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INORGANIC HALOGEN OXIDIZER RESEARCH
FINAL REPORT

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A basic research program was carried out in the area of inorganic halogen oxidizers. The program resulted in 91 papers published in major technical journals, 23 papers presented at international and national meetings, and 14 issued and 4 pending U.S. patents. Major efforts included studies in the areas of nitrogen fluorides, halogen fluorides and oxyfluorides, perchlorates, novel onium salts and sulfur fluorides. In the area of nitrogen fluorides, the most significant

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20. (Continued)

NF4(+)

breakthrough was achieved in NF_4^+ salts and synthetic methods developed under this program have resulted in NF_4^+ based solid propellant NF_3-F_2 gas generators for chemical HF-DF lasers. The most energetic NF_4^+ salt prepared was $(NF_4)_2NiF_6$ which contains 12% more usable fluorine per volume unit than liquid fluorine at its boiling point. In the area of halogen fluorides and oxyfluorides, the outstanding achievements were the discovery and characterization of the novel ClF_3O and ClF_3O_2 molecules and of the ClF_6^+, $ClF_2O_2^+$, ClF_2O^+ and ClF_4O^- ions. In the area of perchlorates, the novel class of fluorocarbon perchlorates and new anhydrous metal perchlorates were discovered. In the area of novel onium compounds, stable salts were synthesized containing OH_3^+, SH_3^+, $NH_2F_2^+$, and $H_3O_2^+$ cations. The complete results of the work under this contract were summarized in 105 technical papers and patents, and are reproduced in Appendix A.

Rockwell International

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INORGANIC HALOGEN OXIDIZER RESEARCH

(1 April 1970 through 31 December 1978)

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PREPARED BY

Exploratory and Laser Reactant Chemisty

Laser Programs

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FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 473, with Drs. R. S. Miller and R. Roberts and Messrs. R. Jackel and R. Hanson as Scientific Officers. This report covers the period 1 April 1970 through 31 December 1978. The program has been directed by Dr. K. O. Christe and, in its early stages, by Dr. D. Pilipovich. The scientific effort was carried out mainly by Drs. K. O. Christe and C. J. Schack and Mr. R. D. Wilson with contributions from Drs. E. C. Curtis, W. W. Wilson, I. B. Goldberg, D. Pilipovich, R. I. Wagner, J. F. Hon, C. B. Lindahl, H. H. Rogers, M. D. Lind, A. E. Axworthy, and H. R. Crowe (all at Rockwell International). Other contributors to these research efforts, at no cost to the contract were: W. Sawodny and W. Kuhlmann (University of Ulm, Germany), R. Bougon (French Atomic Energy Commission), A. Roland (University of California, Berkeley), E. Jacob (M.A.N., Munich, Germany), P. Pulay (Hungarian Academy of Sciences), S. J. Cyvin and J. Brunvoll (University Trondheim, Norway), A. J. Edwards (University of Birmingham, England), D. Naumann and H. Willner (University of Dortmund, Germany), and S. P. Mishra and M. C. R. Symmons (University of Leicester, England). The program was administered by Drs. L. R. Grant, B. Tuffly, and E. A. Lawton.

CONTENTS

Appendix A

Appendix B

INTRODUCTION

This is the final report of a research program carried out at Rocketdyne between 1 April 1970 and 31 December 1978. The purpose of this program was to explore the synthesis and properties of energetic inorganic halogen oxidizers. Although the program was directed toward basic research, applications of the results were continuously considered. Whereas at the onset of the program, the emphasis was mainly on energetic ingredients for propellant applications, in the later stages it shifted more toward chemical lasers. A typical example for the usefulness of such goal-oriented basic research is the application of the NF_4^+ salt chemistry developed under this program. These NF_4^+ salts have become the principal ingredients in solid propellant NF_3-F_2 gas generators for chemical HF-DF lasers.

Only completed items of research, which have been summarized in manuscript form, are included in this report. A total of 82 technical papers were published and 4 papers are in press in major scientific journals. In additon, 23 papers were presented at international and national conferences. A further testimony to the creativity of this program is the fact that it resulted in 14 U.S. patents issued and 4 pending.

The complete results of the work under this contract were summarized in 105 technical papers and patents, and are reproduced in Appendix A.

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104. "Reactions of Electropositive Chlorine With Fluorocarbons," by C. J. Schack, 3rd Winter Fluorine Conference, St. Petersburg, Florida (January 1977).

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123. "Method for Producing NF_4BF_4," by K. O. Christe, C. J. Schack, and R. D. Wilson, U.S. 4,107,275 (August 1978).

124. "$(NF_4)_2NiF_6$ High Energy Solid Propellant Oxidizer and Method of Producing the Same," by K. O. Christe, U.S. 4,108,965 (August 1978).

PATENTS PENDING

125. "Novel NF_4^+ Compositions Suitable for Self-Clinkering NF_3-F_2 Gas Generators," by K. O. Christe, C. J. Schack, and R. D. Wilson.

126. "Novel High Detonation Pressure Explosives," by K. O. Christe.

127. "$N_2F_3^+SbF_6^-$," by C. J. Schack and K. O. Christe.

128. "Self-Clinkering Burning Rate Modifier for Solid Propellant NF_3-F_2 Gas Generators," by K. O. Christe and C. J. Schack.

RESULTS AND DISCUSSION

In view of the very large amount of data generated under this program and their highly diversified nature, we will restrict ourselves to highlight only those areas that are most important and in which our efforts were most heavily concentrated.

NITROGEN FLUORIDE CHEMISTRY

For a long time, nitrogen fluorides have been of great interest as advanced oxidizers for rocket propulsion. Of these, nitrogen trifluoride is the most important compound because it combines a high fluorine and energy content with a remarkable inertness. Its only major drawback is its low boiling point of -129 C. Therefore, the conversion of NF_3 into stable storable solids without significant loss in energy was highly desirable. The first step in this direction was undertaken in 1965 when one of us, under ONR sponsorship at Stauffer Chemical (Ref. 1), discovered the existence of the stable $NF_4^+AsF_6^-$ salt. However, it was not until 1971 when, with the advent of chemical HF-DF lasers, the interest in storable NF_3-F_2 sources was renewed.

It became rapidly obvious that NF_4^+ salts are the most promising oxidizers for solid propellant NF_3-F_2 gas generators. The concept of such a gas generator was conceived (Ref. 2) and, to a large extent (Ref. 3 through 9), developed at Rocketdyne. It offers significant logistics and safety advantages over cryogenic or storable liquid oxidizers.

In a chemical HF-DF laser, F atoms are generated by burning F_2 in a precombustor with a fuel, such as hydrogen:

$$F_2 + H \longrightarrow HF + F\cdot$$

The F atoms are subsequently reacted with a cavity fuel, such as D_2, to produce vibrationally excited DF as the active lasing species:

$$F\cdot + D_2 \longrightarrow DF^* + D$$

In the original solid F atom generator concept (Ref. 2), the F atoms were directly generated by burning the solid propellant grain, thus eliminating the need of a precombustor. This concept is demonstrated for NF_4BF_4 with a small percentage of Teflon serving both as a fuel and a binder. The heat of reaction (Q) is sufficient to dissociate most of the NF_3 and F_2 to F atoms and N_2:

$$NF_4BF_4 + (CF_2)_n \longrightarrow CF_4 + BF_3 + NF_3 + Q$$

$$2NF_3 + Q \longrightarrow N_2 + 6F\cdot$$

From a practical point of view, however, such a direct generation of F atoms is not desirable, since it does not allow the necessary flow controls and flexibility required for operation. Consequently, the concept was modified to that of an NF_3-F_2 molecule generator, using a gas catch tank. Further modification of this concept became necessary, when system analysis data revealed that gaseous byproducts of high molecular weight and low C_p/C_v significantly degrade the performance of a laser. Consequently, an NF_3-F_2 gas generator was desired that would produce no gases other than NF_3 and F_2. The latter objective can be achieved by a so-called clinker system in which the BF_3 byproduct is converted by an alkali metal fluoride to a nonvolatile BF_4^- salt:

$$NF_4BF_4 + KF \xrightarrow{+Q} KBF_4 + NF_3 + F_2$$

Whereas the feasibility of such a clinker system approach has been well demonstrated, the addition of KF lowers the NF_3-F_2 yield per pound of solid propellant and the possibility always exists of having incomplete clinkering.

Realizing these limitations, we have searched for novel NF_4^+ salts containing anions that will yield a nonvolatile fluoride, such as SnF_4 (boiling point = 705 C), after thermal decomposition. No such salts had previously been known, owing to the fact that nonvolatile fluorides are highly polymeric and, therefore, do not behave like strong Lewis acids. This makes the direct synthesis of such salts from NF_3, F_2, and the Lewis acid extremely difficult. We found, however, that $(NF_4)_2SnF_6$ can be prepared (pub. 68) by the following metathetical reaction in HF solution:

$$Cs_2SnF_6 + 2NF_4SbF_6 \xrightarrow{\text{HF sol}} 2CsSbF_6\downarrow + (NF_4)_2SnF_6$$

Further improvements were made by synthesizing novel NF_4^+ salts derived from TiF_4 (pub. 70). Although the usable fluorine content of $(NF_4)_2TiF_6$ (Table 1) is considerably higher than that of $(NF_4)_2SnF_6$, TiF_4 (sublimation pressure of 760 mm at 284 C) is more volatile than SnF_4 (boiling point = 705 C) and may require alkali metal fluoride based clinkering.

TABLE 1. COMPARISON OF THE FLUORINE YIELDS OF PRESENTLY KNOWN NF_3-F_2 GAS GENERATOR SYSTEMS

		Usable F, wt %	
Rank	System	Before	After Burning
1	$(NF_4)_2NiF_6$	64.6	58.6
2	$(NF_4)_2TiF_6$*	55.6	49.6
3	$(NF_4)_2SnF_6$	46.0	40.0
4	$(NF_4)_2TiF_6 \cdot 2.4KF$	39.5	33.5
5	$NF_4BF_4 \cdot 1.2KF$	38.5	32.5
6	$(NF_4)_2GeF_6 \cdot 2.4KF$	37.6	31.6
7	NF_4SnF_5	31.3	25.3
8	$NF_4PF_6 \cdot 1.2KF$	31.2	25.2
9	$NF_4GeF_5 \cdot 1.2KF$	29.0	23.0
10	$NF_4AsF_6 \cdot 1.2KF$	27.3	21.3
11	$NF_4SbF_6 \cdot 1.2KF$	24.0	18.0
12	$NF_4BiF_6 \cdot 1.2KF$	19.7	13.7

*$(NF_4)_2TiF_6$ might require clinkering with KF which would drop its fluorine yield below that of $(NF_4)_2SnF_6$

The usable fluorine content was further increased by synthesizing a NF_4^+ salt of an oxidizing anion. This salt is $(NF_4)_2NiF_6$ (pub. 73, 124)). It has the advantages of containing a doubly charged anion which is "self-clinkering," and an oxidizing anion, thus boosting its usable fluorine content to 64.6 wt % (Table 1). Its potential as an oxidizer and an ingredient for a solid propellant NF_3-F_2 gas generator for chemical HF-DF lasers becomes evident from the following comparison. On thermal decomposition, 1 cm^3 of solid $(NF_4)_2NiF_6$ is capable of producing 12% more useful fluorine values, i.e., in the form of F_2 and NF_3, than liquid F_2 at -187 C. Furthermore, $(NF_4)_2NiF_6$ is a stable solid at ambient temperature that can be safely stored without requiring cryogenic cooling. However, its thermal stability is marginal, which may limit its potential applications.

Since all of the top ranked NF_4^+ salts are prepared by metathetical processes, this process was studied in more detail and was significantly improved. A major breakthrough in the process development was chieved by demonstrating that essentially pure NF_4BF_4 can be produced by metathesis. Furthermore, the synthesis of the NF_4SbF_6 starting material was improved and a novel alternate starting material, i.e., NF_4BiF_6, was synthesized and characterized (pub. 66, 74, 123).

In addition to the above work, a novel uv-photolysis process was developed for the production of NF_4^+ salts (pub. 36, 60). This process provided several novel and some known NF_4^+ salts of extremely high purity which were used (pub. 60) for their thorough characterization. In connection with an on-going ARO program (Ref. 10), the mechanism of the formation and decomposition of NF_4^+ salt was studied and clarified (pub. 83). It was shown that this highly unusual reaction involves the following four equilibria:

$$F_2 \overset{\Delta E}{\rightleftharpoons} 2F\bullet$$

$$F\bullet + NF_3 \rightleftharpoons NF_4^{\bullet}$$

$$NF_4^{\bullet} + MF_5 \rightleftharpoons \dot{N}F_3^{+}MF_6^{-}$$

$$\dot{N}F_3^{+}MF_6^{-} + F\bullet \rightleftharpoons NF_4^{+}MF_6^{-}$$

In the course of this study, the interesting novel NF_3^+ radical cation was prepared and identified (pub. 49, 76, 82).

The possibility of synthesizing NF_4^+ salts in a simple one-step process by direct fluorination of NF_4^+ salts in anhydrous HF solution was also studied. It was found (pub. 55) that the hitherto unknown $NH_2F_2^+$ cation is stable in HF solution, but that the NF_3H^+ cation does not exist, thus explaining the termination of the fluorination reaction at the NF_3 +HF stage.

In addition to the above work on NF_4^+ salts, we have also studied the closely related N_2F^+ (pub. 4) and $N_2F_3^+$ (pub. 81) salts and refuted (pub. 51, 75) claims for $N_2F_5^+$ (Ref. 11) and several novel nitrogen oxyfluorides (Ref. 12).

In summary, the work under this contract has laid the ground work necessary for the development of NF_4^+ salts from exotic laboratory curiosities to extremely useful oxidizers that can be produced on large scale. These salts are useful for solid propellant NF_3-F_2 gas generators for chemical lasers and for high-detonation pressure explosives (pub. 126).

HALOGEN FLUORIDES AND OXYFLUORIDES

Halogen fluorides and oxyfluorides are of great interest as storable liquid rocket propellants. Therefore, it is not surprising that a large percentage of our effort, as shown by 34 publications, was aimed in this direction. The most significant achievements were the discovery and complete characterization of ClF_3O (pub. 11-17) and ClF_3O_2 (pub. 19, 31, 35, 113, 120). Theoretical performance calculations with MMH as fuel (Table 2) show that these oxidizers offer a significant improvement over ClF_3 or $FClO_3$.

We have also studied, in detail, the syntheses and properties of ionic solids derived from chlorine fluorides and oxyfluorides. The two most interesting ions discovered were the ClF_6^+ (pub. 20, 30) and the $ClO_2F_2^+$ cation (pub. 18, 32, 115). Other ions prepared and studied included $ClO_2F_2^-$ (pub. 7), BrF_4^+ (pub. 9), IF_6^-

TABLE 2. PERFORMANCE CALCULATIONS OF LIQUID ROCKET PROPELLANTS

(P_c = 1000, P_e = 14.7 psia, Shifting Composition, Fuel MMH)

Oxidizer	Specific impulse, seconds
ClF_3	283
$FClO_2$	288
$FClO_3$	292
ClF_3O	299
ClF_5	301
ClF_3O_2 [a]	304
$[ClF_5O]$ [a,b]	314

a. Assuming ΔHf° ClF_3O_2 = -32 kcal/mol and ΔHf° ClF_5O = -55.6 kcal/mol based on the known values of other chlorine fluorides and oxyfluorides and the extrapolations given in Ref. 13

b. Hypothetical compound

(pub. 23), IF_4^- (pub. 25), chlorine fluoride cations (pub. 26, 37, 61), BrF_6^+ (pub. 50), BrF_2^+ (pub. 64), and BrF_4O^- (pub. 77). Vibrational spectroscopy and force field computations were used to elucidate the structures and bonding in these ions and in the following molecules: ClF_5 (pub. 1), BrF_3 (pub. 3), BrF_3O (pub. 78) and $FBrO_2$ (pub. 80). In addition, improved syntheses were discovered for ClF (pub. 28) and $FClO_2$ (pub. 47), and the reaction chemistry of chlorine fluorides with hydroxyl compounds (pub. 21) and of Cl_2F^+ with xenon (pub. 33) was investigated. All these studies significantly contributed to the understanding of halogen fluorides, and reviews on halogen fluorides (pub. 39) and chlorine oxyfluorides (pub. 57) were written.

PERCHLORATES

Based on its high energy content and unusual kinetic stability, the perchlorato group is an extremely important ingredient in energetic oxidizers. With the discovery of chlorine perchlorate and bromine perchlorate under this contract (pub. 111), two very useful synthetic reagents became available for the introduction of perchlorato groups into molecules. The potential of these new reagents was thoroughly investigated and is demonstrated by the fact that 22 publications and patents were generated in this area. Among the novel compounds prepared in this manner are the fluorocarbon perchlorates (pub. 29, 42, 43, 46, 79, 86, 89, 92, 97, 99, 104), anhydrous metal perchlorates (pub. 59, 118), and halogen perchlorates (22, 40, 114, 116). The fluorocarbon perchlorates have potential as energetic ingredients in solid propellants, and the anhydrous metal perchlorates show promise for high detonation pressure explosives (pub. 126). In addition, an improved process for the production of $NO_2^+ClO_4^-$ was discovered (pub. 119), based on the reaction of ozone with chlorine nitrate.

NOVEL ONIUM SALTS

Protonation studies in anhydrous super acids, such as $HF\text{-}SbF_5$, led to the discovery of numerous novel solid onium salts. These salts include the following onium cations: OH_3^+ (pub. 53, 121), SH_3^+ (pub. 54, 117), $NH_2F_2^+$ (pub. 55), and H_2OOH^+ (pub. 85, 108). The OH_3^+ salts are of significant interest. They are the most stable onium salts presently known and are solid super acids. They are extremely powerful Friedel Craft type catalysts, capable of rapidly polymerizing epoxides and resulting in high crosslinking (Ref. 14). Furthermore, the formation of OH_3^+ salts offers an excellent method for removal of water from HF (pub. 53, 74). The fact that OH_3^+ salts are stable solid super acids is also of significance because it allows their safe transportation and storage without the corrosivity and potential danger of spills associated with conventional liquid acids.

Other onium salts discovered include $SH_3^+SbF_6^-$, the first known example of a stable unsubstituted sulfonium salt (pub. 54, 117). In view of the fact that the corresponding ammonium (NH_4^+) salts had been known for many centuries, it was very surprising that these simple sulfonium salts had not been discovered sooner. Other interesting onium ions include $NH_2F_2^+$ and H_2OOH^+. Both cations are of significant interest for laser-related applications. The former can undergo a highly exothermic HF elimination to give excited NF_2 and the latter might react with halogens to give excited molecular oxygen.

SULFUR FLUORIDES

Sulfur fluorides are of interest not only because they serve as excellent model compounds for the isoelectronic chlorine fluorides but, also, because they are good energetic oxidizers. For example, characterization of SF_5O^- (pub. 27) and SF_4O (pub. 71) was important to allow the prediction of the spectroscopic properties of the yet unknown isoelectronic ClF_5O and ClF_4O^+ species. The SF_5Br molecule (pub. 69) is of interest as a model compound for laser-induced sulfur isotope separation. In addition to these sulfur fluorides, we have characterized SF_5^- (pub. 24) and SF_4 (pub. 38, 61, 84). The vibrational assignment of the latter were unusually challenging and serve as a model for those in related pseudo-trigonal bipyramidal molecules.

MISCELLANEOUS

In addition to the above main areas of interest, the following miscellaneous studies were undertaken. A simple process for the purification of fluorine was discovered (pub. 72) and the new SeF_5Cl molecule was prepared (pub. 8) and characterized (pub. 10). The oxidation of $(CF_3)_2NO$ (pub. 41) and $XeOF_4$ (pub. 56) with oxidizers, such as PtF_6, was investigated. Known and novel O_2^+ salts (pub. 48, 62) were prepared and characterized, and the structures of XeF_5^+ (pub. 63), $PH_2F_4^-$ (pub. 65) and CF_3O^- (pub. 52) were determined.

CONCLUSION

The results from this contract have demonstrated that the field of inorganic halogen oxidizers is an extremely promising and rewarding area of research. There are many potential uses for novel energetic compounds in traditional and new applications, such as rocket propellants, explosives and chemical lasers, and continuing efforts in this direction are definitely warranted. Furthermore, the production of this program proves the feasibility and benefits that can be expected from well-planned, goal-oriented basic research and program continuity.

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APPENDIX A

TECHNICAL PAPERS/PATENTS

Spectrochimica Acta, Vol. 27A, pp. 631 to 635. Pergamon Press 1971. Printed in Northern Ireland

Matrix isolation study of ClF_5

(*Received* 18 *May* 1970)

Abstract—The infrared spectra of ClF_5 have been recorded in argon and nitrogen matrices. The previously suggested and very unusual triple coincidence of two deformational and one stretching mode at about 480 cm^{-1} has been experimentally confirmed. The observed Cl^{35}–Cl^{37} isotope splittings permit assignment of the bands to the individual modes. Spectroscopic evidence is presented for association of ClF_5 in the pure solid and in Ar matrix at low dilution ratios.

THE vibrational spectrum of ClF_5 has been reported by BEGUN *et al.* [1]. A square-pyramidal structure of symmetry C_{4v} was assigned to ClF_5 by comparison with the spectra of BrF_5, IF_5, and $XeOF_4$. However, the spectrum of ClF_5 exhibited in the range of the fundamental vibrations two bands less than the number observed for the remaining square-pyramidal molecules of this series. A triple coincidence of one stretching (ν_4) and two deformational (ν_3 and ν_8) modes at about 480 cm^{-1} and a double coincidence of ν_1 and ν_7 in the infrared spectrum at about 730 cm^{-1} were suggested [1] to obtain the proper number of fundamental vibrations for symmetry C_{4v}. Since the occurrence of stretching and deformational modes in the same frequency range is quite unusual and since the assignment of BEGUN *et al.* [1] results in an unexpectedly low intensity for ν_2 in the Raman spectrum, additional experimental data on the vibrational spectrum of ClF_5 appeared to be very desirable. In this paper we wish to report the infrared spectrum of matrix-isolated and pure, solid ClF_5.

EXPERIMENTAL

Chlorine pentafluoride (from North American Rockwell) was purified by treatment with anhydrous CsF followed by fractional condensation through traps kept at −111 and −126°. The material retained in the −126° trap was used. It was handled in a well passivated 304 stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellow-seal valves (Hoke Inc., 425 1F 4Y). The apparatus used for the low-temperature matrix isolation studies has been described elsewhere [2] and was directly connected to the metal vacuum system. The ClF_5–inert gas mixtures were prepared in different mole ratios by standard manometric techniques using research grade Ar (99·9995% min.) or prepurified N_2 (99·997% min.) from The Matheson Co. The infrared spectra of matrix isolated and pure ClF_5 were recorded at 4°K on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1} using CsI windows. In addition the spectrum of solid ClF_5 was taken on a Perkin–Elmer Model 337 spectrometer using a conventional Pyrex-glass low-temperature infrared cell equipped with an internal AgCl window cooled with liquid nitrogen. The infrared instruments were calibrated by comparison with standard calibration points [3].

RESULTS AND DISCUSSION

Figure 1 depicts the infrared spectra of matrix isolated ClF_5. Traces A and B show 2·36 and 22 μmole of ClF_5 in argon matrix at a mole ratio of 1:400. Trace C shows 0·7 μmole of ClF_5 in argon at a MR of 1:10000. Trace D was recorded after subjecting the sample of C to a controlled warm up to 37°K followed by recooling to 4°K. Trace E shows 0·7 μmole of ClF_5 in

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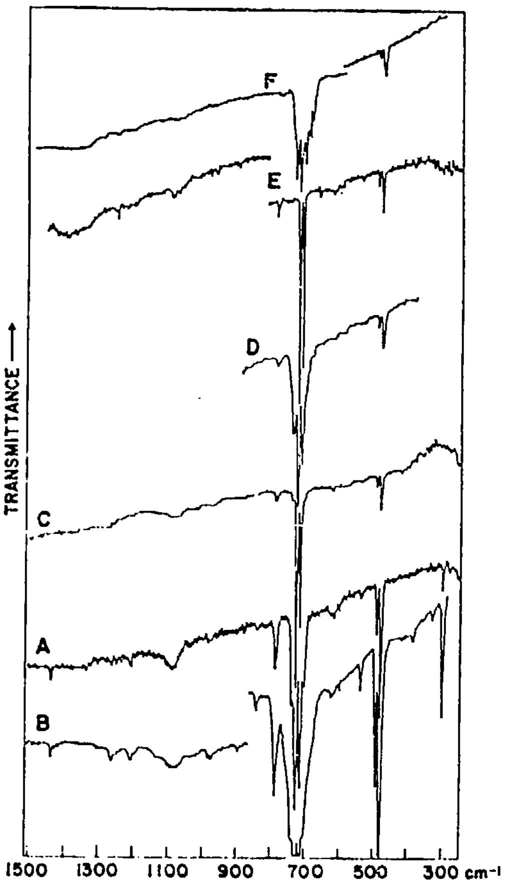

Fig. 1. Infrared spectra of matrix isolated ClF_5. Traces A and B (MR 400), C (MR 10000) in Argon, E (MR 10000) in N_2; traces D and F show samples of traces C and E, respectively, after controlled diffusion.

N_2 at a MR of 1:10000 and F depicts the same sample after being subjected to controlled diffusion at 33°K. Figure 2 shows the individual bands at 10-fold scale expansion under higher resolution conditions to demonstrate the band splittings. The observed frequencies together with the observed and computed isotope splittings are listed in Table 1. Figures 3 and 4 depict the infrared spectra of pure ClF_5 at different concentrations recorded at 4 and 77°K, respectively.

As can be seen from Figs. 1 and 2, the structure of the bands at about 720 cm^{-1} depends strongly upon the nature of the matrix material, the dilution ratio, and temperature cycling. The simplest spectrum was obtained for ClF_5 in N_2 at a MR of 1:10000 (trace E) and, hence, is assumed to be characteristic for monomeric ClF_5. The bands at about 480 cm^{-1} show no detectable dependence upon these effects and, therefore, will be discussed first. Based on the assignments previously suggested by Begun *et al.* [1] a triple coincidence is expected at 480 cm^{-1}. However, $\nu_4(B_1)$ is only active in the Raman spectrum and, hence, the 480 cm^{-1} band should split in the infrared spectrum into two components, $\nu_3(A_1)$ and $\nu_8(E)$. Furthermore, both bands are expected to be split into two components each owing to the Cl^{35} and Cl^{37} isotopes. The Cl^{35}–Cl^{37} ratio should be 3:1. Assuming the normal modes to be 100% characteristic (which is a somewhat crude approximation), the isotope splittings should be 9·9 and 3·7 cm^{-1} for $\nu_3(A_1)$

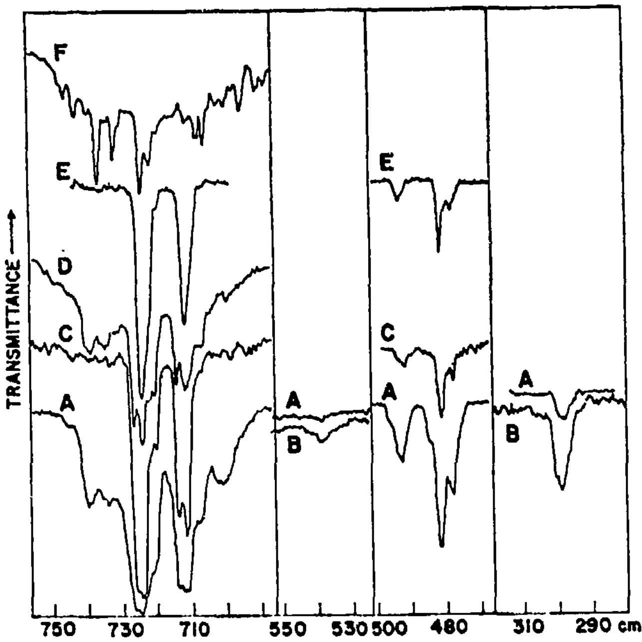

Fig. 2. Infrared spectra from Fig. 1 recorded at 10-fold scale expansion under high resolution conditions.

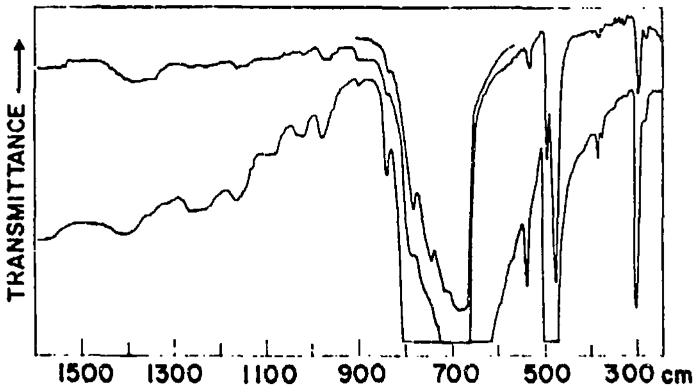

Fig. 3. Infrared spectrum of pure, solid ClF_5 at 4°K at three different concentrations.

and $\nu_8(E)$, respectively. Indeed, two band pairs were observed (see Fig. 2) exhibiting a 3:1 intensity ratio and an isotope splitting of 10 and 3·3 cm^{-1}, respectively. Consequently, the 493 and 482 cm^{-1} bands are assigned to the Cl^{35} isotope components of $\nu_2(A_1)$ and $\nu_8(E)$, respectively. The observed combination bands (see Table 1) suggest for $\nu_4(B_1)$ a frequency of about 486 cm^{-1}, a value close to that observed in the Raman spectrum of liquid ClF_5 [1] thus confirming the triple coincidence.

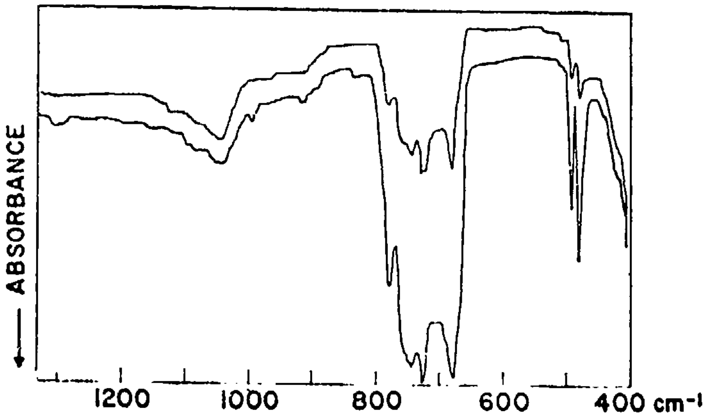

Fig. 4. Infrared spectrum of pure, solid ClF_5 at 77°K at two different concentrations.

Table 1. Infrared spectrum of matrix isolated ClF_5

Obs. frequency	Assignment	Cl^{35}-Cl^{37} Obs.	Isotope splitting Calc.
1444 vw	$\nu_1 + \nu_7(E)$; gives $\nu_1 = 718$		
1265 w	$\nu_2 + \nu_7(E) = 1265$		
1210 w	$\nu_4 + \nu_7(E)$; gives $\nu_4 = 484$		
984 vw	$2\nu_3(A_1) = 986$		
975 w	$\nu_3 + \nu_8(E) = 975$		
840 vw	$\nu_2 + \nu_9(E) = 838$		
790 mw	$\nu_3 + \nu_9 = 792$		
786 w, sh	$\nu_4 + \nu_9(E)$; gives $\nu_4 = 487$		
782 vw, sh	$\nu_8 + \nu_9(A_1 + B_1 + B_2) = 781$		
726 vs	$\nu_7(E)$ Cl^{35}	12.8	12.8
713 s	$\nu_7(E)$ Cl^{37}		
722 w, sh	$\nu_1(A_1)$ Cl^{35}?		
530 w	$\nu_2(A_1)$		0
493 mw	$\nu_3(A_1)$ Cl^{35}	10	9.0
483 sh, w	$\nu_3(A_1)$ Cl^{37}		
482 m	$\nu_8(E)$ Cl^{35}	3.3	3.7
479 mw	$\nu_8(E)$ Cl^{37}		
299 mw	$\nu_9(E)$ Cl^{35}	2.5	4.4
296 sh, w	$\nu_9(E)$ Cl^{37}		

For the 720 cm^{-1} infrared region two band pairs, $\nu_7(E)$ and $\nu_1(A_1)$, are expected with an isotope splitting of 12·8 and 7·2 cm^{-1}, respectively. Of these two fundamentals, $\nu_7(E)$ is of considerably higher relative intensity in the infrared, whereas $\nu_1(A_1)$ appears as a strong, polarized Raman band [1]. As can be seen from Fig. 2, trace E, two bands were observed in the 720 cm^{-1} region exhibiting a 3:1 intensity ratio and a frequency difference of 12·8 cm^{-1}. Consequently, both bands should be assigned to the two isotopic bands of $\nu_7(E)$. The higher frequency band shows a weak shoulder at 722 cm^{-1} which might represent $\nu_1(A_1)$ Cl^{35}. This frequency value is close to the value of 718 cm^{-1} estimated for $\nu_1(A_1)$ from the combination band, $\nu_1 + \nu_7$. However, no conclusive assignment of the 722 cm^{-1} shoulder to $\nu_1(A_1)$ can be made since the corresponding Cl^{37} isotope band would be masked by the much more intense $\nu_7(E)$ Cl^{37} band. Since the frequency of $\nu_1(A_1)$ is well established by the Raman spectrum [1] no further effort was made to unequivocally locate $\nu_1(A_1)$ in the infrared spectrum. However, the shape of the $\nu_7(E)$ bands shows an interesting dependence upon various effects. Thus, in argon matrix at an MR of 1:10000 (trace C) both bands are split by about 2·3 cm^{-1} into two components.

In addition to this matrix site splitting, a concentration dependence was found. At a MR of 1:400 in argon matrix (traces A and B) additional bands appeared between 740 and 700 cm^{-1} which are most likely due to associated ClF$_5$ molecules. This effect was also demonstrated by carrying out two controlled diffusion experiments on ClF$_5$ isolated at high dilution ratios (1:10000) in argon and in nitrogen matrices. In both cases new bands appeared after temperature cycling (traces D and F) with frequencies similar to those observed at low dilution ratios. The effect of association was further demonstrated by recording the spectrum of pure, solid ClF$_5$ (Fig. 3). Again, $\nu_7(E)$ showed considerable band broadening and frequency shifts, whereas the remaining bands exhibited almost no change. Even for solid, pure ClF$_5$ some variation of the band shape has been observed. The spectrum of a sample condensed on an AgCl window cooled with liquid N$_2$ showed two prominent bands at about 725 and 742 cm^{-1} (see Fig. 4). It was demonstrated that this change is not due to a simple temperature effect by allowing the sample depicted in Fig. 3 to slowly warm up from 4 to 77°K while continuously recording its spectrum. No changes in the spectrum could be detected. Hence, the difference in band shapes might be due to different deposition techniques resulting in various degrees of association or crystal ordering effects.

In addition to $\nu_7(E)$, $\nu_3(A_1)$, and $\nu_8(E)$, the following fundamentals were observed in good agreement with the previously published spectrum [1]: $\nu_2(A_1)$ at 539 and $\nu_9(E)$ at 299 cm^{-1}. The spectrum of ClF$_5$ in argon matrix at MR 1:400 (trace B) shows two weak bands at 383 and 330 cm^{-1}. These are close to the values of 375 and 346 cm^{-1} previously assigned [1] to $\nu_6(B_2)$ and $\nu_5(B_1)$, respectively. These should be only Raman active but may have become infrared active owing to the above mentioned association effects.

In summary, the assignments and in particular the unusual triple coincidence of two deformation and one stretching mode at 480 cm^{-1}, previously suggested by Begun *et al.* [1] for ClF$_5$, have been confirmed experimentally. For $\nu_7(E)$ interesting association and matrix effects were observed.

Acknowledgment—I am indebted to Drs. E. C. Curtis and D. Pilipovich for helpful discussions This work was supported by the Office of Naval Research, Power Branch.

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Bromine Perchlorate

BY C. J. SCHACK,* K. O. CHRISTE, D. PILIPOVICH,
AND R. D. WILSON

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Recently we reported the synthesis of a novel chlorine oxide, chlorine perchlorate.[1] This preparation was accomplished by the reaction

$$MClO_4 + ClSO_3F \longrightarrow MSO_3F + ClOClO_3 \quad (M = NO_2, Cs) \quad (1)$$

It has now been found that the related bromine compound bromine perchlorate can be prepared by this method using bromine(I) fluorosulfate.

$$MClO_4 + BrSO_3F \xrightarrow{-20°} MSO_3F + BrOClO_3 \quad (2)$$

In addition, a second method involving the oxidation of elemental bromine with chlorine perchlorate was discovered

$$Br_2 + 2ClOClO_3 \xrightarrow{-45°} Cl_2 + 2BrOClO_3 \quad (3)$$

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[1] C. J. Schack and D. Pilipovich, *Inorg. Chem.*, 9, 1387 (1970).

TABLE I

INFRARED SPECTRA OF $BrOClO_3$ AND RELATED COMPOUNDS

Freq, cm^{-1}, and rel intens					Assignment in point group C_s	Approx description of mode
$HOClO_3$[a] Gas	$FOClO_3$[b] Gas	$ClOClO_3$[c] Gas	$BrOClO_3$ Gas	$BrOClO_3$ Matrix		
			2300 w		$\nu_2 + \nu_9$ (A'') = 2299	
1326 s 1263 vs	1298 vs	1282 vs	1275 vs	1279 vs 1262 vs 1253 m	ν_1 (A') ν_9 (A'')	$\nu_{asym}(ClO_3)$
1050 s	1049 s	1041 s	1039 s	1037 s	ν_2 (A')	$\nu_{sym}(ClO_3)$
3560 s	885 m	752 w	683[d] m	686 m	ν_3 (A')	ν(O–X)
725 s	666 s	652 s	648 s	651 vs 643 ms	ν_4 (A')	ν(–Cl–O)
579 s		561 ms	570 ms	572 mw 566 m	ν_5 (A') ν_{10} (A'')	$\delta_{scissors}(ClO_3)$ $\delta_{asym}(ClO_3)$
519 w		511 w	509 m	516 m	ν_6 (A')	$\delta_{umbrella}(ClO_3)$
430 w				387 w	ν_{11} (A'')	$\delta_{twist}(ClO_3)$

[a] Reference 3. [b] Only four bands reported.[2] [c] Reference 1. [d] A comparable band has been observed at 690 cm^{-1} in the spectrum of $BrONO_2$: C. J. Schack, unpublished results.

This reaction proceeded quantitatively and yielded a purer product than the fluorosulfate reactions.

Bromine perchlorate is a red liquid which freezes below −78°. It is unstable at ambient temperature and decomposes slowly at approximately −20°. A reproducible, measurable vapor pressure of 5 mm was obtained at −23°. The instability of the compound precluded reliable measurements at higher temperatures. The formulation as $BrOClO_3$ is based on the quantitative synthesis according to eq 3, its elemental analysis, and the infrared spectrum. Further support for this formulation was obtained from the quantitative reaction with HBr to form Br_2 and $HClO_4$ and the qualitative reaction with AgCl to form Br_2, Cl_2, and $AgClO_4$.

Figure 1 shows the replotted infrared spectrum of gaseous and matrix-isolated $BrOClO_3$. Good-quality spectra were difficult to obtain owing to the thermal instability of the compound. The vibrational spectrum of $BrOClO_3$ is very comparable to that of other covalent perchlorates—$ClOClO_3$,[1] $FOClO_3$,[2] and $HOClO_3$.[3] From the vibrational spectrum a structure of symmetry C_s (*i.e.*, the only symmetry element is a symmetry plane in the plane of the paper) can be derived for $BrOClO_3$

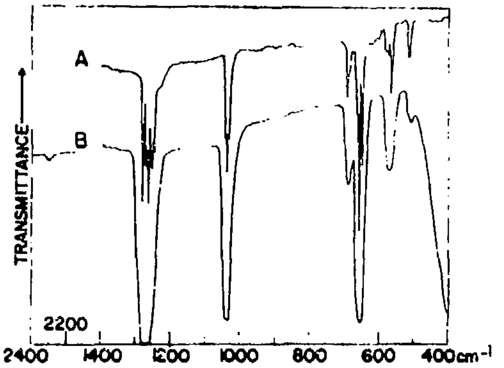
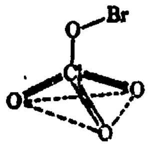


Figure 1.—Infrared spectra of $BrOClO_3$: trace A, 2.5 μmol of sample in Ar matrix (mixture ratio 400) at 4°K; trace B, gas at 20 mm pressure in a cell of 5-cm path length.



This structure is analogous to those of the related molecules $ClOClO_3$, $FOClO_3$, and $HOClO_3$. Table I lists the observed frequencies together with their assignment for symmetry C_s and the values for comparable bands in similar compounds. The decreasing thermal stability of the halogen perchlorates in the order $FOClO_3$ > $ClOClO_3$ > $BrOClO_3$ might be related by the increasing polarizability of the terminal halogen atoms.

Experimental Section

Materials and Apparatus.—All materials were handled in a well-passivated (with ClF_3 followed by covalent perchlorates) 304 stainlesss steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellow-seal valves (Hoke Inc., 4251F4Y). Outside of the vacuum line materials were manipulated in the dry nitrogen atmosphere of a glove box. The apparatus used for the low-temperature matrix-isolation study has been described elsewhere[4] and was directly connected to a metal–Teflon FEP vacuum system. The $BrOClO_3$–Ar mixtures were prepared in a mole ratio of 1:400 by standard manometric techniques using research grade Ar (99.9995% minimum purity from The Matheson Co.). Owing to the thermal instability of $BrOClO_3$, preparation of the gas mixture and its deposition on the cold (4°K) CsI window was done in less than 2 min. The infrared spectra of gases were taken in stainless steel cells of 5-cm path length equipped with AgCl windows. All spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard calibration points.[5]

Preparation of $BrOClO_3$. Method A.—Prepassivated 30-ml stainless steel cylinders were loaded with weighed amounts of either NO_2ClO_4 or $CsClO_4$ in the drybox. A less than equimolar amount of $BrSO_3F$ was then condensed into the cylinder from the vacuum line and the reaction was allowed to proceed at −20° for 5 days or longer. On cooling the cylinder to −196°, varying small amounts of noncondensable gases were observed. The volatile products were separated by fractional condensation in U traps cooled to −45, −64, and −196°. Unreacted $BrSO_3F$, if present, was retained at −45° while the trap cooled to −196° contained only small amounts of the by-products $FClO_3$ and $FClO_2$. Bromine perchlorate was trapped at −64°.

Method B.—A prepassivated 30-ml stainless steel cylinder was loaded at −196° with Br_2 (1.36 mmol) that had been dried over P_4O_{10} followed by $ClOClO_3$ (2.76 mmol). The cylinder was left at −45° for 5 days. After recooling first to −78° and later at −64° the material volatile at those temperatures was pumped out and trapped at −78, −112, and −196°. This consisted of Cl_2 (1.38 mmol), $ClOClO_3$ (0.04 mmol), and $BrClO_4$ (0.1 mmol) as indicated by their vapor pressure and/or infrared spectra. Based on one Cl_2 molecule from each Br_2 reacted, the Cl_2 yield was quantitative within experimental error. The product $BrOClO_3$ (0.469 g, 2.61 mmol) was decomposed by heating at 50° for 3 days. The evolved O_2 was identified by its vapor pressure at −196° and by mass spectroscopy. The halogens were separated

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(2) H. H. Agahigian, A. P. Gray, and G. D. Vickers, *Can. J. Chem.*, **40**, 157 (1962).

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(4) K. O. Christe and D. Pilipovich, *J. Amer. Chem. Soc.*, **93**, 51 (1971).

(5) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Nat. Bur. Stand.*, **64**, 841 (1960).

by fractional condensation after the small amount of BrCl present was thermally decomposed at reduced pressure. Recovered Br_2 (1.30 mmol), Cl_2 (1.32 mmol), and O_2 (5.14 mmol) gave an observed mole ratio of 1.00:1.02:3.95 (theory 1:1:4). *Anal.* Calcd for $BrClO_4$: Br, 44.55; Cl, 19.76; O, 35.68. Found: Br, 44.3; Cl, 20.0; O, 36.1.

Bromine Perchlorate Reactions.—The reaction of $BrOClO_3$ and AgCl was examined only qualitatively. Thus, samples of $BrOClO_3$ were allowed to stand in infrared cells with AgCl windows for several hours. Bands due to $BrOClO_3$ gradually disappeared and those of the ClO_4^- ion[6] grew and were accompanied by the bands of ClO_2 which was formed in minor amounts. In addition, Br_2, Cl_2, and small quantities of gases not condensable at −196° were generated.

A sample of $BrOClO_3$ (2.2 mmol) contained in a 30-ml cylinder was allowed to react with HBr (3.21 mmol) for 1 hr at −78°. Vacuum fractionation of the volatile products at −30, −78, and −196° gave unreacted HBr (1.02 mmol), identified by its infrared spectrum, and Br_2 (2.18 mmol), identified by its vapor pressure. The least volatile fraction was a nearly colorless liquid of low volatility, identified as $HClO_4$ by its infrared spectrum[6] and vapor pressure.[7] No unreacted $BrOClO_3$ was observed.

Acknowledgment.—We are pleased to acknowledge support of this work by the Office of Naval Research, Power Branch.

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Spectrochimica Acta, Vol. 27A, pp. 931 to 936. Pergamon Press 1971. Printed in Northern Ireland

Vibrational spectrum of bromine trifluoride

(*Received* 21 *July* 1970)

Abstract—The infrared spectrum of matrix isolated BrF_3 has been recorded. All six fundamental vibrations expected for a T-shaped molecule of symmetry C_{2v} were observed. A modified valence force field and some thermodynamic properties have been computed for BrF_3.

RECENTLY, SELIG and coworkers [1] have reported the complete vibrational spectrum of gaseous BrF_3. It is difficult to obtain the vibrational spectrum of monomeric BrF_3 owing to its low vapor pressure at ambient temperature, its tendency to disproportionate at elevated temperature, its association in the liquid phase, and its corrosiveness. In this note, we wish to report the results of an independent study of the vibrational spectrum of solid BrF_3. In our study these difficulties were circumvented by the use of low-temperature, matrix-isolation techniques.

EXPERIMENTAL

The apparatus used for the low-temperature, matrix-isolation studies was similar to that previously described [2]. Bromine trifluoride (from The Matheson Company) was purified by fractional condensation, the material retained at −23° being used. It was handled in a passivated (with ClF_3 and BrF_3) stainless steel/Teflon FEP vacuum system connected directly to the sample inlet system. The BrF_3–Ar mixtures were prepared by standard manometric techniques using research grade Ar (99.9995% min. from The Matheson Company). The infrared spectra were recorded at 4°K on a Perkin–Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard calibration points [3]. The Raman spectrum of liquid BrF_3 was recorded using a Coherent Radiation Laboratories Model 52 Ar ion laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to approximately −25° and a d.c. ammeter. Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics. A stainless steel cell having Teflon O-rings and sapphire windows was used as sample container. The design of this cell was similar to that of GASNER and CLAASSEN [4].

RESULTS AND DISCUSSION

Figure 1 depicts the infrared spectrum of BrF_3 in argon matrix at 4°K. Since BrF_3 even in the gas phase shows a tendency to associate [5], the spectrum was recorded at the following argon to BrF_3 mole ratios (MR): 100, 200, 400, 800, and 1600. The relative intensity of some of the bands decreased with increasing MR. Therefore, the spectra of only the two samples with the lowest and highest MR value are shown in Fig. 1.

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[3] E. K. PLYLER, A. DANTI, L. R. BLAINE and E. D. TIDWELL, *J. Res. Natl Bur. Stand.* 64, 841 (1960).
[4] E. L. GASNER and H. H. CLAASSEN, *Inorg. Chem.* 6, 1937 (1967).
[5] For a review of the literature on BrF_3 until 1965, see L. STEIN, *Halogen Chemistry* (Edited by V. GUTMANN), Vol. 1, Chapter 3. Academic Press (1967).

In all spectra the two characteristic absorptions of SiF_4, i.e. ν_3 and ν_4 at about 1030 and 390 cm^{-1}, respectively [6], were observed. The formation of SiF_4 was due to interaction of BrF_3 with sections of the metal vacuum line, and extensive passivation of the line with ClF_3 and BrF_3 was required to keep the SiF_4 concentration at an acceptably low level. At high SiF_4 levels, an additional band at 660 cm^{-1} appeared in some of the spectra. Based on its relative intensity in different spectra, this band does not appear to be related to any other band. Hence, it is assigned to the diatomic molecule BrF for which a frequency of about 670 cm^{-1} was reported based on band spectra [7] and low resolution infrared spectra of Br_2–BrF_3 mixtures [8]. Thus, it appears that small amounts of silicon, present in the steel, can reduce BrF_3 to BrF with SiF_4 being the by-product.

The Raman spectrum of liquid BrF_3 (which always shows a yellow color) has been redetermined with the green 5145 Å argon line. This avoids the problems associated with the use of the blue mercury lines. It agrees well with that previously reported [9] and hence is not depicted. This indicates that the broad, unresolved absorption between 400 and 600 cm^{-1} is likely to be due to association in the liquid phase.

The frequencies observed for matrix isolated BrF_3 are listed in Table 1 together with those recently reported [1] for the gas. The agreement between the two sets of data is excellent. The six fundamentals expected for a T-shaped BrF_3 molecule of symmetry C_{2v} [10] were assigned as previously suggested [1, 9]. The coincidence of $\nu_3(A_1)$ and $\nu_6(B_2)$ at 242 cm^{-1} in the gas phase is confirmed by the observation of two bands in the spectrum of the matrix isolated solid. In addition to ν_4 of SiF_4 at 385 cm^{-1}, there are two bands of variable relative intensity at 578 and 502 cm^{-1}. Since their relative intensity decreases with increasing MR, they cannot be due to BrF_3 itself and are tentatively assigned to di- or polymeric species. This tendency of BrF_3 to associate is also demonstrated by the Raman spectrum of the liquid. It shows a strong, polarized band at 673 cm^{-1} which is in good agreement with the values observed for $\nu_1(A_1)$ in the gas and the matrix-isolated solid. Furthermore, it exhibits three weak bands at 337, 268, and 233 cm^{-1}, respectively, having frequencies similar to those assigned to the three deformational modes. The fact that the symmetric F–Br–F stretching mode, $\nu_2(A_1)$, is the most intense band in the Raman spectrum of BrF_3 gas [1] but does not appear as a strong, distinct band in the Raman spectrum of the liquid, indicates strong association in the liquid phase through formation of fluorine bridges involving the two axial and not the equatorial fluorine atom (the terms axial and equatorial refer to a trigonal bipyramidal structure assuming the two localized free electron pairs of the bromine atom to occupy two equatorial positions).

In the infrared spectrum of matrix-isolated BrF_3, a number of weak bands were observed above 700 cm^{-1} (see Table 1) which obviously cannot be attributed to fundamental vibrations. Most of them can be assigned to overtones and combination bands of BrF_3, thus lending additional support to the given assignment.

The infrared spectrum of non-matrix-isolated, solid BrF_3 has previously been reported [11, 12]. Two different spectra were obtained depending on whether the solid had a glassy or crystalline appearance [12]. Both types of spectra showed two prominent absorptions at about 670 and 600 cm^{-1} but showed additional strong absorptions in the range 400–500 cm^{-1}, indicating association similar to that in the liquid phase. In addition, the infrared spectrum of crystalline BrF_3 showed a decrease in the relative intensity of the 600 cm^{-1} band coupled with the appearance of a new, intense, sharp band at 558 cm^{-1}. Judging from the overall appearance of the two types of spectra, that of the glassy solid was simpler and more closely resembled that of matrix-isolated BrF_3. In no case did the spectrum of solid BrF_3 [12] show the bands characteristic for BrF_2^+ [12]

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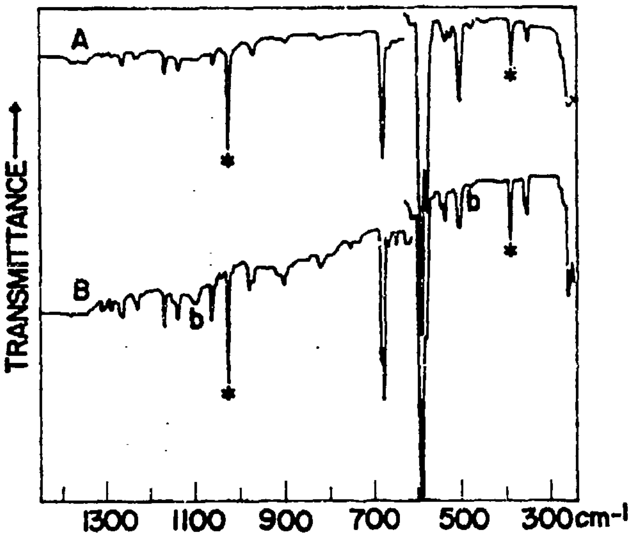

Fig. 1. Infrared spectrum of BrF_3 in argon matrix at 4°K, trace A (MR = 100), trace B (MR = 1600). Bands marked by an asterisk and b are due to SiF_4 and cell window background, respectively.

Table 1. Vibrational spectrum of BrF_3

Gas		Matrix isolated solid IR	Assignment in point group C_{2v}
Raman [1]	IR [1, 9]		
675 s, p	675 s	672 s	$\nu_1(A_1)$ $\nu_{Br-F'}$
612 vvw	614 vs	592 vs	$\nu_4(B_1)$ $\nu_{as\, F-Br-F}$
552 vs, p	552 w	545 mw	$\nu_2(A_1)$ $\nu_{s\, F-Br-F}$
	350 vw	346 mw	$\nu_5(B_1)$ δ_{as} in-plane
	242 s	250 m	$\nu_6(B_2)$ δ out-of-plane
	242 s	235 mw	$\nu_3(A_1)$ δ_s in-plane
	1340 vw	1345 vw	$2\nu_1 = 1344$
	1287 vw	1265 mw	$\nu_1 + \nu_4 = 1264$
		1227 w	$\nu_1 + \nu_2 = 1217$
	1162 w	1170 mw	$2\nu_4 = 1184$
		1138 mw	$\nu_2 + \nu_4 = 1137$
		1062 mw	?
		977 mw	?
		920 w, br	$\nu_1 + \nu_6 = 922$, $\nu_1 + \nu_3 = 905$
		895	$\nu_2 + \nu_5 = 891$
		820 w	$\nu_4 + \nu_3 = 827$
		795 vw, sh	$\nu_2 + \nu_6 = 795$

and BrF_4^- [13] indicating that solid BrF_3 does not exist in the ionic form, $BrF_2^+BrF_4^-$, but prefers association through covalent fluorine bridges. This finding is in good agreement with the results from a crystallographic study on solid BrF_3 [14].

Vibrational force constants

Vibrational force constants were computed for BrF_3 assuming the simplest possible modified valence force field. The kinetic and potential energy metrics were computed by a standard machine method [15] using the geometry determined by microwave spectroscopy [10]. The force constants given in Table 2 were found by trial and error with a time sharing computer. The computed frequencies agreed exactly with the observed values since there were as many force constants as frequencies. The deformation coordinates were weighted by unit distance (1 Å). The force constant designations follow those used for the square-pyramidal interhalogens [16] with f_R for both BrF_3 and BrF_5 referring to the unique fluorine and f_β to the deformation of the angle between that fluorine and the equivalent fluorines.

For comparison, we also report the force constants computed for BrF_5, ClF_5 [17] and ClF_3 [18] assuming a similar force field. Table 2 shows similar trends between BrF_3 and BrF_5 and ClF_3 and ClF_5, although it should be noted that the force constants of ClF_5 are not very certain, since a relatively large interaction force constant is required to fit the frequencies. It is not certain whether this should be $f_{r\beta}$, $f_{R\beta}$, or f_{Rr}. The value for f_α reported for BrF_3 was computed to permit comparison with the similar motion in BrF_5, the E block α deformation. Definition of f_α requires placing fictitious atoms to give BrF_3 the same geometry as BrF_5. These fictitious atoms serve no purpose other than to define f_α and contribute nothing to the molecular motion or force constant [19]. The similarity of f_α for the tri- and penta-fluorides is noteworthy.

Thermodynamic properties

The thermodynamic properties were computed for BrF_3 using the rigid-rotor harmonic-oscillator approximation [20]. The moments of inertia were taken from the microwave data [10] and the vibrational frequencies from this work. The results are given in Table 3.

Table 2. Comparison of the force constants of BrF_3, BrF_5, ClF_3, and ClF_5

	BrF_3	BrF_5[17]	ClF_3[18]	ClF_5[17]
f_R	4·07	4·01	3·88	3·66
f_r	3·10	3·26	2·74	2·75
f_β	1·39	2·32	1·97	2·80
f_α	0·78	0·84	1·03	1·09
f_{rr}'	0·31	0·26	0·38	0·18
$f_{\beta\beta}'$	0·09	0·56	0·17	0.29

Units of the stretching constants are mdyn/Å and of the bending constants mdyn/Å rad^{-2}.

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Table 3. Thermodynamic properties of BrF_3 assuming an ideal gas at 1 atm. pressure

T	$C_p°$	$H° - H_0°$	$-(F° - H_0°)/T$	$S_T°$
0	0	0	0	0
100	9.948	0.847	48.096	56.561
200	13.751	2.041	54.483	64.690
298.15	16.117	3.518	58.866	70.365
300	16.150	3.548	58.939	70.765
400	17.477	5.236	62.522	75.611
500	18.232	7,024	65.551	79.600
600	18.688	8.872	68.180	82.967
700	18.981	10.757	70.505	85.872
800	19.179	12.665	72.588	88.420
900	19.319	14.591	74.476	90.688
1000	19.420	16.528	76.201	92.729
1100	19.497	18.474	77.789	94.583
1200	19.555	20.427	79.260	96.282
1300	19.602	22.385	80.631	97.850
1400	19.638	24.347	81.913	99.304
1500	19.668	26.312	83.118	100.659
1600	19.692	28.280	84.255	101.930
1700	19.713	30.250	85.330	103.124
1800	19.730	32.222	86.350	104.251
1900	19.744	34.196	87.321	105.318
2000	19.757	36.171	88.246	106.332

Units for $C_p°$, $S°$, and $-(F° - H_0°)/T$ are Calories per mole · degree and $H°$ is kilocalories per mole.

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THE VIBRATIONAL SPECTRUM OF THE N_2F^+ CATION

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ABSTRACT

The infrared and Raman spectra are reported for $N_2F^+AsF_6^-$ and $N_2F_2 \cdot 1.3\ SbF_5$. Previous assignments of the two stretching modes for N_2F^+ are confirmed, but the deformational mode occurs at 390 and not at 803 cm^{-1}. Force constants were calculated for N_2F^+ and are compared to those of a series of isoelectronic molecules and ions.

INTRODUCTION

The existence of solid adducts of N_2F_2 and Lewis acids, such as AsF_5 and SbF_5, is well known[1-4]. In all cases an infrared band at about 1060 cm^{-1} was observed which was attributed to the N–F stretching vibration of the N_2F^+ cation. Recently, Shamir and Binenboym reported[5] the Raman spectrum of $N_2F^+AsF_6^-$ and assigned bands at 2370 and 803 cm^{-1} to the two remaining fundamentals of N_2F^+. In this paper we wish to report the infrared and Raman spectra of $N_2F^+AsF_6^-$ and $N_2F_2 \cdot 1.3\ SbF_5$ showing that the deformational mode of N_2F^+ occurs at 390 and not at 803 cm^{-1}.

EXPERIMENTAL

The sample of $N_2F^+AsF_6^-$ was prepared as previously described[1]. Its 1:1 composition was ascertained by quantitative synthesis. The sample of $N_2F_2 \cdot x\ SbF_5$ was prepared in a passivated (with ClF_3) 80 ml Kel-F ampoule equipped with a stainless steel valve. Distilled SbF_5 (12.35 mmoles) was transferred into the Kel-F ampoule in the dry nitrogen atmosphere of a glove box. The ampoule was connected to a stainless steel–Teflon FEP vacuum system and about 20 ml of electrolytically dried[6], liquid HF was added. The SbF_5 was dissolved in

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the HF at ambient temperature, the ampoule cooled to −196°, and a mixture of *cis*- and *trans*-N_2F_2 (total = 25.5 mmoles) containing a small amount of N_2F_4 as impurity was added. The mixture was allowed to warm up to −80° for 3–4 hours and then to ambient temperature for two days under autogenous pressure. Unreacted material (HF and *trans*-N_2F_2) was removed in vacuo at 0°. The material balance and weight increase of the solid residue indicated that SbF_5 had combined with N_2F_2 in a mole ratio of 1.3:1.

The infrared spectra of the solids were recorded on a Perkin Elmer Model 457 spectrophotometer as dry powders between AgBr or AgCl plates or by placing the powder between two single crystal platelets of AgBr and pressing them in a micro pellet press to a disk. The AgBr windows were eventually attacked by the samples with the evolution of bromine. However, useful spectra could be obtained by fast scanning before noticeable attack on the windows occurred. The Raman spectra of the solids were recorded with a Spex Model 1400 spectrophotometer. The green (5145 Å) line of a Coherent Radiation Laboratory Model 52 argon ion laser was used as the exciting line. Glass melting point capillaries or Pyrex glass tubes of 7 mm o.d. with a hollow inside glass cone for variable sample thicknesses were used as sample containers. The former were employed in the transverse viewing–transverse excitation and the latter in the axial viewing–transverse excitation mode.

RESULTS AND DISCUSSION

(*1*) *Synthesis*

The synthesis of the $N_2F_2 \cdot xSbF_5$ adduct deserves some comment. Three different groups have reported the preparation of an adduct of N_2F_2 with SbF_5 but their data disagree. Ruff obtained[2] a 1:2 adduct, $N_2F_2 \cdot 2SbF_5$, by reacting SbF_5 with excess of either *cis*- or *trans*-N_2F_2 at 40–50°. Roesky et al. reported[3] that only the *cis* isomer of N_2F_2 is capable of forming an adduct with SbF_5 resulting in a 1:1 adduct, $N_2F_2 \cdot SbF_5$. Pankratov and Savenkova prepared[4] a 1:1 adduct, $N_2F_2 \cdot SbF_5$, from mixtures of *cis*- and *trans*-N_2F_2 and SbF_5 at −5 to 10° using excess N_2F_2 and pressures of up to 15 atm. Since, according to Pankratov and Sokolov[7], *trans*-N_2F_2 readily equilibrates at ambient temperature to form a 9:1 mixture of *cis*- and *trans*-N_2F_2, *trans*-N_2F_2 should also be capable of forming an SbF_5 adduct by continuous removal of *cis*-N_2F_2 from the equilibrium in the form of solid $N_2F_2 \cdot xSbF_5$.

In the present study we have not attempted to resolve these conflicting reports on either the composition (1:1 versus 2:1) of the adduct or on the ability of *trans*-N_2F_2 to produce an SbF_5 adduct. Our main interest was to determine the vibrational spectrum of N_2F^+. However, in our study several interesting observations were made. The composition of our adduct, $N_2F_2 \cdot 1.3SbF_5$, would seem to indicate that both 1:1 and 1:2 complexes, and mixtures thereof, can be formed. The unreacted N_2F_2 consisted exclusively of the *trans* isomer. Owing to the apparent nonreactivity of the *trans* isomer with Lewis acids and the failure of the *trans* isomer to equilibrate to the *cis* isomer under our reaction conditions, the 1:1.3 composition of our adduct may have been due to the limited amount of *cis*-N_2F_2 present in the mixture. We had chosen HF as a reaction medium to suppress the formation of polymeric anions. Previously, this approach had been successfully applied[8, 9] in the synthesis of $ClF_4{}^+SbF_6{}^-$ and $NF_2O^+SbF_6{}^-$, and in the case of N_2F_2 and SbF_5 it should also result in a well-defined 1:1 adduct provided a large enough excess of *cis*-N_2F_2 is present.

(2) *Vibrational spectra*

Figs. 1–3 show the infrared and Raman spectra of $N_2F^+AsF_6{}^-$ and $N_2F_2 \cdot 1.3SbF_5$. The observed frequencies are listed in Table 1. The Raman spectrum of $N_2F^+AsF_6{}^-$ is in good agreement with that previously reported[5] by Shamir and Binenboym except for the absence of the 803 cm^{-1} band in our spec-

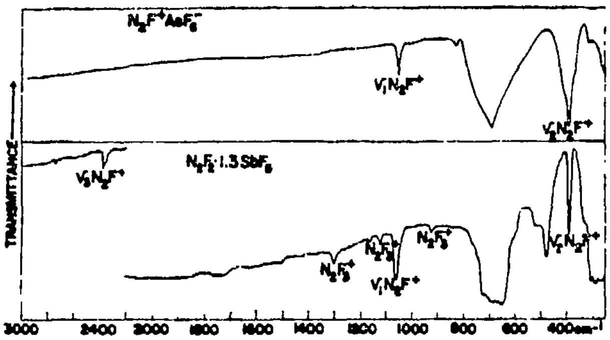


Fig. 1. Infrared spectrum of solid $N_2F^+AsF_6{}^-$ and $N_2F_2 \cdot 1.3SbF_5$ in an AgBr pellet.

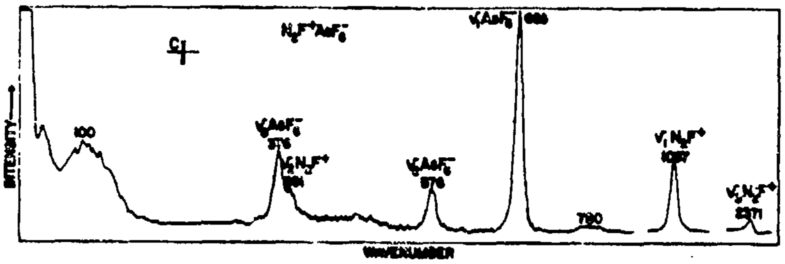


Fig. 2. Raman spectrum of solid $N_2F^+AsF_6{}^-$. C indicates spectral slit width.

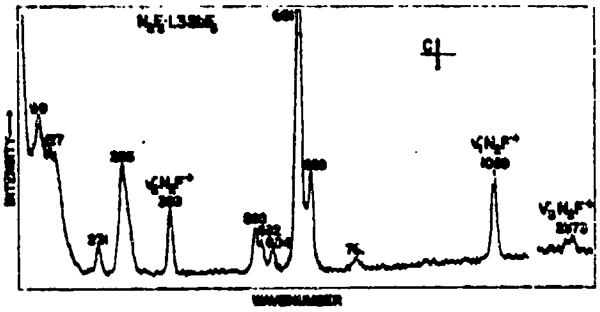


Fig. 3. Raman spectrum of solid $N_2F_2 \cdot 1.3SbF_5$. C indicates spectral slit width.

TABLE 1

VIBRATIONAL SPECTRA OF $N_2F^+AsF_6^-$ AND $N_2F_2 \cdot 1.3SbF_5$ COMPARED WITH THAT OF FCN

Observed frequency					*Assignment (point group)*	
$N_2F_2 \cdot 1.3SbF_5$		$N_2F^+AsF_6^-$		FCN[a]	FXN ($C_{\infty v}$)	AsF_6^- (O_h)
IR	*RA*	*IR*	*RA*	*IR*		
2373 w	2373 (0.3)		2371 (0.5)	2323	$\nu_3(\Sigma^+)$	
1059 ms	1059 (2.3)	1058 ms	1057 (3.1)	1069.4	$\nu_1(\Sigma^+)$	
		830 vw				$\nu_2+\nu_6(F_{1u}+F_{2u})$
	781 (0+)		780 (0+)		$2\nu_2(\Sigma^+)$	
640–720 vs, br	689 (2.5)	698 vs, br				$\nu_3(F_{1u})$
	661 (10)		689 (10)			$\nu_1(A_{1g})$
600 w, sh	604 (0.6)					
	582 (0.5)					
	568 (1.0)		576 (1.8)			$\nu_2(E_g)$
520 mw, sh						
478 ms						
388 ms	389 (1.6)	391 s	391 (0.7)	451.3	$\nu_2(\pi)$	$\nu_4(F_{1u})$
260–300 s	285 (2.7)		376 (3.2)			$\nu_5(F_{2g})$
	231 (0.7)					
	127 99		100			Lattice vibrations

[a] Refs. 10 and 11.

trum. Consequently, we prefer to assign the distinct band of medium intensity at 391 cm^{-1} to the deformational mode, $\nu_2(\pi)$, of N_2F^+. This band at 391 cm^{-1} was also observed[5] by Shamir and Binenboym but they offered no explanation or assignment for this band. Since the 391 cm^{-1} band in $N_2F^+AsF_6^-$ occurs in the range of the AsF_6^- deformational modes and since breakdown of the selection rules for O_h symmetry has been observed for several AsF_6^--containing salts[12, 13], the 391 cm^{-1} band in the AsF_6^- salt cannot unambiguously be assigned to $\nu_2(\pi)$ of N_2F^+. However, if the band at 391 cm^{-1} is indeed due to $\nu_2(\pi)$ of N_2F^+, it should also be observed in the spectra of other N_2F^+ salts containing anions not absorbing in this region. Since for SbF_6^- and $Sb_2F_{11}^-$ no vibrations occur[2,14] in the range 300–450 cm^{-1}, we have prepared a sample of $N_2F_2 \cdot xSbF_5$ and recorded its vibrational spectrum. As can be seen from Figs. 1 and 3, both the infrared and Raman spectrum of $N_2F_2 \cdot 1.3SbF_5$ show a prominent absorption at about 390 cm^{-1} but none at 803 cm^{-1}. Consequently, the band at 390 cm^{-1} may with confidence be assigned to $\nu_2(\pi)$ of N_2F^+.

The spectrum of N_2F^+ was previously compared[5] to that of the isoelectronic N_2O molecule. However, based on bond order and electronegativity considerations, we prefer to compare the spectrum of N_2F^+ with that of the isoelectronic FCN. As can be seen from Table 1, the two stretching modes of N_2F^+ are close to those[10,11] of FCN and, hence, one might expect this analogy to hold also for the deformational mode which in FCN occurs at about 450 cm^{-1}. Based on this comparison a frequency value of 390 cm^{-1} appears more plausible for $\nu_2(\pi)$ of N_2F^+ than that of 803 cm^{-1} previously suggested[5].

The assignments for the remaining bands of $N_2F^+AsF_6^-$ present no difficulties and are listed in Table 1. The observed frequencies and intensities agree well with those predicted for a linear, asymmetric $[N{\equiv}N{-}F]^+$ cation of symmetry $C_{\infty v}$ and for an octahedral AsF_6^- anion[5,9]. For $N_2F_2 \cdot 1.3SbF_5$ three additional bands of low relative intensity were observed at 1300, 1124, and 926 cm^{-1} which can be assigned[2,14] to small amounts of $N_2F_3^+$ present in our sample as an impurity. Infrared spectra, recorded after $N_2F_2 \cdot 1.3SbF_5$ had attacked the AgBr window material, showed the complete absence of the bands assigned to N_2F^+, whereas the bands due to $N_2F_3^+$ had not decreased in intensity. This confirms the previous observation[2] that the N_2F^+ salts are more reactive than the corresponding $N_2F_3^+$ salts. It is interesting to note that for $N_2F_2 \cdot 1.3SbF_5$ the $N{\equiv}N$ stretching mode of N_2F^+ was also observed in the infrared spectrum. However, this band is quite weak and is not easily observed. Since the combining ratio of our $N_2F_2 \cdot xSbF_5$ adduct is intermediate between 1:1 and 1:2, no attempt is made to assign the Sb–F vibrations to individual modes but their frequencies and relative intensities are similar to those previously reported[2,14] for SbF_6^- and $Sb_2F_{11}^-$. Whereas the Raman spectra of $N_2F^+AsF_6^-$ and $N_2F_2 \cdot 1.3SbF_5$ did not show any evidence for a band at 803 cm^{-1} (the frequency previously assigned[5] to ν_2 of N_2F^+), both show a weak band at 780 cm^{-1}. This band appears to belong to the N_2F^+ cation, but its relative intensity is quite low. Further, it does not have a counterpart in the infrared spectrum and its frequency is exactly twice that of the 390 cm^{-1} band. Consequently, it is assigned to the first overtone of ν_2 of N_2F^+.

(3) *Force constants*

For a linear, asymmetric ion of symmetry $C_{\infty v}$, such as N_2F^+, a general valence force field contains four force constants. Since only three frequency values are available, the problem is underdetermined and simplification must be made. Shamir and Binenboym[5] used a modified valence force field for their computation assuming the off-diagonal constant, f_{rR}, to equal zero. However, this assumption is not valid for most of the known force fields of linear XYZ molecules since the influence of f_{rR} upon the diagonal force constants cannot usually be neglected. Therefore, f_{rR} was assumed to have a fixed value, and the N–N and N–F stretching force constants (f_r and f_R, respectively) were computed as a function of f_{rR} (Table 2). The value of f_{rR} was varied over the most probable range (−0.5 to 2.0 mdyne/Å) and computations were made at 0.5 mdyne/Å intervals. A closer estimate of the stretching force constants might be obtained provided one could further narrow the range of possible f_{rR} values.

TABLE 2

STRETCHING FORCE CONSTANTS OF N_2F^+ AS A FUNCTION OF THE ASSUMED VALUE OF THE INTERACTION CONSTANT

(All values in mdyne/Å)

f_{rR}	f_r	f_R
−0.5	19.66	8.82
0	20.48	8.46
0.5	21.23	8.17
1.0	21.92	7.95
1.5	22.57	7.78
2.0	23.19	7.65

A theoretical interpretation of the stretch–stretch interaction force constant as a measure for resonance effects between the two bonds has previously been given by Coulson, Duchesne and Manneback[19] and is in good agreement with the experimental observations. Thus, linear XYZ molecules might be classified into three different groups: (i) molecules with one single and one multiple bond, but without the possibility of resonance, e.g. HCN[16] and HCP[15] for which f_{rR} is negative; (ii) molecules with one single and one multiple bond, where some resonance is possible, e.g. Hal–C≡N, for which f_{rR} was found[17] to be 0.4±0.1 mdyne/Å (but it is not unreasonable to extend the possible range to 0.5±0.5 mdyne/Å); and (iii) molecules with two multiple bonds and stronger resonance, e.g. N_2O and NCO^-,[18] with $f_{rR} > 1$ mdyne/Å. The symmetric molecules and ions, CO_2, NO_2^+, N_3^-,[18] might be included here.

For N_2F^+ the N–N stretching force constant has a value similar to, or slightly lower than, that found for N_2 (22.39 mdyne/Å)[18] throughout the range of probable f_{rR} values. On the other hand, the N–F stretching force constant is the highest one obtained so far for any N–F bond[5,20]; the lowest value possible for N_2F^+ based upon the observed frequencies is 7.45 mdyne/Å. Comparison of this value with those obtained for NF_4^+ (6.22)[21] and NF_2O^+ (6.46 mdyne/Å)[20] indicates that the marked increase cannot be due exclusively to a change in hybridization (i.e. increasing *s*-character of the N–F bond), but strongly suggests partial double bond character. Consequently, N_2F^+ should belong to group (ii) for which f_{rR} might be restricted to the range 0–1 mdyne/Å. Assuming $f_{rR} = 0.5 \pm 0.5$ the stretching force constants become $f_{NN} = 21.23 \pm 0.75$ and $f_{NF} = 8.16 \pm 0.29$ mdyne/Å. Further support for the assumption, $f_{rR} < 1$ mdyne/Å, was obtained by computing a set of force constants for N_2F^+ by the eigenvector method[22,23]. This computation yielded a value of 1.33 mdyne/Å for f_{rR} of N_2F^+. However, for seventeen different linear XYZ molecules the eigenvector method always resulted[24] in f_{rR} values considerably larger than those of the GVFF. Therefore, one might expect f_{rR} of N_2F^+ to be considerably smaller than 1.33 mdyne/Å.

The deformation constant, f_α, of N_2F^+ can be uniquely determined provided the two bond lengths are known. For N_2F^+ this is not the case but, assuming r_{NN}

TABLE 3

FREQUENCIES AND FORCE CONSTANTS OF N_2F^+ COMPARED TO THOSE OF ISOELECTRONIC MOLECULES AND IONS

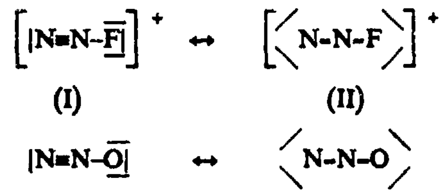
	Species	*Frequency* (cm^{-1})			*Force constants* (*mdyne*/Å)			
		ν_3	ν_1	ν_2	f_r	f_R	f_{rR}	f_α
(i)	$\mathrm{H{-}C{\equiv}P}$[a]	3216.9	1278.4	674.7	8.95	5.59	−0.20	0.15
	$\mathrm{H{-}C{\equiv}N}$[b]	3438.3	2131.8	726.6	18.77	6.23	−0.21	0.21
(ii)	$[\mathrm{N{\equiv}N{-}F}]^+$	2372	1058	390	21.23	8.17	0.5	0.20
	$\mathrm{N{\equiv}C{-}F}$[c]	2323	1069.4	451.3	17.81	8.54	0.39	0.26
	$\mathrm{N{\equiv}C{-}Cl}$[c]	2215.6	744.2	378.4	17.50	5.21	0.44	0.18
	$\mathrm{N{\equiv}C{-}Br}$[c]	2198.3	586.6	341.7	17.51	4.17	0.41	0.15
	$\mathrm{N{\equiv}C{-}I}$[c]	2189.5	485.8	304.5	17.87	3.08	0.50	0.11
(iii)	N∸N∸O[d,e]	2224	1285	589	17.7	11.4	1.2	0.50
	[N∸C∸O]$^-$ [d,e]	2165	1302 1207	632	15.9	11.0	1.4	0.51
	$[\mathrm{O{-}N{-}O}]^+$ [d]	2360	1396	570	17.17		1.19	0.47
	$\mathrm{O{-}C{-}O}$[d]	2349	1286 1388	667	15.61		1.43	0.57
	$[\mathrm{N{-}N{-}N}]^-$ [d]	2036	1344	647	13.15		1.75	0.58

[a] Ref. 15. [b] Ref. 16. [c] Ref. 17. [d] Ref. 18.

[e] The broken lines indicate partial bonds due to appreciable contribution from other mesomeric structures.

to be the same as that in N_2 (1.10 Å)[18] and r_{NF} to be 1.37 Å (r_{NF} in *trans*-N_2F_2 = 1.398 and in NF_3 = 1.371 Å)[25] one obtains for f_α of N_2F^+ a value of 0.202 mdyne/Å or 0.304 mdyne · Å · rad^{-1}. Using the frequency value of 803 cm^{-1}, previously suggested[5] for ν_2 of N_2F^+, f_α would become 0.856 mdyne/Å. Comparison of the frequencies and force constants of N_2F^+ with those of a series of isoelectronic molecules and ions (Table 3) shows that a value of 0.86 mdyne/Å for f_α of N_2F^+ would be out of line. Table 3 also demonstrates that f_α appears to be quite useful for distinguishing single bonds from multiple bonds, especially in cases where no additional experimental data are available to uniquely determine $f_{r\alpha}$. Thomas et al.[26] have recently published a relation having the form $f_r = 37.3/r^{5.71}$ between the valence force constant and bond length of N–N bonds. This relation might be used to crosscheck our estimate of r_{NN} used for the computation of f_α. Assuming f_r = 21.23 mdyne/Å, r_{NN} becomes 1.10 Å which is identical with our estimated value.

The conclusions reached by Shamir and Binenboym[5], that N_2F^+ is linear and asymmetric and that the N–N bond has triple bond character, are certainly correct. Based on the force constant values, contributions of the mesomeric structure (II) to the bonding in N_2F^+ are noticeable,



but must be relatively small contrary to the situation in N_2O where (II) strongly contributes.

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Halogen Perchlorates. Vibrational Spectra

BY KARL O. CHRISTE,* CARL J. SCHACK, AND E. C. CURTIS

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The infrared spectra of gaseous, solid, and matrix-isolated $ClOClO_3$ and the Raman spectrum of liquid $ClOClO_3$ have been measured. All 12 fundamentals expected for symmetry C_s were observed and assigned. The infrared spectra of gaseous and matrix-isolated $BrOClO_3$ have also been recorded. Some vibrational force constants and the thermodynamic properties have been computed.

Introduction

Recently, the existence of the two novel halogen oxides, $ClOClO_3$ and $BrOClO_3$, has been discovered.[1,2] Their chemical and physical properties[1,2] were in accordance with covalent halogen perchlorate structures. In this paper we wish to present spectroscopic data supporting these suggested structures.

Experimental Section

The preparation, purification, and handling of $ClOClO_3$ and $BrOClO_3$ have been reported elsewhere.[1,2] The apparatus used

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(1) C. J. Schack and D. Pilipovich, *Inorg. Chem.*, **9**, 1387 (1970).

(2) C. J. Schack, K. O. Christe, D. Pilipovich, and R. D. Wilson, *ibid.*, **10**, 1078 (1971).

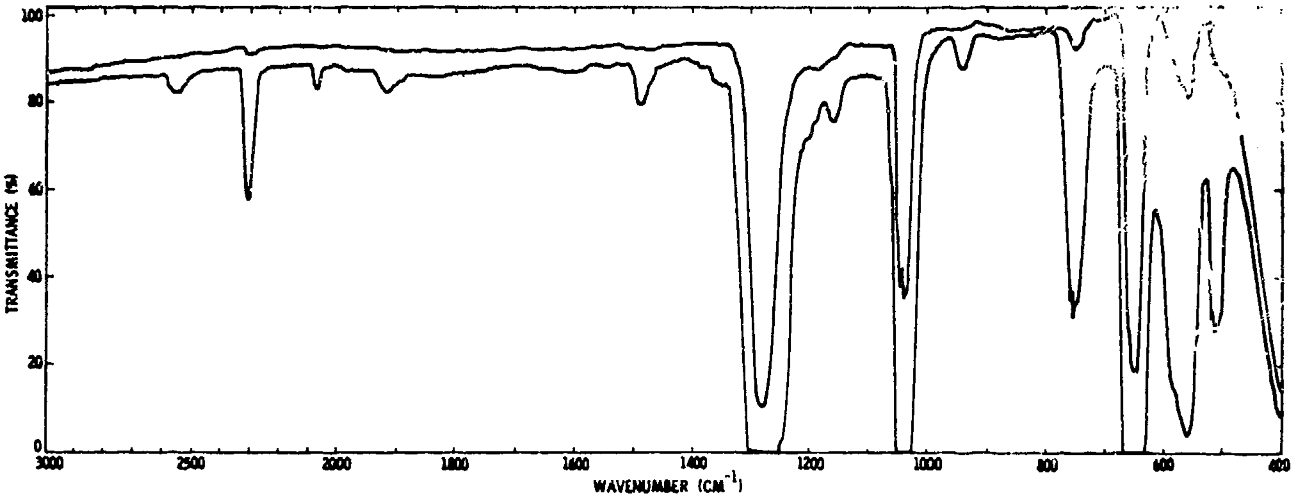

Figure 1.—Infrared spectrum of $ClOClO_3$ at 180 and 8 mm pressure (5-cm path length).

for the low-temperature matrix isolation and infrared spectroscopic studies has previously been described.[3,4] The low-temperature infrared spectrum of solid $ClOClO_3$ was recorded by condensing the sample on the cold (−196°) internal AgCl window of a conventional low-temperature cell. The Raman spectra of liquid $ClOClO_3$ were obtained using Kel-F or Teflon FEP capillaries in the transverse viewing–transverse excitation mode. The capillaries were cooled (−20 to −80°) by a stream of cold gaseous N_2. The intense light from the exciting laser beam (1.3 W at 5145 Å) tended partially to decompose the sample causing gas evolution, thus rendering the recording of spectra difficult. However, reproducible spectra could be obtained by rapidly scanning the spectrum by hand. Under these conditions no lines could be detected due to Cl_2O_7[4,5] which is the major decomposition product in the photolysis of $ClOClO_3$.[1] The Raman instrument used in this study has previously been described.[6]

Results and Discussion

Caution! Halogen perchlorates are shock sensitive[1] *and should be handled with proper safety precautions.*

Figure 1 shows the infrared spectrum of gaseous $ClOClO_3$. The infrared spectra of solid and matrix-isolated $ClOClO_3$ are given in Figure 2. Since chlorine has two natural isotopes (^{35}Cl and ^{37}Cl in a 3:1 mole ratio), the spectra of matrix-isolated species were recorded at 10-fold scale expansion under high-resolution conditions (see Figure 3) to determine the isotopic shifts. Figure 4 shows the Raman spectrum of liquid $ClOClO_3$. Figure 5 shows the infrared spectrum of gaseous and matrix-isolated $BrOClO_3$. The observed frequencies are listed in Table I.

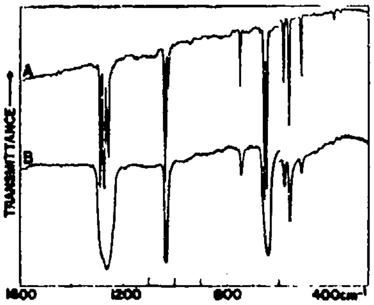

Figure 2.—Infrared spectrum of solid $ClOClO_3$: trace A, 8.2 μmol of sample in Ar matrix (mole ratio = 800) at 4°K; trace B, crystalline solid.

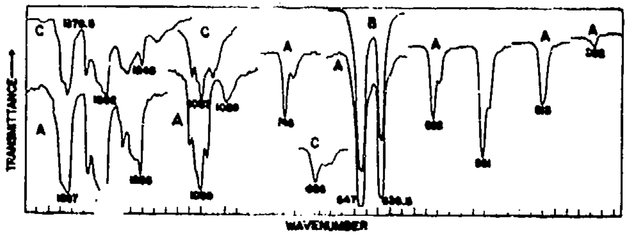

Figure 3.—Infrared spectra of matrix-isolated $ClOClO_3$ and $BrOClO_3$ at 4°K under high-resolution conditions and tenfold scale expansion (1 scale unit = 5 cm⁻¹): trace A, $ClOClO_3$ sample of Figure 2A; trace B, 4.6 μmol of $ClOClO_3$ in Ar matrix (mole ratio = 400); trace C, 2.5 μmol of $BrOClO_3$ in Ar matrix (mole ratio = 400).

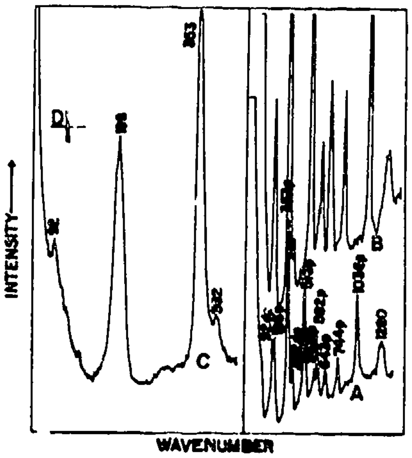

Figure 4.—Raman spectrum of liquid $ClOClO_3$ at −40°. Traces A and B scanned manually; trace C automatically: traces B and C, incident polarization perpendicular; trace A, incident polarization parallel; D, spectral slit width.

The recording of the vibrational spectra of $ClOClO_3$ and $BrOClO_3$ presented several experimental challenges since these two halogen perchlorates are shock and light sensitive, thermally unstable (they decompose at or below ambient temperature), and highly reactive[1,2] (they attack infrared windows such as AgCl causing formation of $AgClO_4$ and Cl_2). Consequently, numer-

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(3) K. O. Christe and D. Pilipovich, *J. Amer. Chem. Soc.*, **93**, 51 (1971).

(4) R. Savoie and P. Giguère, *Can. J. Chem.*, **40**, 991 (1962).

(5) J. D. Witt and R. M. Hammaker, *Chem. Commun.*, 667 (1970), and private communication.

(6) K. O. Christe, *Spectrochim. Acta, Sect. A*, **27**, 463 (1971).

TABLE I
VIBRATIONAL SPECTRA OF $ClOClO_3$ AND $BrOClO_3$

Obsd freq, cm^{-1}						Assignment in point group C_s
$ClOClO_3$				$BrOClO_3$		
Infrared			Raman	Infrared		
Gas	Matrix	Solid	Liquid	Gas	Matrix	
2570 vw						$2\nu_1$
2322 w		2290 w		2300 w		$\nu_1 + \nu_2$, $\nu_8 + \nu_9$
2090 vw		2070 vw				$2\nu_2$
1934 vw						$\nu_1 + \nu_4$
1500 vw						$2\nu_3$
	1289 sh				1280 sh	B^{35}
	1287 vs				1278.5 vs	$\nu_1(^{35}Cl)$ (A′)
	1278 m				1270.5 m	C^{35}
	1274 sh				1265 sh	B^{37}
	1272 sh				1263 sh	$\nu_1(^{37}Cl)$ (A′)
1283 vs	1271 vs	1278 sh	1280 mw	1275 vs	1262 vs	$\nu_9(^{35}Cl)$ (A″)
	1264 mw	1259 vs			1256 sh	C^{37}
	1258 sh	1239 sh			1252 m	D
	1256 m				1246 mw	$\nu_9(^{37}Cl)$ (A″)
					1240 w	
	1044 m				1041 m	
1040 s, PQR	1039 s	1031 vs	1036 vs, p	1039 s	1037 s	ν_2 (A′) and $2\nu_6$
	1036.5 m				1033 m	
	1029 m					
749 mw, PQR	746 m					
	742 mw	743 m	744 ms, p	683 m	686 m	ν_3 (A′)
646 vs	647 vs 638.5 vs	635 vs	643 ms, p	648 s	651 vs 643 s	ν_4 (A′)
580 sh	582 m 579.5 mw	580 m	582 m, p	570 ms	572 mw	ν_5 (A′)
561 m	561 ms 558.5 m	558 ms	561 w, dp		566 m	ν_{10} (A″)
511 mw, PQR	513 m 512 sh	512 m	516 s, p	509 m	516 m	ν_6 (A′)
	382 w	384 vw	382 w, dp		387 vw	ν_{11} (A″)
	355 vw	360 vw	353 vs, p			ν_7 (A′)
			198 ms, p			ν_8 (A′)
			92 w, dp			ν_{12} (A″)

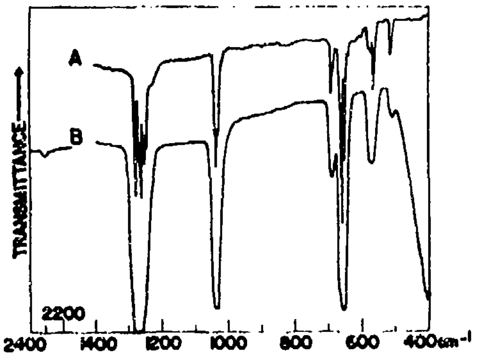
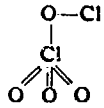


Figure 5.—Infrared spectrum of $BrOClO_3$: trace A, 2.5 μmol of sample in Ar matrix (mole ratio = 400) at 4°K; trace B, gas at 20 mm pressure (5-cm path length).

ous spectra had to be recorded under varying experimental conditions to be able to eliminate bands due to decomposition products.

For a chlorine oxide, having the empirical formula Cl_2O_4, many possible structures can be written. However, the number of observed fundamentals (eight polarized and four depolarized ones), the resemblance between the spectrum of Cl_2O_4 and those of $BrClO_4$, $HOClO_3$,[7] $O_3ClOClO_3$,[4,5] $FClO_3$,[8] $FOClO_3$,[9] and $ClOSO_2F$[10] (see Table II), and its chemical and physical properties[1] can only be explained in terms of the following covalent perchlorate structure of symmetry C_s



For a six-atom molecule of symmetry C_s, a total of 12 fundamentals is expected. Of these, 8 belong to species A′ and should be polarized, and 4 belong to species A″ and should be depolarized. Indeed, three lines (at 561, 382, and 92 cm^{-1}) appear to be depolarized and a fourth one (at 1280 cm^{-1}) may contain a depolarized component. Hence, these four fundamentals are assigned to the four A″ modes. Of these four, the highest and lowest frequency bands can be readily assigned to the antisymmetric ClO_3 stretch and the -O-Cl torsion, respectively. Since the antisymmetric ClO_3 deformation mode should be of higher frequency and infrared intensity than the ClO_3 torsional mode, it is assigned to the 561-cm^{-1} band.

Of the 8 A′ modes, the antisymmetric and symmetric ClO_3 stretches should have the highest frequencies since they involve double bonds. Consequently they are assigned to the bands at 1287 and 1040 cm^{-1}, respectively. The coincidence of the A′ and A″ antisymmetric ClO_3 stretching modes at about 1280 cm^{-1} is supported by the splitting of this band into two intense components in the spectrum of matrix-isolated $ClOClO_3$. Furthermore, the computation of the frequencies of the fundamentals from estimated force constants results in almost identical frequency values for ν_1 and ν_9. The observed ^{35}Cl and ^{37}Cl isotope

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(7) P. A. Giguere and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962).

(8) H. H. Claassen and E. H. Appelman, *Inorg. Chem.*, **9**, 622 (1970).

(9) H. Agahigian, A. P. Gray and G. D. Vickers, *Can. J. Chem.*, **40**, 157 (1962).

(10) K. O. Christe, C. J. Schack, and E. C. Curtis, *Spectrochim. Acta*, *Sect. A*, **26**, 2367 (1970).

TABLE II

FUNDAMENTAL VIBRATIONS OF HALOGEN PERCHLORATES COMPARED TO THOSE OF SIMILAR MOLECULES

Obsd freq, cm⁻¹							Assignment in point group C_s	Approx description of vibration for $YOXO_2Z$
$ClOSO_2F$[a]	$FOClO_3$[b]	$ClOClO_3$	$BrOClO_3$	$HOClO_3$[c]	$O_3ClOClO_3$[d]	$FClO_3$[e]		
1248	1298	1287	1279	1263	1313, 1300	1314	A′ ν_1	$\nu_{as}(XO_2Z)$
855	1049	1040	1039	1050	1060, 1024	1062	ν_2	$\nu_s(XO_2Z)$
703	885	749	683	3560	698, 704		ν_3	$\nu(O-Y)$
831	666	646	648	725		716	ν_4	$\nu(X-O)$
572		580	572	563	598, 571	573	ν_5	$\delta_{scis}(XO_2)$
486		511	509	519	521, 512	549	ν_6	$\delta_{umbrella}(XO_2Z)$
364		355	[278][f]	402	283, 272	414	ν_7	δ_{rock}
<250		198	[159][f]	1200	154		ν_8	$\delta(XOY)$
1481	1298	1271	1262	1326	1300	1314	A″ ν_9	$\nu_{as}(XO_2Z)$
532		561	566	579	567	573	ν_{10}	$\delta_{as}(XO_2Z)$
390		382	387	430	495, 283	414	ν_{11}	Torsion XO_3
<250		92		310			ν_{12}	Torsion O–Y

[a] K. O. Christe, C. J. Schack, and E. C. Curtis, *Spectrochim. Acta, Sect. A*, **26**, 2367 (1970). [b] H. Agahigian, A. P. Gray, and G. D. Vickers, *Can. J. Chem.*, **40**, 157 (1962). [c] P. A. Giguere and R. Savoie, *ibid.*, **40**, 495 (1962). [d] J. D. Witt and R. M. Hammaker, *Chem. Commun.*, 667 (1970), and private communication. [e] H. H. Claassen and E. H. Appelman, *Inorg. Chem.*, **9**, 622 (1970). [f] Computed values.

splittings (see below) confirm these assignments. The complexity of the bands in the 1280- and 1040-cm⁻¹ region renders the assignment to individual bands somewhat uncertain. However, in the matrix spectra of both $ClOClO_3$ and $BrOClO_3$ a similar pattern of band pairs was observed. The splitting of each pair is about 15 cm⁻¹ and the components have a relative intensity of approximately 3:1. The two most intense pairs were chosen to be due to ν_1 and ν_9, respectively. The remaining band pairs (marked by B D in Table I) might be caused by possible Fermi resonance of ν_1 and ν_2 with $2\nu_4$, respectively, and/or matrix site splittings. The bands at 749 and 646 cm⁻¹ should represent the two remaining stretching modes of species A′. Comparison between the spectra of $ClOClO_3$ and $BrOClO_3$ shows that the 749-cm⁻¹ band is shifted to 683 cm⁻¹ in $BrOClO_3$ whereas the 646-cm⁻¹ band exhibits practically no frequency shift. Consequently, the 749 cm⁻¹ must be due to the -O Hal stretching mode and 646 cm⁻¹ represents the O_3Cl O stretch.

There are four frequencies (580, 511, 355, and 198 cm⁻¹) left for assignment to the four deformational modes in species A′. Of these, the Cl O Cl deformation should have the lowest, and the rocking mode, the second lowest frequency. Consequently, they are assigned to 198 and 355 cm⁻¹, respectively. The two remaining frequencies belong to the ClO_2 scissoring and the ClO_3 umbrella deformational modes. Of these two, the umbrella mode should have the higher relative intensity in the Raman spectrum. Furthermore, force constant arguments (see below) favor a higher frequency value for the scissoring mode. This is due to the fact that the scissoring mode involves mainly an angle change between two double bonds, whereas the umbrella mode involves also a change of the angle between the single and double bonds. Consequently, the 580-cm⁻¹ band is assigned to the scissoring, and the 511-cm⁻¹ band, to the umbrella mode. This assignment agrees well with that made for $FClO_3$.[8,11]

Additional support for the above given assignments can be obtained from the observed band contours of gaseous $ClOClO_3$ (see Figure 1). Thus, the bands at 1040, 749, and 511 cm⁻¹, assigned to the A′ modes, ν_2, ν_3, and ν_6, respectively, exhibit a PQR structure close to that expected for parallel bands of an almost symmetric-top molecule.

The vibrational spectrum of $BrOClO_3$ is not as complete as that of $ClOClO_3$ owing to the lack of Raman data. However, nine out of the expected twelve fundamentals were observed. Eight out of the nine observed fundamentals of $BrOClO_3$ show frequencies almost identical with those of $ClOClO_3$ and, hence, were assigned by analogy. The ninth mode exhibits a shift to a lower frequency and is assigned to the O-Br stretching vibration. The magnitude of the shift agrees well with that predicted assuming the O-Br bond strength to be comparable to that of the O-Cl bond and taking the different mass into consideration. Comparison of the vibrational spectra of $ClOClO_3$ and $BrOClO_3$ with those of $HOClO_3$,[7] $O_3ClOClO_3$,[4,5] $FClO_3$,[8] $FOClO_3$,[9] and $ClOSO_2F$[10] (see Table II) shows excellent agreement.

Normal-Coordinated Analysis. The potential and kinetic energy metrics for chlorine and bromine perchlorates were evaluated by a machine method.[12] An assumed geometry was used, with the perchlorate group taken the same as in perchloric acid.[13,14] The remaining parameters, the O-Cl and O-Br bond lengths and the Cl-O-Hal bond angle, were taken to be 1.63 and 1.85 Å and 110°, respectively, based on a comparison with related molecules.[15]

The force constants were adjusted by trial and error with the aid of a time-sharing computer to give a reasonably close fit between the computed frequencies and those reported in Table II. The results obtained for the force constants are $f_{Cl=O} = 8.8$, $f_{Cl-O} = f_{O-Cl} = f_{O-Br} = 2.65$, $f_{O=Cl=O} = 1.9$, $f_{Cl-O-Cl} = 1.4$, and $f_{O=Cl-O} = 1.1$, with the units for the stretching constants being millidynes per ångström and for the bending constants being millidynes per angström per square radian. The bending coordinates were weighted by unit (1 Å) distance. The only significant interactions found were $f_{Cl-O,O=Cl-O}$, which has a value about 0.2 mdyn/(Å radian), and $f_{Cl-O,O-Cl} = f_{Cl-O,O-Br} = 0.35$ mdyn/Å. The isotope shifts were computed using these force constants and are reported in Table III. A somewhat better frequency fit was obtained with slightly different force constants and additional interaction constants with small numerical values, but they were not used here because they are underdetermined

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(11) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **28**, 1128 (1958).

(12) E. C. Curtis, Rocketdyne Report R6768, Oct 1966.

(13) A. H. Clark, B. Beagley, and D. W. J. Cruickshank, *Chem. Commun.*, 14 (1968).

(14) A. H. Clark, B. Beagley, D. W. J. Cruickshank, and T. G. Hewitt, *J. Chem. Soc. A*, 1613 (1970).

(15) L. E. Sutton, *Chem. Soc., Spec. Publ.*, **No. 18** (1965)

TABLE III

COMPARISON BETWEEN OBSERVED AND CALCULATED $^{35}Cl-^{37}Cl$ ISOTOPIC SHIFTS OF $HalOClO_3$

Normal mode	Isotopic shift (cm^{-1}) and rel abund		
	Calcd		Obsd
A′ ν_1	0, 16.2	3:1	0, 15[a,b]
ν_2	0, 4.8	3:1	0, 4.6[b]
ν_3	0, 0.5, 3.1, 3.6	9:3:3:1	0, 3.8[a]
ν_4	0, 0.5, 4.5, 4.9	9:3:3:1	0, 8.5
ν_5	0, 1.8	3:1	0, 2.1[a]
ν_6	0, 0.3, 3.0, 3.3	9:3:3:1	<1.5[a]
ν_7	0, 1.0, 2.8, 3.9	9:3:3:1	Not obsd
ν_8	0, 0.3, 2.5, 2.8	9:3:3:1	Not obsd
A″ ν_9	0, 15.8	3:1	0, 15[a,b]
ν_{10}	0, 1.7	3:1	0, 2.5[a,b]
ν_{11}	0, 0.9	3:1	<1

[a] For $ClOClO_3$. [b] For $BrOClO_3$.

and not particularly transferable between the two perchlorates. The computed potential energy distribution for chlorine perchlorate is given in Table IV.

TABLE IV

POTENTIAL ENERGY DISTRIBUTION FOR CHLORINE PERCHLORATE[a]

A′ ν_1	1287	$0.91f_{Cl-O}$
ν_2	1040	$0.94f_{Cl-O}$
ν_3	749	$0.58f_{O-Cl'} + 0.20f_{ClO-O-Cl'} + 0.15f_{O-Cl-O}$
ν_4	646	$0.78f_{Cl-O} + 0.16f_{O-Cl'} - 0.10f_{Cl-O,O-Cl-O} + 0.10f_{O-Cl-O} - 0.10f_{Cl-O,O-Cl'}$
ν_5	580	$0.92f_{O-Cl-O}$
ν_6	511	$0.44f_{O-Cl-O} + 0.33f_{O-Cl-O} + 0.10f_{Cl-O-Cl}$
ν_7	355	$0.60f_{O-Cl-O} + 0.21f_{O-Cl'}$
ν_8	198	$0.60f_{Cl-O-Cl'} + 0.25f_{O-Cl-O}$
A″ ν_9	1271	$0.94f_{Cl-O}$
ν_{10}	561	$0.99f_{O-Cl-O}$
ν_{11}	382	$1.05f_{O-Cl-O}$

[a] The results do not add up to unity since the less important terms are not shown.

The results for bromine perchlorate were very similar.

Further attempts to refine the force constants using both the usual least-squares methods and the reparameterization method[16] were unsuccessful. This appears to be due to mixing of ν_7 and ν_8. The problem was investigated at some length by varying the interaction constants with the time-sharing computer until we became convinced that any reasonable set of harmonic force constants that fit the other frequencies in the A′ block could not fit ν_7. The same problem occurred with two other molecules with similar geometry, CF_3OF[17] and $ClOSO_2F$.[10]

The failure of the force constants to duplicate the observed $^{35}Cl-^{37}Cl$ isotope splittings for all modes suggests that the chosen valence force field might be too simple. In particular, the frequency shift of 8.5 cm^{-1} observed for ν_4 is about twice that calculated. Since ν_1 is the only mode in the A′ block having an isotope splitting larger than 5 cm^{-1}, mixing between ν_1 and ν_4 is indicated, though difficult to rationalize due to the great dissimilarity of the force constants involved.

Thermodynamic Properties.—The thermodynamic properties for chlorine and bromine perchlorate were computed for the ideal gas using the rigid-rotor harmonic oscillator approximation.[18,19] The vibrational frequencies used were those of Table II. The rotational constants computed from the geometry assumed above were A = 5636, B = 1821, and C = 1808 Mc for chlorine perchlorate and A = 5626, B = 1155, and C = 1150 Mc for bromine perchlorate. The reduced moment of inertia[19] was 24 Gc for chlorine perchlorate and 18 Gc for bromine perchlorate. The thermodynamic properties are given in Tabies V and VI.

TABLE V

COMPUTED THERMODYNAMIC PROPERTIES FOR $ClOClO_3$

T, °K	$C_p°$, cal deg^{-1} mol^{-1}	$H° - H°_0$, kcal mol^{-1}	$-(F° - H°_0)/T$, cal deg^{-1} mol^{-1}	S_0, cal deg^{-1} mol^{-1}
0	0	0	0	0
100	11.451	0.938	51.985	61.362
200	16.471	2.333	59.166	70.829
298.15	20.563	4.161	64.256	78.211
300	20.628	4.199	64.343	78.339
400	23.572	6.418	68.658	84.701
500	25.623	8.883	72.428	90.195
600	27.058	11.522	75.799	95.001
700	28.077	14.281	78.852	99.253
800	28.816	17.128	81.643	103.053
900	29.363	20.038	84.216	106.481
1000	29.778	22.996	86.601	109.597
1100	30.097	25.991	88.823	112.450
1200	30.348	29.013	90.903	115.080
1300	30.549	32.059	92.857	117.518
1400	30.711	35.122	94.701	119.788
1500	30.844	38.200	96.445	121.911
1600	30.954	41.290	98.099	123.905
1700	31.046	44.390	99.673	125.785
1800	31.124	47.498	101.174	127.502
1900	31.191	50.614	102.607	129.246
2000	31.248	53.736	103.980	130.848

TABLE VI

COMPUTED THERMODYNAMIC PROPERTIES FOR $BrOClO_3$[a]

T	$C_p°$, cal deg^{-1} mol^{-1}	$H° - H°_0$, kcal mol^{-1}	$-(F° - H°_0)/T$, cal deg^{-1} mol^{-1}	S_0, cal deg^{-1} mol^{-1}
0	0	0	0	0
100	12.042	0.972	53.975	63.692
200	16.926	2.420	61.434	73.533
298.15	20.898	4.286	66.697	81.073
300	20.961	4.325	66.786	81.202
400	23.819	6.572	71.217	87.649
500	25.809	9.060	75.071	93.191
600	27.202	11.715	78.503	98.027
700	28.190	14.487	81.603	102.299
800	28.907	17.344	84.433	106.112
900	29.438	20.262	87.036	109.549
1000	29.840	23.227	89.446	112.672
1100	30.149	26.227	91.689	115.532
1200	30.393	29.254	93.787	118.166
1300	30.587	32.304	95.757	120.606
1400	30.744	35.371	97.614	122.879
1500	30.873	38.452	99.370	125.005
1600	30.980	41.545	101.035	127.001
1700	31.069	44.647	102.619	128.882
1800	31.145	47.758	104.128	130.660
1900	31.209	50.876	105.569	132.345
2000	31.265	54.000	106.948	133.948

[a] Units are identical with those of Table V.

Acknowledgment.—We are indebted to Dr. D. Pilipovich for continuous encouragement, to Dr J. Silvera for the use of the Raman spectrometer, to Dr. J. D. Witt for the computation of the thermodynamic properties, and to Drs. J. D. Witt and R. M. Hammaker for making their results on Cl_2O_7 available to us prior to publication. This work was supported by the Office of Naval Research, Power Branch.

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(17) P. M. Wilt, Ph.D. Dissertation, Vanderbilt University, 1967; *Diss. Abstr., B*, **28**, 5427 (1968).

(18) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," Wiley, New York, N. Y., 1940.

(19) J. D. Witt (private communication) computed that the barrier to internal rotation is 3.6 kcal based on the assignment given for ν_{11}. This implies that at temperatures below 2000°K internal rotation contributes little to the internal partition function.

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CONTRIBUTION FROM ROCKETDYNE,
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Laser Raman Spectrum of Tetrafluoronitrogen(V) Hexafluoroarsenate(V)

BY K. O. CHRISTE* AND D. PILIPOVICH

Received February 1, 1971

The preparation[1-4] and the vibrational spectrum[5] of $NF_4^+AsF_6^-$ have previously been reported. It was shown that the NF_4^+ cation is tetrahedral.[1-5] Out of the four fundamental vibrations of NF_4^+, the A_1 and the E mode can be observed only in the Raman spectrum. At the time of the previous spectroscopic study,[5] only a very small amount of material and no laser Raman spectrometer were available to us. The observed infrared spectrum was of very good quality; however, owing to a low signal to noise ratio in the Raman spectrum, only tentative assignments could be made at that time for the A_1 and the E mode.

In this note, we wish to report the laser Raman spectrum of $NF_4^+AsF_6^-$ (see Figure 1, trace A). It is shown that ν_1 (A_1) and ν_2 (E) of NF_4^+ occur at 847 and 445 cm^{-1}, respectively. The value of 847 cm^{-1} for ν_1 (A_1) is close to those of 844 and 836 cm^{-1} deduced from the infrared-active[5] combination bands ($\nu_1 + \nu_4$) and ($\nu_1 + \nu_3$), respectively. The symmetry force constants computed with these revised Raman frequencies are $F_{11} = 8.03$ and $F_{22} = 0.74$ mdyn/Å. Adopting for the F_2 block the previously reported values,[5] the internal force constants of NF_4^+ can be calculated (see Table I). These force constants are not unique since in the F_2 block, three force constants had to be computed from two vibrational frequencies using the approximating method of Fadini.[6] For the isoelectronic species, CF_4 and BF_4^-, this method has yielded values close to those of the general valence force field and, hence, may also be a good approximation for NF_4^+. A detailed discussion of the trends observed within this isoelectronic series has previously been given.[5]

TABLE I
FORCE CONSTANTS OF THE ISOELECTRONIC SERIES
NF_4^+, CF_4, BF_4^- (MDYN/Å)

	NF_4^+	CF_4[a]	BF_4^-[a]
f_r	6.22	6.93	4.87
f_{rr}	0.60	0.77	0.62
$f_\alpha - f_{\alpha\alpha'}$	0.98	1.02	0.72
$f_{\alpha\alpha} - f_{\alpha\alpha'}$	0.12	0.16	0.13
$f_{r\alpha} - f_{r\alpha'}$	0.77	0.57	0.43

[a] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer-Verlag, Berlin, 1966, p 69.

The sample used for the present investigation was prepared by the high pressure-temperature method.[4] However, contrary to previous reports,[4] the reaction product was not homogeneous. At the bottom of the Monel reactor, a white, loose solid had accumulated which, according to its elemental analysis, had the approximate composition (in mol %) 93.2 $NF_4^+AsF_6^-$, 5.8 $Ni(AsF_6)_2$, and 1.0 $Cu(AsF_6)_2$. Its vibrational spectrum is depicted by traces A in Figures 1 and 2 and shows the bands expected for the tetrahedral NF_4^+ and the approximately octahedral AsF_6^- ion. About an equal amount of solid product was uniformly distributed over the walls of the reactor. It was pale yellow and, according to its elemental analysis, showed a substantially increased Ni and Cu content. Furthermore, its infrared and Raman spectra (traces B in Figures 1 and 2) show that the bands which in traces A could not be accounted for in terms of octahedral AsF_6^- and tetrahedral NF_4^+ have strongly increased in relative intensity. Therefore, these additional bands must be at-

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(1) K. O. Christe, J. P. Guertin, and A. R. Pavlath, *Inorg. Nucl. Chem. Lett.*, **2**, 83 (1966).

(2) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *ibid.*, **2**, 79 (1966).

(3) J. P. Guertin, K. O. Christe, and A. R. Pavlath, *Inorg. Chem.*, 5, 1921 (1966).

(4) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *ibid.*, **6**, 1156 (1967).

(5) K. O. Christe, J. P. Guertin, A. R. Pavlath, and W. Sawodny, *ibid.*, **6**, 533 (1967).

(6) W. Sawodny, A. Fadini, and K. Ballein, *Spectrochim. Acta*, **21**, 995 (1965).

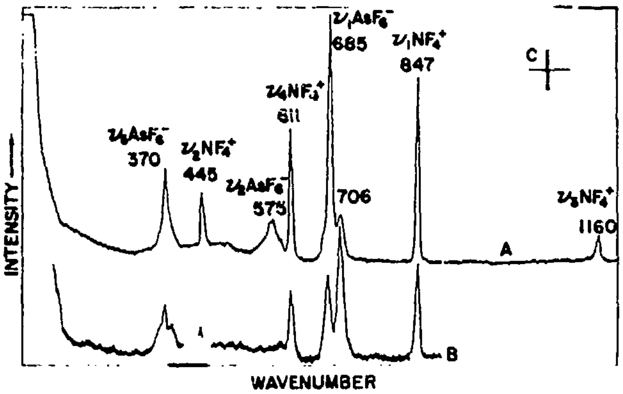

Figure 1.—Replotted Raman spectra of solid $NF_4^+AsF_6^-$ containing smaller (sample I, trace A) and larger (sample II, trace B) amounts of metal salts. C indicates spectral slit width.

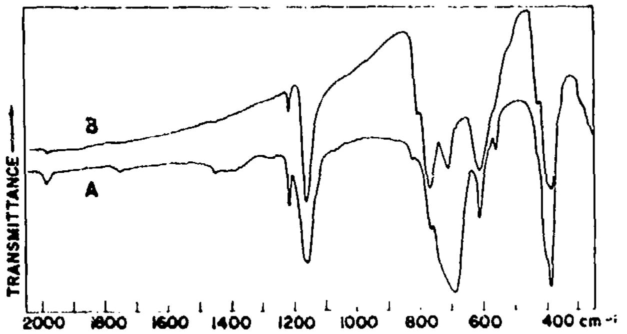

Figure 2.—Infrared spectra of solid $NF_4^+AsF_6^-$. Samples of traces A (AgBr pellet) and B (dry powder between AgCl plates) are identical with those of Figure 1.

tributed to the presence of the metal salts.[7] Furthermore, the previous reports[4] on the hydrolysis of NF_4^+ were confirmed in that NF_3 and O_2 were quantitatively evolved in a 2:1 mole ratio, and no evidence for the formation of nitrogen oxides or oxyfluorides[3] was found.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 1F4Y). Pressures were measured with a Heise-Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nitrogen trifluoride (Air Products) and AsF_5 (Ozark Mahoning Co.) were purified by fractional condensation. Prior to its use, fluorine (Rocketdyne) was passed through a NaF trap to remove HF impurities. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box. The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer as dry powders between AgCl or AgBr windows or in the form of pressed AgBr disks. The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to −25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or melting point capillaries were used as sample containers.

Preparation of $NF_4^+AsF_6^-$. Nitrogen trifluoride (180 mmol), AsF_5 (180 mmol), and F_2 (360 mmol) were heated in a passivated 150-ml Monel cylinder under autogenous pressure to 125° for 20 days. After removal of unreacted starting materials, the cylinder was opened in the glove box and contained about 2.88 g of a solid. About half of the solid had accumulated as a loose white powder (I) at the bottom of the reactor, the rest being distributed in the form of a yellowish layer (II) over the walls of the reactor. *Anal.* Calcd for 93.2 mol % of NF_4AsF_6, 5.8 mol % of $Ni(AsF_6)_2$, and 1.0 mol % of $Cu(AsF_6)_2$: N, 4.50; Ni, 1.21; Cu, 0.22; As, 27.50; total F, 66.59; hydrolyzable F, 6.11; NF_3:O_2 mole ratio, 2.0:1. Found for I: N, 4.64; Ni, 1.21; Cu, 0.23; As, 28.9; total F, 65; hydrolyzable F, 6.2; NF_3:O_2, 2.0:1. Found for II: N, 2.14; Ni, 2.95; Cu, 2.37; As, 28.0; NF_3:O_2, 2.02:1.

Elemental Analysis. For N, Ni, Cu, As, and hydrolyzable F analyses, a weighted sample was hydrolyzed in a Teflon FEP U trap. The total amount of gas (NF_3 + O_2) was measured volumetrically; then NF_3 was separated from O_2 by fractional condensation at −210°, measured, and identified by infrared spectroscopy. The aqueous solution was analyzed for Ni, Cu, and As by atomic absorption, for As by X-ray fluorescence spectroscopy, and for hydrolyzable F both by $Th(NO_3)_4$ titration and by means of a fluoride electrode. For the total fluoride determination, the sample was fused prior to the F^- analysis using the Parr bomb technique (Na_2O_2 + starch).

Acknowledgment.—The author wishes to express his gratitude to Dr. I. Silvera of the Science Center of NAR for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research, Power Branch.

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(7) Since the elemental analysis of the Ni- and Cu-rich sample showed an As content somewhat higher than that expected on the basis of the found N, Ni, and Cu values, we have explored the possible presence of a stable $As_2F_{11}^-$ anion in more detail. Solutions of the salt in HF showed only the ^{19}F nmr lines characteristic for NF_4^+, AsF_6^-, and HF, but no evidence for those previously reported (P. A. W. Dean, R. J. Gillespie, and R. Hulme, *Chem. Commun.*, 990 (1969)) for $As_2F_{11}^-$. When CH_3CN was used as a solvent, interaction with NF_4^+ occurred, resulting in a disappearance of the NF_4^+ signals but in a preservation of the AsF_6^- lines. Again no evidence for the $As_2F_{11}^-$ lines was obtained. Attempts to prepare $Cs^+As_2F_{11}^-$ under conditions similar to those used in the $NF_4^+AsF_6^-$ synthesis, *i.e.*, elevated temperature and pressure, produced exclusively $Cs^+AsF_6^-$. On the basis of these findings and the previously reported instability of $As_2F_{11}^-$ salts (P. A. W. Dean, *et al.*, *Chem. Commun.*, 990 (1969)), the presence of a stable $As_2F_{11}^-$ salt in our sample appears unlikely.

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CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL,
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The Difluorochlorate(V) Anion, $ClO_2F_2^-$. Vibrational Spectrum and Force Constants

BY KARL O. CHRISTE* AND E. C. CURTIS

Received May 3, 1971

The infrared and the Raman spectra of solid $CsF \cdot ClO_2F$ have been recorded. They are consistent with a $ClO_2F_2^-$ anion of symmetry C_{2v}. The structure can be derived from a trigonal bipyramid, where the two F atoms occupy the axial and the two O atoms and the lone electron pair occupy the equatorial positions. A modified valence force field has been computed for $ClO_2F_2^-$, indicating double-bond character for the ClO bonds and rather weak ClF bonds with high ionic contributions.

Introduction

Huggins and Fox have recently reported[1] the existence of $CsClO_2F_2$. However, they did not succeed in obtaining any spectroscopic or structural data on this interesting compound. In this paper, we report the vibrational spectrum and the results of a force-field computation for $CsClO_2F_2$.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ±0.1%). Chloryl fluoride (prepared in this laboratory from $KClO_3$ and F_2[2]) was purified by fractional condensation. Its purity was determined by measuring its vapor pressure and infrared spectrum. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. Because of their hygroscopicity, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on Perkin-Elmer Model 337 and 457 spectrophotometers in the range 4000–250 cm^{-1}.

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(1) D. K. Huggins and W. B. Fox, *Inorg. Nucl. Chem. Lett.*, 6, 337 (1970).

(2) A. Engelbrecht, *Angew. Chem.*, 66, 442 (1954).

TABLE I

VIBRATIONAL SPECTRUM OF $Cs^+ClO_2F_2^-$ AND ITS ASSIGNMENT COMPARED TO THOSE OF SIMILAR MOLECULES AND IONS

Obsd freq, cm^{-1}, and intens										Assignment for XO_2F_2 in point group C_{2v}	Approx description of vibration
$Cs^+ClO_2F_2^-$		XeO_2F_2^{a}									
Ir	Raman	Ir	Raman	ClO_2^- ^{b}	ClO_2^{b}	ClO_2^+ ^{c}	ClO_2F^{d}	ClF_2^{e}	ClF_2^- ^{f}		
1225 1191 vs	1221 (0.8)^g	905 s	902 w	844	1111	1296	1271			$\nu_8(B_2)$	$\nu_{as}(XO_2)$
1070 s	1076 (10) 1064 1055	848 ms	845 vs	786	945	1044	1106			$\nu_1(A_1)$	$\nu_s(XO_2)$
855 vw										$\nu_2 + \nu_6(B_1)$?	
559 m	559 (1.2)	328 ms, sh	333 ms	402	445	521	547			$\nu_2(A_1)$	$\delta_s(XO_2)$
510 vs, br		585 vs	578 w					702	635	$\nu_6(B_1)$	$\nu_{as}(XF_2)$
	480 (1), br									$\nu_5(A_2)$?	τ
330–370 m	363 (10)		490 s					529	475	$\nu_3(A_1)$	$\nu_s(XF_2)$
	337 (8)	324 s 317 ms	313 ms							$\nu_7(B_1)$, $\nu_9(B_2)$	δ_{rock}, δ_{wag}
	198 (0.7)		198 w					328		$\nu_4(A_1)$	$\delta_s(XF_2)$

^{a} H. H. Claassen, *et al.*, *J. Chem. Phys.*, 49, 2531 (1968). ^{b} H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer-Verlag, West Berlin, 1966. ^{c} K. O. Christe, *et al.*, *Inorg. Chem.*, 8, 2489 (1968). ^{d} D. F. Smith, *et al.*, *Spectrochim. Acta*, 20, 1763 (1964). ^{e} H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, 52, 3517 (1970). ^{f} K. O. Christe, *et al.*, *Inorg. Chem.*, 6, 1159 (1967). ^{g} The relative intensities of the Raman bands have not been corrected for the variation of instrument sensitivity with frequency.

The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar ion laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ~−25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or Pyrex or clear Kel-F capillaries were used as sample containers. For the capillaries the transverse viewing–transverse excitation technique and for the conical tube the axial viewing–transverse excitation technique were used.

Preparation of $CsClO_2F_2$.—Dry CsF (7.64 mmol) was placed into a 10-ml prepassivated (with ClF_3) 316 stainless steel cylinder and ClO_2F (22.50 mmol) was added at −196°. The cylinder was kept at −25° for 24 hr and subsequently placed on a mechanical shaker for 24 hr at 25°. Unreacted ClO_2F (16.89 mmol) was removed *in vacuo* at 25°, indicating that 73.4% of the CsF had been converted to $CsClO_2F_2$.

Results and Discussion

Synthesis and Properties.—The synthesis and properties of $CsClO_2F_2$ were in good agreement with those previously reported.[1] The hydrolysis of $CsClO_2F_2$ was studied by exposing a sample of $CsClO_2F_2$ between AgCl plates to atmospheric moisture and by monitoring the changes in its infrared spectrum. It was shown that the decrease of the relative intensity of the bands characteristic for $ClO_2F_2^-$ (see below) was accompanied by the appearance of the bands characteristic[3,4] for the ClO_3^- and HF_2^- anions. This indicates the hydrolysis reaction $ClO_2F_2^- + H_2O \rightarrow ClO_3^- + 2HF$.

Vibrational Spectra.—Figures 1 and 2 show the infrared and Raman spectra, respectively, of solid $CsClO_2F_2$. Weak absorptions owing to ClO_3^- (960, 940, 620, and 480 cm^{-1}) and HF_2^- (1420 and 1230 cm^{-1}) were almost always observed in the infrared spectrum. The appearance of the ClO_3^- and HF_2^- bands in the infrared spectrum is due to the pronounced hygroscopicity of $CsClO_2F_2$ and to the small sample size used for infrared spectroscopy. The observed frequencies are listed in Table I, together with their assignment.

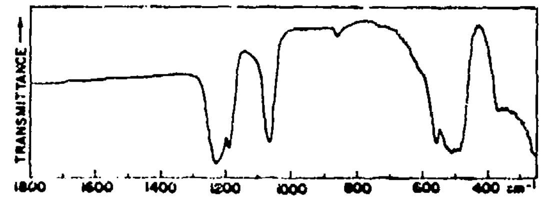

Figure 1.—Infrared spectrum of solid $Cs^+ClO_2F_2^-$ as dry powder in an AgBr disk.

Numerous structural models can be written for $ClO_2F_2^-$. However, their number can be restricted since the chlorine central atom possesses a free electron pair which should be sterically active. Consequently, this chlorine atom should be pentacoordinated, thus resulting in a pseudo-trigonal-bipyramidal structure for $ClO_2F_2^-$. For this structural type, five different arrangements of the ligands are possible. Comparison with the known structures of related molecules, such as substituted phosphorus pentafluorides,[5–10] XeO_2F_2,[11] or $IO_2F_2^-$,[12] shows that the two axial positions are always occupied by the two most electronegative ligands.[13] Theoretical explanations for this behavior have previously been given.[13–16] Therefore, the most plausible structure for $ClO_2F_2^-$ is

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(3) J. L. Hollenberg and D. A. Dows, *Spectrochim. Acta*, 16, 1155 (1960).

(4) J. A. Salthouse and T. C. Waddington, *J. Chem. Phys.*, 48, 5274 (1968).

(5) I. R. Beattie, K. M. S. Livingston, and D. J. Reynolds, *ibid.*, 51, 4269 (1969).

(6) R. R. Holmes, *ibid.*, 46, 3730 (1967), and references cited therein.

(7) J. A. Salthouse and T. C. Waddington, *Spectrochim. Acta, Part A*, 23, 1069 (1967).

(8) J. E. Griffiths, *J. Chem. Phys.*, 49, 1307 (1968).

(9) J. Goubeau, R. Baumgärtner, and H. Weiss, *Z. Anorg. Allg. Chem.*, 348, 286 (1966).

(10) A. J. Downs and R. Schmutzler, *Spectrochim. Acta, Part A*, 23, 681 (1967).

(11) H. H. Claassen, E. L. Gasner, H. Kim, and J. L. Huston, *J. Chem. Phys.*, 49, 253 (1968).

(12) L. Helmholz and M. T. Rogers, *J. Amer. Chem. Soc.*, 62, 1537 (1940).

(13) R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, 6, 749 (1967).

(14) R. J. Gillespie, *ibid.*, 6, 819 (1967).

(15) P. C. Van Der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, 88, 3255 (1966).

(16) L. S. Bartell, *Inorg. Chem.*, 5, 1635 (1966).

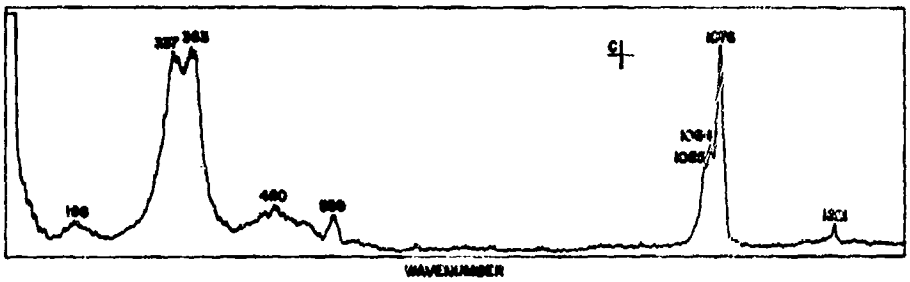
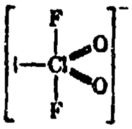


Figure 2.—Raman spectrum of solid $Cs^+ClO_2F_2^-$; sample container, glass capillary; C indicates spectral slit width.



This type of structure has also been suggested[11] for XeO_2F_2 which is isoelectronic with $ClO_2F_2^-$.

The correctness of the proposed model can be tested by inspection of the observed vibrational spectrum. Spectroscopically, this model should contain the elements of the ClO_2^+ cation and the ClF_2^- anion, both of which have recently been characterized.[17-20] The ClO_2^+ cation is preferred over the ClO_2 radical and ClO_2^- anion because ClO_2^+ and $ClO_2F_2^-$ contain a chlorine of the same oxidation state (+V). Furthermore, in $ClO_2F_2^-$, the electron-withdrawing effect of the two highly electronegative fluorine ligands is expected partially to compensate for the bond weakening influence of the formal negative charge. On the other hand, one should expect the two ClF bonds to be rather weak for the following reasons. Generally, in chlorine fluorides, replacement of two fluorine atoms by one doubly bonded oxygen atom significantly weakens the remaining ClF bond.[21] Furthermore, the formal negative charge in anions always decreases the ClF bond strength by increasing the ionic contribution to these bonds. This can be easily understood since the formal negative charge will not be concentrated at the central atom but will be distributed mainly over the highly electronegative fluorine ligands. Since $ClO_2F_2^-$ contains two doubly bonded oxygen atoms and a formal negative charge, the ClF bonds in $ClO_2F_2^-$ should be at least as weak as or weaker than in ClF_2^-. A closer inspection of Table I immediately reveals that the above predictions are indeed correct. The three fundamentals involving only a motion of the ClO_2 part of the ion exhibit frequencies very close to those of ClO_2^+ [17] and ClO_2F.[22] The bands assignable to the three corresponding ClF_2 motions show frequencies somewhat lower than those[20] observed for ClF_2^-.

All nine fundamentals expected for XO_2F_2 of symmetry C_{2v} (these are classified as 4 A_1 + A_2 + 2 B_1 + 2 B_2) were observed if a coincidence of $\nu_7(B_1)$ and $\nu_9(B_2)$ at 337 cm^{-1} is assumed. This double coincidence might account for the surprisingly high relative intensity of the 337-cm^{-1} Raman band and has also been observed[11] for isoelectronic XeO_2F_2. The assignment of the observed bands to the individual modes is straightforward and was made by comparison with the known spectra of the related molecules listed in Table I. Comparison between the corresponding XF modes in XeO_2F_2[11] and $ClO_2F_2^-$ shows that the deformational modes have similar frequencies but that the XeF stretching frequencies are considerably higher than the ClF ones. This is not surprising since Cl and Xe do not belong to the same period of the periodic system. Generally, by going to the next higher period, the electronegativity of the central atom decreases and its size increases, thus resulting in an increase of the XF stretching and a decrease of the XF deformation force constants, respectively. This effect causes the stretching and deformation frequencies to move further apart with increasing mass number and has been observed for several series of related molecules and ions, such as ClF_5, BrF_5, IF_5;[23] SF_5^-, SeF_5^-, TeF_5^-;[24] ClF_2^+, BrF_2^+;[25] or ClF_4^-, BrF_4^-.[26] The assignment of the weak and broad Raman band at 480 cm^{-1} to $\nu_5(A_2)$ should be considered tentative. This band may contain some contribution from $\nu_6(B_1)$; however, its band center at 480 cm^{-1} differs by 30 cm^{-1} from the band center observed for ν_6 in the infrared spectrum (510 cm^{-1}) and, hence, should belong to a different mode. In addition to the bands assigned to fundamental vibrations, a weak band was observed at 855 cm^{-1} in the infrared spectrum of $ClO_2F_2^-$. This band cannot be due to a fundamental vibration and, hence, is assigned to the combination band, ν_2 + $\nu_6(B_1)$. The splitting of $\nu_1(A_1)$ into three components in the Raman spectrum and of $\nu_8(B_2)$ into two components in the infrared spectrum is too large to be due to the two different chlorine isotopes. One would expect the isotope splittings in $ClO_2F_2^-$ to be similar to those found for ClO_2^+ [17] and ClO_2F.[22] Since the $ClO_2F_2^-$ spectra were recorded for crystalline samples, other effects, such as site symmetry splittings, are possible.

In summary, the observed number of bands, their frequencies, and relative intensities in both the infrared and Raman spectra are consistent with the predicted pseudo-trigonal-bipyramidal structure of symmetry C_{2v}. The agreement between the spectrum of $ClO_2F_2^-$ and those of related molecules is excellent.

Force Constants.—A normal-coordinate analysis was carried out to aid in the spectral assignment. The

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(17) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, 8, 2489 (1969).

(18) H. A. Carter, W. M. Johnson, and F. Aubke, *Can. J. Chem.*, 47, 4619 (1969).

(19) A. I. Karelin, K. Nikitina, Yu. Ya. Kharitonov, and V. Ya. Rosolovskii, *Russ. J. Inorg. Chem.*, 15, 941 (1970).

(20) K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, 6, 1159 (1967).

(21) K. O. Christe, unpublished results.

(22) D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, 20, 1763 (1964).

(23) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, 42, 2236 (1965).

(24) K. O. Christe, C. J. Schack, E. C. Curtis, and D. Pilipovich, *Inorg. Chem.* in press.

(25) K. O. Christe and C. J. Schack, *ibid.*, 9, 2296 (1970).

(26) K. O. Christe and C. J. Schack, *ibid.*, 9, 1852 (1970).

kinetic and potential energy metrics were computed by a machine method,[27] assuming the following geometry: $r_{ClF} = 1.79$ Å, $R_{ClO} = 1.43$ Å, $\alpha = \angle OClO = 120°$, $\beta = \angle OClF = 90°$, and $\angle FClF = 180°$. The ClF distance was taken as somewhat larger than those[28] of the two longer bonds in ClF_3 due to the uncommonly low stretching frequencies in $ClO_2F_2^-$. The ClO distance was estimated from the bond length–frequency correlation of Robinson.[29] The bond angles were assumed to be those of an ideal trigonal bipyramid, although they might be slightly reduced due to repulsion by the lone pair in accord with the Gillespie–Nyholm theory.[30]

The force constants were calculated by trial and error with the aid of a time-sharing computer to get exact agreement between the observed and computed frequencies using the simplest possible modified valence force field, *i.e.*, keeping the number of nonzero off-diagonal interaction terms at a minimum. Owing to the underdetermined nature of the problem (17 force constants from 9 vibrational frequencies), unique force constants could not be computed. However, numerical experiments established that some of the principal force constants are quite independent of the chosen interaction constants and, hence, should approach those of a general valence force field. The computed values are $f_R = 8.3$, $f_{RR} = 0.1$, $f_r = 1.6$, and $f_{rr} = -0.1$ mdyn/Å; $f_\alpha = 1.95$, $f_\beta = 1.2$, $f_{\beta\beta}' = 0.57$, and $f_{\beta\beta} = 0.1$ mdyn/Å radian^2; and $f_{r\beta} - f_{r\beta}' = 0.3$ mdyn/Å radian. The deformation coordinates were weighted by unit (1 Å) distance.

The force constants of greatest interest are the stretching force constants since they are a direct measure for the strength of the various bonds. Comparison with the values obtained for a number of related molecules and ions (see Table II) indicates for $ClO_2F_2^-$ double-bond character for the two chlorine–oxygen bonds and unusually weak ClF bonds. The value of the Cl=O stretching force constant, f_R, is slightly lower than those in ClO_2^+ [17] and ClO_2F.[22] This slight decrease might be explained by factors such as the influence of the formal negative charge, change in hybridization due to the altered coordination number of the central atom, and different physical states (solid *vs.* gas). Hence, no attempt will be made to evaluate the relative contributions from each effect.

TABLE II

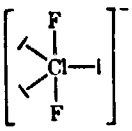
STRETCHING FORCE CONSTANTS (MDYN/Å) OF $ClO_2F_2^-$ COMPARED TO THOSE OF RELATED MOLECULES AND IONS

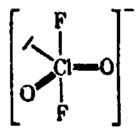
	$ClO_2F_2^-$	$ClO_2^{+\,a}$	$ClO_2{}^b$	$ClO_3^{-\,c}$	ClO_2F^d	$ClF_2^{-\,e}$	$ClF_4^{-\,f}$	ClF^g	$ClF_2^{+\,h}$
f_R	8.3	8.96	7.02	4.26	9.07				
f_{RR}	0.1	−0.45	−0.17	0.11	−0.12				
f_r	1.6				2.53	2.35	2.11	4.36	4.74
f_{rr}	−0.1					0.17	0.23		0.14

[a] Reference 17. [b] M. G. Krishna Pillai and R. F. Curl, Jr., *J. Chem. Phys.*, **37**, 2921 (1962). [c] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer-Verlag, West Berlin, 1966. [d] Reference 22. [e] Reference 20. [f] K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, **374**, 306 (1970). [g] A. H. Nielsen and E. A. Jones, *J. Chem. Phys.*, **19**, 1117 (1951). [h] Reference 25.

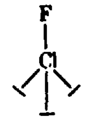
Whereas the ClO bonds in $ClO_2F_2^-$ exhibit double-bond character, the value of the ClF stretching force constant, f_r, of 1.6 mdyn/Å is unusually low. In addition to the reasons discussed above, *i.e.*, oxygen substitution and formal negative charge, weak ClF bonds might be expected since $ClO_2F_2^-$ has a pseudo-trigonal-bipyramidal structure. As pointed out previously,[31] this type of structure appears to be energetically unfavorable as also indicated by the low thermal stability of the CsF·ClO_2F adduct.

Comparison of the stretching force constant of $ClF_2O_2^-$ with that[20] of ClF_2^- is particularly interesting owing to their close structural relationship. Both anions can be derived from a pseudo trigonal bipyramid. In $ClO_2F_2^-$, two of the three free electron pairs on the Cl in ClF_2^- have been replaced by two doubly bonded oxygen atoms without significantly changing the geometry of the rest of the ion, *i.e.*





Hence, a pronounced decrease of the ClF stretching force constant from ClF_2^- (2.35 mdyn/Å)[20] to $ClF_2O_2^-$ (1.6 mdyn/Å) should truly reflect the influence of the doubly bonded oxygen ligands. Comparison of the related pair



shows that the decrease of f_r (see Table II) from ClF to ClO_2F is even larger than for the pair ClF_2^-, $ClO_2F_2^-$. The same trend has been found for a number of other molecules[21] and, hence, appears to be quite general.

The small negative value of the ClF stretch–stretch interaction constant, f_{rr}, is comparable to that found[32] for KrF_2 for which an explanation was given by Coulson.[33] The values found for the OClF and OClO deformation constants are as expected. The large values found for the interaction constant $f_{\beta\beta}'$ and the stretch–bend interaction term, $f_{r\beta}$, are in accord with those obtained for the halogen pentafluoride molecules.[22]

From the above discussion of the stretching force constants, it became obvious that the Cl=O bonds are predominantly covalent, whereas the ClF bonds contain strong contributions from ionic bonds. This finding confirms the previous predictions[24] postulating the following bond model for a trigonal-bipyramidal type moiety with a free electron pair on the central atom. The two most electronegative ligands, *i.e.*, fluorine atoms, occupy the axial positions and the two oxygen atoms and the free electron pair the three equatorial positions of the trigonal bipyramid. The equatorial bonds should have mainly sp^2 character (ignoring the double-bond contributions), whereas the axial bonds involve

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mainly a delocalized p-electron pair of the chlorine central atom for the formation of a semiionic three-center four-electron p–σ bond pair.[20,35–38] For an ideal semiionic three-center four-electron bond, one should therefore expect f_r to have a value about half that of a covalent ClF bond. The low value of 1.6 mdyn/Å obtained for $ClO_2F_2^-$ obviously fulfills these requirements (covalent ClF bonds show stretching force constants ranging from about 3.5 to 4.7 mdyn/Å) and supports the above bond model.

Acknowledgment.—The authors wish to express their gratitude to Drs. D. Pilipovich and C. J. Schack of Rocketdyne for helpful discussions and to Dr. I. Silvera of the Science Center of North American Rockwell for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research, Power Branch.

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Contribution from Rocketdyne,
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Canoga Park, California 91304

Selenium Chloride Pentafluoride

By C. J. Schack,* R. D. Wilson, and J. F. Hon

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The existence of SF_5Cl has been known[1] for some time, while TeF_5Cl has been reported[2] more recently. However, no report concerning the preparation of the intermediate member of the S-Se-Te triad, SeF_5Cl, has appeared. Since the best synthetic routes[3] to SF_5Cl involve chlorination of sulfur fluoride substrates and since this reaction had been found to be enhanced by added alkali metal fluorides,[4] this technique was applied to the formation of SeF_5Cl. We wish now to report the synthesis and characterization of this new compound.

Experimental Section

Apparatus and Materials.—The equipment used in this work has been described[5] and was supplemented with a Perkin-Elmer Model 457 Infracord and a 10-cm, stainless steel infrared cell fitted with AgBr windows. Details concerning the preparation or treatment of ClF, $ClSO_3F$, and CsF have been given.[5] Additional materials were purchased and used as received.

SeF_4.—Selenium tetrafluoride was first prepared from Se powder and ClF according to Pitts and Jache.[6] Later it was determined that ClF_3 performed equally well in this reaction, thereby circumventing the need to prepare ClF. Typically, a prepassivated 30-ml stainless steel cylinder was loaded with Se powder (14.2 g-atoms) in the drybox. Chlorine trifluoride (20.3 mmol) was added at −196° from a vacuum line and the cylinder allowed to warm slowly to ambient temperature where it was maintained for 1 day or until needed. Vacuum fractionation through U traps cooled to −30, −78, and −196° furnished SeF_4 (12.3 mmol) in the highest temperature trap. The purity and identity of the SeF_4 were verified by its vapor pressure[6] and infrared spectrum.[7] Based on the equation 3Se + $4ClF_3$

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$\rightarrow$ $3SeF_4 + 2Cl_2$, the yield was 87%, a value comparable to that found for ClF reactions.

SeF_5Cl.—Selenium chloride pentafluoride was prepared by first forming the solid complex $CsSeF_5$ from CsF and SeF_4.[8] Weighed samples of the complex were placed in prepassivated cylinders and $ClSO_3F$ was added at −196°. After warming to room temperature for several hours or more, the volatile products were separated by fractional condensation at −95, −112, and −196°. Unreacted $ClSO_3F$ was retained at −95° while by-products and impurities such as ClF, $FClO_2$, and Cl_2 passed into the trap cooled to −196°. Pure SeF_5Cl was found in the −112° fraction. From 4.50 mmol of $CsSeF_5$, 4.13 mmol of SeF_5Cl was obtained, corresponding to a yield of 91.7% for the equation $CsSeF_5 + ClSO_3F \rightarrow CsSO_3F + SeF_5Cl$. The presence of uncomplexed CsF in the salt does not inhibit the formation of SeF_5Cl directly but does result in the loss of some $ClSO_3F$ by reaction to form ClF.[9]

Because the system CsF–SF_4–ClF was very effective[4] in producing SF_5Cl, it was expected that CsF–SeF_4–ClF would behave similarly. Such was not the case and unreacted ClF was always fully recoverable after 1 day or several weeks in contact with $CsSeF_5$. However, in the course of preparing SeF_4 from Se and ClF or ClF_3, it was found that excesses of the chlorine fluorides gave detectable yields of SeF_5Cl. To determine the extent of this reaction, 4.19 mmol of SeF_4 and 4.21 mmol of ClF were placed in a 10-ml stainless steel cylinder and kept at ambient temperature for 8 days. Separation of the products by fractional condensation led to the recovery of unreacted SeF_4 and ClF (1.45 mmol of each), as well as trace amounts of SeF_6 and Cl_2. The main product was SeF_5Cl (2.62 mmol), representing a 95% yield based on the SeF_4 that had reacted. With ClF_3, up to 10% yields of SeF_5Cl were obtained but always accompanied by much greater amounts of SeF_6. Thus the direct reaction of SeF_4 and ClF affords an alternate, albeit less efficient, route to SeF_5Cl.

Properties of SeF_5Cl.—Selenium chloride pentafluoride is colorless as a gas, liquid, or solid. It is stable at ambient temperature when stored in clean, dry, passivated stainless steel cylinders. However, contact with glass always resulted in significant decomposition. Even glassware suitably dry and otherwise prepared for the manipulation of ClF_3 did not serve for handling SeF_5Cl. It seems likely that this property hindered the earlier discovery of this compound.

Analysis.—A 0.2001-g sample of SeF_5Cl was hydrolyzed with excess standardized NaOH solution in a glass ampoule fitted with a Teflon Fischer–Porter valve. Fluoride, selenium, and base consumption were determined as reported by Smith and Cady.[9] Fluoride was also determined by the usual thorium nitrate titration. The amount of base consumed was calculated, assuming the hydrolysis equation $SeF_5Cl + 8OH^- \rightarrow SeO_4^{2-} + 4H_2O + 5F^- + Cl^-$. *Anal.* Calcd for SeF_5Cl: Se, 37.71; F, 45.37; OH^- consumed, 8.00 equiv/mol. Found: Se, 37.98; F, 45.18; OH^- consumed, 7.82 equiv/mol.

Molecular Weight.—The molecular weight of the compound as determined by vapor density, assuming ideal gas behavior, was 208 (calcd 209.5).

Vapor Pressure, Boiling Point, and Melting Point.—The vapor (sublimation) pressures of SeF_5Cl over the temperature range −79 to +3° are as follows [T (°C), P (mm)]: −78.7, 6; −64.4, 19; −45.3, 66; −32.2, 142; −23.0, 220; 0.0, 630; 3.5, 729. The pressure–temperature relationship is described by the equation $\log P_{mm} = 7.779 - 1360/T°K$. The normal boiling point calculated from the equation is 4.5°, with a heat of vaporization of 6.22 kcal/mol and a Trouton constant of 22.4. Under its own vapor, the compound melts at −19°. Since part of the pressure–temperature data given are below the melting point, it is actually a sublimation pressure and not a vapor pressure. However, pressure values obtained above and below the melting point were nearly on the same line, indicating little difference in the heats of sublimation and vaporization and consequently a very low heat of fusion.

Infrared Spectrum.—The infrared spectrum of SeF_5Cl in the range 4000–250 cm^{-1} shows several absorptions with the most prominent ones occurring at 745 (vvs), 440 (vs), 420 (s), 385 (w), and 335 cm^{-1} (m). The two highest frequencies and the strongest bands noted are comparable to those of bands of similar intensity and position in related hexacoordinate selenium fluorides. Thus, the two strongest bands for SeF_6[10] occur at 780 and 430 cm^{-1} and for SeF_5OF[11] at 750 and 422 cm^{-1}. That these bands are typical of the SeF_5 group is shown by their presence in a series of substituted SeF_5 compounds.[11] A detailed analysis of the vibrational spectrum of SeF_5Cl is in progress.[12]

Nuclear Magnetic Resonance Spectrum.—The ^{19}F nmr spectrum of SeF_5Cl is shown in Figure 1. It is an AB_4 spectrum and resembles that of SF_5Cl[13] so closely as to be virtually identical. The reported[13] chemical shifts for SF_5Cl when converted to a $CFCl_3$ reference point are −62.3 and −125.6 ppm, respectively, for the axial and equatorial fluorines. For SeF_5Cl, the corresponding values taken from Figure 1 are −71.3 and −132.0 ppm. The only part of the spectrum of SeF_5Cl not identical with the SF_5Cl example is the appearance of the small satellite lines due to ^{77}Se–^{19}F coupling. The observed coupling constant of 629 Hz is furthermore comparable to selenium–fluorine coupling in compounds which contain a chlorine bonded to the selenium central atom as in SeOFCl, where a value of 647 Hz was reported.[14]

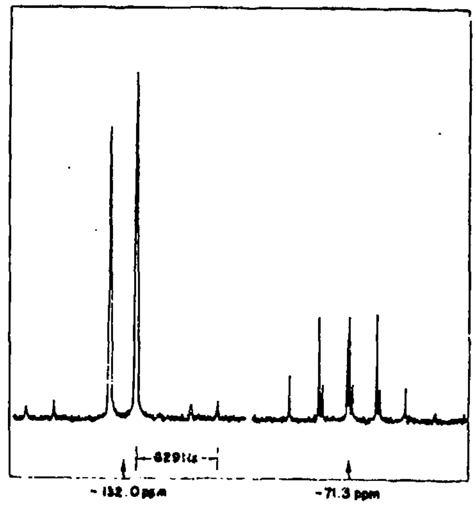

Figure 1.—The ^{19}F nmr spectrum of SeF_5Cl.

Acknowledgment.—The authors gratefully acknowledge support for this work by the Office of Naval Research, Power Branch. We are also indebted to Drs. D. Pilipovich and K. O. Christe for helpful discussion.

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CONTRIBUTION FROM THE NORTH AMERICAN ROCKWELL SCIENCE CENTER, THOUSAND OAKS, CALIFORNIA 91360, AND
ROCKETDYNE DIVISION, NORTH AMERICAN ROCKWELL CORPORATION, CANOGA PARK, CALIFORNIA 91304

The Crystal Structure of $[BrF_4^+][Sb_2F_{11}^-]$

BY M. D. LIND* AND K. O. CHRISTE

Received June 7, 1971

Crystals of the 1:2 adduct formed by BrF_5 and SbF_5 consist of infinite chains of discrete BrF_4^+ and $Sb_2F_{11}^-$ ions coupled by relatively weak fluorine bridges and, accordingly, should be formulated as $[BrF_4^+][Sb_2F_{11}^-]$. This is the first direct evidence for the existence of the BrF_4^+ ion. The crystals are monoclinic with the most probable space group $P2_1/a$, lattice constants $a = 14.19 \pm 0.03$, $b = 14.50 \pm 0.03$, $c = 5.27 \pm 0.01$ Å, $\beta = 90.6 \pm 0.1°$, and four formula units per unit cell; the calculated density is 3.72 g cm^{-3}. The structural parameters were refined by the method of least-squares with visually estimated Weissenberg photographic intensity data. The final value of the conventional agreement index R was 0.14 for 773 reflections having $|F_o|$ greater than $\sigma(|F_o|)$.

Introduction

Previous investigations of solid halogen fluoride adducts have provided evidence that some are predominantly ionic[1–4] and others are predominantly covalent.[5–7] Infrared and Raman spectroscopic studies[4] of the 1:2 adduct[8] formed by BrF_5 and SbF_5 yielded

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equivocal results concerning the nature of this compound because of the large number of possible fundamental vibrations and the low symmetry of the bromine and antimony environments. For the same reasons, the arguments recently presented by Meinert and Gross[9] in favor of the ionic structure are not convincing. To resolve the ambiguity, we have determined the structure from single-crystal X-ray diffraction data. Our investigation was complicated by the marginal stability of the adduct and its tendency to decompose on contact with atmospheric moisture and with glass.

Experimental Section

Preparation of Crystals.—The metal–Teflon FEP vacuum system used and the preparation of $BrF_5 \cdot 2SbF_5$ have been described elsewhere.[4] The single crystals were grown by slow sublimation at 30° in dry N_2. In a dry N_2 glove box, they were transferred to Teflon FEP capillaries, which were subsequently sealed with high melting point Halocarbon wax. A powder X-ray diffraction photograph of crushed single crystals was identical with that of the polycrystalline material from which the single crystals were grown and for which the composition was established by quantitative synthesis.[4]

Crystallographic Data.—Oscillation, Weissenberg, and Buerger precession photographs were obtained with Zr-filtered Mo Kα (λ 0.7107 Å) radiation. These data showed that the crystals have monoclinic symmetry. From the systematic extinctions, $h0l$ with h odd and $0k0$ with k odd, the most probable space group was determined to be $P2_1/a$. The lattice constants, measured from Buerger precession photographs taken at 23°, are $a = 14.19 \pm 0.03$, $b = 14.50 \pm 0.03$, $c = 5.27 \pm 0.01$ Å, $\beta = 90.6 \pm 0.1°$, and $V = 1085$ Å^3. Assuming that the unit cell contains four empirical formula units $BrSb_2F_{11}$ of formula weight 608.4, the calculated density is 3.72 g cm^{-3}. The density of the crystals has not been measured, but the calculated volume per fluorine atom, 18.1 Å^3, is very nearly the value expected for approximately close-packed fluorine atoms.[1,10] For Mo Kα radiation the linear absorption coefficient of the crystals is 9.15 mm^{-1}.

Intensity Data.—The X-ray diffraction intensities were determined from Zr-filtered Mo Kα multiple-film equiinclination Weissenberg photographs by visual comparison with an intensity scale. The specimen was approximately 0.15 × 0.2 × 0.4 mm in dimension with the longest direction nearly parallel to the capillary axis. The axis of rotation was the crystallographic a axis, because it was the axis most nearly aligned with the capillary axis. In each of the reciprocal lattice levels $h = 0$–13, intensities were measured in the range $(\sin \theta)/\lambda \leq 0.65$. A total of 892 independent reflections having intensities above background was measured. Omitted from the intensity measurements were several reflections cut off by the Weissenberg camera beam stop and six reflections too intense to be measured with the intensity scale employed. Within the range of the measurements, there were a large number of reflections too weak to be observed.

After the set of Weissenberg photographs was complete, the $h = 0$ level Weissenberg was repeated to verify that there had been no appreciable decomposition of the crystal. Later, however, the crystal did decompose, and, unfortunately, this happened before its precise shape and dimensions had been recorded; therefore, accurate absorption corrections were impossible, and none was made. We estimate that the errors in intensities caused by absorption are no greater than 8%.

The intensities were reduced to a set of relative structure amplitudes $|F_o(hkl)|$ by application of the appropriate Lorentz–polarization factors and extraction of the square roots.

Determination of the Structure

The four bromine, eight antimony, and sixty fluorine atoms per unit cell are all in the fourfold general positions of space group $P2_1/a$, the equivalent positions of which are x, y, z; $-x, -y, -z$; $^1/_2 + x, ^1/_2 - y, z$; $^1/_2 - x, ^1/_2 + y, -z$. The asymmetric unit of the structure consists of one $BrSb_2F_{11}$ formula unit or eighteen atoms.

The arrangement of the atoms was deduced from the three-dimensional Patterson function and from the three-dimensional Fourier electron density function calculated with phases determined by the bromine and antimony contributions to the structure factors.

The positional parameters were refined by the method of least squares.[11] The function minimized was $\Sigma w(|F_o| - k_h|F_c|)^2$. A modification of the Hughes[12] weighting procedure was used: for $|F_o| > 100$, $w = 100/|F_o|^2$; for $100 \geq |F_o| > 25$, $w = 1/100$; for $|F_o| \leq 25$, $w = 1/625$. Separate scale factors k_h were used for each of the Weissenberg levels. Scattering factors were those for the neutral atoms given by Cromer and Waber.[13] The real parts of the anomalous dispersion corrections for bromine and antimony given by Cromer[14] were applied, but the imaginary parts were neglected.

The thermal parameters were kept isotropic until the agreement index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ had decreased to about 0.20, after which the thermal parameters of the bromine and antimony atoms were allowed to become anisotropic. With anisotropic thermal parameters it was necessary to hold at least one scale factor constant; therefore, the scale factors for levels $h = 0$–2 were alternately held constant in successive least-squares cycles. Anisotropic thermal parameters of the fluorine atoms were not determined because of the large number of variable parameters this would entail.

The final values of the parameters are given in Table I. In the final refinement cycle, the largest parameter change was 18% of the estimated standard error in that parameter value and most were much smaller. After convergence, the agreement index R, defined above, was 0.14 for the 773 reflections having $|F_o|$ greater than σ $(= w^{-1/2})$. Including the 119 reflections having $|F_o|$ observable but less than σ, the index R was 0.15. For the full set of 892 data, the weighted agreement index R_w was 0.17, and the standard deviation of an observation of unit weight SIG1 was 1.2. Table II compares the $|F_o|$ values with the F_c calculated from the final parameter values.[15] F_c's were calculated for the reflections too weak to be observed and were found to be satisfactorily small.

TABLE I

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD ERRORS[a]

	10^4x $(10^4\sigma_x)$	10^4y $(10^4\sigma_y)$	10^4z $(10^4\sigma_z)$	B (σ_B), Å^2
Br	219 (4)	1478 (5)	3015 (10)	2.85[b]
Sb(1)	1510 (4)	6492 (5)	932 (7)	4.29[b]
Sb(2)	3149 (4)	8532 (3)	3945 (9)	3.30[b]
F(1)	997 (30)	613 (28)	4069 (63)	5.06 (1.05)
F(2)	4293 (33)	674 (30)	47 (65)	5.50 (1.14)
F(3)	2837 (34)	1482 (37)	1562 (66)	6.55 (1.22)
F(4)	4191 (31)	2414 (26)	654 (54)	4.70 (1.01)
F(5)	1171 (23)	2525 (19)	4841 (49)	3.21 (0.74)
F(6)	2708 (27)	3450 (26)	3530 (51)	4.15 (0.88)
F(7)	997 (44)	4405 (41)	4796 (92)	7.89 (1.69)
F(8)	4435 (22)	4285 (18)	1386 (43)	2.81 (0.70)
F(9)	2245 (33)	5733 (28)	2641 (68)	5.73 (1.19)
F(10)	806 (53)	6322 (52)	3657 (99)	9.42 (2.17)
F(11)	4049 (34)	6454 (38)	4 (75)	6.55 (1.24)
F(12)	2355 (33)	7615 (27)	2330 (62)	5.07 (1.18)
F(13)	541 (33)	8389 (29)	4292 (62)	5.47 (1.17)
F(14)	3988 (36)	8298 (29)	959 (67)	6.13 (1.36)
F(15)	2480 (26)	9409 (24)	1989 (54)	3.99 (0.85)

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Br	33 (8)	20 (2)	535 (23)	−1 (3)	−42 (6)	−2 (10)
Sb(1)	78 (9)	38 (2)	366 (13)	−2 (3)	−24 (5)	−3 (7)
Sb(2)	32 (8)	25 (2)	655 (16)	4 (4)	39 (4)	−3 (9)

[a] The β_{ij} are for the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The isotropic thermal parameters were calculated as $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

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(15) Table II will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG)[a]

		(a) Br Environment			
Br-F(1)	1.76 ± 0.12	F(1)-F(8)	2.62 ± 0.15	F(1)-Br-F(8)	95.5 ± 5.0
Br-F(8)	1.78 ± 0.09	F(1)-F(13)	2.76 ± 0.18	F(1)-Br-F(13)	101.9 ± 5.5
Br-F(13)	1.80 ± 0.12	F(1)-F(11)	2.47 ± 0.17	F(1)-Br-F(11)	84.6 ± 5.9
Br-F(11)	1.91 ± 0.13	F(8)-F(13)	2.62 ± 0.12	F(8)-Br-F(13)	94.0 ± 4.9
Av	1.81	F(8)-F(11)	2.52 ± 0.17	F(8)-Br-F(11)	85.9 ± 5.3
		F(1)-F(5)	2.81 ± 0.14	F(1)-Br-F(5)	88.5 ± 4.5
Br-F(5)	2.24 ± 0.10	Av	2.60	Av	92.4
Br-F(4)	2.49 ± 0.11				
		F(8)-F(4)	2.76 ± 0.14	F(8)-Br-F(4)	78.5 ± 3.9
		F(13)-F(5)	2.81 ± 0.17	F(13)-Br-F(5)	87.3 ± 4.7
		F(13)-F(4)	3.04 ± 0.14	F(13)-Br-F(4)	88.4 ± 4.8
F(1)-Br-F(4)	168.5 ± 4.2	F(11)-F(5)	3.00 ± 0.16	F(11)-Br-F(5)	92.2 ± 5.1
F(8)-Br-F(5)	175.4 ± 3.5	F(11)-F(4)	3.01 ± 0.20	F(11)-Br-F(4)	85.2 ± 5.3
F(11)-Br-F(13)	173.5 ± 6.1	F(5)-F(4)	3.56 ± 0.14	F(5)-Br-F(4)	97.2 ± 3.7
				Av	88.2
		(b) Sb(1) Environment			
Sb(1)-F(3)	1.62 ± 0.12	F(3)-F(2)	2.51 ± 0.20	F(3)-Sb(1)-F(2)	97.7 ± 6.6
Sb(1)-F(2)	1.72 ± 0.14	F(3)-F(9)	2.47 ± 0.16	F(3)-Sb(1)-F(9)	93.9 ± 6.5
Sb(1)-F(9)	1.76 ± 0.13	F(3)-F(4)	2.40 ± 0.19	F(3)-Sb(1)-F(4)	87.1 ± 6.2
Sb(1)-F(10)	1.77 ± 0.18	F(3)-F(12)	2.64 ± 0.16	F(3)-Sb(1)-F(12)	87.9 ± 6.2
Sb(1)-F(4)	1.86 ± 0.11	F(2)-F(9)	2.59 ± 0.20	F(2)-Sb(1)-F(9)	96.3 ± 6.5
Sb(1)-F(12)	2.15 ± 0.12	F(2)-F(10)	2.17 ± 0.22	F(2)-Sb(1)-F(10)	76.8 ± 8.1
Av	1.81	F(2)-F(4)	2.55 ± 0.16	F(2)-Sb(1)-F(4)	90.7 ± 5.5
		F(9)-F(10)	2.28 ± 0.25	F(9)-Sb(1)-F(10)	80.5 ± 8.0
		F(9)-F(12)	2.74 ± 0.18	F(9)-Sb(1)-F(12)	88.4 ± 5.4
F(2)-Sb(1)-F(12)	172.4 ± 6.1	F(10)-F(4)	2.77 ± 0.20	F(10)-Sb(1)-F(4)	99.2 ± 7.8
F(3)-Sb(1)-F(10)	171.5 ± 10.2	F(10)-F(12)	2.98 ± 0.25	F(10)-Sb(1)-F(12)	98.3 ± 7.7
F(9)-Sb(1)-F(4)	172.7 ± 5.8	F(4)-F(12)	2.70 ± 0.20	F(4)-Sb(1)-F(12)	84.5 ± 6.3
		Av	2.57	Av	90.1
		(c) Sb(2) Environment			
Sb(2)-F(6)	1.81 ± 0.10	F(6)-F(5)	2.65 ± 0.14	F(6)-Sb(2)-F(5)	92.5 ± 4.3
Sb(2)-F(5)	1.86 ± 0.09	F(6)-F(7)	2.88 ± 0.22	F(6)-Sb(2)-F(7)	102.7 ± 6.0
Sb(2)-F(7)	1.87 ± 0.18	F(6)-F(15)	2.76 ± 0.13	F(6)-Sb(2)-F(15)	96.3 ± 4.8
Sb(2)-F(15)	1.89 ± 0.10	F(6)-F(12)	2.50 ± 0.13	F(6)-Sb(2)-F(12)	83.5 ± 4.7
Sb(2)-F(12)	1.94 ± 0.12	F(5)-F(7)	2.74 ± 0.18	F(5)-Sb(2)-F(7)	94.4 ± 5.9
Sb(2)-F(14)	2.01 ± 0.13	F(5)-F(12)	2.56 ± 0.17	F(5)-Sb(2)-F(12)	84.8 ± 5.1
Av	1.90	F(5)-F(14)	2.49 ± 0.13	F(5)-Sb(2)-F(14)	80.1 ± 4.5
		F(7)-F(15)	2.73 ± 0.18	F(7)-Sb(2)-F(15)	93.3 ± 5.8
		F(7)-F(14)	2.75 ± 0.20	F(7)-Sb(2)-F(14)	90.3 ± 6.4
F(5)-Sb(2)-F(15)	166.7 ± 4.0	F(15)-F(12)	2.61 ± 0.14	F(15)-Sb(2)-F(12)	86.3 ± 4.4
F(6)-Sb(2)-F(14)	165.6 ± 5.2	F(15)-F(14)	2.74 ± 0.18	F(15)-Sb(2)-F(14)	89.1 ± 4.9
F(7)-Sb(2)-F(12)	173.8 ± 6.3	F(12)-F(14)	2.63 ± 0.19	F(12)-Sb(2)-F(14)	83.5 ± 5.2
		Av	2.67	Av	89.7
		(d) Bridge Bond Angles			
Br-F(4)-Sb(1)	174.1 ± 6.4	Br-F(5)-Sb(2)	170.8 ± 5.0	Sb(1)-F(12)-Sb(2)	173.0 ± 6.4
		(e) Nonbonded Intrachain Distances			
F(1)-F(9)	3.03 ± 0.16	F(2)-F(7)	3.47 ± 0.20	F(8)-F(15)	3.24 ± 0.14

[a] The limits of error are 3 times the computed estimated standard errors.

Discussion of the Structure

Our results show that the crystals consist of infinite chains of discrete BrF_4^+ and $Sb_2F_{11}^-$ ions coupled by relatively weak fluorine bridges. Accordingly the compound should be formulated as $[BrF_4^+][Sb_2F_{11}^-]$. This conclusion is based on the interatomic distances[16] in the structure, which are given in Figure 1 and Table III. The two fluorine atoms F(4) and F(5) involved in the Sb-F---Br bridges are bonded strongly to the antimony atoms and only weakly to the bromine atoms. The Sb(1)-F(4) and Sb(2)-F(5) distances are both equal to the average Sb-F bond distance in this structure, 1.86 Å. The Br---F(4) and Br---F(5) distances, 2.49 and 2.24 Å, are very long and indicative of rela-

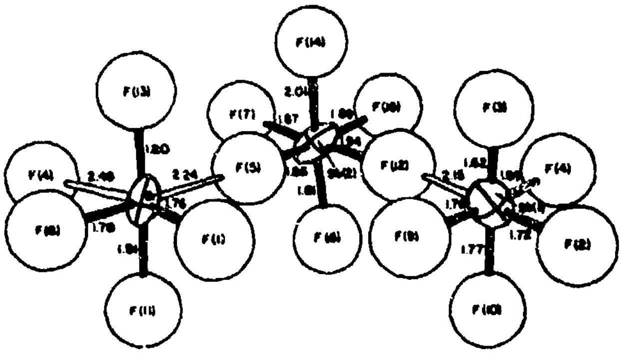

Figure 1.—View in perspective of a segment of the chain structure of $[BrF_4^+][Sb_2F_{11}^-]$ crystals (prepared by the computer program of C. K. Johnston, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965).

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[16] Computed with the program of W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

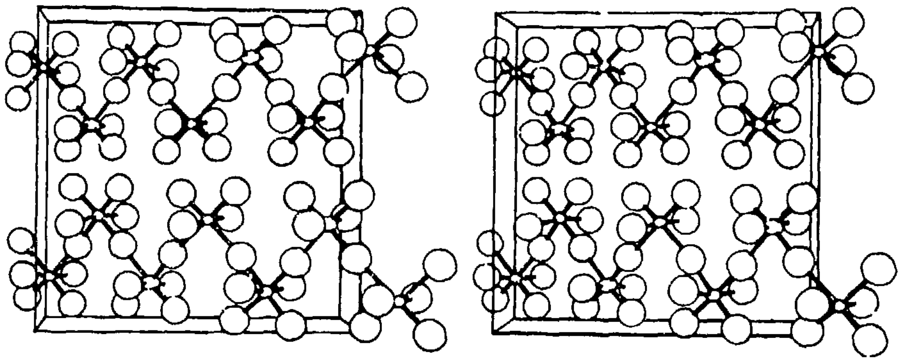

Figure 2.—Stereoscopic view to show the packing arrangement in $[BrF_4^+][Sb_2F_{11}^-]$ crystals (prepared by the computer program of C. K. Johnston, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965). The viewing direction is normal to the 001 planes.

tively weak bonding compared with the other four Br–F bond distances, which average 1.81 Å; this difference is substantially greater than the limits of error in the distances, which are given in Table III. The results rule out the alternative possibility of an essentially covalent structure with strong fluorine bridges.

The bromine atom has four strongly bonded fluorine ligands, F(1), F(8), F(11), and F(13). Including the free electron pair on the bromine atom, the BrF_4^+ structure might be described as a distorted trigonal bipyramid with F(1), F(8), and the free pair occupying the three equatorial positions. Part of the cause for the distortion from an ideal trigonal bipyramid appears to be the presence of the two additional, more remote fluorine ligands, F(4) and F(5), which belong to two neighboring $Sb_2F_{11}^-$ groups. This results in a coordination number of 7 for the bromine atom. For this coordination number, the most likely structures are either a puckered pentagonal bipyramid or an octahedron distorted by having the seventh ligand (the free electron pair) above one of the triangular octahedral faces. As can be seen from Figures 1 and 2 and Table III, the face is that formed by F(4), F(5), and F(11). This results in F(11) being bent toward F(1) and F(8). The free electron pair of the bromine atom is probably not directed at the center of the octahedral face but is probably much closer to the F(4)-F(5) edge because of its greater distance from the bromine atom; thus, the coordination polyhedron approaches a puckered pentagonal bipyramid. This pseudoheptacoordinate structure of BrF_4^+ closely resembles that found by Edwards and Jones[17] for SeF_3^+ in $[SeF_3^+][Nb_2F_{11}^-]$.

The geometry found for BrF_4^+ is in good agreement with that reported for the isoelectronic SeF_4.[18] Gaseous SeF_4 has bond angles of 169 and 100° for the axial and equatorial bonds, respectively, compared to 173 and 96° for BrF_4^+. The deviation of the bond angles of SeF_4 from those of an ideal trigonal bipyramid is due to the nonbonded electron pair being more diffuse than the bonded one, causing an increased repulsion. The equatorial and axial bonds of BrF_4^+ and SeF_4 show a similar difference in average length (0.085 vs. 0.089 Å, respectively), although the experimental BrF_4^+ values are statistically rather insignificant because of the relatively large error limits. As expected, the bond distances in BrF_4^+ are somewhat smaller than those found[3] for the BrF_4^- anion, 1.89 Å.

The $Sb_2F_{11}^-$ ion has the expected fluorine-bridged structure in which each antimony atom is surrounded by an irregular octahedral array of fluorine atoms with one fluorine atom shared by the two antimony atoms. However, the structure of the $Sb_2F_{11}^-$ ion reported here differs somewhat from that reported previously for this ion.[2] The essential difference is the pronounced asymmetry of the Sb---F-Sb bridge in the present case. The Sb(1)---F(12) distance of 2.15 Å indicates a relatively weak bond compared with the other Sb-F bonds in the structure; the difference is well outside the limits of error in the distances. Consistent with the long Sb(1)---F(12) distance, the other Sb(1)-F distances, on the average, are considerably shorter than the Sb(2)-F distances; the former average 1.75 Å, while the latter average 1.90 Å. For comparison, in $[XeF^+][Sb_2F_{11}^-]$ the two Sb-F bridge bonds were found to differ by less than twice the estimated standard error, and the average Sb-F bond distances of the two antimony atoms were found to be very nearly the same.[2] Our results suggest that the $Sb_2F_{11}^-$ ion consists of an SbF_6^- ion and an SbF_5 molecule coupled by a moderately strong fluorine bridge. This view is also supported by the finding[19] that, with excess of SbF_5, SbF_6^- forms not only $Sb_2F_{11}^-$ but also higher polymeric anions $[Sb_nF_{5n+1}^-]$ and that the additional SbF_5 molecules can be removed stepwise by controlled pyrolysis.[20]

The fluorine bridges which couple the BrF_4^+ and $Sb_2F_{11}^-$ ions are formed by cis fluorine atoms F(4), F(5), and F(12). Neglecting the differences in bond distances described above, the cis-fluorine-bridged chain structure of $[BrF_4^+][Sb_2F_{11}^-]$ crystals resembles that proposed[19,21] for liquid SbF_5 and for $[Sb_nF_{5n+1}^-]$ ions in solutions. The nature of the fluorine bridges in the $[BrF_4^+][Sb_2F_{11}^-]$ crystals appears to be very similar to that described for $[BrF_2^+][SbF_6^-]$ crystals, which were found to consist of infinite chains of discrete BrF_2^+ and SbF_6^- ions coupled by weak cis fluorine bridges.[1] In $[BrF_4^+][Sb_2F_{11}^-]$ the Br---F-Sb and Sb---F-Sb bond angles are considerably nearer 180° than are the analogous bridge bond angles in $[BrF_2^+][SbF_6^-]$ and

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$[XeF^+][Sb_2F_{11}^-]$. In $[BrF_4^+][Sb_2F_{11}^-]$ the atoms Br, Sb(1), Sb(2), F(1), F(2), F(4), F(5), F(7), F(8), F(9), F(12), and F(15) are all within 0.3 Å of being coplanar; their common plane is very nearly parallel to the 201 planes. This near coplanarity extends the whole length of any given chain. The planes of adjacent chains (see Figure 2) are parallel but are spaced *c*/2 or *c* apart along the *c* direction. The closest approaches of fluorine atoms bonded to different bromine and antimony atoms within the chains are 3.03, 3.24, and 3.47 Å, all of which are substantially greater than twice the van der Waals radius of fluorine.

The chains are approximately close packed. There is no bridging between chains. The minimum interchain F---F separation is 2.72 Å, which is approximately twice the van der Waals radius of fluorine. The minimum interchain Br---F and Sb---F distance is 3.56 Å, which is approximately the value expected for the sums of the van der Waals radii of the atom pairs.

In summary, this is the first direct evidence for the existence of the BrF_4^+ cation. Although the present experimental data do not allow very precise determinations of bond lengths and angles, valuable information about the structure of this interesting adduct was obtained.

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Selenium Pentafluoride Chloride, SeF_5Cl. Vibrational Spectrum, Force Constants, and Thermodynamic Properties

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The infrared spectrum of gaseous and the Raman spectrum of liquid SeF_5Cl are reported. The observed spectrum is consistent with symmetry C_{4v}. The structure of SeF_5Cl can be derived from an octahedron with one chlorine and five fluorine atoms occupying the six corners. A modified valence force field and thermodynamic properties in the range 0–2000°K were computed for SeF_5Cl.

Introduction

The existence of the novel selenium fluoride chloride, SeF_5Cl, has recently been discovered.[1] In this paper, we wish to report its vibrational spectrum, force constants, and thermodynamic properties.

Experimental Section

The preparation, purification, physical properties, and handling of SeF_5Cl are described elsewhere.[1] The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range of 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard calibration points.[2] Stainless steel cells of 5- or 10-cm path length fitted with AgCl or AgBr windows were used as sample containers. The Raman spectrum of liquid SeF_5Cl was recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to $\sim -25°$, and a dc ammeter. Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics. Clear Kel-F tubes ($\sim$ 2-mm i.d.) were used as sample containers in the transverse viewing–transverse excitation technique.

Results and Discussion

Vibrational Spectrum.—Figures 1 and 2 show the infrared spectrum of gaseous SeF_5Cl and the Raman spectrum of liquid SeF_5Cl, respectively. The observed frequencies are listed in Table I.

Since SeF_5Cl can be considered as a monosubstituted derivative of octahedral SeF_6, it should belong to point group C_{4v}. The 11 normal modes of SeF_5Cl of symmetry C_{4v} can be classified as $4\ a_1 + 2\ b_1 + b_2 + 4\ e$. Of these, all 11 modes will be Raman active, whereas only the a_1 and e modes will be infrared active. Of the Raman lines, the four a_1 modes should be polarized, the rest being depolarized. The assignment of the observed bands to individual modes (Table I) is based on the following arguments. There are four clearly polarized Raman lines at 721, 656, 443, and 385 cm^{-1}. As predicted by theory, these have counterparts in the infrared spectrum. Hence, these four bands must belong to species a_1. The two higher frequency lines are within the range expected for stretching modes of mainly covalent Se–F bonds. They are assigned, respectively, to the SeF and the symmetric SeF_4 stretching vibrations on the basis of their relative Raman intensities.[3] Similarly, the SeCl stretching mode should be of higher Raman intensity than the SeF_4 umbrella deformation.[3] Therefore, the 443-cm^{-1} band is assigned to the SeF_4 deformation. This assignment is further supported by the fact that in the infrared spectra of both $SeF_4(OF)_2$ and SeF_5OF[4] very strong infrared bands were observed at about 430 cm^{-1}.

Of the remaining six depolarized Raman bands, the 745-, 424-, and 336-cm^{-1} lines have counterparts in the infrared region and, consequently, belong to species e. The very intense infrared band at 745 cm^{-1} obviously represents the antisymmetric SeF_4 stretching vibration. For $SeF_4(OF)_2$ and SeF_5OF, this mode was observed[4] at 743 and 750 cm^{-1} respectively. By analogy with the known spectrum[5] of the SF_5Cl molecule, one might

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TABLE I

VIBRATIONAL SPECTRUM OF SeF$_5$Cl

Obsd freq, cm^{-1}		Assignment for point group C_{4v}
Infrared, gas	Raman, liquid	
1449 vw		$2\nu_1 = 1442$ (A$_1$)
1380 w		$\nu_5 + \nu_8 = 1381$ (E)
865 vw		$\nu_3 + \nu_9 = 861$ (E)
821 w		$\nu_3 + \nu_4 = 824$ (A$_1$)
745 vvs	745 (0.3) dp	ν_8(e)
729 ms, sh	721 (1.8) p	ν_1(a$_1$)
654 w	656 (10) p	ν_2(a$_1$)
. . .	636 (0.6) dp	ν_5(b$_1$)
587 vw		$\nu_7 + \nu_{11} = 593$ (E)
529 w		
468 w, sh		
440 vs	443 (2.2) p	ν_3(a$_1$)
421 s	424 (0.4) dp	ν_9(e)
384 mw	385 (8.5) p	ν_4(a$_1$) Cl^{35}
. . .	380 dp	ν_7(b$_2$) + ν_4(a$_1$) Cl^{37}
334 m	336 (1.2) dp	ν_{10}(e)
	213 (1.4) dp	ν_{11}(e)

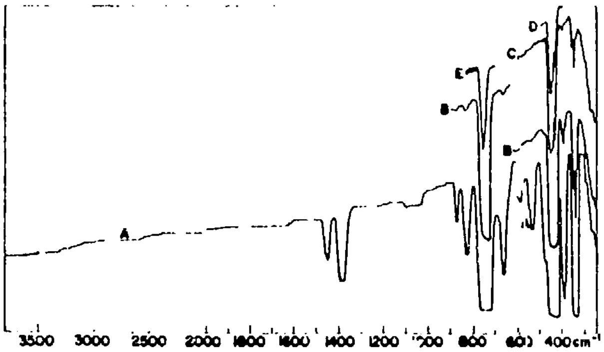

Figure 1.—Infrared spectrum of gaseous SeF$_5$Cl at 434 (A), 40 (B), 10 (C), 2 (D), and 1.5 mm (E) pressure in a 10-cm cell; window material AgBr.

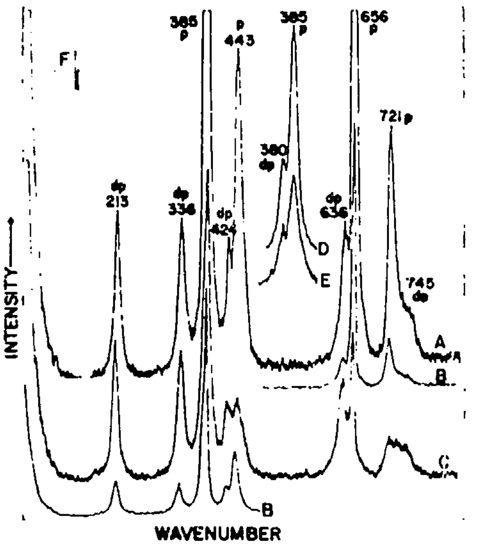

Figure 2.—Raman spectrum of liquid SeF$_5$Cl: traces A, B, and D, incident polarization perpendicular; traces C and E, incident polarization parallel. Traces A and B were recorded at different recorder voltages; traces D and E, under higher resolution. Experimental conditions were identical for A and C and for D and E, except for change of direction of polarization. F indicates spectral slit width.

expect the F–SeF$_4$ wagging to have the highest and the ClSeF$_4$ wagging mode to have the lowest frequency of the three remaining e modes, with the antisymmetric in-plane SeF$_4$ deformation being intermediate. Consequently, the bands at 424 and 336 cm^{-1} are assigned to the F–Se–F$_4$ wagging and the antisymmetric in plane SeF$_4$ deformation modes, respectively. Since the infrared spectrum was not recorded below 250 cm^{-1}, it is not known if the 213-cm^{-1} Raman band has indeed a counterpart in the infrared spectrum. However, the assignment of the 213-cm^{-1} Raman line to the fourth e mode, the Cl–SeF$_4$ wagging mode, appears very plausible for the following reasons. The SeCl stretching mode, ν_4, occurs at a frequency (385 cm^{-1}) considerably lower than those of the three SeF$_4$ stretching modes. Hence, the Cl–SeF$_4$ deformation frequency should be lower than 300 cm^{-1} and must be assigned to 213 and not to 380 cm^{-1}, the only remaining alternative.

TABLE II

FUNDAMENTAL FREQUENCIES OF SeF$_5$Cl AND SF$_5$Cl[a]

		SF$_5$Cl	SeF$_5$Cl
a$_1$	ν_1 ν(XF′)	855	729
	ν_2 ν_{sym}(XF$_4$)	707	654
	ν_3 δ_{sym}(XF$_4$) out of plane	602	440
	ν_4 ν(XCl)	402	384
b$_1$	ν_5 ν_{sym}(XF$_4$) out of phase	625	636
	ν_6 δ_{as}(XF$_4$) out of plane	. . .	. . .
b$_2$	ν_7 δ_{sym}(XF$_4$) in plane	505	380
e	ν_8 ν_{as}(XF$_4$)	909	745
	ν_9 δ(FXF$_4$)	579	421
	ν_{10} δ_{as}(XF$_4$) in plane	441	334
	ν_{11} δ(ClXF$_4$)	287	213

[a] Frequency values taken from ref 3.

For the assignment of the remaining three (2 b$_1$ and b$_2$) modes, we are left with only two Raman lines. The unobserved Raman line is assumed to be the antisymmetric out-of-plane SeF$_4$ deformation mode, ν_6. The fact that this mode has not been observed is not surprising. For the structurally similar halogen pentafluorides (ClF$_5$, BrF$_5$, and IF$_5$) and for SF$_5^-$ and TeF$_5^-$,[6] all belonging to point group C_{4v}, this mode was not observed. Of the two available Raman lines (636 and 380 cm^{-1}), the higher frequency value obviously belongs to the symmetric out-of-phase SeF$_4$ stretching mode, leaving the 380-cm^{-1} band to be assigned to the SeF$_4$ scissoring mode.

In the infrared spectrum of the gas, several bands of very low relative intensity were observed which cannot be attributed to fundamental vibrations. Most of them can satisfactorily be assigned to overtones and combination bands (see Table I).

The above given assignments rest mainly on the Raman lines, the polarization measurements, relative intensities, and the presence or absence of counterparts in the infrared spectrum. It appears interesting to examine to what extent the infrared band contours agree with theoretical predictions. It should be kept in mind, however, that band contours are sometimes subject to unpredictable changes and, hence, do not always agree with the predictions. Ideally, the a$_1$ modes should show PQR structure as expected for parallel bands of a symmetric-top molecule with I_A and I_B being similar to I_C. Indeed, ν_3 and ν_4 show the expected band shape. The band shape of ν_1 is not clear-cut; however, its band shape may have been influenced by Coriolis interaction with ν_8(e), which occurs at almost the same frequency. The band contour of ν_2 does not show a sharp PQR structure. This was also the case for ν_2 of SF$_5$Cl.[3,5]

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(6) K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, in press.

The band contour of ν_9(e) agrees with that expected for a perpendicular band, but that of ν_{10} closely resembles that of the parallel bands. It is interesting to note that ν_{10}(e) of SF_5Cl[3] and the corresponding ν_9(e) mode of ClF_5[7] also showed a PQR structure different from those of the remaining perpendicular bands in species e. The fact that the band contour of the lowest perpendicular band resembles those of the parallel bands has been observed for a number of symmetric-top molecules and can be attributed to first-order Coriolis perturbations.[8] In summary, the band contours of SeF_5Cl agree well with those[3] observed for SF_5Cl, even though differing somewhat from those predicted on the basis of the rigid-rotor, harmonic-oscillator approximation.

Comparison between the vibrational spectra of SF_5Cl[3,5] and SeF_5Cl shows good agreement. However, the SeF_5Cl data and results from force constant calculations[9] indicate that for SF_5Cl, the original assignment of the S–Cl wagging mode, ν_{11}(e), to the 287-cm^{-1} band by Cross, *et al.*,[5] should be retained. The revision of this assignment by Griffiths[3] was based on the fact that he observed an infrared counterpart for the 396-cm^{-1} Raman band. The latter, however, might equally well be interpreted as the ^{37}Cl isotope band of the S–Cl stretching mode, ν_4, at 402 cm^{-1}, the splitting and relative intensity being in good agreement with predictions. Furthermore, the infrared spectrum of SF_5Cl showed[3] a broad band at about 280 cm^{-1} which might represent the counterpart to the Raman band at 271 cm^{-1}. Hence, the original assignment[5] for ν_{11} does not violate the selection rules and results in a more reasonable frequency value. The high relative intensity of the 396-cm^{-1} band in the Raman spectrum of SF_5Cl and its infrared activity also argue against its proposed assignment[3] to ν_6 since for all the remaining related molecules, it either has not been observed or has been of very low intensity. Consequently, we propose that for SF_5Cl, ν_6 either has not been observed or is hidden underneath the intense ν_4 band. In summary, the vibrational spectrum of SeF_5Cl is consistent with symmetry C_{4v}. Ten out of eleven fundamentals were observed and assigned in agreement with the selection rules for C_{4v}.

Force Constants.—A normal-coordinate analysis was carried out to aid the spectral assignment. The kinetic and potential energy metrics were computed by a machine method,[9] assuming the following geometry and coordinate definitions: $R_{SeF'} = 1.68$ Å, $D_{SeCl} = 2.14$ Å, $r_{SeF} = 1.68$ Å, $\alpha = \angle$FSeF $= 90°$, $\beta = \angle$F'SeF $= 90°$, and $\delta = \angle$ClSeF $= 90°$, where F' refers to the axial (unique) fluorine ligand. The deformation coordinates were weighted by unit (1 Å) distance. The bond lengths were estimated using the Schomaker–Stevenson rule.[10]

The force constants were calculated by trial and error with the aid of a time-sharing computer to get exact agreement between the observed and computed frequencies using the simplest possible modified valence force field. Unique force constants could not be computed since the general valence field has 38 constants and there are only ten observed frequencies. However, numerical experiments showed that some of the principal force constants are quite independent of the chosen interaction constants and, hence, should approach those of a general valence force field. The computed values are $f_R = 4.42$, $f_D = 2.75$, $f_r = 4.31$, $f_{rr} = 0.07$, and $f_{rr'} = 0.35$ mdyn/Å; $f_\alpha = 1.26$, $f_\beta = 1.92$, $f_\delta = 1.16$, $f_{\beta\beta'} = 0.30$, and $f_{\delta\delta'} = 0.18$ mdyn/Å radian^2; and $f_{D\delta} = 0.28$ mdyn/Å radian. The two interactions $f_{\beta\beta'}$ and $f_{\delta\delta'}$ were determined from only one symmetry force constant value making the assumption $f_{\beta\beta'}/f_{\delta\delta'} = f_\beta/f_\delta$.

The values of the stretching force constants f_R and f_r of SeF_5Cl are not significantly different indicating similar bonding for both the axial and the equatorial fluorine ligands. Furthermore, their magnitude (4.3–4.4 mdyn/Å) approximates those obtained for other mainly covalent, hexavalent selenium compounds such as SeF_6 (5.01 mdyn/Å),[11] SeO_2F_2 (4.44 mdyn/A),[12] or SeO_3F^- (4.23 mdyn/Å)[12] with bond orders[12–14] close to 1. The slight decrease of the stretching force constant values from SeF_6[11] toward SeF_5Cl parallels that found for the analogous pair SF_6[15] and SF_5Cl[12] (see Table III).

TABLE III

STRETCHING FORCE CONSTANTS (IN MDYN/Å) OF SeF_6 AND SeF_5Cl COMPARED TO THOSE OF SF_6 AND SF_5Cl

	SF_6[a]	SF_5Cl[b]	SeF_6[c]	SeF_5Cl
R		4.83		4.42
	5.26		5.01	
f_r		4.52		4.31

[a] Reference 15. [b] Reference 12. [c] Reference 11.

It can be explained by the substitution of one fluorine atom in XF_6 by a less electronegative ligand, such as Cl. This causes an increased polarity ($S^{\delta+}$–$F^{\delta-}$) of the remaining SF bonds. Since stretching force constants reflect only the contributions from covalent bonding,[13,14] their value should correspondingly decrease. The interaction constants are in accord with our experience with similar molecules.[6] The value given for $f_{D\delta}$ was determined from $\sqrt{2}(f_{D\delta} - f_{D\beta}) \approx 0.4$, which was required to fit ν_3 and ν_4. This is not too surprising considering the mixing of the two modes (see Table IV).

TABLE IV

POTENTIAL ENERGY DISTRIBUTION FOR SeF_5Cl[a]

a_1	ν_1	729	$0.88f_R$
	ν_2	654	$0.90f_r$
	ν_3	440	$0.41f_D + 0.36f_\beta + 0.21f_\delta + 0.11f_R$
	ν_4	384	$0.58f_D + 0.15f_\beta + 0.15f_\delta$
b_1	ν_5	636	$0.95f_r$
	ν_6	(336)	$0.54f_\beta + 0.33f_\delta$
b_2	ν_7	380	$1.10f_\alpha - 0.10f_{\alpha\alpha'}$
e	ν_8	745	$1.00f_r$
	ν_9	421	$1.04f_\beta - 0.16f_{\beta\beta'}$
	ν_{10}	334	$0.79f_\alpha$
	ν_{11}	213	$1.02f_\delta - 0.16f_{\delta\delta'}$

[a] Contributions of less than 0.10 are not listed.

No evidence was found for the similar terms $f_{R\beta}$, $f_{r\beta}$, and $f_{r\delta}$ being nonzero, although this cannot be ruled out and might be expected from our experience with similar molecules[6] or from orbital following arguments.

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TABLE V

COMPUTED THERMODYNAMIC PROPERTIES OF SeF$_5$Cl[a]

T, °K	C_p°	$H° - H°_0$	$-(F° - H°_0)/T$	S°
0	0	0	0	0
100	12.035	0.895	51.149	60.103
200	21.720	2.604	58.534	71.554
298.15	27.800	5.062	64.494	81.472
300	27.885	5.113	64.600	81.644
400	31.338	8.091	69.959	90.186
500	33.331	11.333	74.746	97.412
600	34.548	14.732	79.053	103.605
700	35.336	18.228	82.954	108.994
800	35.870	21.790	86.512	113.750
900	36.248	25.397	89.778	117.998
1000	36.524	29.037	92.795	121.832
1100	36.731	32.700	95.596	125.323
1200	36.891	36.381	98.208	128.526
1300	37.016	40.077	100.656	131.484
1400	37.116	43.784	102.957	134.231
1500	37.197	47.499	105.128	136.795
1600	37.264	51.223	107.183	139.198
1700	37.320	54.952	109.134	141.458
1800	37.367	58.686	110.989	143.593
1900	37.406	62.425	112.759	145.614
2000	37.440	66.167	114.450	147.534

[a] Units for C_p°, S°, and F° are calories, moles, and degrees Kelvin; for H° units are kilocalories and moles.

Coriolis coupling coefficients were computed for SeF$_5$Cl in the belief that the e-block band contours could support the assignment. The computed values using the above given force constants were $\zeta_8 = 0.5$, $\zeta_9 = 0.5$, $\zeta_{10} = -0.4$, and $\zeta_{11} = 0.7$. However, the values of the moments of inertia are such that these values for ζ do not result in very distinctive band shapes.[8] The band shapes are further complicated by the natural chlorine and selenium isotopes and by hot bands. Although the observed band shapes are not inconsistent with those predicted, the contours could not be used to verify the computed ζ's.

The potential energy distribution was computed using the above force constants and is shown in Table IV. The assignment listed in Table I is supported by these values. The mixing of ν_3 and ν_4 is large, so that, strictly, one is not a stretching and one a deformational mode, but rather a symmetric and antisymmetric combination of the two motions.

Thermodynamic Properties.—The thermodynamic properties were computed for this molecule using the rigid-rotor, harmonic-oscillator[16] approximation. The results are given in Table V. The frequencies used were those of Table II, assuming a computed value of 336 cm^{-1} for ν_6. The moments of inertia used were $I_x = I_y = 312$ and $I_z = 214$ amu Å^2 computed from the geometry assumed above, with a symmetry factor of 4.

Acknowledgment.—We are indebted to Dr. D. Pilipovich for continuous encouragement and to Dr. J. Cape for the use of the Raman spectrometer. This work was supported by the Office of Naval Research, Power Branch.

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CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
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Chlorine Trifluoride Oxide. I. Preparation and Properties

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Chlorine trifluoride oxide, ClF_3O, has been prepared by either direct fluorination of Cl_2O, $NaClO_2$, or $ClONO_2$, or by glow discharge of F_2 in the presence of solid Cl_2O. A number of physical properties are reported as well as the ^{19}F nmr spectrum and the mass cracking pattern.

Introduction

Chlorine trifluoride oxide, ClF_3O, was prepared and characterized at Rocketdyne in 1965.[1] However, these results were not reported in the open literature. Recently, Bougon, Isabey, and Plurien have independently discovered[2] ClF_3O. In this paper, we report several synthetic routes and some physical and spectroscopic properties for ClF_3O.

Experimental Section

Materials and Apparatus.—Chlorine nitrate, $ClONO_2$, was prepared by the method of Schack.[3] Dichlorine oxide, Cl_2O, was generated as required from a Cl_2–HgO mixture as reported[4] by Schack and Lindahl. Mercuric oxide was prepared by the method of Cady.[5] Sodium chlorite was purchased from Matheson Coleman and Bell. Alkali metal fluorides were obtained from American Potash and Chemical Co. Prior to their use, they

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[1] D. Pilipovich and R. D. Wilson, U. S. Patent, to be issued, 1972.

[2] R. Bougon, J. Isabey, and P. Plurien, *C. R. Acad. Sci., Ser. C*, 271, 1366 (1970).

[3] C. J. Schack, *Inorg. Chem.*, 6, 1938 (1967).

[4] C. J. Schack and C. B. Lindahl, *Inorg. Nucl. Chem. Lett.*, 3, 387 (1967).

[5] G. H. Cady, *Inorg. Syn.*, 5, 156 (1957).

were fused, allowed to cool in the glove box, and subsequently ground.[6] Fluorine of 99+% purity was produced at Rocketdyne. Metal reactors were either Monel or 304 stainless steel Hoke cylinders equipped with high-pressure Hoke Y3002H needle valves. All manipulations were carried out either in well-passivated (with ClF_3) metal–Teflon FEP vacuum systems or in the dry nitrogen atmosphere of a glove box, except for the glow discharge reaction which was run in a Pyrex glass vessel with copper electrodes.

Infrared spectra were taken on a Beckman IR7 fitted with CsI and NaCl interchange and a Perkin-Elmer Model 337 grating spectrophotometer. The infrared cell used was constructed of nickel and fitted with AgCl windows or CsI windows protected by Teflon FEP film. The ^{19}F nmr spectra were recorded using a Varian high-resolution nmr spectrometer operating at 56.4 Mc. The samples were sealed in Teflon FEP tubes. Mass spectra were obtained with a CEC Model 21-103 C mass spectrometer using an ionizing voltage of 70 eV and a high-range magnet current of 0.60 mA.

Fluorination of Dichlorine Oxide.—*Caution!* Owing to the shock sensitivity of chlorine oxides, proper precautions (*i.e.*, shielding, etc.) must be taken. One explosion was encountered in the course of this work during the purification of about 5 g of Cl_2O.

In a typical experiment, powdered CsF was loaded into a passivated 300-ml 304 stainless steel cylinder in a glove box. The cylinder was then attached to a vacuum line, and after evacuation 246 cm³ (11 mmol) of Cl_2O was condensed into the cylinder at −196°. The cylinder was warmed to −78° to permit the Cl_2O to liquefy and contact the CsF. After recooling to −196°, 2 l. of F_2 was added and the cylinder was then maintained at −78° for 6 days. The unreacted F_2 was removed by pumping at −196°. The cylinder contents was then warmed to ambient temperature and fractionated through traps maintained at −95 and −196°. The chlorine trifluoride oxide (8.9 mmol) was trapped at −95° and corresponded to a yield of 75 mol %/mol of Cl_2O used. The −196° trap contained ClF_3, ClF, and some ClO_2F.

Fluorination of Cl_2O Absorbed on Mercuric Salts.—Yellow HgO and Cl_2 were allowed to interact at −80° for 24 hr in a 304 stainless steel cylinder. Fluorine was added at −196° and the reaction was allowed to proceed for several days at −80°. The reaction products were separated by fractional condensation and consisted of mostly ClF_3 and ClO_2F. In addition, ClF_5 and ClF_3O were obtained in low yields.

Glow-Discharge Fluorination of Solid Cl_2O.—Dichlorine oxide was deposited at −196° as a solid on the walls of a U-shaped Pyrex glass discharge vessel. During discharge, gaseous fluorine at 20 mm pressure was circulated over the solid in a closed-loop system. After consumption of 5 mol of F_2/mol of Cl_2O, the unreacted F_2 was removed at −196° and the products were separated by fractional condensation in a metal–Teflon FEP vacuum system. The main products were ClF_5 (∼45 mol %) and ClO_2F. In addition, the products contained some ClF_3 and 1 to 2% of ClF_3O.

Fluorination of $NaClO_2$.—Sodium chlorite (33 mmol) was placed in a 300-ml 304 stainless steel cylinder. Fluorine (45 mmol) was added at −196°. The mixture was allowed to warm to −80° and was kept at this temperature for 16 hr. The reaction products consisted of mostly ClO_2F, ClF_3, ClF, and Cl_2, but contained also a small amount of ClF_3O.

Fluorination of Chlorine Nitrate.—Chlorine nitrate (29.7 mmol) and F_2 (110 mmol) were condensed into a passivated 75-ml 304 stainless steel cylinder cooled to −196°. The cylinder was then maintained at −35°, resulting in an initial pressure of 480 psi. After 4 hr, the reactor was cooled to −196° and the noncondensables were removed. The products were separated by fractional condensation using cold traps at −95, −142, and −196°. The −95° fraction contained 19.3 mmol of ClF_3O, representing a 65% yield based on $ClONO_2$. The −142° fraction contained ClO_2F and Cl_2 while FNO_2 was trapped at −196°.

Purification of ClF_3O.—An alternate method of purifying ClF_3O may be used when significant amounts of ClF_3 are present and repeated fractionations of larger quantities of materials are not practical. Chlorine trifluoride oxide contaminated with substantial quantities of ClF_3 and ClO_2F was condensed onto KF (at −196°) and then maintained at ambient temperature for 24 hr. The cylinder was cooled to 0° and the ClO_2F, which does not form a stable adduct with KF, was removed by pumping. Pure ClF_3O was removed *in vacuo* at 50–70°, while ClF_3 remained complexed.

Elemental Analysis.—Chlorine and fluorine were determined by potentiometric titration with $AgNO_3$ solution and by $Th(NO_3)_4$–alizarin titration, respectively, after the combustion of a sample of ClF_3O with anhydrous NH_3 in a metal–Teflon FEP ampoule. (Caution!)

Oxygen was directly determined by reaction of ClF_3O with NaCl according to

$$3NaCl + ClF_3O \longrightarrow 3NaF + {}^1/_2O_2 + 2Cl_2$$

The technique involved condensing a measured quantity of ClF_3O onto reagent grade NaCl contained in a passivated cylinder. The cylinder was then heated to 100° to ensure complete reaction. After cooling to −196°, the noncondensables were measured using a Toepler pump. The gas was identified as O_2 by mass spectrometry. *Anal.* Calcd for ClF_3O: Cl, 32.7; F, 52.5; O, 14.7. Found: Cl, 32.6; F, 52.5; O, 13.1.

Results and Discussion

Synthesis.—The synthesis of ClF_3O is readily carried out through the fluorination of an inorganic, covalent hypochlorite. Those that have received the most attention in this study were dichlorine oxide, Cl_2O, and chlorine nitrate, $ClONO_2$. The fluorination of the dangerous[7] Cl_2O proceeds according to the following equations.

$$2F_2 + Cl_2O \longrightarrow ClF_3O + ClF$$

$$3F_2 + Cl_2O \longrightarrow ClF_3O + ClF_3$$

When no catalyst is used or if KF and NaF are present as catalysts, ClF is the main by-product. When the more basic alkali metal fluorides, RbF and CsF, are used, ClF_3 is the favored coproduct. The formation of ClF_3 rather than ClF is presumably associated with the more ready formation of ClF_2^- intermediates with RbF and CsF. A similar catalytic effect has been noted[8] in the preparation of ClF_5 from ClF_3 in the presence of alkali metal fluorides.

Yields of ClF_3O from Cl_2O are rather variable and may be affected by the particular alkali fluoride present. Yields of over 40% have been consistently obtained and have reached over 80% using either NaF or CsF. Since NaF does not form[9] an adduct with ClF_3O, stabilization of the product by complex formation does not seem to strongly influence the ClF_3O yields.

Owing to unpredictable explosions experienced[7] with liquid Cl_2O, attempts were made to circumvent the Cl_2O isolation step. For this purpose, the crude Cl_2O, still absorbed on the mercuric salts, was directly fluorinated. Again, ClF_3O was formed, but its yield was too low to make this synthetic route attractive.

The fluorination of solid Cl_2O to ClF_3O proceeded at temperatures as low as −196° provided the fluorine was suitably activated by methods such as glow discharge. Unactivated fluorine does not interact with Cl_2O at −196°, and after completion of the discharge unreacted F_2 was removed at −196°. Consequently, the observed ClF_3O could not have formed by fluorina-

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(6) We are indebted to Mr. M. G. Warner of our laboratories for devising this technique of preparing active alkali metal fluorides. The method produces salts of activity comparable to the precipitation method used by C. T. Ratcliffe and J. M. Shreeve, *Chem. Commun.*, 674 (1966), but is more convenient.

(7) Extreme caution should be used in handling Cl_2O. We have found that the material is readily exploded during adiabatic compression in a U tube, and even inexplicably during routine handling.

(8) D. Pilipovich, W. Maya, E. A. Lawton, H. F. Bauer, D. F. Sheehan, N. N. Ogimachi, R. D. Wilson, F. C. Gunderloy, Jr., and V. G. Bedwell, *Inorg. Chem.*, 6, 1918 (1967).

(9) K. O. Christe, C. J. Schack, and D. Pilipovich, *ibid.*, 11, 2205 (1972).

tion of Cl_2O during warm-up of the reaction products. The relatively low yields of ClF_3O (1 to 2%) could be partially due to the high reactivity of ClF_3O toward glass, although little interaction is to be expected at −196°, and the transfer of the products to a metal system was done rapidly and at the lowest possible temperature.

The low-temperature fluorination of $NaClO_2$ produced ClF_3O in low yields. However, the low yields and poor reproducibility make this route unattractive.

The fluorination of chlorine nitrate, $ClONO_2$, proceeds according to

$$2F_2 + ClONO_2 \longrightarrow ClF_3O + FNO_2$$

This reaction offers the most convenient route to ClF_3O for several reasons: (1) less fluorine is required than in the fluorination reactions of Cl_2O yielding ClF_3 as a coproduct, (2) the great difference in the volatilities of the products FNO_2 and ClF_3O ($\Delta T_{bp} \sim 100°$) permits an easy separation by fractional condensation, and (3) chlorine nitrate can be made more conveniently and, most importantly, does not appear to be hazardous in its handling. The yields of ClF_3O using $ClONO_2$ as a starting material are somewhat higher than those from Cl_2O.

In the fluorination of both Cl_2O and $ClONO_2$, side reactions compete with the actual fluorination step. These are caused by the thermal decomposition of the starting materials due to inefficient removal of the heat of reaction. Hence, the rate of the competing reactions is markedly affected by the reaction temperature. At reaction temperatures near or above ambient, the decomposition of the hypochlorite appears to be favored and little or no ClF_3O is formed, resulting in rapid, rather uncontrolled reactions. Apparently, thermal decomposition preceding the fluorination step yields only intermediates incapable of producing ClF_3O. Thus, in order to maximize the desired fluorination reaction, long reaction times at low temperature ($T < 0°$) are indicated.

Properties.—Pure ClF_3O is colorless as a gas or liquid and white in the solid state. It boils at 29° and freezes at −42°. Vapor pressures were measured over the range −23 to 31° and the data were fitted to the equation $\log P_{mm} = 8.433 - 1680/T(°K)$. Measured vapor pressures at the noted temperatures are [T (°C), P (mm)]: −23.0, 54.5; −12.4, 98; 0, 200; 5.9, 253; 15.6, 410; 21.0, 525; 25.0, 635, and 31.9, 822. The latent heat of vaporization is 7.7 kcal/mol and the derived Trouton constant is 25.4, indicating some association in the liquid phase. The density at 20° of 1.865 g/ml is similar to those observed for ClF_3[10] and ClF_5.[8] The molecular weight was determined from the vapor density and found to be 106.0 (calcd for ClF_3O, 108.5). The good agreement indicates little or no association in the gas phase at the pressures used ($P < 1$ atm). A complete elemental analysis was carried out for ClF_3O and confirms its composition. The physical properties reported in this paper agree well with those reported[2] by Bougon, *et al.*

Chlorine trifluoride oxide resembles most chlorine fluorides in its corrosive and oxidizing properties. However, it appears to be somewhat more corrosive than either ClF_3 or ClF_5. Care must be taken to passivate all equipment with ClF_3 (or preferably ClF_3O) prior to manipulating ClF_3O. Just as do ClF_3[11] and ClF_5,[8] ClF_3O forms chloryl fluoride upon contact with a number of hydroxylic reagents. The gas reacts rapidly with flamed-out quartz even at low pressures.

Mass Spectrum.—A stable mass cracking pattern for ClF_3O has been obtained. Observed ions[12] (excluding m/e due to ^{37}Cl isotopes) were [m/e, ion, abundance (%)]: 89, ClF_2O^+, 80.6; 70, $ClFO^+$, 100.0; 54, ClF^+, 21.23; 51, ClO^+, 14.78; 35, Cl^+, 29.35; 19, F^+, 27.29; and 16, O^+, 13.19. Several features of the mass cracking pattern are noteworthy. A comparison with the spectrum of IOF_5,[13] for example, shows that IOF_5 gives a significant parent peak (32%) while ClF_3O has no detectable peak at the same ionizing voltage. Also the ions ClF_2O^+ and $ClFO^+$ have a very high intensity which precludes an extensive thermal rupture of the ClO bond prior to electron bombardment.

Infrared Spectrum.—The infrared spectrum of ClF_3O has been recorded over the range 4000–240 cm^{-1}, showing the following absorptions (cm^{-1}, intensity): 1220, s; 678, vs; 667, vs; 490, ms (broad); 413, w; 319, m; and 245, mw. A detailed study of the vibrational spectrum of the gas and the liquid will be given in a separate paper.[14]

^{19}F Nmr Spectrum. The ^{19}F nuclear magnetic resonance spectrum of ClF_3O has been investigated in both the liquid and gaseous state. A single broad line is observed for the neat liquid at −262 ppm relative to the external standard $CFCl_3$. Similarly, only a single line ascribable to ClF_3O has been found in the gas-phase spectrum at −327 ppm relative to the same standard. This significant shift to a lower field, when going from the liquid to the gas, lends further support to the association in the liquid phase derived from the vapor pressure measurement and the Raman spectrum of the liquid.[14] Attempts to observe a splitting of the ^{19}F resonance line by cooling of either neat ClF_3O or solutions in ClF_5 were unsuccessful. This indicates a rapid exchange in the liquid phase and line broadening in the liquid and gas phase due to interaction with the large chlorine quadrupole moment. This line broadening is sufficient to obscure any information concerning chemical shift differences and spin–spin coupling between the nonequivalent fluorines even in the gas phase.

Pyrolysis. It was of interest to determine whether the thermal decomposition of ClF_3O would result in the elimination of F_2, as do ClF_3[15] and ClF_5,[16] or O_2, as do IOF_5[17] and $FClO_2$.[18] When ClF_3O was heated to 280° in Monel, for 16 hr, 70% of the ClF_3O was decomposed to ClF_3 and oxygen, while in stainless steel decomposition was already complete at 200°. Under dynamic conditions at $T > 350°$, ClF_3O decomposed again according to

$$ClF_3O \xrightarrow{\Delta} ClF_3 + {}^1/_2O_2$$

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[10] A. A. Banks and A. J. Rudge, *J. Chem. Soc.*, 2779 (1955).

[11] R. Bougon, M. Carles, and J. Aubert, *C. R. Acad. Sci., Ser. C*, **265**, 179 (1967).

[12] This pattern is corrected for SiF_4, ClO_2F, Cl_2, ClO_2, COF_2, O_2, and HF, all of which were generated through reaction with the inlet system of the mass spectrometer.

[13] C. J. Schack, D. Pilipovich, S. N. Cohz, and D. F. Sheehan, *J. Phys. Chem.*, **72**, 4697 (1968).

[14] K. O. Christe and E. C. Curtis, *Inorg. Chem.*, **11**, 2196 (1972).

[15] H. Schmitz and H. J. Schumacher, *Z. Naturforsch. A*, **2**, 362 (1947).

[16] H. F. Bauer and D. F. Sheehan, *Inorg. Chem.*, **6**, 1736 (1967).

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and not to the unknown chlorosyl fluoride, ClFO, and F_2. Its thermal stability thus appears to be intermediate between that of ClF_3[15] and ClF_5.[16] The reaction chemistry of ClF_3O will be described in a separate paper.[19]

Acknowledgment.—We are pleased to acknowledge support for this work by the Office of Naval Research, Power Branch. We wish to thank Mr. S. Cohz for the mass-spectral work, Drs. J. S. Muirhead and J. D. Ray for the ^{19}F nmr measurements, and J. Quaglino for the density measurement. We are also indebted to Dr. E. A. Lawton for his help and encouragement.

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CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
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Chlorine Trifluoride Oxide. II. Photochemical Synthesis

BY D. PILIPOVICH,* H. H. ROGERS, AND R. D. WILSON

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Chlorine trifluoride oxide, ClF_3O, was synthesized from several gaseous reaction systems using uv activation. The fluorination of both ClO_2F and ClO_3F, using ClF_5 or F_2 as fluorinating agents, gave excellent yields of ClF_3O. In addition, the direct photochemical synthesis of ClF_3O from the elements Cl_2, F_2, and O_2 was successfully achieved. Other systems yielding ClF_3O were ClF_3-O_2 and ClF–IF_5O. Attempts were unsuccessful to photochemically prepare either BrF_3O from BrF_3 and O_2 or BrF_7 from BrF_5 + F_2.

Introduction

Halogen fluorides can be readily synthesized by direct fluorination of the corresponding halogens at appropriate temperatures and pressures.[1] Consequently, little attention has been devoted to their photochemical synthesis. When the novel chlorine oxyfluoride, ClF_3O, was discovered[2,3] in 1965, its original synthesis involved handling of the treacherous[3] starting material, Cl_2O. Therefore, alternate approaches, such as photochemical reactions, were studied which might yield ClF_3O. Of initial interest to us was the use of uv irradiation to achieve the "deoxygenation" of either ClO_2F or ClO_3F. One of these, ClO_2F, had previously been shown[4] to degrade thermally to give ClF and O_2. A stepwise deoxygenation of these oxyfluorides *via* the intermediate (and unknown) chlorosyl fluoride, $ClOF$, might in the presence of F_2 yield ClF_3O. In addition, the alternate approach, *i.e.*, the photochemical addition of oxygen to various chlorine fluorides, was investigated. Of particular interest was whether ClF_3 could combine with oxygen to form ClF_3O and the direct synthesis of ClF_3O from the elements, Cl_2, F_2, and O_2. After the successful completion of our study, Bougon, Isabey, and Plurien independently discovered[5] the formation of ClF_3O when exposing a mixture of ClF_3 and OF_2 to uv irradiation. In this paper, we report the results of our original photochemical studies.

Experimental Section

Materials and Apparatus.—Perchloryl fluoride was purchased from Pennsalt Chemical Co. and used as received after verifying its purity through its infrared spectrum and vapor tension at −80°. Chloryl fluoride was synthesized by a modification of Woolf's procedure[6] and involved the fluorination of $NaClO_3$ with ClF_3. Fluorine was produced at Rocketdyne and Cl_2 and ClF_3 were obtained from the Matheson Co. The ClF_3 was purified by complexing with KF, removing volatiles at ambient temperature, and subsequently pumping off ClF_3 at temperatures above 140°. Chlorine pentafluoride was prepared according to the method of Pilipovich, *et al.*,[7] while chlorine monofluoride was synthesized from ClF_3 and Cl_2.[8] Bromine pentafluoride (Matheson) was treated with F_2 at ambient temperature until the material was colorless. It was purified by fractional condensation through traps kept at −64 and −95°. The BrF_5 was retained in the −95° trap and showed no detectable impurities. The preparation and purification of IF_5O[9] and ClF_3O[3] have previously been described.

All the results listed in this paper was obtained with a Hanovia high-pressure Hg lamp, No. 679-A-36 (power input 450 W). The spectral energy distribution of radiated Hg lines for the lamp includes (Å, W): 2967, 4.3; 2652, 4.0; 2537, 5.8; 2482, 2.3; 2380, 2.3; and 2224, 3.7, according to the manufacturer's specifications. In addition, this lamp emits lines of shorter wavelength down to about 1700 Å (quartz limit). The distance between the lamp and the cell window was about 2 in.

The photolyses were carried out in a cell consisting of a stainless steel cylindrical body (3 in. long, 3 in. i.d., and 388 cm^3 volume). One end of the cell was sealed with a welded plate. The other end was a machined flange onto which a 4-in. diameter optical grade sapphire window was clamped. A vacuum seal was obtained by using Teflon O-rings. Provision was made to condense materials into the cell *via* a stainless steel coldfinger (3 in. long, $^3/_8$ in. o.d.) appended to the main cell body. An outlet was provided which was connected to a stainless steel–Teflon FEP vacuum line for product work-up. Cooling coils were brazed onto the outside of the cell body, and cold methanol was circulated to provide the cooling. The cell wall temperature was automatically controlled to within 3° of a preset temperature over the range −60° to ambient temperature. A removable metal lamphousing was positioned over the sapphire window and dry N_2 was passed over the window to cool the window, prevent condensation prior to the irradiation, and exclude atmospheric oxygen which might act as a filter for short wavelength uv radiation.

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TABLE I

PHOTOCHEMICAL FORMATION OF ClF_3O FROM HALOGEN OXYFLUORIDES

Expt no.	Reaction time, min	Temp, °C	Reactants,[b] cm³	Products,[b] cm³	Yield of ClF_3O, %[c]
1	60	15	ClF_5, 56.3; ClO_2F, 56.9	ClF_5; ClO_2F; ClF_3 (trace)	0
2	60	−40	ClF_5, 55.6; ClO_2F, 55.6	ClF_3O, 26; ClF_3 60	47
3	60	−40	ClF_5, 57.2; ClO_2F, 61.8	ClF_3O, 29; ClF_3 50; ClO_2F, 25	79
4	60	−60	F_2, 65.9; ClO_2F, 61.3	ClF_3O, 18; ClF_3, 10; ClO_2F, 33	64
5[a]	120	−60	ClO_2F, 120.5	ClO_2F, 50; ClF, 43; ClO_3F, 8; O_2	0
6[a]	60	−60	ClF, 67.5; O_2, 67	ClF, 51; ClF_3, 9; ClO_2F (trace); Cl_2	0
7[a]	60	−40	ClF_3O, 69.4	ClF_3O, 49.6; ClF_3; O_2	
8[a]	60	−60	ClF_3O, 61.7	ClF_3O, 56.8	
9[a]	180	−60	ClF_5, 31.5	ClF_5, 21.1; ClF, 10.2; F_2, 10.2	0
10	15	−60	ClF, 101.0; IF_5O, 51.4	ClF_3O, 5; ClF, 69.3; Cl_2; IF_5	10
11	60	−60	ClF, 95.0; IF_5O, 57.0	ClF_3O, 15; 79.5; Cl_2; ClO_2F, IF_5	26

[a] Control experiments. [b] All gas volumes in this paper are cm³ at STP. [c] Based on moles of oxyfluoride reacted.

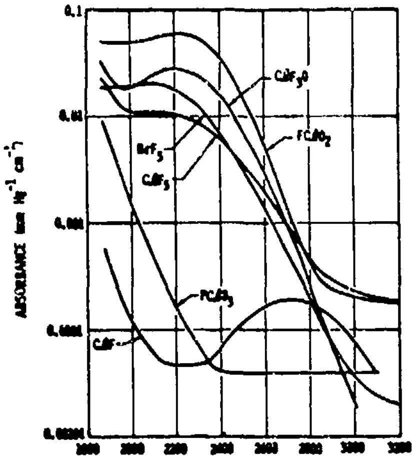

Figure 1.—Ultraviolet absorption spectra for ClF, ClF_5, ClF_3O, ClO_2F, ClO_3F, and BrF_5.

Photochemical Synthesis.—With the cell at ambient temperature and the condensing tube at −196°, the condensable reactants were loaded into the cell, followed by the addition of F_2 and/or O_2. The amount of each reactant introduced was determined by volumetric measurements made in the vacuum system external to the cell. The flow of N_2 was started over the cell window and the methanol cell-coolant flow was started. The condensing tube was allowed to reach the cell-body temperature, and after the reactants had mixed, the lamp was turned on. A shutter between the lamp and cell window was only removed when the lamp current had reached its full operating level. After the desired period of irradiation, the cell was warmed to ambient temperature and its contents fractionated in the vacuum line. The ClF_3O was trapped at −95°, measured volumetrically, and identified by its ir spectrum.[10] The other reaction products were similarly separated and identified by infrared spectroscopy, vapor pressure, and gas density measurements.

Absorption Spectra.—Uv spectra were obtained with a Cary Model 14 recording spectrophotometer. The cells were of 10-cm path length and constructed from 1-in. o.d. nickel tubing. Ultraviolet grade Linde sapphire windows were held in place with flanges and Teflon O-rings. Hoke M482m Monel bellows valves were used as cell closures. Prior to the introduction of the sample, the cell was passivated with F_2 and ClF_3.

Results

Uv Absorption Spectra.—The absorption spectra of some of the starting materials were recorded to obtain insight into the uv activation processes. These spectra are shown in Figure 1. The results for ClF_5 extend the work of Gatti, *et al.*,[11] to wavelengths shorter than 2640 Å. Likewise, the ClF spectrum extends that reported by Schmitz and Schumacher.[12] Schmitz and Schumacher have also reported[13] the uv spectrum of ClF_3.

Synthesis of ClF_3O from Halogen Oxyfluorides.—The results of the reactions of F_2, ClF, and ClF_5 with ClO_2F, ClO_3F, or IF_5O are given in Table I. The reaction temperatures employed ranged from +15 to −60°. The yield of ClF_3O at 15° was zero while at −60° yields as high as 79% were observed (based on 1 mol of ClF_3O from each mole of oxyfluoride reacted). Control experiments to determine the rate of decomposition of ClO_2F and ClF_3O were carried out. After 1 hr at −40 and −60°, ClF_3O had decomposed to the extent of 28.5 and 8.0%, respectively. Surprisingly, ClO_2F decomposed at a rate of about 29%/hr at −60°. Furthermore, the control experiment (expt 6, Table I) showed a low level of oxygenation of ClF to ClO_2F.

Synthesis of ClF_3O from the Elements.—The results for the synthesis of ClF_3O from the elements, Cl_2, F_2, and O_2, at −60° are shown in Table II. The conversions to ClF_3O increased with increasing reaction time ranging from a trace after 15 min to 44.6% after 360 min. Most of the Cl_2 and F_2 were converted to ClF_3 during the first 15 min of irradiation (expt 1). The effective irradiation wavelengths for the reaction were established through the use of different filters. No ClF_3O was formed using either a Pyrex or Vycor filter

TABLE II

PHOTOCHEMICAL FORMATION OF ClF_3O FROM THE ELEMENTS[a] AT −60°

Expt no.	Reaction time, min	Products,[b] cm³			% Cl_2 converted to	
		ClF_3O	ClF_3	ClO_2F	ClF_3O	ClF_3
1	15	Trace	45.2		Trace	84
2	30	1.3	50.5	0.8	2.3	93
3	60	7.3	38.3	1.8	13.3	70
4	90	9.7	46.8	0.4	16.7	80
5	180	15.9	32.9	2.9	29.7	61
6	240	21.4	31.9		39.0	58
7	360	25.0	29.4	0.4	44.6	52
8[c]	60	0	37.7	3.9	0	71
9[d]	60	0	49.3	0.8	0	88
10[e]	180	7.5	40.1	4.9	13.2	71

[a] The ratio of Cl_2:F_2:O_2 in all experiments was 1:3:10 with the total amount of gas being about 400 cm³ and the total pressure being about 780 mm (*i.e.*, approximately 28 cm³ of Cl_2, 85 cm³ of F_2, and 285 cm³ of O_2). [b] Remainder of products were ClF, F_2, and O_2. These were not measured. [c] Pyrex filter used. [d] Vycor filter used. [e] Oxygen filter used.

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(10) K. O. Christe and E. C. Curtis, *Inorg. Chem.*, **11**, 2196 (1972).

(11) R. Gatti, R. L. Krieger, J. E. Sicre, and H. J. Schumacher, *J. Inorg. Nucl. Chem.*, **28**, 655 (1966).

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(13) H. Schmitz and H. J. Schumacher, *ibid.*, **38**, 363 (1950).

and the yield of ClF_3O was drastically reduced by using a crude oxygen filter (*i.e.*, flowing oxygen rather than nitrogen for cooling the cell window).

Synthesis of ClF_3O from ClF_3 and O_2.—The results for the synthesis of ClF_3O from ClF_3 and O_2 at −60° are shown in Table III. Here again the conversions to ClF_3O increase with increasing reaction time with about 21% ClF_3O formed after 360 min. The amounts of ClF_3O formed from ClF_3–O_2 mixtures and from the elements are compared in Figure 2 as a function of the irradiation time. It may be seen that even though the elements are rapidly converted to a ClF_3–O_2 mixture, a much longer induction period occurs when starting with a ClF_3–O_2 mixture and about four times more ClF_3O forms from the elements during a 6-hr experiment.

TABLE III

PHOTOCHEMICAL FORMATION OF ClF_3O FROM ClF_3 AND O_2[a] AT −60°

Expt no.	Reaction time, min	Products,[b] cm³		% ClF_3 converted to ClF_3O	% ClF_3 recovered as ClF_3
		ClF_3O	ClF_3		
1	60	0	29 4	0	98
2	90	1.3	32.5	3.9	97
3	180	3.2	29.1	9.6	87
4	360	6.6	25.3	20.8	79

[a] ClF_3:O_2 ratios of about 1:10 were used in all experiments with the total amount of gas being about 340 cm³ and the total pressure being about 670 mm (*i.e.*, approximately 31 cm³ of ClF_3 and 310 cm³ of O_2). [b] Remainder of products were ClF, F_2, and O_2. These were not measured.

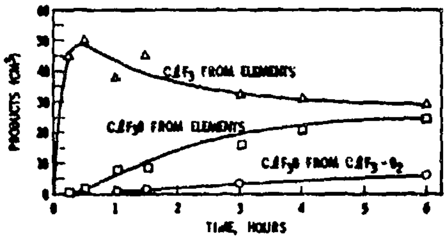

Figure 2.—Photochemical conversion as a function of irradiation time at −60°.

Attempted Synthesis of BrF_5O.—Mixtures of BrF_5 and O_2 (mole ratio of 1:9), after exposure to uv irradiation for 1 to 3 hr at −40 to −60°, consisted exclusively of the unchanged starting materials. Similarly, the photolysis of BrF_5–F_2 mixtures (mole ratio of 1:9) did not result in the formation of any novel compound, such as BrF_7. The unreacted BrF_5 was quantitatively recovered after completion of the experiment.

Discussion

The results obtained in this study demonstrate that uv photolysis constitutes a convenient high-yield synthesis for ClF_3O. The starting materials used for the photolysis reactions are quite different from those used in the chemical syntheses.[3] They are more readily available and safer to handle than $ClONO_2$ or the shock-sensitive[4] Cl_2O.

A wide choice of starting materials exists for the photochemical synthesis of ClF_3O. It appears that the photolysis of almost any system capable of producing active oxygen and either ClF, ClF_3, or ClF_5 will produce ClF_3O. Thus, ClF_3O has been prepared from any of the following reaction systems: Cl_2–F_2–O_2, ClF_3–O_2, ClO_2F–ClF_5, ClO_3F–ClF_5, ClO_2F–F_2, and ClF–IF_5O. It may be seen from the data in Tables I, II, and III that starting with the elements or the ClF_3–O_2 mixture results in better yields of ClF_3O but the halogen oxyfluorides give much faster rates of formation of ClF_3O (in cm³/hr). The failure to observe ClF_3O in the ClF–O_2 system (expt 6, Table I) is most likely due to the short reaction time (60 min). Thus, a 1-hr initiation period was required for the ClF_3–O_2 system (expt 1, Table III) before any ClF_3O could be detected in the products. The number of possible reaction systems has recently been further extended by the independent work of Bougon, *et al.*[5] The latter authors reported the preparation of ClF_3O by photolysis of the ClF_3–OF_2 system.

When considering the results obtained in the present investigation, it should be noted that some of the reactants and products were present in quantities which caused their partial condensation on the reactor walls. The vapor pressure data presented in Table IV indicate the amount of each species which will remain uncondensed at −40 and −60° and thus can participate in the photochemical reaction. It can be seen, for example, that at −60° most of the ClF_3O condenses and, hence, is not subject to decomposition by the irradiation. These vapor pressure considerations might also explain why ClF_3O photolyzes more rapidly at −40 than at −60° (expt 7 and 8 of Table I) and why ClO_3F photolyzes faster than ClF_3O (expt 5 and 8 of Table I).

TABLE IV

VAPOR PRESSURE AND CALCULATED MAXIMUM VOLUME OF VAPOR IN REACTOR

	Vapor pressure, mm		Vapor volume, cm³ at STP[f]	
	−40°	−60°	−40°	−60°
ClF_3O[a]	22	5	13.1	3.3
Cl_2[b]	>400	>100	>230	>65
ClF_5[c]	220	72	131	47
ClF_3[b]	47	10	28	7
ClF[b]	>760	>760	>490	>450
ClO_3F[d]	1000	398	597	260
ClO_2F[e]	143	37	91	23

[a] Reference 3. [b] D. R. Stull, *Ind. Eng. Chem.*, 39, 517 (1947). [c] Reference 7. [d] R. L. Jarry, *J. Phys. Chem.*, 61, 498 (1957). [e] H. Schmitz and H. J. Schumacher, *Z. Anorg. Allg. Chem.*, 249, 238 (1942). [f] In 388-cm³ reactor, assuming ideal vapor pressure.

The most convenient and practical reaction system for the photochemical synthesis of ClF_3O is obviously the one starting from the elements Cl_2, F_2, and O_2. As can be seen from Table II and Figure 2, the synthesis of ClF_3O from the elements produces ClF_3 at a rapid rate during the first half-hour with yields around 90%. This implies that the synthesis of ClF_3O from the elements is closely related to that starting from ClF_3 and O_2, although the different rates and the existence of a 1-hr initiation period for the ClF_3–O_2 system are unexpected. The purpose of the present study was not to study the kinetics of any particular reaction, but rather to screen different reaction systems for their potential as a practical synthesis of ClF_3O. An independent, detailed kinetic study of these systems is in progress in our laboratory and will be published at a later time.[14] Consequently, the discussion of the possi-

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(14) A. Axworthy and K. Mueller, unpublished results.

ble reaction mechanisms will be limited in this paper to the most apparent aspects.

The selection of reaction temperatures below −25° is beneficial for the synthesis of ClF_3O. At reaction temperatures of −40° and below, the vapor pressure of ClF_3O is quite low, thus minimizing its photolytic decomposition according to

$$ClF_3O \xrightarrow{h\nu} ClF_3 + {}^1/_2O_2$$

This decomposition path has been noted also during its pyrolysis and is consistent with the observation (expt 1, Table I) that at 15° no ClF_3O is formed from a system capable of producing it at a lower temperature.

The photolysis of either ClO_2F or ClO_3F in the presence of F_2 or ClF_5 gave ClF_3O in high yields. The observed (expt 5, Table I) degradation of ClO_3F to ClF, ClO_2F, and O_2 indicates a stepwise decomposition of ClO_3F, according to

$$ClO_3F \longrightarrow ClO_2F + {}^1/_2O_2$$
$$ClO_2F \longrightarrow ClOF + {}^1/_2O_2$$
$$ClOF \longrightarrow ClF + {}^1/_2O_2$$

The following data support this assumption. The decomposition of ClO_3F yields a substantial amount of ClO_2F, while the oxygenation of ClF to ClO_2F (expt 6, Table I) is very inefficient. Thus, the product of the first decomposition step of ClO_3F should be ClO_2F.

Some indications concerning the nature of the key intermediates were obtained from experiments involving the use of various filters during uv irradiation (Table II). The insertion of a Vycor filter (10% transmittance at 2250 Å) precluded the formation of ClF_3O from the elements. This result suggested the importance of oxygen activation in the "fixation" step. This assumption was substantiated by passing O_2 between the lamp and the cell, which vastly decreased the ClF_3O yield (compare expt 5 and 10, Table II).

Having thus established the importance of oxygen activation, it would be tempting to propose the combination of ClF_3 with an oxygen atom to form ClF_3O. This, however, appears unlikely since the rate of formation of ClF_3O from ClF_3 and O_2 is much slower, particularly during the initial stages of the reaction, than the rate of formation from Cl_2, F_2, and O_2 (see Figure 2). It has been noted (expt 9, Table I) that ClF_3 slowly generates ClF upon uv irradiation and it is possible that ClF, and not ClF_3, combines with O. The suggested reaction sequence would be

$$ClF_3 \rightleftarrows ClF + F_2$$
$${}^1/_2O_2 \longrightarrow O$$
$$ClF + O \rightleftarrows ClOF$$
$$ClOF + F_2 \longrightarrow ClF_3O$$

The unknown compound, ClOF, would be a plausible intermediate for both the oxygenation of ClF_3 and the deoxygenation of ClO_2F or ClO_3F (see above).

In the ClO_3F- and ClO_2F-containing systems, the postulated ClOF intermediate might be formed in two different ways: (1) by direct deoxygenation of ClO_2F or ClO_3F, and (2) by recombination of ClF with atomic oxygen. If (2) were the preferred reaction path, the rate of ClF_3O formation should be comparable for both the ClF_3–O_2 and the ClO_3F–F_2 systems, since both ClO_3F and ClF_3, upon photolysis, yield ClF at comparable rates (expt 5 and 9, Table I). However, this is not the case. The rate of ClF_3O formation for the ClO_3F–F_2 system is much higher than that found for the ClF_3–O_2 system. Therefore, it appears that at least some of the unstable ClOF intermediate must be fixed by fluorine during the deoxygenation of ClOF or ClO_2F. Attempts were unsuccessful to extend the above described technique toward the syntheses of the yet unknown molecules, BrF_5O and BrF_7.

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CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
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Chlorine Trifluoride Oxide. III. Vibrational Spectrum, Force Constants, and Thermodynamic Properties

BY KARL O. CHRISTE* AND E. C. CURTIS

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The infrared spectra of gaseous, solid, and matrix isolated ClF_3O and the Raman spectra of gaseous and liquid ClF_3O are reported. Nine fundamental vibrations were observed, consistent with symmetry C_s. The vibrational spectrum of ClF_3O agrees well with a trigonal-bipyramidal model with two fluorine atoms at the apexes and one fluorine atom, one oxygen atom, and one localized free electron pair at the remaining corners. A modified valence force field was computed for ClF_3O. These data indicated that the axial ClF bonds (f_r = 2.34 mdyn/Å) are considerably weaker than the equatorial one (f_R = 3.16 mdyn/Å) and that the bond order of the ClO bond is close to two (f_D = 9.37 mdyn/Å). The Raman spectrum of the liquid and the infrared spectrum of the solid indicate association through the axial fluorine atoms. Thermodynamic properties were computed for ClF_3O in the range 0-2000°K.

Introduction

As part of our extensive study[1-5] of the novel chlorine oxyfluoride, ClF_3O, we have investigated the vibrational spectra of the molecule. In their recent paper, Bougon, *et al.*, have proposed[6] a structure of symmetry C_{3v} for ClF_3O on the basis of infrared and Raman spectra. In this paper, we report the complete vibrational spectrum, force constants, and thermodynamic properties of ClF_3O. The vibrational spectra, force constants, and structure of the two ions, ClF_2O^+ and ClF_4O^-, derived from ClF_3O are discussed elsewhere.[7,8]

Experimental Section

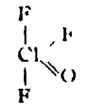
The preparation of ClF_3O and its purification and handling have previously been described.[2,3] The ClF_3O samples used in this investigation had a purity of better than 99.8% and our spectra did not reveal any impurities. The infrared spectra were recorded either on a Beckman Model IR-7 spectrophotometer with NaCl and CsI interchange in the range 4000-200 cm^{-1} or a Perkin-Elmer Model 457 spectrophotometer in the range 4000-250 cm^{-1}. The instruments were calibrated by comparison with standard gas calibration points.[9] The gas cells were made of 304 stainless steel and had a path length of 5 cm. Silver chloride and CsI windows were used in the ranges 4000-450 and 450-200 cm^{-1}, respectively. The inside of the CsI windows was protected against chemical attack by Teflon FEP sheet (1-mil thickness). To ensure close contact between the CsI window and the Teflon sheet, a thin film of Halocarbon grease (high-temperature grade from Halocarbon Products) was put on the CsI window prior to attaching the Teflon sheet. The Teflon sheet did not come loose or show blisters even upon evacuation of the cell provided all gas pockets between the CsI window and the thin Teflon sheet were carefully eliminated before assembling the cell. Compensation for bands due to the window material was achieved by placing an empty cell into the reference beam.

The apparatus, materials, and technique used for the matrix isolation study have previously been described.[10,11] Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of ~1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier, and a dc ammeter. Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics. A stainless steel cell with Teflon O-rings and sapphire windows was used for obtaining the spectra of gases and liquids. The design of this cell was similar to that of a cell described previously.[11]

Results and Discussion

Vibrational Spectra. Figure 1 shows the infrared spectrum of gaseous ClF_3O recorded at various sample pressures. Figures 2 and 3 show the Raman spectra of gaseous and liquid ClF_3O, respectively. Figure 4 shows the infrared spectra of pure and N_2-matrix isolated ClF_3O at 4°K. Figure 5 shows the most intense infrared bands of matrix isolated ClF_3O under high resolution conditions allowing the determination of the ^{35}Cl-^{37}Cl isotopic shifts. Table I lists the observed frequencies which can be attributed to fundamental vibrations. Table II lists the infrared frequencies attributed to overtones and combination bands.

In ClF_3O, the chlorine central atom possesses a nonbonding valence-electron pair. In related molecules (*e.g.*, SF_4 and ClF_5), such an electron pair appears to be sterically active, and similar behavior is anticipated here. The resulting structure can best be described as a trigonal bipyramid. In this type of structure, the apical positions are always occupied by the most electronegative ligands.[13] Hence, structure I of symmetry



I

C_s (possessing one symmetry plane as the only symmetry element) might be expected for ClF_3O. The arrangement of the axial FClF group may not be exactly linear owing to the different degrees of repulsion expected from the three equatorial ligands. However, possible deviations from 180° should be relatively small and symmetry C_s would be retained. A second structure of symmetry C_s (II) can be written for ClF_3O in which one fluorine and one oxygen atom occupy the axial positions. However, comparison with related

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(1) D. Pilipovich, R. D. Wilson, and H. F. Bauer, U. S. Patent, to be issued, 1972.

(2) D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, **11**, 2189 (1972).

(3) D. Pilipovich, H. H. Rogers, and R. D. Wilson, *ibid.*, **11**, 2192 (1972).

(4) C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, *ibid.*, **11**, 2201 (1972).

(5) K. O. Christe, C. J. Schack, and D. Pilipovich, *ibid.*, **11**, 2205 (1972).

(6) R. Bougon, J. Isabey, and P. Plurien, *C. R. Acad. Sci., Ser. C*, **271**, 1366 (1970).

(7) K. O. Christe, E. C. Curtis, and C. J. Schack, *Inorg. Chem.*, **11**, 2212 (1972).

(8) K. O. Christe and E. C. Curtis, *ibid.*, **11**, 2209 (1972).

(9) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Nat. Bur. Stand.*, **64**, 841 (1960).

(10) K. O. Christe and D. Pilipovich, *J. Amer. Chem. Soc.*, **93**, 51 (1971).

(11) K. O. Christe, *Spectrochim. Acta, Part A*, **27**, 631 (1971).

(12) E. L. Gasner and H. H. Claassen, *Inorg. Chem.*, **6**, 1937 (1967).

(13) R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **6**, 749 (1967).

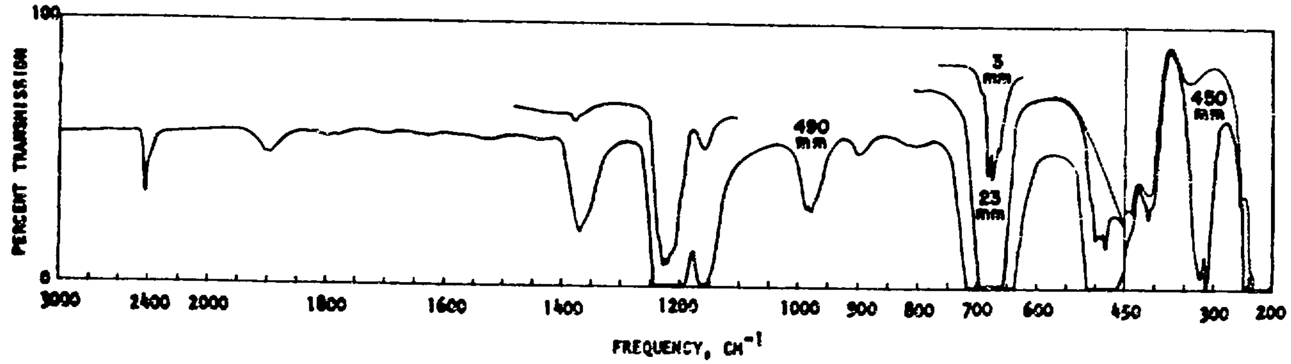
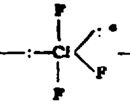
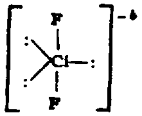
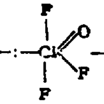
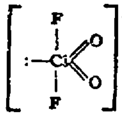
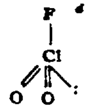


Figure 1.—Infrared spectrum of gaseous ClF$_3$O at various sample pressures. The broken lines indicate the cell background in this particular region.

Table I
Vibrational Spectra of ClF$_3$O Gas and Liquid Compared to Those of Similar Molecules and Ions

Observed frequencies, cm^{-1}, and relative intensities														
 [a]			 [b]						 [c]		 [d]			
Gas		Liquid Raman	Ir	Raman	Gas		Solid Matrix ir	Liquid Raman	Ir	Raman	Gas Ir	Liquid Raman	Assignment for ClF$_3$O in point group C_s	Approx description of mode
Ir	Raman				Ir	Raman								
					1228									
					1224	1222 (1.5) p	1223 s	1224 (1.0) p	1225					
					1218 s				1191 vs	1221 (0.8)			$\nu_1(A')$	$\nu(^{35}Cl{=}O)$
751 s	752 s, p	753 ms			1213	1211 (0.5) p	1212 m		1070 s	1076 (10)			$\nu_1(A')$	$\nu(^{37}Cl{=}O)$
					701	694 (2.6) p	686 s	689 (2.7) p			630 s	602 (2) p	$\nu_3(A')$	$\nu(^{35}Cl{-}F')$
					684	688 sh, p	678 m						$\nu_3(A')$	$\nu(^{37}Cl{-}F')$
702 vs			635 vs		676 vs		652 vs						$\nu_7(A'')$	$\nu_{as}(F^{35}ClF)$
					666		641 s		510 vs				$\nu_7(A'')$	$\nu_{as}(F^{37}ClF)$
							499 m						$\nu_8(A'')$	$\delta_{rock}(O^{35}ClF')$
					501	500 (1)		497 sh	330–370 m	378 (8)				
							498 sh						$\nu_8(A'')$	$\delta_{rock}(O^{37}ClF')$
					491 ms	489 (1)	486 mw						$\nu_2(A')$	$\delta_{sciss}(O^{35}ClF')$
		514 vs					484 w						$\nu_2(A')$	$\delta_{sciss}(O^{37}ClF')$
530 m	529 vs, p			475 (10)	481	482 (10) p	478 mw	466 (10)	330–370 m	363 (10)			$\nu_4(A')$	$\nu_s FClF$
		502 vs												
					412 w	414 (0.2) dp	414 w	405 (0.5) sh					$\nu_9(A'')$	τ
442 w	431 w, dp	424 vw			323 313 m	319 (0.1)	323 mw	316 (0.3) p	330–370 m	337 (8)			$\nu_5(A')$	$\delta_s FClF$ out of FClF plane ≡ $\delta_{wag} OClF'$
328 s	329 w, p	321 vw			230 mw	224 (0.4) p		227 (1.2) p?		198 (0.7)			$\nu_6(A')$	$\delta_s FClF$ in FClF plane

[a] H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, 52, 3517 (1970). [b] K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, 6, 1159 (1967). [c] K. O. Christe and E. C. Curtis, *ibid.*, 11, 583 (1972). [d] D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, 20, 1763 (1964).

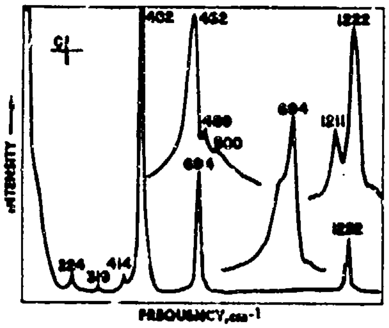


Figure 2.—Raman spectrum of gaseous ClF_3O at a sample pressure of 490 mm. The inserts show the three most intense bands at higher resolution and scale expansion. C indicates equivalent slit width

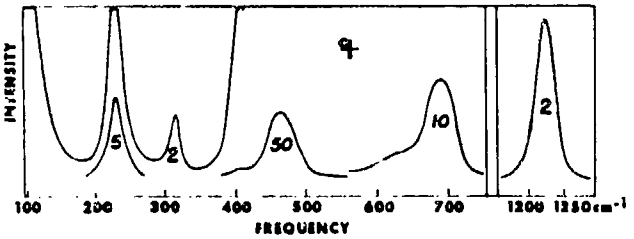


Figure 3.—Raman spectrum of liquid ClF_3O. C indicates equivalent slit width.

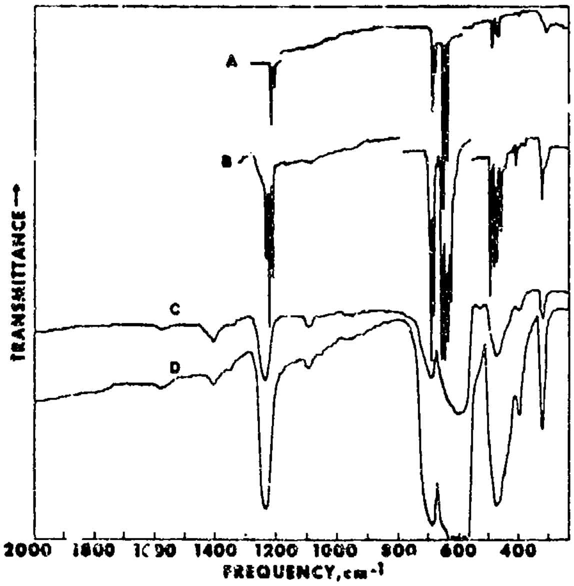
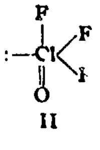


Figure 4.—Infrared spectra of solid ClF_3O at 4°K: (A) 1.0 μmol of ClF_3O in 10,000 μmol of N_2; (B) 10 μmol of ClF_3O in 10,000 μmol of N_2 after controlled diffusion at 27°K; (C and D) pure ClF_3O at two different concentrations.



II

molecules and the observed $^{35}Cl-^{37}Cl$ isotopic shifts (see below) eliminate this model. If the free electron pair of the chlorine atom in ClF_3O would not be sterically active, a tetrahedral molecule of symmetry C_{3v} would result, as proposed[4] by Bougon, *et al.*

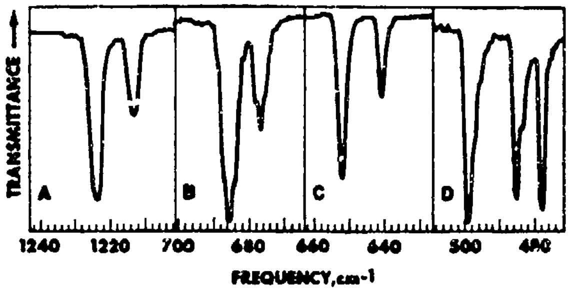
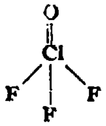


Figure 5.—Infrared spectra of ClF_3O in N_2 matrix at 4°K recorded at tenfold scale expansion under high resolution conditions: (A) 2.9 μmol of ClF_3O (matrix ratio (mr) 1:1000); (B) 2.0 μmol (mr 1:10,000); (C) 0.24 μmol (mr 1:10,000); (D) 10 μmol (mr 1:1000).

TABLE II

OVERTONES AND COMBINATION BANDS OBSERVED IN THE INFRARED SPECTRUM OF ClF_3O GAS

Frequencies, cm^{-1}		
Obsd	Calcd	Assignment
800 vvw, br	475 + 318 = 793	$(\nu_8 + \nu_5)$
899 vw	408 + 491 = 899	$(\nu_4 + \nu_3)$ or $(\nu_4 + \nu_8)$
980 w	2 × 491 = 982	$2\nu_3$ or $2\nu_8$ or $(\nu_3 + \nu_8)$
1161 mw	491 + 680 = 1171	$(\nu_3 + \nu_7)$ or $(\nu_8 + \nu_7)$
1372 mw	2 × 680 = 1360	$2\nu_7$
1899 vw	680 + 1221 = 1901	$(\nu_7 + \nu_1)$
2436 w	2 × 1221 = 2442	$2\nu_1$



III

For structures I and II, one would expect nine fundamental vibrations active in both the infrared and Raman spectrum. For structure III, one would expect only six fundamental vibrations, again, active in both the infrared and Raman spectrum. Since nine fundamental vibrations were unambiguously observed for ClF_3O (see Table I), structure III can be ruled out. Consequently, assignments for ClF_3O were made in point group C_s (see Table I) contrary to the conclusions[4] reached by Bougon, *et al.*, on the basis of incomplete experimental data. Further evidence against symmetry C_{3v} is based on the band shapes observed for the infrared spectrum of the gas showing that ClF_3O cannot be a symmetric top molecule. For example, in the case of C_{3v}, the Cl=O stretching mode at about 1220 cm^{-1} should show well-separated PQR branches. Since the geometry of ClF_3O of symmetry C_s can be estimated (see below), the three principal moments of inertia were computed for structure I resulting in $A = 0.216$, $B = 0.129$, and $C = 0.0934$ cm^{-1}. Based on these values, the infrared band contours were estimated for ClF_3O, according to the method of Ueda and Shimanouchi.[14] The observed band contours were consistent with those predicted. However, they cannot be used to distinguish structures I and II due to the interference by the ^{37}Cl isotope bands, the double and triple coincidences of bands in the infrared spectrum occurring at about 680 and 490 cm^{-1}, respectively, and the fact that most bands are blends of the A, B, and C type.

The assignments (see Table I) for ClF_3O in point group C_s (structure I) are based on the following argu-

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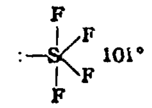
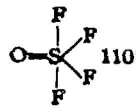
(14) T. Ueda and T. Shimanouchi, *J. Mol. Spectrosc.*, 28, 350 (1968).

ments. The band at about 1220 cm^{-1} occurs at a frequency much too high for any Cl—F fundamental vibration and, hence, must be assigned to the stretching vibration involving the Cl=O double bond. Comparison with related Cl—F containing compounds[15–18] indicates that of the three Cl—F stretching vibrations, at least two should show a frequency higher than 600 cm^{-1} (see Table I). Indeed two bands were observed at about 690 and 650 cm^{-1}. These were assigned to the equatorial Cl—F and the antisymmetric axial FClF stretching vibrations, respectively. These assignments were made on the basis of the observed ^{35}Cl–^{37}Cl isotopic shifts (see below), the relative infrared and Raman intensities, and the Raman polarization measurements. The fourth stretching vibration, *i.e.*, the symmetric FClF mode, should be polarized and of the highest relative intensity in the Raman spectrum. Furthermore, it should be relatively weak in the infrared spectrum and show no detectable Cl isotopic shift if the F–Cl–F group is approximately linear. Hence, this mode must be assigned to the band at about 480 cm^{-1}.

The remaining five bands must be assigned to deformation modes. Of these, three involve a motion of the doubly bonded oxygen atom and, consequently, should occur at higher frequencies. The two lowest frequency bands are assigned to the two F—Cl—F bending modes, ν_5 and ν_6, by analogy with ClF_3.[15] Of the remaining modes, the torsional motion should result in a band of very low intensity in both the infrared and the Raman spectrum. Obviously, only the 414-cm^{-1} band fulfills these requirements. The two highest frequency bands should belong to the F′—Cl=O scissoring and the rocking mode. On the basis of the observed and computed (see below) Cl isotopic shifts, we prefer to assign the scissoring mode, $\nu_3(A')$, to the 480-cm^{-1} band and the rocking mode, $\nu_8(A'')$, to 500 cm^{-1}. These assignments are supported by simple valence force field arguments and by comparison with the vibrational spectra of the related species, ClF_3,[15] ClF_2^-,[16] $ClF_2O_2^-$,[17] and ClO_2F[18] (see Table I).

Force Constants and Bonding.—The potential and kinetic energy metrics for chlorine trifluoride oxide were computed by a machine method.[19] The geometry assumed for this computation was $D(ClO) = 1.42$ Å, $R(ClF') = 1.62$ Å, $r(ClF) = 1.72$ Å, $\alpha(OClF') = 120°$, $\beta(OClF) = \gamma(FClF') = 90°$, based on the observed geometry for ClF_3[20] and a correlation between ClO bond length and stretching frequency.[21] In the absence of structural data, we assumed the oxygen atom, the fluorine atom, and the lone pair to require about the same space and, hence, to be about 120° apart. However, comparison with the known geometry of the trigonal-bipyramid type molecules SF_4[22] and SF_4O[23] indicates that the repulsion from a double bonded





oxygen atom should be intermediate between that of a free electron pair and that of a fluorine ligand. Consequently, the true structure of ClF_3O might be expected to deviate somewhat from that used for our computations.

The symmetry coordinates used for ClF_3O are given in Table III. The bending coordinates were weighted by unit (1 Å) distance so the stretching force constants have units of mdyn/Å, the deformation force constants units of mdyn Å/radian², and the stretch–bend interaction constants mdyn/radian. The *G* matrix and *Z* transformation were found by the computer and, hence, are not given here.

TABLE III

SYMMETRY COORDINATES FOR ClF_3O

A′	S_1	$D(ClO)$
	S_2	$R(ClF')$
	S_3	$\alpha(OClF')$
	S_4	$(1/\sqrt{2})[r_1(ClF) + r_2(ClF)]$
	S_5	$(1/\sqrt{2})[\beta_1(OClF) + \beta_2(OClF)]$
	S_6	$(1/\sqrt{2})[\gamma_1(FClF') + \gamma_2(FClF')]$
A″	S_7	$(1/\sqrt{2})[r_1(ClF) - r_2(ClF)]$
	S_8	$(1/\sqrt{2})[\beta_1(OClF) - \beta_2(OClF)]$
	S_9	$(1/\sqrt{2})[\gamma_1(FClF') - \gamma_2(FClF')]$

The force constants were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. The computed force constants are given in Table IV. An uncertainty estimate is difficult to make. However, numerical experiments with this and similar molecules indicate the uncertainties in the valence force constants to be 0.2 to 0.3 for Cl=O and 0.2 mdyn/Å for Cl—F. The force constants of greatest interest are the stretching force constants since they are a direct measure for the strength and covalent character of the various bonds. The value of 9.37 mdyn/Å obtained for $f_{Cl=O}$ is similar to those computed for ClO_2F (9.07 mdyn/Å)[18] and ClO_2^+ (8.96 mdyn/Å)[24] indicating double bond character. The value of 2.34 mdyn/Å computed for the axial Cl—F stretching force constant f_r is almost identical with that of 2.34 mdyn/Å, previously calculated[16] for ClF_2^-. The corresponding interaction constant, f_{rr}, is also very similar for both species. The relatively low value of f_r in ClF_2^- has previously been interpreted[16] in terms of semiionic three-center four-electron bonds. The same rea-

TABLE IV

INTERNAL FORCE CONSTANTS OF ClF_3O[a]

f_D	9.37	f_{rr}	0.26
f_R	3.16	$f_{\beta\beta}$	0.11
f_r	2.34	$f_{\gamma\gamma}$	0.13
f_α	1.84	$f_{r\beta} = -f_{r\beta'}$	0.25
f_β	1.69	$f_{\beta\gamma} = f_{\beta\gamma'}$	0.22
f_γ	1.87		

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian², and stretch–bend interaction constants in mdyn/radian.

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(15) H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, 53, 3517 (1970).

(16) K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, 6, 1159 (1967).

(17) K. O. Christe and E. C. Curtis, *ibid.*, 11, 35 (1972).

(18) D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, 20, 1763 (1964).

(19) E. C. Curtis, *Spectrochim. Acta, Part A*, 27, 1989 (1971).

(20) D. F. Smith, *J. Chem. Phys.*, 21, 609 (1953).

(21) E. A. Robinson, *Can. J. Chem.*, 41, 3021 (1963).

(22) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, 39, 3172 (1963).

(23) J. L. Hencher, D. W. Cruickshank, and S. H. Bauer, *ibid.*, 48, 518 (1968).

(24) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, 8, 2489 (1969).

soning[16] holds for the axial ClF bonds of ClF_3O and, hence, will not be repeated here. It should be pointed out, however, that in ClF_3O, enhancement of the ionic character of the axial ClF bonds is due to oxygen substitution, whereas in ClF_2^- it is due to the formal negative charge. Since the influence of oxygen substitution on the remaining ClF bonds has previously been discussed[17] at length for $ClO_2F_2^-$, it will not be reiterated. The value of 3.16 mdyn/Å computed for the equatorial ClF bond of ClF_3O is considerably larger than that of the axial bonds indicating[16] predominantly covalent bonding. In summary, the results from the force constant analysis are in excellent agreement with a generalized bonding scheme previously discussed[25] for a large number of halogen fluorides and suggest that the overall bonding in ClF_3O might be described by the following approximation. The bonding of the three equatorial ligands (including the free electron pair on Cl as a ligand and ignoring the second bond of the Cl=O double bond) is mainly due to a sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves mainly one delocalized p-electron pair of the chlorine atom for the formation of a semiionic three-center four-electron pσ bond.

The deformation force constants computed for ClF_3O are as expected. The values for interaction constants cannot be unique; those not given in Table IV were assumed zero. The values for f_{rr}, $f_{\beta\beta}$, $f_{\gamma\gamma}$, and $f_{r\beta}$ are in accord with those for similar molecules.[26] Fitting ν_5 and ν_6 required nonzero values for $f_{\beta\gamma}$ and $f_{\beta\gamma'}$. Similarly, ν_7 and ν_8 required nonzero values for $f_{r\beta}$ and $f_{r\beta'}$. While these four interaction constants are strictly indeterminant, numerical experiments showed that the observed frequencies could not be fitted with significantly different values.

The computed potential energy distribution is given in Table V. The results were normalized, but the sums do not add up to 1.0 since the less important terms are not listed. As can be seen from Table V, most vibrations are highly characteristic except for ν_5 and ν_6, which are almost an equal mixture of the symmetry coordinates, S_5 and S_6. The ν_5 and ν_6 modes can be visualized as a symmetric bending motion of the two axial fluorine atoms in a plane perpendicular to the direction of the lone pair, and ν_6 as a symmetric bending motion in the plane containing the lone pair.

TABLE V

POTENTIAL ENERGY DISTRIBUTION FOR ClF_3O

Assignment		Frequency, cm⁻¹	Potential energy distribution
A′	ν_1	1223	$0.96f_D$
	ν_2	694	$0.76f_R + 0.16f_\alpha$
	ν_3	490	$0.76f_\alpha + 0.17f_R$
	ν_4	482	$0.90f_r + 0.10f_{rr}$
	ν_5	319	$0.61f_\gamma + 0.53f_\beta - 0.14(f_{\beta\gamma} + f_{\beta\gamma'})$
	ν_6	227	$0.41f_\beta + 0.30f_\gamma + 0.09(f_{\beta\gamma} + f_{\beta\gamma'})$
A″	ν_7	652	$0.89f_r + 0.14f_t - 0.09(f_{r\beta} + f_{r\beta'})$
	ν_8	500	$0.97f_\beta$
	ν_9	414	$0.80f_\gamma$

The ^{35}Cl–^{37}Cl isotopic shifts computed for ClF_3O from the above force constants are listed in Table VI.

TABLE VI

OBSERVED AND COMPUTED ^{35}Cl–^{37}Cl ISOTOPIC SHIFTS FOR ClF_3O

Normal mode		Isotopic shift, cm⁻¹ Computed	Obsd
A′	ν_1	11.8	10.9
	ν_2	9.0	8.8
	ν_3	2.7	2.0
	ν_4	0	0
	ν_5	1.4	
	ν_6	0.8	
A″	ν_7	11.2	11.2
	ν_8	0.5	1.2 or less
	ν_9	0	

As can be seen, the agreement between the observed and computed shifts is good and lends further support to the assignments suggested above. Thus, the possibility of assigning the bands at 686, 652, and 478 cm⁻¹ to $\nu_{sym}(ClF_2(eq))$, $\nu_{asym}(ClF_2(eq))$, and $\nu(ClF(ax))$, respectively, of structure II can be ruled out based upon the lack of observing any ^{35}Cl–^{37}Cl isotopic splitting for the 478-cm⁻¹ band.

Association in the Liquid and Pure Solid.—The relatively high boiling point and Trouton constant[2] of ClF_3O imply its association in the liquid phase. More specific evidence about the nature of this association can be obtained from the vibrational spectra recorded for the liquid and the solid and from a controlled diffusion experiment carried out for matrix isolated ClF_3O. Principally, association could involve either oxygen or fluorine bridges. In the case of fluorine bridges, distinction might be made between equatorial and axial fluorine bridges. The stretching frequencies of the bonds involved in the bridging should decrease when going from the gas or matrix isolated solid to the liquid or pure solid. On the other hand, the bonds not involved in the bridging should show no decrease or possibly a very small increase in frequency. Comparison between the infrared spectra of matrix isolated (trace A, Figure 4) and pure solid ClF_3O (trace C, Figure 4) reveals that the Cl=O stretching mode frequency increases by about 10 cm⁻¹, that the equatorial ClF stretching mode shows no detectable change, but that the antisymmetric axial FClF stretching frequency decreases by about 50 cm⁻¹. Similarly, the controlled diffusion experiment carried out for matrix isolated ClF_3O (trace B, Figure 4) shows the appearance of new bands on the high-frequency side of $\nu(Cl{=}O)$ and $\nu(Cl–F')$ and on the low frequency side of $\nu_{as}(FClF)$. Furthermore, a weak band observed at 468 cm⁻¹ in the infrared spectrum of matrix isolated ClF_3O must be due to associated ClF_3O owing to its strong increase in relative intensity upon controlled diffusion. In addition, the Raman spectrum of the liquid (Figure 3) shows a pronounced frequency decrease only for $\nu_{sym}(FClF)$. Consequently, association appears to involve exclusively the axial fluorine atoms. This finding agrees with the association proposed[27] by Frey, Redington, and Aljibury for the structurally related, trigonal-bipyramidal molecules SF_4 and ClF_3.

A decrease of the volatility of ClF_3O due to extensive self-ionization (*i.e.*, $2ClF_3O \rightleftarrows ClF_2O^+ ClF_4O^-$) in the liquid or solid phase can be ruled out since it should result in more dramatic changes in the spectra upon phase change. Furthermore, no evidence for the presence of

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(25) K. O. Christe, paper presented at the Fourth International Fluorine Symposium, Estes Park, Colo., July 1967.

(26) K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, **357**, 125 (1968).

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TABLE VII

THERMODYNAMIC PROPERTIES FOR ClF_3O

T, °K	$C_p°$, cal/mol	$H° - H_0°$, kcal/mol	$-(F° - H_0°)/T$, cal/(mol deg)	$S°$, cal/(mol deg)
0	0	0	0	0
100	9.721	0.837	49.255	57.624
200	14.932	2.072	55.613	65.971
298.15	18.593	3.732	60.159	72.675
300	18.646	3.766	60.237	72.790
400	20.875	5.751	64.108	78.486
500	22.260	7.913	67.478	83.305
600	23.160	10.187	70.470	87.448
700	23.771	12.536	73.159	91.067
800	24.200	14.936	75 .02	94.271
900	24.512	17.372	77.838	97.141
1000	24.744	19.835	79.900	99.736
1100	24.921	22.319	81.813	102.103
1200	25.059	24.818	83.595	104.277
1300	25.168	27.330	85.255	106.288
1400	25.256	29.851	86.834	108.156
1500	25.328	32.380	88.314	109.901
1600	25.387	34.916	89.715	111.538
1700	25.437	37.458	91.044	113.078
1800	25.479	40.003	92.309	114.533
1900	25.514	42.553	93.516	115.912
2000	25.545	45.106	94.668	117.221

the bands characteristic for ClF_2O^+[7] and ClF_4O^-[3] could be detected in the spectra of liquid or solid ClF_3O.

Thermodynamic Properties.—The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation.[28] These properties are given for the range 0–2000°K in Table VII.

Acknowledgment.—The authors wish to express their gratitude to Dr. D. Pilipovich for continuous encouragement of this work and stimulating discussions, and to Mr. R. D. Wilson for his help in the preparation of some of the samples. We are indebted to Dr. J. Cape of the Science Center of North American Rockwell Corporation for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research, Power Branch, and by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under Contract AF 49(638)-1734.

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Chlorine Trifluoride Oxide. IV. Reaction Chemistry

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Reactions of chlorine trifluoride oxide, ClF_3O, with Cl_2, Cl_2O, $ClOSO_2F$, N_2F_4, HNF_2, and NF_2CFO are reported. In these reactions, ClF_3O either fluorinates, oxygenates, or both oxygenates and fluorinates the substrates. The interaction of ClF_3O with PtF_6 is also described. In this reaction, ClF_3O liberates F_2 and forms the new complex, $ClF_2O^+PtF_6^-$. Characterizing data for the complex are given.

Introduction

In the preceding papers,[1-3] we reported the preparation and properties of the new chlorine oxyfluoride, ClF_3O. Since ClF_3 is a powerful oxidative fluorinating agent, it was anticipated that ClF_3O would be similarly reactive as a fluorinating, as well as an oxygenating agent. This paper describes some of the reaction chemistry of ClF_3O.

Experimental Section

Apparatus.—Experimental techniques used in these studies were essentially the same as those described elsewhere.[1-4] Debye–Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in quartz capillaries (~0.5 mm o.d.). Gas chromatographic analyses were performed using the method of Dayan and Neale.[5] A Hanovia utility lamp (catalog no. 30620) was used for the photolyses.

Materials.—The preparation and purification of ClF_3O, Cl_2O, $ClOSO_2F$, HNF_2, and NF_2CFO are described elsewhere.[1,6-9] Chlorine (Matheson Co.), tetrafluorohydrazine (Allied Chemical Corp.), and platinum hexafluoride (Ozark Mahoning Co.) were purchased and purified by fractional condensations.

Reactions of Chlorine Trifluoride Oxide. With Chlorine.—At room temperature, chlorine and ClF_3O do not interact. An equimolar mixture (100 cm^3, 4.46 mmol each) of the two when heated at 200° for 16 hr in a 30-ml stainless steel cylinder did result in complete consumption of the ClF_3O. The products were separated by fractional condensation at −142 and −196° and analyzed by infrared spectroscopy and gas chromatography. Chlorine monofluoride was the principal product (262 cm^3, 11.7 mmol) with only a small amount of ClO_2F (6.7 cm^3, 0.3 mmol) and unreacted Cl_2 (15.7 cm^3, 0.7 mmol) being observed. Noncondensables (O_2) were also produced. When kept at 100° for 2 days, ClF_3O reacted with Cl_2 only partially (~30%) to give ClF_3, ClF, and ClO_2F as the major reaction products.

With Dichlorine Monoxide.—Chlorine trifluoride oxide (76.5 cm^3, 3.42 mmol) and an equal quantity of Cl_2O were separately condensed at −196° into a Kel-F reactor fitted with a Teflon valve. (Previous experiments in stainless steel cylinders resulted in extensive decomposition of the Cl_2O, apparently due to

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(4) K. O. Christe, C. J. Schack, and D. Pilipovich, *ibid*, **11**, 2205 (1972).

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(8) E. A. Lawton, E. F. C. Cain, D. F. Sheehan, and M. G. Warner, *J. Inorg. Nucl. Chem.*, **17**, 188 (1961).

(9) G. W. Fraser and J. M. Shreeve, *Inorg. Chem.*, **4**, 1497 (1965).

reaction with the fluorinated metal surface.) The reactor was allowed to warm slowly to ambient temperature. After a total reaction period of 15 hr, the sample was separated by fractional condensation at −95, −112, −142, and −196°. Unreacted Cl_2O and ClF_3O were recovered (134 cm³, 5.98 mmol total), together with ClF (17.5 cm³, 0.78 mmol) and ClO_2F (10.3 cm³, 0.46 mmol).

With Chlorine Fluorosulfate.—Equimolar amounts (34.2 cm³, 1.53 mmol) of ClF_3O and $ClOSO_2F$ were separately condensed into a prepassivated 10-ml stainless steel cylinder at −196°. The cylinder was allowed to warm to ambient temperature and to stand for 5 days. The reaction products were separated by several fractional condensations in a series of U traps cooled to −80, −95, −142, and −196°. Some unreacted ClF_3O was found, but all the $ClOSO_2F$ had been consumed. The materials formed were SO_2F_2 (13.0 cm³, 0.58 mmol), $S_2O_5F_2$ (9.17 cm³, 0.43 mmol), ClF (26.8 cm³, 1.20 mmol), and ClO_2F (24.0 cm³, 1.07 mmol).

With Tetrafluorohydrazine.—At ambient temperature, chlorine trifluoride oxide and N_2F_4 do not react. An equimolar mixture of the two (99.4 cm³, 4.44 mmol each) was heated in a stainless steel cylinder at 130° for 65 hr before separating the products by fractional condensation. No unreacted N_2F_4 was recovered, but 45.7 cm³ of ClF_3O (2.04 mmol) remained. The principal nitrogen containing product was NF_3 (120 cm³, 5.35 mmol), some of which may have been lost by incomplete condensation in the trap cooled to −196°. Nitrosyl fluoride (62.6 cm³, 2.80 mmol) and ClF (53.8 cm³, 2.40 mmol) were also obtained along with trace amounts of FNO_2, NF_3O, and ClO_2F. At 100° for 24 hr, ClF_3O and N_2F_4 reacted in the same fashion but somewhat less than half the N_2F_4 was consumed.

Photolysis with Tetrafluorohydrazine.—Measured amounts of ClF_3O (85.6 cm³, 3.82 mmol) and N_2F_4 (48.0 cm³, 2.14 mmol) were condensed into a stainless steel cylinder cooled to −196°. The cylinder was equipped at its upper end with a uv grade sapphire window (5-in diameter). After warming to ambient temperature, the contents of the cylinder was irradiated for 2 hr with a Hanovia utility lamp before separating the products. Multiple fractional condensations through U-traps cooled to −78, −95, −142, and −196° were used for this purpose. Considerable amounts of unreacted ClF_3O (60.2 cm³, 2.69 mmol) were recovered, but all the N_2F_4 had been consumed. The products were NF_3 (68.5 cm³, 3.06 mmol), FNO + FNO_2 (15.5 cm³, 0.69 mmol), ClF (23.2 cm³, 1.04 mmol), and ClF_3 (2.3 cm³, 0.10 mmol) The chlorine trifluoride was isolated with an equivalent amount of FNO owing to the formation of the $NO^+ClF_4^-$ complex[10] in the trap cooled to −78°. The discrepancy in the nitrogen material balance for the reaction is ascribed to the incomplete condensation of NF_3 at −196° since no solid residues were observed in the reactor. Mixtures of ClF_3O and N_2F_4 were also irradiated in a cylinder with a 1-in. diameter sapphire window. In these experiments, very little reaction occurred even with prolonged irradiation (2 days) and approximately 90% of the reactants was recovered. The products were NF_3O, NF_3, FNO, ClF_3, and ClF.

With Difluoramine (*Caution!*)[11] **and Difluoraminocarbonyl Fluoride.**—A Kel-F reactor fitted with a Teflon valve was used to avoid the incompatibility problems of ClF_3O (and generated HF) with glass and HNF_2 with metal. From the glass line, HNF_2 (61.0 cm³, 2.72 mmol) was loaded at −142°, and after attachment of the container to the metal line, ClF_3O (35.9 cm³, 1.60 mmol) was condensed in at the same temperature. The closed reactor was warmed to −78° for 15 min before fractionation in the metal line was started through U traps cooled to −78, −95, −142, and −196°. The two warmest traps contained HF (not measured) and ClF_3O (8.1 cm³, 0.36 mmol). The −142° fraction was an approximately equimolar mixture of ClO_2F and Cl_2 (total 6.2 cm³, 0.28 mmol) with a trace of ClF_3. The −196° fraction consisted of NF_3O (19.5 cm³, 0.87 mmol), NF_2Cl (19.4 cm³, 0.87 mmol), and N_2F_4 (10.0 cm³, 0.45 mmol). No unreacted HNF_2 was observed, although the N_2F_4 may have arisen in part from the decomposition of HNF_2 in the metal system during work-up.

A similar reaction was observed between excess ClF_3O and NF_2CFO (46 cm³, 2.05 mmol). However, in this case, the predominant N–F product was N_2F_4 (18 cm³, 0.8 mmol) and COF_2 (46 cm³, 2.05 mmol), with much less NF_3O and NF_2Cl (~5 cm³ each).

With Platinum Hexafluoride.—Platinum hexafluoride (32.2 cm³, 1.44 mmol) and ClF_3O (48.4 cm³, 2.16 mmol) were combined at −196° in a prepassivated 10-ml Monel cylinder. The contents of the cylinder was allowed to warm up slowly to room temperature and was kept at this temperature for 15 hr. Subsequently, the cylinder was cooled to −196° and 14.8 cm³ (0.66 mmol) of material volatile at −196° was removed. The volatile material was identified as F_2 by its vapor pressure at −196° and mass spectrum. The contents of the cylinder was allowed to warm to ambient temperature, and 14.8 cm³ (0.66 mmol) of volatile material was removed at this temperature which consisted, according to its infrared spectrum, of ClF_3O. The cylinder was opened in the glove box and contained 0.57 g of a bright yellow solid, which was identified by vibrational spectroscopy as $ClF_2O^+PtF_6^-$. Therefore, PtF_6 (1.44 mmol) had reacted with ClF_3O (1.50 mmol) in a mole ratio of 1:1.04, producing F_2 (0.66 mmol) and the solid complex, $ClF_2O^+PtF_6^-$.

Results and Discussion

Chlorine trifluoride oxide reacts with numerous materials causing oxidation through both fluorination and oxygenation. With hydrogen-containing species, these reactions may occur at quite low temperature and with hydrocarbon-type compounds are generally explosive. However, many chlorine, fluorine, or oxygen substituted compounds, even with lower valent central atoms, react only slowly at ambient temperature, or not at all. Thus, no reaction was observed at room temperature between ClF_3O and chlorine, chlorine fluorides, chlorine oxyfluorides, and the nitrogen fluorides, FNO, FNO_2, NF_3, and N_2F_4. However, elevated temperatures or uv photolysis have resulted in appreciable reaction of all compounds examined.

Reactions of chlorine and ClF_3O were carried out as a means of assessing the possible courses by which the oxyfluoride might undergo reduction. Basically, this could occur through fluorination or oxygenation of the Cl_2 starting material. A controllable fluorination reaction would be particularly desirable since it might yield the unknown compound, FClO. Whereas at 25°, no interaction was detected, at 200° the following reaction occurred

$$ClF_3O + Cl_2 \longrightarrow 3ClF + 0.5O_2$$

It is tempting to interpret this equation in terms of direct oxygen elimination from ClF_3O, followed by equilibration[12] of ClF_3 and Cl_2 to ClF. However, the following evidence suggests the participation of chlorine in the initial reduction step: (1) ClF_3O alone does not undergo substantial thermal degradation under these conditions;[1] and (2) experiments at lower temperature showed ClF_3, ClF, and ClO_2F as major reaction products. These results might be rationalized by assuming the following reaction sequence involving FClO as an unstable intermediate.

$$\begin{array}{l} 2ClF_3O + 2Cl_2 \longrightarrow 2[FClO] + 4ClF \\ 2[FClO] \longrightarrow ClO_2F + ClF \\ ClO_2F \longrightarrow ClF + O_2 \\ \hline 2ClF_3O + 2Cl_2 \longrightarrow 6ClF + O_2 \end{array}$$

The thermal decomposition of ClO_2F in quartz to ClF

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[10] R. D. Whitney, R. O. MacLaren, T. J. Hurley, and C. R. Fogle, *J. Amer. Chem. Soc.*, **86**, 4340 (1964).

[11] *Caution!* Difluoramine should not be cooled below −142° because of its pronounced tendency to explode after being in the solid state. In addition, chlorine fluorides or oxyfluorides must be free from chlorine oxide impurities for reactions with difluoramine since such impurities often cause explosive deflagration.

[12] H. Schmitz and H. J. Schumacher, *Z. Naturforsch. A*, **2**, 359 (1947).

and O_2 has previously[13] been demonstrated. The fact that this reaction appears to proceed in our experiments at lower temperature might be explained by the catalytic influence[14] of metal fluorides. As an alternative, the decomposition of the unstable FClO may vary with reaction temperature. Thus, at lower temperature, FClO might decompose to ClO_2F and ClF, whereas at higher temperature it might yield directly ClF and O_2. The assumption of an unstable FClO intermediate is reasonable. Numerous chlorine fluoride reaction systems, such as ClF_3–H_2O,[14] ClF_3–$HONO_2$,[15] or ClF_3O–Cl_2O (see below), are best interpreted by assuming the formation of an unstable FClO intermediate. In addition, our repeated efforts to synthesize and isolate a stable FClO moiety[15] have been unsuccessful.

Chlorine monoxide and ClF_3O reacted slowly at room temperature. The use of an inert material for the reactor (Kel-F) allowed the course of the reaction to be determined without extensive, interfering side reactions.

$$ClF_3O + Cl_2O \longrightarrow 2ClF + ClO_2F$$

Again, the fluorination of a chlorine atom (of Cl_2O) appears to be a plausible first reaction step, followed by the formation and decomposition of an unstable FClO intermediate (see above). This reaction of Cl_2O and ClF_3O may also account, at least in part, for the less than theoretical yields of ClF_3O in its synthesis from Cl_2O.[1]

Chlorine fluorosulfate and ClF_3O reacted at ambient temperature forming the products described by the following equations

$$ClF_3O + 2ClOSO_2F \longrightarrow S_2O_5F_2 + ClO_2F + ClF$$

$$ClF_3O + ClOSO_2F \longrightarrow SO_2F_2 + ClO_2F + ClF$$

which account for 60 and 40%, respectively, of the $ClOSO_2F$ consumed. The formation of $S_2O_5F_2$ obviously involves a complex process, including at some point the abstraction of oxygen from the SO_3F group. Indeed, the failure to find either $S_2O_6F_2$ or SO_3F_2 as products suggests that SO_3F radicals are not involved in the reaction. Further, it appears that the overall process may be quite similar to that noted[1] in the preparation of ClF_3O from Cl–O–X species (where X is any other radical, such as Cl, NO_2, or SO_3F). Namely, fluorination of the chlorine atom of the hypochlorite group facilitates O–X bond rupture in preference to the Cl–O bond-breaking process. Such a mechanism would yield SO_3F radicals which can either be fluorinated to SO_2F_2 or can react with additional $ClOSO_2F$ to give $S_2O_5F_2$. However, direct fluorination at the sulfur of $ClOSO_2F$ cannot be excluded as an alternate route to SO_2F_2. The chlorine compounds produced, ClF and ClO_2F, are again the same as those generally obtained from ClF_3O on reaction with Cl–O-containing compounds as expected for an unstable FClO intermediate.

Tetrafluorohydrazine and ClF_3O reacted at an appreciable rate only above 100°. Nitrogen trifluoride and nitrosyl fluoride were obtained in fair agreement with the stoichiometry shown.

$$ClF_3O + 2N_2F_4 \longrightarrow 3NF_3 + FNO + ClF$$

The nitrogen fluoride products are the result of oxygenation and fluorination by ClF_3O. Overall, the reaction is quite similar to that reported[16] for N_2F_4 and OF_2 which also yielded NF_3 and FNO in a 3:1 ratio. Only a trace of the more highly oxidized nitrogen fluoride, NF_3O, was observed. However, this indicated that alternate conditions might more fully take advantage of the ability of ClF_3O to fluorinate and oxygenate. To this end, ultraviolet irradiations of N_2F_4–ClF_3O mixtures were carried out. It was found that limitation of the intensity of the uv irradiation (through the use of a small reactor window, 1-in. diam) allowed greater amounts of NF_3O to be formed than in the thermal reaction. But these quantities were still small, about 5 mol %/mol of N_2F_4. Increasing the window area (and hence the admitted light) by a large factor led to complete conversion of the N_2F_4 to NF_3, FNO, and FNO_2. No attempts were made to maximize conditions for oxidizing N_2F_4 to NF_3O using ClF_3O.

Chlorine trifluoride oxide and difluoramine underwent smooth, fast reaction at temperatures where pure ClF_3O is a solid. Three N–F-containing compounds, NF_3O, $ClNF_2$, and N_2F_4, were formed and the first two of these were always produced in nearly equimolar amounts. Thus, the major reactions may be

$$\begin{array}{l} ClF_3O + 2HNF_2 \longrightarrow [FClO] + 2HF + 2NF_2\cdot \\ 2NF_2\cdot + [FClO] \longrightarrow NF_2Cl + NF_3O \\ \hline ClF_3O + 2HNF_2 \longrightarrow NF_2Cl + NF_3O + 2HF \end{array}$$

accompanied by the following competing reactions

$$\begin{array}{l} 2NF_2\cdot \longrightarrow N_2F_4 \\ 2[FClO] \longrightarrow ClO_2F + ClF \\ ClF + HNF_2 \longrightarrow HF + NF_2Cl \\ \hline 2[FClO] + HNF_2 \longrightarrow ClO_2F + NF_2Cl + HF \end{array}$$

The high yield of NF_3O (70% based on ClF_3O consumed) noted here is remarkable when compared to previously reported[17,18] and unreported[19,20] yields obtained under a variety of conditions.

The reaction between difluoraminocarbonyl fluoride, F_2NCFO, and ClF_3O yielded again NF_3O and $ClNF_2$ in nearly equimolar amounts. However, the yields were much lower (20% based on ClF_3O consumed) with N_2F_4 being the main N–F containing product. By analogy with the HNF_2–ClF_3O reaction (see above), the following reaction sequence might be proposed

$$\begin{array}{l} ClF_3O + 2F_2NCFO \longrightarrow 2COF_2 + [FClO] + 2NF_2\cdot \\ 2NF_2\cdot + [FClO] \longrightarrow NF_2Cl + NF_3O \\ \hline ClF_3O + 2F_2NCFO \longrightarrow NF_2Cl + NF_3O + 2COF_2 \end{array}$$

with the competing reactions being identical with those written for the ClF_3O–HNF_2 reaction.

The formation of the ClF_2O^+ cation by the reaction

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(13) M. J. Heras, P. J. Aymonino, and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, **23**, 161 (1959).

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(17) (a) N. Bartlett, J. Passmore, and E. J. Wells, *Chem. Commun.*, 213 (1966); (b) N. Bartlett and S. P. Beaton, *ibid.*, 167 (1966); (c) N. Bartlett, S. P. Beaton, and N. K. Jha, *ibid.*, 168 (1966).

(18) W. B. Fox, *et al.*, *J. Amer. Chem. Soc.*, **88**, 2604 (1966).

(19) E. A. Lawton and D. Pilipovich, U. S. Patent 3,505,015 (April 7, 1970); British Patent 1,104,711 (Feb 15, 1965).

(20) Just as Bartlett and coworkers showed that PtF_6 or OsF_6 reacts with FNO to give low or trace amounts of NF_3O, so also ClF_5 and FNO have been noted to form slight amounts of NF_3O: D. Pilipovich and H. F. Bauer, unpublished results.

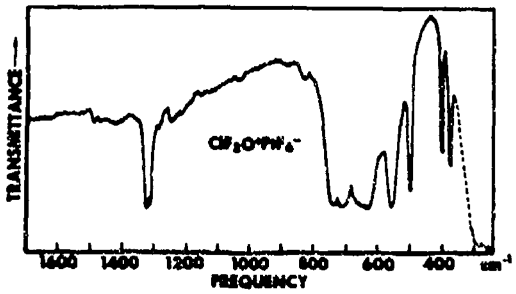

Figure 1.—Infrared spectrum of solid $ClF_2O^+PtF_6^-$ as AgCl disk.

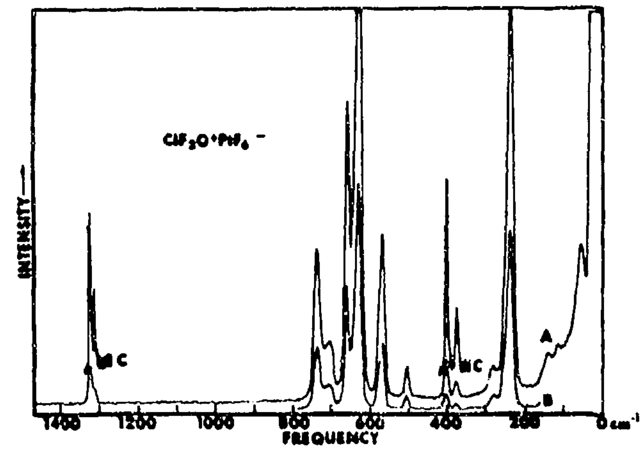

Figure 2.—Raman spectrum of solid $ClF_2O^+PtF_6^-$ at three different recorder voltages: exciting line 6471 Å; spectral slit width for curves A and B 8 cm⁻¹; for curve C 2 cm⁻¹.

of ClF_3O with strong Lewis acids is reported elsewhere.[4,21] The same cation was found to result from the interaction of platinum hexafluoride and ClF_3O, according to

$$ClF_3O + PtF_6 \longrightarrow ClF_2O^+PtF_6^- + 0.5F_2$$

While all the reactions described earlier in this report showed ClF_3O functioning as an oxidizing agent, here it can be seen that platinum hexafluoride is the more powerful oxidizing agent. However, the oxidation is confined to one of the fluorine ligands of ClF_3O and does not affect the oxidation state of the chlorine central atom which would result in the most interesting ClF_5O molecule. All the PtF_6 reacted and excess ClF_3O was recovered unchanged.

The bright yellow, crystalline solid, $ClF_2O^+PtF_6^-$, was characterized by vibrational spectroscopy. Figures 1 and 2 show the infrared and Raman spectrum, respectively, of the solid. Table I lists the observed frequencies together with their assignment. All bands expected for ClF_2O^+ [21] have been observed with proper frequencies and intensities. In addition to the ClF_2O^+ bands, the vibrational spectrum shows the bands characteristic[22] for PtF_6^-. Consequently, the solid obtained from the ClF_3O–PtF_6 reaction has the ionic composition $ClF_2O^+PtF_6^-$.

The X-ray powder diffraction pattern of ClF_2O^+-PtF_6^- is listed in Table II. The observed lines were indexed on the basis of an orthorhombic unit cell with $a = 9.94$, $b = 11.12$, and $c = 8.21$ Å. Assuming that the volume of the oxygen atoms will be comparable to that of the fluorine atoms, and neglecting contributions from the highly charged central atoms to the volume (as suggested by Zachariasen[23,24]), an average volume of 17–18 Å³ can be expected for each fluorine or oxygen atom in $ClF_2O^+PtF_6^-$. Thus, values of 17.8 and 17.0 Å³ have been reported for $IF_6^+AsF_6^-$ [25] and NF_4^+-AsF_6^-,[26] respectively. Based on this assumption, one can deduce six molecules per unit cell for $ClF_2O^+PtF_6^-$, resulting in an average volume of 16.81 Å³ per F or O atom. The powder pattern of $ClF_2O^+PtF_6^-$ is similar

TABLE I

VIBRATIONAL SPECTRUM OF $ClF_2O^+PtF_6^-$ AND ITS ASSIGNMENT COMPARED TO THAT OF $ClF_2O^+AsF_6^-$ [a]

Observed frequency, cm⁻¹				Assignment (for ClF_2O^+ in C_s)
$ClF_2O^+PtF_6^-$		$ClF_2O^+AsF_6^-$		
Ir	Raman	Ir	Raman	
1326 ms	1324 (0.6)[b]	1331 ms	1333 (2)[b]	$\nu_1(A')$ ³⁵Cl
1313 mw	1311 (0.2)	1319 mw	1320 (1)	$\nu_1(A')$ ³⁷Cl
737 s	737 (2.7)	750 br, s	757 br (3)	$\nu_2(A')$
705 s	705 (0.8)	695 vs	696 (1)	$\nu_5(A'')$
643 vs	658 (4.2)	395 vs		XF_6^-
630 sh	630 (10)	675 sh, w	674 (10)	
	575 sh			
564 s	564 (2.9)	561 ms	563 (3)	
508 s	506 (0.5)	509 ms	511 (2)	$\nu_3(A')$
401 ms	401 (0.7)	407 s	406 (2)	$\nu_6(A'')$
		388 s		XF_6^-
386 ms	386 (0.2)	378 sh	378 sh	$\nu_4(A')$
	280 (0.3)		371 (4)	XF_6^-
	239 (7.9)			
	140 (0.3)			Lattice modes
	115 (0.2)			
	58 (1.0)			

[a] K. O. Christe, E. C. Curtis, and C. J. Schack, *Inorg. Chem.*, 11, 2212 (1972). [b] Uncorrected Raman intensities.

TABLE II

X-RAY POWDER DATA FOR $ClF_2O^+PtF_6^-$

d, Å Obsd	d, Å Calcd	Intensity	hkl
7.43	7.43	mw	110
5.47	5.50	m	111
4.95	4.97	mw	200
4.25	4.26	vs	201
4.09	4.10	s	002
3.72	3.70	ms	030
3.61	3.60	vw	112
3.38	3.37	w	031
3.31	3.31	s	300
3.17	3.17	m	310
3.02	3.04	w	212
2.98	2.99	ms	231
2.86	2.85	w	320
2.77	2.78	m	040
2.59	2.57	m	302
2.48	2.49	m	400
2.33	2.34	mw	322
2.20	2.20	ms	223
2.14	2.15	vw	051
2.07	2.07	vw	313
2.04	2.03	m	250
1.99	1.99	mw	500
1.93	1.93	ms	501

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(25) K. O. Christe and W. Sawodny, *Inorg. Chem.*, 6, 1783 (1967).

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to that observed[27] for $ClO_2^+AsF_6^-$. The latter has a tetragonal unit cell with $a = 10.39$ and $c = 8.03$ Å. The unit cell of $ClF_2O^+PtF_6^-$ might be derived from the $ClO_2^+AsF_6^-$ cell by assuming orthorhombic distortion due to the lower symmetry of the ClF_2O^+ cation. Further evidence for the formulation of the solid as $ClF_2O^+PtF_6^-$ can be deduced from the fact that the X-ray powder diffraction patterns of $ClF_2O^+AsF_6^-$[4] and $ClF_2O^+PtF_6^-$ are almost identical.

Acknowledgment.—We are pleased to acknowledge support for this work by the Office of Naval Research, Power Branch. We are indebted to R. B. Cook of Cary Instruments for recording the Raman spectrum.

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Chlorine Trifluoride Oxide. V. Complex Formation with Lewis Acids and Bases

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Chlorine trifluoride oxide, ClF_3O, exhibits amphoteric character. With the strong Lewis bases CsF, RbF, and KF it forms the stable, white, crystalline adducts, $CsF \cdot ClF_3O$, $RbF \cdot ClF_3O$, and $KF \cdot ClF_3O$, respectively. With the weaker base FNO it neither forms a complex nor chemically interacts at temperatures as low as −95°. With the Lewis acids SbF_5, AsF_5, and BF_3 it forms white, crystalline 1:1 adducts, whereas with SiF_4 it forms a 2:1 adduct. The thermal stability of these adducts decreases in the order: $ClF_3O \cdot SbF_5 > ClF_3O \cdot AsF_5 > ClF_3O \cdot BF_3 > (ClF_3O)_2 \cdot SiF_4$. The dissociation pressure–temperature relation has been measured and thermodynamic data are calculated for the process $(ClF_3O)_2 \cdot SiF_4(s) \rightleftharpoons 2ClF_3O(g) + SiF_4(g)$. The tendencies of adduct formation are compared for ClF_3O, ClF_5, ClO_2F, ClF_3, and ClF and are correlated with the structural stability of the halogen fluorides and their corresponding ions.

Introduction

Halogen fluorides and oxyfluorides generally exhibit amphoteric character.[1] Consequently, we considered that ClF_3O might also form complexes with strong Lewis acids and bases. In this paper we report on the syntheses and some of the properties of a number of adducts derived from ClF_3O.

Experimental Section

Materials and Apparatus.—Experimental techniques used in these studies were essentially the same as those described elsewhere.[2-4] The preparation and purification of ClF_3O and FNO are described elswhere.[6,7] The alkali metal fluorides were fused in a platinum crucible and powdered in a drybox prior to use. Arsenic pentafluoride (from Ozark Mahoning Co.), BF_3, and SiF_4 (both from the Matheson Co.) were purified by fractional condensation. Antimony pentafluoride (from Ozark Mahoning Co.) was purified by vacuum distillation at ambient temperature. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra.

Preparation of Alkali Metal Fluoride-ClF_3O Adducts.—Dry CsF (66.0 mmol) was placed into a 90-ml prepassivated Monel cylinder, and purified ClF_3O (106.4 mmol) was added at −196°. The cylinder was kept at ambient temperature for 30 days. Unreacted ClF_3O (40.5 mmol) was removed *in vacuo* and identified by its infrared spectrum. The cylinder was opened in the glove box and contained 17.1 g of a stable, white, crystalline solid (weight calculated for $Cs^+ClF_4O^-$, 17.18 g). Therefore, CsF (66.0 mmol) had reacted with ClF_3O (65.9 mmol) in a mole ratio of 1:0.998 producing the complex $Cs^+ClF_4O^-$.

Similarly, RbF (92.0 mmol), when combined with ClF_3O (93.5 mmol) at −196° and shaken at ambient temperature for 2 days, reacted with ClF_3O (67.15 mmol) producing the complex $Rb^+ClF_4O^- \cdot 0.28RbF$.

Pure ClF_3O (purity 99+%) was loaded into a 316 stainless steel cylinder containing a large excess of dry KF. After the contents of the cylinder was kept at ambient temperature for 30 days, practically all of the ClF_3O had complexed with KF.

The FNO-ClF_3O System.—Nitrosyl fluoride (25.6 mmol) and ClF_3O (12.8 mmol) were combined at −196° in a Teflon FEP U trap. The mixture was allowed to warm to −79° and was kept at this temperature for 24 hr. It remained at all times a water-clear liquid and no sign of solid formation could be observed. The vapor pressure above the liquid was about 115 mm. The contents of the trap was cooled to −95°, and FNO (25.5 mmol) was removed by vacuum distillation. The residue (12.7 mmol) was shown by its infrared spectrum to be essentially pure ClF_3O. Hence, ClF_3O and FNO do not form a stable complex at −95°.

Preparation of ClF_3O·Lewis Acid Adducts.—Boron trifluoride (4.00 mmol) and ClF_3O (3.22 mmol) were combined at −196° in a Teflon FEP container. The mixture was allowed to warm up slowly to ambient temperature and was kept at this temperature for 12 hr. Unreacted BF_3 (0.74 mmol) was removed *in vacuo* at 20° and identified by its infrared spectrum. The white, crystalline residue had no detectable dissociation pressure at 20°. Therefore, ClF_3O (3.22 mmol) had reacted with BF_3 (3.26 mmol) in a mole ratio of 1:1.01, producing the complex $ClF_3O \cdot BF_3$.

Similarly, AsF_5 (16.4 mmol) and ClF_3O (13.2 mmol) were combined at −196°. After keeping the mixture at 20° for 2 hr, unreacted AsF_5 (2.8 mmol) was removed *in vacuo* at 20°. Therefore, ClF_3O (13.2 mmol) had reacted with AsF_5 (13.6 mmol) in a mole ratio of 1:1.03 producing the white, crystalline, stable complex, $ClF_3O \cdot AsF_5$.

Silicon tetrafluoride (3.79 mmol) was combined with ClF_3O (5.02 mmol) at −196°. When the mixture was allowed to warm up to about −80°, complex formation occurred. Unreacted SiF_4 (1.21 mmol) was removed *in vacuo* at −64° and identified by its infrared spectrum. Therefore, ClF_3O (5.02 mmol) had reacted with SiF_4 (2.58 mmol) in a mole ratio of 2:1.03, producing the white, crystalline complex $(ClF_3O)_2 \cdot SiF_4$.

Antimony pentafluoride (104 mmol) and ClF_3O (20.9 mmol) were combined in a 150-ml prepassivated Monel cylinder at −196°. The contents of the cylinder was kept in an electrically heated oven at 135° for 6 days under autogenous pressure. Unreacted SbF_5 was removed by vacuum distillation at 130°.

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(4) K. O. Christe and E. C. Curtis, *ibid.*, 11, 2196 (1972).

(5) C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, *ibid.*, 11, 2201 (1972).

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(7) K. O. Christe, *Inorg. Chem.*, 11, 1220 (1972).

The cylinder was opened in the glove box and contained 7.8 g of a white, crystalline solid (calculated weight for 20.9 mmol of $ClF_3O \cdot SbF_5$, 6.8 g; for 20.9 mmol of $ClF_3O \cdot 2SbF_5$, 11.3 g). Therefore, ClF_3O had reacted with SbF_5 in a mole ratio of 1:1.22.

Dissociation Pressure Measurements.—The $(ClF_3O)_2 \cdot SiF_4$ complex was prepared in a Teflon FEP container directly connected to a Heise, Bourdon-tube-type gauge (0–1500 mm ± 0.1%). The temperature of the cooling bath was determined with a copper–constantan thermocouple. To be certain that an equilibrium existed at each temperature reading, a sample of the gas above the solid complex was pumped off and a constant pressure was reestablished. True equilibrium existed at a given temperature if the pressures, before and after the pumping off procedure, were identical. Equilibrium pressures were always approached from below a given temperature. The following temperature (°C)–vapor pressure (mm) relation was observed: −30.9, 4; −24.5, 8; 0.9, 72; 6.0, 124; 15.7, 257; and 20.8, 380. The best fit of log P *vs.* T^{-1} (in °K) was obtained by the method of least squares.

X-Ray Powder Data.— Debeye-Scherrer powder patterns were taken as previously described.[6]

Results and Discussion

Synthesis. —Chlorine trifluoride oxide and the alkali metal fluorides, CsF, RbF, and KF, when combined at ambient temperature, produced the 1:1 complexes, $CsF \cdot ClF_3O$, $RbF \cdot ClF_3O$, and $KF \cdot ClF_3O$, respectively. For CsF a practically quantitative conversion to $CsF \cdot ClF_3O$ was achieved, whereas for RbF the conversion to $RbF \cdot ClF_3O$ was only 78%. In the case of RbF, however, a considerably shorter reaction time and a nearly stoichiometric amount of starting materials were employed in the synthesis. Hence, the conversion of RbF to $RbF \cdot ClF_3O$ could almost certainly be increased by using an excess of ClF_3O, a longer reaction time, and a slightly increased reaction temperature. The fact that a high conversion to the corresponding alkali metal salt becomes increasingly difficult with decreasing atomic weight of the alkali metal has also been observed in the case of the ClF_2^- and ClF_4^- salts.[8,9] This might be due to various effects such as changes in lattice energy, solubility in the excess halogen fluoride or oxyfluoride, and stability of the adducts.

No indication for the formation of a stable complex between FNO and ClF_3O was found at temperatures as low as −95°. The fact that only a liquid phase was observed at relatively low temperatures where pure ClF_3O (mp, −42°) is a solid indicates high miscibility or solubility of ClF_3O in FNO. The vapor pressure of ~115 mm observed at −78.8° above the liquid phase is only slightly lower than the value of 137 mm calculated for an ideal 1:2 mixture from Raoult's law.

Chlorine trifluoride oxide forms stable 1:1 adducts with the Lewis acids AsF_5 and BF_3. In spite of the excess Lewis acid employed in the syntheses, no evidence for the formation of di- or polymeric anions, such as $B_2F_7^-$ [10–12] or $As_2F_{11}^-$,[12,13] was obtained. However, in the case of SbF_5, a product having the composition (according to its infrared spectrum and the material balance) of $ClF_2O^+SbF_6^- \cdot 0.28ClF_2O^+Sb_2F_{11}^-$ was obtained. The formation of some $Sb_2F_{11}^-$ salt[14–16] is not surprising since a large excess of SbF_5 was used in the synthesis. No attempts were made to optimize the reaction conditions for the synthesis of $ClF_2O^+SbF_6^-$. However, using a large excess of ClF_3O, decreasing the reaction temperature, and adding the SbF_5 (preferably in a solvent such as HF[12]) slowly to the excess ClF_3O should result in a better defined 1:1 adduct.

The difunctional Lewis acid SiF_4, when combined with ClF_3O at about −80°, forms the expected 1:2 complex. The lower temperature required for the synthesis of $(ClF_3O)_2 \cdot SiF_4$ is due to the decreased thermal stability of the adduct.

Properties. The 1:1 adducts of ClF_3O with SbF_5, AsF_5, and BF_3 are white, crystalline solids showing no measurable dissociation pressure at ambient temperature. The thermal stability of the Lewis acid adducts decreases in the order $ClF_3O \cdot SbF_5 > ClF_3O \cdot AsF_5 > ClF_3O \cdot BF_3 > (ClF_3O)_2 \cdot SiF_4$. Thus, $ClF_3O \cdot SbF_5$ is stable at 130° *in vacuo*, whereas $(ClF_3O)_2 \cdot SiF_4$ reaches a dissociation pressure of 760 mm at 31°. Based on the observed dissociation pressure–temperature data, a plot of log P_{mm} *vs.* T^{-1} (in °K) for the heterogeneous equilibrium

$$(ClF_3O)_2SiF_4(s) = 2ClF_3O(g) + SiF_4(g)$$

is a straight line. The equation log $P_{mm} = 11.8018 - 2712.3/T$ represents these data in the temperature range −30.9 to 20.8°. The standard error of the estimate of log P was 0.008 which corresponds to 2% deviation in pressure. The index of correlation (ρ) is 0.999938.

By extrapolation, a dissociation pressure of 1 atm was obtained at 30.9°. At 25° the dissociation pressure amounts to 408 mm. From the slope of the log P_{mm} *vs.* T^{-1} curve, $\Delta H_d° = 37.24$ kcal mol^{-1} was found.[17] From $\Delta F°_T = -RT \ln Kp_{atm}$, a free energy change, $\Delta F°_{298} = 1.846$ kcal mol^{-1}, and from $\Delta S°_T = (\Delta H° - \Delta F°_T)T^{-1}$, an entropy change, $\Delta S°_{298} = 118.7$ cal deg^{-1} mol^{-1}, were found for the dissociation process at 25°. A heat of formation of $(ClF_3O)_2 \cdot SiF_4(s)$, $\Delta H_f°_{298} = 488.4 \pm 6$ kcal mol^{-1}, was calculated based upon $\Delta H_f°_{298}[SiF_4(g)]$[18] $= 385.980$ kcal mol^{-1} and $\Delta H_f°_{298}[ClF_3O(g)]$[19] $= -32.6 \pm 3$ kcal mol^{-1}. The uncertainty in the heat of formation value is mainly due to the uncertainty in the value of the heat of formation of aqueous HF[20] used for calculating $\Delta H_f°_{298}$ of ClF_3O. The heat of dissociation,[17] 37.24 kcal mol^{-1}, obtained for $(ClF_2O^+)_2SiF_6^{2-}$ is of the same order of magnitude as the value obtained for the similar ionic 2:1 adduct $FCl_2^+AsF_6^-$ (32.8 kcal mol^{-1}).[21]

The Lewis base adducts $Cs^+ClF_4O^-$, $Rb^+ClF_4O^-$, and $K^+ClF_4O^-$ show no measurable dissociation pressure at ambient temperature. However, the least stable of these adducts *i.e.*, $K^+ClF_4O^-$, can be slowly dissociated *in vacuo* at ambient temperature. The increasing stability of the salts with increasing size of the

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[13] P. A. W. Dean, R. J. Gillespie, and R. Hulme, *Chem. Commun.*, 990 (1969).

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[17] It is not strictly correct to infer that the measured heat of reaction for the dissociation process equals the thermodynamic heat of dissociation. This would only be appropriate if the complex were in the gas phase or if the heat of sublimation of the complex were zero. However, for convenience, $\Delta H_d°$ will be used throughout the text to mean the heat of reaction of a complete dissociation process of the type complex(s) = gas + gas.

[18] "JANAF Interim Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1961.

[19] O. Kalman, unpublished results.

[20] J. D. Cox and D. Harrop, *Trans. Faraday Soc.*, **61**, 1328 (1965).

[21] K. O. Christe and W. Sawodny, *Inorg. Chem.*, **8**, 212 (1969).

alkali metal cation is similar to that found for the corresponding ClF_2^- and ClF_4^- salts.[8,9]

All of the described ClF_3O adducts are hygroscopic solids. They react violently with water and organic materials. The stable materials were stored in closed Teflon FEP containers at ambient temperature for several years without any signs of decomposition.

Structure of the Adducts.—X-Ray powder diffraction patterns were obtained for $ClF_2O^+AsF_6^-$, $ClF_2O^+BF_4^-$, and $Cs^+ClF_4O^-$. Table I lists the calculated and observed spacings for $ClF_2O^+AsF_6^-$ and $ClF_2O^+BF_4^-$. The patterns of both compounds were tentatively indexed in the orthorhombic system. The unit cell dimensions calculated for these data for $ClF_2O^+AsF_6^-$ are $a = 9.94$, $b = 10.78$, and $c = 8.16$ Å. These values are very similar to those obtained for $ClF_2O^+PtF_6^-$ ($a = 9.94$, $b = 11.12$, and $c = 8.21$ Å).[5] By analogy with $ClO_2^+AsF_6^-$ [22] and $ClF_2O^+PtF_6^-$ [5] one can deduce six molecules per unit cell for $ClF_2O^+AsF_6^-$. This results in a reasonable[23,24] value of 16.2 Å^3 for the average volume per F or O atom neglecting contributions from the highly charged central atoms. For $ClF_2O^+BF_4^-$ the unit cell dimensions are $a = 13.21$, $b = 13.62$, and $c = 9.63$ Å. These unit cell dimensions compare favorably with those of orthorhombic $Cs^+BF_4^-$ ($a = 5.83$, $b = 7.65$, and $c = 9.43$ Å),[25] assuming the $ClF_2O^+BF_4^-$ unit cell to be four times larger than that of $Cs^+BF_4^-$. Therefore, the unit cell of $ClF_2O^+BF_4^-$ should contain 16 molecules resulting in a plausible[23,24] value of 15.5 Å^3 for the average volume per F or O atom. The diffraction pattern of $Cs^+ClF_4O^-$ was rather faint and contained too many lines to allow its indexing.

TABLE I

X-RAY POWDER DATA FOR $ClF_2O^+AsF_6^-$ AND $ClF_2O^+BF_4^-$

$ClF_2O^+AsF_6^-$ d, Å				$ClF_2O^+BF_4^-$ d, Å			
Obsd	Calcd	Intens	hkl	Obsd	Calcd	Intens	hkl
7.42	7.41	m	110	6.63	6.63	ms	200
5.47	5.46	m	111	4.82	4.82	m	002
4.98	4.97	mw	200	4.53	4.53	w	102
4.73	4.73	w	120	4.29	4.29	s	130
4.48	4.50	w	021	4.09	4.10	s	031
4.25	4.25	vs	201	3.75	3.74	w	230
4.09	4.09	s	121, 002	3.64	3.69	w	320
3.77	3.77	vw	102	3.40	3.40	vs	040
3.67	3.66	s	220	3.31	3.31	m	400
3.56	3.56	vw	112	3.03	3.03	w	240
3.37	3.37	vw	130	2.87	2.88	w	241
3.30	3.30	s	300, 031	2.81	2.82	w	213
3.15	3.15	w	202	2.67	2.67	m	150
2.96	2.96	m	311	2.61	2.62	w	051
2.92	2.92	w	230	2.59	2.59	w	510
2.73	2.73	mw	003, 222	2.56	2.57	w	151
2.60	2.60	vw	140	2.44	2.44	mw	251
2.55	2.55	w	113	2.33	2.33	m	114
2.49	2.49	w	400	2.20	2.20	m	600
2.34	2.34	vw	331	2.15	2.15	m	601
2.18	2.18	mw	421	2.06	2.06	w	343
2.14	2.14	mw	402	2.04	2.04	vw	621
2.08	2.08	vw	412	1.922	1.926	mw	170
2.02	2.02	mw	341	1.894		mw	
1.957	1.957	w	510, 323	1.840		w	
1.913	1.907	m	052	1.791		w	
1.883	1.885	w	143	1.759		w	
1.838	1.834	mw	403	1.714		vw	
1.762	1.764	vw	512	1.694		mw	
1.717	1.718	vw	314	1.572		w	
1.649		vw		1.544		vw	
1.594		m		1.520		vw	
1.585		w		1.503		w	
1.531		w		1.467		w	
1.486		w		1.446		w	
1.433		vw		1.410		mw	
1.418		vw		1.337		w	
1.387		w		1.314		w	
1.377		w		1.286		w	
1.358		vw		1.267		w	
1.334		vw		1.228		w	
1.318		w		1.131		w	
1.301		vw		1.106		w	
1.285		vw		1.079		w	
1.260		w		1.065		w	
1.241		w					
1.216		vw					
1.194		vw					
1.177		vw					

The vibrational spectra were recorded for $Rb^+ClF_4O^-$, $Cs^+ClF_4O^-$, $ClF_2O^+BF_4^-$, $ClF_2O^+AsF_6^-$, and $ClF_2O^+SbF_6^-$ and are entirely consistent with ionic structures. A detailed discussion of the spectra and their assignment together with force constant calculations and bond-order considerations are published in separate papers.[26,27]

General Considerations.—In the past the self-ionization of halogen fluorides has been overemphasized.[1] This was mainly due to the ease with which most of the reaction chemistry of the amphoteric halogen fluorides could be explained by it. However, except for BrF_3, little or no evidence has been found supporting this postulated self-ionization. Furthermore, no attempts have been made to rationalize and correlate the available data on the tendency of various halogen fluorides to form adducts with Lewis acids or bases. Since reliable data are now available on the complex formation of pentavalent ClF_5,[18] ClF_3O, and ClO_2F,[28,29] of trivalent ClF_3,[9,30-34] and of monovalent ClF,[4,21,37,38] a meaningful comparison can be made.

A priori, the following trends might be expected within this series. (i) Compounds showing a strong tendency to form stable adducts with Lewis acids (and, hence, having considerable base character) should show a decreased tendency to form adducts with Lewis bases, and *vice versa*. (ii) The fluoride donor (*i.e.*, Lewis base) properties of a halogen fluoride should increase with increasing electron density on the fluoride ligands. Consequently, replacement of two fluorine ligands by one less electronegative oxygen ligand without changing the oxidation state of the central

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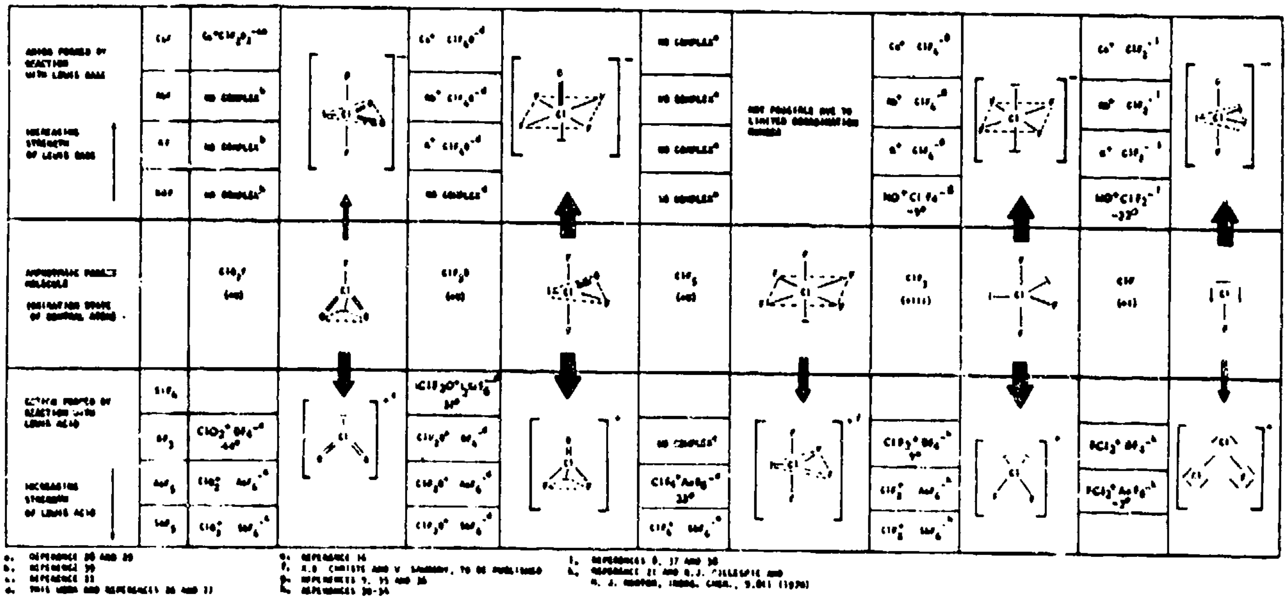

Figure 1.—Relative acid–base strength of various amphoteric halogen fluorides derived from their tendency to form adducts with strong Lewis acids and bases. Compounds of marginal stability are in larger type with the numbers indicating the temperature (°C) at which the dissociation pressure above the solid equals ~80 mm.

atom (*i.e.*, $ClF_5 \rightarrow ClF_3O \rightarrow ClFO_2$) or replacement of two fluorine ligands by one free electron pair with change of the oxidation state of the central atom (*i.e.*, $ClF_5 \rightarrow ClF_3 \rightarrow ClF$) should increase the basicity of a halogen fluoride molecule. Hence, one would expect ClF_5 to have more acid character than either ClO_2F or ClF. Furthermore, one would expect these trends to be continuous.

Figure 1 shows the observed data. The size of the arrows indicates the tendency to form adducts. As can be seen both predictions made *a priori* cannot be the dominating factors. There is no continuous trend from ClF_5 toward either ClO_2F or ClF. Furthermore, ClF_3O and ClF_3 show a pronounced tendency to form adducts with both Lewis acids and Lewis bases. Consequently, the tendency to form adducts cannot depend strongly on the acid strength of the parent molecule. However, there seems to be a correlation between the tendency to form adducts and the structures of the parent molecule and the resulting ions. If, for example, the structure of the parent molecule is derived from the energetically less favorable trigonal bipyramid[27] and if the resulting ions belong to the energetically more favorable octahedral of tetrahedral type, we observe a strong tendency toward adduct formation. This explains the surprising fact that ClF_3O and ClF_3 tend to form stable adducts with both Lewis acids and Lewis bases. The converse should also hold; *i.e.*, octahedral or tetrahedral molecules should show a weak tendency to form ions belonging to the trigonal-bipyramid type. This has been noted for IOF_5 which does not form an adduct with SbF_5[39] and for ClO_2F which forms only a marginally stable adduct with CsF.[28,29] Chlorine pentafluoride and ClF deserve special mention for the following reasons. ClF_5 does not form any adducts with strong Lewis bases.[16] This is most likely due[16] to a limitation of the coordination number of pentavalent chlorine to six (counting the free, sterically active electron pair as a ligand). Chlorine monofluoride forms with Lewis acids only 2:1 adducts.[31] This can be explained by the instability of a hypothetical Cl^+ cation which would possess only an electron sextet. The relatively high stability of the ClF_2^- anion in spite of its trigonal-bipyramid type structure may be due to its high symmetry.[37,38]

In summary, it is difficult to understand and predict relative acid–base properties of amphoteric halogen fluorides on the basis of the properties of the molecule itself. However, comparison of the structural stability of the parent molecule with that of the corresponding ions allows a qualitative interpretation. A method of predicting the structure of unknown halogen fluoride ions and molecules has previously been discussed[40] and should be particularly useful here.

Acknowledgment.—The authors are pleased to acknowledge support for this work by the Office of Naval Research, Power Branch.

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CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION,
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Chlorine Trifluoride Oxide. VI. The Tetrafluorooxychlorate(V) Anion, ClF_4O^-. Vibrational Spectra and Force Constants

BY KARL O. CHRISTE* AND E. C. CURTIS

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The infrared and Raman spectra of $Cs^+ClF_4O^-$ and $Rb^+ClF_4O^-$ have been recorded. Nine fundamental vibrations have been observed consistent with a C_{4v} structure analogous to that of XeF_4O and ClF_5. An assignment of the fundamental vibrations is proposed and a modified valence force field has been calculated. The bonding in ClF_4O^- is best described by a mainly covalent Cl=O double bond and two semiionic three-center, four-electron p–p σ Cl–F bond pairs.

Introduction

ClF_3O forms adducts[1] with strong Lewis acids and bases. In this paper, we present proof for the structure of the ClF_3O ·Lewis base complexes.

Experimental Section

The materials, apparatus, and the preparation of $Rb^+ClF_4O^-$ and $Cs^+ClF_4O^-$ have previously been described.[1] The infrared and Raman spectra were recorded as previously reported.[2]

Results and Discussion

Vibrational Spectra. Figures 1 and 2 show the vibrational spectra of solid $Rb^+ClF_4O^-$ and $Cs^+ClF_4O^-$, respectively. Table I lists the observed frequencies. For comparison, the values reported for ClF_4^- [3] and ClF_5[4,5] are included. Since ClF_4O^- and ClF_4^- are pseudo-isoelectronic with $XeOF_4$ and XeF_4, respectively, the values reported for the latter two molecules[4,6] are also listed.

Comparison with the known structures of isoelectronic ClF_5 [4] and pseudo-isoelectronic $XeOF_4$ [6] suggests for ClF_4O^- symmetry C_{4v}. For this point group, the nine normal modes of vibration are classified as $(3A_1 + 2B_1 + B_2 + 3E)$. Of these, all nine modes are Raman active, while only the three A_1 and the three E modes are infrared active. However, for the related compounds listed in Table I, the antisymmetric XF_4 out-of-plane deformation mode is either inactive for point group D_{4h} or of such low intensity for point group C_{4v} that it has not been observed. Further complications might be expected due to the fact that we are not dealing with the isolated ClF_4O^- ion but with a solid in which the ClF_4O^- ions might occupy lattice sites having a symmetry lower than C_{4v}. This site symmetry lowering might particularly influence the doubly degenerate E modes and cause their splitting into two components. The observation of seven or eight Raman bands (assuming two of the three E modes to split into their degenerate components), with two of them having none and one of them having only a very weak counterpart in the infrared spectrum, is consistent with the above considerations.

The assignments for ClF_4O^- were made by comparison with the known spectra of ClF_4^-,[3] ClF_5,[4,5] XeF_4,[6,7] and $XeOF_4$.[4] The band at about 1200 cm^{-1} occurs at a frequency much too high for any Cl–F fundamental vibration and, hence, is assigned to the Cl=O stretching vibration, $\nu_1(A_1)$. The shoulder on the lower frequency side of the 1200-cm^{-1} band is due to the ^{37}Cl isotope. The strongest Raman band, at about 460 cm^{-1}, should belong to the totally symmetric ClF_4 stretching vibration, $\nu_2(A_1)$. Similarly, the strongest infrared band at about 580 cm^{-1} should be due to the antisymmetric ClF_4 stretching vibration, $\nu_7(E)$, which is split into its two degenerate components. The second strongest Raman band at about 350 cm^{-1} obviously should represent the symmetric out-of-phase ClF_4 stretching mode $\nu_4(B_1)$. The frequencies and relative intensities of $\nu_2(A_1)$ and $\nu_4(B_1)$ of ClF_4O^- are in good agreement with those reported[3] for ClF_4^-.

The remaining five modes are deformation modes. The $O-ClF_4$ deformation mode, $\nu_8(E)$, involves mainly a motion of the double-bonded oxygen and, hence, should have the highest frequency. It is assigned to the band at about 400 cm^{-1}, assuming again a splitting into its degenerate components. By analogy with the related molecules listed in Table I, the antisymmetric in-plane ClF_4 deformation mode should have the lowest frequency and is therefore assigned to the band at about 210 cm^{-1}. For the remaining three modes, we are left with only two frequencies. Since the antisymmetric out-of-plane XF_4 deformation mode, $\nu_5(B_1)$, has not been observed for any of the compounds given in Table I, it is assumed to be the unobserved mode. There are two frequencies at about 340 and 280 cm^{-1} left for assignment to the ClF_4 umbrella deformation, $\nu_3(A_1)$, and the ClF_4 scissoring mode, $\nu_6(B_2)$. These two modes can easily be distinguished based upon their relative infrared intensities. The ν_3 mode should be of high intensity, whereas ν_6 should ideally be only Raman active. Consequently, the bands at 340 and 280 cm^{-1} are assigned to $\nu_3(A_1)$ and $\nu_6(B_2)$, respectively. The frequencies of $\nu_3(A_1)$ and $\nu_4(B_1)$ almost coincide. The possibility that for $Rb^+ClF_4O^-$ the 339-cm^{-1} infrared band is the counterpart of the 350-cm^{-1} Raman band is not likely owing to its high relative intensity and the relatively large frequency difference of 11 cm^{-1}. Comparison of the ClF_4^- frequencies with those of ClF_4O^- and ClF_5 involving only the approximately square-planar ClF_4 part reveals the following trend. The ClF_4O^- anion has the lowest frequencies, ClF_4^- is inter-

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TABLE I

VIBRATIONAL SPECTRA OF $Rb^+ClF_4O^-$ AND $Cs^+ClF_4O^-$ AND THEIR ASSIGNMENT COMPARED WITH THOSE OF ClF_4^-, ClF_5, $XeOF_4$, AND XeF_4

Observed frequencies, cm^{-1}, and relative intensities												Assignment for XZF_4 in point group		
$Rb^+ClF_4O^-$		$Cs^+ClF_4O^-$		ClF_4^- [a]		ClF_5 [b]		$XeOF_4$ [b]		XeF_4 [c,d]				
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	C_{4v}		Type of vibration
1216 s	1211 (0.6)	1201 s	1203 (0.6)			722 m	709 (3)	926 s	920 (2)			A_1	ν_1	ν XZ
462 w	461 (10)	457 w	456 (10)		505 (10)	541 m	538 (1)	576 m	567 (10)		543 (10)		ν_2	ν_{sym} in-phase XF_4
339 s	[350] [e]	339 s	[345] [e]	425 m		493 s	480 (10)	294 s	285 (0+)	291 s			ν_3	δ_{sym} out-of-plane XF_4
	350 (4.3)		345 (4)		417 (10)		480 (10)		527 (4)		502 (8)	B_1	ν_4	ν_{sym} out-of-phase XF_4
							[346] [e]		[230]				ν_5	δ_{asym} out-of-plane XF_4
283 vw	285 (0.4)	280 vw	283 (0.4)		288 (1)		375 (1)		233 (1)		235 (0+)	B_2	ν_6	δ_{sym} in-plane XF_4
600 550 } vs	599 (0.1) 557 (0.4)	600 560 } vs	593 (0.2) 564 (0.3)	500–680 vs, br		732 vs		608 vs		586 vs		E	ν_7	ν_{asym} XF_4
415 394 } s	416 (1.4) 395 (0.1)	415 396 } s	416 (1.4) 397 (0.1)			482 s	[480]	361 s	365 (2)				ν_8	δ ZXF
	213 (0.6)		204 (0.7)			302 s	296 (0.4)		161 (0+)	[250]			ν_9	δ_{asym} in-plane XF_4

[a] Reference 3. [b] References 4 and 5. [c] Reference 6. [d] Reference 7. [e] Frequency values listed in brackets were not observed directly. They were either obscured by stronger bands in the same region or estimated from combination bands or force constant calculations.

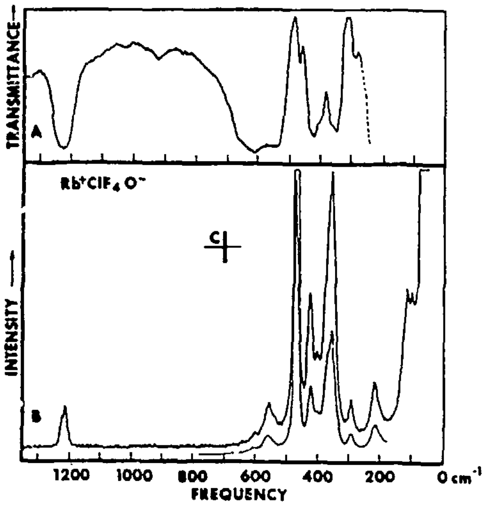

Figure 1.—Vibrational spectrum of solid $Rb^+ClF_4O^-$: (A) infrared spectrum as AgBr disk; (B) Raman spectrum at two different recorder voltages, exciting line 4880 Å; C indicates spectral slit width.

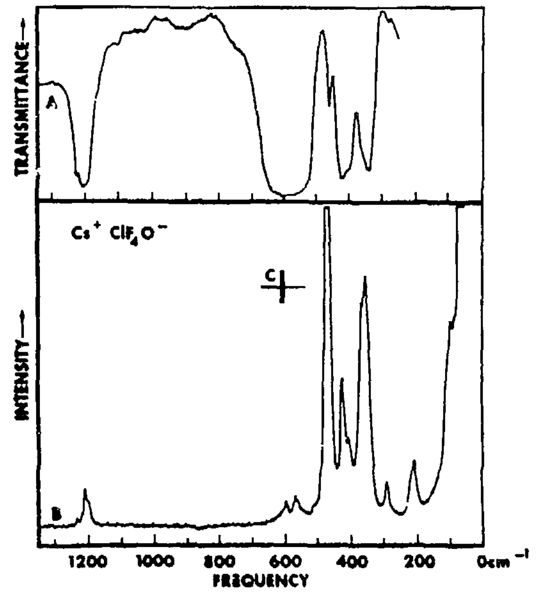

Figure 2.—Vibrational spectrum of solid $Cs^+ClF_4O^-$: (A) infrared spectrum as AgBr disk; (B) Raman spectrum, exciting line 4880 Å; C indicates spectral slit width

mediate, and ClF_5 exhibits the highest frequencies. This is not surprising, since ClF_4O^- possesses, in addition to a bond-weakening formal negative charge, an oxygen ligand. The pronounced weakening effect on ClF bonds upon oxygen substitution has previously been discussed in detail for $ClO_2F_2^-$ [8] and, hence, will not be reiterated.

The difference in the vibrational spectra of ClF_4O^- and isoelectronic $XeOF_4$ can be rationalized in the following way. The two symmetric XF_4 stretching modes do not involve a motion of the central atom. Hence, no mass effect of the central atom is expected, and $XeOF_4$ with the stronger X–F bond shows the higher frequencies for these two modes. For the antisymmetric XF_4 stretching mode, the frequencies become similar for $XeOF_4$ and ClF_4O^- due to a pronounced mass effect. The deformation modes of $XeOF_4$ all show lower frequencies than the corresponding modes of ClF_4O^-. This is due to the increased size of the central atom in $XeOF_4$ which facilitates angle deformations. For ClF_4O^-, an overlap of the range of stretching and deformation vibrations occurs. This unusual overlap has previously been recognized and discussed[3] for the structurally related ClF_4^- anion and requires relatively weak Cl–F bonds and a small central atom. Furthermore, a comparison between the pairs ClF_4O^-–ClF_4^- and $XeOF_4$–XeF_4 shows for the chlorine fluoride stretching modes a frequency decrease from ClF_4^- toward ClF_4O^-, whereas for the xenon fluorides the trend is reversed. This is due to the difference in the electronegativity of the central atoms. In the case of the xenon compounds, the addition of an oxygen ligand (which is more electronegative than xenon) to xenon results in a slight further electron-density withdrawal from xenon. This increases the effective electronegativity of xenon and makes it more similar to that of fluorine, thus increasing the contribution of covalent bonding to the Xe—F bond. In the case of chlorine fluorides, the multivalent chlorine atom is more electronegative than oxygen. Hence, oxygen addition lowers the effective electronegativity of chlorine, thus causing an increase in the polarity of the Cl—F bond. This effect of oxygen substitution has been observed for the following related pairs:

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(8) K. O. Christe and E. C. Curtis, *Inorg. Chem.*, **11**, 35 (1972).

ClF_3–ClF_3O,[2] ClF_2^-–$ClF_2O_2^-$,[8] ClF–$ClFO_2$,[8] and ClF_2^+–ClF_2O^+,[9] and, hence, appears to be quite general. This interpretation assuming a reversed polarity of the X=O bond in chlorine oxyfluorides and $XeOF_4$ is further supported by the observed ^{19}F nmr shifts. Thus, the fluorine ligands in XeF_4 are more shielded than those in $XeOF_4$, whereas the fluorine ligand in $FClO_2$ is less shielded than that in $FClO_3$.[10]

Force Constants and Bonding.—The potential and kinetic energy metrics for the tetrafluorooxychlorate anion were computed by a machine method.[11] The geometry was assumed to be that of an ideal square-pyramid with D(Cl–O) = 1.42 Å, based on a correlation between stretching frequency and bond length,[12] and with r(Cl–F) = 1.75 Å, which is somewhat longer than the long bonds in ClF_3.[13] The bond angles, α and β, are defined as ∠O–Cl–F and ∠F–Cl–F, respectively, and were assumed to be 90°.

The force constants were found by trial and error with the aid of a computer, requiring exact fit between the observed and computed frequencies. The results are given in Table II. The values shown for the interaction constants, while not unique, were the simplest set that would give an exact fit. Since the force constants are underdetermined, a statistically meaningful uncertainty estimate cannot be made. Numerical experiments showed that assuming different interaction constants, and constraining them to plausible values, would result in valence force constants differing from these shown by less than 0.2. These estimated uncertainties are felt to be conservative. The potential energy distribution for this force field is shown in Table III.

TABLE II

FORCE CONSTANTS OF ClF_4O^- [a]

f_R	9.13		
f_r	1.79	$f'_{\beta\beta}$	0.29
f_β	1.33	$f'_{\alpha\alpha}$	0.08
f_α	0.61	$f_{r\beta}$	0.15
f_{rr}	0.25	$f''_{r\beta}$	−0.15
f'_{rr}	0.04		

[a] Stretching force constants in mdyn/Å and deformation force constants in mdyn Å/radian^2.

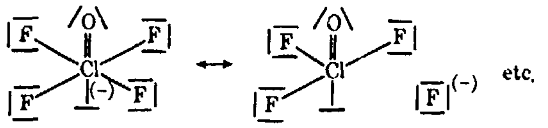
The two constants of greatest interest are the stretching force constants. The value of 9.13 mdyn/Å found for the Cl=O stretching force constant, f_R, is within the range expected for a covalent Cl=O double bond. For example, values of 9.37, 9.07, and 8.3 mdyn/Å were found for the chlorine oxyfluorides, ClF_3O,[2] ClO_2F,[14] and $ClO_2F_2^-$,[8] respectively. The fact that the value of f_R in ClF_4O^- is slightly lower than than in ClF_3O can be explained by the negative charge on the central atom in ClF_4O^-. The low value of 1.78 mdyn/Å obtained for the Cl—F valence force constant, f_r, is similar to that of 1.6 mdyn/Å obtained for $ClO_2F_2^-$.[8] These low values are due to the formal negative charge and oxygen substitution (see above). The negligible change in the Cl—O order (when compared with normal Cl=O double bonds), coupled with a pronounced decrease in the Cl—F bond order, implies that the negative charge in ClF_4O^- is, to a large extent, located on the fluorine ligands and not on the chlorine central atom or oxygen atom.

TABLE III

POTENTIAL ENERGY DISTRIBUTION[a] FOR ClF_4O^-

Assignment		Frequency, cm^{-1}	Potential energy distribution
A_1	ν_1	1203	$0.98f_R$
	ν_2	456	$0.77f_r + 0.21f_{rr}$
	ν_3	339	$0.80f_\beta + 0.17f'_{\beta\beta}$
B_1	ν_4	345	$1.34f_r - 0.37f_{rr}$
	ν_5	(218)[b]	$0.82f_\beta + 0.17f'_{\beta\beta}$
B_2	ν_6	283	$0.89f_\alpha + 0.11f'_{\alpha\alpha}$
E	ν_7	578	$0.97f_r + 0.17f_\beta$
	ν_8	406	$1.11f_\beta$
	ν_9	204	$1.04f_\alpha - 0.13f'_{\alpha\alpha}$

[a] Only the more important terms are given. [b] Computed frequency.



The pseudo-octahedral C_{4v} structure of ClF_4O^- could be explained by two different bond models: (1) an sp^3d^2 hybridization of the valence electrons of chlorine resulting in mainly covalent Cl–F bonds and (2) a model[15–18] involving mainly two delocalized p-electron pairs of the chlorine atom for the formation of two semi-ionic three-center, four-electron p–p σ bonds with the four fluorine atoms. Mainly covalent sp hybridization is assumed for the Cl–O σ bond and the free electron pair. For model 1, we would expect for the Cl–F valence force constant a value in the range 2.8–3.6 mdyn/Å. For model 2, f_r should be between 1.6 and 2.5 mdyn/Å. The value of 1.78 Å observed for the Cl–F stretching force constant in ClF_4O^- strongly favors model 2.

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Chlorine Trifluoride Oxide. VII. The Difluorooxychloronium(V) Cation, ClF_2O^+. Vibrational Spectrum and Force Constants

BY KARL O. CHRISTE,* E. C. CURTIS, AND CARL J. SCHACK

Received September 8, 1971

The vibrational spectra have been recorded for the solid 1:1 adducts, $ClF_3O \cdot BF_3$, $ClF_3O \cdot AsF_5$, and $ClF_3O \cdot SbF_5$, and for $ClF_3O \cdot BF_3$ in HF solution. These spectra are entirely consistent with the ionic structures, $ClF_2O^+BF_4^-$, $ClF_2O^+AsF_6^-$, and $ClF_2O^+SbF_6^-$, respectively. Six fundamental vibrations have been observed for ClF_2O^+, consistent with symmetry C_s. The structure of ClF_2O^+ can be derived from a tetrahedron with the chlorine atom located at the center and with two fluorine atoms, one oxygen atom, and one free electron pair at the four corners. The vibrational spectrum and structure of ClF_2O^+ closely resemble those of isoelectronic SOF_2. An assignment of the fundamental vibrations is proposed for ClF_2O^+, and a modified valence force field has been calculated. A mainly covalent bond model is considered most likely for ClF_2O^+.

Introduction

Chlorine trifluoride oxide possesses amphoteric character and forms adducts with BF_3, AsF_5, SbF_5, and SiF_4.[1] In this paper, we report the vibrational spectra and a structural study of some of these adducts.

Experimental Section

The preparation of the ClF_2O^+ containing salts, the apparatus, handling procedures, and the techniques used for recording the vibrational spectra have previously been described.[1-3]

Results and Discussion

Vibrational Spectra.—Figures 1 and 2 show the infrared and Raman spectra of solid $ClF_2O^+BF_4^-$ and $ClF_2O^+AsF_6^-$, respectively. Figure 3 shows the Raman spectrum of $ClF_2O^+BF_4^-$ in HF solution. The observed frequencies are listed in Table I and are compared with those reported for isoelectronic SOF_2.[4] The vibrational spectrum of the 1:1.2 $ClF_3O–SbF_5$ adduct was also recorded. The infrared spectrum of a dry powder sample showed, in the range 4000–400 cm^{-1}, absorptions at the following wave numbers: 1339 sh, w, 1331 s, 1319 m, 740 s, 710 vs, 658 vs, 600 s, 559 mw, 510 ms, and 401 mw. The Raman spectrum of the solid showed bands at the following wave numbers (relative intensity): 1329 (4), 1316 (2), 741 (5), 686 (1), 670 (5), 637 (10), 590 (1), 554 (2), 504 (3), 397 (3), 377 (0+), and 282 br (4).

The adducts between ClF_3O and Lewis acids could be either ionic or fluorine bridged coordination complexes. The simplicity of the observed spectra, the shift of the Cl═O stretching vibration to higher frequencies when compared to that in ClF_3O,[5] and the occurrence of all bands characteristic for the corresponding anion suggest that solid $ClF_3O \cdot AsF_5$ and $ClF_3O \cdot BF_3$ have the ionic structures $ClF_2O^+AsF_6^-$ and $ClF_2O^+BF_4^-$, respectively. The Raman spectrum of $ClF_2O^+BF_4^-$ in HF solution closely resembles that of the solid, indicating the presence of discrete ions in both the solid state and HF solution. Table I shows the observed vibrational spectra, together with their assignment. The vibrational spectra of AsF_6^- and BF_4^-, respectively, are well known and hence will be discussed first.

An octahedral ion, such as AsF_6^-, has O_h symmetry. The six normal modes of vibration are classified as $A_{1g} + E_g + 2F_{1u} + F_{2g} + F_{2u}$. Of these, only the two F_{1u} modes will be infrared active, while only the A_{1g}, E_g, and F_{2g} modes will be Raman active, assuming that the selection rules are valid and that the octahedron is not distorted. The remaining F_{2u} mode is inactive in both the infrared and Raman spectrum. For $ClF_3O \cdot AsF_5$, all five active modes belonging to AsF_6^- were observed, the observed frequencies and intensities being similar to those of other AsF_6^- containing complexes, such as $ClF_2^+AsF_6^-$,[6] $NF_4^+AsF_6^-$,[7] $NF_2O^+AsF_6^-$,[8] $IF_6^+AsF_6^-$,[9] and $ClO_2^+AsF_6^-$.[10] Several deviations from the selection rules for O_h were observed. The $\nu_2(E_g)$ mode should be Raman active only but was also observed in the infrared spectrum. Furthermore, the two triply degenerate modes, ν_3 and ν_4, in species F_{1u} show shoulders in the infrared spectrum. This breakdown of the selection rules has also been observed for the infrared spectra of most of the other AsF_6^- containing salts.[6-10] It could be due to site symmetry lowering, slight distortion of the AsF_6^- octahedron, or weak fluorine bridges.

A tetrahedral ion, such as BF_4^-, has T_d symmetry. The four normal modes of vibration are classified as $A_1 + E + 2F_2$. Of these, all four modes are expected to be Raman active, whereas only the two F_2 modes should be infrared active. However, crystal-field effects or slight distortion of the BF_4^- tetrahedron can result in the A_1 mode also becoming infrared active. For $ClF_2O \cdot BF_3$, all four modes belonging to BF_4^- were observed and assigned by analogy with the known spectra of $K^+BF_4^-$,[11-14] $ClF_2^+BF_4^-$,[6] $ClO_2^+BF_4^-$,[10] and $FCl_2^+BF_4^-$.[15,16]

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TABLE I

VIBRATIONAL SPECTRA OF ClF_2O^+ SALTS COMPARED WITH THAT OF SOF_2

Observed frequencies, cm^{-1}, and relative intensities								Assignment		
$ClF_2O^+BF_4^-$			$ClF_2O^+AsF_6^-$		SOF_2[a]					
Raman										
HF soln	Solid	Ir	Raman	Ir	Raman (gas)	Raman (liq)	Ir (gas)	OXF_2 (C_s)	AsF_6^- (O_h)	BF_4^- (T_d)
1333 (3.5) 1323 sh } P	1333 (4) 1321 sh (2) }	1334 s 1322 m }	1333 (2) 1320 (1) }	1331 ms 1319 mw }	1339 1329 } (10)	1308 (10)	1341 1331 } s	$\nu_1(A')$		
		1295 m								$\nu_1 + \nu_4(F_2)$
	1020 (0+), br	990–1150 vs								$\nu_3(F_2)$
				820 sh					$\nu_1 + \nu_6(F_{2u})$	
77 .), P	771 (3)	772 w								$\nu_1(A_1)$
741 (10), P	731 (10)	734 m	757 br (3)	750 br, s	808 (10)	804 (6)	808 s	$\nu_2(A')$		
710 sh, dp	695 (5)	694 s	696 (1)	695 vs	747 (4)	716 (0)	747 vs	$\nu_5(A'')$		
				695 vs					$\nu_3(F_{1u})$	
			674 (10)	675 sh, w					$\nu_1(A_{1g})$	
			563 (3)	561 ms					$\nu_2(E_g)$	
	530 sh (1)	532 w								$\nu_4(F_2)B^{10}$
	519 (2)	521 sh								$\nu_4(F_2)B^{11}$
512 (2.5), P	513 (3)	514 s	511 (2)	509 ms	530 (8)	528 (8)	530 w	$\nu_3(A')$		
402 (1.9)	404 (4)	405 m	406 (2)	407 sh	390 (4)	399 (7)	393 w	$\nu_6(A'')$		
				383 s					$\nu_4(F_{1u})$	
383 (1)	384 (2)	383 m	378 sh (1)	378 sh	390 (4)	380 (5)	378 vw	$\nu_4(A')$		
			371 (4)						$\nu_5(F_{2g})$	
355 (0+)	356 (1)	356 mw								$\nu_2(E)$

[a] See ref 4.

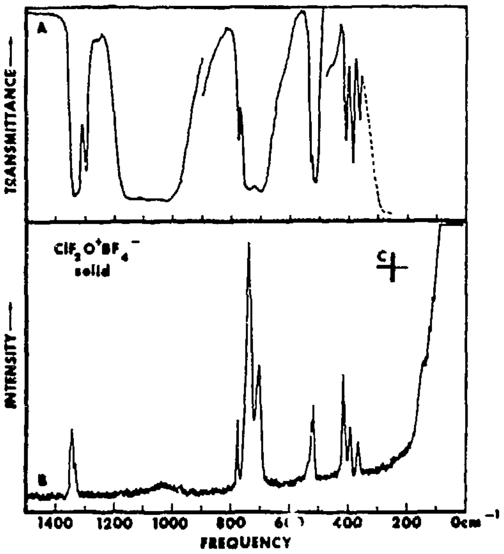

Figure 1.—Vibrational spectrum of solid $ClF_2O^+BF_4^-$: (A) infrared spectrum recorded as a AgCl disk; (B) Raman spectrum, exciting line 4880 Å. C indicates spectral slit width.

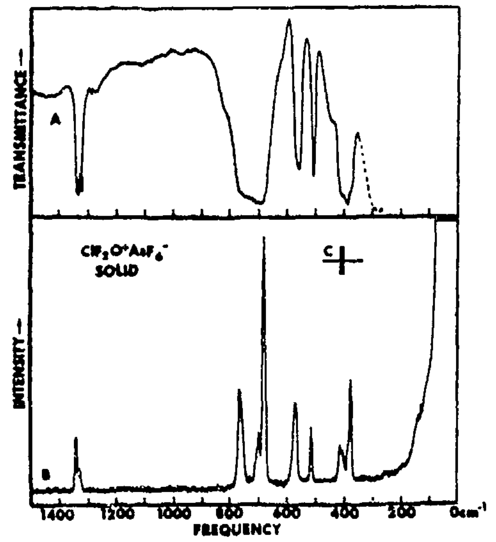

Figure 2.—Vibrational spectrum of solid $ClF_2O^+AsF_6^-$.

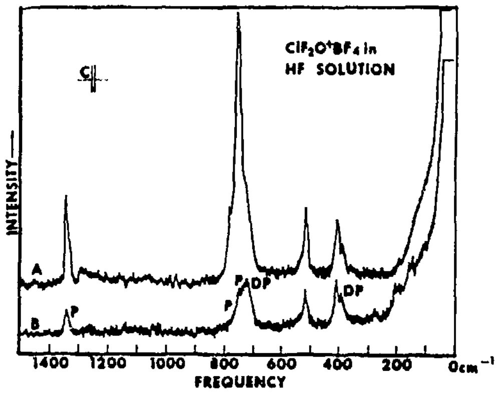

Figure 3.—Raman spectrum of $ClF_2O^+BF_4^-$ in HF solution: traces A and B, incident polarization perpendicular and parallel, respectively. C indicates spectral slit sidth.

The six remaining bands observed in the spectra of both $ClF_2O^+AsF_6^-$ and $ClF_2O^+BF_4^-$ complexes should be due to ClF_2O^+. A four-atom ion of the type ZXY_2, such as ClF_2O^+, could have C_{2v} or C_s symmetry. Distinction between symmetry C_{2v} and C_s should be possible by means of polarization measurements on the Raman bands. For symmetry C_{2v}, we would expect three polarized Raman bands, whereas for C_s, four of them should be polarized. The Raman spectrum of $ClF_2O^+BF_4^-$ in HF solution (Figure 3) shows that of the bands assigned to ClF_2O^+, three bands (1333, 741, and 512 cm^{-1}) are clearly polarized and one (710 cm^{-1}) is depolarized. It is difficult to determine the polarization state of the remaining two lines at 404 and 384 cm^{-1}, respectively. However, polarization measurements[4] for isoelectronic SOF_2, which has a Raman spectrum very similar to that of ClF_2O^+, indicate that the less intense lower frequency mode is weakly polarized, and, hence, should be assigned to $\nu_4(A')$. Intuitively, however, one might expect the $\nu_4(A')$ mode to result in a more intense Raman line than $\nu_6(A'')$. Unfortunately, Figure 3 does not allow a clear-cut distinction between the two possible assignments. Consequently, assignments for ClF_2O^+ were made by complete analogy with SOF_2, which was shown[17] to

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[17] R. C. Ferguson, *J. Amer. Chem. Soc.*, **76**, 850 (1954).

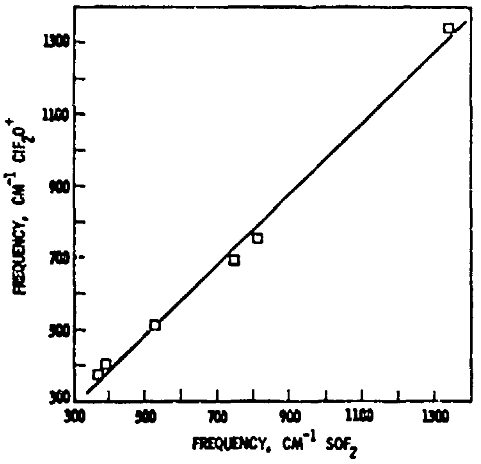

Figure 4.—Correlation between the vibrational frequencies of ClF_2O^+ and those of SF_2O.

have symmetry C_s. A plot of the vibrational frequencies of ClF_2O^+ against those of SOF_2 (see Figure 4) shows an approximately linear correlation. This linearity, together with relative band intensity considerations and the results from the force constant calculations (see below), supports the assignments given in Table I, although a possible reversal of the assignments of $\nu_4(A')$ and $\nu_6(A'')$ cannot entirely be excluded.

The spectra of both ClF_2O^+ and SOF_2 species show a frequency splitting of $\nu_1(A')$. Whereas for SOF_2 the splitting is due to Fermi resonance[4] between $\nu_1(A')$ and $\nu_2 + \nu_3(A')$, the splitting for ClF_2O^+ is due to the ^{35}Cl and ^{37}Cl isotopes. In ClF_2O^+, the combination band $\nu_2 + \nu_3$ has too low a frequency to account for the splitting of the band at about 1330 cm^{-1}. Furthermore, the frequency splitting of 12.5 cm^{-1}, observed under high resolution conditions, agrees well with the value of 12.6 cm^{-1} calculated for $^{35}ClF_2O^+$ and $^{37}ClF_2O^+$.

The vibrational spectrum obtained for the adduct $ClF_3O \cdot 1.22SbF_5$ clearly shows the bands characteristic for the ClF_2O^+ cation at 1331, 1319, 740, ~700, 510, 401, and 377 cm^{-1}. The remaining bands can be attributed to either SbF_6^- or polymeric anions such as $Sb_2F_{11}^-$.[18-20] Consequently, the formulation of the adduct as $ClF_2O^+SbF_6^-$ (containing some $ClF_2O^+Sb_2F_{11}^-$) appears to be appropriate. Similarly, the 1:1 adduct[21] obtained in the reaction between ClF_3O and PtF_6 contains the ClF_2O^+ cation and, hence, is best described as $ClF_2O^+PtF_6^-$. The infrared spectrum[21] of $ClF_2O^+PtF_6^-$ shows, in the range 520–350 cm^{-1}, no absorptions due to the anion and, hence, proves that the three ClF_2O^+ deformation modes occur at about 500, 400, and 380 cm^{-1}.

Force Constants.—Two sets of force constants were computed for ClF_2O^+, assuming $\nu_6 > \nu_4$ (set I) and $\nu_4 > \nu_6$ (set II). Since SOF_2 and $SeOF_2$ are isoelectronic and have similar vibrational frequencies,[4] their force constants were reevaluated by the same method for comparison. The potential and kinetic energy metrics were computed with a machine method[22] using the geometries shown in Table II. The ClO and ClF bond lengths for ClF_2O^+ were estimated by comparison with similar molecules. The correlation noted by Robinson[23] between stretching frequencies and bond lengths predicts a value of 1.39 Å for the ClO bond length, which is only slightly shorter than that accepted here. The bond angles in ClF_2O^+ were estimated to be slightly larger than those in SOF_2, assuming that the mutual repulsion between the ligands will increase with decreasing ionic radius of the central atom.

TABLE II

BOND DISTANCES (Å) AND BOND ANGLES (DEG) ASSUMED FOR ClF_2O^+, SOF_2, AND $SeOF_2$

	ClF_2O^{+a}	SOF_2^b	$SeOF_2^c$
R(X=O)	1.41	1.412	1.576
r(X—F)	1.62	1.585	1.7255
β(O=X—F)	108	106.82	104.82
α(F—X—F)	93	92.82	92.22

[a] Estimated. [b] Reference 17. [c] I. C. Bowater, R. D. Brown, and F R. Burden, *J. Mol. Spectrosc.*, **28**, 461 (1968).

The force constants were computed by trial and error with the aid of a computer, requiring exact fit between the observed and computed frequencies. The results are given in Table III where the force constants not shown were assumed to be zero. The values shown for the interaction constants, while not unique, were the simplest set that would give an exact fit. Since the force constants are underdetermined, a statistically meaningful uncertainty estimate cannot be made. Numerical experiments show that assuming different interaction constants, constrained to plausible values, resulted in valence force constants differing from those shown in Table III by less than 0.2. These uncertainties are estimates and are felt to be conservative. Of the two sets of force constants obtained for ClF_2O^+, set I ($\nu_6 > \nu_4$) is more plausible since it results in f_β (∠O=Cl—F) being larger than f_α (∠F—Cl—F). The good agreement between the force constants of the three species, ClF_2O^+ SOF_2, and $SeOF_2$, adds further credibility to our assignments for ClF_2O^+. Table IV shows the potential energy distribution for set I of ClF_2O^+. For set II, the results were similar, except for an appreciably larger contribution from $f_{\beta\beta}$ to ν_6. The potential energy distribution for SOF_2 and $SeOF_2$ was quite similar to that of ClF_2O^+. Only the

TABLE III

VIBRATIONAL FORCE CONSTANTS OF ClF_2O^+, SOF_2, AND $SeOF_2$[a]

	ClF_2O^+			
	$\nu_6 > \nu_4$	$\nu_4 > \nu_6$	SOF_2	$SeOF_2$
f_R	11.21	11.20	10.84	7.87
f_r	3.44	3.44	4.03	3.57
f_β	1.72	1.65	1.73	1.28
f_α	1.59	1.78	1.52	1.04
$f_{\beta\beta}$	0.32	0.21	0.43	0.23
f_{rr}	0.25	0.39	0.42	0.37

[a] Stretching constants in mdyn/Å and deformation constants in mydn Å/radian^2.

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TABLE IV

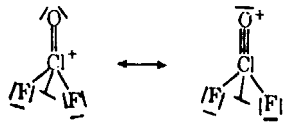
POTENTIAL ENERGY DISTRIBUTION FOR ClF_2O^+

Assignment		Frequency, cm⁻¹	Potential energy distribution
A′	ν_1	1333	$0.97f_R$
	ν_2	731	$0.80f_r + 0.07f_\alpha + 0.06f_\beta + 0.06f_{rr}$
	ν_3	513	$0.76f_\beta + 0.14f_{\beta\beta} + 0.05f_r$
	ν_4	384	$0.91f_\alpha + 0.08f_r$
A″	ν_5	695	$0.96f_r + 0.14f_\beta - 0.07f_{rr}$
	ν_6	404	$1.09f_\beta - 0.20f_{\beta\beta} + 0.11f_r$

more important terms are given in Table IV. These data show that the normal modes assigned to the observed vibrational frequencies are a good representation of the group vibrations described by the symmetry coordinates.

Force constants have previously been computed for both SOF_2 and $SeOF_2$. Our values for $SeOF_2$ are very similar to those reported by Paetzold.[24] For SOF_2, however, our results do not agree with those computed by Cotton and Horrocks.[25] The largest discrepancy was found for f_α[26] for which Cotton and Horrocks[25] report an abnormally high value of 3.47 mdyn Å/radian². This value appears much too high for this type of deformation vibration and cannot be explained by the slightly higher frequency value of 410 cm⁻¹ assumed for ν_4 by Cotton and Horrocks.[25]

The two constants of greatest interest are the two stretching force constants. Table V, showing a comparison of the Cl—O valence force constants of similar molecules and ions, reveals that f_R in ClF_2O^+ is larger by about 1.8 mdyn/Å than the largest value known for any other Cl=O containing compound. Whereas the formal positive charge on the central atom in ClF_2O^+ will certainly contribute to the high f_R value, it cannot account for it solely. Contributions from the resonance structures below could explain the high



f_R value in ClF_2O^+. The following observation seems noteworthy. In ClF_4O^-, the Cl–O valence force constant value[2] is about the same as those in similar compounds, but the Cl F valence force constant decreases dramatically. In ClF_2O^+, it is the ClO valence force constant which increases significantly, whereas the ClF valence force constant is within the usual range. This seems to indicate that the effective electronegativity of pentavalent chlorine is intermediate between those of oxygen and fluorine. Hence, in ClF_2O^+ the positive charge is partially located on the oxygen atom, whereas in ClF_4O^- the negative charge is mainly located on the fluorine ligands.

TABLE V

Cl-O VALENCE FORCE CONSTANTS AS A FUNCTION OF THE OXIDATION NUMBER AND FORMAL ELECTRICAL CHARGE OF THE CENTRAL ATOM

Species	f_R, mdyn/Å	Oxidation state of the central atom	Formal electrical charge on the central atom
ClF_2O^+	11.21	+V	Positive
ClO_3F[a]	9.41	+VII	
ClF_3O[b]	9.37	+V	
ClF_4O^-[c]	9.13	+V	Negative
ClO_2F[d]	9.07	+V	
ClO_2^+[e]	8.96	+V	Positive

[a] W. Sawodny, A. Fadini, and K. Ballein, *Spectrochim. Acta*, **21**, 995 (1965). [b] Reference 5. [c] Reference 2. [d] D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, **20**, 1763 (1964). [e] Reference 10.

The relatively high values obtained for both the ClO and ClF valence force constants in ClF_2O^+ indicate that the bonding in ClF_2O^+ is best described by a mainly covalent bond model employing sp³ hybridized orbitals of the chlorine atom for the two Cl–F bonds, the Cl O σ bond, and the free electron pair. Bond models involving semiionic three-center, four electron p-p σ bonds[27–30] are not possible owing to the geometry of ClF_2O^+ (absence of linear F–Cl–F groups) and would result in a considerably lower value for the Cl F valence force constants.

In summary, the ClF_3O·Lewis adducts investigated in this study are ionic and contain the ClF_2O^+ cation. The structure and bonding of this cation strongly resemble those of isoelectronic SOF_2. The close correlation between the two isoelectronic couples, ClF_2O^+–SOF_2 and ClF_4O^- $XeOF_4$, respectively, demonstrates that the analogy between halogen fluorides and isoelectronic chalcogen or noble gas fluorides is likely to hold also for the oxyfluorides.

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[26] It should be pointed out that the definition of the angles α and β in our work and that of ref 23 is reversed. Furthermore, the value of f_α in ref 23 was normalized for distance to allow a better comparison.

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THE DIFLUOROPERCHLORYL CATION, $ClO_2F_2^+$

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Cations containing a +V chlorine central atom are well known. Thus, ClO_2^+ (1-3), ClF_2O^+ (4,5), and ClF_4^+ (6,7) have been prepared and characterized. However, to our knowledge, no reports have been published on the existence of a cation derived from heptavalent chlorine. In this paper, we wish to report the successful synthesis of a +VII chlorine containing cation, $ClO_2F_2^+$.

The difluoroperchloryl cation, $ClO_2F_2^+$, was prepared in the form of its PtF_6^- salt by reacting $FClO_2$ with PtF_6 in a sapphire reactor at 25°. The following competing reactions were observed:

$$2FClO_2 + 2PtF_6 \longrightarrow ClO_2^+PtF_6^- + ClO_2F_2^+PtF_6^-$$

and

$$2FClO_2 + 2PtF_6 \longrightarrow 2ClO_2^+PtF_6^- + F_2$$

Based on the weight increase observed for the nonvolatile reaction product and the amount of F_2 evolved, the yield of $ClO_2F_2^+$ salt was found to be about 10%. The infrared spectrum of the stable, yellow solid recorded as an AgCl disk showed the bands listed in Table I in addition to those characteristic for ClO_2^+ (1) and PtF_6^- (8). Their assignment to $ClO_2F_2^+$ is supported by comparison with the spectrum of isoelectronic SO_2F_2 (9), the pronounced shifts of the ClO_2

stretching modes to higher frequencies, and the observed $^{35}Cl-^{37}Cl$ isotopic shifts (see Table I). Comparison of the observed isotopic shifts with those computed (assuming for $ClO_2F_2^+$ symmetry C_{2v}, tetrahedral bond angles and 100% characteristic modes) shows an excellent agreement. Additional evidence for the formation of $ClF_2O_2^+$ was obtained from its reaction with FNO, yielding ClF_3O_2 (10).

TABLE I

Infrared Stretching Vibrations (cm^{-1}) of $ClO_2F_2^+$ and SO_2F_2 and Their Assignment in Point Group C_{2v} Together with Observed and Computed $^{35}Cl-^{37}Cl$ Isotopic Shifts

$ClO_2F_2^+$				SO_2F_2		Assignment
Frequency	Intensity	$\Delta\nu_{obs.}$	$\Delta\nu_{calcd.}$	Frequency	Intensity	
1484	vs	16.5	15.1	1502	vs	ν_6 (B_1), $\nu asXO_2$
1249	s	8.5	8.0	1269	s	ν_1 (A_1), $\nu symXO_2$
829	vs	10	9.4	885	vs	ν_8 (B_2), $\nu asXF_2$
757	s	< 7	5.5	848	s	ν_2 (A_1), $\nu symXF_2$

Acknowledgement

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CHLORINE TRIFLUORIDE DIOXIDE, ClF_3O_2

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The existence of $ClO_2F_2^+$, a cation containing a +VII chlorine central atom, has recently been discovered (1). This cation had been prepared in low to moderate yields by the fluorination of $FClO_2$ with the powerful fluorinating agent, PtF_6 (2). Since the $ClO_2F_2^+$ salt can be considered as an adduct between ClF_3O_2 and a strong Lewis base, it appeared possible to prepare the parent compound, ClF_3O_2, by reacting $ClF_2O_2^+PtF_6^-$ with a strong Lewis base.

A sample of $ClO_2^+PtF_6^-$ containing about 10% of $ClF_2O_2^+PtF_6^-$ was treated at -78° in a sapphire reactor with a large excess of FNO for several days. No material noncondensible at -196° (i.e. F_2) was observed. The products, volatile at 25°, were removed and separated by fractional condensation through a series of traps kept at -126, -132, -142, and -196°. The -142° fraction contained a novel compound which was identified by its infrared spectrum as ClF_3O_2. The observed frequencies and band contours are listed in Table I and are in excellent agreement with those expected for a trigonal bipyramidal structure of symmetry C_{2v}.

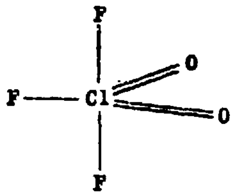

TABLE I

Infrared Spectrum of ClF_3O_2 and its Assignment

Frequency (cm^{-1})	Intensity	Observed Band Contour	Assignment for Point Group C_{2v}
1334	s	B-type	ν_{10} (B_2), νasClO_2
1096	s	C	ν_1 (A_1), νsymClO_2
699	vs	A, PQR	ν_7 (B_1), $\nu\text{asClF}_2\text{ax}$
687	vs	C	ν_2 (A_1), νClFeq
601	ms	A, PQR	ν_8 (B_1), $\delta\,\text{wagClO}_2$
~530	mw	C	ν_3 (A_1), $\delta\text{scissClO}_2$

The solid residue obtained from the FNO displacement reaction showed the correct weight change expected for conversion into $NO^+PtF_6^-$. Its identity as $NO^+PtF_6^-$ was confirmed by infrared spectroscopy.

Chlorine trifluoride dioxide is white as a solid and colorless as a liquid. It appears to be stable at 25°. Its volatility is intermediate between that of ClF_5 and $FClO_3$ as expected on the basis of the molecular weights. Thus, ClF_5 is completely condensed at -126°, ClF_3O_2 passes through a trap kept at -132°, whereas $FClO_3$ passes through a trap kept at -142°. The observed stability and lack of color demonstrate that our product cannot be identical with the previously reported violet and unstable $ClF \cdot O_2F_2$ (3) and $ClF_3 \cdot O_2$ (4) addition compounds supposedly having the empirical composition ClF_3O_2.

Acknowledgement

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THE HEXAFLUOROCHLORINE (VII) CATION, ClF_6^+

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It was recently shown (1) by Christe that PtF_6 can oxidatively fluorinate $FClO_2$ to form the novel $ClO_2F_2^+$ cation according to:

$$2FClO_2 + 2PtF_6 \xrightarrow{25^\circ} ClO_2^+PtF_6^- + ClO_2F_2^+PtF_6^-$$

The infrared spectrum of the solid reaction product exhibited, in addition to the bands characteristic of the $ClO_2F_2^+$, ClO_2^+, and PtF_6^- ions, a new band of medium intensity at 890 cm^{-1}. This band could not be assigned to any known species. The yield of $ClO_2F_2^+$ obtained from the PtF_6 fluorination reaction at 25° was relatively low, owing to the following competing reaction:

$$2FClO_2 + 2PtF_6 \longrightarrow 2ClO_2^+PtF_6^- + F_2$$

In order to suppress this competing reaction, we have studied the $FClO_2$-PtF_6 system at -78°. When PtF_6 was exposed for 48 hours to an excess of $FClO_2$ at -78°, the following unexpected reaction occurred:

$$6FClO_2 + 6PtF_6 \xrightarrow{-78^\circ} 5ClO_2^+PtF_6^- + ClF_6^+PtF_6^- + O_2$$

The observed $FClO_2$-PtF_6 combining ratio, weight gain, and O_2 evolution deviated by less than 3% from those calculated for the above equation. The infrared spectrum of the solid reaction product showed $ClO_2^+PtF_6^-$ as the main product, a trace of $ClO_2F_2^+$, and a strong 890 cm^{-1} absorption. The identity of the novel, stable species having an 890 cm^{-1} infrared absorption as ClF_6^+ was unambiguously established by ^{19}F nmr and vibrational spectroscopy, and its reaction chemistry. The ^{19}F nmr spectrum of the product dissolved in HF contains two sets of quadruplets at -391 ppm relative to $CFCl_3$ (external standard). The observed splitting is due to chlorine-fluorine spin spin coupling and the two naturally occurring Cl isotopes. The coupling constants are $J\ ^{35}ClF = 337$ and $J\ ^{37}ClF = 281$ cps and are the first reported examples of well resolved chlorine-fluorine spin spin coupling. The pronounced down-field shift and the ineffectiveness of chlorine quadrupole relaxation are convincing evidence for the presence of an octahedral ClF_6^+ cation.

The vibrational spectrum of ClF_6^+ is given in Table I and is compared to that of isoelectronic SF_6 (2,3).

TABLE I

Vibrational Spectrum of ClF_6^+ and its Assignment

Frequency (cm^{-1}), intensity				Assignment for
ClF_6^+		SF_6		Point Group O_h
IR	RA	IR	RA	
	679 vs		769 vs	ν_1 (A_{1g})
	580 m		640 m	ν_2 (E_g)
890 vs		948 vs		ν_3 (F_{1u})
582 m		615 m		ν_4 (F_{1u})
	513 m		522 m	ν_5 (F_{2g})

As can be seen, the observed spectrum closely resembles that of SF_6 and confirms the octahedral structure of ClF_6^+. The 890 cm^{-1} infrared band shows a ^{35}Cl-^{37}Cl isotopic splitting. The observed value of about 13 cm^{-1} is in excellent agreement with the value of 12.5 cm^{-1} computed for octahedral ClF_6^+, assuming 100% characteristic modes.

A displacement reaction between $ClF_6^+PtF_6^-$ and FNO was carried out under conditions similar to those which had successfully been used for the synthesis of ClF_3O_2 from $ClO_2F_2^+PtF_6^-$ and FNO (4). Since ClF_6^+ can be considered as a Lewis acid adduct of ClF_7, the products from the FNO displacement reaction should allow some conclusions concerning the stability of the hypothetical compound ClF_7. The following results were obtained for the displacement reaction:

$$ClF_6^+PtF_6^- + FNO \xrightarrow{-78^\circ} NO^+PtF_6^- + ClF_5 + F_2$$

This indicates that ClF_7 under the given reaction conditions is unstable at temperatures as low as -78° towards decomposition into ClF_5 and F_2.

Both cations, $ClO_2F_2^+$ (1) and ClF_6^+, are now well characterized. This suggested the possible synthesis of the intermediate ClF_4O^+ cation from ClF_3O and PtF_6. At 25°, the main reaction was:

$$2ClF_3O + 2PtF_6 \xrightarrow{25^\circ} 2ClF_2O^+PtF_6^- + F_2$$

In addition, small amounts of $FClO_2$ and ClF_5 were observed among the volatile reaction products. When the reaction temperature was lowered to -45°, the main products were again $ClF_2O^+PtF_6^-$ and F_2. However, small amounts of $ClO_2F_2^+$ and $ClF_6^+PtF_6^-$ had also formed. No evidence for the presence of any ClF_4O^+ could be obtained. This suggests that tetrahedral

$ClF_2O_2^+$ and octahedral ClF_6^+ are more favorable products than the pseudo trigonal bipyramidal ClF_4O^+.

In the low-temperature reaction between $FClO_2$ and PtF_6, the yield of ClF_6^+ can be at best 1/6 based on PtF_6. Since Roberto had previously obtained (5) for the ClF_5-PtF_6 system a solid showing a strong 890 cm^{-1} infrared absorption, we have also studied this system in order to increase the possible yield of ClF_6^+ to 50% and to verify that the products from both systems contain the same species, ClF_6^+. Two reactions were carried out at 25° with uv irradiation. When unfiltered uv irradiation was used, the reaction was complete in several hours:

$$2ClF_5 + 2PtF_6 \xrightarrow[uv]{unfiltered} ClF_2^+PtF_6^- + ClF_6^+PtF_6^- + F_2$$

Using a Pyrex-water filter, a reaction time of two weeks was required with the products being:

$$2ClF_5 + 2PtF_6 \xrightarrow[uv]{Pyrex\ filter} ClF_4^+PtF_6^- + ClF_6^+PtF_6^-$$

Since unfiltered uv light can decompose ClF_5 into $ClF_3 + F_2$ (6) and since ClF_2^+ salts are more stable than ClF_4^+ salts (7), the observed displacement of ClF_4^+ by ClF_3 is not surprising. The results from our vibrational spectroscopic study confirm that the products obtained from the reactions of PtF_6 with either $FClO_2$, ClF_3O, or ClF_5 contain indeed the identical new species, ClF_6^+.

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On the Reactions of Chlorine Fluorides with Hydroxyl Compounds

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A systematic study was carried out of the reactions of ClF, ClF_3, ClF_5, and ClO_2F with a monofunctional ($HONO_2$) and a bifunctional (HOH) hydroxyl compound. The nature of the observed reaction products depends upon which reagent is used in excess but can be rationalized for both hydroxyl compounds on a common basis. The observed analogies and additional experimental data allow some generalizations concerning the nature of some of the intermediate reaction products.

Introduction

Most of the studies dealing with chlorine fluorides have been concentrated on three aspects: their syntheses and physical properties, their use as fluorinating agents, and their ability to form adducts. Their reaction chemistry, in particular that involving hydroxyl compounds, has been largely neglected. This may have been partially due to the violent nature of most of the reactions and the great experimental difficulties encountered in working with most of these systems. Thus, only the reactions of ClF, ClF_3, and ClO_2F with H_2O,[1,2] of ClF with an excess of $HONO_2$,[3] and of an excess of ClF_5 with H_2O[4] have been reported. In this paper, we wish to report the results of a systematic study of ClF, ClF_3, ClF_5, and ClO_2F with monofunctional ($HONO_2$) and bifunctional (HOH) hydroxyl compounds with either reagent in excess.

Experimental Section

Caution! Most of these reactions are extremely vigorous and can produce shock-sensitive materials. They should be carried out on a small scale only with appropriate shielding and safety precautions.

Materials and Apparatus.—The materials used in this work were manipulated in a Monel vacuum line equipped with Teflon FEP U traps. For reactions involving an excess of halogen fluoride, the line was well passivated with ClF_3. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Chlorine monofluoride was prepared by heating an equimolar mixture of Cl_2 and ClF_3 to 150° for several hours in a stainless steel cylinder. Chlorine trifluoride (The Matheson Co.) and ClF_5 (Rocketdyne) were commercial materials. The preparation of $ClF_2{}^+AsF_6{}^-$ has previously been described.[5] Chloryl fluoride was prepared from $KClO_3$ and F_2 by the method[6] of Woolf and Cl_2O was prepared from HgO and Cl_2 by the method[7] of Schack. Nominally anhydrous $HONO_2$ was prepared from fuming nitric acid by distillation from concentrated H_2SO_4. All volatile materials were purified prior to use by fractional condensation. Their purities were determined by measurements of their vapor pressures and infrared spectra. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer in the range 4000–400 cm^{-1} using a 5-cm stainless steel cell fitted with AgCl windows. Mass spectra were recorded on a quadrupole mass spectrometer (Electronic Associates Inc. Model Quad 300) using a stainless steel–Teflon FEP inlet manifold.

Reaction of Excess ClF with $HONO_2$.—Anhydrous $HONO_2$ was condensed into one U of a double-U Teflon FEP trap, weighed (5.70 mmol), and cooled to −196°. Chlorine monofluoride (12.8 mmol) was condensed at −196° into the second U of the trap. The U containing $HONO_2$ was allowed to warm up to the melting point (−42°) of $HONO_2$. Then, the temperature of the U containing ClF was gradually increased and both compounds were allowed to interact slowly. First, a brownish color developed. The contents of both U's were combined in one U and kept at −78° for 10 min. The formation of a white solid was observed. The mixture was allowed to warm up to 23° and was kept at this temperature for 30 min. It was cooled again to −196°, at which temperature no noncondensable material was observed and was then during warm up subjected to fractional condensation. The individual fractions were measured by volume and/or weight and identified by their vapor pressures and infrared and mass spectra. The reaction products consisted of $ClONO_2$ (5.7 mmol), HF, and unreacted ClF (7.0 mmol).

Reactions of ClF with Excess HOH.—Chlorine monofluoride (2.34 mmol) and HOH (1.17 mmol) were combined at −196° in a Teflon FEP ampoule. Upon warming of the ampoule from −196 to −78°, melting of the mixture occurred and a dark brown liquid was formed. After keeping the mixture at −78° for 20 hr, the reaction products were separated and consisted of Cl_2O (0.65 mmol), Cl_2 (0.42 mmol), ClO_2 (0.21 mmol), HF, and O_2.

A second reaction carried out at 25° showed as the only products ClO_2, Cl_2, and O_2 in a mole ratio of 1:2:0.25 and HF.

Reaction of ClF with Cl_2O.—Chlorine monofluoride (2.33 mmol) and Cl_2O (1.63 mmol) were combined at −196° in a Teflon FEP U trap. The mixture was allowed to warm to −78° and was kept at this temperature for 15 hr. The color of the liquid reaction mixture had changed after this period from an original dark brown to yellow. The products were separated and consisted of ClO_2F (0.81 mmol), Cl_2 (1.65 mmol), and unreacted ClF (1.50 mmol).

Reaction of $HONO_2$ with Excess ClF_5.—In order to establish the stoichiometry of the reaction, $HONO_2$ (8.60 mmol) was combined with a large excess of ClF_5 (18.5 mmol) at −196°. Upon warm up, a violent reaction occurred which required moderation by cooling and a brownish color developed. After completion of the reaction at −78°, the products were separated and shown to consist of NO_2F, ClO_2F, ClF, HF, and 10 mmol of unreacted ClF_5 as expected for a 1:1 reaction. Since ClF_5 forms an adduct with NO_2F which complicates the separation of the reaction products, subsequent experiments were carried out with ratios of the starting materials close to 1:1. Typically, ClF_5 (10.5 mmol) was slowly admitted into a Teflon FEP U trap containing $HONO_2$ (10.5 mmol) at a temperature slightly above the melting point of $HONO_2$. Initially, an orange color (indicating the presence of ClO_2) developed, followed by solidification of the mixture. When no further ClF_5 uptake took place at −78°, the remaining ClF_5 was added at −196°. The reaction was completed by temperature cycling between −78 and −196° and no noncondensable material was observed at −196°. Fractional condensation of the reaction products showed NO_2F (10 mmol), HF (9 mmol), ClO_2F (5.9 mmol), and ClF (4.4 mmol).

Reaction of ClF_3 with Excess $HONO_2$.—Nominally anhydrous $HONO_2$ (10.4 mmol) and ClF_3 (3.45 mmol) were combined at −78° in a Teflon FEP U trap. The ClF_3 was added in increments, and after each addition, the mixture was allowed gradually to warm up until reaction occurred. During the ClF_3 additions, the reaction mixture turned orange, indicating the formation of ClO_2. After completion of the ClF_3 addition, the mix-

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ure was kept for 8 hr at −78°. The reaction mixture consisted of ClO_2 (1.7 mmol), $ClONO_2$ (1.7 mmol), HF (10 mmol), N_2O_5, and O_2. No unreacted ClF_3 was recovered.

Reaction of Excess ClF_5 with $HONO_2$.—Chlorine pentafluoride (4.0 mmol) and $HONO_2$ (3.36 mmol) were condensed at −196° into the separate bends of a double-U Teflon FEP trap. The $HONO_2$ was warmed to its melting point and ClF_5 vapor was allowed to contact the liquid $HONO_2$ phase. A vigorous reaction took place. At first, a brown color developed, and upon addition of all the ClF_5, two liquid layers formed. The upper one containing most of the material was colorless, whereas the lower one was brown. The mixture was allowed to interact for several minutes at −78° and was then allowed to warm to ambient temperature, at which point the brown color disappeared. Recooling of the mixture to −196° showed the absence of noncondensable material. The reaction products consisted of ClO_2F (1.66 mmol), ClF_5 (2.4 mmol), NO_2F (3.3 mmol), and HF.

Reaction of ClF_5 with Excess $HONO_2$.—Chlorine pentafluoride (1.39 mmol) and $HONO_2$ (6.76 mmol) were combined at −196° in a Teflon FEP U trap. A vigorous reaction took place upon melting, which was moderated by intermittent cooling with liquid N_2. After completion of the reaction, the brown liquid product was kept at 23° for 10 min and then recooled to −196°. The reaction products consisted of O_2 (0.42 mmol), ClO_2F (0.55 mmol), $ClONO_2$ (0.29 mmol), ClO_2 (0.36 mmol), N_2O_5, and HF.

Reaction of ClF_5 with Excess HOH.—Chlorine pentafluoride (2.00 mmol) and HOH (5.00 mmol) were combined at −196° in a Teflon FEP U trap. A vigorous reaction started upon melting of the ClF_5, which was controlled by intermittent cooling with liquid N_2. The yellow to orange mixture was kept at 23° for 3 hr before being recooled to −196°. The products consisted of ClO_2 (1.35 mmol), ClO_2F (0.35 mmol), ClO_3F (0.18 mmol), O_2 (<0.5 mmol), and HF.

Reaction of ClO_2F with Excess $HONO_2$.—Chloryl fluoride (2.35 mmol) and $HONO_2$ (2.16 mmol) were combined at −196° in a Teflon FEP U trap. The mixture was allowed to warm up and to react. The resulting homogeneous brown solution was kept for 30 min at 23°, at which temperature gas evolution was observed. The reaction products were O_2 (0.25 mmol), ClO_2 (0.48 mmol), ClO_2F (1.86 mmol), N_2O_5, $HONO_2$, and HF. Since only 0.49 mmol of ClO_2F reacted, the amount of $HONO_2$ available (2.16 mmol) presented a true excess.

Hydrolysis of $ClF_2^+AsF_6^-$ in HF Solution.—To a mixture of $ClF_2^+AsF_6^-$ (21.7 mmol) and anhydrous HF (5 ml liquid), wet HF (5 ml containing 20.6 mmol of H_2O) was slowly added at −78°. At first a brownish red color developed which gradually changed to yellow. After keeping the mixture at −78° for 1 hr, the volatiles were removed *in vacuo*. The solid residue was shown by infrared spectroscopy to consist of $ClO_2^+AsF_6^-$ and $ClF_2^+AsF_6^-$.

Results and Discussion

The following reaction systems were studied: excess ClF + $HONO_2$, excess ClF_3 + $HONO_2$, excess ClF_5 + $HONO_2$, ClF_3 + excess $HONO_2$, ClF_5 + excess $HONO_2$, ClO_2F + excess $HONO_2$, and ClF_5 + excess HOH. The reactions between excess ClF_5 and HOH,[4] between ClF and excess $HONO_2$,[3] and between ClF, ClF_3, or ClO_2F and HOH with either reagent in excess[1,2] have previously been reported. In order to establish the nature of some of the intermediate products, the ClF–Cl_2O system, the low-temperature reaction of ClF with an excess of water, and the hydrolysis of $ClF_2^+AsF_6^-$ in HF solution were also studied. Consequently, complete experimental data are now available for a systematic evaluation of the reactions between chlorine fluorides and mono- and bifunctional hydroxyl compounds. The following equations (some of them expressed in multiples for easier comparison) summarize the observed reactions:

excess ClF + HOX

$$\mathrm{4ClF + 4HONO_2 \longrightarrow 4HF + 4ClONO_2} \qquad (1)$$

$$\mathrm{5ClF + 2HOH \longrightarrow 4HF + ClO_2F + 2Cl_2} \qquad \text{(2)[1,2]}$$

ClF + excess HOX

$$\mathrm{4ClF + 4HONO_2 \longrightarrow 4HF + 4ClONO_2} \qquad \text{(3)[3]}$$

$$\mathrm{4ClF + 2HOH \longrightarrow 4HF + 2Cl_2 + O_2} \qquad \text{(4)[1,2]}$$

$$\mathrm{4ClF + 2HOH \xrightarrow{low\ temp} 4HF + 2Cl_2O} \qquad (4a)$$

$$\mathrm{10ClF + 5HOH \xrightarrow{25^\circ} 10HF + 2ClO_2 + 4Cl_2 + {}^1/_2O_2} \qquad (4b)$$

excess ClF_3 + HOX

$$\mathrm{2ClF_3 + 2HONO_2 \longrightarrow 2HF + ClO_2F + ClF + 2NO_2F} \qquad (5)$$

$$\mathrm{2ClF_3 + 2HOH \longrightarrow 4HF + ClO_2F + ClF} \qquad \text{(6)[1,2]}$$

ClF_3 + excess HOX

$$\mathrm{4ClF_3 + 12HONO_2 \longrightarrow 12HF + 2ClO_2 + 2ClONO_2 + 5N_2O_5 + {}^1/_2O_2} \qquad (7)$$

$$\mathrm{4ClF_3 + 6HOH \longrightarrow 12HF + 2Cl_2 + 3O_2} \qquad \text{(8)[1,2]}$$

$$\mathrm{[\equiv 2ClO_2 + ClOCl + {}^1/_2O_2]} \qquad (8a)$$

excess ClF_5 + HOX

$$\mathrm{ClF_5 + 2HONO_2 \longrightarrow 2HF + ClO_2F + 2NO_2F} \qquad (9)$$

$$\mathrm{ClF_5 + 2HOH \longrightarrow 4HF + ClO_2F} \qquad \text{(10)[4]}$$

ClF_5 + excess HOX

$$\mathrm{2ClF_5 + 8HONO_2 \longrightarrow 8HF + 4N_2O_5 + 2ClO_2F} \qquad (11)$$

$$\mathrm{2ClO_2F + 2HONO_2 \longrightarrow 2HF + N_2O_5 + 2ClO_2 + {}^1/_2O_2} \qquad (11a)$$

or

$$\mathrm{2ClF_5 + 10HONO_2 \longrightarrow 10HF + 4N_2O_5 + 2ClONO_2 + 2O_2} \qquad (11b)$$

$$\mathrm{2ClF_5 + 5HOH \longrightarrow 10HF + 2ClO_2 + {}^1/_2O_2} \qquad (12)$$

ClO_2F + excess HOX

$$\mathrm{2ClO_2F + 2HONO_2 \longrightarrow 2HF + 2ClO_2 + N_2O_5 + {}^1/_2O_2} \qquad (13)$$

$$\mathrm{2ClO_2F + HOH \longrightarrow 2HF + 2ClO_2 + {}^1/_2O_2} \qquad \text{(14)[1,2]}$$

Cl_2O + excess ClF

$$\mathrm{2Cl_2O + ClF \longrightarrow ClO_2F + 2Cl_2} \qquad (15)$$

Several reactions require some specific comments. According to ref 1 and 2 eq 6 can be followed by additional more or less slow reactions resulting in the formation of some Cl_2 and O_2 and of traces of ClO_3F. Equation 8 might be rewritten by substituting the observed amounts of Cl_2 and O_2 by the appropriate chlorine oxides (eq 8a). This assumption is supported by the fact that in the ClF–H_2O system, depending upon the reaction conditions, either Cl_2 and O_2 (eq 4) or ClO_2, Cl_2, and O_2 (eq 4b) or Cl_2O (eq 4a) can be obtained as the principal products. The reaction products observed for the reaction of ClF_5 with excess $HONO_2$ can be rationalized by assuming that ClO_2F is formed as the primary product (eq 11) which reacts only slowly with additional $HONO_2$, according to (eq 11a), thus leaving an appreciable amount of ClO_2F unconverted. This assumption was confirmed by reaction 13, which showed that this reaction is indeed slow. In addition, a side reaction generating $ClONO_2$ and oxygen occurs (eq 11b). For reaction 12, substantial amounts of ClO_2F and ClO_3F were found in the reaction product. The observation of some ClO_3F is not surprising since it has previously been shown[3] that the hydrolysis of ClO_2F is quite slow. The hydrolysis of some of the ClO_2F produces nascent oxygen, which, in turn, can rapidly oxidize ClO_2F to ClO_3F. Since ClO_3F is resistant to hydrolysis,[8] it will build up as a product.

A general comparison between the reactions of $HONO_2$ and those of HOH shows an excellent agreement. The reaction products and the changes in the oxidation states of Cl are analogous for each equation pair. The only exceptions are reactions 1 and 2. The difference is due to the fact that $ClONO_2$, under the given conditions, does not interact with ClF, whereas Cl_2O even at −78° does, yielding ClO_2F and Cl_2 (eq 15). The fact that the products differ depending upon which reagent is used in excess is not surprising. If an excess of the fluorinating agent is used, ClO_2F is always one or often the only chlorine-containing reaction product independent of the oxidation state of the chlorine fluoride starting material. The only exception is again reaction 1 for the above-mentioned reason, *i.e.*, inability of ClF to fluorinate $ClONO_2$ under the given conditions. If an excess of the hydroxyl compound is used, the main reaction products are chlorine oxides (most frequently ClO_2) and chlorine nitrate. In the case of excess $HONO_2$, any NO_2F present will form N_2O_5 and HF. In the case of ClF the formation of several intermediates was experimentally confirmed suggesting for the low-temperature reaction of ClF with HOH the sequence

$$\mathrm{ClF + HOH \longrightarrow HF + HOCl} \qquad (16)$$

$$\mathrm{HOCl + ClF \longrightarrow HF + ClOCl} \qquad (17)$$

In the presence of an excess of ClF, fluorination of Cl_2O can occur according to eq 15. This reaction was shown to be quantitative at temperatures as low as −78°. In the presence of an excess of water at −78°, Cl_2O is the principal product. In addition to Cl_2O formation, reaction 4b also occurs at −78° and becomes at 25° the dominant reaction. Under the reaction conditions of ref 1 and 2, ClO_2 can decompose further to Cl_2 and O_2 (eq 4). The fact that pure Cl_2O does not readily disproportionate at temperatures between −78 and 25° to ClO_2 and Cl_2 suggests the participation of less stable intermediates such as possibly HOCl or ClO radicals in the ClO_2 formation step.

In the case of ClF_3 and ClF_5 the first reaction should be again the elimination of HF. This reaction is extremely fast and exothermic and often proceeds explosively, even at low temperature

$$\mathrm{ClF_n + HOX \longrightarrow ClF_{n-1}OX + HF} \qquad (18)$$

The next steps could involve either the reaction of $ClF_{n-1}OX$ with additional HOX

$$\mathrm{ClF_{n-1}OX + HOX \longrightarrow ClF_{n-2}(OX)_2 + HF} \qquad (19)$$

or an intramolecular fluorination, *i.e.*, XF elimination

$$\mathrm{ClF_{n-1}OX \longrightarrow ClF_{n-2}O + XF} \qquad (20)$$

Reaction 19 should also be followed by steps such as (20) or by X_2O elimination if there are no or only relatively unreactive fluorine atoms left in the molecule

$$\mathrm{ClF_{n-2}(OX)_2 \longrightarrow ClF_{n-2}O + X_2O} \qquad (21)$$

Thus, by either sequence, one might expect to obtain FClO as a intermediate in the reactions of ClF_3. However, the following facts indicate that this intermediate would be quite unstable. The photochemical synthesis[9] and reaction chemistry[10] of ClF_3O are best interpreted in terms of an unstable FClO intermediate. In addition, an attempt was made to prepare and isolate FClO, according to

$$\mathrm{ClF_2{}^+AsF_6{}^- + HOH \xrightarrow{HF\ soln} ClO^+AsF_6{}^- + 2HF} \qquad (22)$$

$$\mathrm{ClO^+AsF_6{}^- + FNO \longrightarrow NO^+AsF_6{}^- + FClO} \qquad (23)$$

However, instead of $ClO^+AsF_6^-$, only $ClO_2^+AsF_6^-$ and unreacted $ClF_2^+AsF_6^-$ were found for (22).

Similarly, one might have expected to observe ClF_3O, which is known to be stable,[11,12] as an intermediate in the reactions of HOX with an excess of ClF_5. The fact that it was not observed either suggests an alternate sequence such as

$$\mathrm{ClF_5 + 2HOX \longrightarrow ClF_3(OX)_2 + 2HF} \qquad (24)$$

$$\mathrm{ClF_3(OX)_2 \longrightarrow ClO_2F + 2XF} \qquad (25)$$

or indicates that ClF_3O is much more reactive toward HOX than is ClF_5.

In many of these systems, the final products show that the Cl-containing starting material has disproportionated in the course of the reaction. Suitable intermediates which could readily disproportionate might be ClO, HOCl, HOClO, and FClO.

In summary, it appears that the reactions of chlorine fluorides with a monofunctional ($HONO_2$) and a bifunctional (HOH) hydroxyl compound can be rationalized on a common basis. The observed reaction patterns should be very useful for predicting the products of the reactions of chlorine fluorides with other hydroxyl compounds. The partial hydrolysis of chlorine fluorides does not offer a synthetic route toward chlorine oxyfluorides, except for ClO_2F.

Acknowledgment.—I am indebted to Drs. D. Pilipovich and C. J. Schack for stimulating discussions. This work was supported by the Office of Naval Research, Power Branch.

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Contribution from Rocketdyne,
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Iodine Tris(perchlorate) and Cesium Tetrakis(perchlorato)iodate(III)

By KARL O. CHRISTE* and CARL J. SCHACK

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The syntheses and some properties of the novel iodine perchlorates $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$ are reported. Their vibrational spectra were recorded and confirm their formulation as covalent perchlorates. A square-planar configuration is proposed for the $I(OClO_3)_4^-$ anion, whereas $I(OClO_3)_3$ appears to be polymeric.

Introduction

The preparation of iodine tris(perchlorate) from iodine, ozone, and anhydrous $HClO_4$ is described in ref 1. However, a cross-check with the original publication,[2] from which the preparation was abstracted, reveals that the original paper deals only with a compound having the empirical composition $I(ClO_4)_3 \cdot 2H_2O$. Numerous attempts have been reported to prepare iodine perchlorates in organic solvents from I_2 and $AgClO_4$. Whereas the experimental data were consistent with the formation of iodine perchlorates as unstable intermediates, all attempts to isolate and characterize these compounds were unsuccessful, owing

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(1) M. Schmeisser in "Handbook of Preparative Inorganic Chemistry," Vol. 1, G. Brauer, Ed., Academic Press, New York, N. Y., 1963, p 330.

(2) F. Fichter and H. Kappeler, *Z. Anorg. Allg. Chem.*, 91, 134 (1915).

to their incompatibility with the solvent. In this paper, we report the successful preparation and isolation of $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$.

Experimental Section

Materials and Apparatus.—Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Iodine (reagent grade, Mallinckrodt) was resublimed before use. Anhydrous CsI (ROC/RIC, 99.9% minimum purity) was used without further purification. Chlorine perchlorate and $CsIBr_2$ were prepared and purified by the methods of Schack and Pilipovich[3] and Cremer and Duncan,[4] respectively. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl, AgBr, or BaF_2 windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to $\sim -25°$, and a dc ammeter. Glass melting point or Kel-F capillaries were used as sample containers in the transverse viewing–transverse excitation technique. The low-temperature spectra were recorded by the method of Miller and Harney.[5]

Preparation of $I(OClO_3)_3$.—Iodine (0.915 mmol) was loaded into a 10-ml prepassivated Teflon FEP ampoule closed off by a Hoke 316 stainless steel valve (425 1F4Y). Chlorine perchlorate (8.18 mmol) was added at −196°. The ampoule was kept at −50° for 70 hr. At this point, the dark iodine color had disappeared and a pale yellow (due to the presence of Cl_2) solid had formed. Upon cooling to −196°, the ampoule did not contain any noncondensable reaction products. The ampoule was slowly warmed to −45°. The volatile products were separated by fractional condensation and identified by infrared spectroscopy and their vapor pressure. They consisted of Cl_2 (2.70 mmol) and $ClOClO_3$ (2.74 mmol). The white, solid residue weighed 776 mg, in excellent agreement with the weight (777 mg) calculated for a complete conversion to $I(OClO_3)_3$.

A sample of $I(OClO_3)_3$ (775 mg, 1.82 mmol) was allowed to warm up from −45 to 23°. Close to 23°, it formed a brownish paste. Recooling of the sample to −196° showed no noncondensables. The sample was warmed up again to 23° and kept at this temperature for 12 hr while the volatile products were pumped off and separated by fractional condensation. The volatile material consisted of Cl_2O_7 (1.9 mmol) and smaller amounts of Cl_2O_6 and lower chlorine oxides. The pale yellow, nonvolatile residue had the following composition: ClO_4^-, 21.7%; total iodine, 61.0%; iodometric titration assuming an oxidation state of +5, I = 62.0%. The infrared spectrum of the solid showed the presence of the ClO_4^- anion. Additional Cl_2O_7 could be removed from the solid by heating it for several hours to 60° *in vacuo*. The infrared spectrum still showed the presence of ClO_4^-. The weight of the solid had decreased to 366 mg.

Attempted Preparation of $IOClO_3$.—Iodine (1.25 mmol) and $ClOClO_3$ (2.50 mmol) were allowed to react as described for $I(OClO_3)_3$. The iodine color had completely disappeared; however, no products volatile at −45° had formed. The nonvolatile residue was a white solid showing orange and gray-green spots. Upon slight warm-up, the sample turned black and decomposed.

Preparation of $Cs^+I(OClO_3)_4^-$.—A 10-ml prepassivated stainless steel cylinder was loaded with powdered CsI (1.15 mmol), followed by $ClOClO_3$ (6.10 mmol) at −196°. The reaction was allowed to proceed by warming the cylinder to −45°, where it was maintained for 5 weeks. On recooling to −196°, no noncondensable gases were observed. Volatile products were pumped from the reactor for several hours while and after it had warmed to ambient temperature. Separation of these species was effected by fractional condensation and identification by infrared and vapor pressure measurements. They consisted of Cl_2 (2.34 mmol) and unreacted $ClOClO_3$ (1.45 mmol). The solid product was pale yellow and weighed 749 mg, indicating a 99% conversion of the CsI to $Cs^+I(OClO_3)_4^-$ had occurred.

Attempted Preparation of $Cs^+I(OClO_3)_2^-$.—Chlorine perchlorate (6.27 mmol) was allowed to react with $CsIBr_2$ (2.76 mmol) at −45°. No unreacted $ClOClO_3$ was recovered and the volatile products consisted of Cl_2, Br_2, and BrCl only. The solid reaction product was inhomogeneous. The infrared spectra of the upper layers showed the presence of perchlorato groups, whereas for the lower layers these were absent.

Elemental Analysis.—Weighed samples were hydrolyzed in water. The amounts of total iodine and perchlorate were determined by X-ray fluoresecence spectroscopy and by a specific ion electrode (Orion Model 92-17), respectively. The oxidation state of iodine was found by iodometric titration.

Results and Discussion

Caution! Chlorine perchlorate is shock sensitive[3] and samples of both $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$ have exploded even at low temperature while recording their laser Raman spectra. Proper safety precautions must be taken when working with these compounds.

Syntheses and Properties.—The novel compound iodine tris(perchlorate) was prepared by the low-temperature reaction of iodine with an excess of $ClOClO_3$. Its composition was established by quantitative synthesis: $I_2 + 6ClOClO_3 \rightarrow 2I(OClO_3)_3 + 3Cl_2$, with the material balance for all components being 99+%. The compound is a white solid, stable at −45°. During its synthesis, no explosions were encountered; however, when exposed to a laser beam, explosive decomposition occurred even at low temperatures. It decomposes upon warming to ambient temperature. Depending upon the warm-up conditions (*i.e.*, warm-up rate and pressure) differences in the decomposition behavior were observed. Thus, the melting to a brownish paste was not observed in all cases, and in some instances, the appearance of orange and brown colors was observed, which might be ascribed to the formation of ClO_2 and lower chlorine oxides, respectively. The following observations were made for the decomposition process: (1) the volatile decomposition products consisted mainly of Cl_2O_7 but also contained smaller amounts of Cl_2O_6 and lower chlorine oxides; (2) the solid residue contained only iodine in the +5 oxidation state and its infrared spectrum showed the presence of the ClO_4^- anion;[6] (3) upon pyrolysis or longer exposure to the laser beam, the Raman spectrum of the solid is identical with that previously reported[7] for I_2O_5 (see Figure 1, trace B); (4) the elemental analysis and material balance of the solid are in fair agreement with those calculated for a mixture of 62.4 mol % IO_2ClO_4 and 37.6 mol % I_2O_5. Upon extended pyrolysis, the percentage of I_2O_5 increases. These observations are best interpreted in terms of an initial Cl_2O_7 elimination, $I(OClO_3)_3 \rightarrow [OIOClO_3] + Cl_2O_7$, followed by an internal redox reaction yielding

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(5) F. A. Miller and B. M. Harney, private communication.

(6) J. W. Nebgen, A. D. McElroy, and H. F. Klodowski, *Inorg. Chem.*, 4, 1796 (1965).

(7) P. M. A. Sherwood and J. J. Turner, *Spectrochim. Acta, Part A*, 26, 1975 (1970).

+5 iodine, lower chlorine oxides, IO_2ClO_4, and I_2O_5. It is not surprising that mainly Cl_2O_7 and some chlorine oxides of low oxidation state were observed and not Cl_2O_6 as might be expected according to $I(OClO_3)_3 \rightarrow IO_2ClO_4 + Cl_2O_6$. It is well known that the perchlorate ion does not oxidize CsI whereas ClO_3^- or ClO_2^- does. Hence, Cl_2O_7 might also be a less effective oxidizing agent than Cl_2O_6 or the lower chlorine oxides.

Attempts to prepare iodine monoperchlorate from stoichiometric amounts of iodine and $ClOClO_3$ failed. Apparently, $ClOClO_3$ oxidizes iodine rapidly to oxidation states higher than +1. The resulting mixed iodine chloride perchlorate with a formal oxidation state of +2 would be expected to be highly unstable and susceptible to disproportionation and decomposition.

The salt $Cs^+I(OClO_3)_4^-$ was prepared according to $Cs^+I^- + 4ClOClO_3 \rightarrow Cs^+I(OClO_3)_4^- + 2Cl_2$. Its composition was again ascertained by quantitative synthesis. It is a pale yellow solid and is stable at ambient temperature. Its decomposition has been studied less extensively than that of $I(OClO_3)_3$. However, the Raman spectra (Figure 1, trace A, and Figure 2, traces B and C) demonstrate the formation of a common intermediate decomposition product which is not I_2O_5 and does not contain the ClO_4^- anion. The formation of this intermediate might be favored by the laser light.

Attempts to prepare $Cs^+I(OClO_3)_2^-$ according to $Cs^+IBr_2^- + 2ClOClO_3 \rightarrow Cs^+I(OClO_3)_2^- + 2BrCl$ were unsuccessful. Part of the product was converted to +3 iodine salts while some of the $Cs^+IBr_2^-$ starting material was recovered unchanged.

Considering the low thermal stability and high reactivity of $I(OClO_3)_3$, it is not surprising that previous attempts[8-11] had failed to prepare and isolate these compounds from organic solvents. From the properties of $I(OClO_3)_3$, it also appears unlikely that the product obtained[3] by Fichter and Kappeler was indeed a dihydrate of $I(OClO_3)_3$. Other possible structures such as $IO_2ClO_4 \cdot 2HOClO_3$ might be written for their product which approach the reported[3] composition.

Vibrational Spectra.—Figures 1 and 2 show the Raman spectra of $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$, respectively. The spectra of both compounds had to be recorded at low temperature to avoid (explosive) decomposition in the laser beam. For $Cs^+I(OClO_3)_4^-$, which is the more stable of the two compounds, a spectrum was obtained which was essentially free of decomposition product bands (trace A, Figure 2). Traces B and C show the same sample at various stages of decomposition and allow the identification of the bands belonging to the decomposition products. It was not possible to obtain a spectrum of $I(OClO_3)_3$ free of decomposition products. However, the decomposition product was identical with that observed for $Cs^+I(OClO_3)_4^-$ (trace C, Figure 2). Therefore, the bands due to $I(OClO_3)_3$ itself can be readily identified. The spectrum of the product obtained by vacuum pyrolysis of $I(OClO_3)_3$ at 60° is shown as trace B in Figure 1. It is distinct from that in the low-temperature decomposition and is identical with

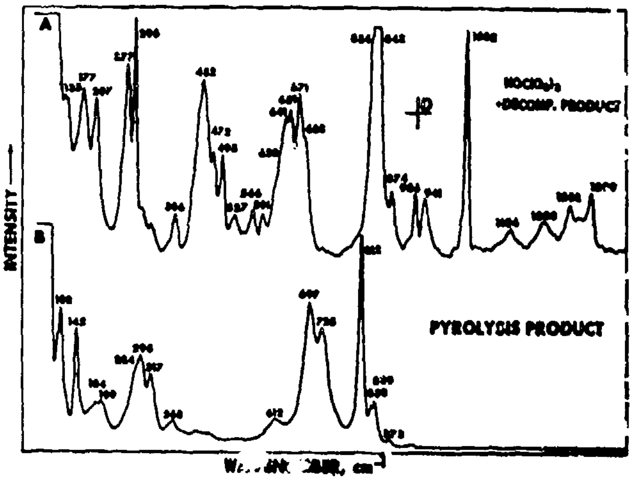

Figure 1.—Raman spectra of $I(OClO_3)_3$, recorded at −60° (trace A), and of its decomposition product (trace B) obtained by vacuum pyrolysis at 60°. D indicates spectral slit width.

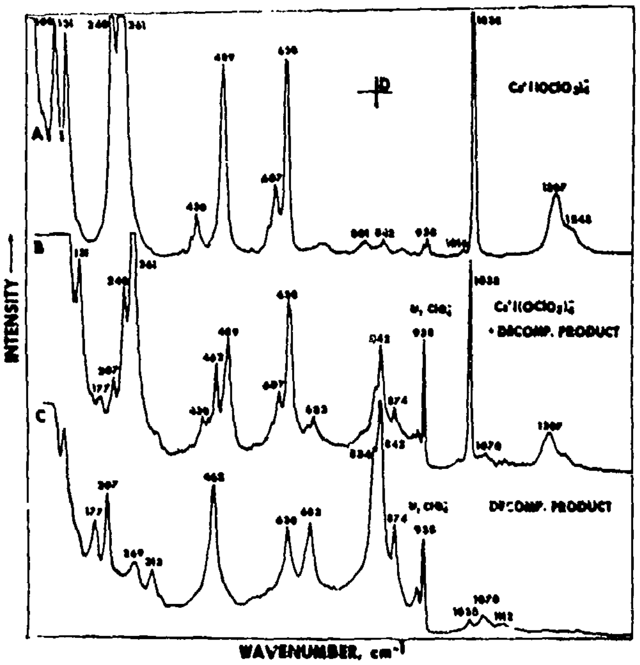

Figure 2.—Raman spectra of $Cs^+I(OClO_3)_4^-$, recorded at −70° (trace A), and of its decomposition products (traces B and C).

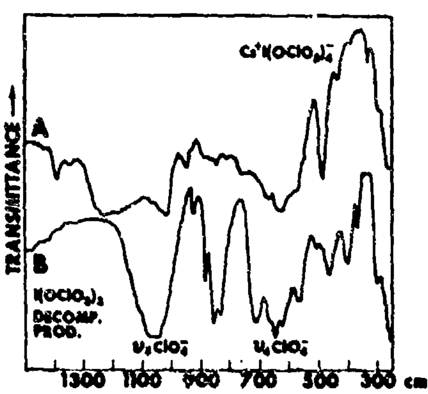

Figure 3.—Infrared spectra of $Cs^+I(OClO_3)_4^-$ (trace A) and of the $I(OClO_3)_3$ decomposition product (trace B) as AgBr disks.

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TABLE I

VIBRATIONAL SPECTRUM OF $Cs^+I(OClO_3)_4^-$ COMPARED TO THOSE OF $ClOClO_3$ AND $BrOClO_3$

Obsd freq, cm^{-1}, and intens					
$ClOClO_3$[a]		$BrOClO_3$[a]	$Cs^+I(OClO_3)_4^-$		
Ir	Raman	Ir	Ir	Raman	Approx description of mode
1283 vs	1280 mw	1275 vs	1230 vs	1243 w, sh 1207 mw	Antisym ClO_3 str
1040 s	1036 vs	1039 s	1015 vs	1038 s 1016 vw	Sym ClO_3 str
646 vs	643 ms	648 s	630 vs	630 s	O–Cl str
580 sh	582 m		570–650 vs	607 mw	ClO_3 scissor, δ_{as} ClO_3
561 m	561 w	570 ms			
511 mw	516 s	509 m	485 s	489 s	δ umbrella ClO_3
			430 vw	430 mw	
				261 vs	ν sym in-phase IO_4
				240 s	ν sym out-of-phase IO_4
				131 ms 106 ms	IOCl def

[a] Reference 13.

that reported[7] for I_2O_5. Figure 3 shows the infrared spectrum of $Cs^+I(OClO_3)_4^-$ and that of the $I(OClO_3)_3$ decomposition product. The latter shows strong absorptions characteristic for the ClO_4^- ion.[8] Since covalent perchlorates generally attack silver halide windows with ClO_4^- formation, the spectrum was also recorded using BaF_2 windows. It was identical with that shown in Figure 3.

The spectrum of $Cs^+I(OClO_3)_4^-$ will be discussed first due to its simplicity. Comparison with the known spectrum of other covalent halogen perchlorates[3,12,13] reveals that the compound contains exclusively covalent, monodentate perchlorato groups. A listing of the observed frequencies together with a tentative assignment is given in Table I. The slight frequency decrease of some of the perchlorato bands on going from halogen mono(perchlorates) to the tetrakis(perchlorato)iodate(III) anion may be explained by the formal negative charge in the latter. A similar decrease has also been observed for the corresponding halogen fluorosulfates.[14–16] The vibrational spectrum of $I(OClO_3)_4^-$ is analogous to that[15] of $I(OSO_2F)_4^-$ and suggests a similar structure for both anions. In agreement with Carter, Jones, and Aubke,[15] we suggest a square-planar configuration for the IO_4 skeleton by analogy with that found for the corresponding tetrafluorohalogenate(III) anions, ClF_4^- and BrF_4^-.[17,18] For the IO_4 skeletal stretching modes, we propose an assignment different from that made previously[15] for $I(OSO_2F)_4^-$. The two symmetric IO_4 stretching modes should both be of very high intensity in the Raman spectrum and be separated by less than 100 cm^{-1}.[17,18] Furthermore, they should be observed for both ions, $I(OClO_3)_4^-$ and $I(OSO_2F)_4^-$. Therefore, the assignment of the bands at 261 and 240 cm^{-1} to the symmetric in-phase and symmetric out-of-phase IO_4 stretching modes, respectively, appears more plausible than that previously suggested.[15] On the basis of the available data, it cannot be decided whether or not the chlorine atoms are coplanar with the IO_4 group.

For $I(OClO_3)_3$, the Raman spectrum (Figure 1, trace A) is rather complex in the 1100–1300-cm^{-1} region. By analogy with the halogen trifluorides and halogen tris(fluorosulfates),[15] these features might be explained in terms of two nonequivalent types of perchlorato groups. The substantial shift to lower frequencies of two of these bands (1203 and 1126 cm^{-1}) indicates strong bridging as expected for a polymeric structure. The bands occurring in the following regions are tentatively assigned to the following type of vibrations: 1100–1300 cm^{-1}, antisymmetric ClO_3 stretch; 920–1040 cm^{-1}, symmetric ClO_3 stretch; 600–690 cm^{-1}, scissoring deformation of ClO_3; 440–500 cm^{-1}, umbrella deformation of ClO_3 and IO stretch; 270–300 cm^{-1}, IO_3 stretching modes; 100–200 cm^{-1}, I–O–Cl bending modes. Again, the bands assigned to the IO_x stretching modes have almost identical counterparts in the $I(OSO_3F)_3$ spectrum,[15] indicating the close structural relationship between these halogen perchlorates and the corresponding fluorosulfates.

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On Alkali Metal Fluoride–Iodine Pentafluoride Adducts

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The syntheses and properties of novel 1:3 adducts between alkali metal fluorides and IF_5 are described. Infrared and Raman spectra are reported for $CsF \cdot 3IF_5$, $CsIF_6$, $RbIF_6$, KIF_6, and a mixture of $RbIF_6$ with $RbF \cdot 3IF_5$. The previously reported discrepancies in the vibrational spectra of IF_6^- salts can be rationalized by assuming mixtures of 1:1 and 1:3 adducts. Powder diffraction X-ray data are given for KIF_6, $RbIF_6$, and $CsIF_6$. Partial pyrolysis, vibrational spectroscopy, and differential thermal analyses show no evidence for the existence of distinct 1:2 adducts as intermediate products from the decomposition of the 1:3 adducts. The previous conclusions are confirmed that IF_6^- is not octahedral and does not have a symmetry higher than C_{3v}. The FNO–IF_5 and FNO–BrF_5 systems were briefly studied. Whereas BrF_5 does not form an FNO adduct, IF_5 combines with FNO to form a white, crystalline 1:1 adduct having a dissociation pressure of about 30 mm at 21°.

Introduction

The vibrational spectra of the alkali metal fluoride–iodine pentafluoride adducts were previously studied by at least four different research groups.[1–4] All four groups reached the same conclusion that the IF_6^- anion is not octahedral. This conclusion was also supported by the results of a recent Mössbauer study.[5] However, the vibrational spectra reported by the four groups for IF_6^- differed strongly and no plausible explanation could be offered for these discrepancies. Recently, Klamm and Meinert reported[6] the formation of IF_4Cl by treating CsCl with IF_5. Their failure to isolate and characterize this novel, yellow, volatile compound was attributed[6] to rapid reaction with the glass container. Our attempts to duplicate Klamm and Meinert's observations[6] in an inert metal–Teflon reaction system were unsuccessful. The most volatile yellow reaction product was, as expected, Cl_2. However, from the material balance, it became obvious that the solid residue was not the expected $Cs^+IF_6^-$ but the novel $CsF \cdot 3IF_5$ adduct. Furthermore, the vibrational spectra of $CsF \cdot 3IF_5$ showed bands previously attributed[1,2] to

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$CsIF_6$, indicating that most of the discrepancies in the previously reported data may have been due to varying mixtures of $Cs^+IF_6^-$ and $CsF \cdot 3IF_5$. Consequently, a systematic study of the alkali metal fluoride–iodine pentafluoride system was carried out, the results of which are reported in this paper. The existence of the $CsF \cdot 3IF_5$ adduct has also been discovered in an independent study by Hyde[7] but has not been published.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nitrosyl fluoride was prepared from NO and F_2 at −196°. Iodine pentafluoride (Allied Chemical) and BrF_5 (Matheson) were treated with F_2 until colorless. All materials were purified prior to use by fractional condensation. The alkali metal fluorides were fused in a platinum crucible and powdered in a drybox prior to use. Because of their hygroscopicity, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ∼−25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with hollow inside glass cones for variable sample thicknesses or Pyrex or clear Kel-F capillaries were used as sample containers. For the capillaries, the transverse viewing–transverse excitation technique and for the conical tubes, the axial viewing–transverse excitation technique were used.

X-Ray powder diffraction patterns were taken using a Phillips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in quartz capillaries (∼0.5-mm o.d.). The densities were measured by the displacement method using a perfluorinated amine (FC 43, 3M Co.) to fill the pycnometer.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used to obtain the dta data. The samples were sealed in aluminum pans, and heating rates of 10°/min in N_2 were used.

Preparation of the Adducts.—Dry CsF (19.02 mmol) was placed into a 30-ml prepassivated 316 stainless steel cylinder and purified IF_5 (80.08 mmol) was added at −196°. The cylinder was placed on a shaker at 60° for 2 days. Unreacted IF_5 was removed at 25° by pumping for 3 hr. The cylinder contained 15.370 g of a stable, white, crystalline solid (weight calculated for $CsF \cdot 3IF_5$ 15.551 g). Therefore, CsF (19.02 mmol) had reacted with IF_5 (56.24 mmol) in a mole ratio of 1:2.96 producing the adduct $CsF \cdot 3IF_5$.

Finely powdered $CsF \cdot 3IF_5$ (10.81 mmol) when heated *in vacuo* to 90° for 12 hr lost IF_5 (21.63 mmol) forming the salt $Cs^+IF_6^-$.

Similarly, RbF (21.06 mmol) was combined with IF_5 (161.34 mmol) in a 150-ml prepassivated Monel cylinder and shaken at 60° for 144 hr. Unreacted IF_5 (114.59 mmol) was removed at 20° by pumping for 5 hr. Therefore, RbF (21.06 mmol) had reacted with IF_5 (46.75 mmole) in a mole ratio of 1:2.22 corresponding to a 73.98% conversion of RbF to $RbF \cdot 3IF_5$. More IF_5 (11.47 mmol) was slowly removed by an additional 15 hr of pumping at 25°. At this point the $RbF:IF_5$ ratio corresponded to 1:1.73.

Finely powdered $RbF \cdot 1.73\ IF_5$ (5.775 g) when heated *in vacuo* to 95° for 14 hr lost IF_5 (2.630 g, 11.85 mmol). A white, crystalline, stable solid resulted which according to the material balance had the composition $RbF \cdot 0.73IF_5$ or 27 mol % RbF + 73 mol % $RbIF_6$.

Potassium fluoride (37.87 mmol) was combined with IF_5 (101.21 mmol) in a 30-ml stainless stell cylinder. The cylinder was shaken for 50 hr at 60°. Unreacted IF_5 (17.61 mmol) was removed at 20° by pumping for 3 hr. Therefore, KF (37.87 mmol) had reacted with IF_5 (83.60 mmol) in a mole ratio of 1:2.21. Upon continued pumping at 25°, the solid kept losing additional amounts of IF_5. Pyrolysis at 60° *in vacuo* for 14 hr resulted in a white, stable, crystalline product having the composition $KF \cdot 0.95IF_5$.

Sodium fluoride, when heated to 60° for 50 hr on a shaker in the presence of a large excess of IF_5, did not combine with the latter to form a stable adduct.

Gaseous FNO was added in increments at 25° to liquid IF_5 (15.96 mmol) contained in a Teflon FEP U trap. Upon FNO addition, the mixture turned yellow and a slightly exothermic reaction occurred. After addition of 5.32 mmol of FNO (corresponding to $FNO \cdot 3IF_5$), the mixture was still liquid. The addition of an additional 5.32 mmol of FNO resulted in partial solidification. A total of 18.98 mmol of FNO was added and the temperature of the mixture was cycled several times between −196 and +25°. Unreacted FNO (2.89 mmol) was removed *in vacuo* at −24°. Hence, FNO (16.09 mmol) had reacted with IF_5 (15.96 mmol) in a mole ratio of 1:0.99 to form a white, crystalline solid. This solid had a dissociation pressure of about 30 mm at 21°. The vapor phase above the solid was shown by infrared spectroscopy to consist of equimolar amounts of FNO and IF_5.

Bromine pentafluoride (4.20 mmol) and FNO (8.40 mmol) were combined at −196° in a Teflon FEP U trap. Upon warm-up, the mixture melted forming a yellowish liquid. The mixture remained liquid at −64° and could be completely removed *in vacuo* at this temperature, not yielding a solid at any time. Hence, no stable solid adduct is formed at temperatures as low as −64°.

Results and Discussion

Syntheses and Properties.—The formation of distinct 1:3 and 1:1 adducts for the alkali metal fluoride–iodine pentafluoride systems was established by syntheses. Thus, KF, RbF, and CsF, can combine with more than an equimolar amount of IF_5. For CsF an almost theoretical conversion to a stable 1:3 adduct was achieved. This 1:3 adduct can be pyrolyzed under vacuum at 90° to form the known 1:1 adduct. When $CsF \cdot 3IF_5$ was slowly heated in a sealed glass capillary under 1 atm of N_2, the material became pasty at 105–110° and partial melting started at about 123°. At 140–150°, IF_5 started to distil off the solid, and the glass container was attacked. A sample of $CsIF_6$ started to attack the glass container at ∼160°, the temperature at which partial melting began. The dta data are in fair agreement with these observations. Thus, $CsF \cdot 3IF_5$ showed a gradual, continuous endotherm starting at about 153° indicating the loss of IF_5. The slight temperature difference might be due to the faster heating rate used for the dta study. No evidence for a stepwise decomposition, *i.e.*, for the formation of a distinct, intermediate 1:2 adduct was obtained. The dta curve of $CsIF_6$ showed an endotherm from 223 to 227°.

The isolation of clearly defined $RbF \cdot 3IF_5$ and $KF \cdot 3IF_5$ adducts is more difficult owing to their marginal stability at 25° and the relatively low volatility of IF_5 which must be used in excess for their syntheses. Furthermore, the conversion of RbF to an IF_5 adduct was found to be slow. After 2 days the conversion to $RbF \cdot 3IF_5$ was only 45% and after 6 days only 74%. It is unlikely that at this point the product consisted mainly of $RbIF_6$ and some $RbF \cdot 3IF_5$ since a mixture of

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(7) Hyde, G. A. Olin Corp., private communication.

TABLE I

X-RAY POWDER DATA FOR KIF$_6$, RbIF$_6$, AND CsIF$_6$

KIF$_6$			
d, Å			
Obsd	Calcd	Intens	*hkl*
7.82	7.86	mw	110
6.94	6.80	m	200
6.36	6.39	m	111
4.53	4.53	vs	300
3.92	3.93	vs	220
3.77	3.78	w	310
3.68	3.68	m	003 221
3.50	3.50	w	302
3.41	3.40	m	400
3.21	3.20	w	222
3.09	3.11	m	312
2.92	2.89	m	402
2.77	2.75	m	004
2.71	2.71	w	500 322 104
2.58	2.58	vw	114 420
2.55	2.55	vw	331 204
2.35	2.35	w	304
2.16	2.17	w	105
2.14	2.14	w	521
2.02	2.02	m	414
1.947	1.945	w	530
1.901	1.901	m	315 33[illegible]
1.861	1.861	w	621
1.835	1.835	m	006
1.796	1.799	m	325
1.745	1.743	w	540
1.707	1.709	w	524
1.574	1.570	w	007
1.481	1.477	w	732
1.461	1.461	mw	902 227 813

RbIF$_6$			
d, Å			
Obsd	Calcd	Intens	*hkl*
7.10	6.91	w	200
6.57	6.57	w	111
4.63	4.61	w	300
3.99	3.99	vs	220
3.76	3.78	mw	221
3.50	3.49	m	113 400
3.27	3.29	w	222
3.13	3.11	m	213
2.97	2.97	m	402 303
2.83	2.84	m	104
2.77	2.77	w	500
2.49	2.49	w	510 502
2.41	2.42	mw	332
2.21	2.21	m, b	205 520
2.06	2.07	m, b	522
1.994	1.996	mw, b	440
1.937	1.937	m	006
1.897	1.893	mw	621
1.870	1.870	mw	702
1.838	1.838	m	415
1.784	1.784	w	306
1.746	1.746	w	712
1.605	1.603	w	811 525
1.535	1.535	w	900 227
1.493	1.493	mw	813 634
1.467	1.469	w	643
1.442	1.443	mw	108 733

CsIF$_6$			
d, Å			
Obsd	Calcd	Intens	*hkl*
7.39	7.23	w	200
6.80	6.78	w	111
4.13	4.13	vs	220
3.90	3.90	m	221
3.61	3.58	s	400
3.39	3.39	mw	222
3.26	3.28	m	320
3.07	3.07	m	402
2.92	2.91	m	104
2.85	2.86	w	500
2.57	2.57	w	502
2.47	2.46	m	422
2.26	2.26	m	205 521
2.12	2.13	m	305
2.05	2.05	w	612 603
1.992	1.992	mw	424 620
1.955	1.955	mw	621
1.932	1.932	mw	702 116
1.886	1.886	mw	415 622
1.833	1.833	w	540 443
1.787	1.787	w	800 226
1.657	1.658	mw	811

73% RbIF$_6$ and 27% RbF was obtained upon pyrolysis of the product at a temperature at which RbIF$_6$ is stable. To obtain mainly the 3:1 adducts of IF$_5$ with either RbF or KF, removal of unreacted IF$_5$ must be stopped as soon as the IF$_5$ removal rate decreases sharply. Otherwise, the products will contain larger amounts of RbIF$_6$ and KIF$_6$, respectively. A mixture of RbF (27%), RbIF$_6$ (23%), and RbF·3IF$_5$ (50%), having the empirical composition RbF·1.73IF$_5$ when heated in a sealed glass capillary, did not show a sharp melting point but started to become cloudy at 130–140° and to decompose slowly with IF$_5$ evolution. A sample of RbF (27%) and RbIF$_6$ (73%) started to become cloudy at ~170° with attack of the glass container. The dta curve for the RbF–RbIF$_6$–RbF·3IF$_5$ sample showed the onset of an endotherm at 137° which reached its maximum at 162°. The RbF–RbIF$_6$ sample showed only a large exotherm starting at 249° which is ascribed to attack on the aluminum container. A sample of KIF$_6$ containing ~5 mol % KF when heated in a sealed glass tube started to give off some IF$_5$ at ~130°. Its dta curve showed the onset of a large endotherm at ~180° followed by a second endotherm centered at about 240°. Sodium fluoride did not form any adduct with IF$_5$ under reaction conditions similar to those used for the remaining alkali metal fluoride adducts.

The fact that CsF and RbF form well-defined 1:3 adducts with IF$_5$ and are not just CsIF$_6$ or RbIF$_6$ containing varying amounts of loosely attached IF$_5$ is supported by the following arguments. A well-defined, stable 1:3 adduct was isolated for CsF. This CsF·3IF$_5$ adduct shows a distinct vibrational spectrum and X-ray powder diffraction pattern (see below). The partially pyrolyzed RbF·3IF$_5$ adduct of the empirical composition RbF·1.73IF$_5$ showed only the bands characteristic of the 1:1 and the 1:3 adducts.

Nitrosyl fluoride does not form a solid 1:3 adduct with IF$_5$. However, it forms a solid 1:1 adduct which has a dissociation pressure of about 30 mm at 21°. This is in contrast to previous reports by Seel and coworkers,[8,9] who reported FNO·IF$_5$ to be a liquid com-

[8] F. Seel and N. Massat, *Z. Anorg. Allg. Chem.*, 280, 186 (1955).

[9] F. Seel and W. Birnkraut, *Angew. Chem.*, 73, 531 (1961).

plex. No adduct formation was observed between BrF_5 and FNO at temperatures as low as −64°.

X-Ray Powder Data.—Table I lists calculated and observed X-ray powder diffraction data for KIF_6, $RbIF_6$, and $CsIF_6$ indexed in the hexagonal system. From these data the following unit cell dimensions were calculated: KIF_6, a = 15 [illegible] = 11.00 Å; $RbIF_6$, a = 15.97, c = 11.61 Å; [illegible]$_6$, a = 16.52, c = 11.89 Å. Density measurements resulted in the following densities: KIF_6, d^{24} = 3.55 g cm^{-3}; $CsIF_6$, d^{24} = 4.05 g cm^{-3}. These density values indicate 18 "molecules" of $MeIF_6$ per unit cell (KIF_6, d_{calcd} = 3.55 g cm^{-3}; $CsIF_6$, d_{calcd} = 3.98 g cm^{-3}). Bougon, Charpin, and Soriano recently reported[10] rhombohedral unit cells for the related adducts, $KBrF_6$, $RbBrF_6$, and $CsBrF_6$. Since these rhombohedral unit cells can be referred to hexagonal ones,[10] the possibility of indexing the $MeIF_6$ patterns in the rhombohedral system was examined. However, some of the observed reflections do not belong to one of the following two categories: $-h + k + l = 3n$ and $h - k + l = 3n$. Hence, the possibility of rhombohedral unit cells must be ruled out for the IF_6^- salts. The fact that the $MeIF_6$ unit cells contain 6 times as many molecules as the $MeBrF_6$ ones agrees well with the lower symmetry suggested for IF_6^- on the basis of the observed vibrational spectra.[1-4,10,11] The powder pattern of $CsF\cdot3IF_5$ was distinct from that of $CsIF_6$ but could not be indexed. The density of $CsF\cdot3IF_5$ was measured and found to be d^{24} = 3.42 g cm^{-3}.

Vibrational Spectra.—Figure 1 shows the infrared spectra of KIF_6, $RbIF_6$, $CsIF_6$, $CsF\cdot3IF_5$, and $RbF\cdot1.7IF_5$. Figures 2 and 3 show the corresponding Raman spectra. The observed frequencies are listed in Table II. As can be seen, the spectra of the 1:1 and 1:3 adducts show a marked difference. Furthermore, the spectrum of partially pyrolyzed $RbF\cdot3IF_5$ shows only bands due to $RbIF_6$ and $RbF\cdot3IF_5$. This is evidence for the nonexistence of a distinct 1:2 adduct as an intermediate decomposition product.

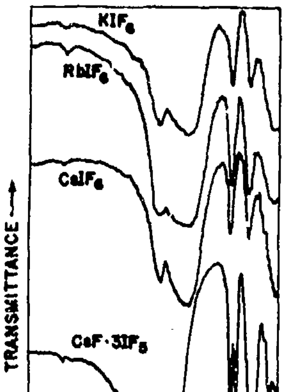

Figure 1.—Infrared spectra of the IF_6 adducts as dry powders in AgBr disks.

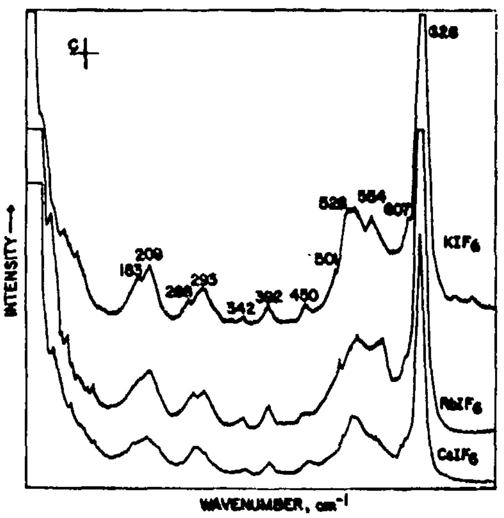

Figure 2.—Raman spectra of KIF_6, $RbIF_6$, and $CsIF_6$. C indicates spectral slit width.

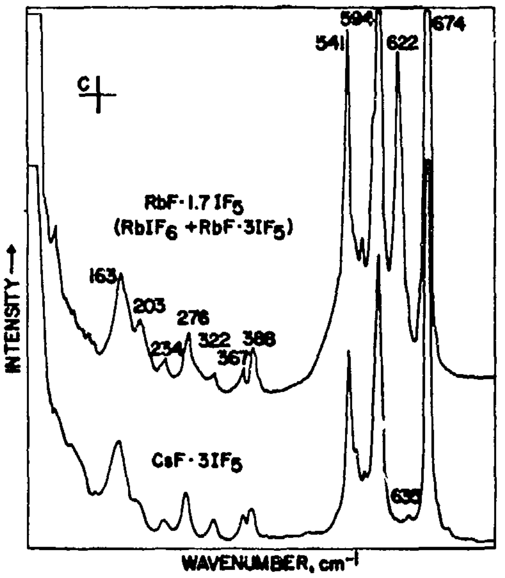

Figure 3.—Raman spectra of $CsF\cdot3IF_5$ and $RbF\cdot1.73IF_5$.

The large number of bands observed for $MeIF_6$ (at least 12 or 13) rules out symmetries higher than C_{3v} for IF_6^-. Distinction between eclipsed or staggered models (differing by one infrared-active stretching mode[4]) cannot be made due to the unresolved band shape of the 520-cm^{-1} infrared band. In addition, the large number of "molecules" (18) per unit cell can be expected to cause the spectra to deviate somewhat from that of the free ion. Hence, conclusions based on such subtle spectral differences would be purely speculative.

Similarly, it is difficult to interpret the vibrational spectrum of $CsF\cdot3IF_5$. The spectrum is not a simple composite of those of $CsIF_6$ and free IF_5 as one might expect for an ideal molecular adduct. An example of such an ideal molecular adduct of IF_5 was found[12] by Sladky and Bartlett for $XeF_2\cdot IF_5$. However, some of the bands of $CsF\cdot3IF_5$ have frequencies somewhat sim-

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[10] R. Bougon, P. Charpin, and J. Soriano, *C. R. Acad. Sci., Ser. C*, **272**, 565 (1971).

[11] J. Shamir and I. Yaroslavsky, *Isr. J. Chem.*, **7**, 495 (1969).

[12] F. O. Sladky and N. Bartlett, *J. Chem. Soc. A*, 2188 (1969).

TABLE II
VIBRATIONAL SPECTRA OF KIF_6, $RbIF_6$, $CsIF_6$, $CsF \cdot 3IF_5$, AND $RbF \cdot 1.7KF_6$
[OBSERVED FREQUENCY (cm^{-1}), INTENSITY]

KIF₆		RbIF₆		CsIF₆		CsF·3IF₅		RbF·1.7KF₆	
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman
						677 s	674 (10)	677 s	674 (10)
						635 sh	635 (0+)		
625 sh	628 (10)	620 sh	622 (10)	620 sh	620 (10)				622 (3)
609 s	607 sh	599 s	598 sh	599 s	599 sh			610 vs	
							593 (5.3)		594 (5)
						584 vs	585 sh	584 ms	585 sh
						569	568 (0+)		565 (0.4)
	554 (2)		562 (2)		554 sh	552	557 (0+)	550 s	557 sh
570–500		570–500		570–500		545 sh	543 (3.0)		541 (3)
vs, b	528 (2.4)	vs, b	528 (2)	vs, b	527 (2)				530 sh
	501 (0+)		501 (0+)		502 sh				
	450 (0.3)		447 (0+)		451 (0.3)				
393 ms	392 (0.6)	391 ms	391 (0.5)	390 ms	391 (0.5)			391 s	388 (0.5)
						385 m	382 (0.5)		
						369 m	367 (0.3)	370 mw	367 (0.2)
	342 (0+)		348 (0+)		347 (0+)				
341 ms		337 ms		335 ms				335 sh	
						320 s	319 (0.4)	318 s	322 (0.1)
290 w	293 (1.0)	288 sh	292 (0.7)					285 sh	292 sh
268 ms	268 sh	260 ms	270 sh	260 ms	275 (0.8)	271 m	271 (0.9)	260 s	276 (0.5)
							231 (0.2)		234 (0.2)
	209 (1.5)		208 (1.1)		199 (1.1)				203 (0.6)
	183 sh						186 (0.2)		186 (0.6)
							157 (1.5)		163 (1)

ilar to those[13,14] of IF_5. Hence, the possibility of a nonideal molecular adduct cannot be ruled out. The increased deviation of the spectrum from that of free IF_5 might be explained by the ionic lattice (Cs^+ and IF_6^- ions) polarizing the soft IF_5 molecule and thereby distorting it. We have observed that single crystals of $CsF \cdot 3IF_5$ can be obtained from IF_5 solutions, and, therefore, the exact structure of this interesting adduct could be studied by X-ray diffraction.

Comparison of the results of this study with those reported earlier[1-4] resolves the previously unexplainable discrepancies. The two sets of Raman data reported[2] by Christe were due to the 1:1 and 1:3 adducts, respectively. The data reported[2] by the Argonne group were due to the 1:3 adduct, whereas the Glasgow group worked with a 1:1 adduct showing several additional unexplainable bands. Klamm, *et al.*, reported[3] the best set of data for KIF_6 and $CsIF_6$. They are in good agreement with those found in the present study for the 1:1 adducts. The fact that a number of experienced investigators mistook the 1:3 adducts for 1:1 adducts demonstrates that quantitative syntheses and elemental analyses may in some rare instances be insufficient for characterizing new adducts. For the MeF + IF_5 reaction, incomplete conversion of MeF to $MeF \cdot 3IF_5$ resulted in material balances and elemental analyses closely corresponding to those expected for pure $MeIF_6$.

The BrF_6^- and IF_6^- anions present a very interesting structural problem. Vibrational spectra indicate that IF_6^- is of low symmetry, whereas BrF_6^- appears to be of higher symmetry and possibly to have a symmetry center.[10] This dissimilarity might be due to the different size of the central atom resulting for BrF_6^- in a maximum coordination number of 6 and, consequently, a sterically inactive free electron pair. For the larger iodine atom, the maximum coordination number is 7 and the free electron pair should become sterically active. Hence, a determination of the exact structure of both ions, which are isoelectronic with XeF_6, is very desirable. Since the size of the central atom in XeF_6 should be intermediate between those of Br and I in BrF_6^- and IF_6^-, respectively, one might expect the structure of XeF_6 to contain contributions from both the BrF_6^- and IF_6^- structures, possibly giving rise to a dynamic pseudo Jahn–Teller effect.[15,16] Consequently, the existence of a stable 1:1 adduct between FNO and IF_5 was examined. In the case of a stable adduct, single crystals could be grown by sublimation and studied by X-ray diffraction techniques. However, the appreciable dissociation pressure of $FNO \cdot IF_5$ and the relatively low volatility of IF_5 prevented the successful growth of suitable single crystals. In this context, the possibility of synthesizing $NO^+BrF_6^-$ was also examined.

The vibrational spectrum of IF_4^-, recently reported[11] by Shamir and Yaroslavsky, strongly resembles those of the IF_6^- salts. The following facts cast some doubt on the conclusions reached by Shamir and Yaroslavsky for IF_4^-: (i) their IF_4^- salt was prepared from CsI and IF_5 which under slightly different reaction conditions yield $CsIF_6$;[17] (ii) CsCl + IF_5 yield $CsIF_6$; (iii) the spectrum resembles that of IF_6^-; (iv) a C_{2v} structure is completely unexpected for IF_4^-.

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[13] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

[14] H. Selig and H. Holzman, *Isr. J. Chem.*, **7**, 417 (1969).

[15] L. S. Bartell, *J. Chem. Phys.*, **46**, 4530 (1967).

[16] R. D. Burbank and N. Bartlett, *Chem. Commun.*, 645 (1968).

[17] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 2373 (1960).

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Vibrational Spectra and Force Constants of the Square-Pyramidal Anions SF_5^-, SeF_5^-, and TeF_5^-

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The adducts of CsF with SeF_4 and SF_4 have been prepared and characterized by vibrational spectroscopy. The observed spectra closely resemble those of BrF_5 and ClF_5, respectively, indicating ionic structures with square-pyramidal anions of symmetry C_{4v}. Force constants have been computed for the series SF_5^-, SeF_5^-, and TeF_5^- and are compared to those of the isoelectronic ClF_5, BrF_5, and IF_5 molecules, respectively.

Introduction

The chalcogen tetrafluorides SF_4, SeF_4, and TeF_4 are known to be amphoteric and to form adducts with Lewis acids and bases. Whereas numerous papers dealing with the vibrational spectra and structure of their Lewis acid adducts have been published,[1-6] of their Lewis base adducts only the complexes of TeF_4 have been studied[7-9] in detail. These TeF_4·(Lewis base) adducts were shown[7-9] to contain a TeF_5^- anion of symmetry C_{4v}. The existence of 1:1 adducts between SeF_4 and alkali metal fluorides was reported[10] in 1952 by Aynsley, Peacock, and Robinson. However, their adducts were only characterized by elemental analyses. Whereas Bartlett and Robinson[4] and Tunder and Siegel[11] reported that alkali metal fluorides, such as CsF, do not form adducts with SF_4, Tullock, Coffman, and Muetterties[12] successfully prepared a stable CsF·SF_4 adduct. Furthermore, Tunder and Siegel obtained[11] evidence for a $(CH_3)_4NF \cdot SF_4$ adduct of marginal stability at ambient temperature. No further information has been published on either the SF_4 or SeF_4 adducts.[12a] In this paper, we wish to report the vibrational spectra of the SeF_5^- and SF_5^- anions and their force constants. Since the vibrational spectra of the series of square-pyramidal molecules ClF_5, BrF_5, and IF_5 are known,[13-15] it appeared particularly interesting to compare them with those of the isoelectronic series SF_5^-, SeF_5^-, and TeF_5^-.

Experimental Section

Materials and Apparatus.—Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Selenium tetrafluoride was prepared by the method[16] of Pitts and Jache from selenium powder and ClF and was purified by fractional condensation. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation. The low-temperature infrared spectra of dry powders were obtained by attaching the AgCl windows to a coolable copper block of a conventional, low-temperature Pyrex cell.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ~25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or melting point capillaries were used as sample containers. For the conical tubes, the axial viewing–transverse excitation technique and, for the capillaries, the transverse viewing–transverse excitation technique were used.

Preparation of the Adducts. $Cs^+SF_5^-$.—A 30-ml prepassivated stainless steel cylinder was loaded with powdered CsF (36.2 mmol) and SF_4 (46.9 mmol). The adduct was formed by shaking the cylinder at room temperature for several days, followed by heating to 125° for several more days. On cooling to room temperature, the unreacted SF_4 was removed by pumping. The white solid product that remained in the cylinder was a single fused mass which was chipped from the cylinder. The weight of the solid (7.41 g) indicated that approximately half the CsF charged (5.50 g) had been converted to the adduct. This was confirmed by pyrolyzing *in vacuo* a portion of the adduct at 150° and trapping the evolved gas at −196°. From 0.82 g of the adduct, 1.88 mmol of pure SF_4 was obtained, indicating a mixture of 48 mol % $Cs^+SF_5^-$ and 52 mol % CsF.

$Cs^+SeF_5^-$.—Powdered CsF (13.1 mmol) was loaded into a prepassivated 30-ml stainless steel cylinder followed by SeF_4 (8.04 mmol). The cylinder was allowed to stand at room temperature overnight. Pumping on the cylinder revealed that all the SeF_4 had reacted since no volatile product was recovered. The weight

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(12a) NOTE ADDED IN PROOF.—After submission of this paper for publication, L. F. Drullinger and J. E. Griffiths [*Spectrochim. Acta, Part A*, **27**, 1793 (1971)] reported the vibrational spectrum of the SF_5^- anion. Their spectrum, assignment, and conclusions concerning the structure of SF_5^- agree with those of this study except for the assignment of $\nu_9(E)$. In related molecules and ions this mode is of appreciable intensity and we did not observe the weak infrared band at 288 cm^{-1} assigned by Drullinger and Griffiths to ν_9. Consequently, we prefer to assume a double coincidence between ν_5 and ν_9 as in the case of isoelectronic ClF_5.

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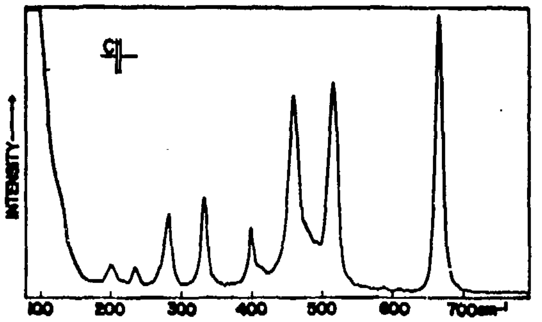


Figure 1.—Raman spectrum of solid $Cs^+SeF_5^-$. The sample container was a glass capillary. C indicates spectral slit width

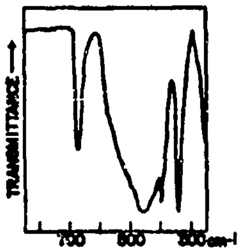


Figure 2.—Infrared spectrum of solid $Cs^+SeF_5^-$. recorded as a dry powder between AgBr plates at −196°.

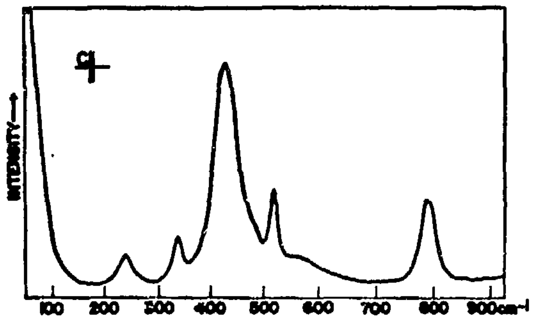


Figure 3.—Raman spectrum of solid $Cs^+SF_5^-$. The sample container was a glass capillary.

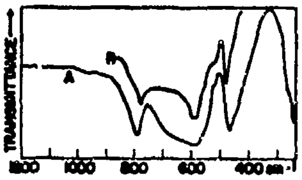


Figure 4.—Infrared spectrum of solid $Cs^+SF_5^-$, recorded as an AgBr disk at ambient temperature (trace A) and a dry powder between AgBr plates at −196° (trace B).

of the white solid adduct (3.25 g) obtained was in agreement with this observation. Therefore, the product was a mixture of 61 mol % $Cs^+SeF_5^-$ and 39 mol % CsF.

Results and Discussion

Synthesis and Properties.—The reaction conditions used for the synthesis of $Cs^+SeF_5^-$ were similar to those[10] used by Aynsley, Peacock, and Robinson. Since the presence of some unreacted CsF was not expected to interfere with the spectroscopic investigation, no attempt was made to achieve complete conversion of CsF to $CsSeF_5$. Our product appeared to be completely stable *in vacuo* at ambient temperature contrary to the claim of Aynsley, *et al.*, who reported[10] slight decomposition under similar conditions.

TABLE I

VIBRATIONAL SPECTRA OF $Cs^+SF_5^-$, $Cs^+SeF_5^-$, AND $Cs^+TeF_5^-$ AND THEIR ASSIGNMENTS COMPARED TO THOSE OF ISOELECTRONIC ClF_5, BrF_5, AND IF_5

Obsd freq, cm⁻¹, and rel intens												Assignment in point group C_{4v}		Approx description of vib
$Cs^+SF_5^-$		$Cs^+SeF_5^-$		$Cs^+TeF_5^-$ [a]		ClF_5 [b,c]		BrF_5 [b]		IF_5 [b]				
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman			
793 s	796 (3.7)	665 vs	666 (10)	618 ms	611 vs	708 m	709 (3)	383 s	682 (7)	710 s	710 s, p	A_1	ν_1	$\nu(XF')$
520 w, sh	522 (2.7)	520 sh	515 (7.5)	[466 vs, br]	504 s	539 w	538 (1)	587 m	570 (10)	(595)[e]	616 vs, p		ν_2	$\nu_s(XF_4)$ in phase
466 s	469 sh	335 s	332 (3.2)	283 m	282 mw	495 mw	[480 (10)]	369 s	365 (2)	318 m	318 m, p		ν_3	$\delta_s(XF_4)$ umbrella
...	[435 (10)][d]	...	460 (7.0)	...	[472 s]	...	[480 (10)]	...	535 (10)	...	604 m	B_1	ν_4	$\nu_s(XF_4)$ out of phase
...	269 sh	...	236 (0.6)	...	...	...	...	...	...	...	...		ν_5	$\delta_{as}(XF_4)$ out of plane
...	342 (1.6)	...	282 (2.6)	...	231 mw	...	375 (1)	...	312 (1)	...	276 w	B_2	ν_6	$\delta_s(XF_4)$ in plane
590 vs, br	592 sh	475 vs, br	480 sh	[466 vs, br]	[472 s]	725 vs	...	644 vs	...	640 vs	631	E	ν_7	$\nu_{as}(XF_4)$
430 sh	[435 (10)[d]	398 mw	399 (1.9)	336 m	338 mw	484 m	[480 (10)]	415 m	414 (1)	372 m	372 w		ν_8	$\delta(F'XF_4)$
...	241 (1.2)	...	202 (0.7)	164 mw	...	299 mw	296 (0.4)	...	237 (0+)	...	200 vw		ν_9	$\delta_{as}(XF_4)$ in plane

[a] Data from ref 7. [b] Data from ref 13, 14. [c] Data from ref 15. [d] Frequencies in brackets indicate coincidences with other modes, thus resulting in increased relative intensities. [e] Frequency estimated from combination bands.

The CsF·SF$_4$ adduct was prepared by the method[12] of Tullock, *et al.*, confirming the existence of a stable complex. Again, no attempt was made to achieve complete conversion of CsF to Cs$^+$SF$_5^-$.

Vibrational Spectra.—Figures 1 and 2 show the Raman and infrared spectra, respectively, of the solid CsF·SeF$_4$ adduct. Figures 3 and 4 show the corresponding spectra of solid CsF·SF$_4$. The observed frequencies are listed in Table I. The Raman spectra are of better quality than the infrared spectra as is generally the case for this type of compound. Consequently, assignments will be based mainly on the Raman spectra. The absorption between 300 and 240 cm^{-1} in the infrared spectra is mainly due to the AgBr window material.

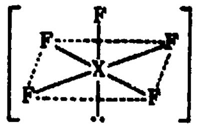
Since the chalcogen tetrafluoride–Lewis acid adducts[1-6] and CsF·TeF$_4$[7-9] were shown to be ionic, the same might be expected for the CsF adducts of SF$_4$ and SeF$_4$. In the pentafluorochalcogenate(IV) anions, the central atoms possess a free electron pair which should be sterically active. Hence, these anions should have a square-pyramidal structure of symmetry C_{4v} similar to that of the isoelectronic halogen pentafluoride series.[13]

For a pentafluorochalcogenate(IV) anion, XF$_5^-$, of symmetry C_{4v}, nine fundamental vibrations should be observed. These are classified as $3\ A_1 + 2\ B_1 + B_2 + 3\ E$. All nine modes should be Raman active whereas only the A$_1$ and E modes should be infrared active. Table I lists the vibrational frequencies of the two isoelectronic series SF$_5^-$, SeF$_5^-$, TeF$_5^-$ and ClF$_5$, BrF$_5$, IF$_5$. As can be seen from Table I, the vibrational frequencies of the two series are very similar. In particular, the Raman spectra of SF$_5^-$ and SeF$_5^-$ strongly resemble those of ClF$_5$ and BrF$_5$, respectively,[13] considering the expected frequency decreases when going from the neutral molecules to the anions. Since the assignments for the halogen pentafluorides are well established,[13-16] the spectra of SF$_5^-$ and SeF$_5^-$ can be assigned (see Table I) by complete analogy. For TeF$_5^-$, the previously reported[7] assignments have been slightly revised to fit the overall intensity and frequency patterns. Greenwood, *et al.*, assigned[7] the symmetric out-of-phase stretching vibration ν_4 to a weak Raman band at 572 cm^{-1} and the antisymmetric stretching vibration ν_7 to a strong Raman band at 472 cm^{-1}. This assignment results in ν_4 having a higher frequency than ν_2 which was not observed for any other member in this series. It appears more satisfactory to assign the strong Raman line at 472 cm^{-1} to ν_4 and to assume that the low-intensity Raman counterpart of the intense infrared band at 466 cm^{-1} is hidden under the 472-cm^{-1} band.

Comparison of the vibrational spectra of the XF$_5^-$ series with those of the isoelectronic XF$_5$ molecules[13-16] reveals several interesting features. The Raman spectra of the corresponding members of each series are very similar. The frequency trends within each series are consistent. Thus, the stretching modes ν_2 and ν_4, involving very little motion of the central atom, show frequency values reflecting the expected change in bond strength, whereas the stretching modes ν_1 and ν_7, involving a motion of the central atom, exhibit an additional mass effect. The deformational modes show, as expected, a pronounced frequency increase with decreasing size of the central atom.

An unexpected, but explicable, feature in the spectra of SeF$_5^-$ and TeF$_5^-$ is the unusual occurrence of the antisymmetric XF$_4$ stretching mode, $\nu_7(E)$, at a frequency lower than that of the totally symmetric XF$_4$ stretching mode, $\nu_2(A_1)$. In SF$_5^-$ the frequency value of ν_7 is only 68 cm^{-1} higher than that of ν_2. Since the mass of the central atom increases from SF$_5^-$ toward TeF$_5^-$ and since only the frequency of ν_7 is mass dependent, for SeF$_5^-$ and TeF$_5^-$ this frequency becomes lower than that of ν_2. A similar unusual occurrence of the symmetric out-of-phase stretching mode, $\nu_2(E_g)$, at a frequency higher than that of the totally symmetric $\nu_1(A_{1g})$ mode was recently established for the octahedral IF$_6^+$ ion.[17] These two cases demonstrate the possibilities for incorrect assignments[7,18] when ignoring relative intensities of bands and frequency trends in related molecules.

In summary, the vibrational spectra of SF$_5^-$, SeF$_5^-$, and TeF$_5^-$ show that these anions are isostructural with ClF$_5$, BrF$_5$, and IF$_5$. Consequently, the following square-pyramidal structure of symmetry C_{4v} can be assigned to these anions



Force Constants.—Force constants were computed for the three isoelectronic pairs SF$_5^-$–ClF$_5$, SeF$_5^-$–BrF$_5$, and TeF$_5^-$–IF$_5$. The required potential and kinetic energy metrics were computed with a machine method[19] adopting the geometries given in Table II.

TABLE II

ASSUMED MOLECULAR PARAMETERS FOR SQUARE-PYRAMIDAL PENTAFLUORIDE IONS AND MOLECULES

	SF$_5^-$ [a]	ClF$_5$ [b]	SeF$_5^-$ [a]	BrF$_5$ [c]	TeF$_5^-$ [d]	IF$_5$ [e]
R, Å	1.62	1.62	1.68	1.68	1.86	1.83
r, Å	1.72	1.72	1.78	1.78	1.95	1.87
β, deg	90	90	84.5	84.5	79.0	82

[a] Assumed values. [b] Values assumed in ref 13. [c] R. D. Burbank and F. N. Bensey, Jr., *J. Chem. Phys.*, 27, 982 (1957). [d] Reference 9. [e] Unpublished electron diffraction data by T. G. Hewitt, A. G. Robiette, and G. M. Sheldrick referred to by S. J. Cyvin, J. Brunvoll, and A. G. Robiette, *J. Mol. Struct.*, 3, 259 (1969).

The force constant definitions used are those of Begun, Smith, and Fletcher,[13] except that the deformation coordinates are weighted by unit (1 Å) distance. The force constants were adjusted by trial and error, assuming the simplest possible modified valence force field, to give an exact fit between the observed and computed frequencies. Since an excellent transferability of interaction force constants was noted for the pairs SeF$_5^-$–BrF$_5$ and TeF$_5^-$–IF$_5$, the interaction constants were assumed precisely equal and all force constants were adjusted for a best fit by the reparameterization method.[19] The results are given in Table III. For the pair SF$_5^-$–ClF$_5$, the transferability was not quite so good. Hence, Table III gives different interaction constants for this pair. The similarity of the interaction constants reported for these molecules is remarkable.

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TABLE III

FORCE CONSTANTS[a] FOR SOME XF_5 MOIETIES COMPUTED FOR BrF_5–SeF_5^- AND IF_5–TeF_5^- FORCING TRANSFERABILITY OF INTERACTION TERMS AND FOR ClF_5 AND SF_5^- BY REQUIRING A PERFECT FIT

	ClF_5	SF_5^- [b]	BrF_5	SeF_5^-	IF_5	TeF_5^-
f_R	3.47	4.12	4.03	3.82	4.82	3.56
f_r	2.67	2.06	3.24	2.41	3.82	2.27
f_β	2.86	2.26	2.23	1.95	2.10	1.86
f_α	1.14	0.86	0.82	0.63	0.72	0.54
$f_{rr'}$	0.24	0.52	0.27		0.36	
$f_{\beta\beta'}$	0.75	0.55	0.32		0.43	
$f_{\alpha\alpha'}$	0.01	0.11	0.04		0.04	
f_{rr}	0.16	0.23	0.15		0.06	
$f_{R\beta}$	0.4	0.25				
$f_{r\beta}$	0.15	0.15				
$f_{r\beta''}$	−0.15	−0.15				
f_r/f_R	0.77	0.50	0.82	0.63	0.79	0.64

[a] Stretching constants in mdyn/Å, deformation constants in mdyn/Å radian^2, and stretch–bend interaction constants in mdyn/Å radian. [b] For SF_5^-, $f_{\alpha\beta}$ was also computed and has a value of 0.20 mdyn/Å radian^2.

The values reported for $f_{R\beta}$, $f_{r\beta}$, and $f_{r\beta''}$ for the pair ClF_5–SF_5^- can be accounted for by orbital-following arguments. Numerical experiments indicated no need to assume other interaction constants and convincingly showed that the observed frequencies could not be fitted unless values were accepted near those shown.

Comparison of the general trends within XF_5 and XF_5^- series shows a remarkable difference. Whereas the deformation force constants in each series have comparable values and follow the same trends, the valence force constants f_R and f_r show reverse trends. Thus, for the XF_5 group, the lightest member, ClF_5, shows the lowest stretching force constant values, but for XF_5^- the heaviest member, TeF_5^-, exhibits the lowest f_R value. However, a closer inspection of the trends of the valence force constants of fluorides throughout the periodic system[20] reveals a general reversal of the direction of that trend either within or close to the sixth main group. Furthermore, increasing stretching force constant values from chlorine to the corresponding bromine fluorides were also found for the ClF_3 and BrF_3 molecules[21] and the ClF_4^- and BrF_4^- anions.[22,23]

The usefulness of stretching force constants for the distinction between mainly covalent and semiionic three-center four-electron (3c-4e) bonds has previously been demonstrated for numerous halogen fluorides.[23,24] The square-pyramidal pentafluorides of the present study contain two types (*i.e.*, axial and equatorial) of fluorine ligands and a comparison of their stretching force constants should permit some conclusions concerning the nature of their bonds. Since ionic bonds do not contribute to the stretching force constants, semiionic bonds ideally should exhibit values half as large as those of covalent bonds. As can be seen from Table III, the f_r/f_R ratios of the pentafluorochalcogenate anions range from 0.50 for SF_5^- to 0.64 for TeF_5^-. This indicates strong contributions from semiionic 3c-4e p–pσ bonds[25–28] to the bonding of the four equatorial fluorine ligands and mainly covalent character for the single axial fluorine bond. This finding agrees with a model involving an sp hybrid of the central atom for the sterically active, free-electron pair and the single, axial fluorine atom while two p electrons of the central atom form two semiionic 3c-4e bond pairs with the remaining four equatorial fluorine atoms.

Acknowledgment.—We are indebted to Dr. I. Silvera of the Science Center of NAR for the use of the Raman spectrometer. This work was supported by the Office of Naval Research, Power Branch, and by the Air Force Office of Scientific Research under Contract AF49(638)-1734.

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Contribution from Rocketdyne, a Division of North American Rockwell Corporation, Canoga Park, California 91304, and the Lehrstuhl fuer Anorganische Chemie, Universitat, Dortmund, Germany

The Tetrafluoroiodate(III) Anion, IF_4^-

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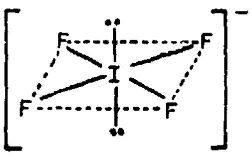
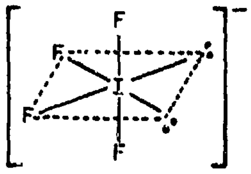
The salts $CsIF_4$ and Cs_3IF_6 were prepared and characterized by infrared and Raman spectroscopy. The vibrational spectra observed for IF_4^- are consistent with a square-planar structure of symmetry D_{4h}. The Raman spectrum previously reported for IF_4^- and interpreted in terms of a nonplanar structure of symmetry C_{2v} can be attributed to IF_6^-. Force constants were computed for IF_4^- and are compared to those of BrF_4^-, ClF_4^-, and XeF_4.

Introduction

The existence of salts containing the IF_4^- anion was first reported[1] in 1960 by Hargreaves and Peacock. When studying the reaction between CsI and IF_5, they obtained depending upon the reaction conditions different products. At elevated temperature the solid product was reported[1] to be $CsIF_6$ whereas at ambient temperature it was believed to be $CsIF_4$. In 1961, Asprey, Margrave, and Silverthorn reported[2] the syntheses of IF_4^- salts by direct fluorination of iodides. In 1969, Shamir and Yaroslavsky published[3] the Raman spectrum of "$CsIF_4$" prepared by the method[1] of Hargreaves. They observed nine bands and concluded[3] that IF_4^- is not square planar (I) but possesses structure II. These results were quite unexpected since the related ClF_4^- and BrF_4^- anions and the isoelectronic XeF_4 molecule are all square planar.[4-7] Recently, Christe pointed out[8] that the Raman spectrum, attributed[3] by Shamir and Yaroslawsky to IF_4^-, closely resembles that of IF_6^-. Hence, it appeared interesting to study the vibrational spectrum of a sample of $CsIF_4$ which had been prepared from IF_3 and CsF by the method[9] of Schmeisser, *et al.*


D_{4h}, I


C_{2v}, II

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*Address correspondence to this author at Rocketdyne.

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Table I. Vibrational Spectrum of $CsIF_4$ and Its Assignment Compared to Those of Isoelectronic XeF_4, BrF_4^-, and ClF_4^- and Those of the Approximately Square-Planar Part of IF_5

Obsd freq, cm^{-1} (intens^a)											
$CsIF_4$		$CsBrF_4$^{b}		$CsClF_4$^{c}		XeF_4^{d}		IF_5^{e}		Assignment in point group D_{4h}	Approx description of vibration
Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman		
	522 (10)		523 (10)		505 (10)		543 (10)		616 vs	ν_1 (A_{1g})	$\nu_s(XF_4)$ in phase
271 ms		317 s		425 s		291 ms		318 m	318 m	ν_2 (A_{2u})	$\delta_s(XF_4)$ out of plane
	195 (0+)		246 (0.7)		288 (1)		235 (0+)		276 w	ν_3 (B_{1g})	$\delta_s(XF_4)$ in plane
	455 (7.2)		449 (7.9)		417 (9)		502 (8.2)		604 m	ν_4 (B_{2g})	$\nu_s(XF_4)$ out of phase
448 vs		478 vs		590 vs		586 vs		640 vs		ν_6 (E_u)	$\nu_{as}(XF_4)$
			[183]^f						200 vw	ν_7 (E_u)	$\delta_{as}(XF_4)$ in plane

^{a} Uncorrected Raman intensities. ^{b} Reference 6. ^{c} Reference 4. ^{d} Reference 11. ^{e} References 12, 13. ^{f} Frequency taken from the $NO^+BrF_4^-$ spectrum.

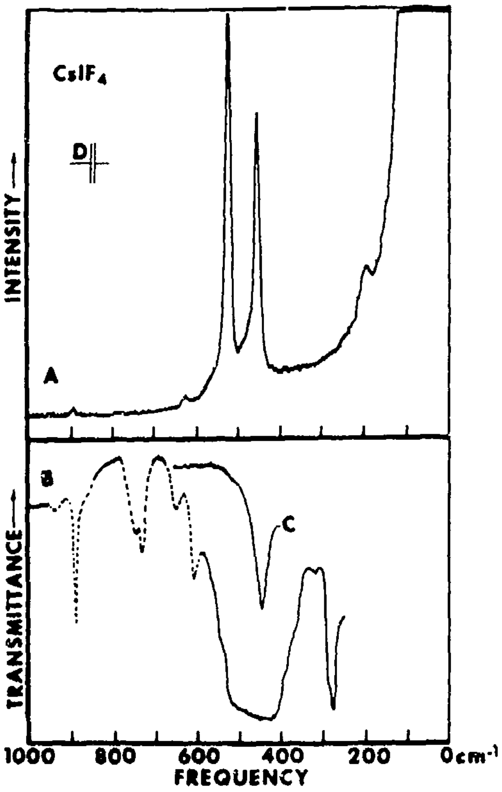

Figure 1. Vibrational spectrum of $CsIF_4$. Traces A, B, and C represent the Raman spectrum of the solid, the infrared spectrum of the solid, and the infrared spectrum of a CH_3CN solution, respectively. D indicates the spectral slit width.

Experimental Section

The preparation and characterization of $CsIF_4$ and Cs_3IF_6 has previously been described.[9,10] Owing to their hygroscopic nature the compounds were handled outside of the vacuum line in the dry nitrogen atmosphere of a glove box.

Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. Spectra were obtained of dry powders as AgBr or AgCl pellets and of CH_3CN solutions in a Wilks minicell between AgCl plates. Raman spectra were recorded on a Cary 83 spectrophotometer using the 4880-A exciting line of an Ar ion laser. Glass melting point capillaries were used as sample containers in the transverse viewing-transverse excitation technique.

Debye-Scherrer powder patterns were taken using a Philips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in quartz capillaries of 0.5-mm o.d.

Results and Discussion

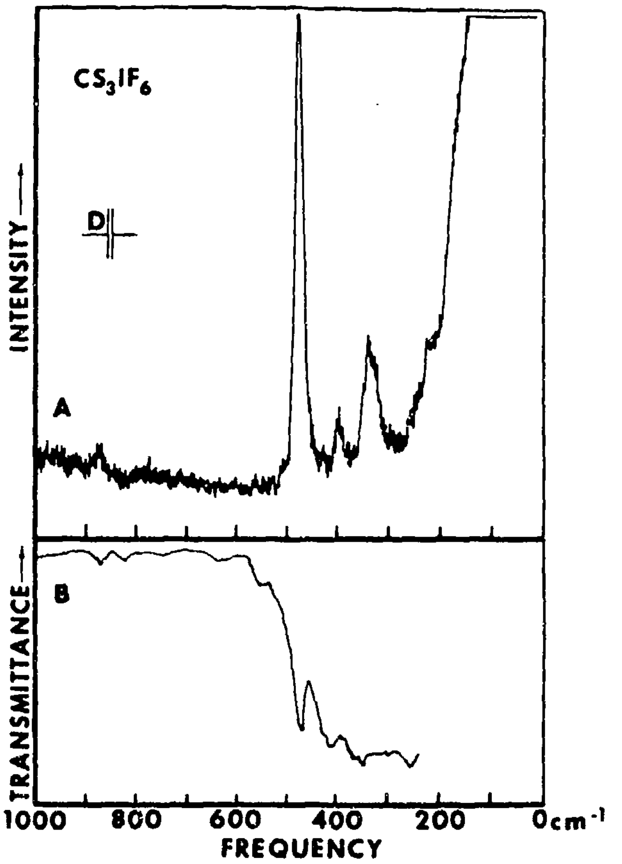

Figure 2. Raman (trace A) and infrared (trace B) spectra of solid Cs_3IF_6.

Vibrational Spectra. Figures 1 and 2 show the vibrational spectra of $CsIF_4$ and Cs_3IF_6. As can be seen, the spectra of $CsIF_4$ and Cs_3IF_6 are quite distinct. This indicates that for Cs_3IF_6 a formulation as $CsIF_4 \cdot 2CsF$ is unlikely. The observed frequencies are listed in Table I. The X-ray powder diffraction patterns of $CsIF_4$ and Cs_3IF_6 (Table II) also differ strongly from each other and from those of the $CsIF_6$ and the $CsF \cdot 3IF_5$ adducts[8] and consequently are very useful for distinguishing between the different adducts.

The vibrational spectrum observed in this study for $CsIF_4$ is very different from that[3] previously reported. It is simpler (only three Raman bands) and strongly resembles those of square-planar XeF_4,[11] BrF_4^-,[6] and ClF_4^-.[4] In addition to the three Raman bands two infrared bands were observed following the rule of mutual exclusion. These observations are entirely consistent with a centrosym-

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Table II. X-Ray Powder Data for $CsIF_4$ and Cs_3IF_6

$CsIF_4$				Cs_3IF_6			
d, A	Intens	*d*, A	Intens	*d*, A	Intens	*d*, A	Intens
4.41	vw	1.854	vw	3.48	ms	1.801	mw
4.16	w	1.814	w	3.41	m	1.776	vw
3.82	m	1.688	w	3.35	w	1.759	vw
3.75	vs	1.567	vw	3.27	vs	1.735	vw
3.66	vw	1.538	s	3.03	mw	1.710	m
3.57	m	1.509	ms	2.96	mw	1.653	w
3.41	m	1.478	vs	2.87	w	1.607	w
3.35	ms	1.455	w	2.65	w	1.555	mw
3.27	vw	1.432	w	2.60	ms	1.496	w
3.12	vw	1.399	mw	2.39	ms	1.460	w
3.05	mw	1.356	m	2.32	vw	1.416	m
2.91	w	1.294	ms	2.25	vw	1.370	w
2.56	vw	1.257	mw	2.20	vw	1.336	mw
2.51	vw	1.193	mw	2.106	mw	1.310	mw
2.38	ms	1.138	m	2.030	m	1.281	vw
2.27	s	1.127	vw	1.990	m	1.265	w
2.23	w	1.112	m	1.959	mw	1.223	w
2.207	w	1.079	m	1.892	w	1.153	w
2.088	w	1.067	m				
2.013	vs	1.009	m				
1.986	w	0.945	m				
1.947	vw	0.879	mw				
1.901	vw	0.867	mw				
1.881	s						

metric square-planar structure of symmetry D_{4h} (model I). They also indicate that the Raman spectrum previously assigned[3] to IF_4^- was not due to IF_4^- but to IF_6^-.[8]

Assignments for the IF_4^- anion in point group D_{4h} are given in Table I and were made based upon the following considerations. For IF_4^- of symmetry D_{4h}, the seven normal modes are classified as $A_{1g} + A_{2u} + B_{1g} + B_{2g} + B_{1u} + 2\,E_u$. Of these, only the A_{1g}, B_{1g}, and B_{2g} modes will be Raman active, whereas the A_{2u} and the two E_u modes will be infrared active. The B_{1u} mode is inactive in both the infrared and Raman spectra. Comparison with the modes belonging to the square-planar part of IF_5[12,13] (see Table I) shows that the E_u deformation vibration of IF_4^- should occur below 250 cm^{-1}, the lower limit of our spectrometer. The assignment of the observed bands to the individual modes (see Table I) was done in complete analogy with XeF_4[11], BrF_4^-,[6] and ClF_4^-[4] and, hence, needs no further discussion. Since the E_u stretching mode is very broad for all solid tetrafluorohalogenate(III) salts, we have also recorded the infrared spectra of $CsIF_4$ and $CsBrF_4$ in CH_3CN solution. For each salt a single sharp band centered at 448 and 478 cm^{-1}, respectively, was observed. This permits the accurate determination of the band centers and also eliminates the possibility[6] of symmetry D_{2h} for which the doubly degenerate E_u mode of D_{4h} should split into its components. Several less intense bands were observed for $CsIF_4$ above 600 cm^{-1}. These were of varying relative intensity and, hence, are attributed to impurities or hydrolysis products.

The vibrational spectrum of Cs_3IF_6 shows bands at about 480, 405, 345, 255, and 225 cm^{-1} in both the Raman and infrared spectra. Their number and activity rule out an octahedral structure for IF_6^{3-} as one might also expect from the fact that IF_6^- is not octahedral.[8] Unfortunately, the observed spectrum does not allow a reliable determination of the symmetry of IF_6^{3-}. However, the pronounced difference in the vibrational spectra of IF_4^- and IF_6^{3-} should be useful for distinguishing the two ions.

Table III. Symmetry and Internal Force Constants (mdyn/A) of ClF_4^-, BrF_4^-, IF_4^-, and XeF_4 Computed for Different Modified Valence Force Fields Using the Frequency Values of Table I

	ClF_4^-				BrF_4^-			IF_4^-						XeF_4		
Computing method	$F_{67} \equiv 0$		$F_{77} \equiv \min$		$F_{67} \equiv 0$	$F_{77} \equiv \min$	$F_{67} \equiv {}^1/_2\lvert F_{67}(\max) - F_{67}(\min)\rvert$	$F_{67} \equiv 0$		$F_{77} \equiv \min$		$F_{67} \equiv {}^1/_2\lvert F_{67}(\max) - F_{67}(\min)\rvert$		$F_{67} \equiv 0$	$F_{77} \equiv \min$	$F_{67} \equiv {}^1/_2\lvert F_{67}(\max) - F_{67}(\min)\rvert$
ν_7	150	250	150	250	183			100	200	100	200	100	200	200		
$F_{11} = f_r + 2f_{rr} + f_{rr'}$	2.853				3.060			3.052						3.302		
$F_{22} = f_\gamma$	0.630				0.577			0.514						0.597		
$F_{33} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'}$	0.232				0.169			0.106						0.155		
$F_{44} = f_r - 2f_{rr} + f_{rr'}$	1.946				2.258			2.319						2.822		
$F_{66} = f_r - f_{rr'}$	1.832	1.711	1.925	2.004	1.69	1.764	1.890	1.724	1.705	1.734	1.748	1.802	1.806	2.962	3.001	3.137
$F_{67} = \sqrt{2}(f_{r\alpha} - f_{r\alpha'})$	0	0	0.061	0.166	0	0.065	0.253	0	0	0.015	0.059	0.156	0.178	0	0.063	0.302
$F_{77} = f_\alpha - f_{\alpha\alpha'}$	0.085	0.253	0.083	0.231	0.145	0.142	0.164	0.046	0.184	0.046	0.182	0.057	0.192	0.183	0.193	0.231
f_r	2.116	2.055	2.162	2.202	2.18	2.212	2.274	2.205	2.196	2.210	2.217	2.244	2.246	3.012	3.032	3.099
f_{rr}	0.227				0.20			0.183						0.120		
$f_{rr'}$	0.284	0.344	0.237	0.198	0.48	0.448	0.385	0.481	0.491	0.476	0.469	0.442	0.440	0.050	0.031	−0.037
Probable values of																
f_r	2.13 ± 0.07				2.227 ± 0.047			2.221 ± 0.025						3.055 ± 0.044		
f_{rr}	0.23				0.20			0.183						0.120		
$f_{rr'}$	0.27 ± 0.07				0.433 ± 0.047			0.466 ± 0.025						0.007 ± 0.044		

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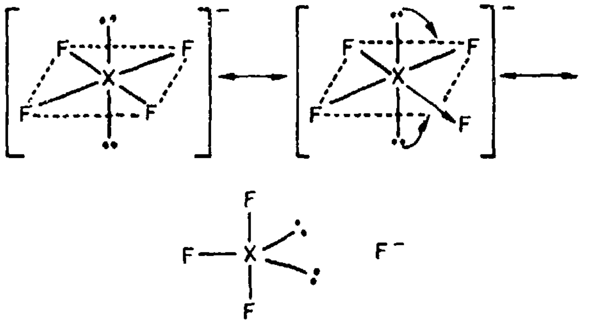
Force Constants. Table III shows the symmetry and some of the internal force constants of IF_4^-. For comparison the force constants obtained for XeF_4 and BrF_4^- and ClF_4^- are also listed. Except for the E_u block all the symmetry force constants are unique. The E_u block is underdetermined since only two frequency values are available for the determination of three force constants. It has recently been shown[14-16] that in similar underdetermined systems consisting of one stretching and one deformation mode, mathematical constraints such as minimizing or maximizing the value of one of the symmetry force constants can be used to narrow down the range of the possible solutions. In particular, one might expect[14,16] that in strongly coupled systems the values of the general valence force field (GVFF) will fall within the range given by $F_{67} = 0$ as the lower and by F_{77} = minimum as the upper limit. These ranges were computed for IF_4^-, BrF_4^-, ClF_4^-, and XeF_4 and are listed in Table III. It can be seen that for the very weakly coupled (heavy central atom) IF_4^- and XeF_4 the resulting valence force constant range becomes so narrow that it might not include any more the GVFF values. The condition $F_{67} = {}^1/_2\,|F_{67}(\max) - F_{67}(\min)|$ has been suggested[17] by Sawodny as a conservative empirical upper limit for weakly coupled systems and was used to determine the uncertainties in the valence force constants of BrF_4^-, IF_4^-, and XeF_4 listed in Table III. These relatively small uncertainties suggest that the given values are good approximations of the GVFF.

For most of the square-planar species of Table III, including IF_4^-, ν_7 has not been observed. Consequently, force fields were also computed assuming minimum and maximum values covering the most likely range for ν_7. The results shown in Table III demonstrate that the values of f_r, f_{rr}, and $f_{rr'}$ are very little influenced by changing the value of ν_7. Comparison of the uncertainty limits of IF_4^- with those of BrF_4^- and ClF_4^- show that these increase, as expected, with increasing coupling, *i.e.*, decreasing mass of the central atom.

Analysis of the results given in Table III allows the following conclusions. (i) The series ClF_4^-, BrF_4^-, IF_4^- shows the expected smooth trends. Whereas, the value of the stretching force constant, f_r, remains almost constant, the deformation force constants markedly decrease with increasing size of the central atom. (ii) The relatively low values of f_r in all three ions indicate strong ionic contributions to the halogen–fluorine bonds. The values are about half of those obtained for mainly covalent single bonds and may be interpreted in terms of semiionic three-center four-electron p-σ bonds.[4,6] (iii) The value of the stretch-stretch interaction constant, f_{rr}, decreases from ClF_4^- to IF_4^-. It reflects decreasing repulsion between the right angular fluorine ligands with increasing radius of the central atom. (iv) The surprisingly large positive values of the collinear F–X–F stretch–stretch interaction constant, $f_{rr'}$, can be explained by the following orbital-following model. Stretching of one X–F bond will tend to make the remaining XF_3 part to partially adopt the structure of the XF_3 molecule which is known to have one short equatorial and two long axial X–F bonds. Hence, the stretching of one X–F bond should cause a bond shortening of the collinear X–F bond as depicted by the mesomeric structures



The increase in the $f_{rr'}$ value from ClF_4^- to IF_4^- can be explained by the increasing ease with which the two free valence electron pairs of the central halogen atom can follow the stretching of the X–F bond. The fact that XeF_4 has a considerably smaller $f_{rr'}$ value than IF_4^- might be due to the lower polarity of the X–F bond in XeF_4 as is also indicated by its higher f_r value (3.02 mdyn/Å).

In summary, the observed vibrational spectrum and force constant analysis strongly support a square-planar structure of symmetry D_{4h} for IF_4^-. These results confirm the suggestion[8] that the previously reported[3] Raman spectrum was not due to IF_4^- but due to IF_6^-.

Registry No. $CsIF_4$, 36245-63-3; Cs_3IF_6, 28223-33-8.

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Contribution from Rocketdyne, a Division of North
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A Fluorine-19 Nuclear Magnetic Resonance Study of Chlorine Fluoride Cations

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Fluorine-19 nuclear magnetic resonance spectra are reported for HF solutions of ClF_6^+, ClF_4^+, ClF_2^+, $ClO_2F_2^+$, and ClF_2O^+ and for NF_2O^+ salts. Several exchange processes between the cations and anions and the solvent were observed, depending on the temperature and the acidity of the solvent. The acidity of the HF solvent was varied by the addition of AsF_5. It is shown that ClF_6^+ is octahedral and splitting owing to both ^{35}Cl-F and ^{37}Cl-F spin-spin coupling has been observed for the first time. The spectrum of ClF_4^+ is analogous to that of SF_4, indicating similar structures for these two isoelectronic species. For each of the remaining chlorine fluoride cations, only one signal was observed, indicating the presence of equivalent fluorine ligands with chlorine quadrupole relaxation preempting the observation of ClF spin-spin coupling. Contrary to previous reports, NF_2O^+ shows a triplet of equal intensity and line width. Chemical shifts are given for ClF and $FClO_2$ in the liquid phase.

Introduction

Halogen fluorides are known[1] to form adducts with numerous Lewis acids. It has been shown by vibrational spectroscopy and in some instances by X-ray diffraction studies that these adducts are predominantly ionic in the solid state.[1] Raman spectra of HF solutions have been reported only for $IF_6^+AsF_6^-$ [2] and ClF_2O^+ salts.[3,4] Except for a recently published note on the ^{19}F nmr spectrum of $IF_6^+AsF_6^-$ in HF solution,[5] no high-resolution nmr data have been reported for halogen fluoride adducts. This lack of nmr data is due to rapid chemical exchange between most of these cations and the HF solvent[6] even at low temperatures. This chemical exchange, however, can be suppressed by acidification of the HF solvent as was recently reported for SF_3^+ salts[7] and $IF_6^+AsF_6^-$.[5] In this paper, we report the results of our ^{19}F nmr study on chlorine fluoride cations.

Experimental Section

The preparation and characterization of $ClF_6^+PtF_6^-$,[8] $ClF_4^+SbF_6^-$,[9] $ClF_2O^+AsF_6^-$,[10] $ClF_2O^+PtF_6^-$,[11], $NF_2O^+AsF_6^-$,[12] and $ClF_2O_2^+PtF_6^-$ [13] have previously been described. The adducts between ClF_3 and BF_3, AsF_5, or SbF_5 were freshly prepared using a Monel Teflon-FEP vacuum system. The material balances observed for the ClF_2^+ adducts deviated by less than 0.5% from those calculated for 1:1 adducts. The purification and handling of HF has previously been described.[2,4] Chloryl fluoride and ClF were prepared from $KClO_3$ and ClF_3 and from Cl_2 + ClF_3, respectively. Chlorine trifluoride (The Matheson Co.) and AsF_5 (Ozark Mahoning Co.) were purified by fractional condensation prior to their use.

Teflon-FEP tubes ($^1/_8$-in. i.d., 0.015-in. wall thickness) were used as sample containers. The stable solids were transferred into the passivated (with ClF_3) tubes in the dry N_2 atmosphere of a glove box. Their amount was determined by weighing and volumetrically measured amounts of AsF_5 and HF were added at −196° on the vacuum line. The tubes were closed by Hoke valves during the transfers and were heat-sealed under vacuum. The loaded Teflon tubes were inserted into standard glass nmr tubes and $CFCl_3$ was added as an external standard.

The ^{19}F nmr spectra were recorded at 56.4 MHZ on a Varian high-resolution nmr spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique with an accuracy of ±1 ppm.

Results and Discussion

The observed ^{19}F nmr chemical shifts are given in Table I. Figure 1 shows the difference in temperature dependence between an acidified and nonacidified HF solution. Figure 2 shows the multiplet structures of several of the resonances. The following compounds were studied in both HF and HF-AsF_5 as a solvent: $ClF_2^+BF_4^-$, $ClF_2^+AsF_6$, $ClF_2^+SbF_6^-$, $ClF_5 \cdot 1.36SbF_5$, $ClF_6^+PtF_6^-$, $ClF_2O^+AsF_6^-$, $ClF_2O^+PtF_6^-$, $ClF_2O_2^+PtF_6^-$, and $NF_2O^+AsF_6^-$. For the ClF_2^+ and ClF_2O^+ salts, acidification of the HF solvent with AsF_5 was required to observe the resonance lines due to the cations. This acidification, however, causes rapid exchange between the anion and HF, thus resulting in a single line for the anion, HF, and AsF_5. Without AsF_5 addition, the anion resonances can be observed as separate lines, but only a single line is observed for the cation and HF. The fact that one of the lines contains, in addition to HF, the resonance due to either the anion or cation was substantiated by peak area measurements on samples of known composition, such as $ClF_2O^+AsF_6^-$ (see footnote *k* of Table I), the observed chemical shifts, and their temperature dependence. The solubility of the salt in HF decreases with decreasing temperature. Hence, cooling of the sample results in a pronounced chemical shift for the line due to HF and the ion exchanging with it, but not for that of the nonexchanging counterion. A similar dependence of the exchange mechanism on the acidity of the solvent has previously been observed by Azeem and coworkers for SF_3^+ salts.[7] By analogy with the SF_3^+ compounds, the rapid exchange between ClF_2^+ and HF in nonacidified HF might be explained by $ClF_2^+ + HF_2^- \rightleftarrows ClF_3 + HF$. The addition of AsF_5 suppresses the HF_2^- formation and, hence, the exchange between ClF_2^+ and HF, but enhances the exchange between AsF_6^- and HF according to $AsF_6^- + H_2F^+ \rightleftarrows AsF_5 + 2HF$. For the HF solutions of $ClF_2^+BF_4^-$, $ClF_2^+SbF_6^-$, $ClF_4^+SbF_6^-$, and HF-ClF_3 mixtures, Raman spectra were also recorded. For the ClF_2^+ and ClF_4^+ salts, all bands expected for the individual ions were observed. Their frequencies deviated by less than 10 cm^{-1} from those observed for the solid adducts but showed no splitting of bands or violations of the symmetry rules. This suggests that in both the solid state and HF solution, the same discrete ions are present and

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Table I. ^{19}F Nmr Spectral Data of Chlorine Fluoride Adducts in HF and HF–AsF_5 Solutions

Sample compn (mole ratio)	Temp, °C	δ, ppm ($CFCl_3$ ext ref)	Assignment	Notes
HF	15	199.6	HF	*a*
	−65	194.8	HF	*a*
HF, AsF_5 (20:1)	15	189	HF, AsF_5	*a*
	−65	186	HF, AsF_5	*a*
HF, AsF_5 (4:1)	15	134	HF, AsF_5	*a*
	−65	129	HF, AsF_5	*a*
$ClF_2^+AsF_6^-$, HF	−10	167	HF, ClF_2^+	*b*
		64	AsF_6^-	*b*
$ClF_2^+AsF_6^-$, HF, AsF_5 (14:300:1)	40	152	HF, $ClF_2^+AsF_6^-$, AsF_5	*c*
	−15	181	HF, AsF_5, ClF_2^+	*d*
		67	AsF_6^-	*d*
	−75	195	HF, AsF_5	*a*
$ClF_2^+AsF_6^-$, HF, AsF_5 (21:300:6)	10, −40	171, 185	HF, AsF_5, AsF_6^-	*b*
		23, · · ·	ClF_2^+	*b*
$ClF_2^+AsF_6^-$, HF, AsF_5 (2:30:14)	38	87	HF, AsF_5, AsF_6^-	*c*
		26	ClF_2^+	*c*
	30, 0	87	HF, AsF_5, AsF_6^-	*c*
		22	ClF_2^+	*e*
	−10, −25, −40	96, 102, 107	HF, AsF_5, AsF_6^-	*c*
		22	ClF_2^+	*a*
	−50, −60	111	HF, AsF_5	*c*
$ClF_2^+SbF_6^-$, HF (2:27)	50	175	HF, ClF_2^+	*d*
		~110	SbF_6^-	*f*
	35, 10	175, 183	HF, ClF_2^+	*a*
	−30	194.5	HF	*a*
$ClF_2^+SbF_6^-$, HF, AsF_5 (2:24.4:3.2)	30	146	HF, AsF_5	*c*
		122	SbF_6^-	*d*
		23	ClF_2^+	*c*
	10, −30, −70	143, 146, 150	HF, AsF_5	*c*
		122, 122, 127	SbF_6^-, HF absorbed on solid ClF_2^+-SbF_6^-?	*d*
		23, 23, · · ·	ClF_2^+	*a*
$ClF_2^+BF_4^-$, HF (2:15)	20, −60	162	HF, $ClF_2^+BF_4^-$	*c*
$ClF_5\cdot 1.36SbF_5$, HF (1:13)	40	190	HF, $ClF_4^+SbF_6^- \times SbF_5$	*d*
	0, −30	195, 197	HF	*e*
		125	SbF_6^-, $Sb_2F_{11}^-$	*c*
		−265	ClF_4^+	*e*
$ClF_5\cdot 1.36SbF_5$, HF, AsF_5 (1:15:3)	0, −20, −60	133	HF, AsF_5, SbF_6^-, $Sb_2F_{11}^-$	*e*
		−265	ClF_4^+	*e*
	−80	−274	ClF_4^+ } axial and equatorial fluorines	*g*
		−256	ClF_4^+	
$ClF_6^+PtF_6^-$, HF (1:50)	30	198	HF	*a*
		−389	ClF_6^+	*g, h*
$ClF_6^+PtF_6^-$, HF, AsF_5 (1:50:12)	40, −60	130	HF, AsF_5	*c*
		−388	ClF_6^+	*g, h*
		320	PtF_6^{2-}?	*i*
$ClF_2O^+AsF_6^-$, HF (1:11.8)	30	170	HF	*f*
		67.5	AsF_6^-	*j*
	10, −30	195	HF	*a*
		68	AsF_6^-	*d*
$ClF_2O^+AsF_6^-$, HF, AsF_5 (1:10.6:2)	20, −60	133, 142	HF, AsF_5, AsF_6^-	*c*
		−273.7, −270.8	ClF_2O^+	*a, k*
$ClF_2O^+PtF_6^-$, HF (1:34)	25	201.2	HF	*a*
		−273.2	ClF_2O^+	*a*
$ClF_2O^+PtF_6^-$, HF, AsF_5 (1:19:3.2)	20, −60	145	HF, AsF_5	*a*
		−272	ClF_2O^+	*a*
		320	PtF_6^{2-}?	*i*
$ClF_2O_2^+PtF_6^-$, HF, AsF_5	30	135	HF, AsF_5	*a*
		−310	$ClF_2O_2^+$	*c*
$NF_2O^+AsF_6^-$, HF (1:14)	−45	190	HF	*c*
		69	AsF_6^-	*c*
		−331	NF_2O^+	*c*
$NF_2O^+AsF_6^-$, HF, AsF_5 (1:9:2)	30	125	HF, AsF_5	*c*
		−330	NF_2O^+	*g, l*

[a] Sharp singlet. [b] See Figure 1. [c] Broad singlet. [d] Very broad singlet. [e] Broad singlet becoming narrower with decreasing temperature. [f] Very, very broad line. [g] See Figure 2. [h] Two sets of quadruplets of equal intensity with $J_{^{35}ClF}$ = 337 and $J_{^{37}ClF}$ = 281 ± 2 Hz. [i] Weak triplet with 1:4:1 peak area ratio and $J_{^{195}PtF}$ = 2090 ± 10 Hz. [j] Poorly resolved quadruplet of about equal intensity with $J_{^{75}AsF}$ of about 900 Hz. [k] Peak area measurements at 20° resulted for ClF_2O^+:HF, AsF_5, AsF_6^- in a ratio of 10:139 (calcd 10:133). [l] Sharp triplet of equal intensity with J_{NF} of 250 Hz.

that the additional splittings and symmetry rule violations observed for the solids are due to lowering of the site symmetry or slight distortion of the ions. If these additional splittings and symmetry rule violations were indicative of *strong* covalent fluorine bridges, one should observe more pronounced frequency shifts when comparing the spectra of the solids with those of the HF solutions. Furthermore, it demonstrates the difference in time scale between nmr and vibrational spectroscopy for chemical exchange reactions. Whereas, the exchange rate between HF and ClF_2^+

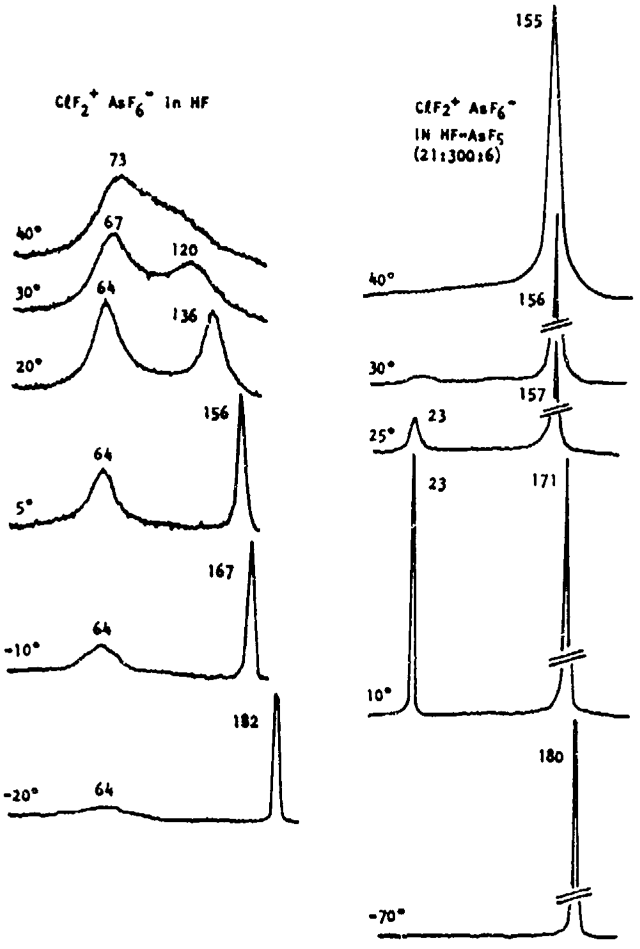

Figure 1. Temperature dependence of the ^{19}F nmr spectra of $ClF_2^+AsF_6^-$ in HF and HF-AsF_5 solution. Chemical shifts and temperatures are given in ppm from external $CFCl_3$ and °C, respectively.

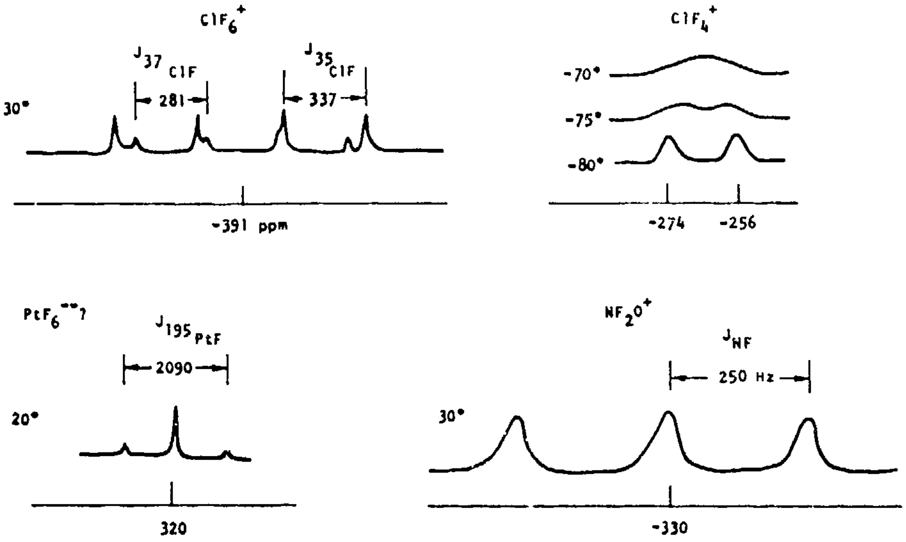

Figure 2. ^{19}F nmr spectra of several selected ions.

is fast enough to prevent observation of separate nmr signals, it is too slow to cause a collapse of the Raman lines. The Raman spectra of the HF–ClF_3 mixtures exhibited only the bands characteristic of ClF_3.[14] The absence of the characteristic ClF_2^+ lines[15,16] indicates that ClF_3 in HF is not ionized according to $ClF_3 + HF \rightarrow ClF_2^+ + HF_2^-$. However, this type of ionization has recently been demonstrated[3] for the structurally related ClF_3O molecule in HF solution.

In the following paragraphs, the individual compounds will be discussed in more detail.

ClF_2^+ Salts. Figure 1 demonstrates how acidification of the solvent and temperature variation influence the spectrum. Without acidification, only one broad line is observed above 40° due to rapid exchange between all three species, HF, ClF_2^+, and AsF_6^-. At 30°, separation into two peaks is noticeable. The chemical shift of one of the peaks (64 ppm) changes very little on further cooling, which suggests that the peak is due to AsF_6^-.[17,18] The chemical shift of the second peak steadily increases with decreasing temperatures and approaches at −60° that of pure HF. Evidently, this peak is due to rapidly exchanging ClF_2^+ and HF. The steady increase of the shift is caused by the decreasing solubility of $ClF_2^+AsF_6^-$ in HF with decreasing temperature as can also be seen from the decreasing relative intensity of the 64-ppm signal.

Solutions acidified with AsF_5 also show two peaks. The low-field resonance exhibits an almost temperature-independent shift of 23 ppm and is assigned to ClF_2^+. Above 30°, the line is extremely broad, while below 20° it is a sharp singlet which decreases in relative intensity with decreasing temperature owing to increasing precipitation of $ClF_2^+AsF_6^-$. The high-field resonance is due to rapidly exchanging HF, AsF_5, and AsF_6^-. Its chemical shift increases with decreasing temperature until essentially all of the AsF_6^- has precipitated. It then remains constant and corresponds to that expected for a HF–AsF_5 mixture.

Samples were studied containing different amounts of AsF_5 to determine how much AsF_5 was required to observe a separate line for ClF_2^+. When the HF contained 0.33 mole % AsF_5, no separate ClF_2^+ signal could be observed;

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(14) H. Selig, H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, 52, 3517 (1970).

(15) K. O. Christe and W. Sawodny, *Inorg. Chem.*, 6, 313 (1967).

(16) R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 9, 616 (1970).

(17) E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 81, 1084 (1959); J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, 41, 1016 (1963).

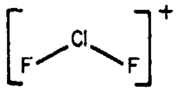
(18) K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, *Inorg. Chem.*, 6, 533 (1967).

however, addition of 2 mole % produced a separate ClF_2^+ line. Hence, the observation of a separate ClF_2^+ line cannot be caused by the formation of a stoichiometric adduct between AsF_5 and $ClF_2^+AsF_6^-$ or HF.

The spectra observed for $ClF_2^+SbF_6^-$ in HF and HF-AsF_5 solution are similar to those of the AsF_6^- salt. One difference was the observation of a broad signal for the HF-AsF_5 solution at about 120 ppm which is assigned to SbF_6^-.[7] Another effect was observed for the latter solution. With decreasing temperature, the solubility of $ClF_2^+SbF_6^-$ decreased as expected, and below −30° the signals attributable to ClF_2^+ and SbF_6^- had essentially disappeared. Further cooling to −70°, however, caused the HF solvent peak to become somewhat narrower and produced a new broad peak at 127 ppm. The intensity of the latter did not decrease with decreasing temperature. Based on its chemical shift, the temperature dependence of its intensity, and its absence in pure HF-AsF_5, it is tentatively assigned to HF bonded to the surface of the precipitated $ClF_2^+SbF_6^-$ salt by strong hydrogen bridges.

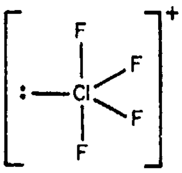
For $ClF_2^+BF_4^-$ in HF, only a single line was observed at 162 ppm between 20 and −60°. This lack of splitting into individual peaks might be explained by the low thermal stability of $ClF_2^+BF_4^-$ (1 atm dissociation pressure at 9°)[19] thus providing a ready anion-cation exchange mechanism, according to $ClF_2^+BF_4^- \rightleftarrows ClF_3 + BF_3$.

The observation of a sharp singlet for ClF_2^+ in its AsF_6^- and SbF_6^- salts is in excellent agreement with the bent structure of symmetry C_{2v}



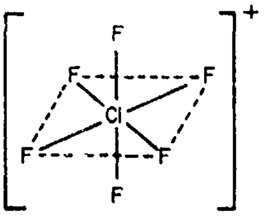
derived for this cation from single-crystal X-ray diffraction studies[20,21] and from vibrational spectroscopy.[15,16] In ClF_2^+, both fluorine ligands should be equivalent and chlorine quadrupole relaxation should preempt the observation of Cl-F spin-spin coupling. The change in chemical shift between ClF_3 and ClF_2^+ of +83 ppm is in the same direction as those observed for IF_7 and IF_6^+,[5] SF_4 and SF_3^+,[7] SF_4O and SF_3O^+,[22] and NF_3O and NF_2O^+,[23] though it is difficult to rationalize why cation formation does not generally result in increasing deshielding of the fluorine ligands.

The ClF_4^+ Cation. The $ClF_5 \cdot 1.36SbF_5$ adduct exhibits a broad resonance at −265 ppm in both HF and HF-AsF_5 mixtures at temperatures between 0 and −30°. Based on its chemical shift, it can be ascribed to a chlorine fluoride species containing chlorine in a high oxidation state. At lower temperatures, the solubility of $ClF_5 \cdot 1.36SbF_5$ in HF becomes very low. In HF-AsF_5, however, the solubility is sufficiently high to allow the observation of this signal in the range −70 to −80°. Below −70°, the −265-ppm resonance separates into a doublet of equal intensity with chemical shifts of −274 and −256 ppm (see Figure 2). This low-temperature splitting is analogous to that observed[17] by Muetterties and Phillips for isoelectronic SF_4. It strongly indicates the presence of a ClF_4^+ cation containing two pairs of nonequivalent fluorine ligands. These could rapidly exchange at higher temperatures by either an intermolecular[17] or an intramolecular pseudorotational Berry mechanism[24] to give a single peak. It was not possible (freezing point of HF) to lower the temperature sufficiently to observe the expected[17] triplet fine structure of the two resonances and to determine the F-F coupling constants. The observation of two pairs of nonequivalent fluorine ligands for ClF_4^+ agrees well with the structure of symmetry C_{2v}



suggested on the basis of vibrational spectra.[9,25] Due to the small difference in chemical shifts between the two ClF_4^+ resonances at −274 and −256 ppm, their assignment to the axial and equatorial fluorine atoms, respectively, should be considered tentative. This assignment is in line with the suggestion[26] by Muetterties and coworkers that in trigonal-bipyramidal species the axial fluorine ligands occur at a lower field than the equatorial ones.

The ClF_6^+ Cation. For salts containing the ClF_6^+ cation, two sharp sets of quadruplets of equal intensity were observed at −391 ppm in both HF and HF-AsF_5 solution (see Figure 2). The lack of exchange between ClF_6^+ and HF is not surprising since an equilibrium such as $ClF_6^+ + HF_2^- \rightleftarrows ClF_7 + HF$ is impossible owing to the nonexistence[8] of stable ClF_7. The peak area ratio between the two sets was 3:1, indicating that they are due to the ^{35}Cl and ^{37}Cl isotopes, having a natural abundance of 75.4 and 24.6%, respectively. The splitting of the signals into quadruplets of equal intensity can be explained by spin-spin coupling between Cl ($I = ^3/_2$) and F. This Cl-F spin-spin coupling, however, is usually not observed for chlorine fluorides due to rapid relaxation caused by interaction of the chlorine quadrupole moment with an unsymmetric electric field gradient. Consequently, the observation of well resolved Cl-F spin-spin coupling for ClF_6^+ is strongly indicative of a spherically symmetric electric field about the Cl nucleus.



This confirms that indeed ClF_6^+ has symmetry O_h as suggested on the basis of its vibrational spectrum.[8] Previously, only one case of a partially resolved Cl-F spin-spin coupling was observed for $FClO_3$[27,28] which has an almost spherically symmetric electric field. For $FClO_3$, $J_{^{35}ClF}$ was

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(21) H. Lynton and J. Passmore, *Can. J. Chem.*, 49, 2539 (1971).

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(27) S. Brownstein, *Can. J. Chem.*, 38, 1597 (1960).

(28) J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, 41, 3063 (1963).

estimated to be 310[27] or 289 Hz[28], but an estimate of $J_{^{37}\mathrm{ClF}}$ was preempted by large line widths. For $\mathrm{ClF_6^+}$, $J_{^{35}\mathrm{ClF}}$ and $J_{^{37}\mathrm{ClF}}$ are 337 and 281 ± 2 Hz, respectively. The observed ratio of $J_{^{35}\mathrm{ClF}}:J_{^{37}\mathrm{ClF}} = 1.199$ is in excellent agreement with the value of 1.202 calculated from the ratio of the magnetic moments of the two chlorine isotopes.[29] The observed full line width at half-height is only 15 Hz for $\mathrm{ClF_6^+}$, compared to about 430 Hz for $\mathrm{FClO_3}$.[27] This indicates that the electric field about the Cl nucleus in $\mathrm{ClF_6^+}$ is, as expected, much more spherical than that in $\mathrm{FClO_3}$. In addition, the center of the $^{37}\mathrm{ClF_6^+}$ resonance is shifted by 0.15 ± 0.02 ppm upfield from that of $^{35}\mathrm{ClF_6^+}$. This shift may be explained[30] by the difference in the vibrational amplitudes of the two Cl isotopes. The heavier isotope has a smaller vibrational amplitude causing the electrons of the fluorine atom to be less polarized and resulting in increased $^{19}\mathrm{F}$ shielding. A similar change in chemical shift (0.053 ppm) in the same direction has been observed[31] for the isoelectronic $^{32}\mathrm{SF_6}$ and $^{34}\mathrm{SF_6}$ isotopes. The fact that the isotopic shift for $\mathrm{ClF_6^+}$ is several times larger than that for $\mathrm{SF_6}$ is in line with the observed large increase[31] from $\mathrm{SiF_6^{2-}}$ toward $\mathrm{SF_6}$.

In addition to the solvent lines, a weak resonance was observed in acidified HF at 320 ppm. This signal consists of a triplet showing a 1:4:1 peak area ratio and a coupling constant of 2090 ± 10 Hz (see Figure 2). These observations suggest that the resonance is due to a platinum species. Of the naturally occurring platinum isotopes, only $^{195}\mathrm{Pt}$ (abundance 33.7%) has a nuclear spin ($I = {}^1/_2$). Spin-spin coupling between F and $^{195}\mathrm{Pt}$ would result in two satellites, each with peak areas equal to one-fourth of that of the central peak. Assignment of the 320-ppm signal to $\mathrm{PtF_6^-}$ is unlikely for the following reasons: (1) its peak area is much too small when compared to those of the counterions, (2) no signal was observed in this range for other $\mathrm{PtF_6^-}$ salts, and (3) $\mathrm{PtF_6^-}$ is paramagnetic[32] and a large anisotropic downfield shift might be expected similar to that observed for $\mathrm{PtF_6}$ (−5550 and −3000 ppm).[33] Since $\mathrm{PtF_6^{2-}}$ is the only diamagnetic tetravalent or higher valent platinum fluoride, we tentatively assign the 320-ppm signal to this anion.

The $\mathrm{ClF_2O^+}$ Cation. The $^{19}\mathrm{F}$ nmr spectra of both $\mathrm{ClF_2O^+AsF_6^-}$ and $\mathrm{ClF_2O^+PtF_6^-}$ show a sharp singlet at about −273 ppm, which is assigned to $\mathrm{ClF_2O^+}$. This indicates two equivalent fluorine atoms for $\mathrm{ClF_2O^+}$ in good agreement with the structure of symmetry C_s proposed[3,4] on the basis of vibrational spectra. The remaining features of the spectra are analogous to those discussed above for $\mathrm{ClF_2^+}$ and $\mathrm{ClF_6^+}$ salts and, hence, are not reiterated.

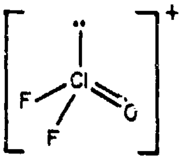
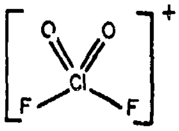


Table II. Summary of $^{19}\mathrm{F}$ Nmr Shifts and Coupling Constants of Liquid Chlorine Fluorides and Oxyfluorides and of Their Cations in HF Solution

Compd	Temp, °C	Chem shift, ppm (from ext $\mathrm{CFCl_3}$)	Coupling constant, Hz	Ref
$\mathrm{Cl}F_2(\mathrm{F})$	−60	−114.3, −121.8, doublet	$J_{\mathrm{FF}} = 421$	*a-c*
$\mathrm{ClF_2}(F)$		−15.0, −7.7, −0.4, triplet		
$\mathrm{Cl}F_4(\mathrm{F})$		−247, doublet	$J_{\mathrm{FF}} = 130$	*d*
$\mathrm{ClF_4}(F)$		−412, quintet		
$\mathrm{ClF_3O}$	10	−262		*e*
$\mathrm{FClO_2}$	−80	−315		*a*
$\mathrm{FClO_3}$		−287, quartet	$J_{^{35}\mathrm{ClF}} = 289$	*f*
$\mathrm{ClF_2^+}$	10	23		*a*
$\mathrm{Cl}F_2(\mathrm{F_2})^+$	−80	−256		*a*
$\mathrm{ClF_2}(F_2)^+$	−80	−274		*a*
$\mathrm{ClF_6^+}$	40	−388, quartet	$J_{^{35}\mathrm{ClF}} = 337$, $J_{^{37}\mathrm{ClF}} = 281$	*a*
$\mathrm{ClF_2O^+}$	20	−272		*a*
$\mathrm{ClF_2O_2^+}$	30	−310		*a*

[a] Data from this study. [b] In addition to the first-order splitting, the −114.3, −121.8, and −7.7-ppm resonances show second-order splitting. [c] Reference 36. [d] D. Pilipovich, W. Maya, E. A. Lawton, H. F. Bauer, D. F. Sheehan, N. N. Ogimachi, R. D. Wilson, F. C. Gunderloy, Jr., V. E. Bedwell, *Inorg. Chem.*, 6, 1918 (1967). [e] D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, *Inorg. Chem.*, 11, 2189 (1972). [f] Reference 28; H. Agahigian, A. P. Gray, and G. D. Vickers, *Can. J. Chem.*, 40, 157 (1962).

The $\mathrm{ClF_2O_2^+}$ Cation. A sample containing about 10 mole % of $\mathrm{ClF_2O_2^+PtF_6^-}$ showed a broad, weak singlet at −310 ppm. Since it cannot be attributed to any known chlorine fluoride species, it is tentatively assigned to $\mathrm{ClF_2O_2^+}$.[33a] Its chemical shift and lack of splitting are consistent with the structure of symmetry C_{2v} as indicated by its vibrational spectrum.[13]



The $\mathrm{NF_2O^+}$ Cation. The $^{19}\mathrm{F}$ nmr spectrum of $\mathrm{NF_2O^+}$ has previously been reported[23] to consist of a partially resolved 4:5:4 triplet at −331 ppm with $J_{\mathrm{NF}} = 250$ Hz and the outer members of the triplet being broader than the central member. As can be seen from Figure 2, acidification with $\mathrm{AsF_5}$ of an HF solution of $\mathrm{NF_2O^+AsF_6^-}$ results in a well-resolved triplet of equal intensity and bandwidth as expected for $\mathrm{NF_2O^+}$. Whereas the previously reported[23] peak area ratio and relative line width are not confirmed, the observed chemical shifts and coupling constants are in excellent agreement.

Summary

Table II summarizes all presently known $^{19}\mathrm{F}$ nmr spectra of chlorine fluorides and oxyfluorides and of their cations. As can be seen, data are now available for all compounds except for the very recently discovered[34] oxyfluoride $\mathrm{ClF_3O_2}$[34a] and the $\mathrm{Cl_2F^+}$ cation.[35] We have redetermined the chemical shifts of ClF and $\mathrm{FClO_2}$ in the liquid phase since only measurements on the gas have previously been report-

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(29) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 188.

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(32) N. Bartlett and S. P. Beaton, *Chem. Commun.*, 167 (1966).

(33) R. Blinc, E. Pirkmajer, J. Slivnik, and I. Zupancic, *J. Chem. Phys.*, 45, 1488 (1966).

(33a) Note Added in Proof. The assignment of the −310-ppm signal to $\mathrm{ClF_2O_2^+}$ has in the meanwhile been confirmed for $\mathrm{ClF_2O_2^+BF_4^-}$ and $\mathrm{ClF_2O_2^+AsF_6^-}$ (K. O. Christe and E. C. Curtis), to be published.

(34) K. O. Christe, *Inorg. Nucl. Chem. Lett.*, 8, 457 (1972).

(34a) Note Added in Proof. $\mathrm{ClF_3O_2}$ shows a second-order splitting $\mathrm{AB_2}$ pattern centered at −413 ppm with $J_{\mathrm{FF}} = 443$ Hz and $J/\nu_0\delta = 1.0$ (K. O. Christe and R. O. Wilson), to be published.

(35) K. O. Christe and W. Sawodny, *Inorg. Chem.*, 8, 212 (1969).

ed.[36] In addition, we have redetermined the chemical shifts for liquid ClF_3 since there is some confusion in the literature[17,37,38] concerning its exact values. Most of the data of Table II can be qualitatively rationalized by assuming increasing deshielding of the fluorine ligands with increasing oxidation state of the chlorine central atom (see trends for ClF-ClF_3-ClF_5, ClF_2^+-ClF_4^+-ClF_6^+, or ClF_2O^+-$ClF_2O_2^+$). The effect of oxygen substitution is more difficult to understand. For example, the fluorine in $FClO_2$ is more deshielded than that in $FClO_3$. Also, the high shielding of F in ClF and the increased shielding in the cations when compared to their parent molecules are unexpected. Clearly, our present understanding of the nature of ^{19}F chemical shifts is insufficient to rationalize all these observations.

Registry No. HF, 7664-39-3; AsF_5, 7784-36-3; $ClF_2^+AsF_6^-$, 19154-21-3; $ClF_2^+SbF_6^-$, 30669-19-3; $ClF_2^+BF_4^-$, 36544-26-0; ClF_5, 13637-63-3; SbF_5, 7783-70-2; $ClF_6^+PtF_6^-$, 36609-91-3; $ClF_2O^+AsF_6^-$, 36544-27-1; $ClF_2O^+PtF_6^-$, 36544-28-2; $ClF_2O_2^+PtF_6^-$, 36609-92-4; $NF_2O^+AsF_6^-$, 25562-24-7; ClF, 7790-89-8; $FClO_2$, 13637-83-7; $FClO_3$, 7616-94-6; $ClF_2(F_2)^+$, 36544-30-6.

Acknowledgment. We are indebted to Dr. C. J. Schack and R. D. Wilson for their help and to the Office of Naval Research, Power Branch, for financial support.

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(36) L. G. Alexakos and C. D. Cornwell, *J. Chem. Phys.*, 41, 2098 (1964).

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(38) C. H. Dungan and J. R. Van Wazer, "Compilation of Reported F^{19} NMR Chemical Shifts," Wiley-Interscience, New York, N. Y., 1970, No. 819.

[Reprinted from Inorganic Chemistry, 12, 620 (1973).]

Contribution from Rocketdyne, a Division of North American Rockwell Corporation, Canoga Park, California 91304, and the Abteilung fur Anorganische Chemie, Universitat, Ulm, Germany

Vibrational Spectrum and Force Constants of the SF_5O^- Anion

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The $CsF{\cdot}SF_4O$ adduct has been prepared and characterized by infrared and Raman spectroscopy. All eleven fundamental vibrations expected for a pseudooctahedral anion of symmetry C_{4v} have been observed and are assigned. A modified valence force field has been computed for SF_5O^- and suggests an SO bond order of approximately 1.5.

Introduction

The existence of a $CsF{\cdot}SF_4O$ adduct has been reported[1] in 1960 by Smith and Englehardt and in 1964 by Ruff and Lustig.[2] However, no details were given regarding its preparation or properties. In a subsequent paper Lustig and Ruff described[3] the synthesis of $Cs^+SF_5O^-$ from CsF and SF_4O in CH_3CN solution. The ionic formulation of this adduct was substantiated[3] by its ^{19}F nmr spectrum which showed a characteristic AB_4 pattern. The vibrational spectrum of this interesting compound is essentially unknown, since only four infrared absorptions were published.[3] In this paper we wish to report the complete vibrational spectrum of the SF_5O^- anion and the results from a force constant computation.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Sulfur oxide tetrafluoride was prepared by the method[3] of Ruff and Lustig from SF_2O and F_2 and was purified by fractional condensation. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1} with an accuracy of $\pm 2\ cm^{-1}$ for sharp bands. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded with an accuracy of $\pm 2\ cm^{-1}$ using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 A. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ~−25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or melting point capillaries were used as sample containers. For the conical tubes the axial viewing–transverse excitation technique and for the capillaries the transverse viewing–transverse excitation techniques were used.

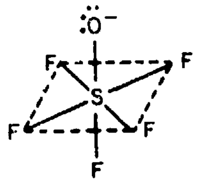
Preparation of $CsSF_5O$. A prepassivated (with ClF_3) 30-ml 316 stainless steel cylinder was loaded with dry, powdered CsF (9.93 mmol). Purified SF_4O (16.1 mmol) was added to the cylinder at −196°. After warming to ambient temperature overnight, the cylinder was heated at 90° for 5 days. Upon recooling to room temperature, all volatiles were removed *in vacuo* and trapped at −196°. The recovered SF_4O (7.32 mmol) indicated that 88.5% of the CsF had been converted to $CsSF_5O$. Confirmation of this was obtained by pyrolyzing a sample of the complex at approximately 250° for 10 min while pumping the evolved gas through a trap cooled to −196°. The evolved gas was identified as SF_4O and the amount found corresponded to an 82% conversion of CsF to $CsSF_5O$. A similar experiment exposing KF to SF_4O at temperatures up to 125° for several days did not result in any complexing.

Results and Discussion

Synthesis and Properties. In the absence of a solvent, heating was required to achieve a significant conversion of CsF to $CsSF_5O$. The conversion obtained in the present study is comparable to that of 76% previously achieved[3] by the use of CH_3CN as a solvent. The reversibility of the formation reaction was demonstrated by a pyrolysis experiment which resulted in SF_4O as the only volatile product. $CsSF_5O$ is a white, crystalline solid and does not show any detectable dissociation pressure at ambient temperature; attempts to synthesize the analogous potassium salt failed under similar reaction conditions. This is not surprising since the stability of salts of this type generally decreases with decreasing cation size.

Vibrational Spectra. Figures 1 and 2 show the Raman and the infrared spectra, respectively, of $CsSF_5O$. The absorption between 300 and 250 cm^{-1} in the infrared spectrum is due to the AgBr window material. The observed frequencies are listed in Table I.

Analogy with isoelectronic SF_5Cl[4,5] and the typical AB_4 ^{19}F nmr pattern previously reported[3] for SF_5O^- suggests the following square-bipyramidal structure of symmetry C_{4v} for SF_5O^-



For this ion of symmetry C_{4v} 11 fundamentals are expected. These are classified as $4\ A_1 + 2\ B_1 + B_2 + 4\ E$. All 11 modes should be Raman active, whereas only the A_1 and E modes should be infrared active. The assignment of the observed bands to the individual modes is given in Table I and is supported by the following arguments. The very intense infrared band at 1154 cm^{-1} must be due to the SO stretching mode. As expected for an A_1 mode it was also observed in the Raman spectrum. Its high frequency rules out any alternate assignment. Comparison with the cor-

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Table I. Vibrational Spectrum of $CsSF_5O$ Compared to Those of SF_5Cl and IF_5O

Obsd freq, cm^{-1}, and intens						Assignment in point group C_{4v}		Approximate description of vibration
$CsSF_5O$		SF_5Cl[a]		IF_5O[b]				
Ir	R	Ir	R	Ir	R			
1154 vs	1153 (1)	402 s	403 (10) p	927 s	928 (4) p	A_1	ν_1	$\nu(XY)$
735 vs	722 (0.2)	855 vs	833 (0.2) p	680 s	680 (10) p		ν_2	$\nu(XF)$
697 m	697 (10)	707 s	704 (3.0) p	640 w	640 (9+) p		ν_3	$\nu_{sym}(XF_4)$
506 s	506 (1)	602 s	603 (0.2) p	360 s	c		ν_4	δ_{sym}(out-of-plane XF_4)
	541 (3.3)		625 (0.7) dp		640 (9+) p	B_1	ν_5	ν_{sym}(out-of-phase XF_4)
	472 (0.2)			(275)[d]			ν_6	δ_{asym}(out-of-plane XF_4)
	452 (0.9)		505 (0.2) dp		305 (1) dp	B_2	ν_7	δ_{sym}(in-plane XF_4)
785 vs, br	780 (0.1) br	909 vs	927 (0.2) dp	710 vs	700 (0+) sh	E	ν_8	$\nu_{asym}(XF_4)$
606 s	607 (2.2)	287 vw	271 (0.6) dp	369 s	374 (1) dp		ν_9	$\delta(YXF_4)$
530 sh	530 (2)	579 mw	584 (0.1) dp	342 s	340 (4) dp		ν_{10}	$\delta(FXF_4)$
325 mw		441 m	442 (0.8) dp	e	205 (0+)		ν_{11}	δ_{as}(in-plane XF_4)

[a] L. H. Cross, M. L. Roberts, P. Goggin, and L. A. Woodward, *Trans. Faraday Soc.*, 56, 945 (1969); J. E. Griffiths, *Spectrochim. Acta, Part A*, 23, 2145 (1967); K. O. Christe, C. J. Schack, and E. C. Curtis, *Inorg. Chem.*, 11, 583 (1972). [b] D. F. Smith and G. M. Begun, *J. Chem. Phys.*, 43, 2001 (1971). [c] Band masked by ν_9 and ν_{10}. [d] Not observed; value estimated from combination band. [e] Below frequency range of spectrometer used.

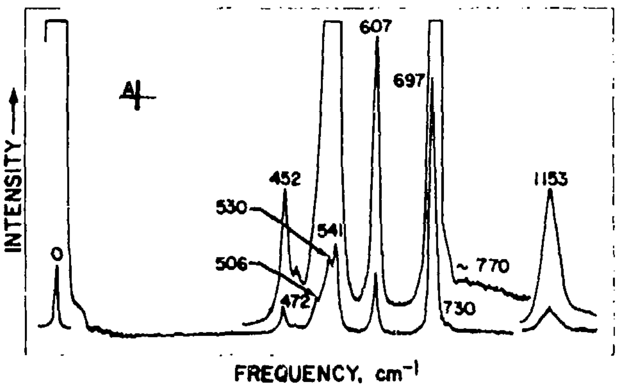

Figure 1. Raman spectrum of solid $Cs^+SF_5O^-$. A indicates spectral slit width.

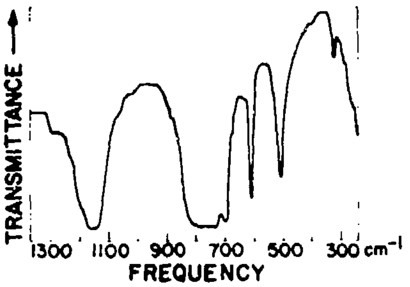

Figure 2. Infrared spectrum of solid $Cs^+SF_5O^-$ as an AgBr disk.

responding mode in SF_3O^+ (1538 cm^{-1})[6] and SF_4O (1380 cm^{-1})[7] shows the expected frequency decrease with an increasing formal negative charge. The SF_5O^- anion should have four additional stretching modes. Three of these belong to the approximately square-planar SF_4 part and one involves the unique fluorine ligand. Of these, the totally symmetric SF_4 stretching mode of species A_1 should result in the most intense Raman line and is consequently assigned to the Raman band at 697 cm^{-1}. As expected for species A_1, this Raman band has an infrared counterpart. The antisymmetric SF_4 and the SF stretching modes in SF_5Cl are both of very high intensity in the infrared and of very low intensity in the Raman spectrum[4,5] and occur at frequencies higher than that of $\nu_{sym}(SF_4)$ (A_1). Consequently, for SF_5O^- these two modes are assigned to the two weak Raman lines at 780 and 722 cm^{-1}, respectively. Of these two, the 780-cm^{-1} line is attributed to $\nu_{as}(SF_4)$ owing to its width, lower Raman intensity, and larger frequency separation from $\nu_{sym}(SF_4)$ (A_1). Both Raman bands show as expected a very intense infrared counterpart. Owing to the broadness of $\nu_{as}(SF_4)$, these two bands are poorly resolved in the infrared spectrum. The broadness of ν_{as} was also observed for several other approximately square-planar XF_4 groups, such as BrF_4^-,[8] ClF_4^-,[9] or those in SF_5^- and SeF_5^-,[10] and hence appears to be quite general. The remaining, yet unassigned, stretching mode, ν_{sym}(out-of-phase SF_4) (B_1), should be of medium Raman intensity, should ideally have no infrared counterpart, and should occur in the range 500–600 cm^{-1}. Since both the 506- and 607-cm^{-1} Raman lines show very intense infrared counterparts, only the 530- or the 541-cm^{-1} line might belong to $\nu_{sym}(SF_4)$ (B_1). Based upon its higher Raman intensity and frequency, we prefer to assign 541 cm^{-1} to $\nu_{sym}(SF_4)$ (B_1).

There are six frequencies left for assignment to the six deformational modes. Of these, the O–SF_4 wagging mode (E) should have the highest frequency since it involves a motion of the oxygen atom which has partial double-bond character (see below). Furthermore, this mode should result in a relatively intense band in both the infrared and Raman spectra. Consequently, this mode is ascribed to 607 cm^{-1}. By comparison with SF_5Cl,[4,5] SF_5^-,[10] and SeF_5Cl[11] one would expect δ_{asym}(in-plane SF_4) (E) to have the lowest frequency of the SF_5 group deformational modes and to be infrared active. Consequently, this mode is assigned to the 325-cm^{-1} infrared band. Of the remaining two yet unassigned infrared-active deformational modes, the δ_{sym}(out-of-plane SF_4) or umbrella mode (A_1) should result in a very intense infrared band of relatively high frequency.[4,5,10,11] Consequently, this mode is assigned to 506 cm^{-1}, leaving 530 cm^{-1} for assignment to the F–SF_4 wagging mode (E). The two remaining, yet unassigned in-

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Table II. Symmetry Force Constants of SF_5O^- [a]

A_1	ν_1	1154	$F_{11} = f_D$	6.46
	ν_2	733	$F_{22} = f_R$	3.75
	ν_3	697	$F_{33} = f_r + 2f_{rr} + f_{rr}'$	5.43
	ν_4	506	$F_{44} = {}^1/_2(f_\beta + 2f_{\beta\beta} + f_{\beta\beta}' + f_\gamma + 2f_{\gamma\gamma} + f_{\gamma\gamma}' - 2f_{\beta\gamma} - 4_{\beta\gamma}' - 2f_{\beta\gamma}'')$	2.52
			$F_{12} = f_{RD}$	0.66
B_1	ν_5	541	$F_{55} = f_r - 2f_{rr} + f_{rr}'$	3.28
	ν_6	472	$F_{66} = {}^1/_2(f_\beta - 2f_{\beta\beta} + f_{\beta\beta}' + f_\gamma - 2f_{\gamma\gamma} + f_{\gamma\gamma}' - 2f_{\beta\gamma} + 4f_{\beta\gamma}' - 2f_{\beta\gamma}'')$	3.19
B_2	ν_7	452	$F_{77} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha}'$	1.46
E	ν_8	785	$F_{88} = f_r - f_{rr}'$	2.84
	ν_9	607	$F_{99} = f_\gamma - f_{\gamma\gamma}'$	2.22
	ν_{10}	530	$F_{1010} = f_\alpha - f_{\alpha\alpha}'$	2.62
	ν_{11}	325	$F_{1111} = f_\beta - f_{\beta\beta}''$	1.21
			$F_{89} = f_{r\gamma} - f_{r\gamma}''$	0.40
			$F_{810} = \sqrt{2}(f_{r\alpha} - f_{r\alpha}')$	0.50
			$F_{811} = f_{r\beta} - f_{r\beta}''$	0.28

[a] Stretching constants in mdyn/A, deformation constants in mdyn/A radian^2, and stretch-bend interaction constants in mdyn/A radian.

frared-inactive modes of species B_1 and B_2, respectively, belong to the Raman lines at 472 and 452 cm^{-1}. Since, for numerous structurally related species, δ_{asym}(out-of-plane SF_4) (B_1) either has not been observed or was of very low intensity,[8,9,12] this mode is assigned to the very weak Raman line at 472 cm^{-1}. Hence, the last yet unassigned Raman line at 452 cm^{-1} should represent δ_{sym}(in-plane SF_4) (B_2).

Comparison of the SF_5O^- assignment with that made for SF_5Cl[4,5] (it should be noted that the assignment given in ref 7 for ν_{11} (E) is likely to be incorrect[11]) shows satisfactory agreement (see Table I). The slight discrepancy in the relative Raman intensities observed for ν_{10} (E) between the two species might be ascribed to increased coupling between ν_9 and ν_{10} in SF_5O^- due to O being more similar in mass to F than Cl. This might result in a symmetric and antisymmetric rather than in a characteristic F-SF_4 and OSF_4 wagging motion. This assumption appears to be supported by the spectrum[13] of isoelectronic IF_5O (see Table I) for which the Raman intensity of ν_{10} is higher than that of ν_9.

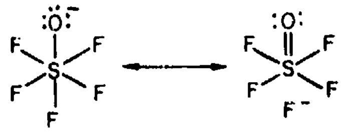
Of the four infrared bands previously reported[3] for $CsSF_5O$ only the two weaker ones agree with our observations. Furthermore, the previously suggested[3] assignment of the SO stretching mode to a broad band centered at 718 cm^{-1} is obviously incorrect.

In summary, all 11 fundamentals of SF_5O^- have been observed and an assignment is offered. The observed vibrational spectrum definitely supports the proposed structural model of symmetry C_{4v}.

Force Constants. A normal-coordinate analysis was carried out to aid the spectral assignment. The kinetic and potential energy metrics were computed by a machine method,[14] assuming the following geometry and coordinate definitions: $R_{SF}' = r_{SF} = 1.60$ Å, $D_{SO} = 1.47$ Å, α (FSF) = β (F'SF) = γ (OSF) = 90°, where F' refers to the axial (unique) fluorine ligand. The symmetry coordinates used were identical with those reported[13] for IF_5O. The bond lengths were estimated by comparison with similar molecules using the correlation[15] noted by Gillespie and Robinson between stretching frequencies and bond lengths. The deformation coordinates were weighted by unit (1 Å) distance.

The force constants were calculated by trial and error with the aid of a time-sharing computer to get exact agreement between the observed and computed frequencies using the simplest possible modified valence force field. Unique force constants could not be computed since the general valence field has 36 constants and there are only 11 observed frequencies. It was found, that for the A_1 block the values of F_{11} and F_{22} were strongly influenced by the value of the interaction constant F_{12}. Since in isoelectronic SF_5Cl[16] and in IF_5O[13] the equatorial and axial fluorine atoms do not significantly differ in their stretching force constants and since in SF_5O^- the equatorial SF stretching force constant f_r is about 3.6 mdyn/Å, we prefer for SF_5O^- a force field with $F_{22} = F_R \approx f_r$. Surprisingly, the interaction constant $F_{13} = 2f_{rD}$ had little influence on the frequencies of ν_1 and ν_3. Hence, its value might be comparable to that of F_{12} although it is not required for obtaining a fit between the computed and observed frequencies. The computed symmetry force constants are listed in Table II. The interaction constants not listed were assumed to be zero.

The following values were obtained for the more important internal force constants: $f_D = 6.46, f_R = 3.75, f_r = 3.60, f_{RD} = 0.66, f_{rr} = 0.54$, and $f_{rr}' = 0.75$ mdyn/Å. Significantly larger values of about 4.6 and 7.7 mdyn/Å are possible for f_R and f_D, respectively, by assuming a much smaller value for f_{RD}. However, the resulting large difference between f_R and f_r renders such a force field less likely. In spite of these uncertainties in the force constants, certain conclusions can be reached. The value of the SO stretching force constant f_D (6.5 mdyn/Å) is much lower than those of 10-12 mdyn/Å generally found for S=O double bonds.[15,16] Its value is comparable to that found for the SO_4^{2-} anion (7.44 mdyn/Å[16]) indicating for SF_5O^- a SO bond order of about 1.5. Furthermore, the values of the SF stretching force constants, f_R and f_r, are somewhat lower than those generally found for covalent SF bonds (4.5-6 mdyn/Å[16]) indicating significant ionic contributions to the SF bonds in SF_5O^-. These results are best interpreted in terms of the resonance structures



etc.

These structures together with orbital-following effects could also account for the unusually strong coupling between the SO and SF stretching modes suggested by the force constant computation.

Registry No. $CsF \cdot SF_4O$, 37862-11-6.

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THE PREPARATION OF CHLORINE MONOFLUORIDE

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ABSTRACT

A procedure is described for the synthesis of chlorine monofluoride from chlorine and chlorine trifluoride.

INTRODUCTION

Chlorine monofluoride is a very vigorous and useful reagent which exhibits a diversity of reaction paths. Thus fluorinating, chlorinating, and chlorofluorinating reactions are well known[1] as well as amphoteric behavior in forming Lewis acid and base complexes[1,2]. Despite this broad utility, specific details regarding the synthesis of ClF are lacking. The experiments reported herein describe a simple, laboratory scale, procedure for the preparation of ClF.

DISCUSSION

Although ClF can be prepared from the elements[3], it is generally preferable to employ ClF_3 and Cl_2 according to the equation:

$$ClF_3 + Cl_2 \xrightarrow{\Delta} 3ClF$$

This reaction was first reported[4] by Schmits and Schumacher. In their work and in later applications[5,6] the reactions were carried out at temperatures in the range of 250 - 350°C and at unspecified pressures and/or times. Therefore, it appeared desirable to better define the most significant parameters, i.e., temperature, pressure, and time. The following table summarizes some of our typical results.

TABLE I

Reaction Data For 1.06 ClF_3 - 1.00 Cl_2

Run No.	T°C	Max. Pressure psi	Time, hr.	ClF_3 Recovered	% Yield Purified ClF
1	120	160	65	Yes	65
2	150	200	18	Yes	79
3	150	620	18	No	95
4	180	375	5	No	92
5	180	670	6	Trace	92

From these experiments it is evident that a temperature of 120°C is too low for obtaining a high yield in a reasonable time. However, a temperature of 180°C, still much lower than those most often used, is quite satisfactory for producing complete reaction in a short time, over a broad pressure range. At 150°C a slightly higher yield was achieved, perhaps due to reduced wall reactions. The longer time required, 18 hr., is still a convenient overnight period. In all cases a 5-7 mole percent excess of ClF_3 was used to ensure sufficient material for the desired reaction since inevitably some fluorine is "lost" through formation of metal fluorides. These conditions have been successfully tested on a reaction scale of a few mmoles to about one mole of ClF.

EXPERIMENTAL

Commercial (The Matheson Co.) ClF_3(98%) and Cl_2 (99.5%) were used without further purification. Stainless steel (304), single ended, high pressure (1800 psi) cylinders (Hoke, Inc.) were used together with stainless steel (316) valves (Hoke, Inc.) and bourdon tube gauges (The Matheson Co.). Clean, assembled reactors were passivated with ClF_3 at ambient temperature before use. Measured amounts of ClF_3 and Cl_2 were condensed into the cylinder held at -196°C. After warming to ambient temperature, the loaded reactors were heated to the final reaction temperature in an oven or with heating tape. Because the temperature-pressure maximums employed were well below ratings for the equipment, small reactors could be placed completely (valve, gauge and all) and safely in an inexpensive drying oven set at the desired temperature. The heating cycle was conducted in an outdoor, pressure safe facility. On completion of the reaction, the contents of the cooled cylinders were separated by fractional condensation in a metal-Teflon vacuum line. A trap cooled to -142°C (methylcyclopentane slush) was used to retain impurities such as Cl_2, ClF_3, and $FClO_2$, while the ClF was condensed in a trap held at -196°C. The purity of the ClF was determined by gas chromatography[7] and its infra-red spectrum.

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Halogen Perchlorates. Additions to Perhaloolefins

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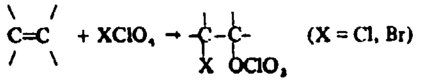
The recently discovered halogen perchlorates, Cl_2O_4 and $BrClO_4$, have been found to react with perhaloolefins by adding across the carbon–carbon double bond. These reactions proceeded quickly at low temperatures, in the absence of a solvent, to furnish the previously unknown perhaloalkyl perchlorates in high yield. Compounds prepared in this manner were $ClCF_2CF_2ClO_4$, $ClCF_2CFClClO_4$, $Cl_2CFCFClClO_4$, $CF_3CFClCF_2ClO_4$, $BrCF_2CFClClO_4$, and $CF_3CFBrCF_2ClO_4$. Characteristic data for these surprisingly stable compounds are reported. All the new perchlorates reacted with alkali metal fluorides to form the corresponding acid fluorides and either $FClO_3$ or mixtures of $FClO_3$, Cl_2, and O_2.

Introduction

Compounds which contain terminal halogen–oxygen single bonds have been reported to add to olefin double bonds through cleavage of the X–O single bond. For example, halogen fluorosulfates (X–OSO_2F),[1,2] chlorine nitrate (Cl–ONO_2),[3] and haloxyperfluoromethanes (X–OCF_3)[4-6] all participate in such reactions. As part of a systematic investigation of the recently discovered halogen perchlorates, Cl_2O_4 ($ClOClO_3$)[7] and $BrClO_4$ ($BrOClO_3$),[8] their reaction with perhaloolefins was examined. Rapid and generally smooth reaction was found which produced the new class of compounds, perhaloalkyl perchlorates



$$\mathrm{>C{=}C<} + XClO_4 \rightarrow \underset{X}{\overset{|}{-C}}-\underset{OClO_3}{\overset{|}{C}}-$$

(X = Cl, Br)

These reactions occurred in high yield (~90%) at low temperatures and have been used to prepare $ClCF_2CF_2ClO_4$, $ClCF_2CFClClO_4$, $Cl_2CFCFClClO_4$, $CF_3CFClCF_2ClO_4$, $BrCF_2CFClClO_4$, and $CF_3CFBrCF_2ClO_4$. Although thermally stable at ambient temperature, the alkyl perchlorates were susceptible to catalytic decomposition with alkali metal fluorides at these same temperatures. Catalyzed decompositions gave quantitative yields of the respective acid fluorides and provided a useful procedure for their identification.

Experimental Section

Apparatus and Materials. The equipment used in this work has been described.[9] Chlorine perchlorate and bromine perchlorate were prepared as reported.[7,8] The haloolefins used were purchased and purified by fractional condensation except tetrafluoroethylene which was prepared by pyrolyzing Teflon. Cesium fluoride and potassium fluoride were fused and then powdered in a drybox prior to use.

Halogen Perchlorate Additions. General Method. In general the reactions of the halogen perchlorates and haloolefins were conducted in a Teflon U trap on the vacuum line. A known quantity of the halogen perchlorate was maintained in the trap at −78°. At this temperature these perchlorates are liquid and have little vapor pressure. An excess of the gaseous olefin was added to this trap incrementally or at a continuous rate such that a pressure of 20–30 mm was not exceeded. The rate of the observed pressure drop was appreciably increased if the liquid phase was agitated. Some reactions were run by condensing all the reactants in a Pyrex bulb at −196° and then warming first to −78° and finally to room temperature. No problems were encountered with this method for the $CF_3CF{=}CF_2$–Cl_2O_4 system on a 4-mmol scale. However, using this method with the $CF_2{=}CFCl$–Cl_2O_4 system on the same scale resulted in an explosion. Therefore additional reactions were not conducted in this manner. Product work-up was easily accomplished by fractional condensation since the perhaloalkyl perchlorates were considerably less volatile than any unreacted material present or any by-products formed. All the perhaloalkyl perchlorates prepared were colorless, mobile liquids which did not freeze down to −78°. The compounds were stable and storable at ambient temperature in clean and dry Pyrex or stainless steel containers. Purity, as determined by gas chromatography, was generally 98+%, even after 1 year at ambient temperature. Details of the synthesis and characterizations follow. The ^{19}nmr data are shown in Table II and the infrared bands of the perchlorate compounds in Table I.

Perfluoropropene–Halogen Perchlorate Reactions. According to the general procedure described above, $CF_3CF{=}CF_2$ (4.20 mmol) was added to Cl_2O_4 (3.56 mmol) over a 20-min period. On fractionation, the product $CF_3CFClCF_2ClO_4$ (3.48 mmol, 97.6% yield) was retained at −78°. The purity of the product was indicated by tensiometric homogeneity, 44 mm at 20.1° and 18 mm at 0.0°. The observed vapor density was 280 g/mol; calculated 285 g/mol. Prominent peaks were noted in the mass spectrum for the *m/e* values corresponding to the ions $C_3F_6Cl^+$, $C_2F_4Cl^+$, CF_2Cl^+, ClO_3^+, CF_3^+ (base peak), ClO_2^+, CF_2O^+, ClO^+, and COF^+. The densities measured in a Pyrex pycnometer at −77.2, 0.0, and 20.0° were 2.01, 1.84, and 1.80 g/ml. For this temperature range, the density, ρ, is given by the equation $\rho = 1.84 - 2.18 \times 10^{-3}t$°C.

Perfluoropropene (4.46 mmol) was added to $BrClO_4$ (4.28 mmol) over 30 min. Pure $CF_3CFBrCF_2ClO_4$ (3.78 mmol, 88.4% yield) was retained at −64° and exhibited vapor pressures of 7 mm at 0.0° and 22 mm at 20.0°. The observed vapor density was 331 g/mol; calculated 329.3 g/mol. Major peaks in the mass spectrum corresponded to the ions $C_3F_6Br^+$, $C_3F_5BrO^+$, $C_2F_4Br^+$, $C_2F_3Br^+$, CF_2Br^+, ClO_3^+, CF_3^+ (base peak), ClO_2^+, CF_2O^+, ClO^+, CF_2^+, and COF^+. The measured densities at −77.4, 0.0, and 21.0° were 2.25, 2.09, and 2.05 g/ml giving a density–temperature relation for this temperature range: $\rho = 2.09 - 2.05 \times 10^{-3}t$°C.

Chlorotrifluoroethylene–Halogen Perchlorate Reactions. During a 4-hr period, $CF_2{=}CFCl$ (8.05 mmol) was added to Cl_2O_4 (7.70 mmol) forming $ClCF_2CFClClO_4$ (7.19 mmol, 93.5% yield) which was retained at −64° on fractionation. Measured vapor pressures were 10 mm at 0.0° and 25 mm at 22.9° and the vapor density was 249 g/mol; calculated 251.5 g/mol. The mass spectrum showed strong peaks for the ions $C_2F_3Cl^+$, $CFCl_2^+$, $C_2F_3O^+$, CF_2Cl^+ (base peak), ClO_3^+, CF_3^+, ClO_2^+, $CFCl^+$, ClO^+, CF_2^+, and COF^+. Densities observed at −77.4, 0.0, and 20.1° were 1.98, 1.83, and 1.79 g/ml. The density–temperature relation for this temperature range is given by the equation $\rho = 1.83 - 1.96 \times 10^{-3}t$°C.

Chlorotrifluoroethylene (2.64 mmol) was allowed to react with $BrClO_4$ (2.45 mmol) over a 1-hr period and furnished $BrCF_2CFClClO_4$ (2.08 mmol, 85% yield) which was trapped at −54° during fractional condensation. The purified material showed vapor pressures of 3 mm at 0.0° and 11 mm at 20.4°.

Tetrafluoroethylene–Chlorine Perchlorate Reaction. The reaction of C_2F_4 (3.16 mmol) and Cl_2O_4 (3.12 mmol) at −78° was quite slow, even with a C_2F_4 pressure of 100 mm, and was allowed to proceed overnight prior to work-up. Fractional condensation at −95° gave $ClCF_2CF_2ClO_4$ (2.86 mmol, 91.5% yield) with an observed vapor density of 233 g/mol; calculated 235 g/mol. The following tempera-

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Table I. Infrared Spectra of Fluorocarbon Perchlorates (4000–400-cm^{-1} Range)

$Cl_2CFCFClClO_4$	$ClCF_2CFClClO_4$	$BrCF_2CFClClO_4$	$ClCF_2CF_2ClO_4$	$CF_3CFClCF_2ClO_4$	$CF_3CFBrCF_2ClO_4$	Tentative assignments
1307 s	1310 s	1311 s	1320 s	1318 s	1318 s	Asym Cl=O str
1296 s	1297 s	1299 s	1295 s	1300 s	1302 s	Asym Cl=O str
1178 m	1232 wm	1224 wm	1198 s	1260 sh	1290 sh	C–F str Region
1130 m	1189 ms	1190 ms	1163 s	1242 s	1255 sh	
1090 m	1140 m	1141 m	1115 s	1182 w	1240 s	
1050 m	1091 m	1088 m		1149 m	1187 vw	
	1054 m	1047 m		1128 m	1170 vw	
					1148 w	
					1123 m	
997 s	1008 s	1004 s	1032 s	1036 s	1033 s	Sym Cl=O str
908 ms	918 m	892 m	970 s	976 s	960 m	
879 m	855 m	820 m	958 s	955 s	924 m	C–O str
818 ms	752 w	749 w	815 w	811 w	805 w	
	660 sh	650 sh	672 m	739 m	737 m	
				670 m	670 sh	
632 s	630 s	630 s	647 ms	653 ms	652 m	Cl–O str
610 sh	580 w	582 w	610 m	620 ms	620 m	
575 w				598 vw	595 vw	
					545 w	

Table II. ^{19}F Nmr Data[a]

Compound	$CF_{3-n}X_n$ ($X = Cl$)	CFX ($X = Cl, Br$)	$CFXClO_4$ ($X = F, Cl$)	COF
$Cl_2CFCFClClO_4$	69.8 [1][b]		76.0 [1]	
$ClCF_2CFClClO_4$	69.0 [2]		79.0 [1]	
$ClCF_2CF_2ClO_4$	72.7 [1]		92.5 [1]	
$CF_3CFClCF_2ClO_4$	78.4 [3]	139.2 [1]	85.8 [2]	
$CF_3CFBrCF_2ClO_4$	76.5 [3]	141.5 [1]	84.7 [2]	
$CFCl_2COF$	65.9 [1]			−7.5 [1]
CF_2ClCOF	65.1 [2]			−10.0 [1]
$CF_3CFClCOF$	80.5 [3]	132.3 [1]		−20.6 [1]
$CF_3CFBrCOF$	78.7 [3]	137.1 [1]		−20.3 [1]

[a] Chemical shift in ppm relative to internal $CFCl_3$. [b] Values in brackets are approximate relative area ratios.

ture–vapor pressure data were noted (°C, mm): −24.1, 10; 0.0, 42; 10.3, 71; 20.4, 113. The vapor pressure–temperature relation is described by the equation $\log p_{\text{mm}} = 7.968 - (1735/T\,°\text{K})$. The extrapolated normal boiling point is 67.8°, with a heat of vaporization of 7.93 kcal/mol and a Trouton constant of 23.3. Intense peaks in the mass spectrum were found for the ions $C_2F_4Cl^+$, CF_2Cl^+ (base peak), ClO_3^+, CF_3^+, ClO_2^+, $CFCl^+$, CF_2O^+, ClO^+, CF_2^+, and COF^+. The density at −76.5, 0.0, and 20.1° was 1.98, 1.80, and 1.75 g/ml. The derived density–temperature equation is $\rho = 1.80 - 2.43 \times 10^{-3}t\,°\text{C}$.

1,2-Dichlorodifluoroethylene–Chlorine Perchlorate Reaction. Chlorine perchlorate (5.75 mmol) was maintained at −35° for its addition to $ClCF{=}CFCl$ (6.03 mmol) so that the reaction could be followed manometrically. Initially the reaction appeared rapid but it soon became sluggish, requiring 10 hr to complete the addition using 40 mm as the maximum reaction pressure. Vacuum fractionation at −35° gave pure $Cl_2CFCFClClO_4$ (5.04 mmol, 87.6% yield). Prominent mass spectral peaks were found for the ions $C_2F_2ClO^+$, $CFCl_2^+$ (base peak), ClO_3^+, ClO_2^+, $CFCl^+$, ClO^+, CCl^+, and COF^+. The vapor pressure was 2 mm at 0.0° and 5 mm at 20.2°. Density measurements at −77.6, 0.0, and 20.0° were 2.06, 1.92, and 1.89 g/ml. The density–temperature relation is given by the equation $\rho = 1.92 - 1.77 \times 10^{-3}t\,°\text{C}$.

Perfluorobutadiene–Chlorine Perchlorate Reaction. An attempt was made to prepare a monoperchlorate-substituted product from a diolefin by treating $CF_2{=}CFCF{=}CF_2$ (2.28 mmol) with Cl_2O_4 (2.34 mmol). The addition proceeded smoothly and less than 0.1 mmol of unreacted material was recovered by pumping on the reaction mixture at −64°. However, when the product was warmed to near room temperature it exploded.

Perhaloalkyl Perchlorate. Alkali Metal Fluoride Reactions. The perhaloalkyl perchlorates were treated with CsF or KF in Pyrex at slightly elevated temperatures. Products of these reactions were separated by fractional condensation and identified by spectral and chromatographic analysis. For the compounds $ClCF_2CF_2ClO_4$, $CF_3CFClCF_2ClO_4$, and $CF_3CFBrCF_2ClO_4$; nearly quantitative yields of $FClO_3$ and the acyl fluorides $ClCF_2COF$, $CF_3CFClCOF$, and $CF_3CFBrCOF$ were obtained on heating overnight at 60°. Chlorodifluoroacetyl fluoride was identified by its infrared spectrum and vapor pressure which agreed with the reported[10] data and that of an authentic sample prepared from $ClCF_2COCl$ and KF.

2-Chlorotetrafluoropiopionyl fluoride has not been reported but was identified by its vapor density: observed, 184 g/mol; calculated, 182.5 g/mol. The vapor pressure was measured over the range −78 to 0° and the equation describing the vapor pressure–temperature relation is $\log p_{\text{mm}} = 7.281 - (1248/T\,°\text{K})$. The calculated normal boiling point is 10.4° with a heat of vaporization of 5.71 kcal/mol. Infrared bands were found at 1860 (s), 1298 (m), 1245 (vs, multiplet), 1142 (s), 968 (s), 760 (w), 700 (m), and 674 (w) cm^{-1}. Together with a weak parent peak, $C_3F_5ClO^+$, the mass spectrum contained intense peaks for $C_2F_4Cl^+$, C_2FClO^+, CF_2Cl^+, CF_3^+ (base peak), $CFCl^+$, CF_2^+, and COF^+.

The corresponding bromine compound $CF_3CFBrCOF$ was identified by its vapor density (observed, 231 g/mol; calculated, 229 g/mol) and the reasonable comparison of its infrared spectrum and boiling point with that reported.[11] Vapor pressure–temperature values were obtained for the range −48.3 to +8.7° (°C, mm): −48.3, 12; −32.0, 36; −18.1, 85; 0.0, 224; 8.7, 328. The derived vapor pressure–temperature equation is $\log p_{\text{mm}} = 8.224 - (1607/T\,°\text{K})$ with a calculated normal boiling point of 27.5° (lit.[11] bp 32°) and a heat of vaporization of 7.35 kcal/mol. Strong mass spectral peaks were found for the ions $C_3F_5BrO^+$ (parent peak), $C_2F_4Br^+$, C_2FBrO^+, CF_2Br^+, $C_2F_4^+$, Br^+, CF_3^+ (base peak), CF_2^+, and COF^+.

For the compounds $ClCF_2CFClClO_4$, $Cl_2CFCFClClO_4$, and $BrCF_2CFClClO_4$ the cesium fluoride catalyzed degradation also produced nearly quantitative yields of the corresponding acid fluorides, $ClCF_2COF$, Cl_2CFCOF, and $BrCF_2COF$. However, the other products were variable amounts of $FClO_3$, Cl_2, and O_2. In addition, the susceptibility of these perchlorates to this reaction varied with $ClCF_2CFClClO_4$ requiring 2 days at 90° for complete decomposition while $BrCF_2CFClClO_4$ was approximately 50% reacted after overnight at room temperature. Chlorodifluoroacetyl fluoride was identified as noted above. Bromodifluoroacetyl fluoride was identified by its infrared spectrum: 1875 (vs), 1267 (m), 1198 (s), 1105 (vs), 940 (s), 768 (w), 670 (m), and 555 (w) cm^{-1}, compared to that of an authentic sample.[12]

Dichlorofluoroacetyl fluoride was identified by its vapor density: observed, 148 g/mol; calculated, 149 g/mol. Observed vapor pressure–temperature data were (°C, mm): −65.1, 11; −47.1, 29; −31.7, 60; −24.0, 85; −10.2, 147; 0.0, 212. The equation describing the vapor pressure–temperature relation is $\log p_{\text{mm}} = 6.440 - (1124/T\,°\text{K})$ leading to a calculated normal boiling point of 42.6° and a heat of vaporization of 5.14 kcal/mol. A boiling point of 38–42° (720 mm) has been reported[13] which compares well with the 40° (710 mm) calculated from the equation. Major mass spectral peaks were found for the ions $C_2F_2ClO^+$, $CFCl_2^+$ (base peak), CF_2Cl^+, $CFCl^+$, CCl^+, and COF^+.

Discussion

Caution! The halogen perchlorates and the alkyl perchlo-

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rates are potentially explosive. Safety precautions should be taken in handling and using these materials.

The new class of compounds, perhaloalkyl perchlorates, have been prepared by the reaction of Cl_2O_4 or $BrClO_4$ with perhaloolefins. Excellent yields, good material balances, and molecular weight data served to establish the 1:1 addition stoichiometry. Two modes of addition were considered possible for this interaction. Further, with each mode of reaction, isomeric products could result using unsymmetrical olefins. For example, in addition to rupture of the terminal X–O bond, the possibility existed for rupture of the central XO–Cl single bond thereby producing $XO{-}C{-}C{-}ClO_3$ adducts. However, all the evidence obtained indicated that only one addition isomer was formed from each olefin, that isomer being a perchlorate. This evidence consisted of ^{19}F nmr, infrared, and mass spectra not only of the perchlorates but also of their respective derivatives, acid fluorides.

The infrared spectra of the perhaloalkyl perchlorates (Table I) are quite characteristic with respect to showing definitive bands for a covalent $OClO_3$ group. All the compounds exhibit strong bands at 1295-1320 (doublet), 997-1036, and 630-652 cm^{-1}. These are assigned respectively to the Cl=O antisymmetric and symmetric stretching vibrations and Cl–O stretching vibration. Other covalent perchlorates, $HOClO_3$,[14] $O_3ClOClO_3$,[15] $FOClO_3$,[16] and the parent perchlorates,[7,8] show bands of very similar position, shape, and relative intensity. Hydrocarbon perchlorates have also been shown[17] to have comparable bands associated with the infrared absorption of the perchlorate group. Formulation of the addition compounds as $XO{-}C{-}C{-}ClO_3$ species was precluded by the absence of the very strong band at ~1200 cm^{-1} which has been ascribed[18] to the ClO_3 group directly bonded to carbon.

Although the perchlorate spectra shown in Table I represent only a limited group, it is noteworthy that distinct differences are apparent for vibrations of the $OClO_3$ group when bonded to a CF_2 as opposed to a CFCl unit. With CF_2 the antisymmetric Cl=O stretches are split further (16-25 cm^{-1}) than with CFCl (11-13 cm^{-1}) and are shifted to slightly higher frequencies. The Cl=O symmetric stretches are shifted even further apart occurring at 1032-1036 cm^{-1} for CF_2 compounds and at 997-1004 cm^{-1} for CFCl species. Bands assigned to the singly bonded Cl–O stretch are also shifted, 647-653 cm^{-1} for CF_2 and 630-632 cm^{-1} for CFCl. These correlations indicate the sensitivity of the ClO_4 group to the nature of the group directly bonded to it.

Fluorine nmr data are given in Table II. The peaks were slightly broadened with indications of multiplet structure but were not resolvable owing to small coupling constants. The chemical shifts, area ratios, and number of peaks observed for the acid fluoride derivatives readily defined the structures of those compounds. For the perchlorates, comparison of the chemical shifts and area ratios of the series together with values reported for similar compounds permitted assignment of the peaks. In the case of the ethyl compounds with equal numbers of fluorine substituents on each carbon, $ClCF_2CF_2ClO_4$ and $Cl_2CFCFClClO_4$, the $ClCF_2$ (72.7 ppm) and Cl_2CF (69.8 ppm) assignments were made which are comparable to the known values for these groups in $ClCF_2CF_2OF$ (69.4 ppm) and Cl_2CFCF_2OF (71.8 ppm)[19] and in $ClCF_2CF_2NF_2$ (69.7 ppm) and $Cl_2CFCF_2NF_2$ (72.8 ppm).[20] The remaining peaks are then assigned to the fluorine resonances of the groups CF_2ClO_4 (92.5 ppm) and $CFClClO_4$ (76.0 ppm). For $ClCF_2CFClClO_4$ these considerations led to the assignments $ClCF_2$ (69.0 ppm) and $CFClClO_4$ (79.0 ppm). The alternate formulation, $Cl_2CFCF_2ClO_4$, would require the assignments Cl_2CF (79.0 ppm) and CF_2ClO_4 (69.0 ppm) which are unjustifiably different from established trends. Unequivocal support for the assignments was obtained from the spectra of the decomposition products. Thus $ClCF_2CFClClO_4$ gave exclusively $ClCF_2COF$ whereas $Cl_2CFCF_2ClO_4$ would have produced Cl_2CFCOF. Similar comparisons and observations regarding the propyl perchlorates and their derivatives resulted in the assignments shown in Table II.

The mass spectra of the perchlorates did not show ions for the parent molecules. Ion fragment assignments were corroborated by the presence of isotopic species in the correct abundance. The highest *m/e* values found generally corresponded to loss of the ClO_4 or ClO_3 groups. Base peaks corresponded to and verified the respective terminal units $CFCl_2$, CF_2Cl, and CF_3. The appearance of these ions as base peaks is typical of simple perhaloalkyl compounds in which they are present.[21] Also typical of such compounds is the appearance of fairly intense peaks for recombination or rearranged ion fragments. This phenomenon was observed as with $ClCF_2CFClClO_4$, where Cl_2CF^+ (~15%) and CF_2Cl^+ (100%) peaks were found. Perchlorate ions were absent from the spectra as they are also absent in the spectrum of Cl_2O_4.[7] Ion fragments corresponding to ClO_3^+, ClO_2^+, and ClO^+ were of appreciable magnitude.

Mass spectra of three of the acid fluorides were obtained. The two propyl compounds, $CF_3CFXCOF$, gave spectra consistent with formulations deduced from infrared and ^{19}F nmr data. Prominent peaks corresponded to the ions, $C_2F_4X^+$, CFX^+, and CF_3^+, with the latter being the base peak. Again appreciable peaks were noted for the rearranged ions, CF_2X^+, particularly in the case of the bromine compound. In addition both compounds exhibited parent peaks corresponding to $C_3F_5XO^+$. The remaining acid fluoride, Cl_2CFCOF, did not give a parent ion peak. The largest *m/e* number fitted the ion $C_2F_2ClO^+$. Other features of its spectrum were analogous to the other halocarbons.

The addition of $XClO_4$ compounds to perhaloolefins is undoubtedly directed since in each case only one product was formed. This would not be expected if the reaction involved a free-radical mechanism. The polar nature of the reactants could be expected to effect a directed addition and such an explanation is adequate for the perfluoropropene reactions

$$CF_3CF{=}CF_2 + XOClO_3 \rightarrow CF_3CFXCF_2ClO_4$$

However, the adducts of chlorotrifluoroethylene are not in keeping with this rationale. Here the only product that was isolated, observed by ^{19}F nmr or indicated by derivative formation, was the opposite of that predicted by polarity considerations. Numerous examples of polar additions to $ClCF{=}CF_2$ have been documented.[22] Usually a mixture of isomers results with the relative amounts dependent on specific reaction conditions. Lacking radical conditions the major and sometimes only product is that expected from a

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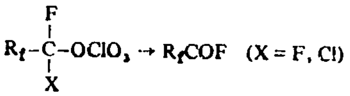
simple polar addition. No examples are known to us in which the alternate adduct is the sole product. Obviously a dominant control is operating but its explanation at this point would be purely speculative.

The overall stability of the perhaloalkyl perchlorates is much superior to that of analogous -OCl compounds.[23] Qualitative tests showed that no decomposition of $CF_3CFClCF_2ClO_4$ occurred on heating in stainless steel at 100° for 72 hr after an initial passivating effect. At 180° complete decomposition in 24 hr produced mainly $CF_3CFClCOF$ with a small amount of COF_2, indicating little carbon–carbon rupture. No decomposition of $ClCF_2CFClClO_4$ was observed after 24 hr at 70° but complete decomposition was found after 72 hr at 100° giving $ClCF_2COF$, $FClO_3$, Cl_2, and O_2. The compound $CF_3CFClCF_2ClO_4$ was insoluble and unaffected by water at ambient temperature.

Alkali metal fluoride catalyzed decomposition of the perchlorates paralleled reported[2,24] reactions of similar fluorosulfate materials. The fluorosulfates produce carbonyl compounds and SO_2F_2 while the perchlorates gave carbonyl compounds and $FClO_3$ or mixtures of $FClO_3$, Cl_2, and O_2. Perchlorates containing $R_fCF_2ClO_4$ structures generated essentially quantitative amounts of $FClO_3$. Perchlorates with $R_fCFClClO_4$ structures gave variable mixtures of $FClO_3$, Cl_2, and O_2. Either type of perchlorate was completely degraded to the respective acid fluoride and was of great assistance in characterizing the perchlorates



$$R_f-\overset{\displaystyle F}{\underset{\displaystyle X}{C}}-OClO_3 \rightarrow R_fCOF \quad (X = F, Cl)$$

Reactions of the $R_fCFClClO_4$ compounds did not yield any acid chlorides and therefore some fluorination by the metal fluoride must have occurred before or after the elimination of ClO_3.

Registry No. $CF_3CF{=}CF_2$, 116-15-4; Cl_2O_4, 27218-16-2; $CF_3CFClCF_2ClO_4$, 38126-25-9; $BrClO_4$, 32707-10-1; $CF_3CFBrCF_2ClO_4$, 38126-26-0; $CF_2{=}CFCl$, 79-38-9; $ClCF_2CFClClO_4$, 38126-27-1; $BrCF_2CFClClO_4$, 38217-36-6; C_2F_4, 116-14-3; $ClCF_2CF_2ClO_4$, 38126-28-2; $ClCF{=}CFCl$, 598-88-9; $Cl_2CFCFClClO_4$, 38126-29-3; $CF_2{=}CFCF{=}CF_2$, 685-63-2; 2-chlorotetrafluoropropionyl fluoride, 28627-00-1; $CF_3CFBrCOF$, 6129-62-0; dichlorofluoroacetyl fluoride, 354-18-7; $ClCF_2COF$, 354-27-8, $BrCF_2COF$, 38126-07-7.

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The Hexafluorochlorine(VII) Cation, ClF_6^+. Synthesis and Vibrational Spectrum

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The ClF_6^+ cation was prepared in the form of its PtF_6^- salt from the reactions of PtF_6 with either $FClO_2$ or ClF_5. A displacement reaction between $ClF_6^+PtF_6^-$ and FNO at −78° yielded only ClF_5 and F_2, indicating that ClF_7 cannot exist under the given reaction conditions. Attempts were unsuccessful to prepare $ClF_6^+BF_4^-$ by low-temperature glow discharge of a ClF_5-F_2-BF_3 mixture, to prepare ClF_6^+ salts from ClF_5, F_2, and the Lewis acid SbF_5, AsF_5, or BF_3 at elevated temperatures and pressures, or to prepare ClF_4O^+ salts either from ClF_3O and PtF_6 or from ClF_3O, F_2, and SbF_5. Iridium hexafluoride was found to be too weak an oxidizer to produce any heptavalent, chlorine-containing cations from $FClO_2$. Vibrational spectra were recorded for PtF_6^- salts of ClF_6^+, ClF_4^+, ClF_2^+, $ClF_2O_2^+$, ClF_2O^+, and ClO_2^+ and for $ClO_2^+IrF_6^-$. Modified valence force fields were computed for the ClF_6^+, PtF_6^-, and IrF_6^- ions.

Introduction

Two preliminary notes on the synthesis of $ClF_6^+PtF_6^-$ from PtF_6 and chlorine fluorides or oxyfluorides have recently been published,[1,2] and the identity of ClF_6^+ was established beyond doubt by ^{19}F nmr spectroscopy.[2,3] The ClF_6^+ cation is of particular interest for two reasons: (1) except for the recently discovered $ClO_2F_2^+$ cation,[4] it is the only known heptavalent chlorine cation and (2) in addition to the NF_4^+ salts,[5-9] it is the only known example of the synthesis of a fluoro cation derived from hitherto unknown compounds (*i.e.*, NF_5 and ClF_7, respectively). In this paper, we give a full account of the synthesis, vibrational spectrum, and force constants of the ClF_6^+ cation.

Experimental Section

Apparatus and Materials. The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellow-seal valves (Hoke, Inc., 425 IF4Y). Pressures were measured with a Heise Bourdon tube type gauge (0–1500 mm ± 0.1%). Because of the rapid hydrolytic interaction with moisture, all materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The spectra of solids were obtained by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a Wilks minipellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded on either a Cary Model 82 or 83 spectrophotometer using the 4880- and 6471-A exciting lines, respectively. Glass melting point capillaries or clear thin-walled Kel-F tubes were used as sample containers in the transverse-viewing-transverse-excitation technique.

Mass spectra were recorded on a Quad 300 (Electronic Associates Inc.) quadrupole mass spectrometer using a passivated all stainless steel inlet system.

Platinum hexafluoride was either purchased (from Ozark Mahoning Co.) or freshly prepared by burning Pt wire in an F_2 atmosphere at −196°, according to the method of Weinstock and his coworkers.[10] Iridium hexafluoride was obtained from Ozark Mahoning Co. Prior to use, both IrF_6 and PtF_6 were purified by fractional condensation at −78° in a dynamic vacuum. Arsenic pentafluoride (Ozark Mahoning Co.) was purified by fractional condensation and SbF_5 (Ozark Mahoning Co.) by distillation. Chlorine pentafluoride (Rocketdyne) was stored over dry CsF to remove any ClF_3 and purified by fractional condensation through traps kept at −112 and −126° with the material retained at −126° being used. Fluorine (Rocketdyne) was passed over NaF to remove HF. Chloryl fluoride was prepared from $KClO_3$ and ClF_3,[11] ClF_3O by fluorination of $ClONO_2$,[12] and FNO from NO and F_2 at −196°. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra.

The $FClO_2$-PtF_6 System. Platinum hexafluoride (17.0 mmol) and $FClO_2$ (46.1 mmol) were combined at −196° in a passivated (with ClF_3) 75-ml stainless steel cylinder. The mixture was allowed to warm up slowly to 25° and was kept at this temperature for 3 days. The cylinder was cooled to −196° and 3.75 mmol of material volatile at this temperature was removed and identified as F_2 by its vapor pressure and mass spectrum. The products volatile at 25° were separated by fractional condensation through traps kept at −78, −126, and −196°. The −126° fraction consisted of $FClO_2$ (28.7 mmol) and the −196° one of $FClO_2$ (0.3 mmol), ClF_5 (0.1 mmol), and a small amount of $FClO_3$. The cylinder contained a stable canary yellow solid (6.618 g), which was identified by infrared spectroscopy as a mixture of $ClO_2^+PtF_6^-$ and $ClO_2F_2^+PtF_6^-$. Hence, PtF_6 (17.0 mmol) had reacted with $FClO_2$ (17.1 mmol) in a 1:1 mole ratio yielding F_2 (3.75 mmol), $ClO_2^+PtF_6^-$ (12.2 mmol = 4.594 g), and $ClO_2F_2^+PtF_6^-$ (4.8 mmol = 2.000 g) as the main products.

Platinum hexafluoride (2.04 mmol) and $FClO_2$ (3.08 mmol) were combined at −196° in a passivated sapphire reaction tube (Varian, Model CS-4250-3). The reactor was rapidly warmed from −196 to −78° and kept at −78° for 48 hr. At the end of this time period, the brown PtF_6 color had completely disappeared and a canary yellow solid had formed. The reactor was cooled to −196° and noncondensable material (0.33 mmol of O_2) was removed. The product volatile at 25° consisted of $FClO_2$ (1.03 mmol). The yellow, solid residue weighed 800 mg and was shown by infrared, Raman, and ^{19}F nmr spectroscopy to be a mixture of $ClF_6^+PtF_6^-$ and $ClO_2^+PtF_6^-$ (weight calculated for a mixture of 1.70 mmol of $ClO_2^+PtF_6^-$ and 0.34 mmol of $ClF_6^+PtF_6^-$ = 796 mg). Hence, PtF_6 (2.04 mmol) had reacted with $FClO_2$ (2.05 mmol) in a 1:1 mole ratio producing O_2 (0.33 mmol) and a 1:5 mole ratio mixture of $ClF_6^+PtF_6^-$ and $ClO_2^+PtF_6^-$.

The ClF_5-PtF_6 System. Platinum hexafluoride (2.70 mmol) and ClF_5 (3.90 mmol) were combined at −196° in a passivated sapphire reactor. The mixture was kept 25° for 24 hr. Since the brown PtF_6 color was still very intense, the tube was exposed to unfiltered uv radiation from a Hanovia Model 616A high-pressure quartz mercury vapor arc. After 24 hr of uv irradiation, the dark brown PtF_6 color

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had disappeared and a yellow to brown solid had formed. The product was kept for 12 hr at −20° without irradiation and its color changed to yellow-orange. The reactor was cooled to −196° and noncondensables (2.58 mmol of F_2) were removed. The reactor was warmed up to 25° and the volatile products were separated by fractional condensation. They consisted of ClF_5 (1.08 mmol) and ClF_3 (0.12 mmol). The yellow solid residue weighed 1.096 g (weight calculated for a mixture of 0.84 mmol of $ClF_6^+PtF_6^-$ and 1.86 mmol of $ClF_2^+PtF_6^-$ is 1.097 g). The identity of this solid as $ClF_2^+PtF_6^-$ and $ClF_6^+PtF_6^-$ was verified by ^{19}F nmr, infrared, and Raman spectroscopy. Hence, PtF_6 (2.70 mmol) had reacted with ClF_5 (2.70 mmol) producing $ClF_6^+PtF_6^-$ (0.84 mmol), $ClF_2^+PtF_6^-$ (1.86 mmol), and F_2 (2.46 mmol). In addition, some of the ClF_5 (0.12 mmol), which had been used in excess, had decomposed to ClF_3 and F_2.

In a second experiment, PtF_6 (5.26 mmol) and ClF_5 (8.02 mmol) were combined at −196° in a sapphire reactor. The mixture was exposed at ambient temperature to uv radiation from a Hanovia Model 616A high-pressure Hg arc using a Pyrex–water filter. After 14 days of irradiation, the PtF_6 color had disappeared and a yellow to orange solid had formed. The volatile products consisted of F_2 (0.23 mmol), ClF_5 (3.23 mmol), and a trace of ClF_3. The solid residue weighed 2.245 g and was, according to its infrared spectrum, a mixture of $ClF_6^+PtF_6^-$ and $ClF_4^+PtF_6^-$. It appears that owing to the long reaction time and uv irradiation, some PtF_6 (0.46 mmol as indicated by the F_2 evolution and by the weight of the solid reaction product) had reacted with the container walls. Hence, PtF_6 (4.80 mmol) had reacted with ClF_5 (4.79 mmol) producing $ClF_4^+PtF_6^-$ (2.40 mmol) and $ClF_6^+PtF_6^-$ (2.40 mmol). The observed weight of the solid product (2.245 g) agreed well with that calculated (2.252 g) for the above reactions.

Displacement Reaction between FNO and $ClF_6^+PtF_6^-$. To a mixture (0.390 g) of $ClF_6^+PtF_6^-$ (0.30 mmol) and $ClF_2^+PtF_6^-$ (0.66 mmol) in a passivated Teflon–FEP ampoule, FNO (6.75 mmol) was added at −196°. The contents of the ampoule were kept at −78° for 12 hr. The ampoule was cooled to −196° and F_2 (0.28 mmol) was removed. The products volatile at ambient temperature were separated by fractional condensation and consisted of FNO (5.76 mmol), ClF_3 (0.64 mmol), and ClF_5 (0.27 mmol). The yellow, solid residue weighed 0.329 g (calculated weight for 0.96 mmol of $NO^+PtF_6^-$ is 0.326 g) and was identified by its infrared spectrum as $NO^+PtF_6^-$.

Reaction between ClF_3O and PtF_6. Platinum hexafluoride (1.87 mmol) and ClF_3O (4.71 mmol) were combined at −196° in a sapphire reaction tube. When the mixture was allowed to warm to 25°, a rapid reaction with gas evolution occurred and the characteristic PtF_6 color disappeared within a few minutes. The mixture was kept at 25° for several hours and was then cooled to −196°. Fluorine (0.78 mmol) was removed at −196° and ClF_3O (2.05 mmol), ClF_5 (0.14 mmol), and $FClO_2$ (0.48 mmol) were removed at 25°. The canary yellow residue weighed 0.749 g (weight calculated for 1.87 mmol of $ClF_2O^+PtF_6^-$ is 0.746 g) and was identified as $ClF_2O^+PtF_6^-$ by its infrared, Raman, and ^{19}F nmr spectrum.

In another experiment, PtF_6 (2.12 mmol) and ClF_3O (5.51 mmol) were allowed to interact at −45° for 12 hr. The volatile products consisted of F_2 (1.60 mmol), ClF_3O (3.35 mmol), $FClO_2$ (0.07 mmol), and a small amount of ClF_5 and PtF_6. The yellow solid residue weighed 0.837 g (weight calculated for 2.12 mmol of $ClF_2O^+PtF_6^-$ is 0.845 g). The infrared spectrum of the solid showed it to be mainly $ClF_2O^+PtF_6^-$ but also revealed the presence of smaller amounts of $ClO_2F_2^+$ and ClF_6^+ salts.

Reaction between $FClO_2$ and IrF_6. Chloryl fluoride (2.57 mmol) and IrF_6 (1.96 mmol) were combined at −196° in a sapphire reactor. The mixture was kept at −78° for 48 hr and then cooled to −196°. All products were condensed at this temperature. At 25°, almost all of the starting materials were recovered unchanged except for 0.011 g of a yellowish solid which was identified by its infrared spectrum as $ClO_2^+IrF_6^-$. The unreacted starting materials were condensed back into the reactor and kept at 25° for 11 days. After this period, the product still showed the original brown color but had partially solidified. The mixture was cooled to −196° at which temperature 0.03 mmol of noncondensable material was removed. The material volatile at 25° consisted of IrF_6 (1.12 mmol), $FClO_2$ (1.88 mmol), and ClF_5 (0.21 mmol). The yellow crystalline solid weighed 0.147 g (0.39 mmol) and was identified by infrared and Raman spectroscopy as $ClO_2^+IrF_6^-$.

Attempted Syntheses of $ClF_6^+SbF_6^-$, $ClF_6^+AsF_6^-$, $ClF_6^+BF_4^-$, and $ClF_2O^+SbF_6^-$. When mixtures of ClF_5, F_2, and AsF_5 in different mole ratios were heated in Monel cylinders for 5–10 days at 125–145° under autogenous pressures of 500–1000 psi, only unreacted starting materials were recovered in addition to very small amounts of metal AsF_6^- salts. Heating the mixture to 160° resulted in partial breakdown of ClF_5 to ClF_3 and F_2.

Heating a BF_3, F_2, and ClF_5 mixture (mole ratio 1:2.7:2) for 8 days to 95° under an autogenous pressure of 450 psi did not result in the formation of a solid product.

Mixtures of ClF_5, F_2, and SbF_5 (mole ratio 1:5:3) were heated for 3–40 days in Monel cylinders at 140–225° under autogenous pressures of ~1000 psi. At 140° and 3 days' reaction time, no F_2 consumption was observed. At 160° and 25 days' reaction time, 6.5% of the F_2 used was consumed due to attack on the cylinder. The solid product was a mixture of ClF_2^+, ClF_4^+, Ni^{2+}, and Cu^{2+} salts of $SbF_6^-\cdot xSbF_5$. Controlled vacuum pyrolysis of this solid resulted in the evolution of ClF_5 at lower and of ClF_3 at higher temperatures. The composition of the solid residues of this stepwise pyrolysis was monitored by infrared and Raman spectroscopy. It was shown that the more stable component having strong absorptions in the infrared and Raman spectra at 825 and 836 cm^{-1} generated only ClF_3 when heated in the presence of CsF. When the reaction between ClF_5, F_2, and SbF_5 was carried out at 225°, $ClF_2^+SbF_6^-$ was formed with F_2 evolution.

Glow discharge of a BF_3, F_2, and ClF_5 mixture (mole ratio 1:1.42:1) at −78° in a Pyrex apparatus at pressures ranging from 20 to 50 mm produced only $ClF_2^+BF_4^-$ and no ClF_6^+ salt.

Heating a mixture of ClF_3O, F_2, and SbF_5 (mole ratio 1:10:5) in a Monel cylinder to 135° for 6 days under an autogenous pressure of 600 psi produced exclusively $ClF_2O^+SbF_6^-\cdot xSbF_5$.

Results and Discussion

Synthesis of ClF_6^+ Salts. Complex fluoro cations of the type XF_{y-1}^+ are generally prepared through fluorine abstraction from the parent compound XF_y by means of a strong Lewis acid. This was first demonstrated in 1949 by Woolf and Emeleus[13] for BrF_3

$$BrF_3 + SbF_5 \rightarrow BrF_2^+SbF_6^- \quad (1)$$

The synthesis of a fluoro cation from a lower fluoride, according to

$$XF + F^+ \rightarrow XF_2^+ \quad (2)$$

is preempted by the fact that fluorine is the most electronegative element. Hence, F^+ should be extremely difficult if not impossible to prepare by chemical means. The first and only known synthesis of a fluoro cation derived from a nonexisting parent compound was achieved[5,9] in 1966, according to

$$NF_3 + F_2 + AsF_5 \rightarrow NF_4^+AsF_6^- \quad (3)$$

This synthesis involved either glow discharge[5] or elevated temperature and pressure.[9] Since tetrahedral and octahedral species exhibit outstanding stability, as demonstrated by CF_4 and SF_6, the successful synthesis of NF_4^+ suggested the feasibility of synthesizing ClF_6^+ salts.

The application of glow discharge to the synthesis of ClF_6^+ salts is limited to the ClF_5–F_2–BF_3 system. Stronger Lewis acids, such as AsF_5, form adducts with ClF_5,[14] thus preventing the use of the low-temperature glow-discharge technique. In the case of BF_3, we did not successfully prepare $ClF_6^+BF_4^-$, owing to rapid breakdown of ClF_5 to ClF_3 and F_2, followed by removal of the ClF_3 from the gas phase by complex formation with BF_3.[15] The possible utility of the second technique, involving elevated temperature and pressure, for the synthesis of ClF_6^+ salts was also examined with BF_3, AsF_5, or SbF_5 as Lewis acids. At lower temperatures, no fluorination of ClF_5 occurred, whereas at higher temperatures, breakdown of ClF_5 to ClF_3 and F_2 was observed. Since ClF_2^+ salts are thermally more stable than the corresponding ClF_4^+ salts, ClF_3 was continuously removed from the $ClF_5 \rightleftarrows ClF_3 + F_2$ equilibrium by complexing until essentially all the ClF_5 was converted to ClF_2^+ and F_2.

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Since the techniques which had successfully been used for the synthesis of NF_4^+ salts did not result in ClF_6^+, other fluorinating agents were investigated. Of particular interest were the third transition series hexafluorides which exhibit an astonishing oxidizing power.[16] It was found[17] that PtF_6 and $FClO_2$, when combined at −196° and allowed to warm up slowly to 25°, interacted according to

$$2FClO_2 + 2PtF_6 \rightarrow ClO_2F_2^+PtF_6^- + ClO_2^+PtF_6^- \qquad (4)$$

The yield of $ClO_2F_2^+$ was not 50% as expected from the above equation, but generally about 25% owing to the competing reaction

$$2FClO_2 + 2PtF_6 \rightarrow 2ClO_2^+PtF_6^- + F_2 \qquad (5)$$

In some of the experiments, small amounts of $ClF_6^+PtF_6^-$ (see below) or ClF_5 and $FClO_3$ were observed, depending on the exact reaction conditions. The formation of some $FClO_3$ is not surprising since it is known that $FClO_2$ readily interacts with nascent oxygen to yield $FClO_3$.[18,19]

Attempts to suppress the competing reaction (eq 5) by changing the reaction conditions (rapid warm-up from −196 to −78° and completion of the reaction at −78°) resulted on one occasion in an entirely different course for the reaction

$$6FClO_2 + 6PtF_6 \rightarrow 5ClO_2^+PtF_6^- + ClF_6^+PtF_6^- + O_2 \qquad (6)$$

The observed material balance was in excellent agreement with eq 6 and the identity of ClF_6^+ was unequivocally established by ^{19}F nmr spectroscopy.[3] Further modification of the reaction conditions (rapid warm-up of the $FClO_2$-PtF_6 mixture from −196 to either −78 or 25° and completion of the reaction at 25°) did not produce detectable amounts of either $ClO_2F_2^+$ or $ClF_6^+PtF_6^-$, but only $ClO_2^+PtF_6^-$ and ClF_5, F_2, and O_2. This indicates that the nature of the reaction products is more influenced by the warm-up rate of the starting materials from −196 to about −78° than by the final reaction temperature. Slow warm-up favors the formation of $ClO_2F_2^+$, whereas rapid warm-up yields ClF_6^+ or ClF_5 and F_2. The above results for the $FClO_2$-PtF_6 system indicated that ClF_5 might be an important intermediate in the formation of ClF_6^+. In order to prove the correctness of this assumption and in order possibly to increase the yield of ClF_6^+, which according to eq 6 can be at best one-sixth based on PtF_6, we have studied also the ClF_5-PtF_6 system. For the latter system, Roberto reported[1] the formation of a ClF_6^+ salt. Owing to the slow reaction rates in the ClF_5-PtF_6 system, we have used uv radiation. Two reactions were carried out at 25°. When unfiltered uv radiation was used, the reaction was complete in several hours, according to

$$2ClF_5 + 2PtF_6 \xrightarrow[uv]{unfiltered} ClF_2^+PtF_6^- + ClF_6^+PtF_6^- + F_2 \qquad (7)$$

and

$$2ClF_5 + 2PtF_6 \rightarrow 2ClF_2^+PtF_6^- + 3F_2 \qquad (8)$$

The relative contributions from (7) and (8) were 62 and 38%, respectively. In addition, some of the ClF_5, which had been used in excess, was recovered in the form of ClF_3 and F_2.

Using a Pyrex-water filter, a reaction time of 2 weeks was required with the products being

$$2ClF_5 + 2PtF_6 \xrightarrow[uv]{Pyrex\ filter} ClF_4^+PtF_6^- + ClF_6^+PtF_6^- \qquad (9)$$

Since unfiltered uv light can decompose ClF_5 into ClF_3 + F_2 [20] and since ClF_2^+ salts are more stable than ClF_4^+ salts,[14] the displacement of ClF_4^+ by ClF_3, observed for (7), is not surprising. The identity of the ClF_6^+ salt obtained from the $FClO_2$-PtF_6 system with that from the ClF_5-PtF_6 system was established by infrared, Raman, and ^{19}F nmr spectroscopy. The unusual nature of these reactions and products ask for a possible rationalization. In spite of the complexity of the $FClO_2$-PtF_6 system, the following assumptions appear plausible.

(a) An initial electron transfer from $FClO_2$ to PtF_6 may take place according to

$$FClO_2 + PtF_6 \rightarrow FClO_2{\cdot}^+PtF_6^- \qquad (10)$$

(b) The resulting $FClO_2{\cdot}^+$ radical cation could either stabilize by generating an active fluorine radical, according to

$$FClO_2{\cdot}^+PtF_6^- \rightarrow ClO_2^+PtF_6^- + F{\cdot} \qquad (11)$$

or act itself as the active fluorinating agent, depending upon the relative lifetimes of these two radicals.[21]

(c) In both cases ($F{\cdot}$ or $ClO_2F{\cdot}^+$), the radical might react either with PtF_6 with F_2 evolution

$$F{\cdot} + PtF_6 \rightarrow F_2 + PtF_5 \qquad (12)$$

followed by

$$PtF_5 + FClO_2 \rightarrow ClO_2^+PtF_6^- \qquad (13)$$

or with $FClO_2$

$$FClO_2 + F{\cdot} \rightarrow F_2ClO_2{\cdot} \qquad (14)$$

(d) The resulting $F_2ClO_2{\cdot}$ radical could readily stabilize by transfer of an electron to PtF_6

$$F_2ClO_2{\cdot} + PtF_6 \rightarrow ClO_2F_2^+PtF_6^- \qquad (15)$$

This sequence would account for the formation of $ClO_2F_2^+$ and for the competitive F_2 evolution reaction. Similarly, the formation of ClF_6^+ from ClF_5 and PtF_6 might involve an intermediate $ClF_5{\cdot}^+$ radical cation and suggests a search for radical cations in these systems. The formation of ClF_6^+ from $FClO_2$ might involve either an intermediate ClF_5 molecule or the direct fluorination of $ClO_2F_2^+$ to ClF_6^+. A definitive answer to these interesting questions concerning the most important intermediates is beyond the scope of the present study.

Properties of ClF_6^+ Salts. The $ClF_6^+PtF_6^-$ salts are canary yellow solids. They were stored at 25° in Teflon-FEP containers for several months without noticeable decomposition and formed stable HF solutions. They are very powerful oxidizers and react explosively with organic materials or water. Contrary to a previous statement,[1] no evidence was found during our investigation that the ClF_6^+ salts themselves can be explosive.

The Question of the Existence of ClF_7. A displacement reaction between $ClF_6^+PtF_6^-$ and FNO was carried out under conditions similar to those which had successfully been used for the synthesis of ClF_3O_2 from $ClO_2F_2^+PtF_6^-$ and FNO.[4] Since $ClF_6^+PtF_6^-$ can be considered as a Lewis acid adduct between ClF_7 and PtF_5, the products from the

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(21) When the reaction between $FClO_2$ and PtF_6 was carried out at low temperature in an inert solvent such as BrF_5 or $FClO_3$, no detectable amounts of $ClO_2F_2^+$ were formed with the only products being $ClO_2^+PtF_6^-$ and F_2. One might expect a fluorine radical to have a comparable lifetime in either excess $FClO_2$ or the solvents $FClO_3$ or BrF_5, whereas a $FClO_2{\cdot}^+$ radical could stabilize itself by rapid intermolecular exchange with $FClO_2$ only. Therefore, the lack of $ClO_2F_2^+$ formation in $FClO_3$ or BrF_5 solution strongly suggests that the $FClO_2{\cdot}^+$ cation is the active fluorination agent.

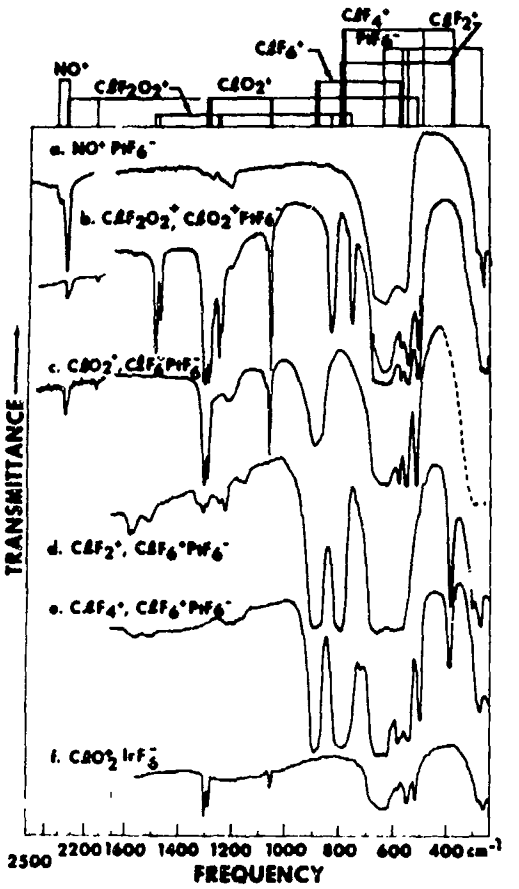

Figure 1. Infrared spectra of the solid products obtained from the following reactions: trace a, displacement reaction between FNO and a mixture of $ClF_2^+PtF_6^-$ and $ClF_6^+PtF_6^-$; traces b and c, $FClO_2 + PtF_6$ at 25 and −78°, respectively; traces d and e, ClF_5 and PtF_6 using unfiltered and filtered uv radiation, respectively; trace f, $FClO_2 + IrF_6$ at 25°. All spectra were recorded as pressed AgBr disks, except for trace c for which a AgCl disk was used.

FNO displacement reaction allow some conclusions concerning the stability of the hypothetical compound ClF_7. The following results were obtained for the displacement reaction

$$ClF_6^+PtF_6^- + FNO \xrightarrow{-78°} NO^+PtF_6^- + ClF_5 + F_2 \qquad (16)$$

This indicates that ClF_7 under the given reaction conditions (−78°) cannot exist.

Iridium Hexafluoride Reactions. Replacement of PtF_6 by IrF_6 in the $FClO_2$ reaction did not result in an oxidative fluorination of Cl(+V) to Cl(+VII). At 25° and long reaction times, only $ClO_2^+IrF_6^-$ and ClF_5 were formed in moderate yields. This demonstrates that IrF_6 is a weaker fluorinating oxidizer than PtF_6 as has previously been demonstrated by Bartlett.[16]

Attempted Synthesis of ClF_4O^+ Salts. The successful syntheses[1,2,4] of the $ClO_2F_2^+$ and the ClF_6^+ cation suggested the possible synthesis of the intermediate ClF_4O^+ cation from ClF_3O and PtF_6. At 25°, the main reaction was

$$2ClF_3O + 2PtF_6 \xrightarrow{25°} 2ClF_2O^+PtF_6^- + F_2 \qquad (17)$$

In addition, small amounts of $FClO_2$ and ClF_5 were observed among the volatile reaction products. When the reaction temperature was lowered to −45°, the main products were again $ClF_2O^+PtF_6^-$ and F_2. However, small amounts of $ClO_2F_2^+$ and $ClF_6^+PtF_6^-$ had also formed. No evidence for the presence of any ClF_4O^+ could be obtained. This suggests that tetrahedral $ClF_2O_2^+$ and octahedral ClF_6^+ are more favorable products than the pseudo trigonal-bipyramidal ClF_4O^+. The formation of small amounts of $ClO_2F_2^+$ and ClF_6^+ (or $FClO_2$ and ClF_5) might be due either to the decomposition of an unstable intermediate, such as ClF_4O^+, into $ClO_2F_2^+$ and ClF_6^+, or at least partially to the formation of some $FClO_2$ from the difficult to handle ClF_3O.[12] Attempts to synthesize $ClF_4O^+SbF_6^-$ from ClF_3O-F_2-SbF_5 at elevated temperature and pressure produced exclusively $ClF_2O^+SbF_6^- \cdot xSbF_5$.[21a]

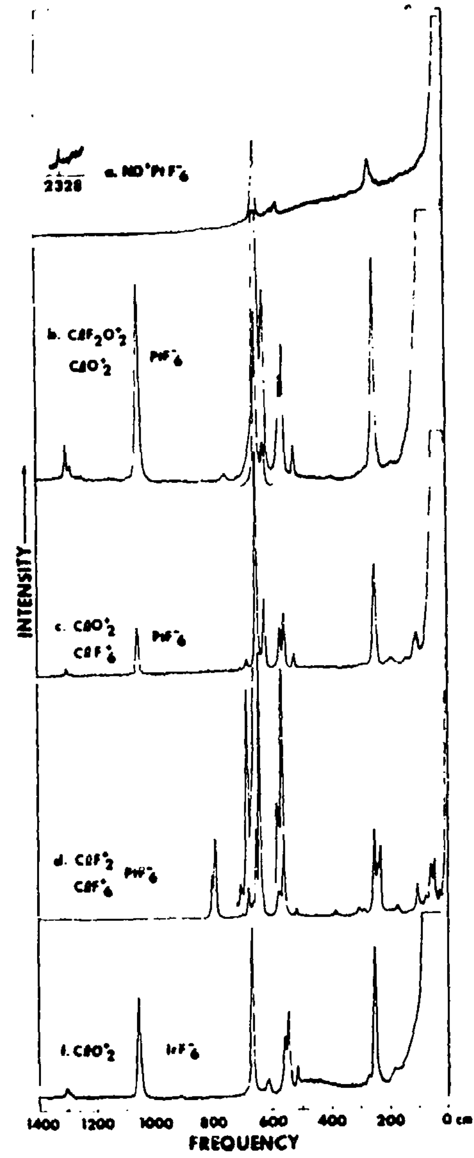

Figure 2. Raman spectra of some of the solid products shown in Figure 1 using the same notations. All spectra were recorded for dry powders in glass melting point capillaries, using the 6471-Å exciting line on a Cary Model 82.

Vibrational Spectra. The infrared and Raman spectra of the solid reaction products are shown by Figures 1 and 2, respectively. The spectrum of $ClF_2O^+PtF_6^-$ was identical with that previously reported[22] and, hence, is not depicted.

[21a] Note Added in Proof. The ClF_3O-PtF_6 reaction was also studied at low temperature in either $FClO_2$ or BrF_5 solution. Furthermore the interaction between $Cs^+ClF_4O^-$ and PtF_6 was investigated either in the absence of a solvent or in $FClO_2$ solution. In all cases the solid reaction product was $ClF_2O^+PtF_6^-$.

[22] C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, *Inorg. Chem.*, 11, 2201 (1972).

Table I. Vibrational Spectra[a] of Several PtF_6^- Salts and of $ClO_2^+IrF_6^-$ and Their Assignment

$NO^+PtF_6^-$

Obsd freq, cm⁻¹ Ir	Obsd freq, cm⁻¹ Raman	Assignment for PtF_6^- in O_h
2385 mw		$\nu(NO)$
2329 ms	2328 (0+)	
1280 w, br		$\nu_1 + \nu_3$ (F_{1u}) PtF_6^-
1212 w, br		$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$) PtF_6^-
880 vw, br		$\nu_3 + \nu_5$ ($A_{2u} + E_u + F_{1u} + F_{2u}$) PtF_6^-
830 vw, br		$\nu_2 + \nu_4$ ($F_{1u} + F_{2u}$) PtF_6^-
640 vs, br		ν_3 (F_{1u}) PtF_6^-
	644 (10)	ν_1 (A_{1g}) PtF_6^-
	589 (0+)	ν_2 (E_g) PtF_6^-
570 s	570 (2)	
295 mw		ν_4 (F_{1u}) PtF_6^-
269 ms		
	249 (4)	ν_5 (F_{2g}) PtF_6^-
	235 sh	

$ClO_2^+, ClF_2O_2^+PtF_6^-$

Obsd freq, cm⁻¹ Ir	Obsd freq, cm⁻¹ Raman	Assignment for ClO_2^+ and $ClF_2O_2^+$ in C_{2v}, for PtF_6^- in O_h
2340 w		$\nu_1 + \nu_3$ (B_1) ClO_2^+
2330		
2115 vw		$2\nu_1$ (A_1) ClO_2^+
1486 s		ν_6 (B_1) $ClF_2O_2^+$
1470		
1297 vs	1299 (0.5)	ν_3 (B_1) ClO_2^+
1283 s	1285 (0.17)	
1245 s	1246 (0+)	ν_1 (A_1) $ClF_2O_2^+$
1237		
1210 w		$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$) PtF_6^-
1052 s	1051 (2.7)	ν_1 (A_1) ClO_2^+
1047 m		
827 s		ν_8 (B_2) $ClF_2O_2^+$
756 s	754 (0.1)	ν_2 (A_1) $ClF_2O_2^+$
640 vs	617 (2.5)	ν_3 (F_{1u}) PtF_6^-
	642 (10)	ν_1 (A_{1g}) PtF_6^-
580 w	564 (1.3)	ν_2 (E_g) PtF_6^-
552 s	552 (1.8)	
530 sh		ν_3 (A_1), ν_7 (B_1), ν_9 (B_2) $ClF_2O_2^+$
	514 (0.4)	
514 s		ν_2 (A_1) ClO_2^+
284 m		ν_4 (F_{1u}) PtF_6^-
265 s		
	239 (2.9)	ν_5 (F_{2g}) PtF_6^-
	180 (0+)	ν_6 (F_{2u}) PtF_6^-

$ClO_2^+, ClF_6^+PtF_6^-$

Obsd freq, cm⁻¹ Ir	Obsd freq, cm⁻¹ Raman	Assignment for ClO_2^+ in C_{2v}, for ClF_6^+ and PtF_6^- in O_h
2340 w		$\nu_1 + \nu_3$ (B_1) ClO_2^+
2330		
1297 vs	1299 (0.3)	ν_3 (B_1) ClO_2^+
1283 s	1285 (0.1)	
1210 w		$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$) PtF_6^-
1053 s	1054 (2.0)	ν_1 (A_1) ClO_2^+
1049 m		
890 s		ν_3 (F_{1u}) ClF_6^+
	679 (0.5)	ν_1 (A_{1g}) ClF_6^+
640 vs		ν_3 (F_{1u}) PtF_6^-
620	618 (3.1)	
	644 (10)	ν_1 (A_{1g}) PtF_6^-
580 ms	569 (1.8)	ν_2 (E_g) PtF_6^-
552 s	554 (2.5)	
516 s	518 (0.6)	ν_2 (A_1) ClO_2^+, ν_5 (F_{2g}) ClF_6^+
	240 (4.5)	ν_5 (F_{2g}) PtF_6^-
	185 (0.2)	ν_6 (F_{2u}) PtF_6^-
	130 (0.1)	Lattice vib
	98 (1.0)	

$ClF_2^+, ClF_6^+PtF_6^-$

Obsd freq, cm⁻¹ Ir	Obsd freq, cm⁻¹ Raman	Assignment for ClF_2^+ in C_{2v}, for ClF_6^+ and PtF_6^- in O_h
1576 w		$\nu_1 + \nu_3$ (B_1) ClF_2^+
1564 w		$\nu_1 + \nu_3$ (F_{1u}) ClF_6^+
1510 w		$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$) ClF_6^+
1298 w		ν_3 (B_1) ClO_2^+
1284		$\nu_1 + \nu_3$ (F_{1u}) PtF_6^-
1240 w		$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$) PtF_6^-
1216		$\nu_2 + \nu_4$ ($F_{1u} + F_{2u}$) ClF_6^+
1160 vw		$\nu_1 + \nu_2$ (A_1) ClF_2^+
890 vs		ν_3 (F_{1u}) ClF_6^+
799 vs	799 (1.3)	ν_3 (B_1) ClF_2^+
789 vs	788 (3.0)	ν_1 (A_1) ClF_2^+
	784 (1)	
733 vw		$\nu_3 + \nu_6$ ($F_{1u} + F_{2u}$) PtF_6^-
	704 (0+)	
	679 (1.0)	ν_1 (A_{1g}) ClF_6^+
655 vs, br	661 (0+)	ν_3 (F_{1u}) PtF_6^-
	651 (2.5)	
	639 (10)	ν_1 (A_{1g}) PtF_6^-
	630 sh	ν_2 (E_g) ClF_6^+
565 s, br	582 (0.8)	ν_2 (E_g) PtF_6^-
	576	
	561 (3.1)	
510 w, sh	513 (0.3)	ν_5 (F_{2g}) ClF_6^+
478 w, sh		
381 s	381 (0.2)	ν_2 (A_1) ClF_2^+
376 sh		
304 m	300 (0.3)	ν_4 (F_{1u}) PtF_6^-
265 s	282 (0.2)	
	249 (3.2)	ν_5 (F_{2g}) PtF_6^-
	236 sh	
	229 (2.5)	
	170 (0.3)	ν_6 (F_{2u}) PtF_6^-
	101 (0.9)	Lattice vib
	72 (0.3)	
	54 (1.5)	
	42 (1.6)	
	26 (0.4)	

$ClF_2O^+PtF_6^-$

Obsd freq, cm⁻¹ Ir	Obsd freq, cm⁻¹ Raman	Assignment for ClF_2O^+ in C_s, for PtF_6^- in O_h
1326 ms	1324 (0.6)	ν_1 (A′) ClF_2O^+
1313 mw	1311 (0.2)	
737 s	737 (2.7)	ν_2 (A′) ClF_2O^+
705 s	706 (0.8)	ν_5 (A″) ClF_2O^+
643 vs	658 (4.3)	ν_3 (F_{1u}) PtF_6^-
630 sh	630 (10)	ν_1 (A_{1g}) PtF_6^-
564 s	575 sh	ν_2 (E_g) PtF_6^-
	564 (2.9)	
506 s	506 (0.5)	ν_3 (A′) ClF_2O^+
401 ms	401 (0.7)	ν_6 (A″) ClF_2O^+
386 ms	386 (0.3)	ν_4 (A′) ClF_2O^+
	280 (0.3)	ν_4 (F_{1u}) PtF_6^-
	239 (7.9)	ν_5 (F_{2g}) PtF_6^-
	140 (0.3)	Lattice vib
	115 (0.3)	
	58 (1.0)	

$ClF_4^+, ClF_6^+PtF_6^-$

Obsd freq, cm⁻¹ Ir	Assignment for ClF_4^+ in C_{2v}, for ClF_6^+ and PtF_6^- in O_h
1560 w	$\nu_1 + \nu_3$ (F_{1u}) ClF_6^+
1515 w	$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$) ClF_6^+
1200 w, br	$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$) PtF_6^-
890 vs	ν_3 (F_{1u}) ClF_6^+
878 sh	
785 vs	ν_8 (B_2), ν_1 (A_1), ν_6 (B_1) ClF_4^+
720 vw	$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$) PtF_6^-
670 vs	ν_3 (F_{1u}) PtF_6^-
630	
580 ms	ν_2 (E_g) PtF_6^-
572 mw	ν_2 (A_1) ClF_4^+
561 sh	ν_7 (B_1) ClF_4^+
545 s	
500 s	ν_3 (A_1) ClF_4^+
382 s	ν_9 (B_2) ClF_4^+
281 sh	ν_4 (F_{1u}) PtF_6^-
271 s	

$ClO_2^+IrF_6^-$

Obsd freq, cm⁻¹ Ir	Obsd freq, cm⁻¹ Raman	Assignment for ClO_2^+ in C_{2v}, for IrF_6^- in O_h
1300 vs	1301 (0.6)	ν_3 (B_1) ClO_2^+
1286 s	1287 (0.2)	
1057 s	1057 (6.1)	ν_1 (A_1) ClO_2^+
	670 (10)	ν_1 (A_{1g}) IrF_6^-
640 vs, br		ν_3 (F_{1u}) IrF_6^-
	618 (0.9)	
580 w	561 (2.5)	ν_2 (E_g) IrF_6^-
548 s	549 (4.5)	
518 s	519 (1.1)	ν_2 (A_1) ClO_2^+
279 m		ν_4 (F_{1u}) IrF_6^-
258 s		
	248 (8.5)	ν_5 (F_{2g}) IrF_6^-
	185 (0.2)	ν_6 (F_{2u}) IrF_6^-

[a] Raman intensities are uncorrected.

Attempts to record the Raman spectrum of the $ClF_4^+PtF_6^-$-$ClF_6^+PtF_6^-$ mixture were unsuccessful owing to rapid sample decomposition by the laser beam. From a large number of experiments, those spectra and products were selected which showed the least amounts of by-products. Depending upon the exact reaction conditions, however, the products sometimes were more complex mixtures of ClO_2^+, $ClO_2F_2^+$, and ClF_6^+ or of ClF_2^+, ClF_4^+, and ClF_6^+. The observed frequencies are listed in Table I.

Since most products contain the PtF_6^- anion, its spectrum will be discussed first. The simplest spectrum is that of $NO^+PtF_6^-$. Our observed spectrum is in good agreement with that previously reported[16,23,24] for this compound. In addition to the reported bands, we have observed an infrared band at 268 cm^{-1}. The crystal structure of $O_2^+PtF_6^-$ (which is isomorphous with $NO^+PtF_6^-$ [16]) has been determined.[25] It was shown that PtF_6^- is approximately octahedral;[25] however, its site symmetry[26] is lower than O_h. This site symmetry lowering can cause splitting of most of the bands and violations of the selection rules expected for symmetry O_h. Since the crystal structures and, hence, the actual site symmetries of PtF_6^- in the other chlorine fluoride salts are unknown and since the observed splittings are relatively small, the assignments for PtF_6^- in Table I were made based on the group symmetry O_h. In addition to the previously assigned bands,[16,23,24] the antisymmetric deformation, ν_4 (F_{1u}), and the normally inactive ν_6 (F_{2u}) mode were observed at about 265 and 180 cm^{-1}, respectively. The spectrum observed for IrF_6^- is in good agreement with that of PtF_6^-. In addition to the previously reported[23] bands, the ν_4 and ν_6 modes were also observed for IrF_6^-.

The vibrational spectra of ClO_2^+,[27] $ClF_2O_2^+$,[4,28] ClF_2^+,[29,30] ClF_2O^+,[22,31,32] and ClF_4^+ [33] have been reported elsewhere. The assignments given in Table I are in excellent agreement with those previously given for these ions and, hence, require no further discussion. Assignments for ClF_6^+, whose identity and octahedral structure have been established beyond doubt by ^{19}F nmr spectroscopy,[3] were made on the basis of the following arguments. For octahedral ClF_6^+, we would expect ideally six normal modes of vibration which are classified as $A_{1g} + E_g + 2\,F_{1u} + F_{2g} + F_{2u}$. Of these, only the two F_{1u} modes will be infrared active, while only the A_{1g}, E_g, and F_{2g} modes will be Raman active, assuming no other solid-state effects such as site symmetry lowering or slight distortion of the octahedron. Three different salts containing $ClF_6^+PtF_6^-$ have been studied. In addition to ClF_6^+, they contain the ClO_2^+ or the ClF_2^+ or the ClF_4^+ cation. All three salts show a strong infrared absorption at 890 cm^{-1}. The frequency of this band is higher than that of any known ClF fundamental vibration and is assigned to the antisymmetric stretching vibration, ν_3 (F_{1u}) of ClF_6^+. This assignment is supported by the following observation. In all three salts, the 890-cm^{-1} band shows a pronounced shoulder at 877 cm^{-1}. The observed frequency difference of about 13 cm^{-1} is in good agreement with the ^{35}Cl-^{37}Cl isotopic shift value of 12.5 cm^{-1} computed for octahedral ClF_6^+, assuming 100% characteristic modes. Of the remaining unassigned bands, the second highest frequency belongs to a relatively intense Raman line at 679 cm^{-1}. Clearly, this line must be due to the totally symmetric stretching mode, ν_1 (A_{1g}). The Raman spectrum of ClF_2^+, $ClF_6^+PtF_6^-$ (trace d, Figure 2) shows a band at 513 cm^{-1}. It has the same frequency as the ClO_2^+ deformation mode but cannot be due to ClO_2^+ since there is no evidence for its more intense ν_1 (A_1) mode at about 1050 cm^{-1}. The 513-cm^{-1} band might be assigned to either ν_2 (E_g) or ν_5 (F_{2g}) of ClF_6^+.

Table II. Fundamental Vibrations of ClF_6^+ Compared to Those of Isoelectronic SF_6

ClF_6^+	SF_6 [a]	Assignment in point group O_h
679	769.4	ν_1 (A_{1g})
630	639.5	ν_2 (E_g)
890	947.9	ν_3 (F_{1u})
582	614.5	ν_4 (F_{1u})
513	522	ν_5 (F_{2g})

[a] Data from ref 35 and 36.

It has previously been shown that the vibrational spectra of ClO_2^+,[27] ClF_2O^+,[31] $ClF_2O_2^+$,[4,28] ClF_5,[34] and ClF_4^+ [33] closely resemble those of isoelectronic SO_2, SF_2O, SF_2O_2, SF_5^-, and SF_4, respectively. A similar relationship might be expected for the isoelectronic pair ClF_6^+-SF_6 (see Table II). Comparison with the vibrational spectrum of SF_6 [35,36] suggests that the 513-cm^{-1} band is due to ν_5 (F_{2g}). This is further supported by the absence of another band below 513 cm^{-1}, which might be assigned to this mode and by the observed combination bands in the infrared spectrum. Generally, octahedral species exhibit two relatively intense combination bands in the infrared spectrum due to $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$. For ClF_6^+, two bands were observed at about 1560 and 1515 cm^{-1}, respectively. The 1560-cm^{-1} band represents $\nu_1 + \nu_3$ (computed frequency 1569 cm^{-1}). Assuming the 1515-cm^{-1} band to be due to $\nu_2 + \nu_3$, a value of 625 cm^{-1} can be assigned to ν_2. Inspection of trace d of Figure 2 reveals a shoulder at 630 cm^{-1}, which is assigned to ν_2 (E_g) of ClF_6^+. Since there is no indication in the infrared spectrum for a combination band at about 1400 cm^{-1} ($890 + 513 = 1403$ cm^{-1}), the 513-cm^{-1} Raman band is assigned to ν_5 (F_{2g}).

An alternate, although less probable, assignment is possible for ν_2 (E_g) of ClF_6^+. Trace d of Figure 2 exhibits two bands at 582 and 576 cm^{-1}, respectively. We prefer, however, to attribute both of them to ν_2 (E_g) of PtF_6^- since the ν_5 (F_{2g}) PtF_6^- bands also show additional splitting and since again no evidence for the corresponding $\nu_2 + \nu_3$ combination band can be found in the infrared spectrum at about 1470 cm^{-1}. Thus all the expected active modes have been assigned for ClF_6^+ except for the antisymmetric deformation, ν_4 (F_{1u}).

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This mode should be infrared active and, by comparison with SF_6, occur in the range 550–610 cm^{-1}. A frequency of 582 cm^{-1} is tentatively assigned to ν_4 on the basis of traces c, d, and e of Figure 1 and by comparison with the infrared spectrum of $ClF_2O^+PtF_6^-$.[22]

Force Constants. A modified valence force field was computed for ClF_6^+ in order to obtain a more quantitative understanding of its relative bond strength. Except for the F_{1u} block, all the symmetry force constants are unique. The F_{1u} block is underdetermined since only two frequency values are available for the determination of three force constants. A third frequency value for the F_{1u} block might be obtained from the ^{35}Cl–^{37}Cl isotopic shifts which would allow the computation of a general valence force field. Unfortunately, the isotopic shift for ν_3 could not be determined with sufficient accuracy. Consequently, the usefulness of mathematical constraints, such as minimizing or maximizing the value of one of the symmetry force constants, was tested for isoelectronic SF_6, for which a general valence force field has been reported.[37] It was found that the condition F_{44} = minimum[38] is the best approximation to the general valence force field, though it yields too high a value for F_{34}, due to appreciable coupling of the bonds.[39] It also results in a rather large negative value (−0.269 mdyn/Å) for the stretch–stretch interaction constant, f_{rr}', which is difficult to rationalize. Using the same condition for computing the force field of ClF_6^+, a comparable negative value (−0.297 mdyn/Å) was obtained for f_{rr}' of ClF_6^+. Since for SF_6 the GVFF value of f_{rr}' is essentially zero, we prefer for ClF_6^+ the condition $f_{rr}' = 0$. The resulting force field is listed in Table III and compared to the GVFF values of SF_6.[37] The force constant of greatest interest is the stretching force constant f_r. Its value is 4.7 mdyn/Å with a conservative uncertainty estimate of ±0.2 mdyn/Å considering the uncertainties in the frequency of ν_4 (F_{1u}) and in the approximating method used for the force constant computation. This value is comparable to those of ClF_2^+ (4.74 mdyn/Å[40]) and of the equatorial Cl-F bonds in ClF_4^+ (4.59 mdyn/Å[33]) but significantly higher than those of the remaining known chlorine fluorides. The high value of f_r in ClF_6^+ can be explained to some extent by the formal positive charge which generally increases the stretching force constant values. It also suggests strong covalent contributions to the bonding. The high f_r value is entirely consistent with the high stability observed for the ClF_6^+ salts and parallels the findings for the NF_4^+ salts.[6–9] In both cases, comparison with the isoelectronic molecules SF_6 and CF_4, respectively, suggested unusual stability, although it proved difficult actually to synthesize these salts. In particular, it appears that the synthesis of ClF_6^+ requires an unusually powerful oxidative fluorinating agent such as PtF_6.

Table III. Symmetry and Internal Force Constants (mdyn/A) of ClF_6^+ Computed for a Modified Valence Force Field Assuming $f_{rr}' = 0$ and Using the Frequency Values of Table II[a]

	ClF_6^+	SF_6
F_{11}	5.161	6.626
F_{22}	4.443	4.578
F_{33}	4.682	5.256
F_{34}	0.726	0.885
F_{44}	0.955	1.035
F_{55}	0.736	0.763
f_r	4.682	5.258
f_{rr}	0.120	0.341
f_{rr}'	0	0.002
$f_{r\alpha} - f_{r\alpha}''$	0.363	0.443

[a] For comparison the GVFF values of SF_6 are also listed.

Table IV. Symmetry and Internal Force Constants (mdyn/A) of PtF_6^- and IrF_6^- Computed for a Modified Valence Force Field Assuming F_{44} = Minimum

	PtF_6^- [a]	IrF_6^- [b]
F_{11}	4.613	5.025
F_{22}	3.573	3.510
F_{33}	3.870	3.861
F_{34}	0.100	0.101
F_{44}	0.308	0.307
F_{55}	0.161	0.172
F_{66}	0.181	0.192
f_r	3.894	3.940
f_{rr}	0.173	0.255
f_{rr}'	0.024	0.079
$f_{r\alpha} - f_{r\alpha}''$	0.050	0.051
$f_\alpha - f_{\alpha\alpha} - f_{\alpha\alpha}' + f_{\alpha\alpha}''$	0.171	0.182
$f_{\alpha\alpha} - f_{\alpha\alpha}' - f_{\alpha\alpha}'' + f_{\alpha\alpha}'''$	−0.010	−0.010

[a] Frequencies used: ν_1 642, ν_2 565, ν_3 640, ν_4 270, ν_5 240, ν_6 180 cm^{-1}. [b] Frequencies used: ν_1 670, ν_2 560, ν_3 640, ν_4 270, ν_5 248, ν_6 185 cm^{-1}.

Table V. Summary of Existing Binary Chlorine Fluorides (Nonexisting Species in Parentheses)

Cl_2F^+ [a]	ClF [b]	ClF_2^- [c]
ClF_2^+ [d]	ClF_3 [e]	ClF_4^- [f]
ClF_4^+ [g]	ClF_5 [h]	(ClF_6^-)[g]
ClF_6^+ [i]	(ClF_7)[i]	(ClF_8^-)

[a] K. O. Christe and W. Sawodny, *Inorg. Chem.*, 8, 212 (1969). [b] O. Ruff, E. Ascher, J. Fischer, and F. Laass, *Z. Anorg. Allg. Chem.*, 176, 258 (1928). [c] K. O. Christe and J. P. Guertin, *Inorg. Chem.*, 4, 905 (1965). [d] J. W. Dale and D. A. MacLeod, private communication, 1950. [e] O. Ruff and H. Krug, *Z. Anorg. Allg. Chem.*, 190, 270 (1930). [f] L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, *J. Amer. Chem. Soc.*, 83, 2955 (1961). [g] K. O Christe and D. Pilipovich, *Inorg. Chem.*, 8, 391 (1969). [h] W. Maya and H. F. Bauer, U. S. Patent 3,354,646 (1967). [i] F. Q. Roberto, *Inorg. Nucl. Chem. Lett.*, 8, 737 (1972); K. O. Christe, *ibid.*, 8, 741 (1972).

Since ν_4 (F_{1u}) and ν_6 (F_{2u}) have been observed for both PtF_6^- and IrF_6^-, a modified valence force field was also computed for these two anions assuming octahedral symmetry and F_{44} = minimum. For PtF_6^- and IrF_6^-, this extremal condition is expected to give a force field close to that of a GVFF owing to the large mass of the central atoms and the resulting weak coupling. The frequencies used for the computation are listed in Table IV, together with the resulting force constants. The value of f_r of PtF_6^- (3.89 mdyn/Å) is intermediate between those of PtF_6 (4.46 mdyn/Å[41]) and PtF_6^{2-} (3.42 mdyn/Å[41]) as expected on the basis of the increasing formal negative charge.

Summary. The successful synthesis of ClF_6^+ and the evidence for the nonexistence of a stable ClF_7 molecule and ClF_6^- anion[14] complete the series of possible binary chlorine fluoride molecules and ions. Table V summarizes the presently known species. The existence of ClF_6^+ suggests the possibility of preparing ClF_5O and efforts to synthesize this new oxyfluoride will be continued.

Registry No. PtF_6, 13693-05-5; $FClO_2$, 13637-83-7; ClF_5,

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(37) A. Ruoff, *J. Mol. Struct.*, 4, 332 (1969).

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(41) H. Siebert, "Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie," Springer-Verlag, Berlin, 1966, p 82.

13637-63-3; FNO, 7789-25-5; ClF_3O, 30708-80-6; IrF_6, 7783-75-7; $ClO_2^+PtF_6^-$, 38123-66-9; $ClO_2F_2^+PtF_6^-$, 36609-92-4; $ClF_6^+PtF_6^-$, 36609-91-3; $ClF_2^+PtF_6^-$, 38123-68-1; $ClF_4^+PtF_6^-$, 38123-69-2; $NO^+PtF_6^-$, 17250-51-0; $ClF_2O^+PtF_6^-$, 36544-28-2; $ClO_2^+IrF_6^-$, 38194-37-5; ClF_6^+, 38217-33-3; PtF_6^-, 38123-72-7; IrF_6^-, 22587-75-3.

Acknowledgment. I am indebted to Dr. C. J. Schack and R. D. Wilson for their help in some of the experiments, to Drs. D. Pilipovich and E. C. Curtis for helpful discussions, and to R. Cook of Cary Instruments for recording the Raman spectra. Financial support of this work by the Office of Naval Research was greatly appreciated.

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Contribution from Rocketdyne, a Division of North
American Rockwell, Canoga Park, California 91304

Chlorine Trifluoride Dioxide, ClF_3O_2. Synthesis and Properties

KARL O. CHRISTE* and RICHARD D. WILSON

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Chlorine trifluoride dioxide was prepared from FNO_2 and $ClF_2O_2^+PtF_6^-$, the latter being synthesized from $FClO_2$ and PtF_6. Physical properties and the ^{19}F nmr spectrum are reported. The nmr spectrum suggests the trigonal-bipyramidal structure I of symmetry C_{2v}. Chlorine trifluoride dioxide forms stable adducts with BF_3 and AsF_5 but not with FNO, FNO_2, or CsF.

Introduction

A brief note on the existence of ClF_3O_2 has recently been published by Christe.[1] In this paper we report details on its synthesis, purification, and properties. The infrared spectra of the gas, the solid, and the matrix-isolated species and the Raman spectra of the gas and the liquid together with a normal coordinate analysis and computation of thermodynamic properties will be published elsewhere.[2]

Experimental Section

Materials and Apparatus. The stainless steel Teflon FEP vacuum system,[3] the glove box, the ^{19}F nmr spectrometer and sampling technique,[4] and the syntheses and purification of PtF_6, $FClO_2$, FNO,[3] FNO_2, BF_3, and $ClF_2O_2^+BF_4^-$ [5] are described elsewhere. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. All equipment was passivated with ClF_3 and BrF_5 prior to its use.

Purification of ClF_3O_2. A sample of $ClF_2O_2^+BF_4^-$ (2.41 mmol), prepared and purified as previously reported,[5] was placed in a passivated Teflon FEP ampoule. Nitryl fluoride (6.83 mmol) was added at −196° and the mixture was kept at −78° for 12 hr with periodic agitation. Volatile products were removed at −78° and separated by fractional condensation through a series of traps kept at −95, −126, and −196°. The −95° trap contained only a very small amount of material which was discarded. The −126° trap contained 2.22 mmol of ClF_3O_2 which according to its infrared spectrum[3] at 700 mm of pressure showed as the only detectable impurity less than 0.1 mol % of $FClO_2$. This sample was used for the subsequent characterization studies. The −196° trap contained the unreacted FNO_2 (4.4 mmol) and a small amount of ClF_3O_2 (0.2 mmol). The solid residue was shown by its weight and infrared spectrum to be $NO_2^+BF_4^-$.

ClF_3O_2–CsF System. Two reactions between ClF_3O_2 (1.5 mmol) and CsF (1.0 mmol) were carried out in 10-ml stainless steel cylinders at 25 and 105°, respectively. At the lower temperature the cylinder was placed on a mechanical shaker for 5 days. The volatile material consisted of F_2, $FClO_2$, and some ClF_3O_2. The solid residue had gained 33 mg in weight and was identified by its infrared spectrum[6] as a mixture of $Cs^+ClO_2F_2^-$ and CsF. When the starting materials were heated to 105° for 68 hr, the ClF_3O_2 had quantitatively decomposed to $FClO_2$ and F_2.

Results and Discussion

Synthesis. The synthesis of ClF_3O_2 is best described by the following reaction sequence.

$$2FClO_2 + 2PtF_6 \rightarrow ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^- \qquad (1)$$

Several side reactions compete with (1) and the yield of $ClF_2O_2^+$ varies greatly with slight changes in the reaction conditions.[3] The ClF_3O_2 is then displaced from its $ClF_2O_2^+$ salt according to

$$ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^- + 2FNO_2 \rightarrow 2NO_2^+PtF_6^- + ClF_3O_2 + FClO_2 \qquad (2)$$

Chloryl fluoride is slightly less volatile than ClF_3O_2. Therefore, most of it can be removed from ClF_3O_2 by fractional condensation in a −112° trap. The remaining $FClO_2$, however, has to be removed by complexing with BF_3.

$$ClF_3O_2 + FClO_2 + 2BF_3 \rightarrow ClF_2O_2^+BF_4^- + ClO_2^+BF_4^- \qquad (3)$$

Since $ClF_2O_2^+BF_4^-$ is stable[5] at 20°, whereas $ClO_2^+BF_4^-$ is not,[7] the latter can be pumped away at 20°. The resulting pure $ClF_2O_2^+BF_4^-$ is then treated with an excess of FNO_2 and the evolved ClF_3O_2 and unreacted FNO_2 are readily separated by fractional condensation through a series of −126 and −196° traps.

$$ClF_2O_2^+BF_4^- + FNO_2 \rightarrow NO_2^+BF_4^- + ClF_3O_2 \qquad (4)$$

Whereas the overall yield of pure ClF_3O_2 based on the PtF_6 used in step 1 was found to be rather low (about 10 mol %), the method was satisfactory to provide enough material to characterize ClF_3O_2. Therefore, no effort was undertaken to search for alternate synthetic routes which might give higher yields of ClF_3O_2.

Properties. Pure ClF_3O_2 is colorless as a gas or liquid and white in the solid state. It melts at −81.2°. Vapor pressures were measured over the range −96 to −32° and the data for the range −64 to −32° were fitted by the method of least squares to the equation

$$\log P\,(\text{mm}) = 7.719 - 1217.2/T\,(°\text{K})$$

with an index of correlation of 0.99998. The extrapolated boiling point is −21.58°. Measured vapor pressures at the noted temperatures are [T (°C), P (mm)]: −95.64, 7.3; −78.73, 25.5; −64.34, 77.5; −57.69, 117.5; −46.32, 226.5; −31.93, 470. The two lowest temperature points were not used for the computation of the vapor pressure equation because the lowest point was measured for solid ClF_3O_2 and the second lowest was too close to the melting point of ClF_3O_2. While at −78.73° the ClF_3O_2 sample was all liquid, the observed vapor pressure was reproducibly lower than expected from the above vapor pressure curve. This indicates that close to the melting point some ordering effect occurs in the liquid causing a decrease of the vapor pressure. The latent heat of vaporization of ClF_3O_2 is 5.57 kcal/mol and the derived Trouton constant is 22.13, indicating little association in the liquid phase. This is in agreement with the low boiling point and the good agreement between the Raman spectra of the gas and of the liquid.[2] The molecular weight was determined from the vapor density and found to be 122.1 (calcd for ClF_3O_2, 124.5). The good agreement in-

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(1) K. O. Christe, *Inorg. Nucl. Chem. Lett.*, 8, 457 (1972).
(2) K. O. Christe and E. C. Curtis, unpublished results.
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(4) K. O. Christe, J. F. Hon, and D. Pilipovich, *Inorg. Chem.*, 12, 84 (1973).
(5) K. O. Christe, R. D. Wilson, and E. C. Curtis, *Inorg. Chem.*, 12, 1358 (1973).
(6) K. O. Christe and E. C. Curtis, *Inorg. Chem.*, 11, 35 (1972).
(7) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, 8, 2489 (1969).

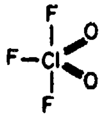
dicates little or no association in the gas phase at the pressures used ($P \sim 1$ atm).

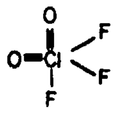
Chlorine trifluoride dioxide resembles chlorine fluorides and oxyfluorides in its corrosive and oxidizing properties. It appears to be marginally stable in a well passivated system at ambient temperature. It is a strong oxidative fluorinator as evidenced by its tendency to fluorinate metal surfaces to metal fluorides with $FClO_2$ formation. It reacts explosively with organic materials and care must be taken to avoid such combinations. The hydrolysis of ClF_3O_2 was not quantitatively studied; however, on one occasion a slight leak in an infrared gas cell containing ClF_3O_2 resulted in the formation of $FClO_3$ and HF indicating the following reaction.

$$ClF_3O_2 + H_2O \rightarrow FClO_3 + 2HF \qquad (5)$$

^{19}F Nmr Spectrum. The ^{19}F nmr spectrum of liquid ClF_3O_2 was measured in the temperature range -20 to $-80°$. It showed at all temperatures one partially resolved signal centered at -413 ppm below the external standard $CFCl_3$. Figure 1 shows the details of the spectrum recorded at $-77°$. The observed signal is in excellent agreement with an AB_2 pattern[8] with $J/\nu_0\delta = 1.0$ (for the computed pattern, see Figure 1). From these data a value of $J_{FF} = 443$ Hz was calculated. The low chemical shift of -413 ppm for ClF_3O_2 is in excellent agreement with a heptavalent chlorine fluoride and compares favorably with those observed[4] for $FClO_2$ (-315 ppm), ClF_6^+ (-388 ppm), and $ClF_2O_2^+$ (-310 ppm). The fact that the resonance of the $ClF_2O_2^+$ cation was observed upfield from that of ClF_3O_2 is difficult to rationalize but seems to be quite general for chlorine fluorides.[4] The fluorine–fluorine coupling constant of 443 Hz observed for ClF_3O_2 is similar to that of 421 Hz observed for the structurally related ClF_3.[4]

Since the chlorine atom in ClF_3O_2 does not possess a free valence electron pair, it is pentacoordinated and the ligands should form a trigonal bipyramid. To account for an AB_2 pattern one has to assume two fluorine atoms in either the axial or the equatorial positions.


I


II

Of these two models, I has to be preferred for the following four reasons. (i) The B_2 part of the AB_2 pattern occurs downfield from the A part and in trigonal-bipyramidal species the resonance for the axial fluorines occurs at a lower field than that of the equatorial ones.[9,10] (ii) In trigonal-bipyramidal molecules the most electronegative ligands generally occupy the axial positions.[11] (iii) The vibrational spectrum[2] is consistent only with model I. (iv) In the structurally related ClF_3O[12] and ClF_3 [13] molecules (in which the oxygen ligands are replaced by one and two sterically active free electron pairs, respectively), both axial positions are occupied by fluorine atoms.

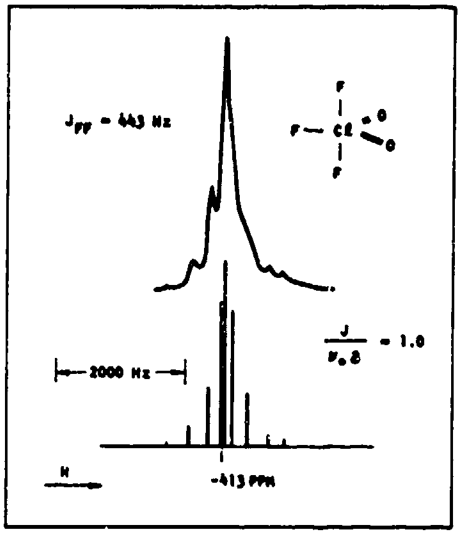


Figure 1. ^{19}F nmr spectrum of liquid ClF_3O_2 at $-77°$ recorded at 56.4 MHz. The chemical shift was measured relative to the external standard $CFCl_3$.

Adduct Formation. Chlorine trifluoride dioxide forms stable adducts with strong Lewis acids, such as BF_3, AsF_5, or PtF_5.[5] These adducts have ionic structures containing the $ClF_2O_2^+$ cation. A detailed discussion of the vibrational and nmr spectra of this cation will be given elsewhere.[5] The high stability of these adducts can be explained by the change from the energetically unfavorable trigonal-bipyramidal structure of ClF_3O_2 to the more favorable tetrahedral $ClF_2O_2^+$ configuration.[14] Contrary to ClF_3,[15] but by analogy with ClF_3O,[14] it does not form stable adducts with FNO or FNO_2 at temperatures as low as $-78°$. This was demonstrated by the various displacement reactions where ClF_3O_2 and unreacted FNO or FNO_2 could be readily removed from the reactor at $-78°$. With the stronger base, CsF, it does not form a stable adduct but decomposes to $FClO_2$ and F_2 with CsF possibly catalyzing the decomposition.

Registry No. $(ClF_2O_2)BF_4$, 38682-34-7; FNO_2, 10022-50-1; ClF_3O_2, 38680-84-1; CsF, 13400-13-0.

Acknowledgment. We thank Drs. D. Pilipovich and C. J. Schack for helpful discussions. We are pleased to acknowledge support of this work by the Office of Naval Research, Power Branch.

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Contribution from Rocketdyne, a Division of North American
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The Difluoroperchloryl Cation, $ClO_2F_2^+$

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Received December 8, 1972

The reaction of $FClO_2$ with PtF_6 yields a product containing $ClO_2F_2^+PtF_6^-$. A synthetic method is described that converts this salt into $ClO_2F_2^+BF_4^-$ or $ClO_2F_2^+AsF_6^-$. All three salts are stable at 25° and according to their infrared, Raman, and ^{19}F nmr spectra are ionic in both the solid state and HF solution. The vibrational spectrum of $ClO_2F_2^+$ closely resembles that of isoelectronic SO_2F_2, suggesting a pseudotetrahedral structure of symmetry C_{2v}. A modified valence force is reported for $ClO_2F_2^+$.

Introduction

A preliminary note on the existence of $ClO_2F_2^+PtF_6^-$ has recently been published by Christe. This salt was prepared from $FClO_2$ and PtF_6.[1] A detailed report on this interesting system, yielding under different reaction conditions $ClF_6^+PtF_6^-$, has been given elsewhere.[2] A ^{19}F nmr chemical shift of −310 ppm relative to external $CFCl_3$ has been tentatively assigned to $ClO_2F_2^+$.[3] A more complete characterization of the $ClO_2F_2^+$ cation in the original PtF_6^- salt, however, was preempted by interference from the PtF_6^- anion and from substantial amounts of by-products such as $ClO_2^+PtF_6^-$. Consequently, efforts were made to prepare $ClO_2F_2^+$ salts containing different anions and to eliminate the undesirable by-products. We have now succeeded in preparing $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$ and in more fully characterizing the $ClO_2F_2^+$ cation. These results are described below.

Experimental Section

Apparatus and Materials. The stainless steel–Teflon-FEP vacuum system, the glove box, the infrared, Raman, and ^{19}F nmr spectrometers and sampling techniques, and the syntheses and purification of PtF_6, AsF_5, and $FClO_2$ have been described elsewhere.[2,3] Nitryl fluoride, prepared from N_2O_4 and F_2, and BF_3 (from The Matheson Co.) were purified by fractional condensation. Debye–Scherrer X-ray diffraction powder patterns were taken as previously described.[4]

Syntheses of $ClO_2F_2^+$ Salts. The synthesis of $ClO_2F_2^+PtF_6^-$ has been described elsewhere.[2] For the synthesis of $ClO_2F_2^+BF_4^-$, a mixture of $ClO_2F_2^+PtF_6^-$ (4.8 mmol) and $ClO_2^+PtF_6^-$ (12.2 mmol) was treated in a passivated (with ClF_3 and BrF_5) 75-ml stainless steel cylinder with FNO_2 (25.3 mmol) at −78° for 48 hr. The reaction products volatile at 25° consisted of $FClO_2$, ClF_3O_2, and unreacted FNO_2 and were separated by fractional condensation through a series of traps kept at −112, −126, −142, and −196°. The −126° fraction contained most of the ClF_3O_2 and some $FClO_2$. Attempts to separate further the ClF_3O_2 and $FClO_2$ mixture by fractional condensation were unsuccessful. Consequently, 2.76 mmol of this mixture was combined with BF_3 (3.00 mmol) at −196° in a passivated Teflon-FEP ampoule and the temperature was cycled several times between −196 and +25°. The product was kept at −78° for several hours and unreacted BF_3 (0.22 mmol) was removed at this temperature *in vacuo*. Removal of volatile material *in vacuo* was continued at 20°. The volatile material (2.60 mmol) consisted according to its infrared spectrum of a 1:1 mixture of $FClO_2$ and BF_3. The white, solid, nonvolatile residue (280 mg, 1.46 mmol) was identified by infrared, Raman, and ^{19}F nmr spectroscopy as $ClO_2F_2^+BF_4^-$.

For the preparation of the AsF_6^- salt, $ClO_2F_2^+BF_4^-$ (0.62 mmol) and AsF_5 (1.43 mmol) were combined at −196° in a passivated Teflon-FEP ampoule. The contents of the ampoule were kept at −78° for 30 min and at 25° for 1 hr. Volatile products were removed at 25° and consisted of unreacted AsF_5 (0.79 mmol) and BF_3 (0.59 mmol). The white, stable solid weighed 185 mg (weight calculated for 0.62 mmol of $ClO_2F_2^+AsF_6^-$ is 183 mg) and was identified as $ClO_2F_2^+AsF_6^-$ by infrared, Raman, and ^{19}F nmr spectroscopy.

Results and Discussion

Syntheses and Properties of $ClO_2F_2^+$ Salts. The synthesis of $ClO_2F_2^+PtF_6^-$ from $FClO_2$ and PtF_6 and its temperature dependence have been discussed elsewhere.[1,2] Since the PtF_6^- anion interfered with the vibrational spectroscopic studies of $ClO_2F_2^+$, the BF_4^- and AsF_6^- salts were prepared according to the reaction

$$ClO_2^+PtF_6^- + ClO_2F_2^+PtF_6^- + FNO_2 \rightarrow FClO_2 + ClF_3O_2 + 2NO_2^+PtF_6^-$$

Unreacted FNO_2 and some of the $FClO_2$ could be separated from ClF_3O_2 by fractional condensation. The remaining $FClO_2$ was separated from ClF_3O_2 by complexing with BF_3. Since the resulting $ClO_2^+BF_4^-$ has a dissociation pressure[5] of 182 mm at 22.1° while $ClO_2F_2^+BF_4^-$ is stable, the former salt could be readily removed by pumping at 20°. Conversion of $ClO_2F_2^+BF_4^-$ to the corresponding AsF_6^- salt was accomplished through displacement of BF_4^- by the stronger Lewis acid AsF_5.

All three salts, $ClO_2F_2^+PtF_6^-$, $ClO_2F_2^+AsF_6^-$, and $ClO_2F_2^+BF_4^-$, are solids, stable at 25°, and react violently with water or organic materials. The PtF_6^- compound is canary yellow, while those of AsF_6^- and BF_4^- are white. The salts dissolve in anhydrous HF without decomposing. They are crystallinic in the solid state and the X-ray powder diffraction patterns of $ClF_2O_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$ are listed in Table I. The powder pattern of $ClO_2F_2^+BF_4^-$ is much simpler than that of $ClO_2F_2^+AsF_6^-$. This is not surprising since the anion and cation in the former salt are both of approximately tetrahedral shape and of similar size. The powder pattern of $ClO_2F_2^+BF_4^-$ can be indexed on the basis of an orthorhombic unit cell with $a = 5.45$, $b = 7.23$, and $c = 13.00$ Å. Assuming four molecules per unit cell and neglecting contributions from the highly charged central atoms to the volume,[6,7] a plausible average volume of 16 Å^3 per F or O atom is obtained. However, the agreement between the observed and calculated reflections is somewhat poor for several lines and, hence, the above unit cell dimensions are tentative.

The thermal stability of $ClO_2F_2^+BF_4^-$ is higher than those of $ClO_2^+BF_4^-$,[5] $ClF_2^+BF_4^-$,[8] or other similar salts. This is in good agreement with the previously made correlations[9] between the stability of an adduct and the structure of the

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Table I. X-Ray Powder Patterns for $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$

$ClO_2F_2^+BF_4^-$		$ClO_2F_2^+AsF_6^-$			
d, A	Intens	*d*, A	Intens	*d*, A	Intens
5.47	s	7.49	w	2.12	w
5.06	m	5.50	ms	2.01	w
4.37	ms	4.98	w	1.94	mw
4.15	w	4.35	ms	1.90	mw
3.70	vs	4.02	w	1.86	w
3.56	s	3.86	s	1.80	w
3.00	m	3.70	w	1.76	mw
2.77	m	3.57	m	1.72	w
2.57	vw	3.40	mw	1.70	mw
2.41	m	3.02	mw	1.65	w
2.18	s	2.77	m	1.62	w
2.08	s	2.69	m	1.59	w
1.86	ms	2.60	w	1.54	w
1.80	w	2.41	w	1.50	w
		2.30	w	1.41	w
		2.20	w	1.37	w
				1.34	w

parent molecule and its ions. Thus, tetrahedral $ClO_2F_2^+$ (see below) should be energetically much more favorable than trigonal-bipyramidal ClF_3O_2.[10,11]

^{19}F Nmr Spectra. A broad singlet at −310 ppm relative to external $CFCl_3$ has previously been observed for $ClO_2F_2^+PtF_6^-$ at low concentration in anhydrous HF and was tentatively assigned to $ClO_2F_2^+$.[3] This tentative assignment is confirmed by the present study. The spectrum of $ClF_2O_2^+BF_4^-$ in HF shows a strong temperature dependence. At 30° it consists of a single peak at 185 ppm relative to external $CFCl_3$. With decreasing temperature the peak at first becomes broader and then separates at about 0° into three signals at −301 ($ClO_2F_2^+$), 146 (BF_4^-),[12] and 194 ppm (HF) which become narrower with further decrease in temperature. The observed peak area ratio of approximately 2:1 for the 146 and −301 ppm signals confirms their assignment to BF_4^- and $ClO_2F_2^+$, respectively, and proves the ionic nature of the $ClF_3O_2 \cdot BF_3$ adduct in HF solution.

The spectrum of $ClF_2O_2^+AsF_6^-$ in HF (which was acidified with AsF_5)[3] consists of two resonances at −307 ($ClO_2F_2^+$) and 105 ppm (HF, AsF_5, AsF_6^-),[3] respectively. Rapid exchange among HF, AsF_5, and AsF_6^- preempted the measurement of the $ClO_2F_2^+$ to AsF_6^- peak area ratio.

Vibrational Spectra. Figure 1 shows the infrared and Raman spectra of solid $ClO_2F_2^+BF_4^-$ and the Raman spectrum of an HF solution of $ClO_2F_2^+BF_4^-$. Figure 2 depicts the infrared and Raman spectra of solid $ClO_2F_2^+AsF_6^-$. Figure 3 shows the infrared spectrum of a mixture of solid $ClO_2F_2^+PtF_6^-$ and $ClO_2^+PtF_6^-$. The observed frequencies are listed in Table II and are compared with those reported for isoelectronic SO_2F_2.[12]

Inspection of Figures 1-3 and of Table II reveals that the spectra of $ClF_3O_2 \cdot BF_3$, $ClF_3O_2 \cdot AsF_5$, and $ClF_3O_2 \cdot PtF_5$ contain the bands characteristic for BF_4^-,[13-16] AsF_6^-,[16-19] and PtF_6^-,[2,20] respectively. Furthermore, the Raman spectra of $ClF_3O_2 \cdot BF_3$ are practically identical for both the solid and its HF solution. These observations, together with the ^{19}F nmr spectrum of the BF_3 adduct in HF solution, establish

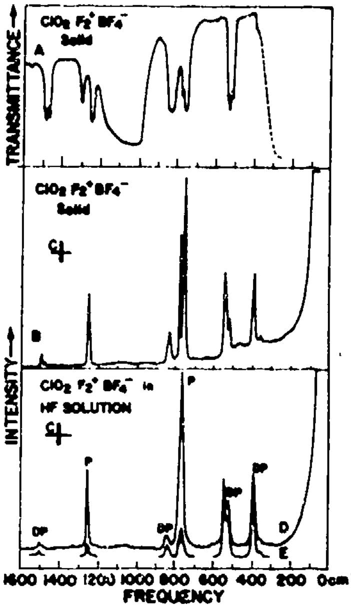

Figure 1. Vibrational spectra of $ClO_2F_2^+BF_4^-$: A, infrared spectrum of the solid as a AgCl disk; B, Raman spectrum of the solid; D and E, Raman spectrum of the HF solution, incident polarization perpendicular and parallel, respectively; exciting line is 4880-A and C indicates spectral slit width.

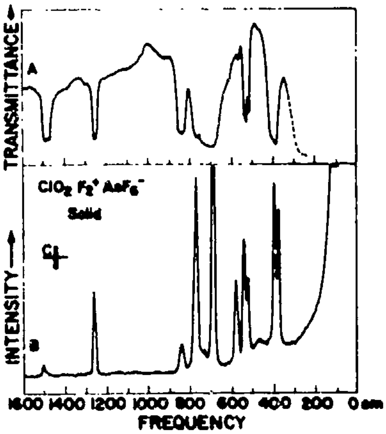

Figure 2. Vibrational spectra of solid $ClO_2F_2^+AsF_6^-$: A, infrared spectrum (AgCl disk); B, Raman spectrum; exciting line 4880 A.

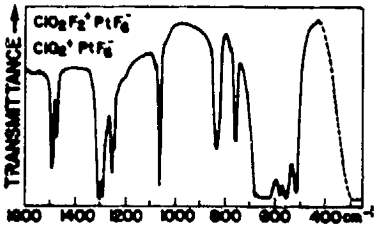

Figure 3. Infrared spectrum of a mixture of solid $ClO_2F_2^+PtF_6^-$ and $ClO_2^+PtF_6^-$ as a AgCl disk.

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Table II. Raman and Infrared Vibrational Spectra of $ClO_2F_2^+$ Salts Compared to Those of SO_2F_2

Obsd freq, cm^{-1}, and rel intens[a]										Assignment (point group)			
SO_2F_2			$ClO_2F_2^+BF_4^-$			$ClO_2F_2^+AsF_6^-$		$ClO_2F_2^+PtF_6^-$ + $ClO_2^+PtF_6^-$					
R[b]		Ir[c]	R										
Gas	Liquid	Gas	HF soln	Solid	Ir	R	Ir	R	Ir	XO_2F_2 (C_{2v})	YF_6^- (O_h)[d]	BF_4^- (T_d)	ClO_2^+ (C_{2v})
									2340 2320 } w				$\nu_1 + \nu_3$ (B_1)
									2115 vw				$2\nu_1$ (A_1)
1502	1497 (1) dp	1502 vs	1495 (0.3) dp	1485 (0.6) 1469 (0.2)	1485 1469 } s	1492 (0.25)	1489 1473 } s		1486 1470 } s	ν_6 (B_1)			
					1295 m							$\nu_1 + \nu_4$ (F_2)	
								1299 (0.5) 1285 (0.17) }	1297 vs 1283 s }				ν_3 (B_1)
1270 vs	1263 (7) p	1269 vs	1252 (4.4) 1244 (1.5) } p	1245 (3.9) 1237 (1.3) }	1245 1237 } s	1252 1244 } (1.9)	1250 1242 } s	1246 (0+)	1245 1237 } s	ν_1 (A_1)			
								1051 (2.7)	1052 s 1047 m }				ν_1 (A_1)
			1050 (0+) br	1050 (0+), br	990–1150 vs, br							ν_3(F_2)	
883	887 (1)	885 vs	834 (0.7) dp	823 (1.6)	824 s	834 (0.6)	832 s		827 s	ν_8 (B_2)			
			771 sh, p	772 (6.3)	772 w							ν_1 (A_1)	
847 vs	846 (10) p	848 vs	761 (10) p	753 (10)	754 s	761 (4.5)	759 s	754 (0.1)	756 s	ν_2 (A_1)			
							700 vs, br	617 (2.5)	640 vs, br		ν_3 (F_{1u})		
						683 (10)		642 (10)			ν_1 (A_{1g})		
						573 (1.9)	564 w	564 (1.3) 552 (1.8) }	580 w 552 s }		ν_2 (E_g)		
543 vbr	547 (6) dp	552.8 544.3 539.4 } s	538 (3.8) 533 sh 517 (1.6) } dp	534 (4.7) 530 sh 515 (1.5) }	534 sh 529 s 516 w }	534 (2.9) 528 sh 514 (1) }	534 sh 527 s 514 m }	514 (0.4)	532 w 514 s	ν_7 (B_1) ν_3 (A_1) ν_9 (B_2)		ν_4 (F_2)	ν_2 (A_1)
388 vbr	389 (4) dp	384.5 w	388 (4.0) dp	394 sh 387 (3.9)	395 w	390 (3.8)	395 sh			{ ν_4 (A_1) { ν_5 (A_2)			
							385 vs		284 m 265 s }		ν_4 (F_{1u})		
						373 (3)			239 (2.9)		ν_5 (F_{2g})		
			355 sh	355 (0.3)								ν_2 (E)	
									180 (0+)		ν_6 (F_{2u})		

[a] Uncorrected Raman intensities. [b] P. Bender and J. M. Wood, Jr., *J. Chem. Phys.*, 23, 1316 (1955). [c] D. R. Lide, Jr., D. E. Mann, and J. J. Comeford, *Spectrochim. Acta*, 21, 497 (1965); G. R. Hunt and M. K. Wilson, *ibid.*, 16, 570 (1960). [d] Assignments for PtF_6^- are made for simplicity on the basis of point group O_h though the site symmetry of PtF_6^- is lower than O_h: K. O. Christe, *Inorg. Chem.*, in press.

Table III. Observed Frequencies (cm^{-1}), Approximate Description of Modes, Computed Symmetry, and Most Important Internal Force Constants of $ClO_2F_2^+$ [a]

					∠OClO, ∠FClF, deg					Obsd isotopic shifts
					124, 96 (I)	114, 105 (II)	109, 109 (III)	124, 96 (IV)	114, 105 (V)	
A_1	ν_1	1241	$\nu_{sym}(ClO_2)$	$F_{11} = f_D + f_{DD}$	11.33 [9.2]	10.66 [10.7]	10.12 [12.4]	11.74 [8.0]	11.38 [8.5]	7.5–8.5
				$F_{12} = 2f_{DR}$				0.50	1.00	
	ν_2	756	$\nu_{sym}(ClF_2)$	$F_{22} = f_R + f_{RR}$	4.28 [5.4]	4.85 [3.4]	4.83 [3.5]	4.08 [6.4]	4.56 [4.9]	~5
	ν_3	514	$\delta_{sym}(ClO_2)$	$F_{33} = 0.56f_\alpha + 0.06f_\beta + 0.38f_\gamma - 0.72f_{\alpha\beta} + 0.06\cdot(f_{\beta\beta} + f_{\beta\beta}' + f_{\beta\beta}'') + 0.59f_{\beta\gamma} - 0.93f_{\alpha\gamma}$ [c]	1.62 [0.6]	1.85 [0.2]	1.79 [1.6]	1.64 [0.4]	1.86 [0.1]	
				$F_{34} = 0.32f_\alpha + 0.13f_\beta - 0.45f_\gamma - 1.01f_{\alpha\beta} + 0.13\cdot(f_{\beta\beta} + f_{\beta\beta}' + f_{\beta\beta}'') + 0.31f_{\beta\gamma} + 0.28f_{\alpha\gamma}$	(0)[b]	(0)[b]	(0)[b]	(0)[b]	(0)[b]	
	ν_4	390	$\delta_{sym}(ClF_2)$	$F_{44} = 0.18f_\alpha + 0.29f_\beta + 0.52f_\gamma - 0.91f_{\alpha\beta} + 0.29\cdot(f_{\beta\beta} + f_{\beta\beta}' + f_{\beta\beta}'') - 1.56f_{\beta\gamma} + 0.63f_{\alpha\gamma}$	1.29 [1.0]	1.06 [1.9]	1.16 [0.1]	1.29 [1.0]	1.07 [1.8]	
A_2	ν_5	390	τ	$F_{55} = f_\beta - f_{\beta\beta} - f_{\beta\beta}' + f_{\beta\beta}''$	1.16	1.16	1.16	1.16	1.16	
B_1	ν_6	1479	$\nu_{asym}(ClO_2)$	$F_{66} = f_D - f_{DD}$	11.48 [18.7]	11.98 [17.9]	12.25 [17.5]	12.66 [16.2]	12.70 [16.4]	15.9–16.7
				$F_{67} = \sqrt{2}(f_{D\beta} - f_{D\beta}')$	(0)[b]	(0)[b]	(0)[b]	1.00	0.60	
	ν_7	530	$\delta_{rock}(ClO_2)$	$F_{77} = f_\beta + f_{\beta\beta} - f_{\beta\beta}' - f_{\beta\beta}''$	1.61 [2.7]	1.78 [3.3]	1.89 [4.5]	1.54 [3.6]	1.71 [3.8]	
B_2	ν_8	830	$\nu_{asym}(ClF_2)$	$F_{88} = f_R - f_{RR}$	4.71 [10.9]	4.50 [11.5]	4.43 [11.7]	4.71 [10.9]	4.50 [11.5]	~11
				$F_{89} = \sqrt{2}(f_{R\beta} - f_{R\beta}')$	(0.5)[b]	(0.5)[b]	(0.5)[b]	(0.5)[b]	(0.5)[b]	
	ν_9	514	$\delta_{rock}(ClF_2)$	$F_{99} = f_\beta - f_{\beta\beta} + f_{\beta\beta}' - f_{\beta\beta}''$	2.01 [2.5]	1.72 [2.2]	1.61 [2.1]	2.01 [2.5]	1.72 [2.2]	
				f_D	11.41	11.32	11.19	12.20	12.04	
				f_{DD}	−0.08	−0.66	−1.07	−0.46	−0.66	
				f_R	4.50	4.68	4.63	4.40	4.53	
				f_{RR}	−0.21	0.17	0.20	−0.32	0.03	

[a] Stretching constants in mdyn/A, deformation constants in mdyn A/radian^2, and stretch-bend interaction constants in mdyn/radian. Values listed in brackets are the computed $^{35}Cl-^{37}Cl$ isotopic shifts (cm^{-1}). Symmetry force constants not shown were assumed to be zero. $f_{\beta\beta}$, $f_{\beta\beta}'$, and $f_{\beta\beta}''$ refer to the interactions between the deformations of two angles having a common oxygen atom, a common fluorine atom, and no common oxygen or fluorine atom, respectively. [b] Assumed values. [c] The numerical coefficients in the *F* matrix are based on the 124 and 96° bond angle geometry.

that these adducts are ionic and contain the $ClO_2F_2^+$ cation. The assignments for the anions are well established and are summarized in Table II. Consequently, only the assignments for $ClO_2F_2^+$ will be discussed in more detail. The $ClO_2F_2^+$ cation is isoelectronic with SO_2F_2 which was shown by microwave spectroscopy to possess symmetry C_{2v}.[21] The SO_2F_2 structure can be derived from a tetrahedron with two oxygen and two fluorine ligands occupying the corners and with the O=S=O angle increased to 123° 58′ and the F–S–F angle compressed to 96° 7′. Comparison of the bands due to $ClO_2F_2^+$ with those previously reported[12,22,23] for SO_2F_2 (see Table II) reveals a pronounced similarity indicating closely related structures and bonding. Therefore, assignments for $ClO_2F_2^+$ were made by analogy with those of SO_2F_2 which were reliably established by infrared,[23] Raman,[22] matrix-isolation,[12] and microwave[12] studies. The analogy appears to include the triple and double coincidences among ν_7 (B_1), ν_3 (A_1), and ν_9 (B_2) at about 530 cm^{-1} and between ν_4 (A_1) and ν_5 (A_2) at about 390 cm^{-1}, respectively. As for SO_2F_2,[12] only tentative assignments to the individual modes can be made for the bands observed in the 520-cm^{-1} region.

The close analogy between the vibrational spectra of isoelectronic $ClO_2F_2^+$ and SO_2F_2 parallels those found for the isoelectronic pairs ClF_2O^+-SF_2O,[16] ClF_6^+-SF_6,[2] ClF_5-SF_5^-,[24] and ClF_4^+-SF_4.[25] It demonstrates the usefulness of knowing the vibrational spectra of the corresponding sulfur compounds for predicting and assigning those of the isoelectronic chlorine fluorides.

Additional evidence for the pseudotetrahedral structure of symmetry C_{2v} of $ClO_2F_2^+$ consists of the $^{35}Cl-^{37}Cl$ isotopic splittings observed for the stretching modes (see Table III and Force Constant section).

Force Constants. Three sets of force constants were computed for $ClO_2F_2^+$ assuming different geometries. Two additional sets were computed requiring agreement between observed and computed $^{35}Cl-^{37}Cl$ isotopic shifts (see Table III). The potential and kinetic energy matrices were computed using a machine method.[26] The three different geometries adopted for $ClO_2F_2^+$ differ only in the bond angles but not in the bond lengths. The bond lengths were estimated to be D(ClO) = 1.41 Å and R(ClF) = 1.53 Å by comparison with related molecules and on the basis of the correlation of Robinson[27] between frequencies and bond lengths. The bond angles of set I, α(∠OClO) = 124°, β(∠OClF) = 108° 15′, and γ(∠FClF) = 96°, were chosen to be identical with those of isoelectronic SO_2F_2.[21] For set III, tetrahedral bond angles were used, and for set II, a geometry was selected intermediate between those of sets I and III. The redundant coordinate was found numerically, and the deformation symmetry coordinates S_3 and S_4 were made orthogonal to it. To demonstrate that the redundancy condition was correct, it was verified that the frequencies of each block taken separately and the corresponding frequencies of the direct sum of all symmetry coordinates were the same.

The force constants were computed by trial and error with

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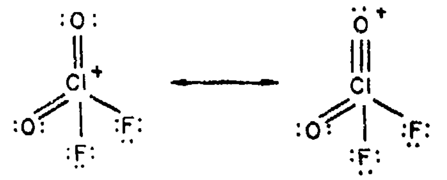
Table IV. Stretching Force Constants (mdyn/Å) of $ClO_2F_2^+$ Compared to Those of Related Compounds

	f_{ClO}		f_{ClF}	f_{ClF}' [a]
$ClO_2F_2^+$	12.1	ClF_6^+ [i]	4.7	
ClF_2O^+ [b]	11.2	ClF_2^+ [j]	4.7	
$FClO_3$ [c]	9.4	ClF_4^+ [k]	4.5	3.2
ClF_3O [d]	9.4	$ClO_2F_2^+$	4.46	
$FClO_2$ [e]	9.1	ClF_3 [l]	4.2	2.7
		$FClO_3$ [c]	3.9	
ClO_2^+ [f]	9.0	ClF_5 [m]	3.5	2.7
ClF_4O^- [g]	8.9	ClF_2O^+ [b]	3.4	
$ClF_2O_2^-$ [h]	8.3	ClF_3O [d]	3.2	2.3
		$FClO_2$ [e]	2.5	
		ClF_2^- [n]		2.4
		ClF_4^- [o]		2.1
		ClF_4O^- [g]		1.9
		$ClF_2O_2^-$ [h]		1.6

[a] ClF bonds for which strong contributions from semiionic three-center, four-electron bonds can be invoked. [b] Reference 16. [c] W. Sawodny, A. Fadini, and K. Ballein, *Spectrochim. Acta*, 21, 995 (1965). [d] K. O. Christe and E. C. Curtis, *Inorg. Chem.*, 11, 2196 (1972). [e] D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, 20, 1763 (1964). [f] Reference 19. [g] K. O. Christe and E. Curtis, *Inorg. Chem.*, 11, 2209 (1972). [h] K. O. Christe and E. C. Curtis, *ibid.*, 11, 35 (1972). [i] K. O. Christe, *ibid.*, in press. [j] K. O. Christe and C. J. Schack, *ibid.*, 9, 2296 (1970). [k] Reference 25. [l] R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.*, 54, 344 (1971). [m] Reference 24. [n] K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, 6, 1159 (1967). [o] K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.*, 374, 306 (1970).

the aid of a computer, requiring exact fit between the observed and computed frequencies. The results are given in Table III where the force constants not shown were assumed to be zero. The values shown for sets I-III were the simplest set that would give an exact fit and, with the exception of F_{89}, represent a diagonal symmetry force field. By analogy with isoelectronic SO_2F_2,[28] a nonzero value was required for F_{89} to fit the observed frequencies. Its value was assumed to be 0.5 to obtain a plausible value for F_{99}. Table III demonstrates the dependence of the force constants on the chosen bond angles and the impossibility to achieve a fit between the observed and the computed ^{35}Cl-^{37}Cl isotopic shifts by simple variation of the bond angles. Numerical experiments confirmed that nonzero off-diagonal symmetry force constants are required to fit the observed isotopic shifts. The results for the more likely geometries I and II are listed as sets IV and V, respectively, in Table III. In the A_1 symmetry block, the only interaction constant capable of sufficiently decreasing the ν_1 isotopic shift is F_{12}. The experimental data do not permit us to distinguish between sets IV and V. However, the variation in the two force constants of greatest interest, f_D and f_R, is relatively small. Consequently, their values might be expected to approach those of a general valence force field. A statistically meaningful uncertainty estimate cannot be made for the force constant values owing to their underdetermined nature and to the lack of exact structural data. However, the numerical data of Table III allow some conclusions concerning the ranges of possible solutions. It should also be mentioned that the observed ^{35}Cl-^{37}Cl isotopic shifts varied slightly depending on the nature of the anion. In $ClO_2F_2^+BF_4^-$ for both the solid state and the HF solution, isotopic shifts of 7.5 and 15.9 cm^{-1} were observed for ν_1 (A_1) and ν_6 (B_1), respectively. For solid $ClO_2F_2^+PtF_6^-$ the corresponding values were 8.5 and 16.6 cm^{-1}.

Of the internal force constants, the stretching force constants are of greatest interest since they can be used as a measure for the relative covalent bond strength. The stretching force constants of $ClO_2F_2^+$ are listed in Table IV and compared to those of related molecules and ions. Comparison of the ClO stretching force constant of $ClO_2F_2^+$ (12.1 mdyn/Å) with those listed in Table IV shows that it is the highest value known for a ClO bond. This is not surprising, since the central atom in $ClO_2F_2^+$ has a high oxidation state (+VII), highly electronegative ligands, and a formal positive charge (cation). The influence of these factors on f_{ClO} has previously been discussed[16] for ClF_2O^+ and, hence, will not be reiterated. By analogy with ClF_2O^+, the only other known species exhibiting a f_{ClO} value of similar magnitude, contributions from the resonance structure



might be invoked[16] to explain the high f_{ClO} value. The value of the ClF stretching force constant (4.46 mdyn/Å) falls within the range expected for a predominantly covalent ClF bond. The interpretation of relatively small differences (~0.3 mdyn/Å) in the ClF stretching force constant values listed in Table IV should be done only with caution since most values were computed from underdetermined systems and might be significantly influenced by the chosen stretch-bend interaction constants.

Registry No. ClF_3O_2, 38680-84-1; BF_3, 7637-07-2; AsF_5, 7784-36-3; $(ClO_2F_2)BF_4$, 38682-34-7; $(ClO_2F_2)AsF_6$, 39003-82-2; $(ClO_2F_2)PtF_6$, 36609-92-4; $(ClO_2)PtF_6$, 38123-66-9.

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ON THE REACTION OF $Cl_2F^+AsF_6^-$ WITH XENON

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In the presence of strong Lewis acids, XeF_2 can act as a powerful fluorinating oxidizer (1,2). For example, it can fluorinate Br_2 or I_2 (3) resulting in the formation of BrF_3 and IF_5, respectively, as shown by the following idealized equation:

$$3\ XeF^+BF_4^- + Br_2 \longrightarrow 2\ BrF_2^+BF_4^- + BF_3 + 3\ Xe$$

followed by dissociation of the thermally unstable $BrF_2^+BF_4^-$ complex to BrF_3 and BF_3 (4). However, to our knowledge, no example has been reported for the reverse reaction of this type, i.e., the oxidative fluorination of Xe by a halogen fluoride under mild conditions. Furthermore, previous studies have shown that both ClF (5) and ClF_3 (6) do not interact with Xe.

We have now found that the addition of a Lewis acid to ClF, which causes Cl_2F^+ formation (7), also increases the oxidizing power of ClF significantly so that it can fluorinate Xe according to:

$$Cl_2F^+AsF_6^- + Xe \longrightarrow XeF^+AsF_6^- + Cl_2$$

followed by the known (8) reaction:

$$2\ XeF^+AsF_6^- \longrightarrow Xe_2F_3^+AsF_6^- + AsF_5$$

These results suggest that the oxidizing power of cations decreases in the following order, $Cl_2F^+ > XeF^+$ or $Xe_2F_3^+ > BrF_2^+$, and that the enhancement of the oxidizing power of an amphoteric molecule by the addition of a strong Lewis acid is not limited to XeF_2 but is probably quite general. Furthermore, the fact that ClF is pseudo-isoelectronic with XeF^+ but acts as a rather mild fluorinating oxidizer, indicates that a specific valence electron configuration is not the main cause for unusual oxidizing power. Rather, it appears that cation formation, i.e., a formal positive charge, is more important.

Experimental Section

Xenon, ClF, and AsF_5 (2.09 mmol each) were combined at -196° in a passivated (with ClF_3) 25 ml sapphire-stainless steel reaction tube. The mixture was allowed to warm up to 25° and was kept at this temperature for one hour. The mixture was recooled to -196° and did not show the presence of any noncondensible material. After removal of the products volatile at 25° by pumping, a white solid residue (83 mg) was obtained. The volatile material was condensed back into the reactor at -196°. The contents were kept at -80° for 1.5 hours. The reactor was allowed to warm to 25° and the volatile products were separated by fractional condensation. They consisted of Xe (1.68 mmol) and a mixture of ClF, Cl_2, and AsF_5 (total of 3 mmol) which could not be separated completely by fractional condensation owing to partial formation of the known $Cl_2F^+AsF_6^-$ (7) and $Cl_3^+AsF_6^-$ (9) adducts. The white solid residue (157 mg) showed the vibrational spectrum and x-ray powder diffraction pattern characteristic (10) for monoclinic $Xe_2F_3^+AsF_6^-$. The latter probably formed from the original $XeF^+AsF_6^-$ (as indicated by the material balance) by loss of AsF_5 during sample preparation in the glove box (8). Previous reports (8,11) on the infrared spectrum and x-ray powder pattern diverge. Our data are in excellent agreement with the data of Bartlett et al. (8), but disagree with those reported by Binenboym et al.(11).

Acknowledgment

This work was supported by the Office of Naval Research, Power Branch. The authors are indebted to Drs. D. Pilipovich and C. J. Schack for helpful discussions and to Dr. N. Bartlett for making his original infrared spectra and x-ray powder patterns of $Xe_2F_3^+AsF_6^-$ available to us.

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Vibrational spectra of trifluoroacetates

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Abstract—Infrared and Raman spectra of $CsI(O_2CCF_3)_4$ and $Cs_2I(O_2CCF_3)_6$ are reported and compared to those of the free trifluoroacetate anion and covalent trifluoroacetyl compounds. The bonding of the trifluoroacetate group in $[I(O_2CCF_3)_4]^-$ is best interpreted as being covalent with strong ionic contributions. The vibrational spectrum of the free trifluoroacetate ion is reassigned.

INTRODUCTION

THE TRIFLUOROACETATE group is frequently used as a ligand in coordination chemistry. In most cases, vibrational spectroscopy is used to postulate either ionic, covalent, monodentate, or bidentate structures. However, these postulates are frequently based exclusively on minor frequency changes or splittings and consequently are not convincing. The recent synthesis [1] of $Cs^+[I(O_2CCF_3)_4]^-$ presented an opportunity to study the vibrational spectrum of a trifluoroacetato ligand expected to be considerably more covalent than metal trifluoroacetates, but more polar than organic trifluoroacetyl compounds. The covalent character of the trifluoroacetato ligand in its iodine (III) compound is suggested by the nature of its analogous perchlorato [2] and nitrato [3] salts, $Cs^+[I(OClO_3)_4]^-$ and $[N(CH_3)_4]^+[I(NO_3)_4]^-$, respectively. In addition, the skeleton of $I(O_2CCF_3)_4^-$ might be expected to have relatively high symmetry since the IF_4^- anion was recently shown [4] to be square planar. When comparing the assignments reported [5–8] for the free trifluoroacetate anion with those more recently reported [9–12] for a number of simple covalent trifluoroacetyl compounds, the need of revising the assignments for the free ion became obvious.

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EXPERIMENTAL

The preparation of $CsI(O_2CCF_3)_4$ and $Cs_2I(O_2CCF_3)_6$ has previously been described [1]. Silver trifluoroacetate was prepared from Ag_2O and CF_3COOH and vacuum dried at 100°C [7]. Sodium and cesium trifluoroacetate were purchased from Peninsular Chemical Research. The infrared spectra of the solids were recorded as dry powders in pressed AgBr disks on a Perkin–Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard calibration points [13]. The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å line of an Ar ion laser and melting point glass capillaries as sample containers in the transverse excitation-transverse viewing mode.

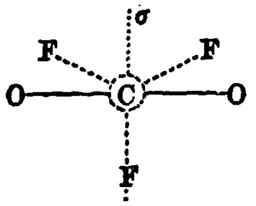
RESULTS and DISCUSSION

Observed spectra

The vibrational spectra of solid $CsI(O_2CCF_3)_4$, $Cs_2I(O_2CCF_3)_6$, NaO_2CCF_3, and AgO_2CCF_3, and of an aqueous solution of NaO_2CCF_3 are shown in Figs. 1 and 2. The observed frequencies are listed in Tables 1 and 2. The Raman spectrum of an aqueous AgO_2CCF_3 solution was also recorded. It closely resembled that of the sodium salt solution and, hence, is not listed. The spectra observed for the metal trifluoroacetates are in good agreement with those previously reported [5–8].

Assignments for the trifluoroacetate ion

A comparison between the assignments reported [5–8] for $CF_3CO_2^-$ and those made for a series of trifluoroacetyl compounds [9] revealed major discrepancies. Consequently, the vibrational spectrum of the free trifluoroacetate was reassigned based on the results of the thorough studies of BERNEY [9] on trifluoroacetyl compounds. For the $CF_3CO_2^-$ anion, a structure of symmetry C_s was assumed based on the known [14] structure of isoelectronic CF_3NO_2. This structure has only one symmetry element, i.e. a symmetry plane perpendicular to the CO_2 plane. Our revised assignments are summarized in Table 1 and were made by analogy with the well established assignments of CF_3COF [9]. The observed intensities and Raman polarization measurements are in good agreement with the predictions for symmetry C_s. For species a', one of the Raman bands (598 cm^{-1}) appears to be depolarized. However, the a' bands can be either polarized or depolarized, and the corresponding Raman band in CF_3COF also showed a high depolarization ratio of 0.78 [9].



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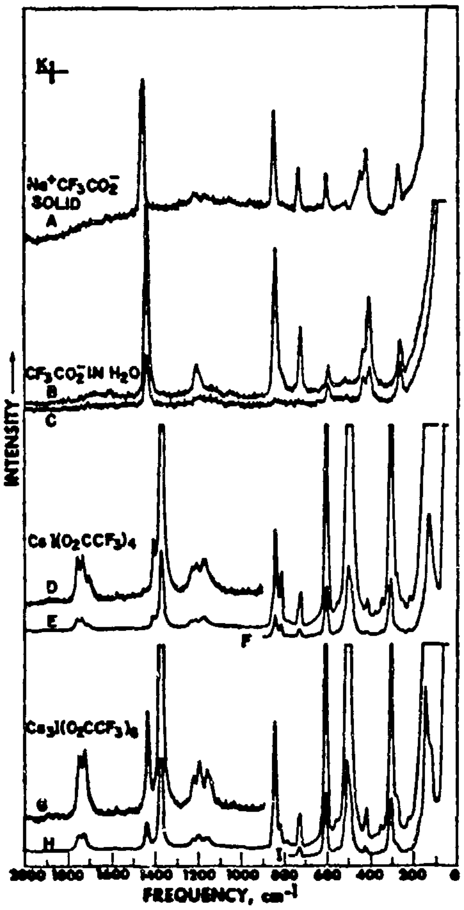

Fig. 1. Raman spectrum of solid $Na^+CF_3CO_2^-$ (trace A), of an aqueous solution of $Na^+CF_3CO_2^-$ traces B and C, incident polarization perpendicular and parallel, respectively, of solid $CsI(O_2CCF_3)_4$ at three different recorder voltages (traces D, E and F), and of solid $Cs_3I(O_2CCF_3)_6$ at three different recorder voltages (traces G, H and I). K indicates spectral slit width; exciting line 4880 Å.

Nature of the iodine–trifluoroacetate bond in $CsI(O_2CCF_3)_4$

Covalent or ionic? The next and most difficult question deals with the nature of the trifluoroacetate ligand in $CsI(O_2CCF_3)_4$. A review of the literature on trifluoroacetate as a ligand reveals numerous studies. However, the conclusions reached are often conflicting. This is due to the fact that most studies deal with trifluoroacetato complexes of metals. In this type of adduct, the trifluoroacetate ligand is essentially a free trifluoroacetate ion [15], which is only weakly bonded to the metal atom. As

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[15] A good example for proving this point is the crystal structure of the $Co(O_2CCF_3)_4^{2-}$ anion in which the trifluoroacetate ligands exhibit in spite of their monodentate nature $C_1—O_1$ and $C_1—O_2$ bond distances identical within experimental error [J. G. Bergman, Jr. and F. A. Cotton, *Inorg. Chem.* 5, 1420 (1966)].

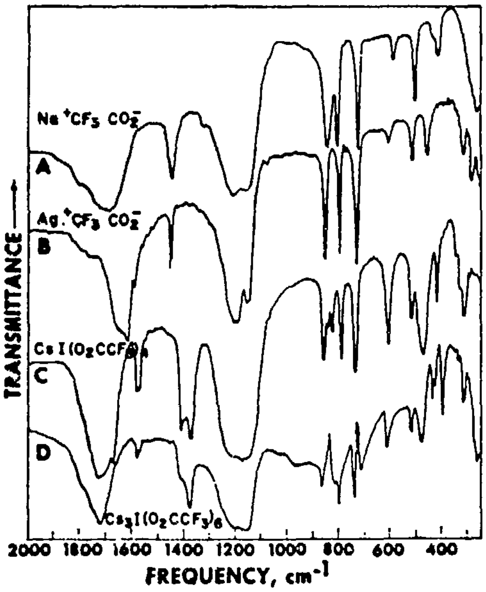

Fig. 2. Infrared spectrum of solid $Na^+CF_3CO_2^-$ (trace A), of solid $Ag^+CF_3CO_2^-$ (trace B), of solid $CsI(O_2CCF_3)_4$ (trace C), and of solid $Cs_3I(O_2CCF_3)_6$ (trace D) recorded as AgBr pellets.

a consequence, the vibrational frequencies of the trifluoroacetato group are very similar to those of the free trifluoroacetate ion and exhibit only small relative changes. Without detailed structural data, such as X-ray diffraction studies, it is difficult to correlate these small frequency shifts with structural parameters. For example, small changes in the O—C—O bond angle due to the size of the metal atom or crystal packing are difficult to separate from effects caused by mono or bidentate coordination.

In $CsI(O_2CCF_3)_4$, the bands due to the $C—CF_3$ part of the trifluoroacetate group are very characteristic and can readily be assigned (see Table 2). Consequently, we will discuss mainly the vibrations associated with the CO_2 group and the IO_4 skeleton. To better understand the nature of the trifluoroacetate group, let us first consider the two extreme cases, i.e. the free trifluoroacetate anion and the highly covalent $CF_3C(O)OCH_3$ molecule [11]. Whereas the average of the two CO stretching frequencies (1500 cm⁻¹ for $CF_3C(O)OCH_3$ and 1559 cm⁻¹ for $CF_3(CO_2^-)$ and, hence, the average CO bond order changes little, their frequency separation (586 cm⁻¹ for $CF_3C(O)OCH_3$ and 242 cm⁻¹ for $CF_3CO_2^-$) is very different. Furthermore, in the covalent trifluoroacetates of the type XO_2CCF_3 bands due to the *X*O vibrations will appear and show increasing frequencies with increasing covalent character of the *X*—O bond. Inspection of the $CsI(O_2CCF_3)_4$ spectrum reveals a CO stretching frequency separation of about 356 cm⁻¹ and the presence of skeletal IO stretching modes as high as 600 cm⁻¹. Since the frequencies of the latter almost approach the frequency range expected for covalent I—O single bonds, the bonding of the trifluoroacetate group in $CsI(O_2CCF_3)_4$ is best described as being covalent with strong

Table 1. Vibrational spectrum (cm^{-1}) of the trifluoroacetate anion and its assignment in point group C_s compared to that of CF_3COF

 $CF_3\overset{O}{C}{-}F$ [9]*		$Na^+CF_3CO_2^-$							$Ag^+CF_3CO_2^-$			
					Raman†							
		Infrared solid			Solid	Aqueous solution			Infrared solid		Raman†‡	Assignment and approximate description of mode
I.R. gas	Raman liquid	[6]	[8]	This work	This work	[6]	[5]	This work	[7]	This work	solid	
		1446 m	1445	1446 m	1454 (10)	1441 (10)	1435 vs, p	1438 (10) p	1450	1451 m	1449 (7)	a′ ν_1 $\nu_{sym}CO_2$
340 m	1338	1213 vs	1212	1212 vs	1210 (0+) br	1211 (1.6)	1205 m, p	1206 (1.3) p	1200	1206 vs	1201 (1)	ν_2 $\nu_{sym}CF_3$
1254 vs		1189 s				1188 (1.2)						ν_3 νFCF_3
806 m	808 p	850 ms	845, 841	847 ms	847 (7.2)	846 (3.2)	844 s, p	844 (6.0) p	845	852 ms	848 (10)	ν_4 ν_{C-C}
761 m	770, 758 p	807 ms		804 ms				810 sh, p	803, 796	794 ms		ν_5 $\delta_{sciss}CO_2$
692 s	694 p	793 ms	724	726 ms	729 (3)	728 (0.4)	729 m, p	727 (2.2) p	722	726 ms		ν_6 δ umbrella CF_3
595 w	596 dp		603	603 mw	602 (2.7)	596 (1.2)	601 m, p	598 (1.2) dp	600	606 mw		ν_7 δFCF_3
390 w	385 p			422 mw	421 (4.5)	410 (1.6)	410 ms, p	409 (2.8) p	445	457 m	450 (2.5)	ν_8 antigear rock§
228 mw	~236			—		224 (0.8)						ν_9 gear rock§
		1689 vs	1685	1688 vs, br		1676 (0+)	1681 mw, dp	1680 (0.3) br	1650, 1620	1640, 1615		a″ ν_{10} $\nu_{as}CO_2$
1214 vs	~1200	1140 s	1143	1158 vs			1143 w	1145 (0.3)	1130	1150 m		ν_{11} $\nu_{as}CF_3$
519 m	520 dp		516	516 m	515 (0+)	505 (0.8)	521 w, dp	520 (0+)	513	517 m		ν_{12} $\delta_{as}CF_3$
426 w	427 dp			441 w	441 (2)	429 (1.2)	437 mw, dp	434 (1) dp	320	319 m		ν_{13} antigear wag§
242 m	246 dp			271 w	270 (2.8)	262 (1.2)	267 m, dp	266 (1.9) dp	284	263 m	280 (1)	ν_{14} gear wag§
60												$\nu_{15}\tau_{C-C}$

* For both CF_3COF and $CF_3CO_2^-$, symmetry C_s was assumed, but for CF_3COF (assuming free rotation of the CF_3 group), the symmetry plane coincides with the COF plane, whereas for CF_3CO_2 it is perpendicular to the CO_2 plane.

† Uncorrected Raman intensities.

‡ The Raman spectrum of an aqueous solution of $Ag^+CF_3COO^-$ was also recorded; since it was almost identical with that of the aqueous $Na^+CF_3COO^-$ solution, it is not listed.

§ For description of this motion, see Ref. [9].

Table 2. Vibrational spectrum (cm^{-1}) of solid $Cs^+I(O_2CCF_3)_4^-$

Infrared	Raman	Assignment
	1750 (0.3)	$\nu_{as}CO_2$ or $\nu_{C=O}$
1710 vs, br	1725 (0.2)	
	1695 (0.1)	
1662 w		816 + 839 = 1655
1571 mw		
1561	1570 (0+)	
1404 m	1405 (0.2)	$\nu_{sym}CO_2$ or ν_{C-O}
1366 s	1369 (1.6)	
	1225 sh	$\nu_{sym}CF_3$
1140–1230 vs	1203 (0.2)	$\nu_{sym}FCF_2$
	1166 (0.2)	$\nu_{as}FCF_2$
854 mw	852 sh	ν_{C-C}
845 vw		
835 vw	839 (2.3)	
830 w	816 (1.3)	
782 mw	781 (0+)	$\delta_{scis}CO_2$
727 m	725 (0.7)	$\delta_{umbrella}CF_3$
602 m	604 (5.2)	$\delta FCF_2 + \nu_{sym}$ out of phase IO_4
	555 (0.1)	
517 mw	520 sh	$\delta_{as}CF_3$
490 sh	501 (7.2)	ν_{sym} in phase IO_4
	490 sh	
470 ms		$\nu_{as}IO_4$
416 mw	418 (0.3)	antigear rock
380 sh	378 (0.1)	
346 vw	346 (0.3)	
329 vw		
310 m		antigear wag?
305 sh	306 (5.8)	δIO_4
293 vw		
275 sh	278 (0.1)	gear wag?
	249 (0.2)	
	218 (0.3)	gear rock?
	130 (10)	δIO_4

ionic contributions. The ionic nature of an X—O_2CCF_3 bond might be expected to increase with decreasing electronegativity of the X atom. Experimental evidence for this trend has been found [16] for the trifluoroacetates of C, Si, Ge, and Sn. Within this series, the C=O stretching frequency decreases from 1852 cm in $CF_3OC(O)CF_3$ [10] to 1750 cm^{-1} in $Sn(O_2CCF_3)_4$ [16], a frequency approaching those observed for $CsI(O_2CCF_3)_4$ (see Table 2). Further proof for the highly covalent nature of the trifluoroacetates of the group IV elements consists of their high volatilities [16]. Unfortunately, only the carbonyl stretching frequencies have been reported for these trifluoroacetates [16], except for $(CH_3)_3SnO_2CCF_3$ which in CCl_4 solution shows CO_2 stretching modes at 1720, 1660, and 1400 cm^{-1} [17]. The fact that a decrease of the carbonyl frequency is generally accompanied by an increase of the C—O frequency has also been recognized by VARETTI and AYMONINO [18].

Monodentate or bidentate? The trifluoroacetate group could function as a monodentate or as a bidentate ligand. In connection with $CsI(O_2CCF_3)_4$, we will discuss

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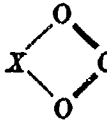
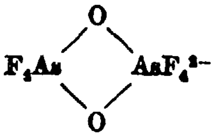
mainly covalent ligands. Again, let us consider the two ideal cases, i.e. a monodentate and a symmetric bidentate trifluoroacetate group. A covalent monodentate group should exhibit a spectrum similar to that observed for $CH_3OC(O)CF_3$ [11], i.e. a high C═O double bond and a low C—O stretching frequency. In addition, the trifluoroacetate group no longer possesses a symmetry plane. This removes the degeneracy between the FCF_2 and the antisymmetric CF_3 stretching mode and allows the observation of a total of three CF_3 stretching modes in the 1100–1300 cm^{-1} frequency range. For a covalent symmetric bidentate, trifluoroacetate group, the two CO bonds should be equivalent, causing a strong mixing of their stretching motions. Instead of a C═O and a C—O stretch, one obtains a symmetric and an antisymmetric CO_2 stretch with a CO bond order about 1.5. The two CO_2 stretching frequencies and their difference should be comparable to those of the free trifluoroacetate anion [19]. A minor decrease in the frequency difference might be expected for the bidentate ligand when compared to the free ion, if one assumes that the XO_2 bonding in  will decrease the CO_2 bond angle from the 120° value in the free ion towards 90°. This decrease in the bond angle would decrease the coupling between the two CO motions and make their frequencies more similar. In addition, one might expect the bidentate ligand to have the same symmetry (C_s) as the free ion and, therefore, to show only two CF_3 stretching modes owing to the degeneracy between ν_3 and ν_{11} (see Table 1). Consequently, distinction between a covalent symmetric bidentate ligand and the free ion may be difficult based upon the CO_2 stretching frequencies alone. However, the appearance of the XO_2 modes in the lower frequency range of the spectrum should clearly distinguish between the two possibilities.

Application of this reasoning to $CsI(O_2CCF_3)_4$ clearly rules out the possibility of a symmetric bidentate structure. To what extent back donation of electrons of the carbonyl group (which is generally a good donor) to iodine in a monodentate structure, such as $I(O_2CCF_3)_4^-$ takes place is difficult to judge from the presently available data and might be a matter of semantics.

Skeletal modes

It was previously shown that the IF_4^- anion is square planar having symmetry D_{4h} [4]. For the IO_4 skeleton in $I(O_2CCF_3)_4^-$ such a planar configuration is unlikely. Comparison with other oxygen bridged species such as $F_5AsOAsF_5^{2-}$ and



suggests X—O—X bond angles of about 140 and 95° [20] for mono- and bidentate

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bonding, respectively, of a trifluoroacetate group. The actual I—O—C bond angle should be influenced by the degree of back donation of electrons of the carbonyl oxygen to iodine and mutual repulsion between the atoms involved. In any case distortion of the IO_4 part from symmetry D_{4h} is expected and a puckered arrangement of the oxygens around iodine is likely.

Comparison of the skeletal modes of $I(O_2CCF_3)_4^-$ with those reported for the related $I(OClO_3)_4^-$ [2] and $I(OSO_2F)_4^-$ [21] anions shows relatively poor agreement. This indicates that the assumed structural models may be too simple and calls for structural studies such as X-ray diffraction, which will yield more accurate information. Similar data are required for $Cs_2\,I(O_2CCF_3)_4$.

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Chlorine Trifluoride Dioxide.
Vibrational Spectrum, Force Constants, and Thermodynamic Properties

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Received March 16, 1973

The infrared spectra of gaseous, solid, and matrix-isolated ClF_3O_2 and the Raman spectra of gaseous and liquid ClF_3O_2 are reported. Twelve fundamental vibrations were observed, consistent with a structure of symmetry C_{2v}. A modified valence force field and thermodynamic properties were computed for ClF_3O_2.

Introduction

A brief note on the existence of ClF_3O_2 was recently published by Christe.[1] In a subsequent paper,[2] more details on its synthesis and physical properties were given. Proof for a pseudo-trigonal-bipyramidal structure of symmetry C_{2v} was obtained[2] from its ^{19}F nmr spectrum, which showed an AB_2 pattern with strong evidence for the two equivalent fluorine atoms occupying the apical positions. In this paper, we report the complete vibrational spectrum, force constants, and thermodynamic properties of ClF_3O_2.

Experimental Section

The synthesis and purification of ClF_3O_2 has previously been described.[1,2] The sample used in this investigation showed no detectable impurities except for small amounts of $FClO_2$ which easily forms during handling and cannot be separated from ClF_3O_2 by fractional condensation.[2] The amount of $FClO_2$ formed, however, could be minimized by thorough passivation of the stainless steel–Teflon FEP vacuum system with BrF_5 and ClF_3. For example, the infrared spectrum of gaseous ClF_3O_2 at 700 mm pressure showed the presence of less than 0.1 mol % of $FClO_2$.

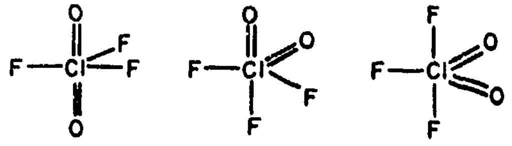
The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range of 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard gas calibration points.[3] The gas cell was made of Teflon and had a path length of 5 cm and AgCl windows. The apparatus, materials, and technique used for the matrix-isolation study have previously been described.[4,5] Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-A line of an Ar ion laser as the exciting line. A stainless steel cell with Teflon O rings and sapphire windows was used for obtaining the spectrum of the gas. The design of this cell was similar to that of a cell described previously.[6] The spectrum of the liquid was obtained using a Teflon FEP capillary as the sample container in the transverse excitation–transverse viewing mode.

Results and Discussion

Vibrational Spectra. Figure 1 shows the infrared spectra of gaseous, solid, and N_2-matrix-isolated ClF_3O_2 and the Raman spectra of gaseous and liquid ClF_3O_2 at various concentrations. The spectra of solid ClF_3O_2 were corrected for small amounts of $FClO_2$. The $FClO_2$ bands were verified by depositing pure $FClO_2$ on top of the ClF_3O_2 sample and observing the relative growth rates of the bands. Figure 2 shows the most intense infrared bands of gaseous and matrix-isolated ClF_3O_2 at higher resolution allowing some conclusions about the band contours and the determination of the ^{35}Cl-^{37}Cl isotopic shifts. Table I lists the observed frequencies. Table II lists the fundamental vibrations of ClF_3O_2 and their assignment compared to those of the related species ClF_3,[7] ClF_3O,[8] $ClF_2O_2^-$,[9] ClF_4^+,[10] and ClO_2^+.[11]

The structure of ClF_3O_2 can be derived from a trigonal bipyramid, in which the two oxygen ligands could occupy both apical (I), one apical and one equatorial (II), or two equatorial (III) positions. (See Chart I.) These three models belong to different point groups and should differ markedly in their vibrational spectra. The observation of a total of 12 fundamentals for ClF_3O_2 (see Figures 1 and 2 and Table I) with a minimum of ten bands being active in the infrared and the Raman spectra, together with the occurrence of four or five polarized Raman bands, rule out point group D_{3h} and favor C_{2v} over C_s. Additional strong evidence for symmetry C_{2v} consists of the relative infrared and Raman intensities and of the frequency separation of the ClF_2 stretching modes, indicating a highly symmetric, *i.e.*, approximately linear, FClF arrangement. Comparison with the vibrational spectra of a number of related species having geometries similar to that of model III (see Table II) also supports model III. This conclusion in favor of model III, reached exclusively on the basis of the observed vibrational spectrum, is in excellent agreement with the observed ^{19}F nmr spectrum[2] and the general observation[12] that, in trigonal-bipyramidal molecules, the most electronegative ligands always occupy the apical positions.

Chart I



	I	II	III
Point group	D_{3h}	C_s	C_{2v}
Total no. of fundamentals	8	12	12
Infrared active	5	12	11
Raman active	6	12	12
Polarized Raman bands	2	8	5

The 12 fundamentals expected for an XY_3Z_2 molecule of symmetry C_{2v} are classified as $5\ A_1 + A_2 + 3\ B_1 + 3\ B_2$. All of these should be active in both the infrared and Raman spectra except for the A_2 mode which should be only Raman

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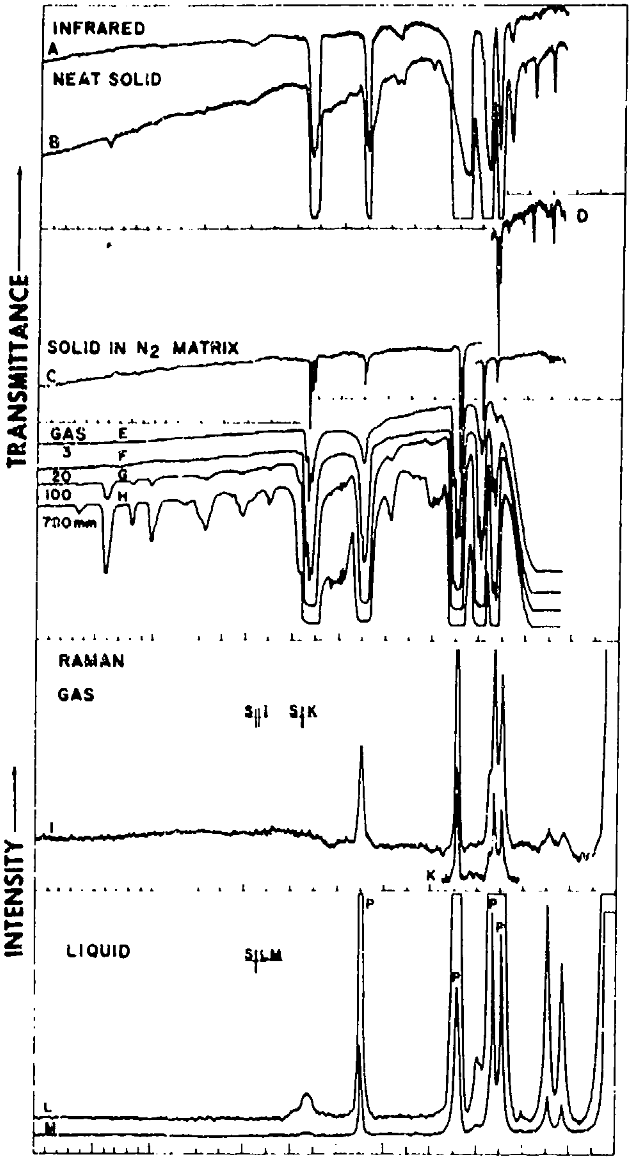


Figure 1. Infrared and Raman spectra of ClF_3O_2. Traces A and B represent the infrared spectra of 22.3 and 230 μmol, respectively, of neat solid ClF_3O_2 at 4°K; traces C and D, the infrared spectra of 0.89 and 20.6 μmol, respectively, of ClF_3O_2 in a N_2 matrix (mole ratio 1:760) at 4°K; traces E–H, the infrared spectra of gaseous ClF_3O_2 at the denoted pressures in a 5-cm path length cell; traces I and K, the Raman spectra of gaseous ClF_3O_2 at 4 atm pressure in a stainless steel cell with sapphire windows; traces L and M, the Raman spectra at two different recorder voltages, respectively, of liquid ClF_3O_2 in a Teflon FEP capillary at 25°; S indicates spectral slit widths and P indicates polarized bands.

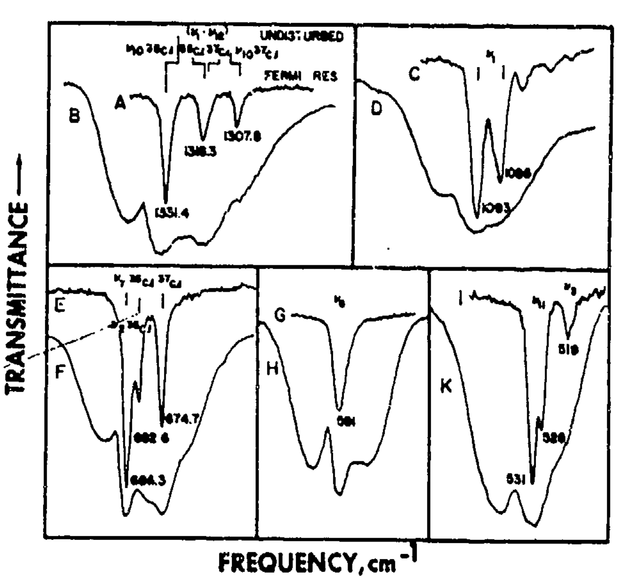


Figure 2. Principal infrared bands of gaseous and N_2-matrix-isolated ClF_3O_2 recorded at tenfold scale expansion under higher resolution conditions. The frequency denotations refer to the matrix-isolation spectra. The frequency scale of the gas bands has been slightly shifted to line up the matrix band centers with the corresponding Q branches of the gas band contours.

active. The strong bands at about 1327 and 1093 cm^{-1} have frequencies too high for any Cl–F stretching modes and, hence, must be assigned to the antisymmetric and symmetric ClO_2 stretching modes, respectively. The antisymmetric axial F–Cl–F stretching mode should occur in the 600–800-cm^{-1} frequency range, be of very high infrared and very low Raman intensity, and by comparison with ClF_3O[8] and ClF_3[7] show a ^{35}Cl-^{37}Cl isotopic shift of about 11 cm^{-1}. Consequently, this mode must be assigned to the bands observed at 686.3 and 674.7 cm^{-1} in the N_2 matrix. The symmetric axial F–Cl–F stretching mode should occur in the 450–570-cm^{-1} frequency range and be of high intensity in the Raman and of very low intensity in the infrared spectrum. There are two intense polarized Raman bands at 520 and 487 cm^{-1}, respectively, which might be assigned to this mode. Since the 487-cm^{-1} band is of much lower infrared intensity (for an ideal linear, symmetric F–Cl–F group, this mode should be infrared inactive and indeed was not observed for gaseous ClF_3O_2), it is assigned to the symmetric axial FClF stretching mode. The fifth stretching mode involving the equatorial fluorine is expected to occur between 650 and 800 cm^{-1}, to be of medium to strong infrared intensity, and to give rise to an intense polarized Raman line. Clearly, this mode must be assigned to the 682.6-cm^{-1} band in the matrix and the 683-cm^{-1} Raman band. Comparison with ClF_3O[8] and ClF_3[7] indicates a ^{35}Cl-^{37}Cl isotopic shift of about 7 cm^{-1} for this mode. Its ^{37}Cl part could not directly be observed for the matrix-isolated sample owing to its accidental coincidence with the much more intense ^{37}Cl antisymmetric FClF stretching mode.

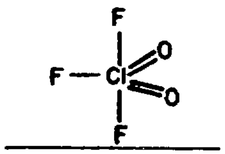
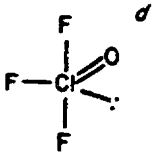
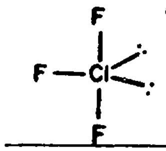
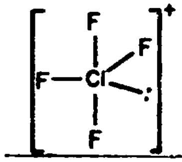
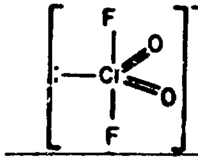
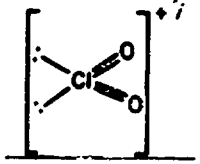
The remaining seven bands must be assigned to the deformation modes. Of these, only the A_2 torsion mode ideally should be infrared inactive. Since the Raman band at about 410 cm^{-1} shows no counterpart in the infrared spectrum of the gas, it is assigned to this torsion mode. The 520-cm^{-1} Raman band is clearly polarized and, hence, must belong to species A_1. Based on its relatively high frequency, it must represent the ClO_2 scissoring mode and not the axial F–Cl–F deformation. Based on the observed Fermi resonance (see below) between the 1327-cm^{-1} band and the 1093 + 222 cm^{-1} combination band, the 222- and 1327-cm^{-1} bands must belong to the same symmetry species. Consequently, the 222-cm^{-1} band must represent the B_2 axial F–Cl–F deformation. There are four bands occurring at about 590, 530, 370, and 290 cm^{-1}, respectively, left for assignment. Two of these represent a rocking and wagging motion, respectively, of the ClO_2 group and, therefore, should have higher frequencies than the two remaining FClF deformations. Assignment of the 591-cm^{-1} band to the ClO_2 wag and of the 531-cm^{-1} band to the ClO_2 rock can be made based on the observed gas-phase band contours and the observed ^{35}Cl-^{37}Cl isotopic splittings (see Figure 2, traces G–K). The 591-cm^{-1}

Table I. Vibrational Spectra of ClF_3O_2 and Their Assignment in Point Group C_{2v}

Obsd freq, cm^{-1}, and intens[a]						
Infrared			Raman			
	Solid					
Gas	Matrix isolated	Neat	Gas	Liquid	Assignment	
2655 vw					2 × 1327 = 2654	$2\nu_{10}\ (A_1)$
2415 vw	2420 2405 vs 2385	2405 vw			1093 + 1327 = 2420	$\nu_1 + \nu_{10}\ (B_2)$
2184 vw		2180 vw			2 × 1093 = 2186	$2\nu_1\ (A_1)$
2012 vw	2012 vw	2010 vw			683 + 1327 = 2010	$\nu_2 + \nu_{10}\ (B_2)$
1860 vw		1850 vw			520 + 1327 = 1847	$\nu_3 + \nu_{10}\ (B_2)$
1776 vw					1093 + 695 = 1788 1093 + 683 = 1776	$\nu_1 + \nu_7\ (B_1)$ $\nu_1 + \nu_2\ (A_1)$
1625 vw					1093 + 531 = 1624	$\nu_1 + \nu_{11}\ (B_2)$
1615 vw		1610 vw			1093 + 520 = 1613 286 + 1327 = 1613	$\nu_1 + \nu_3\ (A_1)$ $\nu_8 + \nu_{10}\ (B_2)$
1579 vw					1093 + 487 = 1580	$\nu_1 + \nu_4\ (A_1)$
1499 vw		1495 vw			2 × 487 + 520 = 1494 683 + 286 + 531 = 1500	$2\nu_4 + \nu_3\ (A_1)$ $\nu_2 + \nu_8 + \nu_{11}\ (B_2)$
1375 vw		1375 vw			683 + 695 = 1378	$\nu_2 + \nu_7\ (B_1)$
1366 vw	1365 vw				2 × 683 = 1366	$2\nu_2\ (A_1)$
1341						
	1331.4 s	1327 s		1320 (0.1) br		$\nu_{10}(^{35}Cl)\ (B_2)$
1331						
vs						
1317	1318.8 ms	1315 m, sh			1093 + 222 = 1315	$\nu_1 + \nu_{12}\ (B_2)$
1306	1307.8 ms	1305 m, sh				$\nu_{10}(^{37}Cl)\ (B_2)$
1230 vs	1230 vw				520 + 695 = 1215	$\nu_3 + \nu_7\ (B_1)$
1218 vw	1218 vw				683 + 531 = 1214	$\nu_2 + \nu_{11}\ (B_2)$
	1207 vw	1200 vw			683 + 520 = 1203	$\nu_2 + \nu_3\ (A_1)$
1195 vw	1203 vw				2 × 592 = 1184	$2\nu_5\ (A_1)$
1186 vw		1150 vw			487 + 695 = 1182	$\nu_4 + \nu_7\ (B_1)$
1174 vw	1173 1169 vw				683 + 487 = 1170	$\nu_2 + \nu_4\ (A_1)$
	1116 vw				417 + 695 = 1112	$\nu_6 + \nu_7\ (B_2)$
					520 + 592 = 1112	$\nu_3 + \nu_5\ (B_1)$
1093 s	1093 ms		1093 (3.5)	1090 (4.1) pol[b]		$\nu_1(^{35}Cl)\ (A_1)$
	1086 m					$\nu_1(^{37}Cl)\ (A_1)$
	1080 vw					
	1073 vw	1070 vw, sh			695 + 372 = 1067	$\nu_7 + \nu_9\ (A_1)$
	1065 vw				2 × 531 = 1062	$2\nu_{11}\ (A_1)$
985 vw					286 + 695 = 981	$\nu_8 + \nu_7\ (B_1)$
978 vw	974 vw	968 vw			2 × 487 = 974	$2\nu_4\ (A_1)$
881 vw					286 + 592 = 878	$\nu_8 + \nu_5\ (B_1)$
856 vw					487 + 372 = 859	$\nu_4 + \nu_9\ (B_1)$
805						
vw	810 vw	806 vw			520 + 286 = 806	$\nu_3 + \nu_8\ (A_1)$
797						
786 vw					417 + 372 = 789	$\nu_6 + \nu_9\ (B_2)$
772 vw		760 sh, vw			487 + 286 = 773	$\nu_4 + \nu_8\ (A_1)$
758 vw					531 + 222 = 753	$\nu_{11} + \nu_{12}\ (A_1)$
702						
695	686.3 vs	655 vs, br				$\nu_7(^{35}Cl)\ (B_1)$
687 sh vs	682.6 m	700 sh, s	683 (10)	675 (6.5) pol		$\nu_2(^{35}Cl)\ (A_1)$
683	674.7 s					$\nu_7(^{37}Cl)\ (B_1)$
679 sh						
593 s	591 ms	570 s		586 (0.1)		$\nu_5\ (B_1)$
543	531 m					$\nu_{11}(^{35}Cl)\ (B_2)$
m		527 m	540 sh	530 sh		
531	528 mw					$\nu_{11}(^{37}Cl)\ (B_2)$
520 sh, mw	519 w	520 sh, w	520 (7.5)	518 (10) pol		$\nu_3\ (A_1)$
	487 vw	473 mw	487 (6.1)	481 (9.0) pol		$\nu_4\ (A_1)$
	417 vw	417 vw		402 (0+)		$\nu_6\ (A_2)$
	372 w	368 w				$\nu_9\ (B_1)$
	287 w	290 w	285 (0.9)	285 (1.6)		$\nu_8\ (A_1)$
			222 (0.7)	222 (1.2)		$\nu_{12}\ (B_2)$

[a] Uncorrected Raman intensities representing the relative peak height; the relative peak widths and, hence, the relative peak heights change from gaseous to liquid ClF_3O_2. [b] Only qualitative polarization measurements could be obtained, owing to the optical activity of the sapphire windows of the gas cell and owing to the tendency of ClF_3O_2 to act as a plasticizer for the Teflon FEP capillaries.

Table II. Vibrational Spectra of ClF$_3$O$_2$ Compared to Those of Similar Molecules and Ions

Obsd freq, cm^{-1}, and intens													
		 [d]		 [f]		 [g]		 [h]		 [i]			
Ir	R	Ir	R	Ir	R	Ir	R	Ir	R	Ir	R	Assignment for ClF$_3$O$_2$ in point group C_{2v}	Approx description of mode[j]
1093 s	1093 (4) p	(1222)		. . .		. . .		1070 s	1076 (10)	1044 s	1044 (10)	A_1 ν_1	Sym ClO$_2$ str
683 m	683 (10) p	686 s	694 (2.4) p	752 s	752 s, p	830–810		. . .				ν_2	ClF$_{eq}$ str
519 w	520 (8) p	. . .		. . .		. . .		559 m	559 (1.2)	521 s	521 (3)	ν_3	ClO$_2$ scissor
487 vw	487 (6) p	478 mw	482 (10) p	530 m	529 vs, p	568 w	567 (7)	330–370 m	363 (10)		. . .	ν_4	Sym F$_{ax}$ClF$_{ax}$ str
287 w	285 (1)	c, e	224 (0.4) p	328 s	329 w, p	c	237 (1)	c	198 (0.7)		. . .	ν_5	F$_{ax}$ClF$_{ax}$ scissor in ClF$_3$ plane
(417)[a]	402 (0+)	412 w	414 (0.2) dp	. . .			474 (1)		480 (1)		. . .	A_2 ν_6	Torsion
695 vs		652 vs		702 vs		770 vs		510 vs			. . .	B_1 ν_7	Antisym F$_{ax}$ClF$_{ax}$ str
592 s	586 (0+)	499 m	500 (1)	. . .		536 mw	538 (2)	330–370 m	337 (8)		. . .	ν_8	ClO$_2$ wag
372 w				442 w	431 w, dp			. . .			. . .	ν_9	Antisym F$_{eq}$ClF$_{ax}$ def in ClF$_3$ plane
1327[b] vs	1320 (0+)	(1222)		. . .		. . .		1225 vs	1221 (0.8)	1296 vs	1296 (1)	B_2 ν_{10}	Antisym ClO$_2$ str
531 m	530 (1)	323 mw[e]	319 (0.1)	. . .		. . .		330–370 m	378 (8)		. . .	ν_{11}	ClO$_2$ rock
c	222 (1)			328 s	329 w	386 m	388 (0+)				. . .	ν_{12}	F$_{ax}$ClF$_{ax}$ scissor out of ClF$_3$ plane

[a] Observed only for solid ClF$_3$O$_2$. [b] Frequency corrected for disturbance by Fermi resonance. [c] Below frequency range of spectrometer used. [d] K. O. Christe and E. C. Curtis, *Inorg. Chem.*, 11, 2196 (1972). [e] According to the potential energy distribution, the 224- and 320-cm^{-1} modes are an almost equal mixture of the corresponding symmetry coordinates and, hence, not very characteristic. [f] H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, 52, 3517 (1970). [g] K. O. Christe and W. Sawodny, to be submitted for publication. [h] K. O. Christe and E. C. Curtis, *Inorg. Chem.*, 11, 35 (1972). [i] K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *ibid.*, 8, 2489 (1969). [j] The modes in the B$_1$ block are highly mixed (see PED, Table VII) and, therefore, difficult to associate with the frequencies.

Table III. Symmetry Coordinates[a] for ClF$_3$O$_2$

A_1	S_1	$(1/\sqrt{2})(\Delta D_1 + \Delta D_2)$
	S_2	ΔR
	S_3	$(1/\sqrt{6})(2\Delta\alpha - \Delta\gamma_1 - \Delta\gamma_2)$
	S_4	$(1/\sqrt{2})(\Delta r_1 + \Delta r_2)$
	S_5	$(1/\sqrt{12})(2\Delta\beta_1 + 2\Delta\beta_2 - \Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$
	S_{r_1}	$(1/\sqrt{3})(\Delta\alpha + \Delta\gamma_1 + \Delta\gamma_2) \equiv 0$
	S_{r_2}	$(1/\sqrt{6})(\Delta\beta_1 + \Delta\beta_2 + \Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3 + \Delta\delta_4) \equiv 0$
A_2	S_6	$(1/\sqrt{4})(\Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 + \Delta\delta_4)$
B_1	S_7	$(1/\sqrt{2})(\Delta r_1 - \Delta r_2)$
	S_8	$(1/\sqrt{4})(\Delta\delta_1 - \Delta\delta_2 + \Delta\delta_3 - \Delta\delta_4)$
	S_9	$(1/\sqrt{2})(\Delta\beta_1 - \Delta\beta_2)$
B_2	S_{10}	$(1/\sqrt{2})(\Delta D_1 - \Delta D_2)$
	S_{11}	$(1/\sqrt{2})(\Delta\gamma_1 - \Delta\gamma_2)$
	S_{12}	$(1/\sqrt{4})(\Delta\delta_1 + \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$

[a] S_{r_1} and S_{r_2} are the redundant coordinates and $\delta_1 = \angle O_1ClF_1$, $\delta_2 = \angle O_1ClF_3$, $\delta_3 = \angle O_2ClF_1$, and $\delta_4 = \angle O_2ClF_3$.

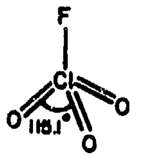
band shows a Q-R branch splitting for $^{35}ClF_3O_2$ of about 8 cm^{-1} comparable to that observed for the antisymmetric FClF stretch, ν_7 (B_1). The 531-cm^{-1} band exhibits a missing Q branch and a P-R branch separation of about 11 cm^{-1} comparable to that observed for the antisymmetric ClO$_2$ stretch, ν_{10} (B_2). Furthermore, the 531-cm^{-1} band shows a larger ^{35}Cl-^{37}Cl isotopic splitting than the one at 591 cm^{-1} in agreement with the values (see Table IV) computed for the ClO$_2$ rocking and wagging motions, respectively. The remaining two bands at 286 and 372 cm^{-1} are assigned to the axial F-Cl-F scissoring mode ν_5 (A_1) and the antisymmetric in-plane ClF$_3$ deformation mode, ν_9 (B_1), respectively. This assignment is based on the observed frequencies and the relative infrared and Raman intensities. The assignment of the 286-cm^{-1} Raman band to an A_1 mode is further supported by the fact that it appears to be weakly polarized. The excellent fit between all the observed and computed combination bands and overtones (see Table I) without violation of the selection rules ($B_1 + B_2 = A_2$ and $A_1 + A_2 = A_2$ combinations are infrared forbidden) also suggests the correctness of the above assignments.

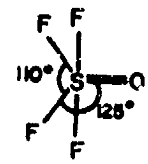
The observation of three relatively intense bands in the N$_2$ matrix for the antisymmetric ClO$_2$ stretching mode, ν_{10} (B_2), requires further explanation. For this mode, a ^{35}Cl-^{37}Cl isotopic splitting of about 15 cm^{-1} might be predicted by comparison with that observed for related ClO$_2^+$.[14] The combination band 1093 + 222 = 1315 cm^{-1} should show a considerably smaller ^{35}Cl-^{37}Cl isotopic splitting of about 8 cm^{-1} (see Table IV) and based on its frequency fall between the ^{35}Cl and ^{37}Cl isotopic bands of ν_{10}. As shown schematically in Figure 2, Fermi resonance between ν_{10} and $\nu_1 + \nu_{12}$ will increase the frequency separation between the ^{35}Cl and ^{37}Cl components of ν_{10} and decrease that between the two isotopic combination bands. This assignment is supported by the observed bandwidths at half-height which are similar (~2.0 cm^{-1}) for the 1331.4- and 1307.8-cm^{-1} bands but larger (~3.0 cm^{-1}) for the 1318.8-cm^{-1} band. The disturbance by Fermi resonance can also account for the strongly increased intensity of the combination band. The fact that the frequency of the 1318.3-cm^{-1} band is closer to 1307.8 cm^{-1} than to 1331.4 cm^{-1} agrees with the observed relative intensities. The 1307.8-cm^{-1} band has lost relatively more of its original intensity as demonstrated by the observed intensity ratio of 1:4.4 for the 1307.8- and 1331.4-cm^{-1} bands. For undisturbed ^{35}Cl-^{37}Cl isotopic species, this ratio should be 1:3.07.

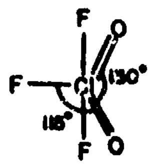
The observed gas-phase infrared band contours are complicated by the ^{35}Cl-^{37}Cl isotopic splittings, Fermi resonance, and two double coincidences of ν_7 with ν_2 and of ν_{11} with ν_3, respectively. However, for most of the bands, the R branches of the ^{35}Cl isotope are well separated (see Figure 2). Since the geometry of ClF$_3$O$_2$ of symmetry C_{2v} can be estimated (see below), the three principal moments of inertia were computed resulting in $A = 0.150$, $B = 0.106$, and $C = 0.095$ cm^{-1}. Based on these values, the infrared band contours were estimated for ClF$_3$O$_2$, according to the method of Ueda and Shimanouchi.[13] Using No. 33 of Ueda's Figure 3,[13] one should expect for the B_1 modes an A-type band contour with a sharp Q branch and a P-R branch separation of about 16 cm^{-1}. As can be seen from Figure 2, the 686- and 591-cm^{-1} bands show the predicted band shape and branch separation and, therefore, may be assigned with confidence to ν_7 and ν_8, respectively. The 1331- and 531-cm^{-1} bands do not show a Q branch as expected for B-type bands of species B_2. Consequently, the observed band contours are consistent with the proposed structure of symmetry C_{2v} and the assignments listed in Table I.

Comparison between the vibrational spectrum of ClF$_3$O$_2$ and those of related species (Table II) shows good agreement and strongly supports the above assignments for ClF$_3$O$_2$. Two features in the ClF$_3$O$_2$ spectrum, however, require further comment. The ClO$_2$ scissoring mode, ν_3 (A_1), is unexpectedly intense in the Raman spectrum. Since the frequency of ν_3 is close to that of the intense ν_2 (A_1) mode and since these motions could easily couple (as indicated by the normal-coordinate transformation L^{-1} and to some extent by the PED), this represents a plausible explanation for its high intensity. Alternate explanations such as Fermi resonance between the symmetric axial FClF stretching mode ν_4 and 222 + 286 = 508 cm^{-1} can be ruled out because they belong to different symmetry species. Resonance between ν_3 and ν_4 can also be eliminated because the observed combination bands involving either ν_3 or ν_4 show a good frequency fit, indicating that the fundamentals are undisturbed. Second, the frequencies of the two axial FClF scissoring modes (in and out of the ClF$_3$ plane, respectively) are strongly influenced by the point group of the corresponding molecules and by the presence or absence of other modes in the same symmetry species and, hence, are difficult to correlate. Furthermore, in ClF$_3$O, these two frequencies are not characteristic and are an almost equal mixture of the corresponding symmetry coordinates.[8]

Force Constants. The potential and kinetic energy metrics for ClF$_3$O$_2$ were computed by a machine method.[14] The geometry assumed for this computation was D(ClO) = 1.40 Å, R(ClF$_{eq}$) = 1.62 Å, r(ClF$_{ax}$) = 1.72 Å, α(OClO) = 130°, β(F$_{eq}$ClF$_{ax}$) = δ(OClF$_{ax}$) = 90°, and γ(OClF$_{eq}$) = 115°, based on the observed geometries of ClF$_3$ [15] and FClO$_3$ [16] and a correlation[17] between ClO bond length and stretching frequency. The deviation of the OClO bond angle from the ideal 120° was estimated by comparison with the known geometries of SF$_4$O[18] and FClO$_3$.[16]







The symmetry coordinates used for ClF$_3$O$_2$ are given in Table III. The bending coordinates were weighted by unit (1 Å) distance so the stretching force constants have units of mdyn/Å, the deformation force constants units of mdyn Å/radian^2, and the stretch-bend interaction constants have units of mdyn/radian. The G matrix and Z transformation were found numerically by the computer and, hence, are not given here.

The force constants were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. Owing to the underdetermined nature (28 symmetry force constants and 12 frequencies) of the problem, a diagonal force field was com-

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Table IV. Observed Frequencies (cm^{-1}), Symmetry Force Constants,[a] and Computed and Observed ^{35}Cl and ^{37}Cl Isotopic Shifts (cm^{-1})

		Freq		F	Δν(comp)	Δν(obsd)
A$_1$	ν_1	1093	$F_{11} = f_D + f_{DD}$	9.14	7.1	7.2
			$F_{13} = (1/\sqrt{3})(2f_{D\alpha} - f_{D\gamma} - f_{D\gamma'})$	0.70		
	ν_2	683	$F_{22} = f_R$	3.35	6.8	~7
			$F_{23} = (\sqrt{2/3})(f_{R\alpha} - f_{R\gamma})$	−0.30		
	ν_3	520	$F_{33} = (1/3)(2f_\alpha + f_\gamma + f_{\gamma\gamma} - 4f_{\alpha\gamma})$	1.27	0.8	~1
	ν_4	487	$F_{44} = f_r + f_{rr}$	2.65	0	
	ν_5	286	$F_{55} = (1/3)(2f_\beta + f_\delta + 2f_{\beta\beta} + f_{\delta\delta} + f_{\delta\delta'} + f_{\delta\delta''} - 4f_{\beta\delta} - 4f_{\beta\delta'})$	1.37	0.5	
A$_2$	ν_6	417	$F_{66} = f_\delta - f_{\delta\delta} - f_{\delta\delta'} + f_{\delta\delta''}$	1.13	0	
B$_1$	ν_7	695	$F_{77} = f_r - f_{rr}$	2.75	11.7	11.6
			$F_{78} = \sqrt{2}(f_{r\delta} - f_{r\delta'})$	0.70		
			$F_{79} = f_{r\beta} - f_{r\beta'}$	0.20		
	ν_8	592	$F_{88} = f_\delta - f_{\delta\delta} + f_{\delta\delta'} - f_{\delta\delta''}$	2.15	0	~0
			$F_{89} = \sqrt{2}(f_{\beta\delta} - f_{\beta\delta'})$	−0.44		
	ν_9	372	$F_{99} = f_\beta - f_{\beta\beta}$	1.31	1.0	
B$_2$	ν_{10}	1327	$F_{10,10} = f_D - f_{DD}$	9.33	16.8	16–17[b]
	ν_{11}	531	$F_{11,11} = f_\gamma - f_{\gamma\gamma}$	1.63	2.2	2.6
	ν_{12}	222	$F_{12,12} = f_\delta + f_{\delta\delta} - f_{\delta\delta'} - f_{\delta\delta''}$	0.78	0.6	

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch–bend interaction constants in mdyn/radian; symmetry force constants not shown were assumed to be zero. [b] Corrected for Fermi resonance interaction with ($\nu_1 + \nu_{12}$).

puted assuming all off-diagonal symmetry force constants equal to zero. In the A$_1$ and B$_1$ block, however, nonzero values were required for several off-diagonal constants to be able to reproduce the observed frequencies. The quality of the resulting force field was examined by comparing the computed ^{35}Cl–^{37}Cl isotopic shifts with those observed. The observed Cl isotopic shifts were then used to improve the force field by introducing off-diagonal constants until the calculated isotopic shifts agreed with the observed ones. Those interaction constants not significantly influencing the isotopic shift were not changed while those introduced were required to achieve a fit between observed and computed isotopic shifts. The force field is still not unique and other solutions are certainly possible. Species A$_1$ contains 15 symmetry force constants. Of these, three off-diagonal terms, *i.e.*, F_{14}, F_{24}, and F_{34}, may be neglected[19] since their corresponding G matrix elements are zero. Therefore, eight frequencies (5 ^{35}Cl + 3 ^{37}Cl) are available for obtaining 12 symmetry force constants. In species B$_1$ and B$_2$ five frequency values are available for obtaining six symmetry force constants. Numerical experiments indicated that plausible force fields and PED values could be achieved only with values reasonably close to those shown in Table IV. The requirement of a large off-diagonal constant for B$_1$ has previously also been found for the structurally related pseudo-trigonal-bipyramidal SF$_4$O molecule.[20]

The internal coordinate stretching force constants can be computed; however, the bending valence force constants cannot be completely separated from the interaction constants without making additional simplifying assumptions (see Table V). The constants of greatest interest are the stretching force constants since they are a measure of the strength of the various bonds. Uncertainty estimates are difficult to make owing to the underdetermined nature of the force field. The value of the Cl=O stretching force constant should have the smallest uncertainty (0.1 mdyn/Å or less) owing to the highly characteristic nature of the ClO$_2$ stretching modes and the use of isotopic shifts for its computation. Its value of 9.23 mdyn/Å is in excellent agreement with that of 9.37 mdyn/Å found for ClF$_3$O[8] and the general valence force field values of 9.07 and 8.96 mdyn/Å reported for FClO$_2$[21] and ClO$_2^+$,[11] respectively. The values of the ClF stretching force constants are comparable to those previously reported for the related pseudo-trigonal-bipyramidal molecules ClF$_3$[22] and ClF$_3$O[8] (see Table VI). In all three molecules, the stretching force constant of the equatorial ClF bond is significantly higher than that of the two axial bonds, although their relative difference decreases with increasing oxidation state of the central atom. The difference in bond strength between equatorial and axial bonds implies significant contributions from semiionic three-center four-electron bonds to the axial ClF bonds. This bonding scheme has previously been discussed in detail[23] for the related pseudo-trigonal-bipyramidal ClF$_2^-$ anion and, hence, will not be repeated.

Table V. Internal Force Constants of ClF$_3$O$_2$[a,b]

$f_D = 9.23$
$f_R = 3.35$
$f_r = 2.70$
$f_\alpha = 1.41$
$f_\beta = 1.40$
$f_\gamma = 1.33$
$f_\delta = 1.30$
$f_{DD} = -0.09$
$f_{rr} = -0.04$
$f_{\beta\beta} = 0.09$
$f_{r\beta} = -f_{r\beta'} = 0.10$
$f_{r\delta} = -f_{r\delta'} = 0.25$
$f_{D\alpha} = 0.61$
$f_{\beta\delta} = -f_{\beta\delta'} = -0.16$
$f_{\delta\delta} = -f_{\delta\delta'} = -0.34$
$f_{\delta\delta''} = -0.17$
$f_{\gamma\gamma} = -0.30$
$f_{R\alpha} = -0.37$

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch–bend interaction constants in mdyn/radian. [b] Only the values of the stretching force constants can be uniquely determined from the symmetry force constants; for the computation of the remaining constants, the following assumptions were made: $f_{r\beta} = -f_{r\beta'}$, $f_{r\delta} = -f_{r\delta'}$, $f_{\beta\delta} = -f_{\beta\delta'}$, $f_{\delta\delta} = -f_{\delta\delta'}$, and $f_{R\gamma} = f_{D\gamma} = f_{\alpha\gamma} = 0$; $f_{\delta\delta}$, $f_{\delta\delta'}$, and $f_{\delta\delta''}$ are the interactions between angles having a common oxygen, fluorine, and no common atom, respectively.

Table VI. ClF Stretching Force Constants (mdyn/Å) of ClF$_3$O$_2$ Compared to Those of Pseudo-Trigonal-Bipyramidal ClF$_3$O,[8] ClF$_3$,[22] ClF$_2^-$,[23] and ClF$_2$O$_2^-$ [9]

	f_R	f_r	f_{rr}	$(f_R - f_r)/f_R$
ClF$_3$	4.2	2.7	0.36	0.36
ClF$_3$O	3.2	2.3	0.26	0.26
ClF$_3$O$_2$	3.4	2.7	−0.04	0.19
ClF$_2^-$		2.4	0.17	
ClF$_2$O$_2^-$		1.6	−0.1	

Inspection of Table VI also reveals that the value of f_r does not depend exclusively on the oxidation state of the central

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[22] R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.*, 54, 344 (1971).

[23] K. O. Christe, W. Sawodny, and J. P. Guertin, *Inorg. Chem.*, 6, 1159 (1967).

atom. Obviously, formal negative charges (as in the anions) and increasing oxygen substitution facilitate[9] the formation of semiionic bonds and, hence, counteract the influence of the oxidation state of the central atom. It is interesting to note that the relative contribution from semiionic bonding to the axial ClF bonds $[=(f_R - f_r)/f_R]$ decreases from ClF_3 to ClF_3O and ClF_3O_2 (see Table VI). This can be attributed to the decreasing electron density around the central atom with increasing oxidation state, thus making it more difficult to release electron density to the axial fluorine ligands as required for the formation of semiionic bonds.

In summary, the bonding in ClF_3O_2 might be described by the following approximation.[24] The bonding of the three equatorial ligands, ignoring the second bond of the Cl=O double bond, is mainly due to an sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves one delocalized p-electron pair of the chlorine atom for the formation of a semiionic three-center four-electron pσ bond.

The potential energy distribution[25] for ClF_3O_2 was obtained from the internal force constants of Table V using a least-squares force field computation code without using least-squares refinement. With this code, we also verified that no computational errors had been made in the trial and error force field computation. The computed PED is given in Table VII. The results were normalized, but the sums do not in all cases add up to 1.0 since the less important terms are not listed. As can be seen from Table VII, most vibrations are reasonably characteristic, except for ν_7 and ν_8, which are mixtures of the symmetry coordinates S_7 and S_8.

Association in the Liquid and Pure Solid. The relatively low boiling point (−21.58°)[2] and Trouton constant (22.13)[2] of ClF_3O_2 imply little association in the liquid phase. This prediction is confirmed by the vibrational spectra of the liquid and the neat solid which exhibit only minor frequency shifts when compared to the spectra of the gas and the matrix-isolated solid. This finding is somewhat surprising since both ClF_3[24] and ClF_3O[8] show a pronounced tendency to associate in the liquid and solid state through bridges involving the axial fluorine atoms. For the pure solid, the infrared spectrum indicates the lowering of symmetry C_{2v} due to slight distortion or a lower site symmetry in the crystal because the A_2 torsion mode, ideally forbidden in the infrared spectrum and not observed for the gas, becomes infrared active. Similarly, the symmetric axial FClF stretching mode, ν_4 (A_1), which was not observed in the infrared spectrum of gaseous ClF_3O_2, gained for solid ClF_3O_2 in relative intensity and was observed as a medium weak band.

Thermodynamic Properties. The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation.[26] These properties are given for the range 0–2000°K in Table VIII.

Table VII. Potential Energy Distribution for ClF_3O_2

	Assignment	Freq, cm^{-1}	PED
A_1	ν_1	1093	$0.99f_D + 0.06f_R - 0.06f_{D\alpha}$
	ν_2	683	$0.71f_R + 0.20f_\alpha - 0.13f_{R\alpha} + 0.10f_\gamma + 0.05f_\beta$
	ν_3	520	$0.50f_\alpha + 0.23f_\gamma + 0.22f_R + 0.12f_{R\alpha} - 0.05f_{\gamma\gamma} - 0.05f_{D\alpha}$
	ν_4	487	$1.02f_r$
	ν_5	286	$0.61f_\beta + 0.28f_\delta + 0.14(f_{\beta\delta} - f_{\beta\delta'}) + 0.07(f_{\delta\delta'} - f_{r\delta}) + 0.05f_\alpha$
A_2	ν_6	417	$1.15f_\delta + 0.30(f_{\delta\delta} - f_{r\delta'}) - 0.15f_{\delta\delta''}$
B_1	ν_7	695	$0.86f_r + 0.39f_\delta - 0.22(f_{r\delta} + f_{r\delta'}) + 0.10(f_{\delta\delta} + f_{\delta\delta'}) + 0.05f_{\delta\delta''}$
	ν_8	592	$0.26f_\delta + 0.25f_r + 0.10(f_{r\delta} + f_{r\delta'}) + 0.07(f_{\delta\delta} + f_{\delta\delta'}) + 0.06f_\beta$
	ν_9	372	$1.10f_\beta - 0.10(f_{\beta\delta} + f_{\beta\delta'}) + 0.08f_\delta - 0.07f_{\beta\beta}$
B_2	ν_{10}	1327	$0.93f_D$
	ν_{11}	531	$0.75f_\gamma + 0.16f_{\gamma\gamma}$
	ν_{12}	222	$1.58f_\delta - 0.41(f_{\delta\delta} + f_{\delta\delta'}) + 0.21f_{\delta\delta''}$

Table VIII. Thermodynamic Properties for ClF_3O_2

T, °K	$C_p°$, cal/mol	$H° - H°_0$, kcal/mol	$-(F° - H°_0)/T$, cal/(mol deg)	$S°$, cal/(mol deg)
0	0	0	0	0
100	10.127	0.847	48.967	57.437
200	16.511	2.179	55.516	66.411
298.15	21.256	4.049	60.375	73.956
300	21.327	4.089	60.459	74.088
400	24.384	6.386	64.711	80.675
500	26.362	8.930	68.484	85.344
600	27.685	11.636	71.881	91.275
700	28.599	14.453	74.968	95.615
800	29.251	17.347	77.795	99.479
900	29.727	20.298	80.400	102.953
1000	30.085	23.289	82.816	106.105
1100	30.360	26.312	85.066	108.985
1200	30.574	29.359	87.171	111.637
1300	30.745	32.425	89.143	114.091
1400	30.883	35.507	91.012	116.375
1500	30.995	38.601	92.775	118.509
1600	31.089	41.705	94.447	120.513
1700	31.167	44.818	96.036	122.400
1800	31.233	47.938	97.551	124.183
1900	31.289	51.064	98.997	125.873
2000	31.337	54.196	100.382	127.480

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Registry No. ClF_3O_2, 38680-84-1.

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Contribution from Rocketdyne, a Division of Rockwell
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A New Synthesis of NF_4^+ Salts and Its Mechanistic Interpretation Involving a New and Exceptionally Powerful Oxidizing Species

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Complex fluoro cations are generally prepared through fluorine abstraction from the parent molecule by means of a strong Lewis acid. This was first demonstrated in 1949 by Woolf and Emeleus[1] for BrF_3.

$$BrF_3 + SbF_5 \rightarrow BrF_2^+SbF_6^- \quad (1)$$

In the case of NF_4^+ salts, this approach was impossible since the parent molecule NF_5 is unknown and unlikely to exist owing to the validity of the octet rule for first row elements such as nitrogen and fluorine. The synthesis of NF_4^+ from NF_3 and F^+ is preempted by the fact that fluorine is the most electronegative element and, hence, F^+ should be extremely difficult, if not impossible, to prepare by chemical means. In 1965, Christe and coworkers experimentally confirmed that NF_4^+ salts can be prepared from NF_3, F_2, and a strong Lewis acid in the presence of an activation energy source.[2] Presently, three methods are known which are capable of producing NF_4^+ salts. These are (1) glow discharge at low temperature,[3,4] (2) heating under high pressure,[5,6]

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and (3) bremstrahlung at −196°.[7] In this note, we describe a fourth method, *i.e.*, uv photolysis, which is capable of producing $\mathrm{NF_4^+}$ salts.

In addition to the great challenge which the preparation of $\mathrm{NF_4^+}$ salts presented to the synthetic chemist, the $\mathrm{NF_4^+}$ formation is of unusual interest from a mechanistic point of view. In view of the second and fourth methods of formation (see above), the originally suggested[3] mechanism cannot be considered satisfactory and a more plausible mechanism is offered. Based on the revised mechanism, we postulate a new intermediate of unusual oxidizing power comparable to that[8] of $\mathrm{PtF_6}$.

Experimental Section

Materials and Apparatus. The materials used in this work were manipulated in a well-passivated (with $\mathrm{ClF_3}$) 304 stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 IF4Y). Pressures were measured with a Heise-Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nitrogen trifluoride (Air Products), $\mathrm{BF_3}$ (Matheson Co.), and $\mathrm{AsF_5}$ (Ozark Mahoning Co.) were purified by fractional condensation. Antimony pentafluoride (Ozark Mahoning Co.) was purified by distillation. Prior to its use, fluorine (Rocketdyne) was passed through a NaF trap to remove HF impurities. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box. The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer as dry powders between AgCl windows in the form of pressed disks. The pressing operation was carried out using a Wilks mini pellet press. Raman spectra were recorded on a Cary Model 83 double monochromator using the 4880-A exciting line and Kel-F capillaries as sample containers. Reactions were carried out either in a sapphire reaction tube brazed to a 304 stainless steel tube (Varian, Model CS-4250-3) having a volume of 23 ml or in a flamed out 1-l. quartz bulb. For the photolyses, unfiltered uv radiation from a Hanovia Model 616A high-pressure quartz mercury vapor arc was used.

Reactions in Quartz. Preparation of $\mathrm{NF_4^+SbF_6^-\cdot xSbF_5}$. Antimony pentafluoride (26.43 mmol) was loaded into the flamed out and passivated (with $\mathrm{ClF_3}$) quartz bulb in the glove box. Nitrogen trifluoride (30.6 mmol) and $\mathrm{F_2}$ (30.6 mmol) were added at −196°. The mixture was allowed to warm to 25°. When exposed to uv irradiation, clouds of suspended solid appeared within seconds inside the bulb. Within 1 hr layers of a white solid formed. Irradiation of the contents was continued for 3 days until the last droplets of liquid ($\mathrm{SbF_5}$) had disappeared and no signs of cloudiness in the gas phase could be detected. The contents of the bulb were cooled to −196° and $\mathrm{O_2}$ and unreacted $\mathrm{F_2}$ (3.1 mmol total) and unreacted $\mathrm{NF_3}$ (25.2 mmol) were removed and separated by fractional condensation. The absence of unreacted $\mathrm{SbF_5}$ was established by pumping for 2 hr at 25° on the solid, resulting in no detectable weight change. Compared to the bulb with $\mathrm{SbF_5}$ only, the bulb containing the solid product had gained 403 mg in weight. The solid was removed from the walls of the reactor by immersion of the bulb into an ultrasonic cleaning bath and removed from the bulb in the glove box. The resulting white powder (~6.1 g) was shown by vibrational spectroscopy to be an approximately equimolar mixture of $\mathrm{SbF_6^-\cdot xSbF_5}$ salts of $\mathrm{NF_4^+}$ [9,10] and $\mathrm{O_2^+}$.[11]

The $\mathrm{NF_3}$–$\mathrm{F_2}$–$\mathrm{AsF_5}$ System. An equimolar mixture of $\mathrm{NF_3}$, $\mathrm{F_2}$, and $\mathrm{AsF_5}$, when exposed in a quartz bulb to uv irradiation, produced a white solid product. It was identified by vibrational spectroscopy[11] and its X-ray diffraction powder pattern[12] as $\mathrm{O_2^+AsF_6^-}$. No $\mathrm{NF_4^+}$ salt could be detected by these methods.

Reactions in Sapphire. Preparation of $\mathrm{NF_4^+AsF_6^-}$. An equimolar mixture of $\mathrm{NF_3}$, $\mathrm{F_2}$, and $\mathrm{AsF_5}$, when kept for 3 days at 25° in a sapphire reactor in the dark, at an autogenous pressure of 6.5 atm, showed no detectable trace of solid formation. Upon exposing the sapphire section of the reactor to unfiltered uv radiation, clouds of suspended solid appeared within seconds inside the reactor resulting in an instant coating on the reactor walls. Continued exposure (for several days) of the reactor to uv radiation did not significantly increase the solid formation. After removal of the volatile reaction products, the weight gain of the reactor varied from 2 to 8 mg in several experiments. The solid residue was identified by vibrational spectroscopy[9,10] as $\mathrm{NF_4^+AsF_6^-}$ and in all cases did not show any detectable impurities.

Preparation of $\mathrm{NF_4^+BF_4^-}$. The $\mathrm{NF_3}$–$\mathrm{F_2}$–$\mathrm{BF_3}$ reaction was carried out in the same way as described for $\mathrm{NF_3}$–$\mathrm{F_2}$–$\mathrm{AsF_5}$. The reactants behaved similarly and the reaction rate decreased sharply with increasing solid deposition on the inside walls of the reactor. The yield of $\mathrm{NF_4^+BF_4^-}$ was between 1 and 2 mg. The infrared spectrum of the solid was in excellent agreement with that previously reported[7] for $\mathrm{NF_4^+BF_4^-}$.

Results and Discussion

When gaseous mixtures of $\mathrm{NF_3}$, $\mathrm{F_2}$, and the strong Lewis acids $\mathrm{SbF_5}$, $\mathrm{AsF_5}$, or $\mathrm{BF_3}$ are exposed to unfiltered uv irradiation, the corresponding $\mathrm{NF_4^+}$ salts are formed rapidly and reproducibly. Using $\mathrm{AsF_5}$ or $\mathrm{BF_3}$ and sapphire reactors, the following reactions occurred.

$$\mathrm{NF_3 + F_2 + AsF_5 \rightarrow NF_4^+AsF_6^-} \tag{2}$$

$$\mathrm{NF_3 + F_2 + BF_3 \rightarrow NF_4^+BF_4^-} \tag{3}$$

However, the yield of the $\mathrm{NF_4^+}$ salt was less than 1%. This low yield appears not to be caused so much by a low reaction rate but by deposition of the solid product on the reactor walls, thus preventing further irradiation of the reactants. In the case of $\mathrm{SbF_5}$ and a quartz reactor, all of the $\mathrm{SbF_5}$ starting material was consumed in less than 3 days. In addition to $\mathrm{NF_4^+}$ formation, the following side reaction occurred.

$$\begin{array}{l}
\mathrm{4F_2 + 2SiO_2 \rightarrow 2SiF_4 + 2O_2} \\
\mathrm{2O_2 + F_2 + 4SbF_5 \rightarrow 2O_2^+Sb_2F_{11}^-} \\
\hline
\mathrm{5F_2 + 2SiO_2 + 4SbF_5 \rightarrow 2SiF_4 + 2O_2^+Sb_2F_{11}^-}
\end{array}$$

Based on the observed material balance and its vibrational spectrum, the product contained approximately equimolar amounts of $\mathrm{NF_4^+}$ and $\mathrm{O_2^+}$ salts.[9-11] As generally the case with $\mathrm{SbF_5}$, polymeric anions,[13] such as $\mathrm{Sb_2F_{11}^-}$ or $\mathrm{Sb_3F_{16}^-}$, were formed. Attempts to use the quartz reactor for the synthesis of $\mathrm{NF_4^+AsF_6^-}$ were unsuccessful. The attack of the quartz reactor occurred at a rate much faster than that of the $\mathrm{NF_4^+}$ formation, thus resulting in $\mathrm{O_2^+AsF_6^-}$ as the principal product.

The relatively low intensity of the uv lamp used in our experiments and the high yield of $\mathrm{NF_4^+SbF_6^-\cdot xSbF_5}$ suggest a quantum yield larger than one, *i.e.*, a chain reaction. Taking all the presently available experimental data on the synthesis of $\mathrm{NF_4^+}$ compounds into consideration, additional conclusions concerning a plausible reaction mechanism can be reached. Based on the glow-discharge synthesis, we had originally invoked the intermediate formation of a $\mathrm{F^+}$ or $\mathrm{NF_3^+}$ cation.[3] Whereas these cations might indeed be produced under glow-discharge conditions, the high ionization potentials of $\mathrm{NF_3}$ (13.00 eV),[14] $\mathrm{F_2}$ (15.69 eV),[15] or F· (17.44 eV)[16] preclude their formation in the uv photolysis, since the maximum energy available from the uv source does not exceed 7 eV.

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Even stronger evidence for an alternate mechanism stems from the thermal synthesis (method 2). Heating to about 120° cannot provide the activation energies required for the formation of NF_3^+, F_2^+, or F^+. However, it has been found for the Cl_2-F_2 dark reaction[17,18] that a temperature of about 120° is sufficient to dissociate some of the F_2 into F· radicals [$D^\circ(F_2)$ is only 37.5 kcal mol^{-1} = 1.62 eV].[19] In spite of the very low F atom concentrations expected at 120°, a chain reaction may result in relatively fast reaction rates. Based on these considerations and the observed fast reaction rate in the NF_3-F_2-SbF_5 photolysis, it seems safe to postulate F_2 dissociation as the first reaction step in the NF_4^+ salt syntheses.

$$F_2 \rightarrow 2F\cdot \qquad (4)$$

The next step could involve the reaction of F· with either NF_3 or a Lewis acid such as AsF_5. Since the hypothetical $NF_4\cdot$ containing only first row elements would violate the octet rule, its formation is very unlikely. Therefore, the second step should be

$$F\cdot + AsF_5 \rightarrow AsF_6\cdot \qquad (5)$$

This step appears plausible since AsF_5 generally acts as an excellent acceptor molecule and changes from a trigonal-bipyramidal to an energetically more favorable octahedral AsF_6 configuration. The $AsF_6\cdot$ radical is pseudo-isoelectronic with SF_6^+ and, hence, a rough estimate for the exothermicity of the reaction

$$AsF_6\cdot + e \rightarrow AsF_6^-$$

can be obtained from the known[20] photoionization threshold of SF_6 (15.29 eV). This high value strongly suggests that the $AsF_6\cdot$ radical is the only likely intermediate capable of oxidizing NF_3, which has a first ionization potential of 13.00 eV.[14] Consequently, the third reaction step in the $NF_4^+AsF_6^-$ formation should be

$$AsF_6\cdot + NF_3 \rightarrow NF_3^+AsF_6^- \qquad (6)$$

In order to maintain a chain reaction, the $NF_3^+AsF_6^-$ could react with F_2 according to

$$NF_3^+AsF_6^- + F_2 \rightarrow NF_4^+AsF_6^- + F\cdot \qquad (7)$$

A crude estimate of the bond energy changes involved in this step can again be obtained by comparison between the isoelectronic species

$$NF_3^+ + F\cdot \rightarrow NF_4^+ \qquad (8)$$

and

$$CF_3\cdot + F\cdot \rightarrow CF_4 \qquad (9)$$

Since the CF_3-F bond energy (139.4 kcal mol^{-1})[21] is considerably higher than that of the F-F bond (37.5 kcal mol^{-1}),[19] reaction 7 should also be exothermic. Chain termination steps could occur by combination of any two of the radicals involved in this mechanism. The overall sequence, eq 4-7, appears to be a very plausible mechanism requiring only a low activation energy for (4), in excellent agreement with the experimental observations.

Solomon and coworkers have studied[22] the kinetics of the thermal decomposition of $NF_4^+AsF_6^-$ to NF_3, F_2, and AsF_5 in the temperature range 175-222° at low pressure. Since Tolberg, *et al.*, have shown[5] that $NF_4^+AsF_6^-$ can be formed in this temperature range from NF_3, F_2, and AsF_5 under high pressure, reversibility of these reactions is indicated. Consequently, the $NF_4^+AsF_6^-$ formation mechanism should allow us also to better understand the thermal decomposition. Solomon, *et al.*, observed[22] that both NF_3 and AsF_5 inhibit the decomposition reaction and suggest that the decomposition mechanism involves the reversible dissociation of the solid to NF_5 and AsF_5, followed by the irreversible decomposition of NF_5 as the rate-determining step. However, the observed fractional-order kinetics could not be explained by an elementary reaction mechanism. The mechanism, suggested[22] by Solomon and coworkers, has several shortcomings. In our opinion, the most serious ones are (1) NF_5 violates the octet rule which is strictly valid for first row elements—promotion of nitrogen electrons to the 3s level would result in a prohibitively large activation energy for the NF_5 formation, (2) the $NF_4^+AsF_6^-$ formation, and (3) the inhibition of the $NF_4^+AsF_6^-$ decomposition by NF_3 addition suggests that the steps involving NF_3 cannot be irreversible. For these reasons and by analogy with the mechanism discussed above for the $NF_4^+AsF_6^-$ formation, a more plausible decomposition mechanism would be

$$NF_4^+AsF_6^- \rightleftarrows NF_3^+AsF_6^- + F\cdot \qquad (10)$$

$$NF_3^+AsF_6^- \rightleftarrows NF_3 + AsF_6\cdot \qquad (11)$$

$$AsF_6\cdot \rightleftarrows F\cdot + AsF_5 \qquad (12)$$

$$2F\cdot \rightarrow F_2 \qquad (13)$$

Because the steady-state F atom concentration would be determined by a number of reactions, including the reverse of reaction 7, a very complex rate expression might be expected. The recombination of F atoms could occur either homogeneously *via* a three-body collision or heterogeneously. The inhibiting effects of NF_3 and AsF_5 could result from the reduction of the steady-state F atom concentration caused by the shifting of the equilibria 10-12 to the left.

The postulate of an $AsF_6\cdot$ radical intermediate which can act as a powerful oxidizer could also explain the following two previously reported[23-25] and highly unusual reactions

$$2O_2 + F_2 + 2AsF_5 \xrightarrow[\text{or uv}]{130^\circ} 2O_2^+AsF_6^- \qquad (14)$$

and

$$Xe + F_2 + AsF_5 \xrightarrow{uv} XeF^+AsF_6^- \qquad (15)$$

Both reactions proceed again under very mild conditions, resulting in the oxidation of two species, O_2 and Xe, with very high first ionization potentials of 12.06 and 12.13 eV, respectively. Reactions 14 and 15 are directly comparable to the following known[8,26,27] PtF_6 reactions

$$O_2 + PtF_6 \rightarrow O_2^+PtF_6^- \qquad (16)$$

and

$$Xe + 2PtF_6 \rightarrow XeF^+Pt_2F_{11}^- \qquad (17)$$

This analogy suggests that the oxidizing power of a Lewis acid-F· radical, such as $AsF_6\cdot$, is comparable to that of PtF_6,

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which is one of the strongest oxidizing fluorinators[8] known. The applicability of the Lewis acid-activated F_2 system, however, seems to be limited to starting materials which themselves do not form stable adducts with the Lewis acid. The given examples demonstrate that the oxidizing power of fluorine can be promoted significantly by the simultaneous use of a strong Lewis acid and an energy source promoting dissociation of F_2 into F· atoms. Consequently, many reactions previously requiring the use of the prohibitively expensive PtF_6 may now be carried out at a reasonable expense by the use of Lewis acid promoted activated fluorine.

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Registry No. F_2, 7782-41-4; NF_3, 7783-54-2; SbF_5, 7783-70-2; AsF_5, 7784-36-3; BF_3, 7637-07-2; $NF_4^+AsF_6^-$, 16871-75-3; $NF_4^+BF_4^-$, 15640-93-4.

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Halogen Pentafluoride-Lewis Acid Adducts[1]

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Vibrational spectra have been recorded for the known adducts $ClF_5 \cdot AsF_5$, $ClF_5 \cdot xSbF_5$ ($x = 1.08$ and 1.36), $BrF_5 \cdot 2SbF_5$, and $IF_5 \cdot SbF_5$. Furthermore, the new adduct $BrF_5 \cdot AsF_5$ has been prepared. It is marginally stable at −95°. The spectra of the ClF_5 adducts are consistent with predominantly ionic structures containing the ClF_4^+ cation. The spectrum of ClF_4^+ is very similar to that of isoelectronic SF_4 thus indicating a pseudo-trigonal-bipyramidal structure of symmetry C_{2v}. All fundamentals have been assigned and a valence force field has been computed for ClF_4^+. The vibrational spectra of $IF_5 \cdot SbF_5$ and $BrF_5 \cdot 2SbF_5$ are compatible with the predominantly ionic structures $IF_4^+SbF_6^-$ and $BrF_4^+Sb_2F_{11}^-$, respectively, established by X-ray diffraction data. Tentative assignments are given for BrF_4^+ and IF_4^+. The ^{19}F nmr spectra of $BrF_5 \cdot 2SbF_5$ and $IF_5 \cdot SbF_5$ in HF solution are also reported.

Introduction

Halogen fluorides exhibit amphoteric character. By combining with strong Lewis acids, they can form cations containing one F^- ion less than the parent molecule. In recent years these salts have received much attention, and numerous papers dealing with their syntheses and structures have been published.[2] Whereas the structures of the halogen mono-, tri-, and heptafluoride adducts are reasonably well established, much less is known about the complexes of the halogen pentafluorides.

Chlorine pentafluoride combines with Lewis acids such as AsF_5,[3] SbF_5,[3,4] and PtF_6.[5,6] Ionic structures containing the ClF_4^+ cation were suggested;[3,5] however, no supporting data were presented. Recently, the ^{19}F nmr spectrum of $ClF_5 \cdot 1.36SbF_5$ in HF-AsF_5 solution was studied.[7] The observation of two resonances of equal intensity at low field is strong evidence for the presence of a ClF_4^+ cation having a pseudo-trigonal-bipyramidal structure of symmetry C_{2v}, analogous to that found[8,9] for isoelectronic SF_4.

Bromine pentafluoride forms with SbF_5 the adduct, $BrF_5 \cdot 2SbF_5$.[10] A brief report on the ^{19}F nmr spectrum of the solid and melt has been published[11] indicating the presence of two different kinds of fluorine ligands; however, the observed area ratio was in poor agreement with that expected for the postulated[11] structure $BrF_4^+Sb_2F_{11}^-$. Recently, the crystal structure of $BrF_5 \cdot 2SbF_5$ has been determined establishing[12] its predominantly ionic nature. After completion of our study,[1] Surles and coworkers have reported[13] the Raman spectra of $BrF_4^+Sb_2F_{11}^-$ and of BrF_5 in SbF_5 solution and proposed a tentative assignment for BrF_4^+. Solutions of BrF_5 in SbF_5 were shown[13] to be highly conductive suggesting an ionic formulation for the $BrF_5 \cdot SbF_5$ adduct.

Iodine pentafluoride forms 1:1 adducts with SbF_5[14] and PtF_5.[15] Recently, the crystal structure of $IF_5 \cdot SbF_5$ has independently been studied by X-ray diffraction by two groups.[16,17] Unfortunately, $IF_5 \cdot SbF_5$ tends to form twin crystals[17] thus rendering the structural determination somewhat difficult. Both groups suggest for $IF_5 \cdot SbF_5$ a mainly ionic structure containing a distorted trigonal-bipyramidal IF_4^+ cation of symmetry C_{2v} and an SbF_6^- anion distorted from symmetry O_h. However, several interesting questions such as the difference in bond length between the axial and equatorial IF bonds remain unresolved. Shamir and Yaroslavsky have reported[18] in a preliminary communication the Raman spectra of a number of adducts including that of $IF_5 \cdot SbF_5$. However, their experimental data are incomplete and, therefore, their conclusions are little convincing.

Experimental Section

Apparatus. The materials used in this work were manipulated either in a well-passivated (with ClF_3) 304 stainless steel vacuum system equipped with Teflon FEP U traps or in the dry nitrogen atmosphere of a glove box. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%).

The Raman spectra of the solids were recorded with a Spex Model 1400 spectrophotometer. The green (5145 A) or the blue (4880 A) line of a Coherent Radiation Laboratory Model 52 Ar ion laser and the red (6328 A) line of a Spectra-Physics Model 125 He-Ne laser were used as exciting lines. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or clear Teflon FEP or Kel-F capillaries (1–4 mm i.d.) were used as sample containers. For the capillaries the transverse viewing–transverse excitation technique was applied. The Raman spectra of the HF solutions were recorded on a Cary Model 83 spectrophotometer using the 4880-A exciting line. The samples were contained in Teflon FEP capillaries which were also used for the ^{19}F nmr spectra.

The infrared spectra of the solids were recorded on a Beckman Model IR-7 with CsI interchange and Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000–250 cm^{-1} as dry powders between AgCl or AgBr plates or thin (2 mils) Teflon FEP sheets. Compensation for bands due to the Teflon FEP window material was achieved by placing an empty cell in the reference beam. Screw-cap metal cells with Teflon FEP gaskets were used as window holders. The low-temperature infrared spectrum of $ClF_5 \cdot AsF_5$ was taken by preparing the complex on the internal window (cooled with liquid nitrogen) of an infrared cell. The body of this cell was made from Pyrex glass, all windows being AgCl. Temperature cycling of the

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internal window *in vacuo* was essential to obtain spectra free of unreacted starting materials.

The ^{19}F nmr spectra were recorded at 56.4 MHz on a Varian high-resolution nmr spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique with an accuracy of ±1 ppm relative to the external standard $CFCl_3$.

Preparation of the ClF_5 Adducts. The purification of ClF_5, SbF_5, AsF_5, and HF and the preparation of the $ClF_5 \cdot$(Lewis acid) adducts has previously been described.[3] Since the melting point and the composition of the $ClF_5 \cdot SbF_5$ samples varied somewhat with the method of preparation, three different samples were investigated. Sample I had the composition $ClF_5 \cdot 1.08SbF_5$ and showed first signs of melting at 88°. It was prepared by adding an SbF_5–HF solution to excess ClF_5. Sample II had the composition $ClF_5 \cdot 1.36SbF_5$ and was prepared by combining SbF_5 dissolved in HF with an excess of ClF_5 at −196° followed by warm-up to 25° and removal of volatile material *in vacuo*. It showed first indications of partial melting at ~35°. With increasing temperature, however, the sample solidified again showing the onset of a second melting at 88°. Sample III had the same composition as sample II and was prepared by treating a part of sample II with excess ClF_5 in a Monel cylinder at 50° for 48 hr with agitation. It melted at about 33° to form a milky, highly viscous liquid. The synthesis of the $ClF_4^+PtF_6^-$ and $ClF_6^+PtF_6^-$ mixture has previously been described.[6]

Preparation of $BrF_5 \cdot 2SbF_5$. Bromine pentafluoride (from The Matheson Co.) was treated with F_2 at ambient temperature until the material was colorless. It was purified by fractional condensation through two traps kept at −64 and −95°. The material retained in the −95° trap showed no detectable impurities in the infrared spectrum.

Bromine pentafluoride (112.3 mmol) was condensed at −196° into a passivated 100-ml Monel cylinder containing 68.8 mmol of SbF_5. The cylinder was heated for 3 days at 120°. Subsequently, unreacted BrF_5 (78.3 mmol) was removed *in vacuo* at ambient temperature leaving behind a white, crystallinic solid. Consequently, BrF_5 (34.0 mmol) had reacted with SbF_5 (68.8 mmol) in a mole ratio of 1:2.02 producing the complex $BrF_5 \cdot 2SbF_5$.

Preparation of $BrF_5 \cdot AsF_5$. Bromine pentafluoride (4.42 mmol) was combined with AsF_5 (13.15 mmol) at −196° in a Teflon FEP U trap. The mixture was allowed to warm up slowly until melting and reaction occurred When the pressure inside the trap reached 1200 mm, the mixture was cooled again to −196°. This procedure was repeated several times until the reaction was complete. Unreacted AsF_5 (8.77 mmol) was removed *in vacuo* at −95° leaving behind a white solid which melted at higher temperature to form an almost colorless liquid. Prolonged pumping on the adduct at −95° resulted in the removal of additional small amounts of AsF_5 indicating that the adduct has a slight dissociation pressure even at −95°. The infrared spectrum of the gas obtained by exhaustive dissociation of the solid showed BrF_5 and AsF_5 in a 1:1 mole ratio. Based on the above given material balance, BrF_5 (4.42 mmol) had combined with AsF_5 (4.38 mmol) in a mole ratio of 1:0.99 producing the complex $BrF_5 \cdot AsF_5$.

Preparation of $IF_5 \cdot SbF_5$. This product was prepared as previously described.[14] The material was a white, crystallinic solid. The material balance was as expected for a 1:1 adduct. *Anal.* Calcd for $ISbF_{10}$: I, 28.9; Sb, 27.8; F, 43.3. Found: I, 29.4; Sb, 27.4; F, 43.0.

Liquid IF_5 and gaseous AsF_5 when combined at 20° with stirring did not form a stable adduct.

Results and Discussion

Syntheses and Properties. The preparation of the ClF_5 adducts has previously been discussed.[3] In the BrF_5–SbF_5 system we could not isolate a 1:1 adduct even when employing a large excess of BrF_5 and temperatures above 100° in the synthesis. The $BrF_5 \cdot 2SbF_5$ complex is a white crystallinic solid. It can be stored in Teflon FEP containers without appreciable decomposition. Exposure to small amounts of moisture or reactive surfaces produces a pink to deep red color due to the formation of Br_2^+ salts.[2] Single crystals of $BrF_5 \cdot 2SbF_5$ can be readily grown by slow sublimation at temperatures slightly higher than ambient. The results of a single-crystal X-ray diffraction study on $BrF_5 \cdot 2SbF_5$ have been reported[12] elsewhere. With AsF_5, however, BrF_5 does form a 1:1 adduct, but its thermal instability preempted its use for structural studies. Upon melting, the complex forms a colorless liquid. If impure BrF_5 is used in the synthesis, the color of the liquid is an intense burgundy red indicating the presence of Br_2^+ ions.[2] The fact that AsF_5 and SbF_5 combine with BrF_5 in different mole ratios might be explained by the pronounced tendency of SbF_5 to form polymeric anions such as $Sb_2F_{11}^-$.

Our data obtained for $IF_5 \cdot SbF_5$ confirm Woolf's reports.[14] Single crystals of $IF_5 \cdot SbF_5$ were grown by slow sublimation at 40°. A single-crystal X-ray diffraction study in our laboratory was discontinued when we learned about the work[15] of Baird and Giles. The fact that AsF_5, a weaker Lewis acid than SbF_5, does not form a stable adduct with IF_5 is not surprising. As previously pointed out,[19] halogen pentafluorides possess an energetically favorable pseudooctahedral structure and show little tendency to form the energetically less favorable pseudo-trigonal-bipyramidal XF_4^+ cations.

^{19}F Nmr Spectra. The ^{19}F nmr spectrum of $ClF_5 \cdot 1.36SbF_5$ in acidified HF has previously been discussed.[7] The observation of two signals of equal intensity at −256 and −274 ppm, respectively, relative to $CFCl_3$ below −60° is strong evidence for a ClF_4^+ cation having two nonequivalent sets of two fluorine ligands.[7]

The ^{19}F nmr spectrum of $BrF_5 \cdot 2SbF_5$ in HF or HF-AsF_5 solution showed, between +20 and −80° for the BrF part of the spectrum, a single resonance at −197 ppm relative to external $CFCl_3$. In the HF-SbF region at 20° a very broad unresolved common peak centered at about 130 ppm was observed indicating fast exchange between the solvent and the anion. In more dilute solutions the HF-$Sb_2F_{11}^-$ signal shifted to about 150 ppm and gained in relative intensity whereas the chemical shift of the BrF_4^+ resonance remained constant. At lower temperatures (−60 to −80°) the peak in the SbF region started to separate into several peaks at about 76, 93, 120, and 127 ppm. Whereas the identity of these peaks could not definitely be established, the chemical shifts of some of them are similar to those (93, 120, and 142 ppm) previously found for $Sb_2F_{11}^-$ in HF solution.[20] The chemical shift of −197 ppm found for BrF_4^+ in HF differs significantly from that (−167 ppm) reported by Meinert and Gross for the melt.[11] This discrepancy might be caused by the different environment.

A solution of $IF_5 \cdot SbF_5$ in HF exhibited between +20 and −80° only one signal at 133 ppm indicating rapid exchange between all species present. Acidification of the solvent with AsF_5 did not influence the exchange rates sufficiently to cause a separation into individual signals.

The fact that the inter- and intramolecular exchange rates decrease in the order $IF_5 \cdot SbF_5 > BrF_5 \cdot 2SbF_5 > ClF_5 \cdot SbF_5$ might be explained by the decreasing size and polarizability of the corresponding halogen pentafluorides.

Vibrational Spectra. The vibrational spectra of the halogen pentafluoride-Lewis acid adducts are shown in Figures 1-10. The infrared spectrum of the $ClF_4^+PtF_6^-$ and $ClF_6^+PtF_6^-$ mixture has previously been given[6] and, hence, is not shown here. The observed frequencies are listed in Tables I and II.

Since the ionic nature and structure of the Lewis acid adducts of ClF_5, BrF_5, and IF_5 have been established by X-ray diffraction,[12,16,17] nmr,[7] and conductivity studies,[13] the discussion of their vibrational spectra can be kept relatively short. The main objective of this study is to demonstrate that the vibrational spectra are consistent with the known

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(19) K. O. Christe, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, 11, 2205 (1972).

(20) R. J. Gillespie and K. C. Moss, *J. Chem. Soc. A*, 1170 (1966); M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, 47, 4159 (1969).

Table I. Vibrational Spectra of $ClF_5\cdot$(Lewis acid) Adducts and Their Assignments Compared to That[a] of SF_4

Obsd freq (cm^{-1}) and rel intens[b]								Assignment (point group)[c]	
SF_4(g)		$ClF_5\cdot AsF_5$[f]		$ClF_5\cdot SbF_5$[g]			$ClF_4^+PtF^-$ $ClF_6^+PtF_6^-$[h]		
					Raman				
Ir[d]	Raman[e]	Ir	Raman	Ir	Solid	HF soln	Ir	XF_4 (C_{2v})	YF_6 (O_h)
1744 vw		1600 vw, br						$\nu_1 + \nu_8$ (B_2)	
1617 vw									
		1390 vw							720 + 671
1281 w		1340 vw		1335 w			1330 w, br	$\nu_2 + \nu_6$ (B_1)	$\nu_1 + \nu_3$ (F_{1u})
867 s	865 (0+)	827 s	830 (2.5)	825 s, sh	822 (2.5)	825 sh	790 vs	ν_8 (B_2)	
891 s	888 (9.0)	796 vs	799 (10)	803 vs	802 (10)	802 (10)		ν_1 (A_1)	
730 vs	730 (0+)							ν_6 (B_1)	
		720 vs	711 (0.3)	669 vs	670 (0.5–2.5)		670–620 vs		ν_3 (F_{1u})
		699 s	695 (0.3)	648 vs	653 (8.6)	656 (8)			ν_1 (A_{1g})
		673 ms	671 (8.0)						
		584 m	579 (4)	579 w	583 (0.6–4)				ν_2 (E_g)
		576 mw							
558 m	553 (10)	568 w	567 (6.5)		568 (5.5)	574 (5.5)		ν_2 (A_1)	
		553 w							ν_2 (E_g)
532 ms	532 (4.0)	536 mw	538 (2.5)	535 ms*	534 (5)*	537 (1)*	545 s, br*	ν_7 (B_2) and	ν_2 (E_g)*
464 vw	475 (1.2)	511 ms**	519 (1)	510 sh	515 (0.2)	515 (0+)	500 s	ν_3 (A_1) and	ν(AsFAs)**
	414 (0+)		473 (1)		475 (0.4)	475 (0.4)		ν_5 (A_2)	
353 ms	350 (0+)	395 s	399 (0.6)	386 m			383 s	ν_9 (B_2)	
				280 s			271 s		ν_4 (F_{1u})
			372 (2.7)		279 (1.4)	277 (1)			ν_5 (F_{2g})
226 w	223 (1.0)		237 (1.1)		235 (0.5)	245 sh		ν_4 (A_1)	

[a] R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.*, 54, 344 (1971). [b] Uncorrected Raman intensities. [c] Assignments for the anion bands are made assuming for simplicity octahedral symmetry, although in most cases the actual symmetry is expected to be lower than O_h. [d] I. W. Levin and C. V. Berney, *J. Chem. Phys.*, 44, 2557 (1966). [e] K. O. Christe and W. Sawodny, *ibid.*, 52, 6320 (1970). [f] The low-temperature infrared spectrum indicates the presence of substantial amounts of $As_2F_{11}^-$. [g] The listed frequencies are those obtained for $ClF_5\cdot 1.08SbF_5$. The relative intensities of the 670-, 583-, and to a lesser extent the 534-cm^{-1} Raman bands varied, indicating different degrees of deviation of SbF_6^- from symmetry O_h or slight inhomogeneity of the sample. [h] Reference 6.

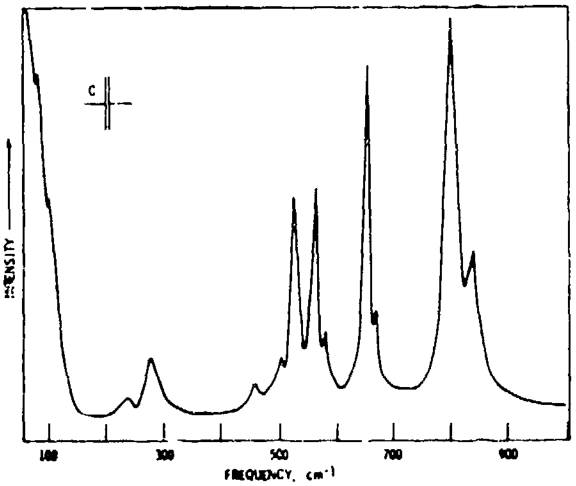

Figure 1. Raman spectrum of solid $ClF_5\cdot 1.08SbF_5$ (sample I) contained in a Teflon FEP capillary. Exciting line was 5145 Å. C indicates spectral slit width.

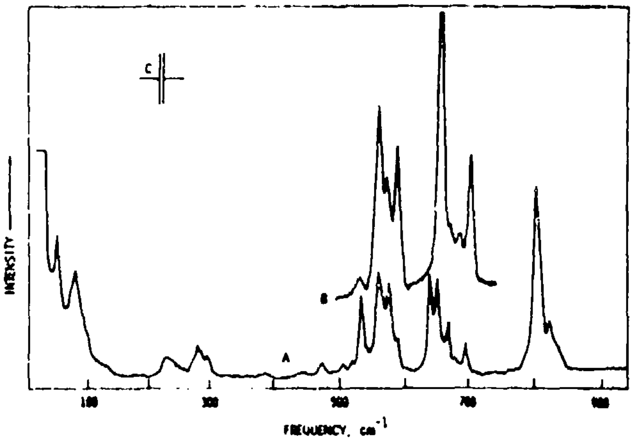

Figure 2. Raman spectrum of solid $ClF_5\cdot 1.36SbF_5$. Traces A and B show samples II and III, respectively. Kel-F capillaries were used as containers with 5145-Å excitation.

ionic structures, to define the principal bands of the $HalF_4^+$ cations, and to examine the plausibility of the given assignments by comparison with the known spectra of isoelectronic chalcogen tetrafluorides and by force field computations.

Chlorine Pentafluoride Adducts. The infrared spectra of the $ClF_5\cdot xSbF_5$ adducts are relatively insensitive to changes in the $ClF_5:SbF_5$ combining ratio owing to the relative broadness of the bands due to the Sb-F vibrations (see Figure 3). In the corresponding Raman spectra (Figures 1 and 2), however, slight changes in the composition of the adducts or in the procedures used for their preparation may cause significant changes. As expected, sample I, having the composition $ClF_5\cdot 1.08SbF_5$, shows the simplest spectrum. With increasing SbF_5 content and tempering, features attributable to polymeric anions such as $Sb_2F_{11}^-$ become more pronounced. Similarly, the low-temperature infrared spectrum of the $ClF_5\cdot AsF_5$ adduct (Figure 5) indicates the presence of the $As_2F_{11}^-$ anion.[21,22] However, the $As_2F_{11}^-$ anion is much less stable than $Sb_2F_{11}^-$ resulting in the facile removal of the second AsF_5 molecule under the conditions[3] used for the synthesis of the Raman sample (1:1 adduct).

The vibrational assignments for ClF_4^+ in point group C_{2v} (see Table I) were made by analogy with isoelectronic SF_4[23-26]

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(21) K. O. Christe and W. Maya, *Inorg. Chem.*, 8, 1253 (1969).

(22) P. A. W. Dean, R. J. Gillespie, R. Hulme, and D. A. Humphreys, *J. Chem. Soc. A*, 341 (1971).

(23) I. W. Levin and C. V. Berney, *J. Chem. Phys.*, 44, 2557 (1966).

(24) K. O. Christe and W. Sawodny, *J. Chem. Phys.*, 52, 6320 (1970).

(25) R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.*, 54, 344 (1971).

Table II. Vibrational Spectra of $BrF_3 \cdot 2SbF_5$ and $IF_5 \cdot SbF_5$ Compared to Those of SeF_4 and TeF_4

Obsd freq (cm^{-1}) and rel intens[a] SeF_4[b] Ir	SeF_4[b] Raman	$BrF_3 \cdot 2SbF_5$ Solid Ir	$BrF_3 \cdot 2SbF_5$ Solid Raman	$BrF_3 \cdot 2SbF_5$ HF soln Raman	Tentative assignment for XF_4 in C_{2v}	Obsd freq (cm^{-1}) and rel intens[a] TeF_4[c] Ir	$IF_5 \cdot SbF_5$ Solid Ir	$IF_5 \cdot SbF_5$ Solid Raman	$IF_5 \cdot SbF_5$ HF soln Raman	Tentative assignment for XF_4 in C_{2v}
723 s	724 w, sh	730 sh	736 sh		ν_8 (B_2)	695 m	728 sh	729 (9)	704 (10)	ν_1 (A_1)
744 ms	749 vs, p		723 (10)	680 sh	ν_1 (A_1)	682 m	719 m	720 (1.6)		ν_8 (B_2)
622 vs		690 vs	704 (2.4)		ν_6 (B_1) + $Sb_2F_{11}^-$ (?)		691 sh	693 (2.2)	663 (8)	SbF_6^- + ν_6(B_1)
		655 vs	660 sh	660 (10)	$Sb_2F_{11}^-$	587 s	668 sh	662 (10)		
		645 sh	651 (6.9)				655 vs			
				600 sh						
	574 s, p	606 mw	606 (4.8)	575 (5)	ν_2 (A_1)		625 m, sh	625 (3)		
		568 m	555 (3.3)		$Sb_2F_{11}^-$	572 vw		614 (4)	609 (9)	ν_2 (A_1)
		540 mw	545 sh	540 (1)			567 w, sh	569 (1.5)	570 sh	SbF_6^-
		488 ms		490 (1)	Sb–F–Sb		520 vw, sh	521 (1.3)		
405 m	400 w	419 m		426 (2)	ν_7 (B_1)	333 w	388 mw	385 (0.8)		ν_7 (B_1)
	366 m, p		385 (0.5)		ν_3 (A_1)	293 mw	345 w	341 (0.4)	325 sh	ν_3 (A_1)
250 vw		369 mw	369 (0.5)	363 (5)	ν_9 (B_2)		311 w	316 (0.2)		ν_9 (B_2)
			295 (1)	280 sh	$Sb_2F_{11}^-$			239 (0.9)		SbF_6^-
			264 (0.7)				288 m	285 (0+)	280 sh	
			230 (0.5)	235 (0+)			263 mw	259 (0.5)	250 sh	
160 vw	162 w, p		219 (0.2)		ν_4 (A_1)			151 (0.4)		ν_4 (A_1)
			45 (1.5)		Lattice mode			72 (1)		Lattice modes
								42 (6)		

[a] Uncorrected Raman intensities. [b] Best values and assignments were taken from K. Ramaswamy and S. Jayaraman, *Indian J. Pure Appl. Phys.*, 8, 625 (1970); L. E. Alexander and I. R. Beattie, *J. Chem. Soc., Dalton Trans.*, 1745 (1972); C. J. Adams and A. J. Downs, *Spectrochim. Acta, Part A*, 28, 1841 (1972). [c] From the last reference given in footnote *b*.

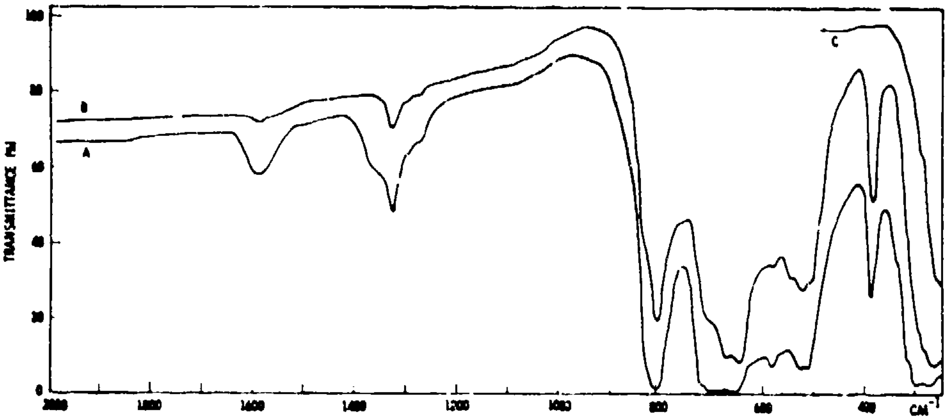

Figure 3. Infrared spectra of solid $ClF_3 \cdot xSbF_5$ as dry powder between AgBr plates: trace A, sample II; trace B, sample I; trace C, AgBr window background.

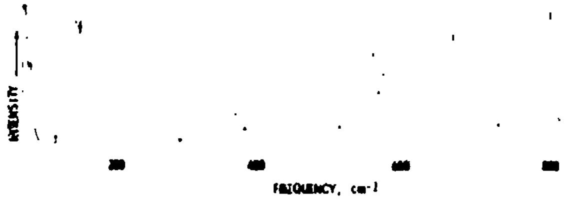

Figure 4. Raman spectrum of solid $ClF_3 \cdot AsF_5$ contained in a Teflon FEP capillary. Exciting was line 5145 Å. Bands marked by an asterisk are due to the Teflon tube.

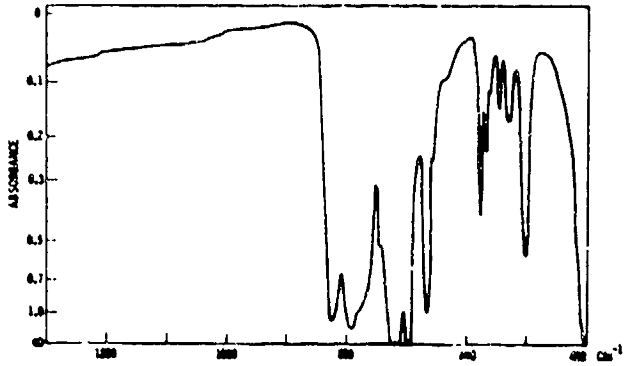

Figure 5. Low-temperature infrared spectrum of solid $ClF_3 \cdot AsF_5$. Window material AgCl.

and by comparison with the known spectra of compounds containing AsF_6^-,[21,27-29] $As_2F_{11}^-$,[21,22] SbF_6^-, and $Sb_2F_{11}^-$[20,28,30-33] anions. In solids, the deviation of the spectra of these anions from those expected for the isolated octahedral ions is very common. It can be caused by effects such as site symmetry lowering, slight distortion of the octahedrons owing to crystal packing and anion–cation interac-

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(26) K. O. Christe, W. Sawodny, and P. Pulay, *J. Mol. Struct.*, in press.

(27) R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 9, 811 (1970).

(28) K. O. Christe, R. D. Wilson, and W. Sawodny, *J. Mol. Struct.*, 8, 245 (1971).

(29) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, *Inorg. Chem.*, 8, 2489 (1969).

(30) K. O. Christe and C. J. Schack, *Inorg. Chem.*, 9, 2296 (1970).

(31) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1969).

(32) R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 9, 616 (1970).

(33) D. E. McKee, C. J. Adams, and N. Bartlett, private communication.

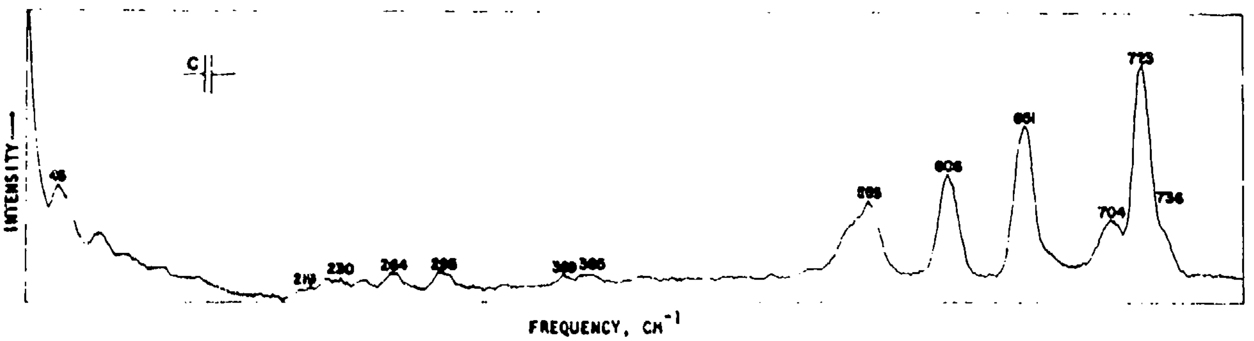

Figure 6. Raman spectrum of solid $BrF_5 \cdot 2SbF_5$ contained in a glass tube with a hollow inside glass cone. Exciting line was 5145 A using the axial viewing-transverse excitation technique.

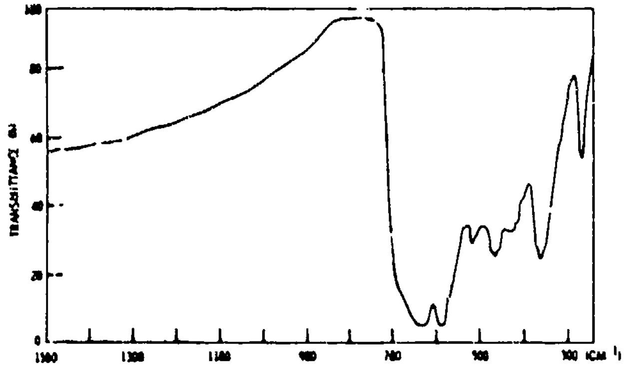

Figure 7. Infrared spectrum of solid $BrF_5 \cdot 2SbF_5$ as a dry powder between AgCl plates.

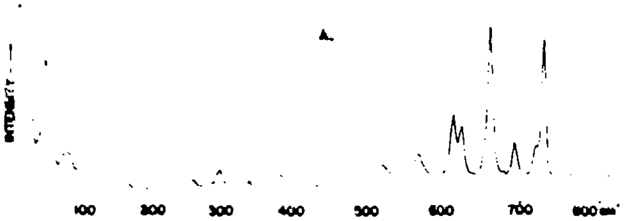

Figure 8. Raman spectrum of solid $IF_5 \cdot SbF_5$ contained in a glass tube with a hollow inside glass cone using 5145-A excitation.

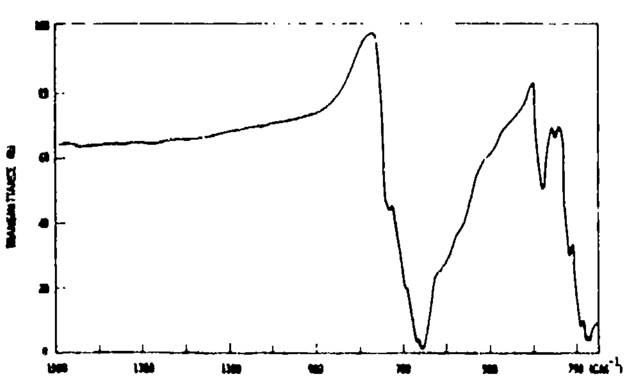

Figure 9. Infrared spectrum of solid $IF_5 \cdot SbF_5$ as a dry powder between AgBr plates.

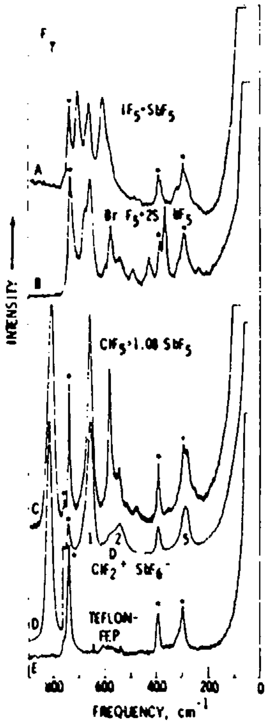

Figure 10. Raman spectra of HF solutions of $IF_5 \cdot SbF_5$ (trace A), $BrF_5 \cdot 2SbF_5$ (trace B), $ClF_5 \cdot 1.08SbF_5$ (trace C), and $ClF_4^+SbF_6^-$ (trace D; the numbers indicate ν_1, ν_2, and ν_5 of octahedral SbF_6^-) in Teflon FEP capillaries using 4880-A excitation. Trace E shows the spectrum of an empty capillary; Teflon bands are marked by and asterisk. F indicates spectral slit width.

tion, and the tendency to form polymeric anions. Unfortunately, the splittings, frequencies, and relative intensities of these bands strongly vary from compound to compound. Therefore, reliable assignments for the cations require the recording of spectra of adducts containing different anions or of solution spectra which usually show the bands characteristic of the unperturbed ions. Contrary to the highly symmetric octahedral XF_6^- anions, the ClF_4^+ cation of symmetry C_{2v} should be very little influenced by solid-state effects because it possesses already its maximum number ($3n - 6 = 9$) of modes.

For the ClF_5 adducts sufficient experimental data (see Table I) are available to distinguish the anion from the cation bands. As can be seen, the spectrum of ClF_4^+ is very similar to that of isoelectronic SF_4.[23,24] This close resemblance is comparable to that found for the isoelectronic pairs SF_2O-ClF_2O^+,[34] SF_2O_2-$ClF_2O_2^+$,[35] SF_6-ClF_6^+,[6] and SF_5^--ClF_5[36] and, therefore, is not surprising. For ClF_4^+, the assignment to the individual modes was made by analogy with SF_4. For SF_4, the assignment of Frey, *et al.*,[25] was used which was recently confirmed[26] by mean-square amplitudes of vibration and force field computations.

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(34) K. O. Christe, E. C. Curtis, and C. J. Schack, *Inorg. Chem.*, 11, 2212 (1972).

(35) K. O. Christe, R. D. Wilson, and E. C. Curtis, *Inorg. Chem.*, 12, 1358 (1973).

(36) K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, 11, 1679 (1972).

Table III. Observed Frequencies (cm^{-1}), Approximate Description of Modes, and Computed Symmetry and Most Important Internal Force Constants[a] of ClF_4^+

					ClF_4^+	ClF_3[b]
A_1	ν_1	800	ν sym eq	$F_{11} = f_r + f_{rr}$	4.54	
				$F_{13} = \sqrt{2}f_{r\beta}$	0.24	
				F_{14}	0.05	
	ν_2	571	ν sym ax	$F_{22} = f_R + f_{RR}$	3.65	
	ν_3	510	δ sciss eq	$F_{33} = f_\beta$	2.65	
				F_{34}	−0.03	
	ν_4	237	δ sciss ax	$F_{44} = 0.31f_\alpha + 0.69f_\gamma$[c]	0.41	
A_2	ν_5	475	τ	$F_{55} = f_\alpha + f_{\alpha'''} - f_{\alpha'} - f_{\alpha''}$	2.08	
B_1	ν_6	795	ν asym ax	$F_{66} = f_R - f_{RR}$	3.23	
				$F_{67} = \sqrt{2}(f_{R\alpha} - f_{R\alpha'})$	0.50	
	ν_7	537	rocking	$F_{77} = f_\alpha - f_{\alpha''} + f_{\alpha'} - f_{\alpha'''}$	2.26	
B_2	ν_8	829	ν asym eq	$F_{88} = f_r - f_{rr}$	4.61	
				$F_{89} = \sqrt{2}(f_{r\alpha} - f_{r\alpha'})$	0.21	
	ν_9	385	δ sciss ax out of plane	$F_{99} = f_\alpha - f_{\alpha'''} - f_{\alpha'} + f_{\alpha''}$	2.54	
				f_r	4.58	4.19
				f_R	3.44	2.70
				f_{rr}	−0.04	
				f_{RR}	0.21	0.36

[a] Stretching constants in mdyn/A, deformation constants in mdyn A/radian^2, and stretch-bend interaction constants in mdyn/radian. [b] Reference 25. [c] In addition to interaction constants which are not listed.

In the spectra of the ClF_5 adducts, nine bands are found which might be attributed to ClF_4^+. Of these, the intense infrared and Raman bands at about 800 cm^{-1} obviously represent the symmetric equatorial ClF_2 stretching mode ν_1. The moderately intense Raman and strong infrared bands at about 825 cm^{-1} then must be the antisymmetric equatorial stretch ν_8. The symmetric axial stretch, ν_2, falls within the range of the ν_2 anion bands, but is clearly identified by the strong Raman band at 574 cm^{-1} in the HF solution. The antisymmetric axial stretching mode, ν_6, should be of very high intensity in the infrared and of very low intensity in the Raman spectrum. By comparison with other pseudo-trigonal-bipyramidal molecules such as ClF_3[37] or ClF_3O_2,[38] it should occur above 700 cm^{-1}. Since there is no additional yet unassigned strong infrared band above this frequency in all of the observed spectra, a coincidence with ν_1 must be assumed. The assignment of ν_4 and ν_9 to the bands at 237 and 385 cm^{-1}, respectively, is clear-cut and needs no further comment. This leaves us with three frequencies, 537, 515, and 475 cm^{-1}, for the assignment to ν_7, ν_3, and ν_5. Since the 475-cm^{-1} band appears to be inactive in the infrared spectrum, we ascribe it to ν_5 which ideally should be forbidden in the infrared spectrum. Based on their relative Raman intensities, when compared to those of SF_4, we prefer to assign ν_3 and ν_7 to 515 and 537 cm^{-1}, respectively. The assignments for ν_3, ν_7, and ν_5 are somewhat tentative. However, a reassignment of these three deformational modes should, owing to their similar frequencies, be of minor influence on the principal force constants.

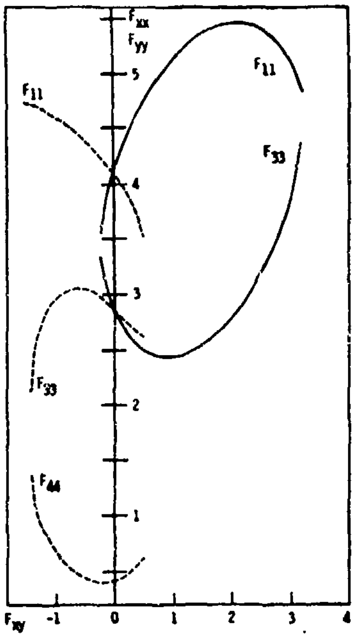

Figure 11. Force constant ellipses for ClF_4^+. The solid and broken curves represent the solutions for F_{11}, F_{33}, and F_{44} as a function of F_{34} and for F_{11} and F_{33} as a function of F_{13}, respectively. Dimensions are in mdyn/A.

Force Constants. The method used for the computation of the ClF_4^+ force field has previously been described.[38] The following geometry was assumed for ClF_4^+: $r(Cl\text{-}F_{eq}) = 1.57$, $R(Cl\text{-}F_{ax}) = 1.66$ Å; $\alpha(F_{ax}ClF_{eq}) = 90$, $\beta(F_{eq}ClF_{eq}) = 97$, $\gamma(F_{ax}ClF_{ax}) = 180°$. The symmetry coordinates were identical with those previously given[23,24] for isoelectronic SF_4, except for $S_3 = \Delta\beta$ and $S_4 = 0.2765\Sigma\alpha_i - 0.8332\gamma$, which are different owing to $\gamma = 180°$ in ClF_4^+ and were found numerically by a previously described[39] machine method.

A general valence force field for ClF_4^+ contains 17 symmetry force constants. Since only nine frequency values are available for their computation, a unique force field cannot be determined. Inspection of the G matrices of ClF_4^+ shows that in the A_1 block G_{12}, G_{23}, and G_{24} are zero and, therefore, F_{12}, F_{23}, and F_{24} can be neglected.[40]

The influence of the remaining off-diagonal F terms on the diagonal F values was determined by computing their values as a function of the off-diagonal F terms. The resulting halves of the force constant ellipses are shown in Figures 11 and 12 and represent the possible mathematical solutions of the force field. It has previously been shown[40] that the most probable range for F_{xy} is limited by the extremal values F_{yy} and F_{xy} = minimum. Inspection of Figures 11 and 12 reveals that even with this constraint small variation of certain off-diagonal force constants can strongly influence the values of the diagonal force constants. Consequently, an uncertainty of about ±0.5 mdyn/Å should be assumed for

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(37) H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.*, 52, 3517 (1970).

(38) K. O. Christe and E. C. Curtis, *Inorg. Chem.*, 12, 2245 (1973).

(39) K. O. Christe and E. C. Curtis, *Inorg. Chem.*, 11, 2196 (1972).

(40) W. Sawodny, *J. Mol. Spectrosc.*, 30, 56 (1969).

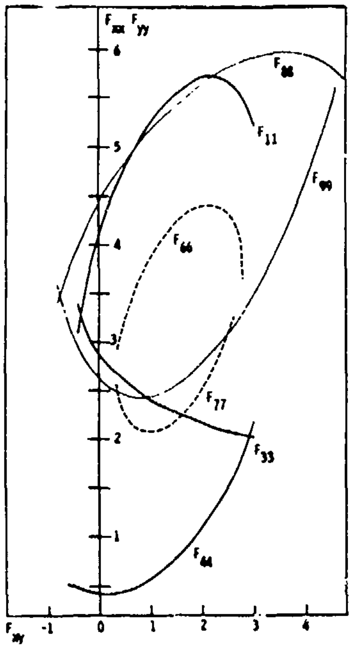

Figure 12. Force constant ellipses for ClF_4^+. The solid, broken, and dotted curves represent the solutions for F_{11}, F_{33}, and F_{44} as a function of F_{14}, for F_{66} and F_{77} as a function of F_{67}, and for F_{88} and F_{99} as a function of F_{89}, respectively.

the stretching force constants F_{11}, F_{66}, and F_{88}. However in spite of these relatively larger uncertainties, Figures 11 and 12 clearly show that the symmetry force constants involving the equatorial bonds (*i.e.*, F_{11} and F_{88}) are significantly larger than those involving the axial bonds (*i.e.*, F_{22} and F_{66}). The frequencies used for the force constant computations of ClF_4^+ are listed in Table III, together with our preferred force field, obtained by the method of stepwise coupling.[41] The fact that ClF_4^+ and isoelectronic SF_4 show similar force fields is not surprising in view of their similar frequencies and *G* matrices.

The significant difference in covalent bond strength between equatorial (4.6 mdyn/Å) and axial (3.4 mdyn/Å) bonds in ClF_4^+ is in excellent agreement with a generalized bonding scheme previously discussed[42] for a large number of halogen fluorides. It suggests that the bonding in ClF_4^+ might be explained, as previously described for the related pseudo-trigonal-bipyramidal species ClF_3, ClF_3O,[39] and ClF_3O_2,[38] by the following approximation. The bonding of the three equatorial ligands (including the free electron pair on Cl as a ligand) is mainly due to an sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves mainly one delocalized p-electron pair of the chlorine atom for the formation of a semiionic three-center four-electron pp σ bond.[43-45]

$BrF_5 \cdot 2SbF_5$ Adduct. The predominantly ionic nature of $BrF_5 \cdot 2SbF_5$ has previously been established[12] by a single-crystal X-ray diffraction study. Owing to the large number of fundamentals expected for $BrF_4^+Sb_2F_{11}^-$ and to the inavailability of other salts containing the BrF_4^+ cation only tentative assignments can be made for BrF_4^+. These are listed in Table II and are based on comparisons with those reported for isoelectronic SeF_4[46-48] and those of other salts containing the $Sb_2F_{11}^-$ anion.[20,28,31,33,49] Our Raman spectrum[1] of solid $BrF_4^+Sb_2F_{11}^-$ has in the meantime been confirmed by Surles, *et al.*,[13] and the proposed assignments[1,13] agree for most of the fundamentals. Since the crystal structure of $BrF_4^+Sb_2F_{11}^-$ is known[12] and the assignments for BrF_4^+ are tentative, no force constant computations were carried out for BrF_4^+.

Table IV. Comparison of the Fundamental Vibrations (cm^{-1}) of ClF_4^+, BrF_4^+, and IF_4^+ with Those of Isoelectronic SF_4, SeF_4, and TeF_4, Respectively

		ClF_4^+	BrF_4^+	IF_4^+	SF_4	SeF_4	TeF_4
A_1	ν_1	800	723	704	891	749	695
	ν_2	571	606	609	553	574	572
	ν_3	510	385	341	475	366	293
	ν_4	237	216	151	226	162	[151][a]
A_2	ν_5	475			414		
B_1	ν_6	795	704	655	730	622	587
	ν_7	537	419	385	532	400	333
B_2	ν_8	829	736	720	867	723	682
	ν_9	385	369	316	353	250	[184.8][a]

[a] Computed values.

$IF_5 \cdot SbF_5$ Adduct. Two independent single-crystal X-ray diffraction studies[16,17] have shown that the $IF_5 \cdot SbF_5$ has the predominantly ionic structure $IF_4^+SbF_6^-$, although the bond lengths and angles found by the two groups for IF_4^+ differ somewhat. The observed vibrational spectrum of $IF_5 \cdot SbF_5$ (see Table II) is consistent with such a predominantly ionic structure. The bands were tentatively assigned by comparison with those of TeF_4,[48] which is isoelectronic with IF_4^+, and those reported for similar SbF_6^- salts[20,30] containing an SbF_6^- anion distorted from symmetry O_h.[50] Our Raman spectrum of $IF_5 \cdot SbF_5$ is in good agreement with that reported[18] by Shamir and Yaroslavski. However, their interpretation suffers from the incorrect assumption of an ideal octahedral SbF_6^- anion. As for $BrF_4^+Sb_2F_{11}^-$, the tentative nature of the IF_4^+ assignments does not warrant a force constant treatment.

In summary, all the experimental data, *i.e.*, X-ray diffraction data, vibrational and ^{19}F nmr spectra, and conductivity measurements, available for the halogen pentafluoride-Lewis acid adducts are consistent with predominantly ionic structures containing $HalF_4^+$ cations. The structure of these cations can be derived from a pseudo trigonal bipyramid with a free valence electron pair occupying one of the equatorial positions. Deviation from this structure increases, as expected, with increasing size and polarizability of the halogen central atom. This results in a decrease of the axial F-Hal-F angle and increasing F bridging from the ClF_5 to the IF_5 adducts. A comparison of the fundamentals assigned to the $HalF_4^+$ cations with those of the isoelectronic chalcogen tetrafluoride series (see Table IV) shows consistent trends and satisfactory agreement.

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Registry No. BrF_5, 7789-30-2; SbF_5, 7783-70-2; AsF_5, 7784-36-3; $ClF_4^+SbF_6^-$, 25481-31-6; $ClF_5 \cdot xSbF_5$, 41646-49-5; $ClF_4^+AsF_6^-$, 41646-46-2; $BrF_4^+Sb_2F_{11}^-$, 36445-03-1; $IF_4^+SbF_6^-$, 41646-48-4; $BrF_5 \cdot AsF_5$, 41646-50-8; ClF_4^+, 36544-30-6; BrF_4^+, 41646-52-0; IF_4^+, 41646-53-1.

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Short communication

Vibrational assignment of SF_4

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In a previous paper [1] we reported the Raman spectrum of gaseous SF_4. The Raman data and a reinterpretation of the infrared band contours suggested the need of revising all assignments for the deformational modes except for $\nu_7(B_1)$. For the four stretching modes, the previous assignment [2–4] was adopted and force constants and mean amplitudes of vibration were computed [1]. In a recent paper [5], Frey, Redington, and Aljibury proposed a reversed assignment for the two antisymmetric stretching modes, $\nu_6(B_1)$ and $\nu_8(B_2)$, based on comparison with the spectra of the structurally related molecules, BrF_3 and ClF_3. More recently, Levin [6] proposed a reassignment of the deformational modes on the basis of Raman and infrared spectra of solid SF_4 and supported his assignment with a CDNO/2 calculation of the infrared intensities. One of Levin's main arguments for revising the assignment of the deformational modes was the observation of two bands at 245 and 205 cm^{-1}, respectively, in the Raman spectrum of solid SF_4. In a subsequent paper [7], however, Berney showed that the 205 cm^{-1} Raman band is due to residual α-SF_4.

Another unsettled question involves the frequencies of the axial and equatorial SF_2 scissoring modes in species A_1. It was shown [8–12] for related trigonal bipyramidal molecules such as PF_5 that these two deformational modes are highly mixed [11] and that a better agreement with the observed mean square amplitudes of vibration can be achieved [10] by assigning the lower frequency to the equatorial deformation. This frequency sequence was also proposed by Levin [6] for SF_4, contrary to our assignment [1] and that of Frey et al. [5] which are more consistent with the fact that in SF_4 the equatorial bonds are considerably shorter and hence stronger than the axial ones [13, 14]. In view of these conflicting assignments,

TABLE 1

ASSIGNMENT OF NORMAL MODES OF SF_4

Species		Approximate description	Assignment		
			I Christe and Sawodny [1]	*II* Frey et al. [5]	*III* Levin [6]
A_1	ν_1	ν sym SF_2 eq	892	892	892
	ν_2	ν sym SF_2 ax	558	558	558
	ν_3	δ sciss SF_2 eq	475	475	245 (233)
	ν_4	δ sciss SF_2 ax in plane	226	228	353
A_2	ν_5	SF_2 twist	414	414	475
B_1	ν_6	ν asym SF_2 ax	867	730	728
	ν_7	SF_2 rocking	532	532	533
B_2	ν_8	ν asym SF_2 eq	730	867	867
	ν_9	δ sciss SF_2 ax out of plane	353	353	206 (228)

TABLE 2

SYMMETRY FORCE CONSTANTS[a,b] OF SF_4 COMPUTED FROM THE ASSIGNMENTS LISTED IN TABLE 1 ASSUMING FOR SETS a $\delta SF_2eq > \delta SF_2ax$ (A_1) AND FOR SETS b $\delta SF_2eq < \delta SF_2ax$ (A_1)

		Ia	*Ib*	*IIa*	*IIa* (*MVFF*)	*IIb*	*IIIa*	*IIIb*
A_1	F_{11}	5.74	5.71	5.74	5.49	5.71	5.83	5.81
	F_{22}	3.48	3.48	3.48	3.48	3.48	3.48	3.48
	F_{33}	1.97	0.57	1.97	2.10	0.57	1.10	0.63
	F_{44}	0.37	1.30	0.37	0.38	1.30	0.41	0.71
	F_{12}	0	0.01	0	0	0.01	0	0
	F_{13}	0.13	0.05	0.13	0	0.05	0.02	0.04
	F_{14}	0.05	0.16	0.05	0	0.16	0.04	0.05
	F_{23}	0.02	0.01	0.02	0	0.01	0	0
	F_{24}	0.01	0.02	0.01	0	0.02	0.01	0.01
	F_{34}	−0.04	−0.03	−0.04	0	−0.03	−0.07	−0.06
A_2	F_{55} ($\nu_5 = 200\ cm^{-1}$)			0.35				
	($\nu_5 = 400\ cm^{-1}$)			1.40				
	($\nu_5 = 600\ cm^{-1}$)			3.15				
B_1	F_{66}	3.66	3.66	2.65	2.35	2.65	2.65	2.65
	F_{77}	2.20	2.20	2.24	2.50	2.24	2.24	2.24
	F_{67}	0.45	0.45	0.60	0.54[c]	0.60	0.60	0.60
B_2	F_{88}	3.33	3.33	4.77	4.62	4.77	4.77	4.77
	F_{99}	2.01	2.01	1.98	2.04	1.98	1.98	1.98
	F_{89}	0.20	0.20	0.17	0	0.17	0.17	0.17

[a] Stretching force constants in mdyn/Å, deformation constants in mdyn Å, and stretch–bend interaction constants in mdyn.

[b] Unless otherwise indicated the listed force fields were computed by the eigenvector method.

[c] Minimum value of F_{67} required for obtaining a real solution.

we have recomputed the force field and mean square amplitudes of vibration for SF_4 hoping that these data might allow us to distinguish between the different assignments [1, 5, 6] (see Table 1).

Since only nine frequency values are available for the computation of seventeen symmetry force constants, a General Valence Force Field (GVFF) cannot be computed. However, it is known that mean square amplitudes of vibration are only slightly influenced by moderate changes in the force field. This was confirmed for SF_4 by calculating mean amplitudes of vibration based on two force fields obtained by two different approximating methods. The first method used was the eigenvector method [15, 16] and the second one was a diagonal MVFF for species A_1 and B_2 combined with the $F_{67} \equiv$ minimum solution for species B_1 since no real values can be obtained for $F_{67} \equiv 0$. The results of these computations are given in Tables 2, 3 and 4 and in Fig. 1. The mean square amplitudes of vibration computed from the two force fields differed by less than 0.001 Å, except for

TABLE 3

STRETCHING FORCE CONSTANTS (in mdyn/Å) AND BOND LENGTHS (in Å) OF SF_4 COMPARED TO THOSE OF RELATED MOLECULES AND IONS

	SF_4				SF_6 [19]	SF_5^- [17]	ClF_3 [5]
	Ia	*IIa*	*IIa* (*MVFF*)	*IIIb*			
f_R (ax)	3.57	3.07	2.92	3.07		2.06	2.70
f_R'	−0.09	0.42	0.57	0.42		0.52	0.36
f_r (eq)	4.54	5.25	5.05	5.33	5.26	4.12	4.19
f_r'	1.21	0.49	0.43	0.48			
R		1.646 ± 0.003^a					1.698 ± 0.003^c
r		1.545 ± 0.003^a			1.56 ± 0.02^b		1.598 ± 0.003

[a] Ref. 14. [b] Ref. 18. [c] D. F. Smith, *J. Chem. Phys.*, 21 (1953) 609.

TABLE 4

COMPUTED AND OBSERVED [13] MEAN SQUARE AMPLITUDES (in Å) OF VIBRATION OF SF_4

	$\langle q^2\rangle_{calc}^{1/2}$						$\langle q^2\rangle_{obs}^{1/2}$
	Ia	*IIa*	*IIa* (*MVFF*)	*IIb*	*IIIa*	*IIIb*	
S–F_1 (ax)	0.050	0.049	0.050	0.049	0.049	0.049	0.047 ± 0.005
S–F_3 (eq)	0.044	0.041	0.041	0.041	0.041	0.041	0.041 ± 0.005
$F_1 \cdots F_2$	0.061	0.061	0.061	0.061	0.061	0.061	0.059 ± 0.01
$F_3 \cdots F_4$	0.063	0.063	0.064	0.094	0.076	0.091	0.068 ± 0.01
$F_1 \cdots F_3$ ($\nu_s = 200\ cm^{-1}$)	0.091	0.091	0.091	0.086	0.096	0.094	0.067 ± 0.005
($\nu_s = 400\ cm^{-1}$)	0.074	0.073	0.074	0.068	0.080	0.077	
($\nu_s = 600\ cm^{-1}$)	0.070	0.069	0.070	0.064	0.076	0.073	
($\nu_s = 800\ cm^{-1}$)	0.068	0.068	0.068	0.063	0.075	0.072	

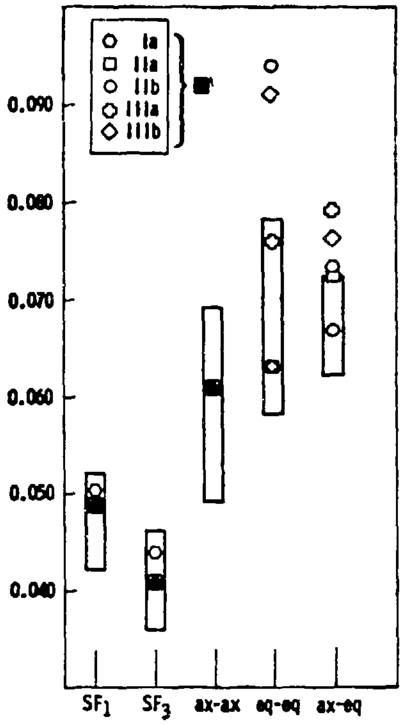


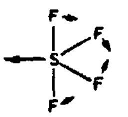
Fig. 1. Mean amplitudes of vibration (Å) of SF_4 for bonded and nonbonded distances. Rectangles represent experimental electron diffraction values ±esd according to ref. 8. Crosses, squares, diamonds, and circles represent amplitudes computed for the different assignments.

$\langle q^2\rangle^{\frac{1}{2}}$ $F_3 \cdots F_4$ using the assignment of Levin [6] which showed a difference of 0.004 Å. Therefore, only the data obtained by the eigenvector method are listed in Tables 2, 3, and 4, except for the preferred (see below) set IIa for which the MVFF values are also given for comparison.

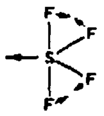
Table 4 and Fig. 1 show that the mean square amplitudes of vibration are useful for discriminating between the different assignments of the deformational modes, but are of little help in finding the correct assignment for the two stretching modes $\nu_6(B_1)$ and $\nu_8(B_2)$. However, the following force field arguments favor set II over set I: (1) Generally, the stretch-stretch interaction constant is relatively small whenever two bonds form an angle close to 90°. For set I, the equatorial interaction constant f_r' exhibits a value of 1.21 mdyn/Å which is unreasonably high for a F–S–F bond angle of 101°. The value of 0.49 mdyn/Å obtained for set II is much more plausible; (2) The value of the second stretch-stretch interaction constant, f_R', shows only for set II a value similar to those observed for the related species, SF_5^- [17], ClF_3 [5], and BrF_3 [5]; (3) The bond length of the equatorial S–F bonds in SF_4 (1.545±0.003 Å) [14] is similar to that in SF_6(1.56±0.02 Å) [18]. Since bond lengths are related to the stretching force constants, one might expect f_r of SF_4 to approach the SF_6 value [19] of 5.26 mdyn/Å. This is true only for set II; (4) The relatively large difference in the length of the equatorial and the axial bonds of SF_4 (0.10 Å) [14] favors set II which shows the larger difference between f_r and f_R; (5) Set II is in better agreement with the values found [17] for SF_5^- if the general decrease in the force constant values owing to the formal negative charge is taken into account. Thus, the proposed [5] reassignment of $\nu_6(B_1)$ and $\nu_8(B_2)$ results in a more satisfactory set of force constants for SF_4, although it remains difficult to rationalize the observed infrared band contours [2, 4].

The question as to which A_1 deformation mode should be assigned to the higher frequency value, can readily be decided based on the computed mean square amplitudes of vibration (see Table 4 and Fig. 1). It should be noted that the $F_1 \cdots F_3$ values reported in our previous paper [1] are incorrect due to a computational error. The revised values are listed as set Ia. It can be seen from Fig. 1 that all b sets (i.e. δ sciss ax > δ sciss eq) result in unacceptably high values for $\langle q^2\rangle^{1/2}$ $F_3 \cdots F_4$. Hence, δ sciss eq > δ sciss ax appears to be a better description of the two A_1 deformational modes of SF_4. It should be kept in mind, however, that both ν_3 and ν_1 are not highly characteristic. The potential energy distribution obtained for the diagonal force field shows that ν_3 is made up of 65 % equatorial and 35 % axial bending motion, and that ν_1 contains significant contributions from both the axial and equatorial bending motions. This high degree of mixing is not surprising [20] since the G matrix elements G_{13}, G_{14}, and G_{34} of SF_4 show large numerical values. The two remaining modes in species A_1 are more characteristic: ν_2 is made up entirely of axial stretching and ν_4 represents 88 % axial bending. As can be seen from Fig. 1, the fit between observed [13] and computed $\langle q^2\rangle^{1/2}$ $F_3 \cdots F_4$ and $F_1 \cdots F_3$ can be improved by increasing somewhat the mixing between ν_3 and ν_4. Additional support for $\nu_3 > \nu_4$ in the chalcogen tetrafluorides was recently obtained [21] by Adams and Downs in a matrix isolation study of SeF_4. The observed selenium isotopic shifts show that the higher frequency value belongs to ν_3.

The high degree of mixing between the equatorial and axial bending motions for ν_3 can be rationalized. Inspection of the normal coordinates of ν_3 shows that this mode is essentially an umbrella type deformation, i.e. a symmetric combination of the equatorial and axial bending motions. The ν_4 deformation might be considered as the corresponding antisymmetric combination of these motions. It should be the mode mainly involved in an intramolecular exchange process as suggested by Berry [22] although higher vibrational levels must be invoked since the normal coordinates show only little motion of the equatorial fluorines in the fundamental. The fact that the potential energy distribution shows ν_4 to be composed mainly of axial bending is due to the fact that the sulfur moves in the same direction as the equatorial fluorines thus suppressing the equatorial scissoring motion.



ν_3, symmetric combination of axial and equatorial bending



ν_4, antisymmetric combination of axial and equatorial bending

Inspection of Fig. 1 also reveals that the assignment proposed [6] by Levin (set IIIb) results in unsatisfactory values for $\langle q^2\rangle^{\frac{1}{2}}$ $F_3 \cdots F_4$ and $F_1 \cdots F_3$ and, therefore, should be rejected. Furthermore, it can be seen that retaining Levin's frequencies [6] for A_1 but reversing the assignment of ν_3 and ν_4 (set IIIa) results in too high a value for $\langle q^2\rangle^{\frac{1}{2}}F_1 \cdots F_3$. This discrepancy cannot be eliminated by increasing the mixing between ν_3 and ν_4, since a small decrease in $\langle q^2\rangle^{\frac{1}{2}}F_1 \cdots F_3$ results in a large increase in $\langle q^2\rangle^{\frac{1}{2}}F_3 \cdots F_4$. A second strong argument against set IIIa was recently put forward by Berney [7]. He showed that the splitting of the 223 cm^{-1} Raman line in the spectrum of the solid is due to the α, β, and γ forms of SF_4 and not due to two different fundamentals, thus eliminating the basis of Levin's reassignment. Furthermore, the observed infrared band contours [4] and Raman polarization measurements on gaseous SF_4 [1] and SeF_4 [23] favor set II over III.

Since the modified valence force field obtained by the eigenvector method [15, 16] is not too different from the diagonal force field, numerical experiments were carried out by varying the off diagonal constants within meaningful limits. Whereas for set IIa, the fit between observed and computed $\langle q^2\rangle^{\frac{1}{2}}F_1 \cdots F_3$ could be improved, for set IIb the large discrepancy in $\langle q^2\rangle^{\frac{1}{2}}F_3 \cdots F_4$ could not be eliminated.

In summary, set IIa is the only assignment which can satisfy both the observed [13] mean square amplitudes of vibration and basic force field arguments. Furthermore, the mean square amplitudes of vibration suggest that for SF_4 the higher frequency A_1 deformational mode ν_3 should be assigned to the equatorial scissoring motion. However, a normal coordinate description of ν_3 and ν_4 as symmetric and antisymmetric combinations, respectively, of the equatorial and axial scissoring motions seems more appropriate.

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HALOGEN FLUORIDES

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ABSTRACT

A selective review of the presently known binary chlorine -, bromine -, and iodine - fluorides is given. Their syntheses, physical and chemical properties, and structures are discussed. Their tendencies to form adducts with Lewis acids and bases are compared, and the structures and relative stabilities of the resulting halogen fluoride ions are summarized. Force constant data are used to demonstrate the occurrence of two types of bonding (semi-ionic and mainly covalent) in this class of compounds and a new rule (described as rule III in the text) is given which allows their prediction and rationalization.

INTRODUCTION

This review deals with selected aspects of halogen fluoride chemistry which are of particular interest to the author. No attempt was made to give a complete coverage of all the data published on halogen fluorides since it would be beyond the scope of this short article. The cited references are those which were most convenient and, therefore, do not imply any priorities. The literature published until the end of 1964 has been summarized in an excellent review by Stein (1) who also lists the previously published reviews. Some of the more recent data have been discussed by Meinert (2), Lawless and Smith (3), Popov (4), and Schmeisser and Naumann (5). A recent review by Gillespie and Morton (6) deals exclusively with interhalogen cations.

Whereas the last halogen fluoride molecule was discovered in 1962, a large number of halogen fluoride ions has been discovered since then and their structures have been established. Essentially all of the possible binary halogen fluoride molecules and ions have now been synthesized and characterized. Owing to the large number of possible oxidation states, coordination numbers, and sterically active free valence electron pairs, this family of compounds is of particular interest from a structural point of view.

HALOGEN FLUORIDE MOLECULES

Table I lists the presently known halogen fluorides including the year of their discovery. As can be seen, all the compounds expected to exist were synthesized before 1963 and their properties have been summarized (1,7) previously. The fact that the heptafluoride of chlorine does not exist (8) can be explained by steric arguments (maximum coordination number of 6 for +VII chlorine).

Table I. Known Halogen Fluoride Molecules

Oxidation State of Central Atom			
+I	ClF b.p. -100°C Ruff (1928)	BrF ~ + 20° Ruff (1933)	IF Unstable Schmeisser (1960)
+III	ClF_3 +12° Ruff (1930)	BrF_3 +126° LEBEAU, Prideaux (1905)	IF_3 Unstable Schmeisser (1960)
+V	ClF_5 -14° Maya (1962)	BrF_5 +41° Ruff (1931)	IF_5 +98° Gore (1871)
+VII			IF_7 +5° Ruff (1930)

General Synthetic Methods

A. Direct Fluorination with Fluorine

All of the halogen fluorides listed in Table I can be synthesized directly from the elements. Variation of the reaction parameters, such as stoichiometry of the reactants and reaction time and pressure, will determine the composition of the product.

$$X_2 + nF_2 \longrightarrow 2XF_n$$

This ease of synthesis also explains why most of these halogen fluorides had been synthesized more than 30 years ago. Only the thermal instability of IF and IF_3 and the lack of low-temperature techniques pre-empted the earlier discovery of IF and IF_3. The late discovery of ClF_5 in 1962 (9) may be explained by the fact that its synthesis from the elements requires both high temperature and high pressure.

Fluorinations requiring elevated temperature appear to be catalyzed by the presence of Lewis bases such as CsF. For example, the fluorination of ClF_3 to ClF_5 in the presence of CsF involves the formation of $Cs^+ ClF_4^-$ as an intermediate and proceeds already at 150° (7). Whereas numerous examples are known where the presence of complex fluoro anions facilitate oxidative fluorinations, the contrary appears to be true for complex fluoro cations (10).

B. Fluorinations Involving Nonmetal Fluorides

Since iodine fluorides are relatively mild fluorinating agents, they can be readily prepared by fluorination of I_2, iodides, or I_2O_5 with nonmetal fluorides such as ClF_3, BrF_3, BuF_5, or SF_4 (1), OF_2 (11), or SF_5OF(12). The latter can also be used to fluorinate Br_2 to BrF_3(12).

C. Conproportionation Reactions

This reaction is particularly useful for the syntheses of the halogen monofluorides (1, 5) according to:

$$X_2 + XF_3 \longrightarrow 3XF$$

All three halogen monofluorides can be obtained in this manner.

D. Fluorinations with Metal Fluorides

Fluorinations involving metal fluorides are useful for producing all three halogen monofluorides. Since BrF and IF readily disproportionate to BrF_3 and IF_5, respectively, the latter compounds can also be prepared in this fashion. Typical examples for this type of reactions involve either AgF(1, 13),

$$AgF + I_2 \longrightarrow AgI + IF \; (\longrightarrow 2I_2 + IF_5)$$

$$AgF + Br_2 \longrightarrow AgBr + BrF \; (\longrightarrow Br_2 + BrF_3)$$

$$AgF + Cl_2 \longrightarrow AgCl + ClF$$

or eutectic melts (13),

$$\begin{array}{l} LiF - NaF - KF + Cl_2 \xrightarrow{Melt} MeCl + ClF \\ MeCl + HF \longrightarrow MeF + HCl \\ \hline HF + Cl_2 \longrightarrow ClF + HCl \end{array}$$

or pseudohalides, such as $ClOSO_2F$ (14),

$$CsF + ClOSO_2F \xrightarrow{-80^{o}} CsSO_3F + ClF$$

The use of eutectic melts is interesting since the alkali metal chloride product can be reconverted to the fluoride by HF, thus allowing the production of ClF from Cl_2 and HF. The last method employing $ClOSO_2F$ is remarkable because it proceeds already at such a low temperature.

E. Photolysis

The photolysis of the Cl_2 $-F_2$, chlorine fluoride $-F_2$, or chlorine oxyfluoride $-F_2$ systems can be used for preparing ClF, ClF_3, and ClF_5 (15 - 18). The photolytic synthesis from the elements parallels the thermal one (method A). Both methods seem to involve as the initiation step, the generation of F atoms from F_2, but in one case the F atoms are generated thermally and in the other case photolytically. Whereas low temperature photolysis of matrix isolated species can be used for structural studies, it is of no importance as a synthetic method for the production of significant amounts of material.

F. Electrolysis

Chlorine fluorides are usually synthesized from Cl_2 and F_2 and F_2 is made by electrolysis. Therefore, the direct electrochemical synthesis of ClF, ClF_3, and ClF_5 from Cl_2 in anhydrous HF was studied (19, 20). It was shown for example that ClF_5 can be formed from ClF_3 with current yields of up to 50% (19) and from Cl_2 with current yields of up to 18% (20). In the latter case, ClF is the main product and substantial amounts of ClF_3 are also produced.

G. Glow Discharge

The original discovery of ClF_5 by Maya in 1962 involved the use of glow discharge (9). Since more convenient syntheses are available for producing all of the known halogen fluorides, apparently few further attempts have been made to exploit this experimental approach. For example, an unsuccessful attempt by Meinert (18) to produce Xe chloride fluoride from Xe, Cl_2, and F_2 resulted in ClF_3 and ClF_5 formation.

H. Fluorinations with PtF_6 and $Kr_2F_3^+$

Inspite of the nonexistence of ClF_7 and BrF_7, the heptavalent ClF_6^+ and BrF_6^+ cations were successfully synthesized (8, 21-23). These cations are more powerful

$$2ClF_5 + 2PtF_6 \longrightarrow ClF_4^+\,PtF_6^- + ClF_6^+\,PtF_6^-$$

$$BrF_5 + Kr_2F_3^+SbF_6^- \longrightarrow BrF_6^+SbF_6^- + 2Kr + F_2$$

oxidizers than F_2 and hence cannot be prepared from F_2. In the case of ClF_6^+ (8, 21, 22), PtF_6 was used as the oxidizing fluorinator. Since PtF_6 does not oxidize BrF_5 to BrF_6^+, even when exposed to unfiltered uv radiation (10), an even stronger oxidizer, $Kr_2F_3^+SbF_6^-$, was required for the synthesis of BrF_6^+ (23). Obviously, the synthesis of such powerful oxidizers is very unusual, difficult, and challenging.

Physical Properties and Handling

The physical properties of the halogen fluoride molecules have previously been summarized (1, 5, 7) and hence, require only little further discussion. Owing to association in the liquid and solid state, the volatilities of ClF_3, BrF, BrF_3, IF, IF_3, and IF_5 (see Table I) are significantly lower than one might expect from their molecular weights. Through formation of fluorine bridges, these halogen fluorides achieve more favorable coordination numbers by dimer or polymer formation as shown in Figure 1 for BrF_3 (24, 25). Spectroscopic evidence for association was also obtained for IF_3 (26) and IF_5 (27).

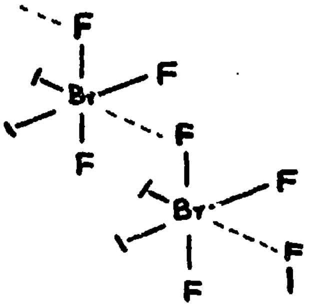


Figure 1. Association of BrF_3 through fluorine bridges

As a further consequence of their unfavorable coordination numbers, BrF, IF, and IF_3 tend to disproportionate according to:

$$3\ BrF \longrightarrow Br_2 + BrF_3$$

$$5\ IF \longrightarrow IF_5 + 2I_2$$

$$5\ IF_3 \longrightarrow 3IF_5 + I_2$$

Unlike BrF and IF, ClF shows little tendency to associate or disproportionate but instead exhibits partial double bond character which may be described by the following mesomeric structures:

$$\underset{\delta+\quad\delta-}{|\overline{\underline{Cl}} - \overline{\underline{F}}|} \longleftrightarrow \underset{(-)\quad(+)}{|\overline{\underline{Cl}} = \overline{F}} \qquad \mu_{exp.} = -0.88D \quad \underset{\delta-\quad\delta+}{Cl - F}$$

These structures were proposed in 1957 by Goubeau (28) and recent measurements of the direction of the dipole moment in ClF (29) indeed confirm this view. It was shown that $\mu_{ClF} = -0.88D$. The small size of the overall dipole moment is due to the opposite direction of this moment in the two mesomeric structures. The observed direction of the dipole moment in ClF with F being the positive end is surprising, particularly in view of the reaction chemistry of ClF. The fact that Cl acts in all known ClF reactions as positive chlorine may be explained by the relatively small net dipole moment and by the polarisability of chlorine being larger than that of fluorine.

All of the halogen fluorides can be handled safely and are not shock sensitive. The chlorine and bromine fluorides are much stronger oxidising fluorinators than the iodine fluorides and, therefore, differ markedly from these in their reaction chemistry. Owing to their high reactivity with water, fuels, and organic compounds, chlorine and bromine fluorides are best handled in well passivated metal-Teflon vacuum systems. Exposure of chlorine fluorides to excess water should be avoided since it results in the formation of shock sensitive chlorine oxides (30, 31).

Selfionization

One of the most significant characteristics of halogen fluorides is their amphoteric nature, i.e., their ability to act as a base towards strong Lewis acids and as an acid towards strong bases. These interactions result in the formation of complex fluoro cations and anions, respectively, according to:

$$Me^{+}\,XF_{n+1}^{-} \xleftarrow[+MeF]{+\text{Lewis base}} XF_n \xrightarrow[+YF_m]{+\text{Lewis acid}} XF_{n-1}^{+}\;YF_{m+1}^{-}$$

This amphoteric nature was first recognized by Woolf and Emeleus (32). Since BrF_3 shows a relatively high specific conductance of 8×10^{-3} ohm $^{-1}$cm^{-1} (33), selfionization was postulated for BrF_3 according to:

$$2BrF_3 \rightleftharpoons BrF_2^{+}\;BrF_4^{-}$$

Whereas this assumption is certainly correct for BrF_3 (keeping in mind that the conductance of BrF_3 is strongly enhanced by aggregation of BrF_3 in the liquid phase, thus requiring only the migration of an electric charge instead of the ion itself), the ability of the remaining halogen fluorides to form complex fluoro ions has generally been construed as a chemical proof for their selfionization. This concept is grossly incorrect since the specific conductances reported for the other halogen fluorides are quite low and often were the lower limits of the experimental equipment. In addition, it should be kept in mind how difficult it is to obtain and retain these extremely reactive materials in a pure state. Therefore, the halogen fluoride molecules, with the exception of BrF_3, are best considered as essentially undissociated molecules. This misconception concerning the selfionization of halogen fluorides has also been criticized recently by Meinert and Gross (34).

Reaction Chemistry

Halogen Monofluoride Reactions

In addition to reactions in which halogen monofluorides act as simple fluorinating agents (1), the following types of reactions are possible.

A. Addition to Multiple Bonds

Halogen monofluorides can readily be added to C=C double bonds:

In the case of BrF and IF, the halogen monofluorides can be substituted by systems such as N-bromo compounds + HF (35), Br_2 + AgF, or I_2 + AgF (36), or $2I_2 + IF_5$ (37 - 39), respectively, without changing the nature of the addition products (40).

The addition of XF to multiple bonds is by no means limited to C=C bonds. Typical examples for other multiple bonds are $N\equiv S$ (41), $S=O$ (42, 43) and $C=O$ (44, 45) as demonstrated by the following equations:

$$N\equiv SF_3 + 2ClF \longrightarrow Cl_2NSF_5$$

$$SO_3 + ClF \longrightarrow ClOSO_2F$$

$$SF_4O + ClF \xrightarrow{CaF} SF_5OCl$$

$$OCF_2 + ClF \xrightarrow{CaF} CF_3OCl$$

B. HF Elimination Reactions

Since the elimination of HF is usually highly exothermic, this type of reactions are often violent and require careful control of the reaction conditions. With hydroxyl groups the following reactions (30, 31) were observed:

$$HONO_2 + ClF \longrightarrow HF + ClONO_2$$

$$HOH + 2ClF \longrightarrow 2HF + Cl_2O$$

It should be kept in mind, however, that the products in these reactions vary depending on which starting material is used in excess and on the exact reaction conditions (30, 31).

The HF elimination reactions are not limited to hydroxyl groups as was demonstrated (46) for HNF_2:

$$HNF_2 + ClF \longrightarrow HF + NF_2Cl$$

C. Oxidative Chlorofluorinations

Generally, ClF acts as a fluorinating agent, however, instances are known in which it can behave as a chlorofluorinating agent (47, 48, 1):

$$SF_4 + ClF \xrightarrow{CaF} SF_5Cl$$

$$CF_3PCl_2 + ClF \longrightarrow CF_3PCl_3F$$

$$CO + ClF \longrightarrow COFCl$$

D. Oxidative Fluorinations

Many reactions are known (1) in which ClF acts as a fluorinating agent. It has recently been shown (49) that strong Lewis acids, such as AsF_5, can strongly enhance the fluorinating power of ClF. Thus, ClF alone does not fluorinate xenon. However, upon addition of AsF_5 the following reaction takes place involving the formation of $Cl_2F^+AsF_6^-$ (50) as an intermediate:

$$Xe + 2ClF \xrightarrow{+AsF_5} XeF^+AsF_6^- + Cl_2$$

E. Disproportionation Reactions

The tendency of halogen monofluorides to disproportionate has been discussed above and, hence, is not reiterated.

Reactions of Higher Valent Halogen Fluorides

Since the higher valent chlorine and bromine fluorides are relatively powerful fluorinators and are easier to handle than F_2, they can be used for the preparation of metal fluorides or oxyfluorides (1). However, owing to their high reactivity, the reaction chemistry of the chlorine and bromine fluorides shows less variation than that of the corresponding iodine fluorides. Few systematic studies of chlorine fluoride reactions with non-metal compounds have been reported. These include reactions with hydroxyl functions (30, 31) and HNF_2 (46). The reaction of excess ClF_3 with $HONO_2$ is of interest, since $FClO_2$ and ClF were the observed products (31) and not FClO as one might expect.

$$2ClF_3 + 2HONO_2 \longrightarrow 2HF + FClO_2 + ClF + 2NO_2F$$

This observation is in excellent agreement with the recently reported evidence for an unstable FClO intermediate in the hydrolysis of ClF_3 in a flow system (51), resulting in its disproportionation into $FClO_2$ and ClF.

The hydrolysis of ClF_5 cannot be carried out step-wise to yield ClF_3O (31) but yields $FClO_2$ as the only product indicating that ClF_3O hydrolyses much faster than ClF_5. However, the statement in a previous review (2) that ClF_5 interacts only slowly with water is clearly incorrect. Chlorine trifluoride can also be used to convert a perfluorinated alcohol (52) or COF_2 (53) to the corresponding peroxides:

$$2(CF_3)_3COH + ClF_3 \longrightarrow (CF_3)_3COOC(CF_3)_3 + 2HF + ClF$$

$$2COF_2 + ClF_3 \xrightarrow{CsF} CF_3OOCF_3$$

Whereas ClF_3 and ClF_5 are powerful oxidizers, a few cases have been reported in which they can act as reducing agents towards stronger oxidizers, such as XeO_3F_2 (54), KrF_2 (55) or PtF_6 (8, 21, 22). In the first case, both ClF_3 and ClF_5 are oxidized to $FClO_3$. With KrF_2, ClF_3 is oxidized to ClF_5, and PtF_6 can oxidize ClF_5 to ClF_6^+.

Most of the known reaction chemistry of BrF_3 and BrF_5 has previously (1) been reviewed. BrF_5 is relatively inert towards strong oxidizers and, therefore, can be used as a solvent for reactions involving strong oxidizers such as PtF_6. It also forms at low temperature a very unstable adduct with pyridine and can be dissolved in cold CH_3CN (56). It also interacts with SO_3 (57) yielding

$BrF_{5-n}(OSO_2F)_n$ type products the structures of which have not been unambiguously established. The formation of ill defined products parallels that observed for the $IF_5 - SO_3$ system, which also involves the formation of $O{=}IF_2OSO_2F$ type compounds (58).

Iodine trifluoride forms numerous adducts with N- containing bases such as pyridine. For the $IF_3 \cdot Py$ adduct, the ionic structure $[IF_2 \cdot Py_2]^+ [IF_4]^-$ was suggested (5). Since the IF_n group is only a relatively weak fluorinator, it is possible to synthesize substituted iodine fluorides. Typical examples are trifluoroacetato (59), perfluoro-alkyl (60-63), and methoxy (64) groups:

$$IF_3 + 3\,(CF_3CO)_2) \longrightarrow I(O_2CCF_3)_3 + 3CF_3COF$$

$$R_fI \xrightarrow[\text{or } BrF_5]{+F_2,\ ClF_3,\ BrF_3,} R_fIF_2 \longrightarrow R_fIF_4$$

$$IF_5 + (CH_3)_3SiOCH_3 \longrightarrow IF_4OCH_3 + (CH_3)_3SiF$$

Iodine pentafluoride exhibits a property rather unique for halogen fluorides. It forms molecular adducts with compounds such as XeF_2 (65 - 67) and XeF_4 (65, 68). It also forms a 2:1 adduct with $CsIF_6$ (69) which had been responsible for much of the confusion concerning the spectra of $Cs^+IF_6^-$ (70 - 73). However, the exact structure of $CsIF_6 \cdot 2IF_5$ has as yet not been established.

HALOGEN FLUORIDE IONS

As a consequence of the above discussed amphoteric nature of the halogen fluoride molecules, a large number of simple and novel ions were discovered and characterized. Since the main progress in halogen fluoride chemistry during recent years has been in this area, a more detailed discussion will be given in the following paragraphs. The syntheses of most of these ions are simple and involve the combination of the corresponding halogen fluoride molecules with either a Lewis acid or a Lewis base. However, the syntheses of ClF_6^+ and BrF_6^+ turned out to be a great challenge (see above) since the corresponding parent molecules, ClF_7 and BrF_7, are unknown.

Existing Ions

Table II summarizes the possibly existing and presently known binary halogen fluoride ions together with their first syntheses. As can be seen all ions are known (8, 21 - 23, 32, 50, 74 - 90) with the exception of ClF_6^-, ClF_8^-, BrF_8^-, Br_2F^+, and I_2F^+. The ClF_6^- anion and ClF_7 were shown (79, 8) not to exist. This is probably due to the fact that for these high oxidation state central atoms the maximum coordination number is limited to six. The existence of ClF_6^+ and the nonexistence of ClF_6^- suggest that in ClF_6^- the free Cl valence electron pair is to some extent sterically active. The limiting coordination number is also a plausible argument for the nonexistence of BrF_8^-. There is no compelling reason why Br_2F^+ and I_2F^+ should not exist. The lack of their discovery can be ascribed to experimental difficulties in preparing and handling the unstable parent compounds, BrF and IF, respectively.

Table II. Halogen Fluoride Ions. Compounds listed in brackets do not exist, those in parentheses may exist but have not as yet been prepared.

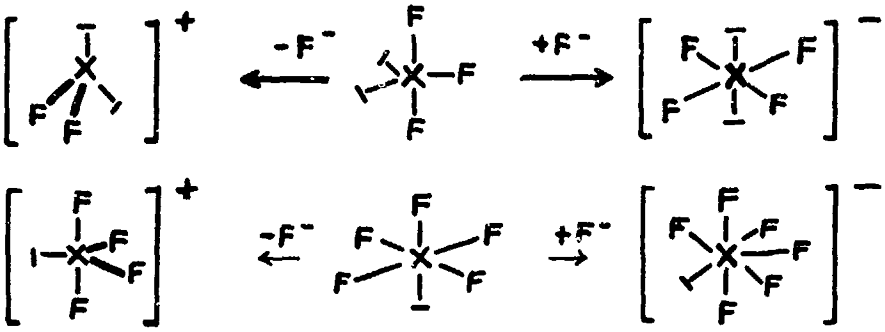
Cl_2F^+ Christe, Sawodny (1969)	ClF	ClF_2^- Christe, Guertin (1965)
ClF_2^+ Dale (1950)	ClF_3	ClF_4^- Asprey et al (1961)
ClF_4^+ Christe, Pilipovich (1967)	ClF_5	$[ClF_6^-]$
ClF_6^+ Roberto, Christe (1972)	$[ClF_7]$	$[ClF_8^-]$
(Br_2F^+)	BrF	BrF_2^- Surles et al (1973)
BrF_2^+ Woolf, Emeleus (1949)	BrF_3	BrF_4^- Sharpe, Emeleus (1948)
BrF_4^+ Schmeisser, Pammer (1957)	BrF_5	BrF_6^- Muetterties (1961)
BrF_6^+ Schrobilgen, Gillespie (1973)	$[BrF_7]$	$[BrF_8^-]$
(I_2F^+)	IF	IF_2^- Meinert, Klamm (1965)
(IF_2^+) Schmeisser, Ludovici (1965)	IF_3	IF_4^- Hargreaves, Peacock (1960)
IF_4^+ Woolf (1950)	IF_5	IF_6^- Emeleus, Sharpe (1949)
IF_6^+ Seel, Detmer (1958)	IF_7	IF_8^- Adams, Bartlett (1972)

Relative Stability of Halogen Fluoride Ions

For a given halogen fluoride, its tendency to form adducts with different Lewis acids or bases decreases with a decrease of their acid or base strength, respectively. Thus, the commonly used Lewis acids and bases can be arranged in the following order of decreasing strength: acids, $SbF_5 > AsF_5 > BF_3 > PF_5 > HF > SiF_4$ bases, $CsF > RbF > KF > FNO > FNO_2$. Considering the relative stability of the products formed, SbF_5 is the most attractive Lewis acid.

Unfortunately, it has several drawbacks. It tends to form polyanions of the type $Sb_2F_{11}^-$, $Sb_3F_{16}^-$, etc., and has a relatively high melting point of 7°. The latter often requires the use of a solvent such as HF to provide a common liquid phase for reactions involving low boiling halogen fluorides. Similarly, FNO and FNO_2 are suitable for quantitative low-temperature complexing but the products lack the stability of the alkali metal salts.

Based on the conclusions from the preceding paragraph, one would predict that the relative stabilities of adducts formed by a given Lewis acid or base with different halogen fluorides is a function of the acid strength of the corresponding halogen fluorides. Thus, a relatively acidic halogen fluoride should tend to form adducts with bases but to a much lesser degree with acids. Inspection of the relative stabilities of adducts of numerous halogen fluorides and oxyfluorides, however, showed (91) that this prediction is incorrect. The dominating factor governing the stability appears to be the structures of the parent molecules compared to those of the ions formed. Favored structures are either pseudo-tetrahedral or pseudo-octahedral. Thus, pseudo-trigonal bipyramidal molecules, such as the halogen trifluorides, show a pronounced tendency to form either pseudo-tetrahedral XF_2^+ cations or pseudo-octahedral XF_4^- anions. On the other hand, pseudo-octahedral pentafluorides show little tendency to form trigonal bipyramidal XF_4^+ or pentagonal bipyramidal XF_6^-.

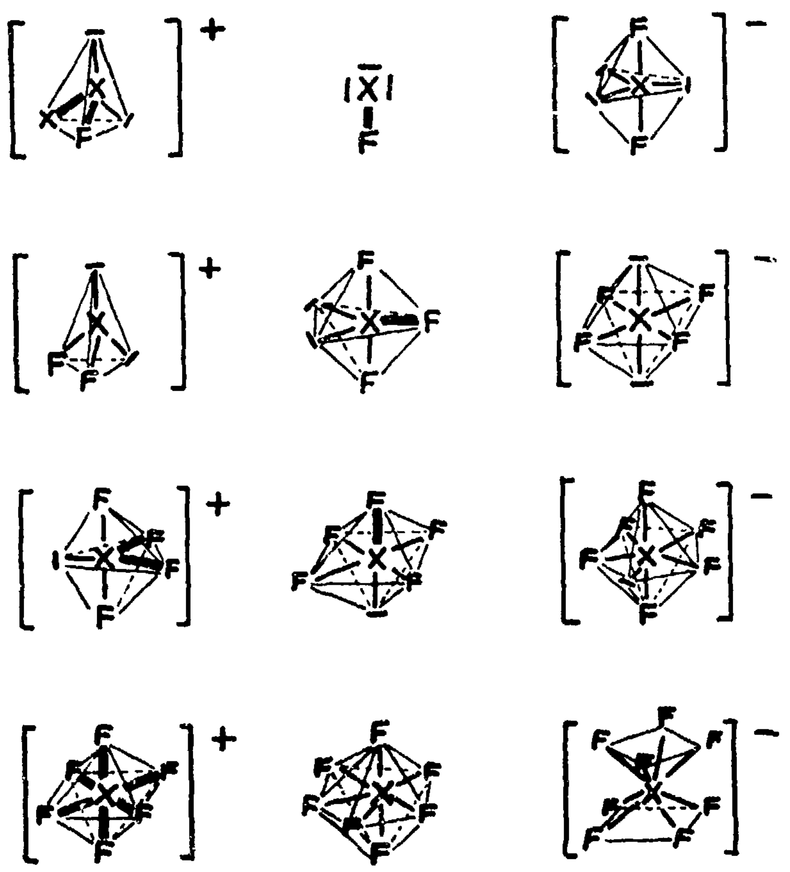


STRUCTURAL RELATIONS AND BONDING

Observed Structures

Figure 2 shows a scheme of the structures encountered for halogen fluoride molecules and ions. More recent results not covered by previous reviews (1 - 6) include X-ray diffraction data for $ClF_2^+SbF_6^-$ (92), $ClF_2^+AsF_6^-$ (93), $BrF_4^+Sb_2F_{11}^-$ (94), BrF_6^- (95), and $IF_4^+SbF_6^-$ (96, 97), microwave and electron diffraction data for BrF_5 and IF_5 (98 - 100), electron diffraction data for IF_7 (101), vibrational spectra for ClF_4^- (102), ClF_5 (103), ClF_3 (24, 104), ClF_6^+ (8), BrF_2^- (80), BrF_3 (24, 25, 104) BrF_4^- (105), BrF_4^+ (101, 106),

Figure 2. Structure of the halogen fluoride moledules and ions. Mainly covalent (two electron) bonds are drawn with heavier lines. For XF_6^- and XF_8^- sufficient data are not yet available. The two shorter bonds in XF_7 are primarily due to liquid repulsion effects.



BrF_6^- (95), IF_3 (26), IF_4^- (107), IF_4^+ (102), IF_6^- (69), IF_7 (27, 108, 109) and IF_5 (27, 110), Moessbauer data for IF_5 and IF_7 (111), nmr spectra for IF_6^+ (109), ClF_2^+ (112), and numerous chlorine fluoride ions (113), a photoionization study of ClF (114), force fields (115, 116) and mean amplitudes of vibration (117) of ClF_5, BrF_5, and IF_5, and mass spectra of ClF (118) and IF_7 and IF_5O (119).

As can be seen from Figure 2, the structures are simple and can be logically predicted if one keeps in mind that free valence electron pairs on the central atom are sterically active and behave as a ligand. For 4, 5, 6, 7, and 8 ligands always the sterically most favorable arrangements are observed, i.e., the tetrahedron, trigonal bipyramid, octahedron, puckered pentagonal bipyramid and the square antiprism, respectively. The only possible exception to the concept of localized free valence electron pairs may be BrF_6^- which contrary to IF_6^- (69) appears to possess a symmetry center (95). A probable explanation for this behavior assumes room for only six localized ligands and a fluxional free electron pair which in a pseudo Jahn Teller effect causes a dynamic distortion of the octahedron. This structural problem resembles that encountered with XeF_6. It appears that the XeF_6 structure is intermediate between those of the BrF_6^- and IF_6^- ions. Since single crystals of BrF_6^- and IF_6^- salts could be prepared, determination of their crystal structures would be very rewarding (69).

Primary Effects, The Three Basic Rules

More details about the structures shown in Figure 2, about the positions occupied by the free valence electron pairs, and about the relative bond strengths can be derived from consideration of the following set of three main rules. Secondary effects, such as the influence of formal positive (in cations) or formal negative (in anions) charges, and of the oxidation state of the central atom, will be discussed in a separate paragraph.

(I) For trigonal and pentagonal bipyramids, the hard sphere model results in different bond lengths for the equatorial and axial ligands.

(II) Free valence electron pairs on the central atom are sterically active, i.e., localized. They are more diffuse than the orbitals of an X-F bond, thus causing increased repulsion from the free pairs and slight distortion from the ideal geometries.

(III) The free valence electron pairs on the central atom seek high s-character; i.e., sp^n hybridization. If the number of ligands is larger than 4 and one or more of them are free valence electron pairs, then as many F ligands form linear semi-ionic 3 center -4 electron bonds as are required to allow the free electron pairs to form an sp^n hybrid with the remaining F lignads. These semi-ionic 3c - 4e bonds are considerably weaker and longer than the mainly "covalent" sp^n hybrid bonds.

Rules I and II are based on Nyholm and Gillespie's valence shell electron pair repulsion (VSEPR) theory (120). Rule III is an extension of I and II required to account for the great differences in bond strength encountered for these compounds (see below).

Examples for the Basic Rules

The following examples are given to illustrate rules I to III.

Rule I: In PF_5, the axial ligands have three neighbors at right angles, whereas the equatorial ones have only two. Therefore, the axial ligands are repelled more strongly resulting in an increased (by 0.04Å (121)) bond length. The same logic applies to IF_7. The crowding of 5 ligands in the base of the pentagonal bipyramid causes an average 7.5° ring puckering, a 4.5° axial bend displacement, and the axial bonds to be shorter by 0.07Å than the equatorial ones (101). However, these two configurations, i.e., the trigonal and pentagonal bipyramids, are quite distinct from the tetrahedron and octahedron, in which all positions are equivalent and, therefore, should, in the absence of other factors, result in identical bond lengths.

Rule II: The increased repulsion from free pairs is shown for ClF_3 (122) in Figure 3. The F^1ClF bond angle deviates by about 3° from that expected for an ideal trigonal bipyramid, and the axial ClF bonds are 0.10 Å longer than the equatorial one. Obviously, there are two consequences from increased repulsion. The first one is a decrease in the bond angle formed by the neighboring ligands and the central atom, and the second one is an increase in the bond lengths of the neighboring XF bonds. If the neighboring FXF bond angle is significantly larger than 90°, the change in bond angle will be more pronounced than the change in bond lengths.

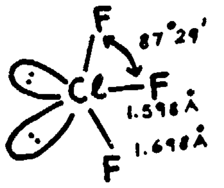


Figure 3. Distortion of ClF_3 from an ideal pseudo-trigonal bipyramidal configuration by increased repulsion from the free valence electron pairs.

Rule III: The principle of a semi-ionic 3c-4e bond (123 - 125) is demonstrated in Figure 4 for a simple species, such as ClF_2^- (74 - 76). Ideally, the two F-ligands form two semi-ionic 3c -4e [p-p] σ bonds with one p electron pair of the chlorine central atom, while the free Cl valence electron pairs form an sp^2 hybrid.

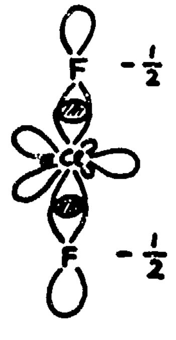


Figure 4. The schematic bonding in ClF_2^- as explained by a semi-ionic 3c-4e bond model

Instead of using this semi-empirical molecular orbital model, the bonding in ClF_2^- can also adequately be described in the valence-bond representation (126) as a resonance hybrid of the following canonical forms: (F-Cl) F^- and F^-(Cl-F). This results in the same average charge distribution as in the molecular orbital model, i.e., $^{-1/2}F-Cl-F^{-1/2}$. A third and the most simple bond model, proposed by Bilham and Linnett (127) for XeF_2 which is pseudo-isoelectronic with ClF_2^-, assumes single electron bonds for each X-F bond. It is relatively immaterial, which of these three descriptions is preferred since all of them result in the same charge distribution, a bond order of about 0.5, and an electron octet for the central atom as previously discussed by Bartlett (128) for the closely related noble gas fluorides.

Whereas the retention of a formal electron octet around the central atom is a very attractive concept, it must be realized that contrary to a previous statement (128) this concept is not applicable to all noble gas related fluorides. In ClF_6^+, for example, the ClF bond order is about one and hence, the bonding is best described by a sp^3d^2 hybridization, i.e., an electron dodecet (8). The same argument applies to TeF_6 having a bond order of about 1 (129) and, hence, the suggested (128) diagonal (based on the position of the central atoms in the periodic table) relation, XeF_4, IF_5, TeF_6 does not hold for the bonding in these molecules.

The Relationship Between Rules I + II and III

Qualitatively, rules I + II and rule III describe the same effect, i.e., the increase in bond lengths by the repulsive effect of a localized free valence electron pair. Rules I and II are derived from the hard sphere model (120) without making any assumptions about the nature of bonding or any possible changes in it when comparing different halogen fluoride bonds. The need for rule III arises from a more quantitative study of these effects, i.e., force constants computed from the observed vibrational spectra (see below for a more detailed discussion). These computations show such dramatic changes in the values of the stretching force constants (see Table III) that the postulate of two different types of bonding, i.e., rule III, becomes necessary. Consequently, rule III is not contradicting rules I and II, but explains the unexpectedly high repulsive effect of certain free valence electron pairs by their increased s-character, i.e., by a change in bonding and hybridization. Based on the assumption of a hard sphere model and ligand crowding, the simultaneous occurrence of semi-ionic 3c-4e bonds and orbitals with high s-character for the free valence electron pairs is very logical. An increase of the X-F bond distances will cause the free valence electron pairs to become shorter and wider and, hence, to assume more s-character (see Figure 5).

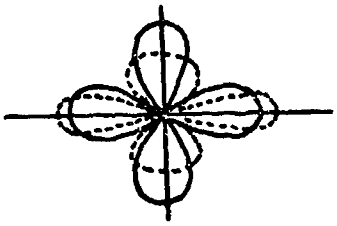
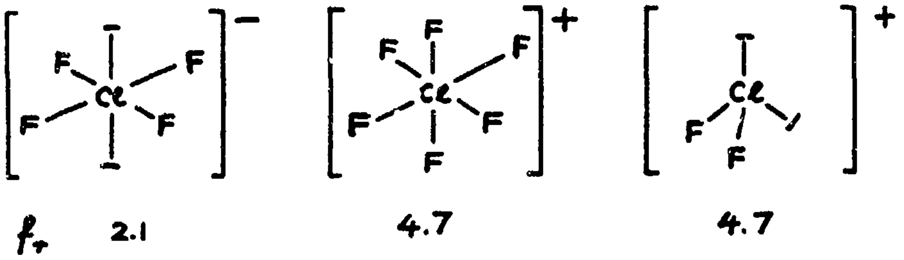


Figure 5. Influence of increasing (broken lines) bond lengths on the spatial distribution of free valence electron pairs assuming a hard sphere model.

Table III. Stretching Force Constants (mdyn/Å) of Binary Chlorine Fluorides

	Mainly Covalent	Semi-ionic
ClF_6^+	4.7	
ClF_4^+	4.7	3.3
ClF_2^+	4.7	
ClF	4.4	
ClF_3	4.2	2.7
ClF_5	3.5	2.7
ClF_2^-		2.3
ClF_4^-		2.1

Figure 6. Comparison of the structures and stretching force constants (mdyn/Å) of ClF_4^-, ClF_6^+, and ClF_2^+



In this respect it appears meaningless to argue whether the formation of semi-ionic bonds causes the free electron pairs to assume more s-character or whether the increased s-character of the free electron pairs causes the semi-ionic bonds. Obviously, both effects go hand in hand as a consequence of the hard sphere model.

The General Validity of Rules I to III

Whereas rules I and II, i.e., the VSEPR theory, have gained general acceptance, rule III as yet is still widely ignored inspite of continuous emphasis by the author since 1967 (130). The application of the three basic rules is by no means limited to halogen-fluorides, but holds essentially for all the non-metal fluorides. As previously shown (130), all the possible compounds can be arranged in isoelectronic groups and the simple knowledge of the total number of ligands and of the number of free valence electron pairs on the central atom is sufficient to predict the symmetry and relative bond strengths of all simple non-metal fluorides.

The tendency to form semi-ionic 3c-4e bonds is most pronounced for the lightest central atoms with high coordination numbers. With increasing size of the central atom, the ligand repulsion decreases and the polarizability of the central atom increases. This tends to make the bond lengths more similar.

Secondary Effect Influencing the Bond Strengths

Obviously, there are numerous other effects which will influence the relatively strength of a bond. However, we feel that their influence is not as strong as that of the three basic rules described above. Among these secondary effects, maybe the most important ones are the influence of a formal negative (in anions) or a formal positive (in cations) charge, the oxidation state of the central atom, and the tendency to form partial double bonds. Of these, the latter has been discussed above for ClF and, therefore, requires no further comment. An increasing oxidation state of the central atom increases its electronegativity and, hence, decreases the electronegativity difference between the central atom and the ligands. As previously pointed out by Goubeau (28) this will increase the covalency of the bond and thereby the bond strength. The influence of formal positive or negative charges can be readily understood. In anions, the formal negative charge will reside mainly on the highly electronegative F ligands. This will increase the polarity of the X-F bonds and, thereby, promote the formation of semi-ionic 3c-4e bonds.

The influence of such secondary effects also preempts the assignment of one numerical value to an ideal single bond in different compounds. Instead, relatively broad ranges (as apparent from Table III) must be assumed for covalent and semi-ionic bonds. Furthermore, it should be kept in mind, that one rarely deals exclusively with one kind of bonding but with contributions from both in varying amounts.

Force Constants

Unfortunately, exact bond lengths are known only for a limited number of halogen fluoride molecules and ions. However, the vibrational spectra and approximate force fields of these compounds are well known. Since the stretching force constants are closely related to the bond lengths and bond strengths, they are very useful for distinguishing semi-ionic 3c-4e (or one electron) bonds from mainly "covalent" (or two electron) bonds.

To demonstrate the wide variation of ClF stretching force constants, a summary of published values is given in Table III. It can be seen that the range of mainly covalent bonds varies from about 4.7 to about 3.5 mdyn/Å whereas semi-ionic bonds show a range from 2.1 to 3.3 mdyn/Å. Even if one takes into account the uncertainties in these force constants caused by the underdetermined nature of the force fields (102, 131, 132), the difference between the two columns in Table III is significant.

Figure 6 is an excellent demonstration that both requirements, i.e., a coordination number > 4 and the presence of at least one free valence electron pair, must be fulfilled for the formation of semi-ionic bonds. Comparison between the f_r values and structures of ClF_2^+ and ClF_4^- also demonstrates that the mere presence of two free valence electron pairs on chlorine without a change in in the nature of bonding cannot account for such a dramatic decrease in the value of the stretching force constant. Although repulsion in the pseudo-tetrahedral ClF_2^+ arrangement should be considerably less than in pseudo-octahedral ClF_4^-, some noticeable effect should be expected. Thus, it can be concluded that rule III, i.e. the assumption of semi-ionic bonding for certain nonmetal fluorides, is a definite requirement for a more quantitative prediction and understanding of the bonding in these compounds.

Based upon the above rules and their experimental confirmation by bond length measurements and force constant computations, the mainly covalent bonds have been marked in Figure 2 with heavier lines. For the seven and eight coordinated species XF_6^- and XF_8^-, respectively, no reliable structural data are as yet available.

Halogen Fluroide-Lewis Acid Adducts, Ionic or Covalent?

Since the very beginning of the discovery of the halogen fluoride-Lewis acid adducts around 1949 (32), there was much controversy as to whether these adducts are ionic or covalent coordination compounds. In the beginning, in the absence of sufficient and good experimental data, it was more or less a matter of conviction and dogmatic thinking and the arguments were correspondingly heated. By now, the predominantly ionic nature of these adducts has been well established and generally accepted, although the importance of fluorine bridging is frequently overemphasized by improper interpretation of observed vibrational spectra. As a consequence, predominantly ionic adducts have been described as strongly fluorine bridged adducts thus confusing the issue. The main argument, improperly used in favor of strong fluorine bridging, is the observation of symmetry lowering for highly symmetric anions in the solid state. Several recent studies (102, 113, 133 - 137) comparing the vibrational spectra of halogen fluoride adducts in the solid state with those of HF solutions, convincingly show that the HF solution spectra exhibit the bands characteristic for the ideal ions, and that the number and frequencies of the cation bands are practically unchanged. This indicates that the observed anion effects are mainly due to site symmetry lowering and/or slight distortion of the highly symmetric anions. Since the cations are usually of low symmetry and therefore already exhibit the maximum number of possible bands, their number remains unchanged. The fact that their frequencies are practically unchanged indicates that fluorine bridging in the solid state is relatively insignificant. The fact that in the known crystal structures the cations (which usually have relatively low coordination numbers) show next nearest fluorine neighbors, is obviously due to dipole - dipole interactions and crystal packing considerations. Consequently, if the next nearest fluorine neighbors are considerably further away from the halogen central atom than the regular fluorine ligands, it appears justified to classify these adducts as predominantly ionic. However, it should be kept in mind that with increasing size of the central atoms the polarizability of the bonds and hereby the influence of these "fluorine bridges" increases, (92, 93) and may for some iodine and xenon compounds indeed become significant.

NUCLEAR MAGNETIC RESONANCE STUDIES

The discovery that acidification of HF with strong Lewis acids slows down the exchange rate between HF and halogen fluoride cations, has allowed the investigation of numerous ions by ^{19}Fnmr spectroscopy (23, 109, 112, 113). The high symmetry of the XF_6^+ cations renders quadrupole relaxation by the halogen central atom ineffective and has thus permitted experimental measurement of halogen-fluorine spin-spin coupling constants (23, 109, 113). Whereas all of the observed nmr data are in excellent agreement with the ionic structures established by other methods, it remains difficult to rationalize the observed chemical shifts (113).

HALOGEN FLUORIDE RADICALS

As yet little work has been done in the area of halogen fluoride radicals. There have been recent reports on the existence of two chlorine fluoride radicals at low temperature. Mamantov and coworkers assigned one (138, 139) of the new species observed (140) in the photolysis of N_2 or Ar matrix isolated $ClF-F_2$ and Cl_2-F_2 mixtures to the $ClF_2\cdot$ radical. They interpreted the observed spectrum in terms of a bent structure. This bent structure, however, is somewhat unexpected and Pimentel suggested (141) that Mamantov's data might just as well be interpreted in terms of a linear ClF_2 radical.

The second known radical, $ClF_4\cdot$, was synthesized by low temperature photolysis of a Cl_2 - CF_3OF or SF_5OF mixture (142). It was identified by esr spectroscopy and a square planar structure was suggested.

The formation of the ClF^+ radical cation was reported (143) by Olah and Comisarov for both the ClF_3 - SbF_5 and ClF_5 - SbF_5 system. However, subsequent studies in other laboratories (144 - 146) refuted their claim.

The existence of a relatively stable ClF_5^+ radical cation has recently been predicted (8) based on observations made for the ClF_5 - PtF_6 system. However, more direct experimental proof will be required to confirm this prediction.

So far very little information on the existence and structure of halogen fluoride radicals is available. However, it appears plausible to predict that the unpaired free electron will reside on the halogen central atom and be sterically active. Consequently the free radicals should show structures analogous to those of the corresponding anions, as shown in Figure 7 for ClF_4^- and $ClF_4\cdot$.

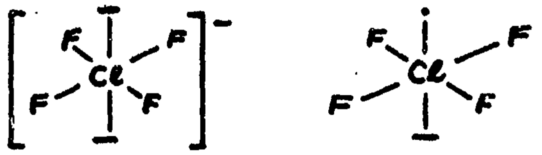


Figure 7. Structural relation between the $ClF_4\cdot$ radical and the ClF_4^- anion.

APPLICATION IN CHEMICAL LASERS

In addition to the continuing interest in halogen fluorides as powerful oxidizers in high energy rocket propellants and as chemical reagents for the preparation of uranium fluorides, a third area of general interest has recently developed. It was realized that energetic fluorides, such as halogen fluorides, are of great potential for chemical lasers. For example, the use of ClF and ClF_3 in chemical HF lasers have been studied in both the U.S. (147) and Russia (148).

CONCLUSIONS AND OUTLOOK

All of the expected binary halogen fluoride molecules and most of the ions derived from them have been synthesized and characterised. Work on the remaining compounds is being actively pursued by several research groups. The structures of most compounds have been established and can be rationalized in terms of a plausible bonding scheme.

Areas for future development include the syntheses of halogen oxyfluorides, of substituted halogen fluorides, and of halogen fluoride radicals and radical ions. Furthermore, the reaction chemistry of most of the halogen fluorides has not yet been studied to any large extent. In addition to their potential use as rocket propellants and in the processing of nuclear fuels, halogen fluorides are expected to become of importance in the field of chemical HF lasers.

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Cesium Bis(perchlorato)bromate(I), $Cs^+[Br(OClO_3)_2]^-$

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The synthesis and some properties of the novel bis(perchlorato)bromate(I) anion are reported. Vibrational spectra were recorded and are consistent with a model containing two covalent, monodentate perchlorato groups and an approximately linear O–Br–O arrangement.

Introduction

Except for fluorine perchlorate,[1] no halogen perchlorates had been reported until 1970. With the recent discovery of chlorine perchlorate ($ClOClO_3$) by Schack[2] a versatile synthetic reagent became available for the preparation of other perchlorates. This led to the syntheses of the novel halogen perchlorates $BrOClO_3$,[3] $I(OClO_3)_3$, and $Cs^+[I(OClO_3)_4]^-$.[4] The covalent monodentate nature of the perchlorato ligand in these compounds was established by vibrational spectroscopy.[2-5] In this paper we wish to report on the synthesis and characterization of the first known example of a perchloratobromate ion.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 IF4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Anhydrous CsBr (ROC/RIC, 99.9% minimum) was used without further purification. Chlorine perchlorate was prepared and purified by the method of Schack and Pilipovich.[2] The purity of volatile materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Dry powders were recorded as pressed disks between AgCl windows. The pressing operation was carried out using a Wilks minipellet press.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[6] for the elimination of plasma lines. Glass melting point capillaries were used as sample containers in the transverse-viewing–transverse-excitation technique.

Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries (~0.5-mm o.d.). For elemental analyses, the solid samples were hydrolyzed in aqueous NaOH. Perchlorate was determined with a specific ion electrode (Orion Model 92-17) and Cs and Br by X-ray fluorescence employing a GE XRD-6VS X-ray fluorescence spectrometer.

Preparation of $CsBr(ClO_4)_2$. A 30-ml prepassivated 316 stainless steel cylinder was loaded with powdered CsBr (1.03 mmol) followed by $ClOClO_3$ (6.76 mmol) at −196°. The reactor was warmed to −45° and stored at that temperature for 2 years. On recooling to −196° a few cubic centimeters of noncondensable gas was noted. Volatile products were pumped from the reactor for several hours while and after it had warmed to ambient temperature. Separation of these materials were effected by fractional condensation. They consisted of Cl_2 (1.41 mmol), a small amount of Cl_2O_6,[7] and unreacted $ClOClO_3$ (4.01 mmol). The solid product was faint yellow and weighed 416 mg, corresponding to a 96% conversion of the CsBr to $CsBr(ClO_4)_2$. *Anal.* Calcd for $CsBr(ClO_4)_2$: Cs, 32.3; Br, 19.4; ClO_4^-, 48.3. Found: Cs, 32.6; Br, 19.0; ClO_4^-, 47.2. X-Ray powder diffraction patterns of the solid showed no lines due to CsBr, $CsBrO_3$, or $CsClO_4$. The product was found to be completely stable at ambient temperature as shown by visual and spectroscopic examination after several months.

A reaction of CsBr (1.42 mmol) and $ClOClO_3$ (4.46 mmol), carried out under similar conditions, was examined after 6 days at −45°. The volatile products consisted of Cl_2 (1.43 mmol), $BrOClO_3$ (1.38 mmol),[3] and unreacted $ClOClO_3$ (1.52 mmol). The white solid residue weighed 332 mg, in excellent agreement with the weight (331 mg) calculated for a complete conversion to $CsClO_4$. The infrared spectrum of the solid showed only bands[8] attributable to the ClO_4^- ion. *Anal.* Calcd for $CsClO_4$: ClO_4^-, 42.8. Found: ClO_4^-, 42.4.

When another of these reactions was examined after 2 months at −45°, the solid product consisted of 32 mol % $CsBr(ClO_4)_2$ and 68 mol % $CsClO_4$ as shown by the observed material balance, vibrational spectroscopy, and analysis.

Results and Discussion

Caution! Chlorine perchlorate is shock sensitive.[2] Proper safety precautions must be taken when working with this compound. Although during our experiments $CsBr(ClO_4)_2$ appeared to be stable, it should be kept in mind that we have previously observed explosive decompositions for the closely related iodine perchlorate compounds.[4]

Synthesis. The experimental data show that CsBr interacts with an excess of $ClOClO_3$ at −45° relatively fast according to

$$CsBr + 2ClOClO_3 \rightarrow CsClO_4 + BrOClO_3 + Cl_2$$

This reaction is followed by the much slower second step

$$CsClO_4 + BrOClO_3 \rightarrow CsBr(ClO_4)_2$$

Acceleration of the second step by raising of the reaction temperature was not feasible owing to the thermal instability of the halogen monoperchlorates. The use of a proper solvent is likely to increase the reaction rate. However, owing to the pronounced incompatibility of halogen perchlorates with most solvents and owing to the slowness of the reaction, studies in this direction were beyond the scope of the present investigation.

The above data demonstrate that the reactivity of CsBr toward $ClOClO_3$ is intermediate between those previously observed for CsCl and CsI.[2,4] Whereas CsCl or $CsClO_4$ do not form any stable adduct with $ClOClO_3$, CsI is readily converted to $CsI(ClO_4)_4$. The fact that iodide is oxidized by $ClOClO_3$ to the +III oxidation state whereas bromide is oxidized only to the +I state is not surprising since iodide is a stronger re-

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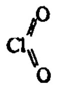
ducing agent than bromide. Our previous attempts[4] to synthesize the iodine(I) salt $CsI(ClO_4)_2$ from $CsIBr_2$ and $ClOClO_3$ resulted only in a mixture of unreacted $CsIBr_2$ and $CsI(ClO_4)_4$. This indicated instability of the iodine(I) salt may be caused by its pronounced tendency to disproportionate and to achieve a higher coordination number.

Properties. The compound $CsBr(ClO_4)_2$ is a faint yellow solid. It was stored for more than 6 months at ambient temperature in dry nitrogen without noticeable decomposition. It is hygroscopic and readily hydrolyzes in water. The solid is crystalline and its X-ray powder pattern is listed in Table I. Surprisingly, the pattern shows little resemblance to that reported[9] for the similar compound $CsBr(SO_3F)_2$.

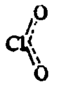
Vibrational Spectrum. Figure 1 shows the infrared and the Raman spectrum of solid $CsBr(ClO_4)_2$. The observed frequencies and their assignments are listed in Table II.

Before discussing these assignments in more detail, the nature of the perchlorate moiety in $CsBr(ClO_4)_2$ must be established. The perchlorate could be present as a ClO_4^- anion or as a covalent perchlorato ligand. In the latter case, the perchlorato group could be either mono- or bidentate. Since bromine(I) has three free valence electron pairs, two bidentate perchlorato ligands would result in a coordination number of 7. This coordination number is not unreasonable in view of the existence[10] of the BrF_6^- anion which has one free valence electron pair on the central atom. The vibrational spectra of the ClO_4^- anion[8] and of covalent monodentate perchlorates, such as $ClOClO_3$ and $BrOClO_3$,[6] are well known and understood. Recently, we have also established the vibrational spectrum of $Ti(ClO_4)_4$, a compound containing four bidentate perchlorato ligands.[11] Since relative bandwidths of the individual bands are very important for distinguishing antisymmetric from symmetric motions, we have added to Figure 1 for comparison the vibrational spectra of the typical covalent monodentate $ClOClO_3$, of the bidentate $Ti(ClO_4)_4$, and of the ClO_4^- anion.

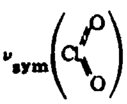
Inspection of Figure 1 immediately rules out for $CsBr(ClO_4)_2$ a structure containing ClO_4^- anions. The spectrum of a typical bidentate perchlorate should show two pairs of strong infrared bands at about 1310 and 1170 and at 880 and 660 cm^{-1}, respectively. These pairs are due to the antisymmetric and symmetric stretching vibrations of the



and the



groups, respectively. The absence of a strong infrared band in the region 800-1000 cm^{-1} and of a strong sharp Raman band above 1100 cm^{-1} for



clearly rules out for $CsBr(ClO_4)_2$ a bidentate perchlorate structure.

A superficial comparison between the spectra of $CsBr(ClO_4)_2$ and $ClOClO_3$ also reveals pronounced differences. However, these differences can be easily reconciled by taking into account that $Br(ClO_4)_2^-$ contains two perchlorato groups. Their motions should strongly couple owing to the approximately linear configuration of the O-Br-O group expected by comparison with pseudoisoelectronic ClF_2^-,[12] KrF_2, and XeF_2.[13] This coupling results in a splitting of each mode into an in-phase and an out-of-phase motion of the two perchlorato groups. The observed bandwidths make it easy to assign the bands to antisymmetric (broad) and symmetric (narrow) vibrations. The agreement between the vibrational spectra of $ClOClO_3$ and $Br(OClO_3)_2^-$ is excellent if one takes the average frequency of each band pair and keeps in mind the expected frequency decrease when going from neutral $XOClO_3$ to the $Br(OClO_3)_2^-$ anion. This frequency trend in the order cation > neutral molecule > anion has been established for numerous halogen compounds[14] and can be explained by the increasing polarity of the bonds.

After establishing the covalent monodentate nature of the perchlorato ligands in $Br(OClO_3)_2^-$, assignments of the observed bands to individual modes can be discussed. Since the highly electronegative perchlorato ligand might be considered as a pseudohalide, the structure of $Br(OClO_3)_2^-$ should be analogous to those found for the pseudoisoelectronic fluorides ClF_2^-,[12] KrF_2, or XeF_2.[13] The central atoms of these species possess three free valence electron pairs and, hence, have a coordination number of 5. This results in a trigonal bipyramid in which the three free valence electron pairs occupy the equatorial positions and the two electronegative ligands the two axial positions. If this analogy is

Table I. X-Ray Powder Data for $CsBr(ClO_4)_2$

d, A	Intens	d, A	Intens	d, A	Intens
5.13	w	2.445	m	1.536	w
3.47	m	2.188	s	1.512	vw
3.40	vs	2.018	ms	1.490	w
2.77	m	1.973	w	1.467	vw
2.579	vw	1.834	w	1.411	m
2.518	m	1.709	ms	1.397	mw

Table II. Infrared and Raman Spectrum of Solid $CsBr(ClO_4)_2$

Obsd freq, cm^{-1}, and intens[a]		Approx description of mode in point group C_2
Ir	Raman	
2930 vw		1115 + 1078 + 720 = 2913
2360 w		1289 + 1078 = 2367
2040 w		1105 + 947 = 2052
1663 vw		947 + 720 = 1667
1300 vs, br	1289 (0.6)	$\nu_{as}(ClO_3)$ in phase (2 A)
1115 vs, br	1105 (0.3) br	$\nu_{as}(ClO_3)$ out of phase (2 B)
1076 vw	1078 (10)	$\nu_{sym}(ClO_3)$ in phase (A)
947 vw	947 (6.2)	$\nu_{sym}(ClO_3)$ out of phase (B)
	933 (1.4)	
	904 (0.1)	
720 vs, br	719 (1.1)	$\nu_{as}(BrOCl)$ out of phase (B)
633 m	633 (1.4)	$\nu_{sym}(BrOCl)$ out of phase (B)
622 mw	625 (0.5)	
581 ms	584 (1.8)	$\delta_{sciss}(ClO_2)$ (A, B)
572 ms	578 (1.8)	$\delta_{as}(ClO_3)$ (A, B)
558 mw	558 (2.1)	$\delta_{umbrella}(ClO_3)$ (A, B)
	466 (1.2)	$\nu_{as}(BrOCl)$ in phase (A)
	450 (1.5)	$\nu_{sym}(BrOCl)$ in phase (A)
	407 (2.7)	$\delta_{rock}(ClO_3)$ (A)
	396 (2.5)	$\delta_{rock}(ClO_3)$ (B)

[a] Uncorrected Raman intensities.

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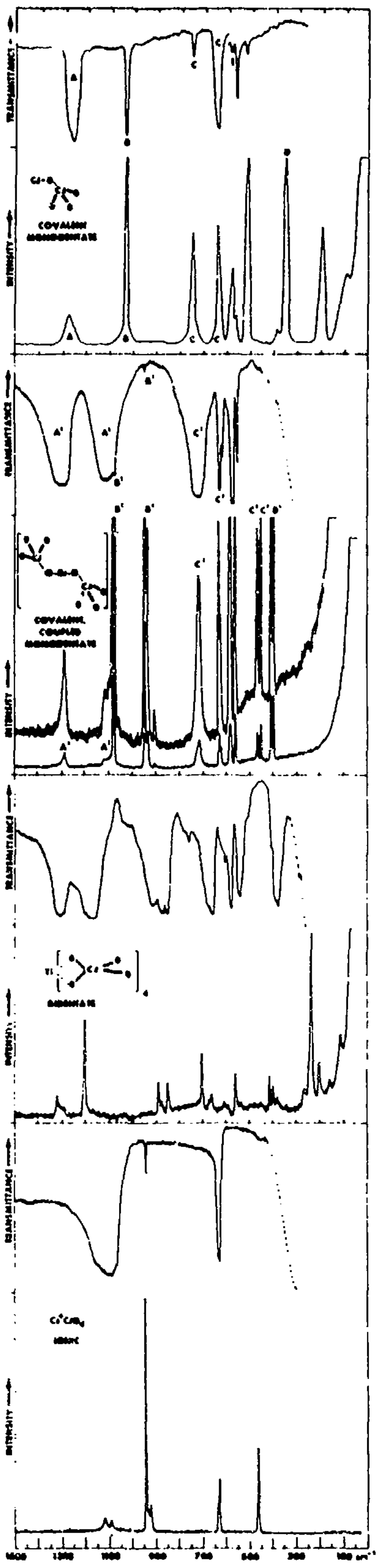
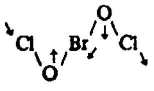
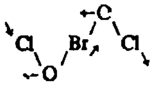
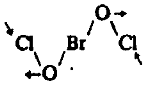
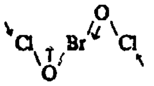


Figure 1. Vibrational spectra of solid $CsBr(ClO_4)_2$, $Ti(ClO_4)_4$, and $CsClO_4$ (infrared spectra recorded as AgCl disks). Raman spectrum of liquid $ClOClO_3$ and infrared spectrum of solid $ClOClO_3$ as a film on a CsI window cooled to 4°K. Spectral slit width used for the recording of the Raman spectra of the solids was 4 cm^{-1}. The bands of $CsBr(ClO_4)_2$ marked by A', B', C', and D' represent the in-phase and out-of-phase motion components of the A, B, C, and D bands, respectively, of $ClOClO_3$.

Table III. Summary of 27 Fundamentals Expected for $Br(OClO_3)_2^-$ in Point Group C_2

ClOBrOCl Skeletal Modes

	ν_{sym}(BrOCl) out of phase (B)
	ν_{asym}(BrOCl) out of phase (B)
	ν_{asym}(BrOCl) in phase (A)
	ν_{sym}(BrOCl) in phase (A)

δ(BrOCl) in plane $\begin{cases}\text{in phase (A)}\\ \text{out of phase (B)}\end{cases}$

δ(BrOCl) out of plane = τ(BrO) $\begin{cases}\text{in phase (A)}\\ \text{out of phase (B)}\end{cases}$

δ(OBrO) in plane (B)

ClO_3 Modes

$\nu_{asym}(ClO_3)\begin{cases}\text{in phase (2 A)}\\ \text{out of phase (2 B)}\end{cases}$

$\nu_{sym}(ClO_3)\begin{cases}\text{in phase (A)}\\ \text{out of phase (B)}\end{cases}$

$\delta_{asym}(ClO_3)\begin{cases}\text{in phase (A)}\\ \text{out of phase (B)}\end{cases}$

$\delta_{sciss}(ClO_3)\begin{cases}\text{in phase (A)}\\ \text{out of phase (B)}\end{cases}$

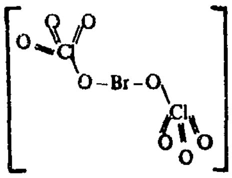
$\tau(ClO_3)\begin{cases}\text{in phase (A)}\\ \text{out of phase (B)}\end{cases}$

$\delta_{umbrella}(ClO_3)\begin{cases}\text{in phase (A)}\\ \text{out of phase (B)}\end{cases}$

$\delta_{rock}(ClO_3)\begin{cases}\text{in phase (A)}\\ \text{out of phase (B)}\end{cases}$

$\tau(OCl)\begin{cases}\text{in phase (A)}\\ \text{out of phase (B)}\end{cases}$

extended to $Br(OClO_3)_2^-$ and if a bond angle of about 100° is assumed for BrOCl with the two ClO_3 groups being in a trans position to minimize their mutual repulsion, the following structure of symmetry C_2 is obtained



The twofold symmetry axis is perpendicular to the ClOBrOCl plane and passes through the Br central atom.

For an 11-atom species of symmetry C_2 one would expect a total of 27 fundamentals. Of these, 13 belong to species A representing the in-phase motions of the two ligands and 14 belong to species B representing the out-of-phase motions and the OBrO in-plane deformation. These 27 modes may be broken down further into nine ClOBrOCl skeletal modes by treating the ClO_3 group as one point of mass. A summary of the 27 fundamentals is given in Table III.

Assignments to the modes involving internal motions of the ClO_3 group can be readily made by comparison with those previously given[5] for $ClOClO_3$ and $BrOClO_3$. As expected, the two antisymmetric ClO_3 stretching modes are nearly degenerate (for $ClOClO_3$ and $BrOClO_3$ splitting into the components was observed only for the matrix-isolated species)[5] and, therefore, result for $Br(OClO_3)_2^-$ in a single broad band. However, the frequency difference of ~10 cm^{-1} observed between the band centers of the infrared and the Raman bands suggests that these modes are not completely degenerate and are of different relative intensities in the infrared and Raman spectra. The assignments are given in Table II and are supported by the observed bandwidths and intensities. For example, the symmetric ClO_3 stretching modes should give rise to very intense, sharp Raman bands with weak infrared counterparts, with the strongest Raman band representing the in-phase motion. The slight splitting observed for the 947-cm^{-1} Raman band does not show the right (3:1) intensity ratio for the ^{35}Cl-^{37}Cl isotopes and, hence, is ascribed to crystal effects.

After assigning the ClO$_3$ modes, four bands in the region 450-750 cm^{-1} remain unassigned. Based on their frequencies, these bands must represent the four skeletal stretching modes. Of the four bands the two lower frequency ones do not show a counterpart in the infrared spectrum and, therefore, must be assigned to the two A modes which do not involve a change of the dipole moment (see Table III). Based on its higher Raman intensity and lower frequency the 450-cm^{-1} band is assigned to ν_{sym}(BrOCl) in phase which involves more of a Br-O stretch than a Cl-O stretch. For the two higher frequencies we prefer to assign the 720-cm^{-1} band to the antisymmetric BrOCl motion based on its strong infrared intensity and large bandwidth. The two components of the 633-cm^{-1} band show the correct intensity ratio of 3:1 for ^{35}Cl and ^{37}Cl isotopes and, hence, this splitting is ascribed to isotope effects.

In summary, the observed spectrum is in excellent agreement with our predictions for a covalent, monodentate perchlorato structure containing a strongly coupled and, therefore, approximately linear OBrO configuration.[15] Except for the torsional modes and the BrO$_2$ and BrOCl in plane deformations (which are expected to be of relatively low frequency and intensity) all of the predicted fundamentals were observed. For the stretching vibrations, the strong coupling causes pronounced frequency splittings owing to in-phase and out-of-phase motions of the two ligands. For the ClO$_3$ deformation modes, such a splitting was not observed except for an 11-cm^{-1} separation of the two rocking modes.

No attempts were made to compute a force field for Br(OClO$_3$)$_2^-$ owing to the size (11 atoms) of the ion, the inavailability of the skeletal deformation frequencies, and an expected[5] strong mixing of the symmetry coordinates of the skeletal stretching modes.

Acknowledgment. We are indebted to Dr. L. Grant for helpful discussions and to the Office of Naval Research, Power Branch, for financial support.

Registry No. CsBr, 7787-69-1; ClOClO$_3$, 27218-16-2; CsBr(ClO$_4$)$_2$, 51108-46-4.

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(15) Quantitative computations have been carried out for M-O-M linkages containing a light central atom: I. R. Beattie and M. J. Gall, *J. Chem. Soc. A*, 3569 (1971). Qualitatively, their arguments should also be valid for our case with Br as a central atom, where the observed frequency separation of the average of the BrOCl stretches of species B from that of the corresponding A modes is 216 cm^{-1}.

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REACTIONS OF THE $(CF_3)_2NO$ RADICAL WITH STRONG OXIDIZERS

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(Received November 24, 1973)

Summary

The reactions of $(CF_3)_2NO$ with PtF_6, MoF_6, ReF_6, $O_2^+SbF_6^-$ and $O_2^+AsF_6^-$ have been studied. The reaction of $(CF_3)_2NO$ with $O_2^+SbF_6^-$ presents a new method of producing CF_3 radicals chemically at low temperature. This was demonstrated by a new and high yield synthesis of $(CF_3)_2NOCF_3$. In addition, the novel compound $[(CF_3)_2NO]_2CF_2$ has been isolated as a by-product from this reaction and was characterized.

Introduction

The bis(trifluoromethyl) nitroxide radical was discovered [1,2] in 1964. Since then, the physical and chemical properties of this unusually stable radical have been studied extensively and were summarized in two recent reviews [3,4]. In its reaction chemistry, $(CF_3)_2NO$ behaves as a pseudohalogen with an oxidizing power similar to or higher than that of Cl_2 [3]. Due to this high oxidizing power, the previously reported studies [3,4] appear to have been limited to combinations with other radicals, additions across double bonds, and reactions with reducing agents. In view of the well-known stability of the $F_2N{=}O^+$ cation [5,6] and of hexafluoroacetone which are isoelectronic with COF_2 and the hypothetical $(CF_3)_2N{=}O^+$ cation, respectively, it seemed interesting to study the behavior of $(CF_3)_2NO$ towards strong oxidizers. If the oxidation could be limited to a simple one-electron transfer from $(CF_3)_2NO$ to an oxidizing species A, the following reaction series would allow not only the synthesis of the $(CF_3)_2N{=}O^+$ cation, but also that of the novel bis(trifluoromethyl)-substituted NF_3O molecule:

$$(CF_3)_2NO + A \rightarrow (CF_3)_2NO^+A^-$$

$$(CF_3)_2NO^+A^- + FNO_2 \rightarrow NO_2^+A^- + (CF_3)_2N(O)F$$

Although we could not limit the oxidation of $(CF_3)_2NO$ to a one-electron transfer without breakage of chemical bonds, several interesting results were obtained which we report in this paper.

Experimental

Materials

Rhenium hexafluoride and MoF_6 (Ozark Mahoning) and CF_3NO (PCR) were purchased. Platinum hexafluoride was prepared by burning Pt wire in an F_2 atmosphere at −196 °C [7]. The O_2^+ salts of AsF_6^- and SbF_6^- were synthesized by the methods of Beal [8] and Shamir [9], respectively. Bis(trifluoromethyl) nitroxide was prepared [10] from Ag_2O_2 and $(CF_3)_2NOH$, with the latter being synthesized as previously described [1]. Prior to use, all volatile starting materials were purified by fractional condensation and their purity was verified by spectroscopic techniques.

Apparatus

The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless-steel vacuum line equipped with Teflon FEP traps and 316 stainless-steel bellow-seal valves (Hoke Inc., 425 IF4Y). Pressures were measured with a Heise–Bourdon tube type gauge (0 - 1500 mm ± 0.1%). Because of the rapid hydrolytic interaction with moisture, all materials were handled outside the vacuum system in the dry nitrogen atmosphere in a glove box.

The infrared spectra were recorded on Perkin–Elmer Model 337 and 457 spectrophotometers in the range 4000 - 250 cm^{-1}. The spectra of gases were obtained using 304 stainless-steel cells of 5 cm path length fitted with AgCl or AgBr windows. The spectra of solids were obtained by pressing two small single-crystal platelets of either AgCl or AgBr into a disk in a Wilks minipellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å exciting line and a Claassen filter [11] for the elimination of plasma lines. Glass melting point capillaries were used as sample containers in the transverse-viewing–transverse-excitation technique.

Mass spectra were recorded on a Quad 300 (Electronic Associates Inc.) quadrupole mass spectrometer using a passivated all-stainless-steel inlet system.

The ^{19}F NMR spectra were recorded at 56.4 MHz on a Varian DA60 NMR spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique.

The $(CF_3)_2NO$–MoF_6 system

Molybdenum hexafluoride (0.90 mmol) and $(CF_3)_2NO$ (1.44 mmol) were combined at −196 °C in a passivated 25 cm^3 sapphire stainless-steel reaction tube (Varian Model CS-4250-3). After warming the mixture to 29 °C for 1 h, only unreacted starting materials were recovered.

The $(CF_3)_2NO$–ReF_6 system

Rhenium hexafluoride (2.01 mmol) and $(CF_3)_2NO$ (1.88 mmol) when kept at 29 °C for 1 h in a sapphire reactor produced a small amount of a non-volatile white solid. To increase the yield of this solid, the starting materials were recombined in the reactor and kept at 29 °C for 100 h. The volatile products were removed, separated by fractional condensation, measured by *PVT* and identified by spectroscopic techniques. They consisted of $(CF_3)_2NOCF_3$ (0.29 mmol), $(CF_3)_2NO$ (1.61 mmol) and ReF_6 (1.92 mmol). The white solid residue (8 mg) was mainly $NO^+ReF_6^-$, but its infrared spectrum also indicated the presence of a new rhenium oxyfluoride anion having strong absorptions at 1059, 1022 and 971 cm^{-1}.

The $(CF_3)_2NO$–PtF_6 system

Platinum hexafluoride (1.78 mmol) and $(CF_3)_2NO$ (3.56 mmol) were combined at −196 °C in a sapphire reactor. The mixture was slowly warmed up until the $(CF_3)_2NO$ started to melt and react. The reaction with PtF_6 was very violent (caution!) and the reaction was immediately quenched by cooling to −196 °C. This procedure was repeated several times until the reaction was essentially complete when the reactor was kept at 25 °C for 1 day. The volatile products consisted of COF_2 and CF_4 (4.04 mmol), $(CF_3)_2NOCF_3$ (0.54 mmol) and $(CF_3)_2NO$ (0.73 mmol). The dark-grey solid residue (570 mg) was identified by vibrational spectroscopy as $NO^+PtF_6^-$.

The $(CF_3)_2NO$–$O_2^+AsF_6^-$ system

In a Teflon–FEP ampoule, $(CF_3)_2NO$ (0.86 mmol) and $O_2^+AsF_6^-$ (0.95 mmol) were combined at −196 °C. The mixture was slowly warmed up to 25 °C and a smooth reaction occurred with gas evolution. The volatile products consisted of O_2 (0.90 mmol), $(CF_3)_2NO$ (0.32 mmol) and CF_4 and COF_2 (0.98 mmol). The white solid residue consisted of $NO^+AsF_6^-$ (0.48 mmol) indicating that some $O_2^+AsF_6^-$ had decomposed irreversibly during the reaction, with the free AsF_5 being absorbed by the metal fluoride surface of the passivated metal line.

The $(CF_3)_2NO$–$O_2^+SbF_6^-$ system

In a 30 cm^3 stainless-steel cylinder, $(CF_3)_2NO$ (1.92 mmol) and $O_2^+SbF_6^- \cdot 0.73SbF_5$ (0.70 mmol) were combined at −196 °C. The mixture was allowed to warm to −21 °C and kept at this temperature for 1 day. The volatile products consisted of O_2 (0.70 mmol), CF_4 and COF_2 (0.74 mmol), $(CF_3)_2NOCF_3$ (0.73 mmol) and $[(CF_3)_2NO]_2CF_2$ (0.16 mmol). The white solid residue consisted of $NO^+SbF_6^- \cdot 0.73SbF_5$ (0.70 mmol).

The CF_3NO–$O_2^+SbF_6^-$ system

When mixtures of CF_3NO and $O_2^+SbF_6^- \cdot 0.73SbF_5$ with either component in excess were kept for several days at ambient temperature, little interaction occurred. Heating to 80 °C was required for $NO^+SbF_6^-$ formation and O_2 evo-

TABLE 1

Mass spectrum* of $[(CF_3)_2NO]_2CF_2$

367, $(CF_3)_2NOCF_2ONC_2F_5^{+}$, (6); 279, $C_2F_5NOCF_2ONCF_2^{+}$, (7);
234, $(CF_3)_2NOCF_2O^{+}$, (0+); 218, $(CF_3)_2NOCF_2^{+}$, (38); 191, $C_2F_4NOCFON^{+}$, (0.7);
168, $(CF_3)_2NO^{+}$, (2.8); 149, $C_2F_5NO^{+}$, (1.4); 133, $C_2F_5N^{+}$, (2.8);
130, $C_2F_4NO^{+}$, (90); 127, CF_3NOCO^{+}, (0.7); 114, $C_2F_4N^{+}$, (29); 111, $C_2F_3NO^{+}$, (0.7);
108, CF_2NOCO^{+}, (0+); 99, CF_3NO^{+}, (1.2); 95, $C_2F_3N^{+}$, (0.2); 92, $C_2F_2NO^{+}$, (1);
83, CF_3N^{+}, (0.3); 80, CF_2NO^{+}, (0.2); 76, $C_2F_2N^{+}$, (0+); 70, $CNOCO^{+}$, (20);
69, CF_3^{+}, (1000); 66, CF_2O^{+}, (32); 64, CF_2N^{+}, (60); 61, $CFNO^{+}$, (3);
57, C_2FN^{+}, (0.2); 50, CF_2^{+}, (104); 47, CFO^{+}, (195); 45, CFN^{+}, (14);
44, CO_2^{+}, (54); 31, CF^{+}, (106); 30, NO^{+}, (340); 26, CN^{+}, (3); 19, F^{+}, (46);
16, O^{+}, (120); 14, N^{+}, (135); 12, C^{+}, (11).

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* Measured at 70 ev. Results quoted as *m/e*, ion, relative intensity.

lution. No evidence was obtained for the formation of any species containing more than one carbon atom. The main products were COF_2, CF_4 and CF_3NO_2.

Properties of $[(CF_3)_2NO]_2CF_2$

The compound is a stable, colorless liquid having vapor pressures of 8 and 16 mmHg at −31.2 °C and 0 °C, respectively. During fractional condensation, it slowly passed a −64 °C trap and was retained at −78 °C. Its mass spectrum is given in Table 1 and its infrared and Raman spectrum in Fig. 1 and Table 2. The ^{19}F NMR spectrum showed a 1:2:1 triplet at 67.96 ppm (CF_3) and a multiplet (~13) at 69.77 ppm (CF_2) above the internal standard $CFCl_3$ with $J(FF) = 6.0$ Hz and an area ratio slightly larger than 6:1. Three additional weak signals were observed at 66.2, 66.9 and 73.6 ppm which were broad singlets. The relative peak area of the low-field signal increased for the neat compound and increased further with increasing temperature. In addition, the CF_3 signal started to show a low-field component with increasing intensity of the low-field CF_2 signals at ~66 ppm. Analysis: Found: C, 15.7; F, 68.1%. $C_5F_{14}N_2O_2$ requires C, 15.54; F, 68.89%.

Results and discussion

Of the strong oxidizers studied, PtF_6 and O_2^+ salts are capable of oxidizing the $(CF_3)_2NO$ radical under the given conditions whereas MoF_6 is not. Rhenium hexafluoride with an electron affinity > 90 kcal mol^{-1} [12] appears capable of slowly oxidizing $(CF_3)_2NO$ at room temperature. These results are in excellent agreement with the apparent [3] high electronegativity of the $(CF_3)_2NO$ radical. This requirement of a strong oxidizing reagent may also explain the lack of $(CF_3)_2NO^+$ formation. Instead of a simple one-electron transfer reaction, an oxidative fission of the N—C bond was observed resulting in the formation of CF_4, NO^+ salts and significant amounts of CF_3 radicals. In the presence of unreacted $(CF_3)_2NO$ radicals, the CF_3 radical undergoes the following reaction

$$CF_3\cdot + (CF_3)_2NO\cdot \rightarrow (CF_3)_2NOCF_3$$

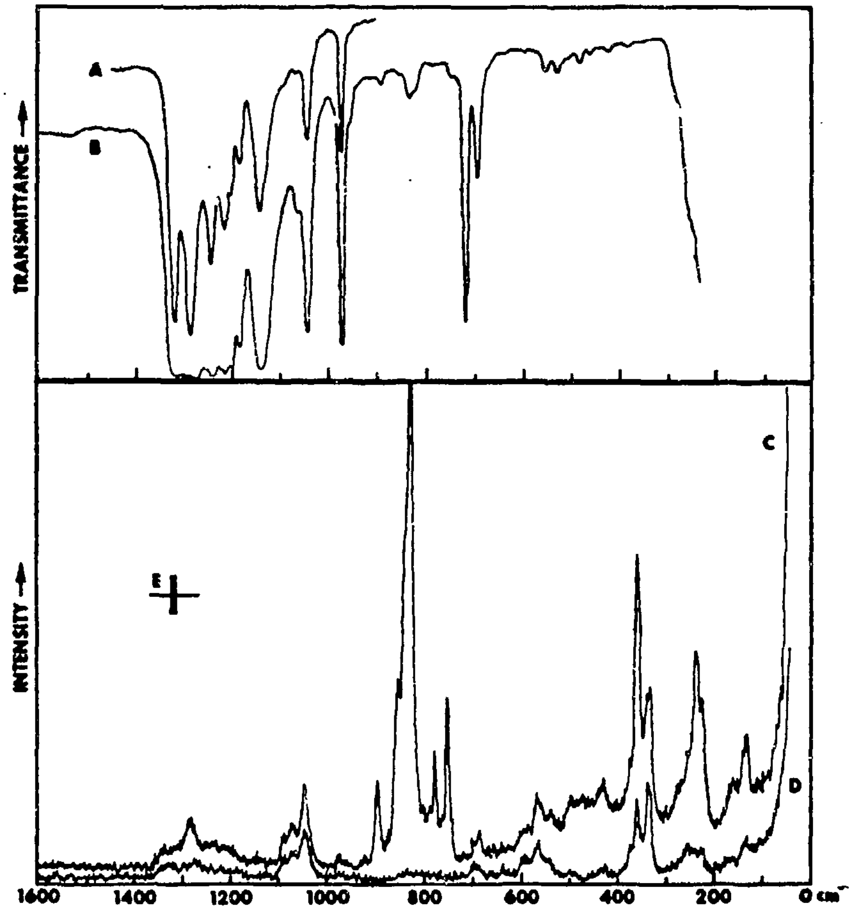
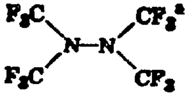
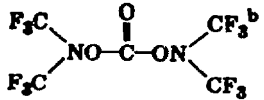


Fig. 1. Vibrational spectrum of $[(CF_3)_2NO]_2CF_2$. A and B: IR spectrum of the gas at 10 and 3 mm, respectively, path length 5 cm, window material AgBr. C and D: Raman spectrum of the liquid with the polarization parallel and perpendicular, respectively. E indicates the spectral slit width.

Thus, these reactions present a new high yield synthesis of $(CF_3)_2NOCF_3$. However, owing to the commercial availability of CF_3NO, the catalytic fluorination of CF_3NO yielding $(CF_3)_2NOCF_3$ in 55% yield [13] appears to be a more attractive synthetic route. A brief study to substitute $(CF_3)_2NO$ by CF_3NO in its reaction with O_2^+ salts did not result in the formation of any two carbon atom species but only CF_3NO oxidation products. This observation agrees with the above postulate that in $(CF_3)_2NO$ an N—C bond is attacked first with CF_4 formation resulting in an excited CF_3NO species which can readily lose a CF_3 radical. The interaction between $(CF_3)_2NO$ and $O_2^+SbF_6^-$ when carried out under suitable conditions (such as gas phase reaction, use of a carrier gas, *etc.*) may have potential for producing CF_3 radicals under mild

TABLE 2

Vibrational spectrum (cm^{-1}) of $[(CF_3)_2NO]_2CF_2$ and its assignment compared to those of $[(CF_3)_2NO]_2CO$ and $[(CF_3)_2N]_2$

					Tentative assignment for $(CF_3)_2NOCF_2ON(CF_3)_2$
IR (gas)	*Raman (liquid)*	*IR (gas)*	*IR (gas)*	*Raman (liquid)*	
1333 (s)	1334(4)	1317 (vs)	1322 (vs)	1325(4)	
1310 (s)					
1292 (s)	1295(3)	1269 (vs)	1291 (vs)	1285(10) (p)	
	1278(2)				
1232 (s)	1239(9) (p)	1237 (vs)	1249 (vs)		CF_3 stretch
		1218 (vs)	1220 (vs)		CF_2 stretch
				1230(6) (br)	
1205 (s)	1203(4)		1205 (m)		
1180 (s)	1176(3)		1189 (m)		
		1132 (vs)	1145 (vs)	1145(0+) (br)	$\nu_{as}(CO_2)$
				1085(2)	
		1096 (m)	1070 (w)	1070(6)	$\nu_{sym}(CO_2)$
		1038 (s)	1047 (s)	1046(18) (p)	$\nu(N-O)$
987 (vs)	987(2) (dp)	975 (-)	976 (s)	975(2)	
			960 (w)		$\nu_{as}(NC_2)$
886 (s)	889(1) (dp)		893 (vw)	895(14) (p)	
	864(1) (p)		852 (sh,vw)	850(20) (p)	
	832(2) (p)		835 (w)	835 (sh,p)	$\nu_{sym}(NC_2)$
			825 (sh)	826(100) (p)	
785 (sh)	764(2) (p)	777 (w)		775(13) (p)	
741 (s)	752(1) (p)	748 (w)	750 (w)	750(23) (p)	
722 (s)	724(2) (p)	713 (s)	719 (s)	718(1)	CF_3 deformation
			699 (m)	693(4)	
				681(5)	
652 (w)	652(3) (p)	668 (w)	640 (vw)	635(0+)	
	592(6) (p)			590(5) (dp)	CF_3 deformation
	582(6)				

561 (m)	566(7) (dp)	555 (w)	562(12) (dp)	CF$_2$ deformation
536 (m)	538(2) (dp)	531 (w)	538(4)	
485 (sh)	489(5) (p)	487 (w)	490(3) (p)	
		427 (vw)	429(6) (p)	
	365 (sh,dp)		368 (sh,dp)	NC$_2$ deformation
	378(28) (p)			
	323(90) (p)		357(55) (p)	
	352(34) (dp)		338(34) (dp)	
250 (m)	252(4) (dp)		253 (sh,dp)	CF$_2$ rock
	237(7) (dp)		239(32) (p)	
	202(2) (dp)		225(4)	
	153(6) (dp)		156(5)	
			130(12) (p)	
	108(3) (dp)		105(0+) (dp)	
	69 (dp)			

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[a] Values from ref. 15.
[b] Values from ref. 16.

conditions by chemical means. However, further experiments in this direction were beyond the scope of the present study.

In addition to $(CF_3)_2NOCF_3$ a new compound, $[(CF_3)_2NO]_2CF_2$, was formed in about 20% yield based on O_2^+ salt. This indicates that significant amounts of the CF_2 diradical are also formed which interact $(CF_3)_2NO$ according to:

$$2(CF_3)_2NO + CF_2 \rightarrow [(CF_3)_2NO]_2CF_2$$

The formation of a carbon species with only two fluorine atoms attached to it, such as CF_2 or COF_2, is not unreasonable since the formation of CF_4 in the first step will create a fluorine deficiency in the system.

The $[(CF_3)_2NO]_2CF_2$ molecule may be considered as a derivative of the previously reported $(F_2NO)_2CF_2$ molecule [14] in which the fluorines attached to the nitrogen atom are replaced by CF_3 groups. The observed mass spectrum (Table 1), vibrational spectrum (Table 2) and ^{19}F NMR data are in excellent agreement with the suggested structure. Tentative assignments for the more important vibrational modes are given in Table 2. These were made by comparison with the previously reported spectra for $(CF_3)_2N{-}N(CF_3)_2$ [15] and $[(CF_3)_2NO]_2CO$ [16]. The general agreement between the vibrational spectra of the three compounds is excellent except for the difference in the relative Raman intensities of $\nu_{sym}(NC_2)$ between $(CF_3)_2N{-}N(CF_3)_2$ and $[(CF_3)_2NO]_2CF_2$. As pointed out previously [15], the Raman intensities observed for these modes in $(CF_3)_2N{-}N(CF_3)_2$ are much lower than those usually found for related $(CF_3)_2N$-type molecules. A more detailed analysis is not warranted due to the size of the molecule and to the possible existence of different rotational isomers as indicated by the NMR spectral data.

The ^{19}F NMR chemical shifts and coupling constant observed for $[(CF_3)_2NO]_2CF_2$ are in excellent agreement with those reported for the related $(CF_3)_2NOCF_2X$-type compounds [17,18]. The chemical shift of the $CF_2(OX)_2$ group appears to decrease with decreasing electronegativity of X resulting in the following order for X: F(84.2) [19], NF_2(84) [14], OCF_3 and $OOCF_3$(79.2) [20], $N(CF_3)_2$(69.8), SO_2F(58.6) [21]. The fact that in addition to the 69.8 ppm CF_2 signal, three other weak signals having similar chemical shifts were observed for $[(CF_3)_2NO]_2CF_2$ indicates the possible existence of rotational isomers which would not be surprising for this bulky molecule.

Acknowledgements

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TRIFLUOROMETHYL PERCHLORATE-PREPARATION AND PROPERTIES

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Recently the addition of chlorine or bromine perchlorate to perhaloolefins was reported (1). The perhaloalkyl perchlorates that were formed exhibited good overall stability especially when contrasted to the known (2) hydrocarbon perchlorates. In an effort to widen the range of available perhaloalkyl perchlorates and to continue the study of the chemistry of chlorine perchlorate, the possible displacement of halogen from perhaloalkyls was investigated.

We now report that the action of chlorine perchlorate on trifluoromethyl iodide at low temperature has resulted in the formation of the simplest perfluoroalkyl perchlorate, CF_3OClO_3. The observed stoichiometry of the preparation was:

$$CF_3I + 2ClOClO_3 \longrightarrow CF_3OClO_3 + Cl_2 + [IClO_4]$$

The identification of this colorless compound was unequivocal, based on its infrared, Raman, mass, and ^{19}F nmr spectra, together with vapor density molecular weight, elemental analysis, and CsF catalyzed decomposition. The infrared spectrum shows the following bands: 1310 (vs), 1275(s), 1250(s), 1130(vs), 1035(vs), 920(m), 725(m), 620(s), 575(w), and 510(vw) cm^{-1}. The 1310, 1035, and 620 cm^{-1} bands are typical of the covalent, monodentate perchlorate group (1, 3). Intense m/e fragments in the mass spectrum were assigned to the ions, ClO_3^+, CF_3^+, ClO_2^+, ClO^+, and COF^+. In addition a weak parent ion peak was noted. The ^{19}F nmr spectrum exhibited only one line at 60.0 ppm, quite close to that of related CF_3O moieties (4, 5). Also, measured quantities of CF_3OClO_3 and $CFCl_3$ reference were used to prove by nmr peak area ratio measurements that the compound contains three fluorine atoms per molecule.

Iodine perchlorate, postulated as the by-product in the preceding equation, is not a monomeric covalent material like the other halogen perchlorates. At ambient temperature, on standing the "$IClO_4$" gradually loses Cl_2 and Cl_2O_7, eventually leading to the formation of I_2O_5. The same solid decomposition product results from the ambient temperature degradation of $I(ClO_4)_3$(6).

The CsF catalysed decomposition of CF_3OClO_3 demonstrated the inherent stability of the molecule since only 30 percent of the sample cleaved during 18 hours at 100°.

$$CF_3OClO_3 \xrightarrow[\Delta]{CsF} COF_2 + FClO_3$$

Higher temperatures produced complete decomposition and quantitative amounts of the products shown.

Several other new perchlorates have been synthesized in similar reactions and will be described shortly.

Experimental Section

Trifluoromethyl iodide (2.02 mmole) and $ClOClO_3$ (4.24 mmole) were combined at -196° in a 30 ml stainless-steel cylinder which was subsequently slowly warmed to -45° during several days. Recooling to -196° showed the absence of noncondensable products. While warming to room temperature, the volatile products evolved were separated by fractional condensation. These consisted essentially of Cl_2 (2.07 mmole), trapped at -196° and CF_3OClO_3 (2.01 mmole), trapped at -112°; the yield of CF_3OClO_3 was 99 percent. The observed molecular weight based on vapor density measurements was 167 versus a value of 168.4 g/mole calculated for CF_3OClO_3. Anal., Calc.: F, 33.84; Cl, 21.04. Found; F, 33.3; Cl, 21.5.

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Infrared and Raman Spectra of Trifluoromethyl Perchlorate

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The gas-phase infrared spectrum and the liquid-phase Raman spectrum of trifluoromethyl perchlorate have been recorded. The spectra show that CF_3OClO_3 contains a covalent monodentate perchlorato group. A total of 19 fundamental vibrations out of 21, expected for a model of symmetry C_s with hindered rotation, were observed and assigned.

Introduction

Few covalent perchlorates are known. Among these are free perchloric acid, $HOClO_3$, and its anhydride, $O_3ClOClO_3$, both of which have been known for many years.[1] More recently the halogen perchlorates $FOClO_3$,[2] $ClOClO_3$,[3] $BrOClO_3$,[4] $Cs^+Br(OClO_3)_2^-$,[5] $I(OClO_3)_3$,[6] and $Cs^+I(OClO_3)_4^-$ [6] have been reported. Alkyl perchlorates are also known but are very treacherous materials[1] and therefore have not been investigated extensively. While spectroscopic studies of O_3-

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$ClOClO_3$,[7,8] $HOClO_3$,[9] and the halogen perchlorates[5,6,10] have been completed, alkyl perchlorates remain unexamined. Renewed interest in the synthesis of new covalent perchlorates[11,12] has shown that perhalogenated alkyl derivatives can be prepared, are stable, and are thus amenable to further study.

For spectroscopic work on alkyl compounds it is best to study the simplest example in order to avoid interference from bands due to large alkyl groups. Recently we succeeded in synthesizing[13] the novel fluorocarbon perchlorate trifluoromethyl perchlorate. Owing to its simplicity this compound is ideally suited for a systematic study of its vibrational spectrum.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Trifluoromethyl perchlorate was prepared from CF_3I and $ClOClO_3$ as reported[13] and was purified by several fractional condensations. The purity of the sample used for this study was verified by its mass spectrum and tensiometric homogeneity. Infrared absorbing impurities were not detected. Pure CF_3OClO_3 is stable and can be manipulated with much less difficulty than any of the halogen perchlorates. A gas sample stored in a stainless steel vessel at room temperature for nearly 2 years was not noticeably changed.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5- or 10-cm path length fitted with AgCl or AgBr windows. The instrument was calibrated by comparison with standard calibration points.[14] The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å line of an Ar ion laser as the exciting line and a Claassen filter[15] for the elimination of plasma lines. Sealed quartz tubes (~ 2-mm i.d.) were used as sample containers for the liquid in the transverse-viewing–transverse-excitation technique. The Raman spectra were recorded at −100° using a device similar to that previously described.[16]

Results and Discussion

Caution! Perchlorates are generally shock sensitive and must be treated with due care. Although trifluoromethyl perchlorate appears quite stable, deflagrations were occasionally encountered in the course of its synthesis.

Vibrational Spectrum. Figure 1 shows the infrared spectrum of gaseous trifluoromethyl perchlorate at several pressures and the Raman spectrum of the liquid. Table I lists the observed frequencies together with their assignments.

Structural Model. In principle several isomeric structures are possible for a compound with the empirical composition CF_3ClO_4. All the observed properties, *i.e.*, low melting point, bp 9.5°, Trouton constant 23.3, vapor-phase mol wt 167, and nmr-equivalent fluorines, together with the direct synthetic method, are consistent with a structure containing a CF_3 group linked to a ClO_4 group through one of the oxygens. Such a structure would be expected to have a bent C–O–Cl link much like the previously studied[2-10] covalent perchlorates and to resemble spectroscopically a mixed ether, B_3A–O–CD_3. Therefore, CF_3OClO_3 should possess structure I of symmetry C_s assuming one F and one double-bonded oxygen atom to be located in the COCl plane. Assuming free rotation of the CF_3 and ClO_3 groups, the molecule would also possess C_s symmetry but some of the XY_3 modes would be degenerate. Assuming hindered rotation a nine-atom molecule of C_s symmetry should exhibit 21 fundamental modes of vibration, all active in both the infrared and the Raman spectra. Of these, 13 belong to species A′ and can be either polarized or depolarized, while 8 belong to species A″ and should be depolarized. The 21 fundamental vibrations arise from 3 skeletal motions and 9 modes each for the CF_3 and the ClO_3 groups. The 9 motions each of the CF_3 and ClO_3 groups may be described as 3 stretching modes, 3 deformational modes, 2 rocking fundamentals, and 1 torsional oscillation. Torsional modes for CF_3[17] and ClO_3[7] groups generally occur at quite low frequencies (beyond the range of our infrared measurements), are weak, and usually are not observed. No evidence for the two torsional fundamentals was found and they will not be considered further in our discussion.

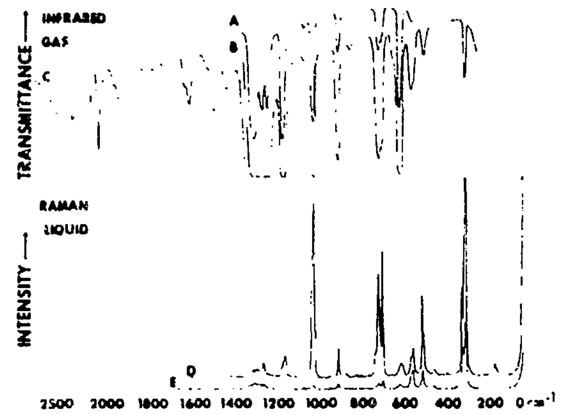

Figure 1. Vibrational spectra of CF_3OClO_3. Infrared spectrum of the gas: A, 5 mm in a 5-cm path length cell with AgCl windows; B and C, 18 and 125 mm, respectively, in a 10-cm path length cell with AgBr windows. Raman spectrum of the liquid at ~−100°: D, incident polarization perpendicular; E, incident polarization parallel; the spectral slit width used was 3 cm^{-1}.

I

Assignment of Stretching Modes. Investigations[17,18] of trifluoromethyl compounds have shown that the CF_3 stretching fundamentals lie in the frequency range 1400–1100 cm^{-1}. Similarly for ClO_3 stretching modes, the frequency range 1350–1000 cm^{-1} has been established.[7,10] In spite of this frequency range overlap, assignments can be made to the modes belonging to the CF_3 and the ClO_3 groups, respectively. The two antisymmetric ClO_3 stretches usually are almost degenerate and splitting into the individual modes is

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Table I. Vibrational Spectra of CF_3OClO_3[a]

Obsd freq, cm^{-1}, and intens[b]		Assignment in point group C_s and approx description of mode
Infrared (gas)	Raman (liquid)	
2595 vw		$\nu_2 + \nu_{14} = 2595$ (A″)
2547 vw		$\nu_1 + \nu_{15} = 2549$ (A″)
2486 w		$2\nu_{15} = 2482$ (A′)
2435 vw		$\nu_2 + \nu_3 = 2436$ (A′)
2345 w		$2\nu_3 = 2342$ (A′)
2290 vw		$\nu_2 + \nu_4 = 2293$ (A′)
2167 vw		$\nu_5 + \nu_{15} = 2155$ (A″) or $\nu_2 + \nu_5 = 2179$ (A′)
2093 w		$\nu_3 + \nu_5 = 2085$ (A′)
2038 vw		$\nu_7 + \nu_{14} = 2036$ (A″)
1964 vw		$\nu_1 + \nu_{16} = 1968$ (A″) or $\nu_2 + \nu_7 = 1971$ (A′)
1942 w		$\nu_8 + \nu_{14} = 1945$ (A″) or $\nu_7 + \nu_{15} = 1947$ (A″) or $\nu_4 + \nu_5 = 1942$ (A′)
1877 vw		$\nu_3 + \nu_7 = 1877$ (A′)
1831 vw		$2\nu_5 = 1828$ (A′) or $\nu_3 + \nu_{16} = 1831$ (A″) or $\nu_2 + \nu_{17} = 1833$ (A″)
1632 vw		$\nu_5 + \nu_6 = 1638$ (A′) or $\nu_3 + \nu_{18} = 1633$ (A″)
1612 w		$\nu_1 + \nu_{12} = 1622$ (A′) or $\nu_5 + \nu_7 = 1620$ (A′) or $\nu_2 + \nu_{11} = 1604$ (A′)
1495 w		$\nu_4 + \nu_{18} = 1490$ (A″)
1438 vw		$\nu_2 + \nu_{13} = 1443$ (A′) or $\nu_6 + \nu_7 = 1430$ (A′)
1308 vs	1330 (0.2) dp[c]	ν_{14}(A″) ν antisym ClO_3
	1300 (0.3) p	ν_1(A′) ν antisym ClO_3
1265 s	1267 (0.5) p	ν_2(A′) ν antisym CF_3
1241 s	1240 (0.1)	ν_{15}(A″) ν antisym CF_3
1171 vs	1169 (0.8) p	ν_3(A′) ν sym CF_3
1074 vw		$\nu_9 + \nu_{10} = 1072$ (A′)
1028 vs	1031 (7.2) p	ν_4(A′) ν sym ClO_3
914 m	917 (1.1) p	ν_5(A′) ν C–O
	880 (0.1) p	$\nu_9 + \nu_{12} = 880$ (A′)
852 vw		$\nu_{10} + \nu_{11} = 851$ (A′)
829 vvw		$\nu_{10} + \nu_{12} = 826$ (A′)
724 m	726 (4.2) p	ν_6(A′) δ sym CF_3
706 sh (PQR)	708 (5.1) p	ν_7(A′) δ antisym CF_3
660 sh	660 (<0.1)	ν_{16}(A″) δ antisym CF_3
615 s	616 (0.5) p	ν_8(A′) ν O–Cl
568 mw	570 (0.7) dp	ν_{17}(A″) δ antisym ClO_3
560 sh	564 (1.1) p	ν_9(A′) δ antisym ClO_3
512 w	516 (3.2) p	ν_{10}(A′) δ sym ClO_3
	490 (<0.1)	$\nu_{12} + \nu_{13} = 494$ (A′)
463 vvw	462 (0.2) dp	ν_{18}(A″) δ rock CF_3
339 sh	342 (3.5) p	ν_{11}(A′) δ wag CF_3
	320 dp?	ν_{19}(A″) δ rock ClO_3
314 mw	316 (10) p	ν_{12}(A′) δ in-plane C–O–Cl
	178 (0.5) p	ν_{13}(A′) δ wag ClO_3

[a] In addition to the listed infrared absorptions very weak bands were observed having the frequencies 2635, 2455, 2220, 2195, 1893, 1780, 1734, 1533, and 1476 cm^{-1} which can readily be assigned to combination bands and overtones. [b] Uncorrected Raman intensities representing relative peak height. [c] Qualitative polarization measurement.

only observed for liquid or matrix-isolated samples.[10] In the infrared spectrum of the gas, they generally appear as a very intense, somewhat broad band near 1300 cm^{-1} and, therefore, are assigned for CF_3OClO_3 to the strong infrared band at 1308 cm^{-1} (see Figure 1). Furthermore, it is expected that their Raman counterparts would be weak. This is the case as shown in Figure 1. For the liquid also partial separation into the almost degenerate components was noted. The higher frequency band, 1330 cm^{-1}, appears depolarized and is therefore assigned to the A″ antisymmetric ClO_3 stretch, while the 1300-cm^{-1} band appears polarized and is assigned to the corresponding A′ mode. The symmetric ClO_3 stretching vibration is normally found in the range 1060–1000 cm^{-1}, well below the CF_3 stretching mode range and is intense in both the infrared and the Raman spectra. Since only one intense band at 1028 cm^{-1} is noted in this region in both spectra, it is assigned to the symmetric ClO_3 stretching vibration. Further support for this assignment is the high degree of polarization[19,20] of the band in the Raman spectrum.

For the three CF_3 stretching vibrations, there remain three bands in the appropriate infrared region (1265, 1241, 1171 cm^{-1}) all of which are strong as expected. Conversely, they are very weak in the Raman spectrum where it is seen that two of the three are highly polarized and one (1240 cm^{-1}) is probably depolarized. The lower frequency polarized band (1169 cm^{-1}) can be readily assigned to the A′ symmetric CF_3 stretching mode which agrees well with previous assignments.[18,20] The other polarized band (1267 cm^{-1}) is then attributable to the antisymmetric CF_3 stretch of species A′ while the corresponding A″ mode is assigned to the 1240-cm^{-1} band. Thus the assignment of all of the six stretching vibrations is straightforward and can be made with confidence.

Immediately below the region for ClO_3 and CF_3 stretching motions is the area in which C–O stretching vibrations are most likely[18-20] to occur, *i.e.*, approximately between 1000 and 900 cm^{-1}. Figure 1 shows that only one intense band occurs in this region. This band at 914 cm^{-1} is moderately intense in both the infrared and the Raman spectra, exhibits the correct infrared band contour for an A′ mode, and is polarized. All of these observations support its assignment as the C–O stretching fundamental. Comparable C–O bands have been reported at 916 cm^{-1} (average value) for CF_3OOOCF_3[20] and at 915 cm^{-1} for CF_3OCl.[21]

Assignment of Deformational Modes. Inspection of the literature[17,18,20] reveals that for simple CF_3-containing molecules the CF_3 deformation vibrations occur in the range of 720–520 cm^{-1}. Similarly, ClO_3 compounds[7,9,10,22] show deformational modes in the range 600–510 cm^{-1}. In addition, the Cl–O single-bond stretch should occur in this frequency region.[7,9,10] Hence, for CF_3OClO_3 we should expect seven fundamentals in the frequency range 720–510 cm^{-1} in excellent agreement with our observations (see Figure 1 and Table I). Of the seven expected, five belong to species A′ and two to species A″. The latter must be depolarized in the Raman spectrum and arise from the antisymmetric CF_3 and ClO_3 deformations. Of these seven observed bands, only one band (570 cm^{-1}) is clearly depolarized while five (726, 708, 616, 564, and 516 cm^{-1}) are polarized and for one (660 cm^{-1}) the polarization ratio is doubtful owing to its very low intensity. Since for all of the reported ClO_3 compounds, the A″ antisymmetric deformation is moderately intense in both the infrared and the Raman spectra, the more intense one (570 cm^{-1}) of the two apparently depolarized bands is assigned to the A″ antisymmetric ClO_3 deformation, and the very weak one at 660 cm^{-1} is assigned to the A″ antisymmetric CF_3 deformation. The low intensity thereby attributed to this CF_3 mode is not unusual since for similar compounds it is sometimes not even observed.[18,23]

In the series of $XOClO_3$ compounds where X = F,[24] Cl,[10] and Br,[10] the internal Cl–O single-bond stretch results in

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a strong infrared band comparable in intensity to the ClO_3 stretching bands. As seen in Figure 1, there is only one such infrared band (615 cm^{-1}) present in the appropriate frequency range and hence should be assigned to the Cl–O stretching mode. The observed frequency for this band (615 cm^{-1}) is only slightly lower than that noted for the related halogen perchlorates (666–646 cm^{-1}).[10,24]

We are left now with four unassigned bands in the 720-520-cm^{-1} region. The two higher frequency (724 and 706 cm^{-1}) infrared bands are also appreciably stronger than the two lower ones (560 and 512 cm^{-1}). Furthermore these higher frequency vibrations occur beyond the 600-510-cm^{-1} range predicted for ClO_3 deformations. Therefore, they are ascribed to the two unassigned CF_3 A′ deformational modes. Since the 724-cm^{-1} band is of higher intensity in the infrared spectrum, it is assigned to the CF_3 umbrella deformation, while the 706-cm^{-1} band is assigned to the CF_3 scissoring deformation. These assignments are analogous to those of other CF_3 moieties[18,20,25] where similar frequency and intensity relationships have been observed.

By analogy with the corresponding CF_3 deformations, the ClO_3 umbrella deformation should be more intense than the ClO_3 scissoring mode in both the infrared and Raman spectra. Therefore, the 512- and the 560-cm^{-1} bands are assigned to the ClO_3 umbrella and scissoring modes, respectively, in good agreement with previous observations.[7,9,10] It should be noted that for all these compounds the frequency of the ClO_3 umbrella deformation is nearly constant (515 ± 6 cm^{-1}) indicating this mode to be highly characteristic.

There are five fundamental vibrations left unaccounted for. Two of these are the CF_3 and the ClO_3 wagging motion belonging to species A′. Another two are the CF_3 and ClO_3 rocking motions of species A″. The fifth fundamental is the C–O–Cl in-plane bending motion which will be considered first. This vibration should occur below 500 cm^{-1} and involve a large change in the polarizability of the molecule. It should therefore appear as an intense Raman band. Since the most intense Raman band in the entire CF_3OClO_3 spectrum occurs at 316 cm^{-1} and is polarized, this frequency must represent this mode. Neither the A′ CF_3 wag nor the A′ ClO_3 wag should produce such a strong Raman band. Comparable data on similar motions in related compounds are extremely limited. Examples that might be useful for comparison are the Cl–O–Cl skeletal bend of O_3Cl–O–ClO_3 and the O–O–O bend in the trioxide CF_3OOOCF_3. The former has been assigned[7,8] to a Raman peak at 161 cm^{-1} while the trioxide bend[20] has been attributed to a peak at 286 cm^{-1}. Whereas the latter assignment is in excellent agreement with our assignment for CF_3OClO_3, the former might be incorrect. Based on our data for CF_3OClO_3, we prefer to reassign the Cl–O–Cl bend in Cl_2O_7 to the very intense Raman band at 286 cm^{-1} and attribute the 161-cm^{-1} band to the ClO_3 wagging motion (see below).

As has been remarked by Durig and Wertz[18] and Witt and Hammaker,[7] the precise assignment of $-XY_3$ rocking motions is difficult owing to the wide range of frequencies involved and the paucity of data. Our assignments for the modes are based on the following observations: (i) the two polarized Raman lines must represent the wagging (A′) motions, and the two depolarized lines, the rocking (A″) motions; (ii) all the assigned CF_3 deformations have higher frequencies than the corresponding ClO_3 modes. Consequently, the higher frequency A′ and A″ modes are attributed to the CF_3 group and the lower ones to the ClO_3 group (see Table I).

A band of very low intensity was noted in the Raman spectrum at 490 cm^{-1} but was not observed in the infrared spectrum. We do not believe that this is a fundamental, although that possibility cannot be completely ruled out. It could be due to a combination ($\nu_{12} + \nu_{13} = 494$ cm^{-1}) or perhaps an impurity.

Summary

The observed infrared and Raman spectra of CF_3OClO_3 are in excellent agreement with a structure of symmetry C_s containing a covalent monodentate perchlorato group. The close agreement between the infrared frequencies of the gas and the Raman frequencies of the liquid indicate that no appreciable association occurs in the liquid phase. Observation of two separate antisymmetric stretching modes for both the CF_3 and the ClO_3 groups indicates hindered rotation for both groups. Except for the two torsional modes, all predicted fundaments were observed and assigned and indicate the need for reassigning the two lowest frequency vibrations in Cl_2O_7.

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Halogen Nitrates

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The low-temperature infrared and Raman spectra of $I(NO_3)_3$ and the Raman spectra of liquid $ClONO_2$, $FONO_2$, FNO_2, and $ClNO_2$ have been recorded. Comparison of the vibrational spectra within the series NO_2^-, FNO_2, $ClNO_2$, $FONO_2$, and $ClONO_2$ allows unambiguous assignments for the halogen nitrate molecules. Raman polarization measurements show that in halogen nitrates the halogen atom is perpendicular to the ONO_2 plane contrary to previous assumptions and to the known planar structure of $HONO_2$ and CH_3ONO_2. The vibrational spectrum of $I(NO_3)_3$ is consistent with predominantly covalent nitrato ligands. However, the complexity of the spectrum suggests a polymeric structure with bridging nitrato groups. Experimental evidence was obtained for the formation of the new and thermally unstable compound $CF_3I(NO_3)_2$ in the CF_3I–$ClONO_2$ system. Attempts to convert this compound into CF_3ONO_2 were unsuccessful.

Introduction

Highly electronegative groups such as perchlorates, nitrates, fluorosulfates, or trifluoroacetates can be considered as pseudohalides. As such they either can form stable anions in the presence of suitable cations or can act as covalent ligands particularly when bonded to highly electronegative elements such as the halogens or oxygen. Whereas the vibrational spectra of the free anions are relatively well understood, those of the corresponding covalent ligands have only recently received more attention. Reliable spectra and assignments are now available for covalent perchlorates,[1-3] trifluoroacetates,[4] and fluorosulfates.[5-7] In spite of extensive infrared spectroscopic studies on halogen nitrates,[8-11] a recent paper, reporting the vibrational spectrum of CF_3OONO_2, demonstrates[12] how poorly understood these spectra are at present.

The question whether the halogen atom in $XONO_2$ is coplanar or perpendicular with respect to the ONO_2 plane added further interest to our study. The consensus[9-12] appears to favor coplanarity based on analogy with the planar structures established for the related molecules $HONO_2$[13] and CH_3ONO_2.[14] However, the assumption of a planar structure for the halogen nitrates is against our intuition. Similarly, Pauling and Brockway suggested[15] for $FONO_2$ a nonplanar structure based on low-precision electron diffraction data, although a planar structure could not be ruled out. Raman polarization measurements should clearly distinguish between a planar and a nonplanar structure provided that unambiguous assignments are available. For this purpose Raman data were also required for the closely related nitryl halides.

Another objective of this study was to characterize $I(NO_3)_3$. This interesting compound was first prepared by Schmeisser and Braendle.[16] It is unstable above 0° and no data concerning its structure have been published. Attempts were also made to synthesize the novel covalent nitrate CF_3ONO_2 which led to the synthesis of the novel compound $CF_3I(NO_3)_2$.

Experimental Section

Caution! Fluorine nitrate is shock sensitive.

Material and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 4251 F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nitryl chloride,[17] $ClONO_2$,[18] and FNO_2[19] were prepared by literature methods. Fluorine nitrate was prepared by direct fluorination of KNO_3 in a stainless steel cylinder.[11] The purity of volatile materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The low-temperature spectrum of $I(NO_3)_3$ was obtained as a dry powder between CsI plates at −196° using a low-temperature transfer technique similar to one previously reported.[20] The instrument was calibrated by comparison with standard calibration points.[21]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[22] for the elimination of plasma lines. Sealed quartz tubes (3-mm o.d.) were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature Raman spectra were recorded using a device similar to one previously described.[23] Polarization measurements were carried out according to method VIII listed by Claassen, *et al.*[22]

Preparation of $I(NO_3)_3$. Resublimed I_2 (1.005 mmol) was placed into a Teflon FEP tube fitted with a stainless steel valve. Freshly fractionated $ClONO_2$ (8.20 mmol) was condensed into the tube at −196°. The mixture was kept at −45° for 1 week. The materials, volatile at −45°, were removed *in vacuo* and separated by fractional condensation. They consisted of unreacted $ClONO_2$ (2.20 mmol) and Cl_2 (3.01 mmol) in excellent agreement with the values calculated for a quantitative conversion of I_2 to $I(NO_3)_3$. The nonvolatile residue was a fluffy light yellow solid which decomposed above 0° under dynamic vacuum yielding N_2O_5 (2.05 mmol) and a tan solid residue. This residue gradually decomposed further as evidenced by the buildup of NO_2-colored fumes above the solid. An infrared spectrum of the solid after several weeks of storage at 25° did not show any absorptions characteristic for N=O double bonds.

The $ClONO_2$–CF_3I System. Chlorine nitrate (4.02 mmol) and CF_3I (1.75 mmol) were combined at −196° in a 30-ml stainless steel cylinder. The reactor was slowly warmed to −45° and kept at this temperature for 6 days. Recooling to −196° did not show any noncondensable material. Products volatile at −78° were removed *in vacuo* and separated by fractional condensation. They consisted of unreacted $ClONO_2$ (0.40 mmol) and Cl_2 (1.79 mmol) in good agreement with the amounts expected for a quantitative conversion of CF_3I to $CF_3I(NO_3)_2$. Warming of the solid residue to 25° yielded N_2O_5 (1.14 mmol), COF_2 (1.07 mmol), and CF_3I (0.65 mmol) in addition to 219 mg of a sticky solid residue of varied orange color.

Results and Discussion

Synthesis and Properties. The interaction between I_2 and excess $ClONO_2$ at −45° produced $I(NO_3)_3$ in quantitative yield according to

$$I_2 + 6ClONO_2 \rightarrow 2I(NO_3)_3 + 3Cl_2$$

Thus, this reaction offers an excellent route to high-purity $I(NO_3)_3$, contrary to a previous statement[16] that, although $I(NO_3)_3$ is formed in this system, it is not of synthetic usefulness.

The properties and thermal instability observed for $I(NO_3)_3$ are in good agreement with those previously reported[16] for the product obtained from the $ICl_3 + ClONO_2$ reaction. The evolution of 1 mol of N_2O_5/mol of $I(NO_3)_3$ in the initial stage of the thermal decomposition indicates the possible formation of $OINO_3$ as an intermediate of marginal stability at 0°

$$I(NO_3)_3 \rightarrow OINO_3 + N_2O_5$$

The subsequent slow decomposition of this intermediate involves a redox reaction in which the +V nitrogen is reduced to the +IV state (N_2O_4) with simultaneous oxidation of the +III iodine. This observation is in excellent agreement with the thermal decomposition of $I(OClO_3)_3$ which yields Cl_2O_7, lower chlorine oxides, and I_2O_5.[2]

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In the CF_3I–$ClONO_2$ system, the observed material balance is in good agreement with the reaction

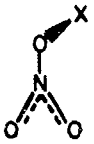
$$CF_3I + 2ClONO_2 \rightarrow CF_3I(NO_3)_2 + Cl_2$$

Again the observation of such an intermediate is in excellent agreement with the closely related $ClOClO_3$ reaction chemistry. Thus, the interaction of R_fI with $ClOClO_3$ produced $R_fI(ClO_4)_2$.[24] When R_f was $(CF_3)_2CF$ or n-C_7F_{15}, the $R_fI(ClO_4)_2$ intermediate was successfully isolated. At 40°, the n-$C_7F_{15}I(ClO_4)_2$ could be converted into R_fOClO_3 by vacuum pyrolysis. For $R_f = (CF_3)_2CF$, however, vacuum pyrolysis at 105° resulted exclusively in decomposition products. For $R_f = CF_3$, the $CF_3I(ClO_4)_2$ intermediate was not isolated; however, a quantitative yield of CF_3OClO_3 was obtainable at −45°.[24,25] Therefore, it appeared interesting to determine whether the novel compound CF_3ONO_2 could be prepared by controlled decomposition of $CF_3I(NO_3)_2$. No evidence for CF_3ONO_2 could be obtained, but CF_3I and about equimolar amounts of N_2O_5 and COF_2 were formed.

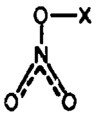
The observation of CF_3I as a decomposition product is interesting. A plausible explanation for its formation can be offered. For $R_fI(ClO_4)_2$, Raman spectra support[24] the ionic structure $[(R_f)_2I]^+[I(ClO_4)_4]^-$. If $CF_3I(NO_3)_2$ had the analogous ionic structure $[(CF_3)_2I]^+[I(NO_3)_4]^-$, as much as 50% of the originally used CF_3I might be recovered in the thermal decomposition of such an intermediate. The difficulty in obtaining CF_3ONO_2 indicates that this compound might be relatively unstable toward decomposition into COF_2. This is in good agreement with previous studies[12,26] aimed at the synthesis of R_fONO_2.

Vibrational Spectra. Figure 1 shows the Raman spectra of $ClNO_2$, FNO_2, $ClONO_2$, and $FONO_2$ and the infrared and the Raman spectrum of $I(NO_3)_3$. The observed frequencies are listed in Tables I and II.

Before the assignment of the fundamentals of the halogen nitrate molecules can be discussed in more detail, it must be established whether $XONO_2$ has structure I or II, *i.e.*, whether X is perpendicular to or coplanar with the ONO_2 plane.

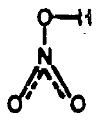


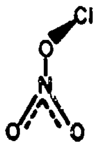
I



II

Whereas in $HONO_2$ intramolecular hydrogen bridging should favor planarity, in $HalONO_2$ the expected mutual repulsion between the halogen and the two oxygen atoms should favor the perpendicular model.





Raman spectroscopy should readily distinguish between models I and II. Both models possess symmetry C_s and nine fundamentals, but for model I three of the fundamentals are antisymmetric with respect to the symmetry plane, whereas for model II only two modes are antisymmetric.

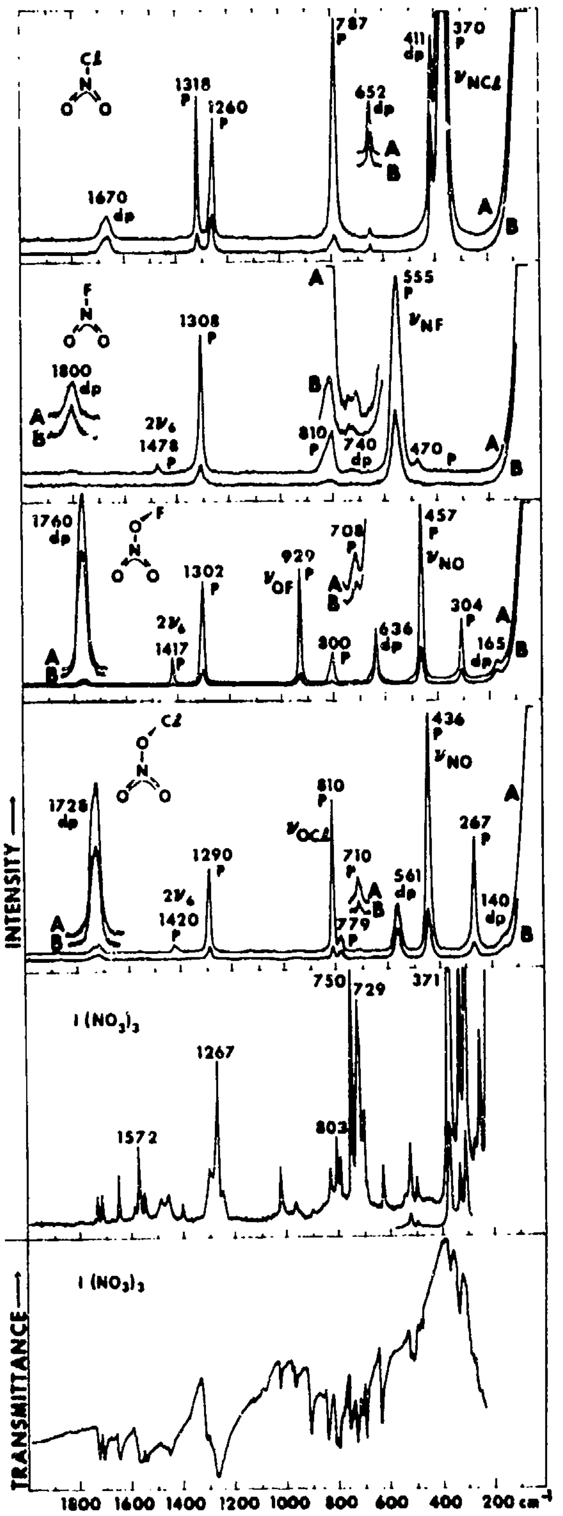


Figure 1. Raman spectra of liquid $ClNO_2$ (recorded at −110°), FNO_2 (−80°), $FONO_2$ (−100°), and $ClONO_2$ (−80°) and of solid $I(NO_3)_3$ (−90°) and infrared spectrum of solid $I(NO_3)_3$ (−196°). Spectral slit width used for the recording of the Raman spectra was 3 cm^{-1}. Traces A and B were recorded with parallel and perpendicular polarizations, respectively. The inserts represent the weaker bands recorded at higher sensitivity and larger slit width. Polarized and depolarized bands are marked by p and dp, respectively.

One mode which for model I belongs to species A″ and for model II belongs to species A′ is the antisymmetric NO_2 stretching vibration. Since no question exists concerning

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Table I. Fundamental Vibrations of NO_2, $ClNO_2$, FNO_2, $FONO_2$, and $ClONO_2$

Approx description of mode	Mode designation			Obsd freq, cm^{-1}								
	NO_2 C_{2v}	XNO_2 C_{2v}	$XONO_2$ C_s[a]	NO_2 Ir gas[b]	$ClNO_2$		FNO_2		$FONO_2$		$ClONO_2$	
					Ir gas[d]	Raman liq[e]	Ir gas[d]	Raman liq[e]	Ir gas[h]	Raman liq[e]	Ir gas[h]	Raman liq[e]
$\nu_{as}(NO_2)$	B_1 (ν_3)	B_1 (ν_4)	A'' (ν_7)	1618 [38][c] vs	1685 [38] vs	1670 (1),[f] 0.75[g]	1792 [41] vs	1800 (1), 0.75	1759 [39] vs	1760 (3), 0.75	1735 [41] vs	1728 (4) dp[i]
$\nu_s(NO_2)$	A_1 (ν_1)	A_1 (ν_1)	A' (ν_1)	1318 [12] s	1286 [10] s	1318 (8), 0.15[j] 1260 (6), 0.32	1310 [12] s	1308 (7), 0.15	1301 [10] vs	1302 (59), 0.16	1292 [12] vs	1290 (30), 0.15
$\delta_{sciss}(NO_2)$	A_1 (ν_2)	A_1 (ν_2)	A' (ν_3)	750 [10] s	793 [11] vs	787 (12), 0.07	822 [14] s	810 (21), 0.10	804 [12] s	800 (17), 0.10	780 [7] ms	779 (6), 0.45
$\nu(NX)$		A_1 (ν_3)	A' (ν_5)		370 [2.2] vs	370 (100), 0.20	568 [1] ms	555 (100), 0.37	454 [0] ms	457 (100), 0.21	434 [2] m	436 (100), 0.21
$\delta(XNO_2)$ in-plane		B_1 (ν_5)	A'' (ν_8)		408 vw	411 (8), 0.75	560		633 [1] m	636 (31), 0.75	560 [3] s	561 (20) dp[i]
$\delta(XNO_2)$ out-of-plane		B_2 (ν_6)	A' (ν_4)		652 [17] m	652 (0.3), 0.75	742 [20] mw	740 (1), 0.75	708 [18] m	708 (0.6), 0.40	711 [17] mw	710 (1), 0.40
$\nu(XY)$			A' (ν_2)						928 [0] m	929 (67), 0.11	809 [6] s	810 (49), 0.07
$\delta(NXY)$ in-plane			A' (ν_6)						303 [1] vw	304 (33), 0.24	270 vvw	267 (47), 0.10
$\tau(NX)$			A'' (ν_9)						152 vvw	165 (4), 0.75		140 (2) dp

[a] For model with *O*–Hal bond being perpendicular to ONO_2 plane. [b] E. T. Arakawa and A. H. Nielsen, *J. Mol. Spectrosc.*, 2, 413 (1958). [c] Values listed in brackets behind infrared frequencies are observed $^{14}N-^{15}N$ isotopic shifts. [d] D. L. Bernitt, R. H. Miller, and I. C. Hisatsune, *Spectrochim. Acta, Part A*, 23, 237 (1967). [e] Data from this study. [f] Values listed in parentheses are uncorrected Raman intensities. [g] *Measured depolarization ratios; depolarized bands 0.75.* [h] R. H. Miller, D. L. Bernitt, and I. C. Hisatsune, *Spectrochim. Acta, Part A*, 23, 223 (1967). [i] The experimentally observed depolarization ratios for these two bands were slightly less than 0.75. However, we believe that these two bands are depolarized and that the observed deviation is due to either experimental conditions or interference from a trace of Cl_2 which has a highly polarized Raman band at 560 cm^{-1} and from the combination band $\nu_s(NO_2) + \nu(NX)(A') = 1726$ cm^{-1}. [j] Splitting due to Fermi resonance between ν_1 and $2\nu_6$.

Table II. Low-Temperature Infrared (−196°) and Raman (−90°) Spectra (cm^{-1}) of Solid $I(NO_3)_3$

Ir	Raman	Ir	Raman
1734 m	1734 (6)	837 m	830 (10)
1715 m	1718 (7)	805 m	803 (18)
1649 m	1649 (11)	793 m	791 (13)
1587 w, sh	1588 (3)	780 w	
1568 m	1572 (18)	775 w	775 sh
1550 m	1551 (6)	754 mw	752 (57)
1485 sh	1489 (5)	729 m	729 (50)
1457 m	1459 (6)		720 sh
1400 sh, br	1402 (4)	710 w	
1313 w		702 w	702 (22)
1300 sh	1301 (10)	690 m	690 (4)
1270 vs	1267 (34)	629 ms	627 (9)
1250 w	1249 (5)		549 sh
1024 mw	1021 (11)	525 mw	524 (14)
1010 w, sh	1008 sh	512 mw	
979 vw			498 (7)
967 mw	966 (3)	490 w	
950 sh	950 sh	478 w	
906 m	902 (1)	370 mw	370 (100)
863 w		335 m	332 (60)
			310 (93)
		280 m	282 (4)
		255 m	255 (30)

the assignment of this mode, its Raman depolarization ratio should answer the planarity question. Figure 1 and Table I show that in $FONO_2$ the antisymmetric NO_2 stretch is clearly depolarized and, hence, the fluorine atom is not coplanar with the rest of the molecule.

Additional support in favor of model I can be derived from polarization data on the XNO_2 deformational modes. For model I the ONO_2 in-plane deformation should be depolarized, whereas for model II the depolarized band should be the ONO_2 out-of-plane deformation. Application of this criterion, however, requires reliable assignments for these modes which, as stated above, were not available owing to an almost complete lack of Raman data on these and related molecules. As can be seen from Figure 1 and Table I, the combination of previously reported infrared data (including $^{14}N-^{15}N$ isotopic shifts)[11,27,28] with the Raman spectra of this study allows unambiguous assignments for all fundamentals of $FONO_2$ and $ClONO_2$. These results convincingly show that the ONO_2 in-plane deformation is depolarized and that the corresponding out-of-plane mode is polarized in agreement only with model I.

Since the assignments for the halogen nitrates are self-evident from the data given in Table I, we can limit ourselves to a comparison with previously reported assignments and some specific comments. For $ClNO_2$ only one previous reference to a Raman study was found in which only one very wide diffuse line centered at about 360 cm^{-1} was observed.[29] The observation of a depolarized line at 411 cm^{-1} in the present study confirms the previous assignment of this frequency to $\nu_5(B_1)$ based on microwave data.[30]

Similarly, our Raman data for FNO_2 are in excellent agreement with the previous assignment[27] which had been confirmed by a microwave study.[31] The observed relative Raman intensities and depolarization ratios of ν_2 and ν_3, when compared to the remaining molecules of Table I, support the conclusion[27] reached by Bernitt, *et al.*, concerning the identity of ν_2 and ν_3. On the basis of the observed ^{14}N-

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^{15}N isotopic shifts, they chose from the two possible force fields[27,32] the one which results in ν_2 being mainly the NO_2 scissoring and ν_3 being mainly the NF stretching mode. A Raman spectrum of liquid FNO_2 has previously been reported[33] and is in fair agreement with our data. Two weak features at 470 and 710 cm^{-1}, respectively, in our Raman spectrum of FNO_2 require some comment. Both were also observed previously,[33] but the 470-cm^{-1} line was subsequently ascribed,[27] together with a line at 926 cm^{-1}, to $FONO_2$ impurity. Since our spectrum does not show any line at about 930 cm^{-1}, a different explanation for the 470-cm^{-1} band is required. It could possibly be due to the difference band $\nu_1 - \nu_2$ which could have borrowed intensity from ν_3 through Fermi resonance. The very weak polarized feature at about 710 cm^{-1} might similarly be explained by Fermi resonance between ν_2 and $\nu_1 - \nu_3$.

For $ClONO_2$ an incomplete Raman spectrum has previously been reported.[11] The five frequencies listed are in good agreement with our results. However, no polarization data were given and the fundamentals were assigned on the basis of the incorrect planar model II. Both of the two most recent assignments reported[11,12] for $ClONO_2$ need revision. Hohorst and DesMarteau assigned three and Miller, *et al.*, two fundamentals incorrectly. Both corrections involve the mode of greatest interest, the N–O stretching mode. The data of Table I (in particular the ^{14}N–^{15}N isotopic shifts and the polarization data) indicate that the similar frequencies of the NO_2 scissoring and the O–Cl stretching modes cause a strong mixing of the corresponding symmetry coordinates. The frequency of 140 cm^{-1} observed for the N–OCl torsional mode results in a barrier to internal rotation of 10.40 kcal mol^{-1} in good agreement with previous estimates and the value of 10.23 kcal mol^{-1} found for $FONO_2$.[11]

For $FONO_2$ no Raman data have been published except for the impurity bands[33] in the spectrum of FNO_2 which were attributed by others[11] to $FONO_2$. By analogy with $ClONO_2$ (see above), the previous assignments[11,12] need revision for three and two fundamentals, respectively.

Several general aspects deserve emphasis. (1) Whereas the XNO_2 out-of-plane deformation is of very low intensity in the Raman spectra and therefore difficult to detect, its first overtone was generally observed as a reasonably intense Raman band. This allows reliable identification of this fundamental. (ii) The symmetric NO_2 stretch and the NO_2 scissoring mode have very characteristic frequencies and occur in the ranges 1285–1300 and 780–820 cm^{-1}, respectively. Therefore, these two modes are useful for identifying XNO_2 groups. The XNO_2 out-of-plane deformation is moderately dependent and the corresponding in-plane deformation is strongly dependent on the mass of X. The large ^{14}N–^{15}N isotopic shifts (17–20 cm^{-1}) observed for the XNO_2 out-of-plane deformation indicates that in this mode mainly the N atom moves, *i.e.*, swings through the XO_2 plane. (iii) The NX stretching mode occurs for all compounds at a surprisingly low frequency, *i.e.*, 370–570 cm^{-1}. This is in agreement with the known thermal instability of these compounds. Contrary to the N–O stretching modes, the O–Hal stretching modes occur in their usual frequency range. They exhibit frequencies much higher than those of the N–O stretches indicating that the N–O single bond is by far the weakest bond in $ClONO_2$ and $FONO_2$.

The low-temperature spectra of $I(NO_3)_3$ (see Figure 1 and Table II) clearly show that the compound is not ionic. In the higher frequency range three clusters of bands centered at about 1570, 1270, and 800 cm^{-1}, respectively, occur, indicating the presence of covalent nitrato group. However, the number of individual bands within these clusters is too high and they are distributed over too wide a frequency range to be comfortably accounted for by a simple in-phase, out-of-phase coupling of the motions of monodentate or bidentate ligands.[3,34] It seems more reasonable to explain the complexity of the spectra by a polymeric structure involving bridging ligands as was previously suggested for the closely related compounds $I(ClO_4)_3$[2] and $I(SO_3F)_3$.[6] We suggest tentative assignments of the clusters to the following types of vibrations: 1750–1450 cm^{-1}, antisymmetric NO_2 stretches; 1300–1200 cm^{-1}, symmetric NO_2 stretches; 830–780 cm^{-1}, NO_2 scissoring; 750–690 cm^{-1}, IO stretches; 370–300 cm^{-1}, N–O stretches. The significant decrease in the N–O stretch frequencies, when compared to those in $FONO_2$ (457 cm^{-1}) and $ClONO_2$ (436 cm^{-1}), indicates increasing polarity of the Hal–O bonds within this series. This is generally true for related compounds and is caused by the increasing electronegativity difference between the halogen and the ligands with increasing atomic weight of the halogen.

Acknowledgment. We are indebted to Dr. L. R. Grant for helpful discussions and to the Office of Naval Research, Power Branch, for financial support.

Registry No. $ClNO_2$, 13444-90-1; FNO_2, 10022-50-1; $FONO_2$, 7789-26-6; $ClONO_2$, 14545-72-3; $I(NO_3)_3$, 52760-88-0; $CF_3I(NO_3)_2$, 52760-89-1.

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Reactions of Ozone with Covalent Hypohalites

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The reactions of pure ozone with a series of covalent hypohalites were examined. With $ClOClO_3$, $ClOSO_2F$, $BrONO_2$, and $BrOClO_3$ oxidative oxygenations of the terminal halogen occurred giving respectively $O_2ClOClO_3$, O_2ClOSO_2F, O_2BrONO_2, and the new compound $O_2BrOClO_3$. Similar conditions with $ClONO_2$ produced exclusively $NO_2{}^+ClO_4{}^-$, constituting a new synthesis of this powerful oxidizer. With $ClOCF_3$ and $BrOSO_2F$ no oxidation was noted. For comparison, chlorine dioxide was also oxidized to chlorine hexoxide using the same experimental conditions. The nature of the products prepared by different methods and all having the empirical composition Cl_2O_6 was investigated by mass and infrared matrix-isolation spectroscopy. It is concluded that above its melting point "Cl_2O_6" has the oxygen-bridged chloryl perchlorate structure $O_2ClOClO_3$. The infrared spectrum of matrix-isolated ClO_2 was also recorded and its $^{35}Cl-^{37}Cl$ isotopic shifts were measured.

Introduction

Covalent hypohalite compounds are highly reactive and synthetically useful reagents.[1] However, nearly all of the known chemistry of these materials centers on their reactions involving cleavage of the halogen-oxygen bond. For example, $BrOSO_2F$ was used[2] to replace the chlorines in CCl_4 giving $C(OSO_2F)_4$, while $ClOSO_2F$ was employed[3] to produce $ClOClO_3$ from $CsClO_4$. In other cases, $ClOSO_2F$[4] and $ClOClO_3$[5] were shown to add across olefinic double bonds forming $Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}OSO_2F$ and $Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OClO_3$ derivatives. It appeared interesting to synthesize the corresponding halites, halates, or perhalates by oxidative oxygenation of the terminal halogen. The only report of such an oxidation was given by Schmeisser and Taglinger[6] on the ozonization of $BrONO_2$ at −78° according to

$$BrONO_2 + 2O_3 \rightarrow O_2BrONO_2 + 2O_2$$

This successful synthesis of bromyl nitrate suggested the possibility of carrying out similar reactions of O_3 with other XO species. Accordingly, we examined the reactions of ozone with $ClOClO_3$, $ClOSO_2F$, $ClONO_2$, $ClOCF_3$, $BrOClO_3$, and $BrOSO_2F$. For comparison, the known[6,7] oxidative ozonizations of $BrONO_2$ and ClO_2 were carried out under our reaction conditions.

Experimental Section

Apparatus and Materials. The equipment used in this work has previously been described.[8] Mass spectra were recorded on a Quad 300 (Electronic Associates, Inc.) quadrupole mass spectrometer using a passivated all stainless steel inlet system. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer using the previously described matrix-isolation technique.[9] Literature methods were used to synthesize $ClOClO_3$,[3] $ClOSO_2F$,[8] $ClONO_2$,[10] $ClOCF_3$,[11] ClO_2,[12] $BrOClO_3$,[13] and $BrONO_2$.[6] Since hypobromites cannot be transferred without decomposition, they were synthesized directly in the ozonization vessel from Br_2 or BrCl and a slight excess of the corresponding hypochlorites. The undesired by-products and impurities were removed prior to addition of solvent and ozone.

Ozone was prepared by glow discharge of O_2 (Matheson Co.) in a Pyrex U tube cooled with liquid nitrogen. A 15-kV power supply provided the discharge through internal copper electrodes and the conversion of O_2 to O_3 was followed manometrically. After volumetric measurement, the O_3 was immediately loaded into a precooled reactor. Approximately 1 mmol of O_3 was obtained from each batch. Larger quantities could be easily prepared but were avoided for safety considerations.

General Method. Essentially the same technique was applied in all the reactions. The freshly prepared, purified, and measured hypohalite was placed in the reactor at −196°. Solvent CF_3Cl or $CFCl_3$, when used, was added, followed by a measured amount of O_3 both being condensed into the reactor cooled to −196°. The closed reactor was maintained at the desired reaction temperature in a freezer for a specified period. Subsequently, the reactor was recooled to −196° and the by-product O_2 pumped away and measured. Solvent, unreacted starting material, and products were separated by fractional condensation in a series of U traps cooled to appropriate temperatures. Product identification was based on combinations of infrared and mass spectroscopy, vapor pressure measurements, and elemental analyses.

Discussion

Caution! Most of the hypohalites employed in this study are potential explosives. Also, the use of pure ozone can be hazardous and two explosions were encountered with it. Safety precautions must be adhered to when working with these materials and the reactions should be limited a millimole scale.

The results of representative reactions are summarized in Table I. The nature of the reactor (*i.e.*, 304 or 316 stainless steel cylinders and FEP Teflon or sapphire tubes all equipped with stainless steel valves) did not appear to influence the course of the reactions.

The $ClOClO_3$-O_3 System. For chlorine perchlorate it was found that oxidation occurred under a variety of conditions according to the equation

$$ClOClO_3 + 2O_3 \rightarrow O_2ClOClO_3 + 2O_2$$

A virtually quantitative conversion of $ClOClO_3$ to Cl_2O_6 was achieved as was also established by a very good oxygen material balance. When short reaction times were used, most of the unreacted O_3 could be recovered undecomposed. This indicates that each O_3 molecule contributed only one oxygen atom to converting Cl_2O_4 to Cl_2O_6. Large excess of O_3 did not cause any further oxidation of $O_2ClOClO_3$. Thus, $O_3ClOClO_3$ (Cl_2O_7) was never observed in these systems.

Properties and Structure of Cl_2O_6. The exact nature of "Cl_2O_6" has as yet not been established. The two most

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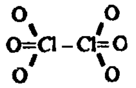
Table I. Ozone Reactions

Hypohalite (mmol)	Amt of O_3, mmol	Solvent	Temp, °C	Time, hr	Products[a] (mmol)
$ClOClO_3$ (1.30)	2.86	None	−78	24	Cl_2O_6 (0.47), $ClOClO_3$ (0.83)
$ClOClO_3$ (1.35)	3.24	CF_3Cl or none	−45	40	Cl_2O_6 (1.35)
ClO_2 (1.23)	3.16	None	−45	18	Cl_2O_6 (0.61)
$ClOSO_2F$ (1.06)	2.30	None	−45	70	ClO_2SO_3F (1.03)
$ClONO_2$ (0.73)	2.55	None	−45	66	NO_2ClO_4 (0.39), $ClONO_2$ (0.33)
$ClONO_2$ (1.08)	3.24	CF_3Cl	−45	42	NO_2ClO_4 (0.74), $ClONO_2$ (0.34)
$ClONO_2$ (1.03)	4.04	CF_3Cl	−45	72	NO_2ClO_4 (0.92), Cl_2
$ClOCF_3$ (1.02)	2.60	None	−45	300	$ClOCF_3$ (0.98), COF_2
$BrOClO_3$ (1.59)	2.98	None	−45	72	$Br_2 + Cl_2 + BrCl$ (1.58), O_2 (7.41)
$BrOClO_3$ (1.29)	3.06	CF_3Cl	−45	72	BrO_2ClO_4 (1.28)
$BrONO_2$ (1.06)	2.80	$CFCl_3$	−45	72	BrO_2NO_3 (1.01)
$BrONO_2$ (1.00)	3.15	$CFCl_3$	−23	100	O_2 (5.42), Br_2, NO_2
$BrOSO_2F$ (1.25)	3.37	None	−45	130	O_2 (5.14), $BrOSO_2F$ (1.20), Br_2, $S_2O_6F_2$

[a] Except where noted, by-product O_2 was always found in ratios expected for nO_3 + substrate → nO_2 + substrate-O_n in addition to small amounts of O_2 resulting from the decomposition of O_3.

likely structures are the symmetric Cl–Cl-bridged model I and the asymmetric oxygen-bridge model II.[14] Another structure suggested[15] as very probable is the double-oxygen-bridged model III. However, several severe shortcomings make this model unlikely. In both versions, IIIA and IIIB, at least one Cl must assume an energetically unfavorable pentacoordination.[16] In addition, IIIA would be a diradical which disagrees with the diamagnetism observed[17] for pure Cl_2O_6.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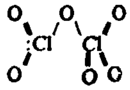
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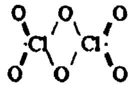
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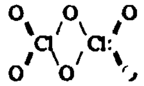
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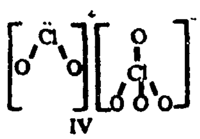
IV

Most frequently, Cl_2O_6 is considered[14,15] to possess structure I based on early work[18] which reported the detection of considerable paramagnetism in the liquid and solid phases. This paramagnetism was attributed to the ClO_3 radical being in equilibrium with the Cl_2O_6 dimer according to $Cl_2O_6 \rightleftharpoons 2ClO_3$. The surprisingly low value of 1.5 kcal/mol for the "dissociation energy" of this supposed quilibrium was generally interpreted as an indication for Cl_2O_6 having structure I with an extremely weak Cl–Cl bond. However, more recently it was shown[17] that the paramagnetic species present in small concentrations in condensed Cl_2O_6 is ClO_2 and that the uv-visible spectrum attributed to gaseous ClO_3 closely resembles that of ClO.[15] Chlorine trioxide radicals are very difficult to obtain and were found in Cl_2O_6 only under extreme conditions, *i.e.*, at −196° after irradiation by ^{60}Co γ irradiation.[17] Additional doubts about the validity of model I stem from its reaction chemistry[14] and the vibrational spectrum of the solid[19] which suggest the ionic structure $ClO_2^+ \cdot ClO_4^-$ (model IV). In view of the different known synthetic methods[3,7,14] for preparing a product of the composition Cl_2O_6 and of the known existence of two forms of $(ClO_3)_n$, *i.e.*, ClO_2[14] and oxygen bridged Cl_2O_4,[3] it appeared desirable to establish the identity of the various Cl_2O_6 compositions and, if possible, to determine the structure of the isolated free species. For this purpose we have studied samples of Cl_2O_6 prepared by three different synthetic methods (eq 1–3).

$$2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2 \quad \text{(ref 7)} \tag{1}$$

$$ClOClO_3 + 2O_3 \rightarrow Cl_2O_6 + 2O_2 \quad \text{(this work)} \tag{2}$$

$$ClOClO_3 \rightarrow Cl_2O_6 \quad \text{(ref 3)} \tag{3}$$

The identical nature of the different Cl_2O_6 samples was established by their elemental analyses after decomposition at elevated temperature, their physical appearance, and properties. They were orange solids melting near 0° to form dark red liquids. They exhibited only several millimeters vapor pressure near ambient temperature. On standing at 22°, slow gas evolution was noted and the gas pressure increased gradually. This was found to be caused by the decomposition of Cl_2O_6 resulting in the formation of ClO_2, Cl_2, and O_2.

Spectroscopic Studies. Additional support for the various Cl_2O_6 compositions being identical was obtained by mass and infrared matrix-isolation spectroscopy. Previous reports on the mass spectrum[20,21] of Cl_2O_6 show some discrepancy. Cordes and Smith[20] observed a weak ClO_3^+ ion as the highest *m/e* from Cl_2O_6. However, Fisher[21] found no ClO_x^+ ions above ClO_2^+, but his samples showed appreciable amounts of $HClO_4$ as impurity. In this work, samples without $HClO_4$ gave a small (5% of base) peak for ClO_3^+. Even samples with $HClO_4$ exhibited a modest but reproducible ClO_3^+ peak after the spectrum was corrected for that impurity.

For the infrared study, Cl_2O_6 samples were isolated in an N_2 matrix (MR 1:1000) at 4°K. All three samples exhibited the same characteristics. Unfortunately, the spectra were rather complex. In agreement with the previous esr study,[17] it was found that the gas phase above liquid Cl_2O_6 consisted mainly of ClO_2. The infrared spectrum of matrix-isolated ClO_2 closely corresponded to the well-known gas-phase spectrum.[22] The ^{35}Cl-^{37}Cl isotopic shifts were measured for the matrix-isolated species. They are compared in Table II with the previous measurements[22-24] which showed considerable discrepancy.

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Table II. ^{35}Cl-^{37}Cl Isotopic Shifts (cm^{-1}) of ClO_2

	^{35}Cl freq	Isotopic shifts				
					Ref 24	
	This study	This study	Ref 22	Ref 23	Ir	Uv
ν_1	950	5.8 ± 0.2		6.41	4.8	5.7
ν_2	452	2.9				3.3
ν_3	1104	11.4	11.5		12.7	

No evidence could be found in our spectra for bands showing the frequencies and intensities expected for a free ClO_3 radical. This result agrees with the previous esr study[17] and indicates either that Cl_2O_6 does not appreciably dissociate into ClO_3 or that the ClO_3 radical is highly unstable and rapidly decomposes into ClO_2 and oxygen. The first alternative is more in agreement with our expectations for a structure containing a strongly polarized oxygen bridge (see below). Thus, the O_2Cl-O bond should be considerably weaker than the O-ClO_3 bond and, therefore, the former should preferentially break. This should result in the formation of ClO_2 and (unstable) ClO_4 instead of ClO_3 radicals.

In addition to ClO_2, the matrix-isolation spectra always exhibited bands due to $HOClO_3$.[25] To positively identify the bands due to $HOClO_3$ in an N_2 matrix, we have prepared a sample of pure $HOClO_3$ and recorded its spectrum. In addition to bands attributable to the monomer, features due to associated $HOClO_3$ were observed. The intensity of the latter was a function of the dilution ratio.

To suppress the bands due to ClO_2 and $HOClO_3$, N_2 was rapidly swept over liquid Cl_2O_6 and immediately frozen out on the cold CsI window of the ir cell. Under these conditions, at least two novel species were observed in addition to ClO_2 and $HOClO_3$. These two species, designated A and B, showed the following principal absorptions (cm^{-1}): A, 1275 (vs), 1043 (s), 1041 (m), 1008 (w), 950, 702 (vs), 658 (w), 648 (w), 620 (w), 585 (s), 512 (w); B, 1240 (s), 1028 (vs), 624 (vs), 484 (vs), 374 (vs). These bands exhibit frequencies and to some extent ^{37}Cl isotopic splittings in agreement with those expected for covalent chlorato or perchlorato compounds. In particular, species A shows a very intense band in the frequency region expected[26] for an antisymmetric stretch of a Cl-O-Cl bridge in addition to bands occurring in the ClO_3 and ClO_2 stretching modes region.[26] Therefore, this set of bands might be due to a Cl-O-Cl-bridged Cl_2O_6 species, such as model II. [The set of bands ascribed to species B somewhat resembles that of $FClO_2$[27] shifted to a lower frequency. This indicates an $XClO_2$ type species with X being less electronegative than F. Possibly, this species could be $HOClO_2$ which might be expected from the hydrolysis of $O_2ClOClO_3$ according to $O_2ClOClO_3 + H_2O \rightarrow HOClO_3 + HOClO_2$.] However, unambiguous identification and assignment of the bands are not possible owing to the size and low symmetry of these species and to the complexity of the rest of the spectrum.

In summary, our spectroscopic studies indicate that the three "Cl_2O_6" species obtained by the three different synthetic methods are indeed identical. Furthermore, the low-temperature, high-yield oxidation of the Cl-O-Cl-bridged starting material $ClOClO_3$ combined with the results from the other more recent studies[14,15,17,19] show that Cl_2O_6 has the oxygen-bridged structure II and not the Cl-Cl-bridged structure I. Therefore, the assumption of a previously postulated[14] rearrangement of Cl_2O_6 from model I to model II used to reconcile its reaction chemistry with a basic Cl-Cl-bridged structure is unwarranted. On the other hand, for the oxygen-bridged structure II transformation into the ionic structure IV should be very facile requiring no significant rearrangements. The low volatility of Cl_2O_6, its high melting point, and its readiness to change to an ionic structure in the solid also indicate for the liquid a strong polarization of the Cl-O-Cl bridge in the direction toward $O_2Cl^+OClO_3^-$. This structural behavior of Cl_2O_6 closely resembles that of N_2O_5 which in the free state has a covalent oxygen-bridged structure but in the solid state has the ionic structure $NO_2^+NO_3^-$.[28]

The $BrOClO_3$-O_3 System. The novel process for oxygenation of the terminal chlorine of $ClOClO_3$ was applied to $BrOClO_3$. Surprisingly, it was found that neat O_3 and $BrOClO_3$ in the temperature range of −78 to −45° reacted to cause their complete degradation to the elements. An effort was therefore made to moderate the reaction through the use of CF_3Cl as a solvent. This was successful and the reaction observed at −45° was

$$BrOClO_3 + 2O_3 \rightarrow O_2BrOClO_3 + 2O_2$$

This stoichiometry was confirmed by an excellent oxygen material balance and by elemental analysis of the product which showed six oxygen atoms were present for each BrCl. The novel compound $O_2BrOClO_3$ is a bright orange solid that does not melt below −35°. Since decomposition begins at higher temperatures and owing to its nonvolatility, we were unable to determine reliably other properties. Additional proof for its composition was obtained by a displacement reaction with FNO_2 carried out at −45°. The following reaction was observed

$$O_2BrOClO_3 + FNO_2 \rightarrow NO_2ClO_4 + [FBrO_2]$$

The displacement was slow, requiring several days. While the solid nitronium perchlorate was found in quantitative yield (1.35 mmol of NO_2ClO_4 from 1.35 mmol of $O_2BrOClO_3$), the $FBrO_2$ decomposed to the elements.

The $ClOSO_2F$-O_3 and $BrOSO_2F$-O_3 Systems. The reaction of chlorine fluorosulfate and ozone was examined in view of the above results and the fact that the predicted product (O_2ClOSO_2F) is well known from other routes.[14,29] The following reaction was observed

$$ClOSO_2F + 2O_3 \rightarrow O_2ClOSO_2F + 2O_2$$

Yields above 90% were readily realized at temperatures up to 0°. The use of a solvent was not required and was not investigated. With a large excess of O_3 additional oxygen uptake was not observed.

Bromine fluorosulfate and ozone reacted only incompletely. The main reaction was decomposition of O_3 to O_2 accompanied by some degradation of the $BrOSO_2F$. No evidence for O_2BrOSO_2F was obtained.

The $ClONO_2$-O_3 System. Ozone and chlorine nitrate did not react at −78° in the absence of a solvent. However, when a solvent was used or the temperature was raised to −45°, chlorine was surprisingly oxidized to the +VII oxidation state as shown

$$ClONO_2 + 3O_3 \rightarrow NO_2^+ClO_4^- + 3O_2$$

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Thus, the covalent hypochlorite group was oxidized to the perchlorate anion. An excellent material balance was obtained for this reaction. Again only one oxygen from each ozone was added to the substrate. Furthermore, it was found that with a deficiency of O_3 or with short reaction periods, the only products were nitronium perchlorate and unreacted chlorine nitrate. Other intermediate oxidation products were not observed and, hence, must have been more reactive than $ClONO_2$. The white solid was readily identified as $NO_2^+ClO_4^-$ by its infrared spectrum[30] and comparison to an authentic sample. This reaction represents a new process for preparing nitronium perchlorate. Its main advantage consists of the elimination of ClO_2, one of the two shock-sensitive materials required for the conventional[31] $NO_2^+ClO_4^-$ synthesis.

The $BrONO_2$-O_3 System. The $BrONO_2$-O_3 reaction has previously been reported[6] to yield O_2BrONO_2. We reinvestigated this system since it now appeared to be a promising synthetic route to the novel and interesting compound $NO_2^+BrO_4^-$. All effort to this end, however, failed since at or below −45°, the only product was O_2BrONO_2, while at higher temperatures, degradation of the bromyl intermediate was encountered.

The CF_3OCl-O_3 System. Prolonged contact of trifluoromethyl hypochlorite with neat ozone at −45° did not result in any oxygenation of the chlorine or other reaction. Thus, CF_3OClO_3, a compound recently obtained by another synthetic approach,[32] was not observed.

General Aspects. Comparison of the results of the present study raises an interesting question. Whereas covalent hypochlorite groups are generally oxidized by O_3 to the O_2ClO group, *i.e.*, to chlorine (+V), the chlorine in $ClONO_2$ is oxidized to the +VII state. This is surprising since $ClOClO_3$ and $ClONO_2$ are both covalent hypochlorites of similar structure and reactivity, and the perchlorato and nitrato group are of similar electronegativity. Comparison of the resulting ozonization products, however, reveals a marked difference. The products, in which the original hypochlorite chlorine is oxidized to the +V oxidation state, are mainly covalent and polarized toward the $ClO_2^+X^-$ type structure where X^- can be, for example, ClO_4^- or SO_3F^-. In the case of $ClONO_2$, however, the hypochlorite chlorine ends up in the anion of the product $NO_2^+ClO_4^-$. Since cations are more difficult to oxidize and are stronger oxidizers than anions of the same oxidation state,[16] oxidation of $ClONO_2$ to $NO_2^+ClO_4^-$ is still possible, while formation of a covalent O_3ClO group or of the hypothetical ClO_3^+ cation is not. The ease of NO_2^+ formation is due to the fact that XNO_2 type compounds, such as FNO_2, are strong Lewis bases, whereas $XClO_2$ type compounds are amphoteric.[14,33]

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Registry No. O_3, 10028-15-6; $ClOClO_3$, 27218-16-2; $O_2ClOClO_3$, 52225-66-8; $BrOClO_3$, 32707-10-[illegible]; $O_2BrOClO_3$, 52225-67-9; $ClOSO_2F$, 13997-90-5; O_2ClOSO_2F, 24114-30-5; $ClONO_2$, 14545-72-3; $NO_2^+ClO_4^-$, 17495-81-7; ClO_2, 10049-04-4.

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Halogen Perchlorates. Reactions with Fluorocarbon Halides

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The reactions of chlorine perchlorate and bromine perchlorate with numerous fluoroalkyl halides were examined. In the case of fluorocarbon iodides, these reactions were generally found to produce high yields of the novel fluorocarbon perchlorates CF_3ClO_4, $CF_3CF_2ClO_4$, n-$C_7F_{15}ClO_4$, $O_4ClCF_2CF_2ClO_4$, and $ICF_2CF_2ClO_4$. Important insight into the mechanism of formation of these compounds was obtained through the isolation of complex intermediates such as $(CF_3)_2CFI(ClO_4)_2$ and n-$C_7F_{15}I(ClO_4)_2$. Based on their vibrational spectra, these intermediates have the ionic structure $[(R_f)_2I]^+[I(ClO_4)_4]^-$. Fluorocarbon bromides reacted less readily but sometimes did produce perchlorate derivatives such as $(O_4ClCF_2CFBr-)_2$, $CF_3CFBrCF_2ClO_4$, and $BrCF_2CF_2ClO_4$. Neither mono nor di, primary nor secondary chlorine contained in saturated R_fCl materials interacted with these halogen perchlorates. These and other related reactions are discussed and characteristic data are given for this new and interesting class of compounds.

Introduction

Until recently the study of covalent perchlorates was restricted to a few derivatives,[1,2] mainly inorganic, because of the extreme shock sensitivity of the known hydrocarbon derivatives. Also the available intermediates for forming covalent perchlorates were quite limited and themselves difficult to manipulate. With the discovery of chlorine perchlorate ($ClOClO_3$ or Cl_2O_4)[3] and bromine perchlorate ($BrOClO_3$ or $BrClO_4$),[4] useful reagents became available for the synthesis of new perchlorate species. This has been realized and has led to the preparation of the new inorganic materials $I(ClO_4)_3$,[5] $CsI(ClO_4)_4$,[5] and $CsBr(ClO_4)_2$[6] and improved syntheses of $Ti(ClO_4)_4$ and $CrO_2(ClO_4)_2$.[7] Furthermore, the reactions of Cl_2O_4 and $BrClO_4$ with perhaloolefins were shown[8] to produce the previously unknown perhaloalkyl perchlorates, in high yield, as illustrated

$$XClO_4 + {>}C{=}C{<} \rightarrow X-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-ClO_4 \quad (X = Cl, Br)$$

Of paramount interest though, was the finding that these fluorocarbon perchlorates were stable, tractable species quite unlike their hydrocarbon and some of their inorganic analogs. Thus it was decided to investigate further this new class of compounds and, in particular, to search for additional preparative routes which result exclusively in the introduction of a perchlorate group without simultaneous addition of bromine or chlorine atoms.

Experimental Section

Caution! The halogen perchlorates and the alkyl perchlorates are potential explosives. Safety precautions should be taken in handling and using these materials.

Apparatus and Materials. The equipment used in this work has been described.[5] Chlorine perchlorate[3] and bromine perchlorate[4] were prepared as reported. The fluoroalkyls were purchased (except where noted) and purified by fractional condensation. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å line of an Ar ion laser as the exciting line and a Claassen filter[9] for the elimination of plasma lines. Sealed quartz tubes (~2-mm i.d.) or glass melting point capillaries were used as sample containers in the transverse-viewing, transverse-excitation technique. While exposed to the laser beam, the sample tube was kept below −80° in a vacuum-jacketed flow tube by flowing a stream of dry N_2 through it. Mass spectra were recorded using a Quad 300 (Electronic Associates, Inc.) quadrupole mass spectrometer equipped with a passivated all stainless steel inlet system. The ^{19}F nmr spectra were recorded on a Varian Model DA60 spectrometer at 56.4 MHz using $CFCl_3$ as internal standard. Chemical shifts and coupling constants were determined by the side-band technique. Analytical data were obtained using Orion specific ion electrodes (F^-, Cl^-, or ClO_4^-) and solutions prepared after Na fusion or hydrolysis. These data together with some physical properties are summarized in Table I.

CF_3I–Cl_2O_4 Reactions. Trifluoromethyl iodide (2.02 mmol) and Cl_2O_4 (4.24 mmol) were combined at −196° in a 30-ml stainless steel cylinder which was subsequently slowly warmed to −45° during several days. Recooling to −196° showed the absence of noncondensable products. While rewarming to room temperature, the volatile products evolved were separated by fractional condensation. These consisted essentially of Cl_2 (2.07 mmol), trapped at −196°, and CF_3ClO_4 (2.01 mmol), trapped at −112°; the yield of CF_3ClO_4 was 99% based on CF_3I. The molecular weight observed by vapor density measurements was 167 *vs.* a value of 168.4 calculated for CF_3ClO_4. Measured quantities of CF_3ClO_4 and $CFCl_3$ reference were used to confirm by ^{19}F nmr peak area ratio measurements that the compound contains three fluorine atoms per molecule. The purity of the product was further indicated by its tensiometric homogeneity. The mass spectrum showed *m/e* peaks for $CF_3ClO_4^+$ (parent), $CF_3ClO_2^+$, CF_3ClO^+, ClO_3^+ (base peak), CF_3^+, ClO_2^+, COF_2^+, ClO^+, CF_2^+, COF^+, CO_2^+, O_2^+, CF^+, and CO^+ ions.

On standing at room temperature, the nonvolatile product of this reaction, "$IClO_4$," evolved O_2, Cl_2, and Cl_2O_7 in a manner similar to $I(ClO_4)_3$[5] eventually leading to the formation of I_2O_5. Occasionally the reaction of CF_3I with Cl_2O_4 deflagrated, particularly when warmed up too rapidly. The deflagration resulted in the generation of much O_2 (*e.g.*, 9.4 mmol from 6.0 mmol of Cl_2O_4), CO_2, COF_2,

Table I. Physical Properties and Analytical Data of Several Novel Fluorocarbon Perchlorates

Compd[a]	Vapor pressure	ΔS, eu	ΔH_v, kcal/mol	Elemental analysis, %			
				Calcd		Found	
				F	Cl	F	Cl
CF_3ClO_4	7.4828, 1301.0 (9.5[b])	23.3	5.94	33.84	21.04	33.3	21.5
$CF_3CF_2ClO_4$	7.6356, 1430.8 (27.7[b])	21.8	6.54	43.49	16.23	42.9	16.0
n-$C_7F_{15}ClO_4$	2[c]			60.84	7.57	60.4	7.42
$ICF_2CF_2ClO_4$	15			23.29	10.86	22.9	10.9
$BrCF_2CF_2ClO_4$	74			27.20	12.69	27.1	12.5
$(-CFBrCF_2ClO_4)_2$	<1			21.89	13.62	21.4	13.8
$C_4F_6(ClO_4)_2Cl_2$	2			26.40	32.84	26.3	32.7

[a] All compounds listed are clear, colorless liquids. [b] $\log P_{mm} = A - B/T(°K)$; bp, °C. [c] In mm at 20°.

Cl_2, and a trace of CF_3Cl. All the iodine was recovered as I_2 and IF_5. No solid residue was produced and no CF_3ClO_4 was obtained.

Trifluoromethyl perchlorate (0.456 mmol) was loaded into a 10-ml cylinder containing ~1 g of CsF cooled at −196°. The closed cylinder was heated at 100° for 18 hr prior to fractionation of the products. Most of the CF_3ClO_4 was recovered (0.321 mmol) unchanged. The decomposition products were $FClO_3$ (0.134 mmol) and COF_2 (0.134 mmol obtained on vacuum pyrolysis of the $Cs^+OCF_3^-$ salt formed).

CF_3CF_2I–Cl_2O_4 Reactions. Perfluoroethyl iodide (1.97 mmol) and Cl_2O_4 4.65 mmol) were allowed to react as described for CF_3I but during the work-up the reactor was initially not warmed above −45°. The only volatile species found were Cl_2 (2.03 mmol) and some Cl_2O_4. However, after 3 days at −25°, the reactor was again examined and additional volatile materials were present. These were $CF_3CF_2ClO_4$ (1.84 mmol) and small amounts of Cl_2 and unreacted CF_3CF_2I. The yield was 94% and the vapor density molecular weight was 216; calculated for $CF_3CF_2ClO_4$, 218.4. The mass spectrum of $CF_3CF_2ClO_4$ exhibited prominent *m/e* peaks for the fragment ions $CF_2ClO_4^+$, $C_2F_5^+$, ClO_3^+, CF_3^+ (base peak), ClO_2^+, ClO^+, CF_2^+, COF^+, CF^+, and CO^+. The "$IClO_4$" solid left in the reactor was as described before.

Other examples of this reaction which were worked up somewhat differently gave the same final result. However, at the intermediate stages there was even more definite evidence for the formation of an $R_fI(ClO_4)_2$ complex. For example, at the completion of the −45° reaction, the reaction cylinder was warmed directly to room temperature while pumping and fractionating the volatiles. After 1.5 hr the cylinder was closed and the fractions obtained were examined. These were one Cl_2 for each C_2F_5I and a little $FClO_3$ but no R_f species from a starting mixture of 1:2 C_2F_5I–Cl_2O_4. After 2 hr at room temperature, the reactor was reopened and was now found to contain "free" $CF_3CF_2ClO_4$ in approximately 95% yield, together with trace amounts of Cl_2 and Cl_2O_7. The stability of $CF_3CF_2ClO_4$ is shown by the fact that a 0.598-mmol sample did not react on contact with 1.6 g of CsF for 1 week at ambient temperature. However, heating the mixture at 120° for 12 hr completely decomposed the perchlorate to $FClO_3$ (0.60 mmol) and CF_3CFO (0.60 mmol obtained on vacuum pyrolysis of the formed $Cs^+CF_3CF_2O^-$).

$(CF_3)_2CFI$–Cl_2O_4 Reactions. 2-Iodoperfluoropropane was prepared from perfluoropropene and I_2–IF_5 by a method similar to that previously reported[10] and its identity was verified by infrared, mass, and ^{19}F nmr spectra. Chlorine perchlorate (3.31 mmol) and $(CF_3)_2CFI$ (1.53 mmol) were allowed to react as in the preceding examples. Fractional condensation of the volatile products on work-up showed Cl_2 (1.55 mmol), Cl_2O_4 (0.36 mmol), and $(CF_3)_2CFI$ (0.09 mmol). The nonvolatile residue weighed 0.703 g, and it did not decompose on standing. The weight calculated for 1.44 mmol of $(CF_3)_2CFI(ClO_4)_2$ was 0.711 g. Examination of the residue in the drybox showed a loose, finely powdered, white solid, mp 71–73° dec. *Anal.* Calcd for $C_3F_7I(ClO_4)_2$: ClO_4, 40.2. Found: ClO_4, 40.6. The solid fumes in air and liberates some I_2 together with oily droplets on treatment with water. When heated at 105° for 16 hr in a 10-ml cylinder, 0.62 mmol produced O_2 (1.13 mmol) and 2.42 mmol of the condensable species CO_2 and Cl_2 with some COF_2 and small amounts of CF_4 and C_2F_6. Iodine was found exclusively as I_2 and IF_5. No solid products were recovered.

ICF_2CF_2I–Cl_2O_4 Reactions. 1,2-Diiodotetrafluoroethane was prepared from $CF_2{=}CF_2$ and I_2. The purified product was allowed to react with 4–6-fold molar equivalents of Cl_2O_4 at and below −45°. Generally the chlorine by-product obtained indicated that even after 1 week only slightly more than one I per ICF_2CF_2I had reacted. In addition to unreacted ICF_2CF_2I and Cl_2O_4, typical products included $ICF_2CF_2ClO_4$ (~60%), ICF_2CF_2Cl (~20%), and Cl_2O_7. Purification of $ICF_2CF_2ClO_4$ was difficult, especially the removal of Cl_2O_7. The $ICF_2CF_2ClO_4$ is a clear, colorless liquid stable at ambient temperature. Under dynamic vacuum it slowly passes through traps cooled to −45°. This compound gave a most definitive mass cracking pattern including an easily detectable parent ion. Important *m/e* peaks noted corresponded to the ions $IC_2F_4ClO_4^+$, $IC_2F_4^+$, $IC_2F_3O^+$, $C_2F_4ClO_4^+$, CF_2I^+, $C_2F_4^+$, $C_2F_3O^+$, ClO_3^+, CF_3^+ (base peak), ClO_2^+ COF_2^+, ClO^+, CF_2^+, COF^+, and CF^+.

When carried out at −25° the reaction deflagrated, giving the usual O_2, Cl_2, CO_2, COF_2 and I_2–IF_5. No nonvolatile products were recovered. With the aid of a solvent (FC-78, 3M Co.) reactions of Cl_2O_4 with both ICF_2CF_2I and $ICF_2CF_2ClO_4$ were carried out at −45°. Again poor results were obtained and poor yields of R_fClO_4 but minor amounts of a viscous, colorless liquid of low volatility (~2 mm at 20°) were recovered. Based on its ^{19}F nmr and infrared spectrum, this material has been identified as the bisperchlorate $O_4ClCF_2CF_2ClO_4$.

$ICF_2CF_2CF_2I$–Cl_2O_4 Reaction. 1,3-Diiodoperfluoropropane was prepared as reported[11] from $AgO_2CCF_2CF_2CF_2CO_2Ag$ and I_2. A 1.29-mmol sample of it was allowed to react with 5.63 mmol of Cl_2O_4 at −45° for several days. Products volatile at −45° consisted of Cl_2 (2.91 mmol) and Cl_2O_4 (0.47 mmol). However when the closed reactor was allowed to warm to room temperature for 4 hr, the nonvolatile product $(O_4Cl)_2ICF_2CF_2CF_2I(ClO_4)_2$, according to the observed stoichiometry, deflagrated. The deflagration products were O_2 (~7 mmol), Cl_2, CO_2, COF_2, CF_4, and some C_2F_6 (~6 mmol total), together with I_2 and IF_5. No nonvolatile species was observed.

n-$C_7F_{15}I$–Cl_2O_4 Reactions. n-Perfluoroheptyl iodide (1.42 mmol) and Cl_2O_4 (3.60 mmol) were allowed to react at −45° for several days and gave Cl_2 (1.48 mmol) and Cl_2O_4 (0.66 mmol) as products volatile at this temperature. After several hours of pumping at room temperature, the white solid product left in the reactor weighed 0.985 g. The weight calculated for 1.42 mmol of $C_7F_{15}I(ClO_4)_2$ was 0.987 g. The solid had a melting point with decomposition of 56–58° and it fumed in air. *Anal.* Calcd for $C_7F_{15}I(ClO_4)_2$: ClO_4, 28.6. Found: ClO_4, 28.3. Upon standing for several days at ambient temperature the solid appeared shiny and sticky as if it were decomposing. Therefore it was heated to 40° under vacuum while collecting the volatile material in cold traps. Traces of Cl_2 and Cl_2O_7 were obtained, along with a clear, colorless, mobile liquid. The mass spectrum of this liquid resembled those reported[12] for n-C_7F_{15}– compounds. Some of the more important characteristic peaks were attributable to the ions $C_7F_{14}ClO_4^+$, $C_7F_{15}O^+$, $C_7F_{15}^+$, $C_nF_{2n-1}O^+$ and $C_nF_{2n-1}^+$ (n = 3–6), and ClO_x^+ (x = 1–3). This liquid was identified as $C_7F_{15}ClO_4$.

A sample of $C_7F_{15}ClO_4$ (0.22 mmol) was heated with 1.1 g of CsF for 1 hr at 110°. This produced $FClO_3$ (0.22 mmol) and $C_6F_{13}CFO$ (0.21 mmol obtained on pyrolysis of the $Cs^+C_7F_{15}O^-$ salt formed). The n-perfluoroheptoyl fluoride was identified on the base of its infrared and mass spectrum, which included the parent ion peak, $C_7F_{14}O^+$.

$BrCF_2CFBrCFBrCF_2Br$–Cl_2O_4 Reactions. Perfluorobutadiene and Br_2 were employed to prepare 1,2,3,4-tetrabromoperfluorobutane.[13] The latter (1.27 mmol) and Cl_2O_4 (7.37 mmol) were allowed to react at −25° for 4 weeks. Vacuum fractionation of the products, while keeping the reactor at 0°, showed the volatile products to be Cl_2 (2.67 mmol), Cl_2O_4 (2.42 mmol), and a large but unmeasured amount of $BrClO_4$. From the recovered materials, it appeared that 2 Br had been replaced by ClO_4 to give $C_4F_6Br_2(ClO_4)_2$. The residue was a stable, clear, colorless liquid with less than 1 mm vapor pressure at room temperature. It was identified as $(O_4ClCF_2CFBr-)_2$ by the comparison of its infrared, mass, and ^{19}F nmr spectra with those of a sample of $(O_4ClCF_2CFBr-)_2$ prepared from bromine perchlorate and perfluorobutadiene (see below).

Samples of $C_4F_6Br_2(ClO_4)_2$ (1.34 mmol) and Cl_2O_4 (2.00 mmol) were allowed to react in a 30-ml cylinder at −45° for 3 weeks. Very little Cl_2 by-product was noted at that time and therefore more Cl_2O_4 was added and the temperature changed to −25° for 5 weeks. The evolved Cl_2 (1.03 mmol) indicated about 40% of the bromine had reacted. However, some degradation was also evident since fluorocarbon acyl fluoride and $FClO_3$ were found. Removal of these volatile species as well as $BrClO_4$ and excess Cl_2O_4 left a clear, colorless, nonvolatile liquid which was characterized by vibrational and ^{19}F nmr spectroscopy.

$CF_2{=}CFCF{=}CF_2$–$BrClO_4$ and –Cl_2O_4 Reactions. Perfluorobutadiene (2.58 mmol) and $BrClO_4$ (5.80 mmol)[14] were gradually warmed from −78 to 0° over several days followed by removal and separation of volatile products which consisted of a small amount of $BrClO_4$ and an unidentified fluorocarbon acyl fluoride. The residue consisted of the clear, colorless, mobile liquid $(O_4ClCF_2CFBr-)_2$ (2.25 mmol, 87% yield). The ^{19}F nmr showed only two types of fluorine with a 2:1 peak area ratio indicating a symmetrical adduct. The mass spectrum was complex and the parent ion was beyond the range of the instrument (*m/e* 500). No ion containing more than 2 Br atoms was found. Several $C-ClO_4^+$ fragments were noted as well as intense ClO_3^+, ClO_2^+, and ClO^+ ions.

Similarly, perfluorobutadiene (2.24 mmol) and Cl_2O_4 (4.98 mmol) were allowed to react at −78 to 0° furnishing $C_4F_6Cl_2(ClO_4)_2$ (2.15 mmol, 96% yield). The infrared spectrum was typical for a covalent perchlorate while the mass spectrum was very complex apparently due to the presence of isomeric species which was also indicated by the ^{19}F nmr spectrum (see Discussion). In the mass spectrum intense ClO_x^+ ($x = 1-3$) ion fragments were observed.

Miscellaneous R_fBr–$XClO_4$ Reactions. 1,2-Dibromoperfluoropropane was prepared from $CF_3CF{=}CF_2$ and Br_2. In a typical reaction, $CF_3CFBrCF_2Br$ (2.01 mmol) and Cl_2O_4 (2.68 mmol) were allowed to react for 3 days at 0° followed by 4 days at room temperature. Several fractional condensations were carried out, after O_2 (3.49 mmol) was removed by pumping, resulting in the isolation of $CF_3CFBrCF_2ClO_4$ (0.90 mmol, 45% yield) as the only detectable fluorocarbon perchlorate. It was identified by comparison to an authentic sample.[8] At −25° for 4 weeks, these same reactants gave a 31% yield of the $CF_3CFBrCF_2ClO_4$.

Bromine perchlorate and $CF_3CFBrCF_2Br$ were allowed to react using these same conditions and produced a 23% yield of $CF_3CFBrCF_2ClO_4$ with all of the unreacted R_fBr being recovered. For this system the possibility was examined for catalytically accelerating the displacement of Br by ClO_4 using added $Cs^+ClO_4^-$ or $NO_2^+ClO_4^-$. However, no effect was noted, with both the reaction rates and yields being unchanged.

1,2-Dibromoperfluorethane (2.01 mmol) and Cl_2O_4 (4.60 mmol) were contacted at −25° for 6 weeks. Separation of the products revealed that most of the $BrCF_2CF_2Br$ (1.70 mmol) was unchanged. A trace of $ClCF_2CF_2Br$ was found, and as the only R_fClO_4, $BrCF_2CF_2ClO_4$ (0.23 mmol, 11% yield). This perchlorate was identified by comparison to an authentic sample prepared from tetrafluoroethylene and $BrClO_4$. Furthermore, the known $BrCF_2CFO$ and $FClO_3$ were formed in qualitative experiments by CsF-catalyzed decomposition.

Tetrafluoroethylene (1.23 mmol), $BrClO_4$ (1.34 mmol), and CF_3Cl (~9 mmol) were allowed to react at −45° for several days. Trapping at −78° separated $BrCF_2CF_2ClO_4$ (1.12 mmol) from the CF_3Cl and other trace products which were more volatile. When no solvent was used to moderate this reaction only decomposition products were obtained. In addition to characterization of $BrCF_2CF_2ClO_4$ by CsF-catalyzed decomposition to $BrCF_2CFO$ and $FClO_3$, other data are presented in the tables.

Dibromodifluoromethane (2.02 mmol) and Cl_2O_4 (8.16 mmol) were added to a 30-ml cylinder cooled at −196°. After 3 weeks at −45°, the products were separated by fractional condensation. Analysis by infrared and gc showed COF_2 (1.9 mmol), COFCl (0.[illegible] mmol), and Cl_2 (4.1 mmol), together with $BrClO_4$ and Cl_2O_7.

Discussion

Fluorocarbon Iodide Reactions. Chlorine perchlorate and fluorocarbon iodides have been found to react vigorously at −45° and below to produce, at first, a complex intermediate of the composition $R_fI(ClO_4)_2$ and eventually the corresponding fluorocarbon perchlorate.[15] The equations for these reactions are

$$R_fI + 2Cl_2O_4 \rightarrow R_fI(ClO_4)_2 + Cl_2$$

$$R_fI(ClO_4)_2 \rightarrow R_fClO_4 + [IClO_4]$$

Yields of R_fClO_4 from these reactions were often high (90+%) and excellent material balances served to define the stoichiometry of the reactions. The vigor of the reaction is exemplified by the fact that with the simplest R_f ($=CF_3-$) occasional deflagrations were encountered, particularly when the requirement of very slow warming of the reactants was not rigorously followed. In other instances, the intermediate deflagrated at some higher temperature (>−45°). These deflagrations always produced much O_2, Cl_2, CO_2, and COF_2 together with small amounts of CF_4, CF_3Cl, and sometimes C_2F_6. Furthermore, all of the iodine originally present as R_fI was always recovered as a mixture of I_2 and IF_5. This is remarkable in view of the fact that the only fluorine in the system was bound to carbon in supposedly inert perfluoralkyl groups. Thus, an interhalogen compound has been formed from a C–F compound.

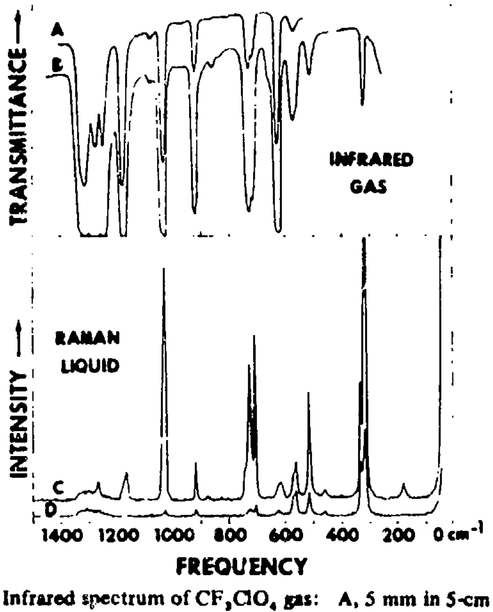


Figure 1. Infrared spectrum of CF_3ClO_4 gas: A, 5 mm in 5-cm path length cell with AgCl windows; B, 18 mm in 10-cm path length cell with AgBr windows. Raman spectrum of liquid CF_3ClO_4 at −100°: C, incident polarization parallel; D, incident polarization perpendicular.

To our knowledge, this is the first time that such an unusual reaction has been observed. This is an efficient process also, since all the iodine is involved. This process probably entails an initial formation of IF, which is known to disproportionate[16] readily to the observed species according to

$$5IF \rightarrow 2I_2 + IF_5$$

The fluorocarbon perchlorates prepared from iodides were CF_3ClO_4, $CF_3CF_2ClO_4$, $C_7F_{15}ClO_4$, $ICF_2CF_2ClO_4$, and $O_4ClCF_2CF_2ClO_4$. Combinations of spectral data (infrared and Raman, Table II and Figures 1 and 2; ^{19}F nmr, Table III; and mass spectra) together with elemental analyses, vapor density molecular weight measurements, and derivative formation were used to identify these new compounds. The results of all these observations were unequivocal, agreed with earlier results for similar compounds,[8] and established these products as covalent monodentate perchlorates.

A combination of infrared and Raman spectroscopy is a very useful tool for establishing the identity of these perchlorates.

Table II. Infrared and Raman Spectra of Fluorocarbon Perchlorates (4000–500-cm^{-1} Range)

CF_3ClO_4		$CF_3CF_2ClO_4$	$BrCF_2$-CF_2ClO_4	$ICF_2CF_2ClO_4$	n-$C_7F_{15}ClO_4$		$(O_4ClCF_2$-$CFCl$-$)_2$	$(O_4ClCF_2$-$CFBr$-$)_2$	Tentative assignment
Ir[a]	Raman[b]	Ir[a]	Ir[a]	Ir[a]	Ir[b]	Raman[b]	Ir[b]	Ir[b]	
					1368 sh	1375 w			
	1330 vw		1320 vs	1320 vs	1350 sh	1332 w	1310 vs	1310 vs	
1308 vs	1300 vs	1308 vs	1305 vs	1303 vs	1295 vs	1300 w	1295 vs	1290 vs	Antisym ClO_3 str
1265 s	1267 vw	1250 vs	1250 s	1288 s	1245 vs		1245 m	1225 ms	
1241 s	1240 vw	1204 s	1204 s	1197 s	1210 vs	1215 vw	1227 m	1190 s	
1171 vs	1169 vw	1180 s	1187 m		1153 vs	1160 w	1180 vs	1150 s	C–F str region
			1168 s			1140 vw	1135 s	1115 sh	
		1093 vs	1112 s	1105 s	1108 m	1112 w	1100 m	1098 w	
			1068 w	1076 w	1052 m	1051 m	1058 w		
1028 vs	1031 s	1035 vs	1037 vs	1038 vs	1028 vs	1035 vs	1032 vs	1028 vs	Sym ClO_3 str
							960 s		
914 m	917 w	930 w	940 s	922 s	947 w	948 vw	943 s	933 m	C–O str
				906 s	900 mw	908 w	892 m	900 m	
		848 mw	850 w		852 w		861 s	860 mw	
					840 w		848 m	843 mw	
			810 w	805 m	825 w	823 w	809 w	804 w	C–C str + certain C–Hal str
					785 w		784 m	780 m	
					770 w	767 s	770 m	762 m	
					750 m	750 w		750 m	
					743 m	742 w	732 w		
724 m	726 m	752 m			728 m	728 s			δ umbrella CF_3
706 sh	708 m				713 ms	714 m			δ scissor FCF_2
660 sh	660 vw	675 s	665 m	670 s	660 s	660 s			δ CF_2
			643 m	640 s	643 s	645 s	650 vs	645 vs	
615 s	616 vw	612 s	615 m	614 s	612 s	617 m	610 vs	608 vs	Cl–O str
568 mw	570 vw	582 m			565 sh	578 w	572 w	570 sh	δ antisym ClO_3
560 sh	564 w								δ scissor $OClO_2$
512 w	516 m[c]	530 w				515 m[d]			δ umbrella ClO_3

[a] Gas. [b] Liquid. [c] Raman peaks below 500 cm^{-1} for CF_3ClO_4 were at 462 (vw), 342 (m), 320 (vw), 316 (vs), and 178 (vw) cm^{-1}. [d] Raman peaks below 500 cm^{-1} for n-$C_7F_{15}ClO_4$ were at 470 (vw), 388 (m), 322 (m), 300 (m), 285 (w), and 223 (mw) cm^{-1}.

Table III. ^{19}F Nmr Data[a,b]

Compd	CF_3-	-CF_2-	>CFX (X = Cl, Br)	-CFX-ClO_4 (X = F, Cl)
CF_3ClO_4	60.4			
$CF_3CF_2ClO_4$	84.6			93.2
$CF_3(CF_2)_5CF_2ClO_4$	81.2	121.9–126.4		88.0
$ClCF_2CF_2ClO_4$		72.7		92.5
$BrCF_2CF_2ClO_4$		68.2		91.4
$ICF_2CF_2ClO_4$		63.3		90.4
$O_4ClCF_2CF_2ClO_4$		92.2		92.2
$ClCF_2CFClClO_4$		69.0		79.0
$Cl_2CFCFClClO_4$			69.8	76.0
$(-CFBrCF_2ClO_4)_2$			125	79.3
$CF_3CFClCF_2ClO_4$	76.5		122	84.7
$CF_3CFBrCF_2ClO_4$	78.4		139	85.8

[a] Chemical shift in ppm relative to internal $CFCl_3$; a peak area ratio measurements agreed with the assignments. [b] Data not from this work are taken from ref 8.

All of the more than 12 members of this class of compounds now known show very strong infrared bands near 1300 cm^{-1} (antisymmetric ClO_3 stretches) and 1030 cm^{-1} (symmetric ClO_3 stretch). In addition, another strong band due to the Cl–O single bond stretch of the O–ClO_3 group appears near 615 cm^{-1} in all -CF_2ClO_4 terminated species and at 630 cm^{-1} in all -$CFClClO_4$ terminated[8] species. Previously[8] we had assigned the Cl–O stretch in -CF_2ClO_4 examples to the bands at ~645 cm^{-1} in those compounds. Now with many more examples available, it is clear that the Cl–O stretch occurs at ~615 cm^{-1} while the ~645-cm^{-1} band is due to a CF_2 deformational mode (see Table II). The C–O stretch for these compounds is also characteristic and is emphasized in Table II along with other significant correlations. Raman spectra alone are less characteristic than the infrared for these materials but they always exhibit a very intense symmetric ClO_3 stretching band at ~1030 cm^{-1}. Infrared and Raman spectra of CF_3ClO_4 and n-$C_7F_{15}ClO_4$ are shown in Figures 1 and 2 as typical representatives of this class of compounds.

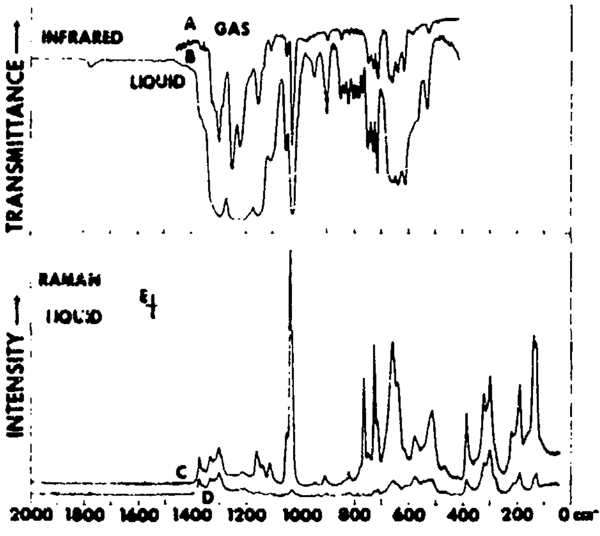


Figure 2. Infrared spectrum of $C_7F_{15}ClO_4$: A, 2 mm of gas in 10-cm path length cell with AgBr windows; B, liquid between AgCl plates. Raman spectrum of liquid n-$C_7F_{15}ClO_4$ at −80°: C, incident polarization parallel; D, incident polarization perpendicular; E, spectral slit width.

Trifluoromethyl perchlorate is the simplest fluorocarbon perchlorate, the "parent" member of the series. Some of its properties were described in a preliminary communication.[17] The stability of this compound is noteworthy. A sample stored in a stainless steel cylinder for nearly 2 years was unchanged. Even at elevated temperature (100° for 18 hr) in the presence of the known decomposition catalyst CsF,[8] only 30% of the material cleaved according to

$$CF_3ClO_4 \xrightarrow[\Delta]{CsF} COF_2 + FClO_3$$

The quantitative decomposition of R_fClO_4 compounds into

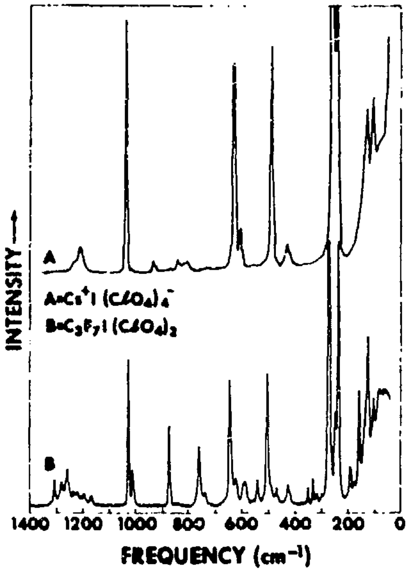


Figure 3. Raman spectra of solids at −100°.

Table IV. Infrared and Raman Spectra of Solid Iodine Perchlorates (cm^{-1}, Intensity)

i-$C_3F_7I(ClO_4)_2$		n-$C_7F_{15}I(ClO_4)_2$		$Cs^+I(ClO_4)_4^-$
Ir	Raman	Ir	Raman	Raman
		1371 ms	1376 mw	
		1337 mw	1332 w	
	1308 w		1295 vw	
1295 vs	1281 w	1278 sh	1278 w	
1250 vs, br	1257 mw	1230 vs, br	1259 w	
	1235 vw		1250 vw	1243 w, sh
	1220 vw		1236 vw	
	1205 vw		1218 vw	1207 mw
1190 sh	1196 vw			
1168 s	1168 vw	1157 s		
		1138 w		
		1074 mw	1074 mw	
		1048 mw	1048 vw	
1032 s	1028 s	1023 s	1023 s	1038 s
	1011 mw			1016 mw
971 s		959 ms	959 m	
874 s	875 m	857 w		
		828 w		
		810 mw	806 m	
765 m	762 m	755 m	755 w	
746 s	741 vw	730 mw	742 m	
718 s				
667 s		675 s	664 w	
640 s	646 s	640 s	639 s	630 s
620 sh	622 w			607 mw
584 m	588 w	584 m	590 w	
		568 m	576 w	
542 m	543 w	533 m		
496 s	502 s	494 m	499 s	489 s
425 w	429 w	423 vw	428 w	430 mw
	352 w	382 w	383 w	
	333 w		345 vw	
	320 vw		322 vw	
	298 vw		311 vw	
	272 vvs		261 vvs	261 vs
	249 w			
	228 vs			240 s
	191 w		197 w	
	175 vw			
	159 ms		152 w	
	129 ms		125 w	131 ms
	106 w			106 ms

their corresponding acyl fluorides and perchloryl fluoride is a very useful characteristic reaction as reported previously.[8] The mass spectrum of CF_3ClO_4 was slightly unusual in that it is the only example of a perfluorocarbon perchlorate for which we have observed a parent ion. Typical of covalent perchlorates in general, no ClO_4^+ ions were found although intense ClO_3^+, ClO_2^+, and ClO^+ ion peaks were present. This is reasonable since the C–O bond energy is almost twice that of the Cl–O bond. The ^{19}F nmr spectrum exhibited only one line at 60.4 ppm, quite close to that of related CF_3O– moieties.[18,19] An analysis of the infrared and Raman spectra of gaseous and liquid CF_3ClO_4 has been completed.[20] Nineteen of the twenty-one fundamental modes of vibration expected for a nine-atom molecule of symmetry C_s with hindered rotation of the CF_3 and ClO_3 groups were observed and assigned. This thorough spectral study is fully consistent with the covalent monodentate perchlorate formulation.

Iodine monoperchlorate, postulated as the by-product in the synthesis equations, seems not to be a monomeric covalent material since it shows no volatility. At ambient temperature, on standing the "$IClO_4$" gradually loses Cl_2 and Cl_2O_7, eventually leading to the formation of I_2O_5. The same solid decomposition product results from the ambient-temperature degradation of $I(ClO_4)_3$.[5]

In view of the facile synthesis noted for CF_3ClO_4, it was of interest to extend the method to analogous perfluoroalkyl iodides. With CF_3CF_2I this led to the formation of $CF_3CF_2ClO_4$ whose characterization was analogous to that used for CF_3ClO_4 proving that this was a covalent perchlorate. However, during the synthesis, observations were made which indicated a complex, metastable intermediate had been formed. At −45° all the by-product Cl_2 was formed but not the $CF_3CF_2ClO_4$. To obtain $CF_3CF_2ClO_4$ it was necessary to raise the temperature somewhat which decomposed the intermediate. From several reactions it was found that this metastable intermediate had the empirical composition $CF_3CF_2I(ClO_4)_2$.

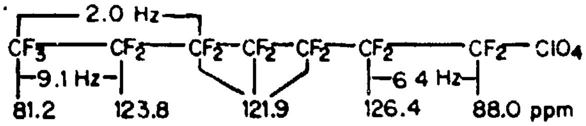
With other precursors, $(CF_3)_2CFI$ and n-$C_7F_{15}I$, it was found that this intermediate was an isolable solid, stable at ambient temperature. The empirical compositions were analogous to those of the ethyl case, *i.e.*, $(CF_3)_2CFI(ClO_4)_2$ and n-$C_7F_{15}I(ClO_4)_2$. These solids fumed in air and formed ClO_4^- and some I_2 on hydrolysis. From their infrared and Raman spectra (Table IV and Figure 3) it was evident that the covalent perchlorate function was still present. However, comparison of the Raman spectra of both solids with that of the salt $Cs^+I(ClO_4)_4^-$ (Table IV and Figure 3), which was obtained from CsI and Cl_2O_4,[5] revealed striking similarities. All of the bands observed for the $I(ClO_4)_4^-$ ion are also shown by these two $R_fI(ClO_4)_2$ solids. They correspond quite closely in both frequency and relative intensity. Furthermore, the only other moderately intense bands in the spectra of the fluorocarbon-containing compounds are in the C–C stretching region and thus not associated with the perchlorate functions. Therefore, it can be concluded the intermediates having the empirical composition $R_fI(ClO_4)_2$ possess the ionic structure $(R_f)_2I^+I(ClO_4)_4^-$. The related ionic structure $(R_f)_2I^+IF_4^-$ has been postulated[21] for solids obtained "not infrequently" from the fluorination of R_fI compounds with ClF_3. However, experimental proof for such a structure was not offered.

That these solid intermediates are the precursors to the covalent R_fClO_4 products was shown for the perfluoroheptyl case. Thus, it was found that, slowly at ambient temperature or more rapidly at 40°, this solid produced n-$C_7F_{15}ClO_4$ and the decomposition products of "$IClO_4$," *i.e.*, Cl_2, O_2, Cl_2O_7, and I_2O_5. Care is required in heating the solid complex. On one occasion when heated just to its melting point under dynamic vacuum, the n-$C_7F_{15}I(ClO_4)_2$ exploded, also the solid tetraperchlorate $(O_4Cl)_2ICF_2CF_2CF_2I(ClO_4)_2$ deflagrated on warming to ambient temperature, as did $(CF_3)_2CFI(ClO_4)_2$ on heating above its melting point.

The high-yield conversion of $(R_f)_2I^+I(ClO_4)_4^-$ to $2R_fClO_4$ is an unusual and very interesting reaction. In addition, the

$(R_f)_2I^+$ cation might be a very useful alkylating reagent for the introduction of perfluoroalkyl groups.

n-Perfluoroheptyl perchlorate exhibited the typical covalent perchlorate mass spectrum and vibrational spectra (Table II). Its ^{19}F nmr spectrum was especially informative with regard to the fluorocarbon part of the molecule but it was more complex than the other R_fClO_4 moieties owing to the presence of several closely similar CF_2 groups. The *n*-$C_7F_{15}ClO_4$ nmr spectrum exhibited five peaks showing relative area ratios of 3:2:6:2:2. A schematic of the analyzed spectrum is shown below.



The lowest field peak at 81.2 ppm (area 3), was shown to be composed of triplets. This peak is assigned to the terminal CF_3 group with coupling to the nearest CF_2 (9.1 Hz) and the next nearest CF_2 (2.0 Hz) groups. Assignment of the next peak, 88.0 ppm (area 2), to the $-CF_2ClO_4$ fluorine resonances can be readily made by comparison with known R_fCF_2OX values.[18,22] This peak is a poorly resolved triplet due to coupling (6.4 Hz) with the adjacent CF_2 group. Since CF_2 groups α to CF_3- are generally of lower field shift than those α to $-CF_2OX$,[18,22,23] the remaining two peaks of area 2 are assigned respectively to the CF_2 (123.8 ppm) α to the terminal CF_3- and the CF_2 (126.4 ppm) α to the $-CF_2ClO_4$ termination. The remaining peak, 121.9 ppm (area 6), is thus assigned to the three central CF_2 groups which are nearly equivalent. This peak is not symmetrical but has a weak shoulder at 122.5 ppm which can be ascribed to a slight nonequivalence of one of the three CF_2's, perhaps the central one in the seven-carbon chain. Further verification of the identity of this perchlorate was obtained through its quantitative CsF-catalyzed decomposition into $FClO_3$ and *n*-$C_6F_{13}CFO$.

The synthesis of 1,2-bis(perchlorato)tetrafluoroethane was attempted from ICF_2CF_2I and Cl_2O_4. In the absence of a solvent, it was found that the consumed Cl_2O_4 amounted to only slightly more than that required for reaction of one I atom. This occurred despite relatively long (1 week) reaction periods at −45°. One of these reactions which had gone smoothly but incompletely at −45° deflagrated while being maintained at −25°. Normally, the volatile products recovered from this reaction were $ICF_2CF_2ClO_4$, ICF_2CF_2Cl (a minor amount usually), Cl_2, and Cl_2O_7. The R_fClO_4 yield (50–60%) was generally nowhere near so good as that obtained with other R_fI compounds.

When a solvent was used to promote the substitution of both iodines in ICF_2CF_2I, $ICF_2CF_2ClO_4$ was still the main product. However, a viscous liquid of low volatility was isolated in very small amounts which was identified as $O_4ClCF_2CF_2ClO_4$ by ^{19}F nmr and ir spectroscopy. The infrared spectrum agreed very well with that of $FSO_3CF_2CF_2SO_3F$[24] when vibrations caused by the different end groups were discounted and only $-OCF_2CF_2O-$ bands were considered. An improved synthetic technique is required to study this perchlorate more fully.

Fluorocarbon Bromide Reactions. Attempts were made to displace bromine from R_fBr substrates in analogy to the corresponding iodine systems. Again reactant ratios of Cl_2O_4 to R_fBr greater than 1 were required since any liberated bromine ($BrCl$ or Br_2) can react with Cl_2O_4 to give $BrClO_4$.[4] The latter might or might not participate in additional displacement of bromine from R_fBr. A 4-week reaction of $BrCF_2CFBrCFBrCF_2Br$ and excess Cl_2O_4 proceeded according to

$$C_4F_6Br_4 + 4Cl_2O_4 \rightarrow C_4F_6Br_2(ClO_4)_2 + 2BrClO_4 + 2Cl_2$$

The ^{19}F nmr spectrum of this bisperchlorate showed it to be a single isomer. It exhibited only two basic types of C–F. These peaks were readily assignable by comparison with known species[8,25] to terminal $-CF_2ClO_4$ fluorine atoms (79.3 ppm) and internal $>CFBr$ fluorine atoms (125 ppm). The resonance characteristic of $-CF_2Br$ fluorines (~60 ppm) was totally absent. Also, the peak area ratio of 2:1 established that this product was wholly $O_4ClCF_2CFBrCFBrCF_2ClO_4$. However, the absorption of the $>CFBr$ fluorines was split into two lines (124.6 and 126.1 ppm) with the low field line having about one-fourth the intensity of the other. The proximity of these peaks indicates strongly that they are due to two different rotational isomers. This is not surprising in view of the many bulky groups on the carbon backbone. With Br atoms on adjacent carbons, the trans isomer would be expected to be preferred as previously demonstrated[26] for $BrCF_2CFBr_2$.

The identification of $O_4ClCF_2CFBrCFBrCF_2ClO_4$ was aided by examining the product of the reaction

$$CF_2{=}CFCF{=}CF_2 + 2BrClO_4 \rightarrow C_4F_6Br_2(ClO_4)_2$$

This interaction proceeded smoothly and efficiently below room temperature to give the identical bisperchlorate in 87% yield. Thus, the first reaction step must have been the following polar 1,2 addition of $BrClO_4$ to the diolefin

$$CF_2{=}CFCF{=}CF_2 + BrClO_4 \rightarrow O_4ClCF_2CFBrCF{=}CF_2$$

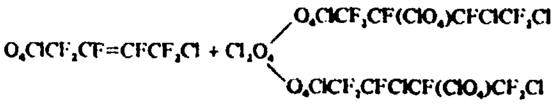
followed by the addition of a second $BrClO_4$ in the same fashion

$$O_4ClCF_2CFBrCF{=}CF_2 + BrClO_4 \rightarrow O_4ClCF_2CFBrCFBrCF_2ClO_4$$

Thus, the symmetrical bisperchlorate is formed with all perchlorate groups in the 1,4 positions as expected on the basis of our previous studies.[8]

The corresponding Cl_2O_4 adduct of perfluorobutadiene was also prepared in 96% yield. The physical appearance, vapor pressure, and infrared spectrum (ClO_4 and C–F bands) of the adduct were much like its Br counterpart. However, the ^{19}F nmr spectrum clearly indicated that a more random addition had occurred. The observed resonances were of three basic types, all of which were well separated and readily assignable:[8,25] (1) 62 ppm $-CF_2Cl$, (2) 83 ppm $-CF_2ClO_4$, and (3) 130 ppm $>CFZ$ (Z = Cl or ClO_4). The finding of both perchlorate and chlorine terminal groups and peak area measurements show that both 1,2 and 1,4 additions occurred as the first step. Equations illustrating the 1,4 addition are

$$CF_2{=}CFCF{=}CF_2 + Cl_2O_4 \rightarrow O_4ClCF_2CF{=}CFCF_2Cl$$



$$O_4ClCF_2CF{=}CFCF_2Cl + Cl_2O_4 \begin{cases} O_4ClCF_2CF(ClO_4)CFClCF_2Cl \\ O_4ClCF_2CFClCF(ClO_4)CF_2Cl \end{cases}$$

Based on peak area measurements and assuming that 1,2 attack gives a single product as discussed for the $BrClO_4$ example, then Cl_2O_4 addition gave somewhat more 1,4 than 1,2 products.

Further substitution of bromine in (O_4ClCF_2CFBr-) by a perchlorato ligand was sought using Cl_2O_4. From the evolved Cl_2, it appeared that ~40% reaction had occurred after 8 weeks at −45 to −25°. In appearance, the liquid product was unchanged—still clear, colorless, and mobile. Its infrared spectrum exhibited minor but distinct differences from the starting material. In particular, the ClO_4 absorptions appeared relatively more intense and broad than they did in the starting material. The ^{19}F nmr spectrum confirmed the changed nature of this liquid compared to the bisperchlorate compound. Rather than just two types of C–F as in the starting material (79.3 ppm for CF_2ClO_4 and 125 ppm for $>CFBr$), this material had three different types of C–F resonances: 81 ppm $-CF_2ClO_4$, 125 ppm $>CFBr$, and 135 ppm $>CFClO_4$. The relative area ratios for these types indicated about 35% of the $>CFX$ fluorines were of the X = ClO_4 type. Furthermore, each of the three types of C–F found consisted of two or more unequal-area peaks of similar shifts (±1 ppm), indicating the presence of different isomers. Since only 35% of the original Br had been substituted, the above nmr spectrum is that of a mixture of starting material with either a tris- or a tetrakisperchlorate. Distinction between these two possibilities is not possible owing to their low volatilities. However, we would expect the formation of the trisubstituted compound to be favored over that of the tetrakisperchlorate.

Another R_fBr compound tested with Cl_2O_4 and $BrClO_4$ was $CF_3CFBrCF_2Br$. Yields of $CF_3CFBrCF_2ClO_4$ as high as 45% were obtained. The product was identical in its physical and spectral properties with the material previously synthesized[8] by $BrClO_4$ addition to the corresponding olefin. Added $Cs^+ClO_4^-$ or $NO_2^+ClO_4^-$ did not catalyze the above reactions.

Further studies with R_fBr species showed that $BrCF_2CF_2Br$ reacted very slowly and incompletely with Cl_2O_4 giving $BrCF_2CF_2ClO_4$ in 11% yield (after purification) according to

$$BrCF_2CF_2Br + 2Cl_2O_4 \rightarrow BrCF_2CF_2ClO_4 + Cl_2 + BrClO_4$$

The infrared and ^{19}F nmr spectra of the product correlate well with those of the known $ClCF_2CF_2ClO_4$[8] and of $ICF_2CF_2ClO_4$ which was discussed above. In addition, it was shown that CsF decomposed this perchlorate to $BrCF_2CFO$ and $FClO_3$ as expected.

Other R_fBr compounds found not to react with either Cl_2O_4 or $BrClO_4$ despite long contact times were CF_3CF_2Br, $BrCF_2CF_2CF_2Br$, and $CF_3CFBrCF_2ClO_4$.

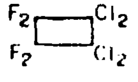
From these various R_fBr–Cl_2O_4 studies, the pattern emerged that some primary and even some secondary Br can be displaced by ClO_4. There are, however, marked differences in the rate and degree of these displacements: $C_4F_6Br_4 > CF_3CFBrCF_2Br > BrCF_2CF_2Br >>> C_2F_5Br$. Furthermore, the reaction appears to be sensitive to the nature of the group adjacent to the C–Br bond. When these are perfluorinated, as in CF_3CF_2Br or $BrCF_2CF_2CF_2Br$ or $CF_3CFBrCF_2ClO_4$, no substitution takes place. If the group is either $-CFBr-$, $-CF_2Br$, or $-CF_2ClO_4$, some substitution occurs.

Attempted Synthesis of Geminal Bisperchlorates. All of the preceding experiments were aimed at the introduction of a single perchlorato group per carbon atom. It appeared very interesting to examine the possibility of synthesizing compounds containing more than one perchlorato group per carbon atom. To this end, dibromodifluoromethane and Cl_2O_4 were allowed to react at -45° for 3 weeks producing the anticipated Cl_2 and $BrClO_4$ by-products. However, the only carbon-containing materials accompanying those compounds were COF_2 and COFCl, accounting for 95 and 5%, respectively, of the carbon in CF_2Br_2. Chlorine heptoxide constituted the other significant product. These moieties most certainly arose from the sequence

$$CF_2Br_2 + 4Cl_2O_4 \rightarrow 2Cl_2 + 2BrClO_4 + [CF_2(ClO_4)_2] \rightarrow COF_2 + Cl_2O_7$$

Apparently geminal ClO_4 groups are unstable toward decomposition into carbonyl compounds and Cl_2O_7.

Fluorocarbon Chloride Reactions. Numerous R_fCl compounds were investigated and it was ascertained that mono or di, primary or secondary chlorine contained in saturated R_fCl materials was unreactive. Those compounds examined that did not react with Cl_2O_4 were CF_3Cl, $ClCF_2CF_2Cl$, $ClCF_2CFCl_2$, $CF_3CFClCF_2Cl$,



$CF_3CFClCF_2ClO_4$, and $C_4F_6Cl_2(ClO_4)_2$. Trichlorofluoromethane did react but gave COFCl and Cl_2O_7 as primary products. Once again apparently geminal ClO_4 groups were unstable with respect to the formation of $>C{=}O$ and Cl_2O_7.

General Considerations. In spite of the large amount of experimental data, it remains difficult to rationalize all of the observed reactions. For the alkyl iodides, a simple halogen elimination reaction according to

$$>\underset{\delta+}{\mathrm{C}}-\underset{\delta-}{\mathrm{Hal}} + \underset{\delta+}{\mathrm{Hal}}-\underset{\delta-}{\mathrm{OClO_3}} \rightarrow >\mathrm{C{-}OClO_3} + \mathrm{Hal{-}Hal}$$

certainly is not applicable, since the isolation of the $(R_f)_2I^+I(ClO_4)_4^-$ intermediate suggests an oxidation of iodine to a +III oxidation state followed by complex rearrangements. In the case of chlorine compounds, such as $CFCl_3$, which interacted with Cl_2O_4, the halogen elimination mechanism shown above is more likely owing to the fact that Cl_2O_4 is probably not a strong enough oxidizer to oxidize Cl to the +III state. Thus, it is possible that the reaction chemistry of the alkyl iodides might be entirely different from that of the corresponding chlorides. Obviously, systematic and more sophisticated kinetic and structural studies should be carried out on these interesting systems to determine reliably the mechanisms involved and to avoid undue speculation.

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Registry No. CF_3ClO_4, 52003-45-9; $CF_3CF_2ClO_4$, 53011-52-2; n-$C_7F_{15}ClO_4$, 53011-53-3; $ICF_2CF_2ClO_4$, 53011-54-4; $BrCF_2CF_2ClO_4$, 53011-55-5; $C_4F_6(ClO_4)_2Br_2$, 53011-56-6; $C_4F_6(ClO_4)_2Cl_2$, 53011-57-7; $CF_3CFBrCF_2ClO_4$, 38126-26-0; i-$C_3F_7I(ClO_4)_2$, 53078-08-3; n-$C_7F_{15}I(ClO_4)_2$, 53078-09-4; $Cs^+I(ClO_4)_4^-$, 53078-10-7; CF_3I, 2314-97-8; CF_3CF_2I, 354-64-3; $(CF_3)_2CFI$, 677-69-0; ICF_2CF_2I, 354-65-4; $ICF_2CF_2CF_2I$, 422-91-3; n-$C_7F_{15}I$, 335-58-0; $BrCF_2CFBrCF_2Br$, 661-94-9; $CF_2{=}CFCF{=}CF_2$, 685-63-2; $CF_3CFBrCF_2Br$, 661-95-0; $BrCF_2CF_2Br$, 124-73-2; $CF_2{=}CF_2$, 116-14-3; Cl_2O_4, 27218-16-2; $BrClO_4$, 32707-10-1.

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(14) An excess of $BrClO_4$ over that required by the 2:1 stoichiometry for reaction of the two olefinic bonds is considered important. Previously[8] a monoperchlorate adduct of $CF_2{=}CFCF{=}CF_2$ had exploded on warming to room temperature. It is believed that a molecule of that type, *i.e.*, $CF_2{=}CFCFXCF_2ClO_4$, with an oxidizable unsaturated link in close proximity to the oxidizing perchlorate group may be inherently unstable.
(15) For succinctness and clarity, the notation ClO_4 is used to denote the covalent perchlorate group $-OClO_3$. Ionic perchlorate is distinguished by a negative change sign, ClO_4^-.
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AN IMPROVED SYNTHESIS OF $FClO_2$

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The literature methods reported (1) for the synthesis of $FClO_2$ are inconvenient, since they either involve the fluorination of shock sensitive chlorine oxides or, as in the case of the $KClO_3 + BrF_3$ reaction (2), result in product mixtures which are difficult to separate. In this note, we report an improved synthesis of $FClO_2$ from $NaClO_3$ and ClF_3 which, in our opinion, is more convenient than the literature methods. It is based on the previous observations (3,4) that gaseous ClF_3 reacts with $KClO_3$ to produce $FClO_2$ in high yield, but it reduces the ClF_3 requirement by 60 percent.

In our method, dry $NaClO_3$ is combined with approximately an equimolar amount of ClF_3 at -196° in a stainless steel cylinder. The mixture is kept at room temperature for about one day. Chloryl fluoride is thus obtained in high yield according to the idealized stoichiometry:

$$6NaClO_3 + 4ClF_3 \longrightarrow 6NaF + 2Cl_2 + 3O_2 + 6FClO_2$$

The products condensible at -196° can be separated either by fractional distillation (bp: Cl_2=-33.8, $FClO_2$=-6, ClF_3=11.75°) or by repeated fractional condensation through a series of U-traps kept at -95, -112, and -126°. The use of well passivated metal, Teflon, or KelF equipment is essential for handling $FClO_2$. The use of larger than stoichiometric amounts of ClF_3 in the above reaction is recommended to avoid the possible formation of chlorine oxides. The substitution of the previously used (3, 4) $KClO_3$ by $NaClO_3$ is significant since KF forms a 1:1 adduct with ClF_3, whereas NaF does not. Therefore, the use of $NaClO_3$ reduces the ClF_3 requirement for the reaction by 60 percent. In summary, the above process incorporates the following advantages: (1) safety, no shock sensitive materials must be handled, (2) better utilization of ClF_3, and (3) good product purity.

We have also examined the synthesis of $FClO_2$ according to Faust et al. (5). According to their claim, $FClO_2$ can be prepared in 50% yield by simply heating a mixture of ClF and O_2 for about one day to 80 - 90°. This process would be superior to any of the previously reported syntheses. However, duplication of the experiments of Faust et al. (5) in our laboratory failed to produce significant amounts of $FClO_2$. For example, heating mixtures of ClF and O_2 in a well passivated (with ClF_3) Monel cylinder to 80 - 90° for one day under an autogenous pressure of 1000 psi produced only a trace of $FClO_2$ (less than 0.1%). We believe that the observation of a trace of $FClO_2$ in the products is not due to $FClO_2$ formation from ClF and O_2 but due to the following well known (6) hydrolysis of ClF during the handling of the starting materials and products:

$$5\,ClF + 2H_2O \longrightarrow 4HF + FClO_2 + 2Cl_2$$

The failure to obtain $FClO_2$ from ClF and O_2 by simple heating agrees with the following observations: (i) chlorine oxyfluorides are extremely difficult to prepare by oxygenation of chlorine fluorides; (ii) thermodynamics favor the decomposition of $FClO_2$ to ClF and O_2 as was also demonstrated by kinetic studies of the thermal decomposition of $FClO_2$ (7, 8).

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Electron Spin Resonance Study of O_2^+ Salts. Influence of Crystal Field Effects and Relaxation

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Electron spin resonance spectra of polycrystalline $O_2^+BF_4^-$, $O_2^+AsF_6^-$, $O_2^+SbF_6^-$, and $O_2^+Sb_2F_{11}^-$ were recorded over the temperature range −190 to +20° at 9.35 GHz. The *g* tensors calculated from simulated spectra of $O_2^+BF_4^-$, $O_2^+AsF_6^-$, and $O_2^+Sb_2F_{11}^-$ at −196° indicated the ions are in sites of orthorhombic or lower symmetry. Two of the components of the *g* tensor were between 1.96 and 2.00. The third component was between 1.73 and 1.76 in agreement with crystal field theory. The line shapes were lorentzian indicating that dipolar broadening is at least partially averaged by thermal motion. Above −196°, the line widths of the spectra increased rapidly indicating a relaxation process which has a small activation barrier. The spectrum of $O_2^+SbF_6^-$ was very broad at −196° and exhibited additional lines of magnetic fields in the region of 1000–1500 G. This may be due to strong exchange between nearest O_2^+ ions. An improved synthesis of $O_2^+BF_4^-$ was described involving low-temperature uv photolysis of a BF_3–F_2–O_2 mixture.

Introduction

The preparation of a variety of dioxygenyl salts has been reported.[1,2] Although electron spin resonance (esr) has been used to confirm the paramagnetic character of dioxygenyl tetrafluoroborate[3,4] and hexafluoroarsenate,[5] no interpretations of these spectra have been reported. An esr spectrum was reported for $O_2^+BF_4^-$ at −196° consisting of one asymmetric line with a peak to peak line width (ΔH_{pp}) between 400 and 500 G and a *g* factor between 1.94 and 1.97.[3,4] The spectrum reported for $O_2^+AsF_6^-$ was characterized by a *g* factor of 1.9880 ± 0.0002 and a temperature-dependent line width of 24 G at −50° and 66 G at 23°.[5] Both the BF_4^- and the AsF_6^- anions are large such that both materials would be expected to exhibit similar spectra. Recently, esr spectra of $O_2^+SbF_6^-$, $O_2^+AsF_6^-$, and $O_2^+Sb_2F_{11}^-$ at temperatures near liquid helium were studied. These spectra were interpreted in terms of near-axial symmetry.[6] Values of $g_\perp$ were about 1.97 and those of $g_\parallel$ were 1.73. In addition, the magnetic susceptibility of these salts and the ^{19}F nmr of $O_2^+AsF_6^-$ were reported.[6]

Esr spectra of concentrated paramagnetic samples generally exhibit a variety of relaxation processes. Dipolar broadening results from the various magnetic fields generated by the close magnetic dipoles acting on the central ion. Exchange processes, cross relaxation, or motion of the magnetic ion can also cause a modulation of the magnetic energy levels and therefore relax the spin states. The O_2^+ ion has the additional possibility of Jahn–Teller relaxation since it is in a nearly degenerate state. In a crystal field which is symmetric with respect to the internuclear axis, two states are separated only by the spin–orbit coupling energy (about 200 cm^{-1}). These effects have not been considered in the interpretation of the esr spectra of compounds of O_2^+.

Esr spectra have been observed for O_2^+ and the isoelectronic species N_2^- and NO in single crystals and adsorbed on surfaces. Detailed studies of O_2^+ on rutile surfaces,[7] N_2^- in single crystals of irradiated azides,[8] and nitric oxide adsorbed on various surfaces[9–11] and generated by irradiation in azides[12] have been reported. Nitric oxide in single crystals and on some surfaces exhibits spectra characteristic of a three-component *g* tensor when the line widths are sufficiently narrow so that all components can be resolved. On some surfaces NO exhibits a spectrum with a broad-line characteristic of apparent axial symmetry; however, simulations assuming axial symmetry do not accurately reproduce the spectra.

Synthetic aspects add further interest to this study. Recent communications[13,14] indicate that the previously reported photochemical synthesis of $O_2^+SbF_6^-$ results in a product which contains appreciable amounts of the dimeric anion $Sb_2F_{11}^-$. In addition, no convenient synthesis has been reported for the preparation of $O_2^+BF_4^-$.

In view of the discrepancies in the esr spectra of O_2^+ and for the purpose of understanding the behavior of O_2^+ in a crystalline environment, we have investigated the esr spectra of this ion in the presence of several counterions. In addition, an improved synthesis is reported for O_2BF_4.

Experimental Section

Preparation of O_2^+ Salts. The $O_2^+AsF_6^-$ and $O_2^+SbF_6^-$ samples were prepared at 200° from O_2, F_2, and AsF_5 or SbF_5, respectively, in Monel cylinders according to the method of Beal, *et al.*[15] Material balances, vibrational spectra,[16] and elemental analyses (oxygen content was determined by displacement reaction with excess FNO at −78° and As or Sb were determined by conventional techniques) showed that the solid products had the compositions $O_2^+AsF_6^-$ and $O_2^+SbF_6^-\cdot0.06SbF_5$, respectively. A sample having the composition $O_2^+SbF_6^-\cdot0.73SbF_5$ was prepared by the above method but by heating the starting materials to 150° for 12 hr. A sample of $O_2^+Sb_2F_{11}^-$ was prepared by uv photolysis of a 1:$^1/_2$:2 mole ratio mixture of O_2–F_2–SbF_5 in a manner similar to that described by McKee and Bartlett.[14]

For the synthesis of $O_2^+BF_4^-$, a 1-l. Pyrex bulb containing equimolar amounts of O_2, F_2, and BF_3, at a total pressure of 800 mm, was exposed for 7 days to uv radiation from a high-pressure mercury lamp (Hanovia 616A, 100 W) equipped with a water filter. The condensing tip of the reactor was kept at −78°. The solid $O_2^+BF_4^-$ accumulated in the cold section of the reactor and was periodically removed at 0° from the walls to the bottom of the reactor by means of an ultrasonic cleaning bath. After completion of the photolysis, products volatile at −78° were removed *in vacuo*. The white solid residue was transferred, while cold, from the Pyrex container to a Teflon–FEP ampoule in an inert-atmosphere glove box. Vibrational spectroscopy[17] and elemental analysis (see above) showed the product to be $O_2^+BF_4^-$. The yield was 51%.

Esr Spectra. Esr spectra were obtained on a modified Varian V-4502 dual-cavity esr spectrometer.[18] The magnetic field was monitored using a sample of Mn^{2+} in forsterite.[19] Each of the six lines from the Mn^{2+} were narrower than 1.5 G, and the splittings and the *g* factor were determined against DPPH ($g = 2.00365$) using a proton resonance probe to calibrate the magnetic field. The esr parameters for Mn^{2+} were $g = 2.00095 \pm 0.00006$ and $a = 86.75 \pm 0.05$ G. To calibrate the field difference from the field corresponding to $g_{Mn^{2+}}$ for each manganous line, the hyperfine Hamiltonian was expanded to second order.

The reference channel was operated at 100-kHz field modulation, and the sample channel was operated at 14.7-kHz with a set of water-cooled coils which allow peak-to-peak modulation amplitudes up to 100 G.[20] In all spectra, the modulation amplitude was less 0.1 of the peak-to-peak line width of the spectrum. Simulations of the powder spectra were carried out by the method of Griscom, Taylor, Ware, and Bray[21] on a CDC 6600 computer with a Calcomp plotter. Three components of a *g* tensor were required to simulate the spectra. Since two components were very close (g_x and g_y) and one component

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Table I. Esr Parameters of Dioxygenyl Compounds at −196°

	g_x	g_y	g_z	ΔH_{pp},[a] G	Δ,[b] cm^{-1}	10^4E,[b] cm^{-1}
O_2AsF_6	2.000	1.973	1.742	80	1480	1.00
O_2BF_4	2.00	1.98	1.78	260	1500	2.0
O_2SbF_6	1.75	Isotropic		2200		
$O_2Sb_2F_{11}$	1.970	1.958	1.729	120	1960	1.20

[a] Lorentzian line width used to simulate the powder spectrum.
[b] Parameters derived from g factors assuming $\lambda = 195\ cm^{-1}$.

(g_z) was at considerably higher fields, the dependence of magnetic field on the intensity was treated by the relationship

$$I \propto \left(\frac{g_x + g_y}{2}\right)^2 \left[\left(\frac{g_z}{g}\right)^2 + 1\right]$$

where I is the intensity and g is the apparent g factor given by $h\nu/\beta H$. This is analogous to the relationship derived by Bleaney.[22]

Samples of the dioxygenyl salt were placed in 4-mm Teflon–FEP or quartz tubes and heat sealed. The Teflon–FEP tubes exhibited a weak spectrum of two lines each about 1 G wide, at points very close to $g = 2$. Under the high powers and high modulation amplitudes used, these lines were broadened and weakened even further. At liquid nitrogen temperatures where large signals were observed, low gains and small modulation amplitudes were used and the Teflon–FEP spectrum was too weak to be detected. Samples prepared in Monel vessels exhibited a weak line about 20 G wide at −196°. This is probably due to a copper or nickel ion impurity. This signal is similar to that previously reported for $O_2^+AsF_6^-$.[5] The samples of antimonates and the arsenates were stored for several weeks at room temperature with no noticeable decrease of signal intensity. The tetrafluoroborate salts were stored at −20° and were also stable for several weeks.

Results and Discussion

Syntheses of O_2^+ Salts. The previous reports on the photochemical synthesis[5] of $O_2^+AsF_6^-$ and the thermal synthesis[15] of $O_2^+SbF_6^-$ were confirmed. For the thermal synthesis of $O_2^+SbF_6^-$ it was found important to keep the reaction temperature sufficiently high, *i.e.*, at about 200°, in order to suppress the formation of $O_2^+Sb_2F_{11}^-$. A reasonable explanation for this temperature requirement is the melting point of $O_2^+Sb_2F_{11}^-$ which was recently reported[12] to be 180–185°. Below 180°, $O_2^+Sb_2F_{11}^-$ can solidify thus escaping further interaction with O_2 and F_2.

The uv photolysis of O_2–F_2–SbF_5 mixtures yields mainly $O_2^+Sb_2F_{11}^-$ and not $O_2^+SbF_6^-$ as originally reported.[5] This finding is in excellent agreement with a recent study by McKee and Bartlett.[14] Since the esr spectra of $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$ (see below) strongly differ, they are useful for distinguishing the two compounds.

The previously reported syntheses[1] of $O_2^+BF_4^-$ required oxygen fluorides, such as O_2F_2 or O_4F_2, as starting materials. Since these oxygen fluorides are difficult to prepare (low-temperature glow discharge, γ irradiation, or photolysis) and, owing to their thermal instability, inconvenient to handle, a direct synthesis from O_2, F_2, and BF_3 appeared desirable. We have found that $O_2^+BF_4^-$ can easily be prepared by uv photolysis of O_2–F_2–BF_3 mixtures. During this photolysis part of the reactor must be kept at −78° to avoid thermal decomposition of the product which is of only marginal thermal stability at ambient temperature. Our yield (~50%) of $O_2^+BF_4^-$ and conversion rates could probably be significantly improved by choosing a reactor geometry more favorable than the cold-finger Pyrex bulb used in our experiment.

Observed Spectra. Parameters determined from the esr spectra of O_2^+ compounds are given in Table I. Although the spectra of $O_2^+Sb_2F_{11}^-$ and $O_2^+AsF_6^-$ at −196° appear characteristic of radicals with axial symmetry, the spectra cannot be accurately simulated unless three independent g factors are used. The experimental and computed spectra of $O_2^+AsF_6^-$ are shown in Figure 1. The spectrum of $O_2^+BF_4^-$ is similar to that described in the literature.[3,4] We observe an asymmetric line with a peak-to-peak width of 430 G. Parameters shown in Table I were determined assuming orthorhombic symmetry. Due to the low resolution of this spectrum, those parameters are not particularly accurate. The spectrum of $O_2^+SbF_6^-$ at −196° appears isotropic with a g factor of about 1.75 and a line width of 2200 G. This spectrum and the spectrum of $O_2^+SbF_6^- \cdot 0.73SbF_5$ are shown in Figure 2. Lines due to gaseous molecular oxygen are identified by an asterisk. The spectrum of $O_2^+SbF_6^- \cdot 0.73SbF_5$ exhibits two components: one component is very broad, and the second component is similar to the spectra of $O_2^+Sb_2F_{11}^-$ and $O_2^+AsF_6^-$. The broad component in the spectrum of $O_2^+SbF_6^- \cdot 0.73SbF_5$ is considerably different from the spectrum of $O_2^+SbF_6^-$. These samples were prepared in Monel which exhibits magnetic behavior. Esr spectra of scrapings from different parts of the bomb were recorded and the spectra showed considerable variation. The line widths varied between 700 and 1100 G and the field corresponding to the mean amplitude between maximum and minimum peaks of the derivative varied between 2100 and 2500 G. It is therefore likely that the low-field component in Figure 2b is due to Monel. Apparently the Monel contributes little to the spectrum shown in Figure 2a.

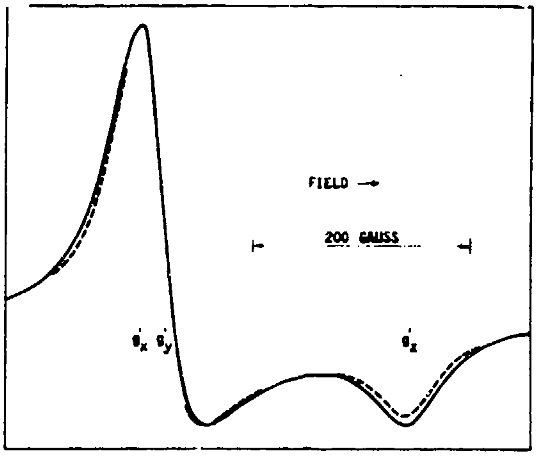

Figure 1. Esr spectrum of dioxygenyl hexafluoroarsenate at −196° (solid line) and computer simulation using the parameters $g_x = 2.000$, $g_y = 1.973$, $g_z = 1.742$, and $\Delta H_{pp} = 80$ G (broken line).

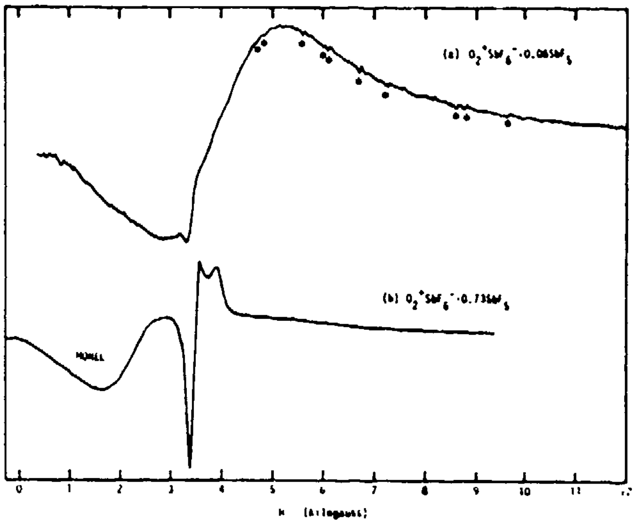

Figure 2. Esr spectra of dioxygenyl fluoroantimonates at −196° (frequency 9.317GHz): (a) sample of composition $O_2^+SbF_6^- \cdot 0.06SbF_5$; (b) sample of composition $O_2^+SbF_6^- \cdot 0.73SbF_5$.

The line widths of the spectra of $O_2^+BF_4^-$, $O_2^+AsF_6^-$, and

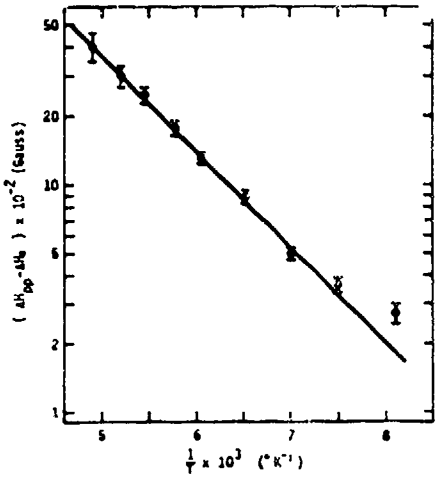

Figure 3. Temperature dependence of the line width of the esr spectrum of dioxygenyl hexafluoroarsenate.

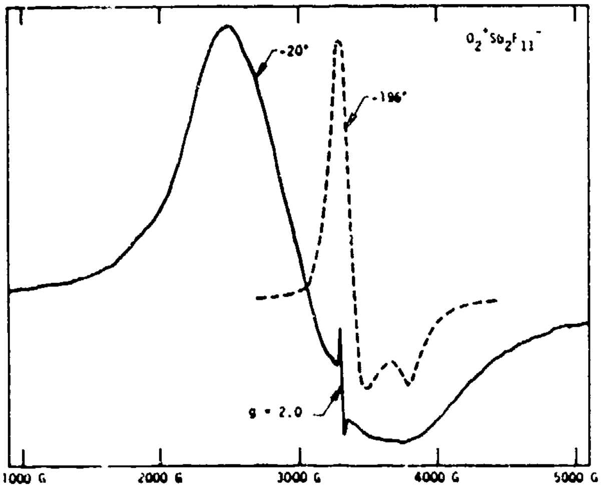

Figure 4. Comparison of esr spectra recorded at −196° (broken line) and −20° (solid line) of $O_2^+Sb_2F_{11}^-$ prepared in quartz. Signal at $g = 2$ is due to an undetermined impurity.

$O_2^+Sb_2F_{11}^-$ and the narrow component of the spectrum of $O_2^+SbF_6^-$·$0.73SbF_5$ increase rapidly at temperatures greater than −170°. The line width of $O_2^+AsF_6^-$ exhibits an exponential dependence on $1/T$ between −160 and −70° as shown in Figure 3. The spectrum of $O_2^+BF_4^-$ appears to behave in a similar way; however within a few degrees of −130° the spectrum disappears when warmed and reappears when cooled. This suggests that a crystal modification occurs at this temperature.

The compounds $O_2^+Sb_2F_{11}^-$, $O_2^+SbF_6^-$, and O_2SbF_6 · $0.73SbF_5$ exhibit different temperature dependences. At −165° the spectrum of $O_2^+Sb_2F_{11}^-$ is broadened and a low-field shoulder begins to appear. As the temperature is increased, the original component broadens out, and an asymmetric line with an apparent g factor of 2.3 emerges from the shoulder. Above −100°, only the "$g = 2.3$" line can be detected as shown in Figure 4. This sample was not prepared in Monel.

The spectrum of $O_2^+SbF_6^-$ at −196° is very broad with ΔH_{pp} about 2300 G and a g factor of 1.75. At higher temperatures, this absorption shifts to higher fields and low-field shoulders emerge. These absorptions become defined at −60° with apparent g factors of 4.69 and 2.83 for the low-field absorptions and approximately 0.9 for the high-field absorption. The high-field absorption can be ascribed to the O_2^+ in which the angular momentum is virtually unquenched. The absorption at $g = 2.83$ is probably due to Monel. The absorption of $g = 4.69$ broadens with temperature. The spectrum of O_2^+-SbF_6^-·$0.73SbF_5$ (Figure 2b) exhibits two components. At temperatures above −196° the sharper component is again broadened. At 20°, only an 800 G wide absorption at $g = 2.80$ can be seen which is probably due to Monel. All spectra described here are reversible as the temperature is increased or decreased.

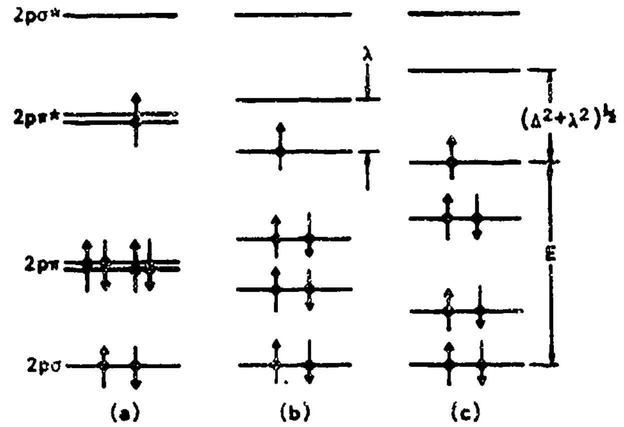

Figure 5. Energy level diagram of the dioxygenyl ion showing the σ- and π-bonding 2p orbitals: (a) energy levels in the absence of spin-orbit coupling and crystal field effects; (b) energy levels with spin-orbit splitting; (c) energy levels with spin-orbit and orthorhombic field splittings.

g Tensor. In the absence of spin-orbit coupling and crystal field effects, the dioxygenyl ion would be in a degenerate state, and the energy level diagram would be given by Figure 5a. Spin-orbit coupling splits the energy levels of the 2pπ and 2pπ* states (Figure 5b). The application of an orthorhombic crystal field further separates the energy levels and quenches the angular momentum (Figure 5c)). Crystal field calculations were carried out in a manner similar to that described by Mergerian and Marshall.[12] The matrix elements of the crystal field potential operator V_{cf} are given by eq 1 where Dirac

$$\langle M_l', M_s' | V_{cf} | M_s M_l \rangle = \Delta \delta_{M_s M_s'} \delta_{M_l \pm 1, M_l'} \tag{1}$$

notation is used, M_l and M_s are the azimuthal quantum numbers for the angular momentum and spin, δ is the Dirac δ function, and Δ is the magnitude of the crystal field energy. The π and π* levels consist of values of M_l which are equal to +1 or −1. The spin-orbit coupling operator only has diagonal elements equal to $\lambda M_l M_s$.

The solution of the secular determinant gives the energies of either the 2pπ or 2pπ* states relative to the energy of the unsplit levels. Each of the two states which result are degenerate in spin, and the energies are given in eq 2.

$$E_1 = {}^1/_2(\Delta^2 + \lambda^2)^{1/2} \tag{2a}$$

$$E_2 = -{}^1/_2(\Delta^2 + \lambda^2)^{1/2} \tag{2b}$$

The wave functions which correspond to these energies are

$$\Psi_{1\alpha}{}^\circ = N_1\left(|1, {}^1/_2\rangle - \left\{\frac{\lambda}{\Delta} - \left[1 + \left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\right\}|-1, {}^1/_2\rangle\right) \tag{3a}$$

$$\Psi_{1\beta}{}^\circ = N_2\left(|1, -{}^1/_2\rangle + \left\{\frac{\lambda}{\Delta} + \left[1 + \left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\right\}|-1, -{}^1/_2\rangle\right) \tag{3b}$$

$$\Psi_{2\alpha}{}^\circ = N_2\left(|1, {}^1/_2\rangle - \left\{\frac{\lambda}{\Delta} + \left[1 + \left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\right\}|-1, {}^1/_2\rangle\right) \tag{3c}$$

$$\Psi_{2\beta}{}^\circ = N_1\left(|1, -{}^1/_2\rangle - \left\{\frac{\lambda}{\Delta} - \left[1 + \left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\right\}|-1, -{}^1/_2\rangle\right) \tag{3d}$$

where N_1 and N_2 are normalization constants given by

$$N_1 = \left(2\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\left\{\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}-\frac{\lambda}{\Delta}\right\}\right)^{-1/2} \quad (4a)$$

$$N_2 = \left(2\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\left\{\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}+\frac{\lambda}{\Delta}\right\}\right)^{-1/2} \quad (4b)$$

The O_2^- ion behaves in a similar way and exhibits the same crystal field splittings. The difference between O_2^- and O_2^+ is that the unpaired electron of O_2^- is considered to be in the state corresponding to energy E_1, while the unpaired electron of O_2^+ is considered to be in the state corresponding to energy E_2.

The *g* tensor for the dioxygenyl ion may be calculated by the method of Kanzig, *et al.*[23] An additional term which contributes to the $2p\pi^*$ levels arises from interaction with the $2p\sigma$ levels. This results in a small admixture of $-{}^1/_2$ spin to wave functions which are predominantly of $+{}^1/_2$ spin, and a small admixture of $+{}^1/_2$ spin to the wave functions which are predominantly $-{}^1/_2$ spin. The additional term added to eq 3c is of the form $(\lambda/E)|0, -{}^1/_2\rangle$, and the term added to eq 3d is of the form $(\lambda/E)|0, {}^1/_2\rangle$. Using second-order perturbation theory, the additional terms added to the basis wave functions are shown in eq 5.

$$\Psi_{2\alpha}' = \Psi_{2\alpha}^\circ - \frac{\lambda}{2E}\frac{\left\{\frac{\lambda}{\Delta}+\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\right\}^{1/2}}{\left[1+\frac{\lambda}{\Delta}^2\right]^{1/2}}|0, -{}^1/_2\rangle \quad (5a)$$

$$\Psi_{2\beta}' = \Psi_{2\beta}^\circ + \frac{\lambda}{2E}\frac{1}{\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}\left\{\left[1+\left(\frac{\lambda}{\Delta}\right)^2\right]^{1/2}-\frac{\lambda}{\Delta}\right\}}|0, {}^1/_2\rangle \quad (5b)$$

The *g* factors can now be calculated using the magnetic Hamiltonian. Fields are independently assumed along the *x*, *y*, or *z* axes of the dioxygenyl ion.

In the absence of the $M_l = 0$ functions, only the wave functions are coupled through $\hat{S}_+$ and $\hat{S}_-$. The addition of the $M_l = 0$ functions allows coupling through $\hat{L}_+$ and $\hat{L}_-$. The *g* factors are obtained by diagonalizing the 2 × 2 matrices formed by application of H_{mag}. This procedure is outlined in more detail by Wertz and Bolton.[24]

The results of these calculations are given in eq 6 which

$$g_z = g_e - 2\left(\frac{\lambda^2}{\lambda^2+\Delta^2}\right)^{1/2} \quad (6a)$$

$$g_x = g_e\left(\frac{\Delta^2}{\lambda^3+\Delta^2}\right)^{1/2} - \frac{\lambda}{E}\left[\left(\frac{\Delta^2}{\lambda^2+\Delta^2}\right)^{1/2} + \left(\frac{\lambda^2}{\lambda^3+\Delta^2}\right)^{1/2} + 1\right] \quad (6b)$$

$$g_y = g_e\left(\frac{\lambda^2}{\lambda^2+\Delta^2}\right)^{1/2} + \frac{\lambda}{E}\left[\left(\frac{\lambda^2}{\lambda^2+\Delta^2}\right)^{1/2} - \left(\frac{\lambda^2}{\lambda^3+\Delta^2}\right)^{1/2} - 1\right] \quad (6c)$$

shows that the g tensor should be comprised of three different principal values provided that *E* is sufficiently small.

Crystal Field Effects. The esr parameters determined from the simulations, which are given in Table I, can be used to calculate the parameters Δ and *E* shown in Figure 5. The *g* factors of $O_2^+AsF_6^-$ and $O_2^+Sb_2F_{11}^-$ are believed accurate to ±0.002, and that of $O_2^+BF_4^-$ is believed accurate to ±0.02. There is some doubt of the spin–orbit coupling constant λ of O_2^+ in a crystal lattice. The values of λ are 195 cm^{-1} for the free ion[25] and 151 cm^{-1} for atomic oxygen. Since the crystal field probably reduces the value of λ from the free ion, the correct value is probably between 151 and 195 cm^{-1}. In principle, the value of λ can also be determined from the solutions of the simultaneous equations (6a)–(6c), but the precision of the *g* factors is not sufficiently accurate for this purpose. Arbitrarily, the free-ion value of λ was used. The values of Δ and *E* which are given in Table I must therefore be considered as upper limits of these energies.

These values can be compared with those determined from spectra of O_2^- and the isoelectronic NO. The comparison of the crystal field parameters of O_2^+ and O_2^- is valid since a similar mixing of orbitals takes place to give shifts of the *g* factor from g_e. In NaI where large negative ions and small positive ions surround the O_2^- ion, the angular momentum is unquenched.[23] However, in other halides[23] values of Δ range from 650 to 1200 cm^{-1} and values of *E* range from 6 × 10^4 to 15 × 10^4 cm^{-1}. The precise values depended upon the sizes of the ions and the symmetry of the lattice sites. The asymmetry was attributed to covalent interaction between the O_2^- and the alkali metal ions since the site of the O_2^- ion aligns in the 110 direction such that the crystal ions are axially symmetric with respect to the O_2^- internuclear axes. In other studies, alkali metal–O_2^- compounds were trapped in an argon matrix at 4°K,[26,27] so that the principal interaction is with one alkali metal ion. In these cases Δ for O_2^- was considerably larger than in alkali metal halides.

Values of Δ and *E* obtained for NO adsorbed on various zeolites agree more closely with the values obtained here for O_2^+. Values of Δ range from 1050 to 1700 cm^{-1}, and values of *E* range between 1.2 × 10^4 and 3.7 × 10^4 and are consistent with a small interaction with the surface.[9] NO adsorbed on MgO and generated in various crystals exhibits larger values of Δ and *E*, and thus the elements of the g tensor are much closer to g_e.[10] Similarly, the N_2^- generated in KN_3[8] is also in sites with greater asymmetry and exhibits *g* factors closer to g_e.

The data of Table I suggest that in $O_2^+BF_4^-$, $O_2^+AsF_6^-$, and $O_2^+Sb_2F_{11}^-$, the O_2^+ cation is in the site of a small orthorhombic field. The origin of the field can be due either to covalent interaction with the fluorine in the complex anion, as suggested from neutron diffraction studies on $O_2^+PtF_6^-$[28] or to an asymmetric arrangement of anions around O_2^+. Values of Δ were also estimated from magnetic susceptibility measurements.[6] If a value for λ of 195 cm^{-1} is assumed, then Δ would be about 1400 cm^{-1}.

Measurements of the spectrum of $O_2^+SbF_6^-$ at −250°[6] indicate that the spectrum is sharpened considerably when the temperature is below −195°, and the O_2^+ ion may also be in an orthorhombic environment.

Temperature Dependence. The spectra of each of the O_2^+ compounds exhibit a strong temperature dependence. In all samples studied, as the temperature is increased, the lines broaden. Only $O_2^+AsF_6^-$ exhibited a spectrum with a single component over a sufficiently large temperature range so that the line width can be investigated as a function of temperature. $O_2^+BF_4^-$ was assumed to be linear over a narrow range of temperature. If the slopes of ln $(\Delta H_{pp} - \Delta H_0)$ *vs.* $1/T$ for $O_2^+AsF_6^-$ and $O_2^+BF_4^-$ are considered to be related to activation energies in an Arrhenius plot, the energy for the relaxation of the spectrum of $O_2^+AsF_6^-$ is 1.92 kcal (690 cm^{-1}) and that of $O_2^+BF_4^-$ is 1.3 kcal (470 cm^{-1}). These values are considerably smaller than the crystal field energies calculated from the *g* factors and suggest that there may be several modes operating to cause relaxation.

Since cross relaxation and exchange interactions are possible modes of relaxations in concentrated paramagnetic samples, attempts were made to form dilute O_2^+ salts in an $NO^+AsF_6^-$ lattice. The simultaneous formation of $NO^+AsF_6^-$ was unsuccessful since the reaction of NO + F_2 + AsF_5 is much faster than that of O_2 + F_2 + AsF_5. The displacement of O_2^+ by NO^+ by exposing $O_2^+AsF_6^-$ to FNO at −77° did not produce the desired cation distribution.

The mechanism of the relaxation process cannot be determined from line width measurements alone since the components of spin–lattice and spin–spin relaxation times cannot be separated. At line widths in the order of 100 G an incident microwave power far in excess of the Klystron output would be required in order to use progressive saturation techniques. Based on other measurements we can speculate on the relaxation mechanism.

Calculations of the dipolar broadening based on the published crystal structure of the dioxygenyl compounds[14,29,30] were carried out according to the model of Van Vleck.[31] In all cases the second moment was about 10^4 G^2. If this is the dominant broadening mechanism, the powder spectrum should be simulated by convoluting the powder spectrum onto a gaussian line shape with a width of more than 100 G peak-to-peak. However, for $O_2AsF_6^-$ and $O_2^+Sb_2F_{11}^-$ lorentzian lines were required. This result indicates that at least some of the dipolar interactions are partially averaged in the lattice even at −196°.

Recent ^{19}F nmr studies of $O_2^+AsF_6^-$ indicate substantial cation motion in the lattice at temperatures above −240°.[6] A similar conclusion was derived from electron diffraction studies of $O_2^+PtF_6^-$.[28] These results suggest that modulation of the crystal field energy[32] is indeed one reasonable mechanism for relaxation of the electron spin. Although the spectrum of $O_2^+SbF_6^-$ is extremely broad at −196°, cooling further sharpens the line.[6] This further suggests that in this lattice there is more room for motion of the O_2^+ ion. $O_2^+BF_4^-$ is also somewhat broader than $O_2^+AsF_6^-$ and $O_2^+Sb_2F_{11}^-$ although the crystal field is stronger. In the $O_2^+BF_4^-$ lattice, the O_2^+ ions are closer, and it is more likely that exchange processes are more significant than in the other materials as a means of relaxation. This would also explain the apparently smaller activation energy.

In the three dioxygenyl–antimonate compounds studied, different low-field absorptions appear at temperatures greater than −130°. This may be the result of strong exchange interactions between neighboring O_2^+ ions. This exchange process may also account for part of the more rapid relaxation of O_2^+ at −196°. One mechanism which may account for the enhanced exchange in the antimonates would be one wherein the SbF_6^- ion acts as a bridge between O_2^+ ions. This is more likely in antimonates than in any of the other materials studied since the antimonates are more polarizable. Figure 4 shows the spectrum of $O_2^+Sb_2F_{11}^-$ at −20°. An asymmetric line with an apparent g factor of 2.3 can be seen.

Although these processes are not completely understood, the different spectra of $O_2^+Sb_2F_{11}^-$ and $O_2^+SbF_6^-$ at −196° appear to be a simple, nondestructive qualitative method to detect the presence of $Sb_2F_{11}^-$ formed in $O_2^+SbF_6^-$ during synthesis. Figure 2a demonstrates that amounts of $Sb_2F_{11}^-$ as low as about 5% can be readily detected by esr.

Conclusions

1. g factors of $O_2^+AsF_6^-$, $O_2^+Sb_2F_{11}^-$, and $O_2^+BF_4^-$ indicate strong orthorhombic symmetry around the O_2^+ ion in the lattice.

2. Values for the orthorhombic crystal field and for the energy separation between σ and π^* states are in agreement with values of O_2^- and NO in single crystals and NO adsorbed on zeolites.

3. Several different relaxation processes to account for the temperature dependence of the line width of the esr spectra were proposed. Modulation of the crystal field by ion motion appears to be a dominant mechanism. The spectrum of $O_2^+SbF_6^-$ undergoes faster relaxation at −196° than each of the other salts.

4. Anomalous spectra for dioxygenyl antimonates above −140° were observed. Absorptions where $g > 2$ may indicate coupling between dioxygenyl ions.

5. Because of the difference between spectra of $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$ or $O_2^+SbF_6^-{\cdot}0.73SbF_5$ at −196°, esr can be used to demonstrate the absence of excess SbF_5 in $O_2^+SbF_6^-$.

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Registry No. O_2AsF_6, 12370-43-3; O_2BF_4, 12228-13-5; O_2SbF_6, 12361-66-9; $O_2Sb_2F_{11}$, 12592-38-0.

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The NF_3^+ Radical Cation. Electron Spin Resonance Studies of Radiation Effects in NF_4^+ Salts

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Exposure of $NF_4^+AsF_6^-$ and $NF_4^+SbF_6^- \cdot 0.8SbF_5$ to ^{60}Co γ rays at 77°K gave two paramagnetic centers, one of which is shown by ESR spectroscopy to contain one nitrogen atom and three equivalent fluorine atoms. Based on its magnetic properties it is identified as pyramidal $\dot{N}F_3^+$, a novel radical cation. The other center exhibits strong interaction of the electron with two fluorine atoms, weaker interaction with the antimony or arsenic central atom, and small interaction with several other fluorine atoms. It is tentatively assigned to the electron-loss species $As\dot{F}_6$, $Sb\dot{F}_6$, or $Sb_2\dot{F}_{11}$ with the unpaired electron largely confined to two fluorine ligands. Irradiation of $NF_4^+BF_4^-$ did not result in well-defined magnetic centers. An improved synthesis of $NF_4^+BF_4^-$ is reported.

Introduction

Although carbon readily forms tetrahedral molecules with electronegative ligands, such as the halogens, the synthesis of the isoelectronic nitrogen compounds has been achieved only recently.[1] Attempts to prepare NF_4^+ salts had been discouraged by theoretical computations[2,3] showing that these salts should be thermodynamically unstable and by the nonexistence of the parent compound NF_5. Once the principle was recognized[1] that NF_4^+ salts can be prepared from NF_3, F_2, and a strong Lewis acid in the presence of a suitable activation energy source, a number of synthetic methods became available. These involve the use of different activation energy sources such as glow discharge,[4,5] elevated temperature and pressure,[6,7] γ irradiation[8] and uv photolysis.[9]

On exposure to high-energy radiation, CF_4 undergoes the dissociative electron-capture process

$$CF_4 + e^- \rightarrow \dot{C}F_3 + F^- \qquad (1)$$

to give $\dot{C}F_3$ radicals which have been detected both in the liquid[10] and solid[10-12] phase. The fact that no evidence for the existence of the $\dot{C}F_4^-$ radical anion was observed is not surprising in view of the validity of the octet rule for first-row elements of the periodic system. A study of the corresponding NF_4^+ system appeared interesting, particularly in view of the recent suggestion[9] that $\dot{N}F_3^+$ and the radicals derived from the Lewis acid–fluorine interaction, such as $As\dot{F}_6$, are the key intermediates in the formation mechanism of NF_4^+ salts. By analogy with CF_4, one might expect that $\dot{N}F_3^+$ might be prepared by γ irradiation of NF_4^+ salts according to

$$NF_4^+ + e^- \rightarrow \dot{N}F_3^+ + F^- \qquad (2)$$

In this paper we report ESR spectroscopic evidence for the existence of the novel radicals $\dot{N}F_3^+$ and $M\dot{F}_6$, in addition to an improved synthesis of $NF_4^+BF_4^-$ by metathesis in HF solution.

Experimental Section

Syntheses of NF_4^+ Salts. A sample of $NF_4^+SbF_6^- \cdot 0.8SbF_5$ was prepared as previously described[7] by heating a 1:1.2 l molar mixture of NF_3, F_2, and SbF_5 in a Monel cylinder to 120° for 2 days under an autogenous pressure of 200 atm. The resulting white solid, having the composition $NF_4^+SbF_6^- \cdot 1.9SbF_5$, was converted to $NF_4^+SbF_6^- \cdot 0.8SbF_5$ by heating under a dynamic vacuum to 200° for 3 days. The compound was analyzed as previously described.[13] The only detectable impurities were small amounts of Ni (0.066 wt %) and Cu (0.03%) in the form of their salts. The synthesis of $NF_4^+AsF_6^-$ has previously been described.[13] Again, the only detectable impurities were Ni (0.98%) and Cu (0.27%).

For the synthesis of $NF_4^+BF_4^-$ by metathesis, commercial HF was dried by shaking it overnight in a 1-l. Monel cylinder with fluorine (10 l./0.7 kg of HF) after which oxygen and residual fluorine (ca. 210 psi) were removed under vacuum at −78°. The metathesis apparatus, fabricated entirely from Teflon and Kel-F, consisted of four identical 1-l. vessels connected in series through valves and filters with a fitting carrying a vacuum line connection, a 60-psi pressure relief valve, and a compound pressure–vacuum gauge (Kel-F-coated diaphragm) between the last two vessels. In addition, each vessel was stirred with a Teflon-coated magnetic stirring bar and equipped with a valve which by-passed the filter for introduction or removal of gaseous or liquid materials. All manipulations of reagents and products were conducted either in an inert-atmosphere glove box or by standard high-vacuum techniques.

A 251.5-g (1.94-mol) quantity of silver fluoride (Cationic, Inc.), which contained 2.1% HF-insoluble impurities, was loaded into the first vessel and 284 g of HF was added. Into the second vessel were placed 400.5 g (0.822 mol) of $NF_4SbF_6 \cdot 0.8SbF_5$ and 148 g of HF. The $AgHF_2$ solution in the first vessel was pressurized to 30 psi with nitrogen and passed through a filter into the stirred NF_4^+ salt–HF solution under autogenous pressure in the second vessel. The resulting NF_4HF_2 solution was separated from the $AgSbF_6$ precipitate by filtration into the evacuated third reaction vessel. After brief pumping to remove the nitrogen pressurizing gas, BF_3 (68 g, 1.0 mol) was added to the third vessel until the total pressure above the liquid remained constant at 19–20 psi. The NF_4BF_4 solution was separated from the precipitated $AgBF_4$ by filtration into the evacuated fourth vessel. After removal of excess BF_3 and solvent HF the residual solid product (101.9 g) was isolated. The composition of the solid (in mole percent) was NF_4BF_4 (89), $NF_4Sb_2F_{11}$ (7.9), and $AgBF_4$ (3.1).

γ Irradiation and ESR Spectra. The NF_4^+ salts were transferred in the dry nitrogen atmosphere of a glove box into passivated 4-mm o.d. quartz tubes which were flame-sealed in vacuo. For the solution study, a 0.24 *M* solution of $NF_4^+SbF_6^- \cdot 0.8SbF_5$ in anhydrous HF was heat-sealed in a Teflon FEP tube.

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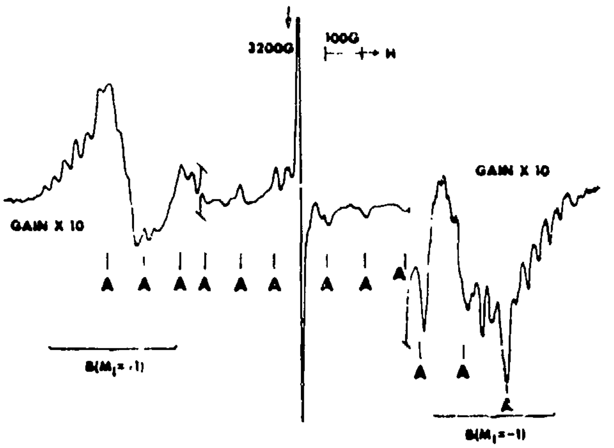


Figure 1. First-derivative X-band ESR spectrum for $NF_4^+SbF_6^- \cdot 0.8SbF_5$ after exposure to ^{60}Co γ rays at 77° K, showing features assigned to species A and B. The intense central component stems in part from paramagnetic centers generated in the quartz tube.

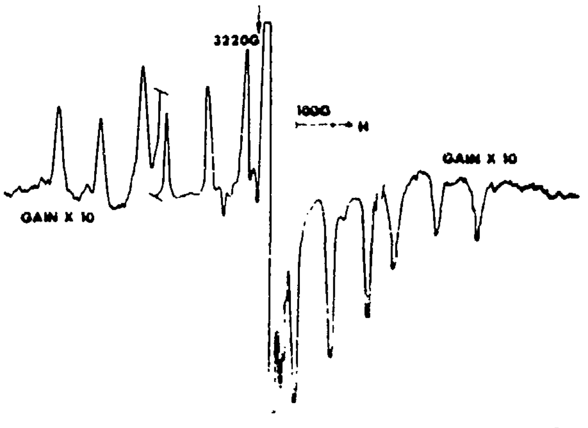


Figure 2. Sample of Figure 1 but after annealing at about 140° K and recooling to 77° K, showing features assigned to radical A.

The sample tubes were cooled to 77°K prior to exposure to ^{60}Co γ rays in a Vickrad cell at a nominal dose rate of about 4 Mrads hr^{-1}. It was necessary to expose samples to high doses (about 10 Mrads) before good ESR signals were obtained.

The ESR spectra were obtained with a Varian E3 spectrometer at 77°K. Samples were annealed by gradual warming to above 77°K and recooling whenever significant changes were observed in the continuously monitored esr signals. Signals were independent of sample tube orientation indicating the absence of sample graining effects.

Results and Discussion

Synthesis. For the preparation of $NF_4^+SbF_6^- \cdot xSbF_5$ and $NF_4^+AsF_6^-$ the previously reported[7] elevated pressure–temperature method was chosen. For that of $NF_4^+BF_4^-$, a metathetical process similar to that of Tolberg, *et al.*[14] was selected which was significantly improved by substituting AgF for the originally used ^{14}CsF. The reaction sequence is best described by eq 3–5. Since $Ag^+HF_2^-$ was used in excess for

$$AgF + HF \xrightarrow{HF} Ag^+HF_2^- \tag{3}$$

$$Ag^+HF_2^- + NF_4^+SbF_6^- \xrightarrow{HF} AgSbF_6\downarrow + NF_4^+HF_2^- \tag{4}$$

$$NF_4^+HF_2^- + BF_3 \xrightarrow{HF} NF_4^+BF_4^- + HF \tag{5}$$

the precipitation of the fluoroantimonate, the rather insoluble $AgBF_4$ precipitated from the $NF_4^+HF_2^-$ solution upon BF_3 addition. This required an additional filtration step. The level of impurities ($NF_4Sb_2F_{11}$ and $AgBF_4$) in the final crude product is determined by the solubility products of $AgSbF_6$ and $AgBF_4$ in HF.

Since the $NF_4^+SbF_6^- \cdot xSbF_5$ starting material can readily be prepared on a large scale,[7] this metathetical process is well suited for the synthesis of larger amounts of $NF_4^+BF_4^-$. Its main drawback is the relatively low product purity. Using CsF the purity is quite low, but with AgF we have been able to obtain purities as high as 89 mol % of $NF_4^+BF_4^-$. The main impurities could significantly be decreased by subsequent recrystallization[14] of the crude $NF_4^+BF_4^-$ from suitable solvents. Whereas the γ-irradiation[8] and uv-photolysis[9] processes yield purer products, they are at present much less amenable to scale up.

Electron Spin Resonance Spectra. The best defined spectra were obtained from $NF_4^+SbF_6^- \cdot 0.8SbF_5$ and typical spectra, obtained before and after annealing, are given in Figures 1 and 2, respectively. The $NF_4^+AsF_6^-$ salt gave very similar results, but $NF_4^+BF_4^-$ proved to be remarkably resistant to ^{60}Co γ rays. Two radical species, A and B, can be detected in the initial spectra (Figure 1), but radical B decayed rapidly on annealing to about 150°K, leaving a well-defined spectrum of A (Figure 2).

Radical A. Well-defined wing (parallel) triplets characteristic of hyperfine coupling to ^{14}N $[I(^{14}N) = 1]$ establish the presence of one strongly coupled ^{14}N nucleus. If the outer sets of triplets are described as the $M_I(^{19}F) = \pm^1/_2$ "parallel" features for $\dot{N}F_3^+$ $[I(^{19}F) = ^1/_2]$ for the three equivalent fluorine atoms, then the $\pm^1/_2$ lines are predicted to fall close to the more intense set of six lines in the central region of the spectrum. However, the apparent $A(^{14}N)$ coupling on these inner features has decreased by about 15 G relative to the outer lines, and hence we suggest that these inner lines contain dominant contributions arising from "anisotropic" features.

Interpretation of ESR spectra for pyramidal radicals of this type is complicated by the fact that the principal values for the three ^{19}F hyperfine tensors lie along three different axes, two of which always differ from those for the ^{14}N hyperfine coupling. Also, there should be a relatively large second-order splitting (δ) of the $M_I(^{19}F) = \pm^1/_2$ lines which can be approximately estimated[15] from $\delta_\parallel = {}^3/_2 A_\perp(^{19}F)/H_\perp$ and $\delta_\perp = {}^3/_4(A_\perp + A_\parallel)/H_\parallel$. From the initial approximate data, we find $\delta_\parallel \simeq 3$ G and $\delta_\perp \simeq 23$ G. Thus the former will be barely defined in our spectra, but the latter result is clearly significant. This problem has been discussed in depth by Coope, *et al.*,[11,16] especially for the isoelectronic radical, $\dot{C}F_3$, and we have followed their procedure in arriving at the parameters listed in Table I. The results for $\dot{C}F_3$[10,12] are included for comparison.

The results for ^{19}F of $\dot{N}F_3^+$ are in good agreement with those[12] of $\dot{C}F_3$ but indicate a small increase in spin density on fluorine on going from $\dot{C}F_3$ to $\dot{N}F_3^+$. Since these are not principal values, we make no attempt to estimate the actual spin density on fluorine from these data. However, the data for ^{14}N can be taken as principal values and hence we can deduce approximate spin densities in the 2s and 2p atomic orbitals that nitrogen contributes to the total MO of the unpaired electron. This we do by dividing the A and $2B$ values by the values for $A°$ (550 G) and $2B°$ (33 G) estimated from recent accurate atomic wave functions.[17] (A and $2B$ are the experimental isotropic and traceless parts of the hyperfine tensor components, and $A°$ and $2B°$ are the corresponding computed values for unit population of the 2s and 2p AO's.) The results (Table II) indicate that the total spin density on nitrogen is about 69%, and the 2p:2s ratio is about 2.8. Only the isotropic ^{13}C datum is known[10] for $^{13}CF_3$, and this gives about 24% spin density in the 2s AO on carbon. The latter value might be somewhat high, since the anisotropic components of ^{19}F in $\dot{N}F_3^+$ and $\dot{C}F_3$ are quite similar (133 and 123 G, respectively) implying that the spin densities on F and

Table I. ESR Data for Radical in γ-Irradiated NF_4^+ Salts, Together with Those for $\dot{C}F_3$

	Hyperfine tensor components, G[a,b]								
	^{14}N, ^{13}C, ^{121}Sb			^{19}F[c]			g values		
Radical	∥	⊥	Iso	∥	⊥	Iso	∥	⊥	Av
$\dot{N}F_3^+$[i]	115	90	98.3	300	100	167	2.003	2.009	2.007
$\dot{C}F_3$[d]				264	80	141.3			
$\dot{C}F_3$[e]			272			143			
$Sb\dot{F}_6$	~30 or ~60 (see text)			630[f,g]	420[f,g] +~30[h]	490		~2.00	

[a] G = 10^{-4} T [b] Errors ~±3G. [c] Data relate to the C_{3v} axes and therefore are not principal values. [d] Reference 12. [e] Reference 10. [f] For two equivalent fluorine atoms. [g] Approximate since number of subcomponents unknown. [h] Weak coupling to other fluoride ligands. [i] The $\dot{N}F_3^+$ signals derived from either NF_4SbF_6 or NF_4AsF_6 had experimentally undistinguishable parameters.

Table II Estimated Spin Densities (%) for $\dot{N}F_3^+$ and $\dot{C}F_3$ on Central Atom

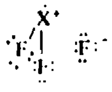
	a_s^2	a_p^2	Total	2p:2s
$\dot{N}F_3^+$	18	50.5	68.5	2.8
$\dot{C}F_3$	24			

hence also on the central atoms should be similar in both species. An alternate although less plausible, explanation might be that the atomic orbitals of the central atom in $\dot{C}F_3$ have more s character (*i.e.*, a stronger contribution from sp^2 hybridization) than those in $\dot{N}F_3^+$. This would imply that $\dot{C}F_3$ is less pyramidal than $\dot{N}F_3^+$.

The implications from the ESR data that in $\dot{N}F_3^+$ the spin density on F is somewhat higher than in $\dot{C}F_3$ and that the atomic orbitals of the central atom in $\dot{C}F_3$ have more s character than those in $\dot{N}F_3^+$ are in accord with arguments based on consideration of the resonance structures I–III.


I


II


III

In $\dot{N}F_3^+$ the formal positive charge and the higher oxidation state of the central atom should increase the effective electronegativity of the NF_2^+ group when compared to that of CF_2. Therefore, for $\dot{N}F_3^+$ the relative contribution from structure II should be higher than for CF_3 hereby increasing the spin density on F in $\dot{N}F_3^+$. Since with an increasing electronegativity difference between X and F the XF bond becomes more ionic, the contribution from the sp^2-hybridized model III to the bonding should be more significant in $\dot{C}F_3$ than in $\dot{N}F_3^+$. In addition, model III for $\dot{N}F_3^+$ would require an unfavorable double positive charge on the NF_2 part of the molecule.

The failure to observe any evidence for the NF_4 radical is not surprising in view of the above-mentioned strict validity of the octet rule for first-row elements. This is in marked contrast with second-row elements, such as phosphorus for which the corresponding PF_4 has been observed.[18,19] We have also studied the irradiation products from HF solutions of $NF_4^+SbF_6^- \cdot 0.8\ SbF_5$ since it is often found that dissociative reactions, such as the hypothetical process

$$NF_4 \rightarrow \dot{N}F_3^+ + F^- \qquad (6)$$

are solvent dependent. Unfortunately, solutions in HF, the only suitable solvent, gave, after irradiation, only very broad uninformative features.

Radical B. The other species (B), lost during mild annealing, is tentatively identified as $Sb\dot{F}_6$ (or $As\dot{F}_6$) or $Sb_2\dot{F}_{11}$ for the following reasons. (1) $\dot{N}F_3^+$ is undoubtedly formed by electron capture, and the most reasonable initial electron loss center is $Sb\dot{F}_6$. (2) The results indicate the presence of two (or, less reasonably, one) strongly coupled ^{19}F nuclei with very weak coupling to magnetic isotopes of antimony or arsenic and possible further ^{19}F nuclei. Electron loss from SbF_6^- is from one of the nonbonding orbitals on fluorine, and a suitable distortion could well tend to isolate the unpaired electron on just two of the ligands. This model provides a reasonable explanation for the observed data. (3) The broad similarity between the results for the arsenic and antimony salts requires a low spin density on the central atom, in accord with the model. (4) Lack of $\dot{N}F_3^+$ radicals in the BF_4^- salt accord with the apparent inability to form $B\dot{F}_4$ radicals from such salts.[18]

Based on the above arguments, we favor the spectral analysis indicated in Figure 1 rather than the alternative of treating the B features as a doublet, on the basis of the relatively small anisotropy. For a distorted radical with the unpaired electron delocalized between two adjacent fluoride ligands, the apparent anisotropy deduced from the powder spectrum must be greatly reduced compared with the real anisotropy or that to be expected from spin confined to just one ligand.

The superhyperfine coupling present on the $M_I(^{19}F) = \pm 1$ lines must then arise from coupling to ^{121}Sb ($I = {}^5/_2$; 57.25% abundance) and to a lesser extent from ^{123}Sb ($I = {}^7/_2$; 42.75% abundance). This will not explain all the resolved features in Figure 1 and hence extra ^{19}F coupling or interaction with the second antimony atom of Sb_2F_{11} must also be present.

It is interesting to compare these results with those for a species formed in irradiated sodium hexafluoroantimonate, originally thought to be SbF_5^- or SbF_6^{2-} [20] but later assigned to an impurity species, $\dot{O}SbF_4$ or $\dot{O}SbF_5^-$.[21] This center had only very weak coupling to ^{19}F (about 5 G) and a near-isotropic coupling to ^{121}Sb in the 60–70-G region. Our present results indicate a coupling to ^{121}Sb of 30 or 60 G. A reduction of the coupling in SbF_6 or $Sb_2\dot{F}_{11}$, when compared to that for $\dot{O}SbF_5^-$, can be rationalized by electronegativity arguments.[21,22]

Although we have been unable to obtain well-resolved ESR spectra for radical B, we conclude that this center is probably $Sb\dot{F}_6$ or $Sb_2\dot{F}_{11}$, with the unpaired electron largely confined to two adjacent fluoride ligands. Other possible assignments that had occurred to us have been rejected for various reasons. For example, the assignment to F_2^-, weakly interacting with neighboring ions, can be ruled out since the observed hyperfine coupling is too small.

Summary

γ Irradiation of NF_4^+ salts at 77°K produces the novel pyramidal cation $\dot{N}F_3^+$ in addition to a second less stable species which is tentatively assigned to the corresponding anion electron-loss species, $Sb\dot{F}_6$, $Sb_2\dot{F}_{11}$, and $As\dot{F}_6$, respectively. The experimental observation of these species lends further credibility to the reaction mechanism previously suggested[9] for the formation and thermal decomposition of NF_4^+ salts. In this mechanism, the $As\dot{F}_6$ radical was postulated to be the crucial intermediate capable of supplying the energy (ionization potential of NF_3 minus the energy released by the formation of the ion pair) required for the oxidation of NF_3 according to

$$As\dot{F}_6 + NF_3 \rightarrow \dot{N}F_3^+AsF_6^- \qquad (7)$$

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Registry No. $NF_4^+SbF_6^-$, 16871-76-4; $NF_4^+AsF_6^-$, 16871-75-3; $NF_4^+BF_4^-$, 15640-93-4; $\dot{N}F_3^+$, 54384-83-7; $\dot{S}bF_6$, 54384-84-8.

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Contribution from Rocketdyne, a Division of
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The Hexafluorobromine(VII) Cation, BrF_6^+. Infrared Spectrum and Force Field

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The syntheses of $BrF_6^+AsF_6^-$ and $BrF_6^+Sb_2F_{11}^-$ from BrF_5 and the corresponding KrF_2·(Lewis acid) adducts have recently been reported by Gillespie and Schrobilgen.[1,2] These BrF_6^+ salts were characterized by ^{19}F nmr and Raman spectroscopy.[2] Since complete vibrational spectra and modified valence force fields are known for ClF_6^+ [3] and IF_6^+,[4-6] similar information on BrF_6^+ was desirable to obtain more quantitative data on the bonding in these unusual high oxidation state cations.

Experimental Section

Apparatus and Materials. The materials used in this work were manipulated in a well-passivated (with ClF_3 and BrF_5) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 4251 F4Y). Pressures were measured with a Heise Bourdon tube type gauge (0 1500 mm ± 0.1%). Because of the rapid hydrolytic interaction with moisture, all materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. The spectra of solids at room temperature were obtained by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a Wilks minipellet press. The powdered sample was placed between the platelets before starting the pressing operation. The low-temperature spectra were recorded at -196° using a cell and transfer technique similar to one previously described.[7] The inner windows of the cell were AgCl; the outer ones, CsI disks. The instrument was calibrated by comparison with standard calibration points.[8]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[9] for the elimination of plasma lines. For low-temperature work a Miller Harney device[10] was used. Passivated quartz, Teflon FEP, or Kel-F capillaries were used as sample tubes in the transverse-viewing, transverse-excitation technique.

Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with copper $K\alpha$ radiation and a nickel filter. Samples were sealed in quartz capillaries (~0.5-mm o.d.).

The purification of BrF_5 and AsF_5 and the preparation of BrF_5·$2SbF_5$ have previously been described.[11] Krypton difluoride was prepared from Kr (Matheson, 99.995%) and F_2 using glow discharge at 183°. Our method was similar to that[12] of Schreiner, *et al.*, except for the elimination of the gas circulation system. The KrF_2 was collected at the end of a run in a tared Teflon FEP U trap maintained at -78°. The only detectable impurity in the KrF_2 was a small amount of N_2O_5 which could be removed by treatment of the crude KrF_2 with BF_3 at -78 and -10°, which converted the N_2O_5 to nonvolatile $NO_2^+BF_4^-$.[13] Pure KrF_2 was obtained by pumping off the volatile material and trapping the KrF_2 at 78°.

Preparation of BrF_6^+ Salts. The $BrF_6^+AsF_6^-$ salt was prepared by the method of Gillespie and Schrobilgen[2] using a KrF_2:AsF_5 mole ratio of 2:1 and a large excess of BrF_5. Complete material balances were obtained for the experiments. The yields of $BrF_6^+AsF_6^-$ were found to range from 5.3 to 7.0 mol % based on KrF_2 and the correct amounts of Kr and F_2 were evolved.

For the synthesis of the SbF_5 salt, weighed amounts of $BrF_4^+Sb_2F_{11}^-$ were dissolved in BrF_5, and KrF_2 was added at -196°. The mixture was kept at 25° until no further gas evolution was observed. Volatile materials were removed at room temperature. The Raman spectrum of the solid residue was identical with that previously reported.[2] Since in a separate experiment we had demonstrated that $BrF_4^+Sb_2F_{11}^-$ can be removed under a dynamic vacuum at 50°, this residue was warmed to 50° for 1 week under a dynamic vacuum. Starting originally with 1.02 mmol of $BrF_4^+Sb_2F_{11}^-$ and 7.63 mmol of KrF_2, 23.2 mg of a white solid residue was obtained which according to its infrared and Raman spectra was mainly $BrF_6^+SbF_6^-$·$xSbF_5$ with x being less than 1.

Results and Discussion

Synthesis and Properties. The synthesis data are in excellent agreement with the reports[2] of Gillespie and Schrobilgen. The following observations deserve some comment. In the previous study[2] no material balances were obtained. In our study the yield of $BrF_6^+AsF_6^-$ was found to be about 6 mol % based on the assumption that 1 mol of KrF_2 could produce 1 mol of BrF_6^+ salt. In addition, it was established that $BrF_6^+SbF_6^-$·$xSbF_5$ can be separated from $BrF_4^+Sb_2F_{11}^-$ by vacuum sublimation. However, the resulting product was not of sufficient quantity and purity to allow further characterization and to determine whether the anion was mainly SbF_6^- or $Sb_2F_{11}^-$. When samples of BrF_6^+ salts were placed in passivated quartz capillaries and flame sealed, Raman spectroscopy showed that at ambient temperature the BrF_6^+ salts attacked the quartz with formation of the corresponding O_2^+ salts. Similarly, the BrF_6^+ salts interacted at ambient temperature with AgCl. The attack of AgCl by $BrF_6^+AsF_6^-$ was much faster than that by the corresponding SbF_5 salt and preempted the recording of $BrF_6^+AsF_6^-$ infrared spectra at room temperature. In Teflon FEP containers the BrF_6^+ salts were stored at room temperature for prolonged periods without noticeable decomposition.

X-Ray Powder Data. The observed and calculated X-ray powder diffraction data for $BrF_6^+AsF_6^-$ are listed in Table I. The pattern was corrected for lines[14] due to $NO_2^+AsF_6^-$ resulting from the interaction[13] between AsF_5 and some N_2O_5 which was present as an impurity in the KrF_2 starting material. The powder pattern of $BrF_6^+AsF_6^-$ very closely resembles that[4,15] of $IF_6^+AsF_6^-$ indicating that the two compounds are isomorphous. By analogy with $IF_6^+AsF_6^-$, it was indexed in the face-centered cubic system with $a = 9.394$ Å. As expected, the unit cell of $BrF_6^+AsF_6^-$ is slightly smaller than that of

Table I. X-Ray Powder Data for $BrF_6^+AsF_6^-$

d, Å Obsd	d, Å Calcd	Intens	h	k	l
4.69	4.69	vs	2	0	0
3.32	3.32	s	2	2	0
2.712	2.712	ms	2	2	2
2.509	2.511	w	3	2	1
2.102	2.100	m	4	2	0
2.002	2.003	w	3	3	2
1.916	1.918	ms	4	2	2
1.661	1.661	m	4	4	0
1.565	1.566	ms	4 6	4 0	2 0
1.486	1.486	mw	6	2	0
1.417	1.416	mw	6	2	2
1.356	1.356	w	4	4	4
1.302	1.303	m	6	4	0
1.278	1.279	vw	7 6 5	2 3 5	1 3 2
1.256	1.255	m	6	4	2
1.193	1.193	w	7 6	3 5	2 1
1.174	1.174	w	8	0	0
1.140	1.141	mw	8 6	2 4	0 4
1.107	1.107	mw	8 6	2 6	2 0
1.077	1.078	w	6	6	2
1.051	1.050	w	8	4	0
1.025	1.025	w	8	4	2
0.940	0.939	w	8 10	6 0	0 0
0.922	0.921	w	10	2	0

$IF_6^+AsF_6^-$ (9.49 Å).[4,15] This relatively small change in the unit cell dimensions is not surprising because the small radii of the +VII halogen ions allow them to occupy interstices in the fluoride packing. Assuming four molecules per unit cell and neglecting contributions to the volume from the highly charged central atoms, a plausible average volume[16,17] of 17.27 Å^3 per F and a calculated density of 3.068 g/cm^3 are obtained.

Weaker lines were observed having mixed, even and odd Miller indices. These are not expected for a simple NaCl structure but can readily be explained[4,15] by scattering from the fluorine atoms grouped around the Br and As atoms with these central atoms occupying the positions of Na and Cl in the NaCl lattice. By analogy with $IF_6^+AsF_6^-$,[15] the space group of $BrF_6^+AsF_6^-$ is *Pa*3.

Vibrational Spectra. The infrared spectra of $BrF_6^+AsF_6^-$ and of $BrF_6^+SbF_6^- \cdot xSbF_5$ after the removal of $BrF_4^+Sb_2F_{11}^-$ are shown in Figure 1. The Raman spectra of $BrF_6^+AsF_6^-$ and of the SbF_5 adduct before the removal of $BrF_4^+Sb_2F_{11}^-$ were identical with those previously reported.[2] The Raman spectrum of the SbF_5 adduct after the removal of BrF_4^+-$Sb_2F_{11}^-$ had its most intense band at 660 cm^{-1} (ν_1 of SbF_6^-) with two pronounced shoulders on its high-frequency side. In addition to weak bands attributable to $Sb_2F_{11}^-$ stretching modes and to the SbF deformational modes in the 300–220 cm^{-1} frequency range, the BrF_6^+ deformation $\nu_5(F_{2g})$ was observed at 406 cm^{-1}.

In addition to the three previously reported[2] Raman-active modes, octahedral BrF_6^+ is expected to exhibit two infrared-active fundamentals. These are the antisymmetric stretch, $\nu_3(F_{1u})$, and the antisymmetric deformation, $\nu_4(F_{1u})$. By comparison with the known frequencies of the closely related ClF_6^+, IF_6^+, SF_6, SeF_6, and TeF_6 species, ν_3 and ν_4 of BrF_6^+ are expected to occur between 760 and 800 and between 400 and 450 cm^{-1}, respectively. Inspection of Figure 1 reveals that in both the AsF_5 and the SbF_5 adduct bands were observed at 775 and 430 cm^{-1}. Furthermore, these bands disappeared when the $BrF_6^+AsF_6^-$ ir sample was allowed to

Table II. Symmetry and Internal Force Constants (mdyn/Å) of BrF_6^+ Compared to Those of Related Octahedral Species[a]

		PF_6^- F_{44} = min	AsF_6^- F_{44} = min	SbF_6^- F_{44} = min	SF_6 GVFF[b]	SF_6	SF_6 F_{44} = min	SeF_6 GVFF[c]	SeF_6	SeF_6 F_{44} = min	TeF_6 GVFF[d]	TeF_6	TeF_6 F_{44} = min	ClF_6^+ $f_{rr'} = 0$	ClF_6^+	ClF_6^+ F_{44} = min	BrF_6^+ F_{44} = min	IF_6^+ F_{44} = min
A_{1g}	$F_{11} = f_r + 4f_{rr} + f_{rr'}$	6.23	5.21	4.77		6.70[e]			5.59[e]			5.44[e]			5.16		4.88	5.61
E_g	$F_{22} = f_r - 2f_{rr} + f_{rr'}$	3.52	3.61	3.52		4.61[e]			4.86[e]			5.03[e]			4.44		5.02	6.00
F_{1u}	$F_{33} = f_r - f_{rr'}$	4.36	3.82	3.86	5.26		5.80	4.88		4.85	4.98		4.95	4.68		5.28	4.82	5.23
	$F_{34} = 2(f_{r\alpha} - f_{r\alpha''})$	0.91	0.33	0.14	0.89		1.10	0.44		0.42	0.24		0.19	0.73		0.96	0.41	0.21
	$F_{44} = f_\alpha + 2f_{\alpha\alpha} - 2f_{\alpha\alpha''} - f_{\alpha\alpha'''}$	0.83	0.55	0.30	1.04		1.02	0.64		0.65	0.40		0.41	0.96		0.93	0.63	0.45
F_{2g}	$F_{55} = f_\alpha - 2f_{\alpha\alpha'} + f_{\alpha\alpha''}$	0.63	0.38	0.21		0.77[e]			0.46[e]			0.28[e]			0.74		0.46	0.32
	f_r	4.39	3.98	3.90	5.28		5.55	4.99		4.98	5.07		5.06	4.68		4.98	4.90	5.42
	f_{rr}	0.45	0.27	0.21		0.35			0.12			0.07			0.12		−0.03	−0.07
	$f_{rr'}$	0.03	0.16	0.04	0.02		−0.25	0.11		0.13	0.09		0.11	0		−0.30	0.08	0.19

[a] Frequencies (cm^{-1}) of ν_1–ν_5 used for force field computations: PF_6^-, 746, 561, 817, 557, 475; AsF_6^-, 682, 568, 696, 385, 369; SbF_6^-, 653, 561, 667, 280, 273; SF_6, 773.5, 641.7, 947.9, 614.5, 525; SeF_6, 706.9, 658.7, 778.5, 436, 405; TeF_6, 697.1, 670.3, 751, 326.5, 314; ClF_6^+, 679, 630, 890, 582, 513; BrF_6^+, 660, 670, 775, 430, 405; IF_6^+, 708, 732, 790, 343, 340. [b] Reference 19. [c] Reference 21. [d] Reference 20. [e] Using Raman frequencies from H. H. Claassen, G. L. Goodman, J. L. Holloway, and H. Selig, *J. Chem. Phys.*, 53, 341 (1970).

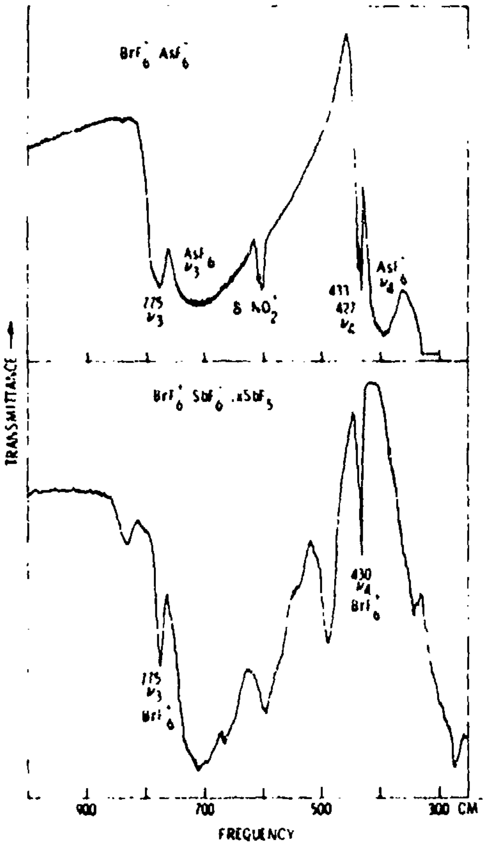

Figure 1. Infrared spectra of $BrF_6^+AsF_6^-$ recorded as a dry powder between AgCl plates at −196° and of $BrF_6^+SbF_6^-\cdot xSbF_5$ recorded as a AgBr disk at 25°. The increase in background at the low-frequency end of the spectra is due to absorption by the windows.

warm to ambient temperature or when the ir sample of the SbF_5 adduct was kept at ambient temperature for several hours. The remaining bands in the infrared spectra changed only little, thus supporting the assignment of the 775- and 430-cm^{-1} bands to ν_3 and ν_4, respectively, of the powerful oxidizing species BrF_6^+. The ready interaction between BrF_6^+ and the silver halide window material can also account for the weakening of the intensity of the BrF_6^+ infrared bands in the room-temperature spectrum of the SbF_5 adduct.

In $BrF_6^+AsF_6^-$, the 430-cm^{-1} band shows a splitting of 6 cm^{-1}. Since the two components are of similar intensity, splitting due to the $^{79}Br^{81}Br$ isotopes must be considered. The following arguments augur against the splitting being caused by the bromine isotopes and favor its attribution to crystal field or site symmetry effects. (i) The SbF_5 adduct does not show a comparable splitting. (ii) The observed splitting of 6 cm^{-1} is much larger than that (~2 cm^{-1}) predicted for the Br isotopes. (iii) The NO_2^+ deformation in the same spectrum shows a comparable splitting. (iv) The site symmetry of BrF_6^+ in space group *Pa*3 is only C_{3i}.

Force Constants. Since both the infrared- and the Raman-active fundamentals are now known, it was interesting to compute a force field for BrF_6^+. This allows a more quantitative comparison of the relative bond strength of BrF_6^+ with those of related species.

Except for the F_{1u} block, all the symmetry force constants of BrF_6^+ are unique. The F_{1u} block is undetermined since only two frequency values are available for the determination of three force constants. Consequently, the usefulness of mathematical constraints, such as minimizing or maximizing the value of one of the symmetry force constants,[18] was tested for the isoelectronic series SF_6, SeF_6, and TeF_6, for which general valence force fields have been reported.[19-21] As can be seen from Table II, the condition F_{44} = minimum very closely duplicates the GVFF values for the two heavier molecules SeF_6 and TeF_6. Therefore, it is also expected to be a very good approximation for the force field of BrF_6^+. The values so obtained for BrF_6^+ are listed in Table II and correlate well with the remaining species of Table II. The modified valence force fields, listed for the lightest isoelectronic series, *i.e.*, PF_6^-, SF_6, and ClF_6^+, are less reliable since the lighter central atoms cause stronger coupling of the stretching and bending modes.

The force constant of greatest interest is the stretching force constant f_r. For BrF_6^+ its value of 4.9 mdyn/Å is the highest found to date for any BrF bond.[23-25] This is not surprising since the covalency and therefore also the force constant of such a bond tend to increase with increasing oxidation state of the central atom and a formal positive charge.[22] Since the Br–F bonds in BrF_6^+ are stronger than those in other bromine fluorides, the reactivity of these salts must be due to the high oxidizing power of BrF_6^+.

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Registry No. $BrF_6^+AsF_6^-$, 51063-29-7; $BrF_6^+SbF_6^-$, 53432-26-1; PF_6^-, 16919-18-9; AsF_6^-, 16973-45-8; SbF_6^-, 17111-95-4; SF_6, 2551-62-4; SeF_6, 7783-79-1; TeF_6, 7783-80-4; ClF_6^+, 38217-33-3; IF_6^+, 21303-14-0; BrF_6^+, 51063-27-5.

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On the Existence of Several New O,N,F-Compounds. A Critical Comment on the Paper by Sicre and Schumacher

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Abstract. It is shown that the infrared spectra previously attributed to the three novel compounds FONO, NO_2F_3, and an unknown are due to the known compounds $HONO_2$, $FONO_2$, and covalent N_2O_5, respectively. The observed chemical and physical properties agree well with this reinterpretation.

Über die Existenz einiger neuer O,N,F-Verbindungen. Ein kritischer Kommentar zur Veröffentlichung von Sicre und Schumacher

Inhaltsübersicht. Es wird gezeigt, daß die Infrarot-Spektren, die zuvor den drei neuen Verbindungen FONO, NO_2F_3 und einer nichtidentifizierten Substanz zugeschrieben wurden, vollständig den bekannten Verbindungen $HONO_2$, $FONO_2$ und kovalentes N_2O_5 zugeordnet werden können. Die beobachteten chemischen und physikalischen Eigenschaften stimmen mit der neuen Interpretation überein.

In the course of a spectroscopic study of halogen nitrates¹), it became obvious that the infrared spectrum reported by Sicre and Schumacher²) for the new compound FONO was inconsistent with such a structure. In addition, these authors have given data for two more new N, O, F-compounds and suggested for one of these the composition NO_2F_3. In view of this inconsistency, we have critically reviewed the given experimental data and succeeded in positively identifying all three compounds as known substances. Sicre and Schumacher had chosen²) the designations X_1, X_2, and X_3 for their new compounds which will be retained in the following discussion to facilitate comparison.

Compound X_1.

This compound could be prepared from NO_2 and small amounts of F_2 only in an aluminium cylinder, the walls of which were coated with a thick layer of aluminium oxyfluoride or corrosion products.

Based on its infrared spectrum, apparent molecular weight of 64.5, and facile conversion to FNO_2, it was identified²) as the FNO_2 isomer FONO. However, a closer inspection of the infrared spectrum attributed to FONO indicated a struc-

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ture containing an XNO_2 group[1]). Comparison with known spectra revealed that the infrared band shapes and frequencies (in cm^{-1}) and relative intensities of X_1 (1713 vs, 1302 vs, 885 s) are in excellent agreement with those reported[3]) for $HONO_2$ (1712 vs, 1311 vs, average of 895 and 879 braches = 887 s). Further support for its identification as $HONO_2$ can be derived from its chemical behavior. Thus it could not be separated by fractionation from compound X_3 which was identified (see below) as N_2O_5.

The following facts indicate that the original reaction product in the $NO_2 + F_2$ reaction was FNO_3 which was subsequently converted by hydrolysis into $HONO_2$. (I) The original product was volatile at −120 °C. (II) Sometimes the infrared spectra showed FNO_2 which was attributed to an isomerization of FONO to FNO_2. However, a plausible explanation for this behavior can be offered. For example, lack of hydrolysis of FNO_2 or secondary reactions of $HONO_2$ with passivated surfaces or strong fluorinating agents such as compound X_2 (=$FONO_2$) could easily generate FNO_2. (III) Clean reactors did not produce any X_1. Only in the presence of substantial amounts of aluminium corrosion products was X_1 formed. The likelihood of such corrosion products containing hydroxyl-groups supports our interpretation that X_1 is formed by hydrolysis of FNO_2 and is $HONO_2$. (IV) The molecular weight determination would not be expected to effectively discriminate between FNO_2 (65) and $HONO_2$ (63). However, from the fact that the determination was carried out at a pressure of 700 mm, it can be concluded that the sample used at this point was still mainly FNO_2. The vapor pressure of $HONO_2$ at ambient temperature is considerably lower than 700 mm.

Compound X_2.

This compound is formed[3]) when NO_2 is reacted with an excess of F_2. As has previously been found[4]), some $FONO_2$ is readily formed under these conditions. Comparison between the infrared spectrum of X_2 (1761 vs, 1294 vs, 927 m, 804 s) and that[5])[6]) of $FONO_2$ (1759 vs, 1301 vs, 928 m, 804 s) reveals that X_2 is indeed $FONO_2$. The minor frequency discrepancy for the 1300 cm^{-1} band is caused by the difficulty in estimating the true band center for X_2 due to overlap with an intense X_1 band. Again the observed band contours of X_2 are identical to those of $FONO_2$ and their chemical and physical properties agree.

When X_2 was allowed to interact with an excess of NO_2 the following reaction was observed:

$$X_2 + \text{excess } NO_2 \rightarrow X_3 + X_1.$$

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If we substitute $FONO_2$ for X_2 and N_2O_5 for X_3 (see below), this observed reaction further confirms the identities of X_2 and X_3:

$$FONO_2 + 2NO_2 \rightarrow FNO_2 + N_2O_5.$$

The formation of X_1 (=$HONO_2$) can be explained by hydrolysis of FNO_2 according to:

$$FNO_2 + H_2O \rightarrow HONO_2 + HF.$$

Compound X_3.

As discussed above, X_3 was formed by interaction of X_2 with an excess of NO_2 and, therefore, was suspected to be N_2O_5. Comparison of the infrared spectrum of X_3 (1 720 vs, 1 240 s) 2)) with that of covalent gaseous N_2O_5 (1 728 vs, 1 247 s) 7)) confirmed our suspicion. The minor discrepancy in the listed frequency values is due to the relative broadness of these bands making estimation of the exact band centers difficult. The observed low volatility of X_3 and its tendency to associate with $HONO_2$ agree with X_3 being N_2O_5.

Conclusion. Without doubt, compounds X_2 and X_3 of Sicre and Schumacher are $FONO_2$ and N_2O_5, respectively, since their spectra, physical and chemical properties all agree with those of the latter ones. There is also no doubt that the infrared spectrum of X_1 which was the only direct experimental proof for FONO, is due to $HONO_2$. Therefore, the existence of FONO has not been established since all the experimental data of Sicre and Schumacher might be explained by assuming FNO_2 which during transfer to or in the infrared cell hydrolyzed to $HONO_2$.

Recently, matrix isolation data have been presented as evidence for the existence of FON and FONO at cryogenic temperatures 8))9)). Although the infrared bands attributed 8)) to matrix isolated FONO are quite different from those of X_1, their frequencies are difficult to reconcile with the proposed FONO structure.

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The CF_3O^- anion: vibrational spectrum of an unusual CF_3 compound

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Abstract—The i.r. and Raman spectra of solid $CsOCF_3$ and the Raman spectra of liquid and gaseous NF_3O have been recorded. The vibrational spectrum of CF_3O^- closely resembles that of isoelectronic NF_3O. For CF_3O^-, six fundamentals were observed and assigned consistent with a pseudo-tetrahedral structure of symmetry C_{3v}. It is shown that the unusual bonding in NF_3O is not unique but also occurs in CF_3O^-. In both isoelectronic XF_3O species, the XO bond possesses almost double bond character whereas the three XF bonds are highly polar implying very strong contributions from resonance structures such as

The occurrence of this type of bonding can be rationalized by the high electronegativity of fluorine and by the importance of the octet rule for first row elements limiting the sum of the bond orders to a maximum of four.

I. INTRODUCTION

When the NF_3O molecule was discovered [1–4] the observed high frequency (1690 cm^{-1}) [5, 6] of the NO stretching mode was very surprising since it implied a NO bond order of approximately two. This interpretation was confirmed by a subsequent electron diffraction study showing a short NO (1.158 Å) and long NF (1.431 Å) bonds [7]. For the theoreticians this posed an interesting problem since it raised the question whether the strict validity of the octet rule for first row elements also holds for NF_3O [8]. A systematic study [9] of the force constants and bond orders of a large number of simple inorganic fluorides showed that for the first row elements the sum of the bond orders does not tend to exceed the maximum allowed by the octet rule. This is in agreement with the results from recent Hartree–Fock computations [10] giving a possible origin for the nonexpansion of the octet among first row elements. However, the severe shortcomings of molecular orbital, underdetermined force field, and approximate bond order computations must be kept in mind when interpreting such data.

It appeared interesting to determine whether the occurrence of abnormally strong XO bonds coupled with highly polar XF bonds is limited to X being N (i.e., NF_3O and the nitrosyl halides), or if it also extends to other first row elements. Of the possible truly isoelectronic [11] species, only two, CF_3O^- and BF_3O^{2-}, have been reported to exist. However, the original reports on BF_3O^{2-} salts by Ray and Mitra [12] were subsequently refuted by Clark and Lynton [13].

The existence of the trifluoromethoxides of Cs, Rb and K was first reported [14] by Redwood and Willis in 1965. Ionic structures containing the CF_3O^- anion were postulated for these salts based on X-ray powder diffraction patterns [14]. These patterns showed the trifluoromethoxides to be isomorphous with the corresponding tetrafluoroborates. In a subsequent paper [15], the same authors reported incomplete i.r. spectra for these trifluoromethoxides. However, these spectra showed more bands than expected for a simple CF_3O^- anion of symmetry C_{3v}. Furthermore, Dear and co-workers found [16] that the fluorinated higher alkoxides of Li and Na can be sublimed without decomposition and, therefore, must possess considerable covalent character. These conflicting data added further interest to our study.

There was also a question concerning the assignment of $\nu_3(A_1)$ and $\nu_5(E)$ of NF_3O. The original assignment [5, 6] for these modes has recently been questioned [17, 18]. Since Raman polarization data should readily distinguish between these two modes, we have also recorded the Raman spectra of liquid and gaseous NF_3O. After completion of our study, the Raman spectrum of gaseous NF_3O has been published [19]. It is in excellent agreement with our measurements and resulted in a reassignment of ν_3 and ν_5.

II. EXPERIMENTAL

Materials and apparatus

Cesium trifluoromethoxide was prepared from CsF and COF$_2$ in dry CH$_3$CN as previously described [14]. The conversion of CsF to CsOCF$_3$ was 70 mole%. Nitrogen trifluorideoxide (Allied Chemical) was purified by fractional condensation and showed no impurities detectable by i.r. spectroscopy. Volatile materials used in this work were manipulated in a stainless steel-Teflon FEP vacuum line. Solid products were handled in the dry nitrogen atmosphere of a glove box.

Vibrational spectra

The i.r. spectra of the solids were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1} as dry powders pressed between thin AgCl windows. The pressing operation was carried out using a Wilks mini pellet press.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å exciting line of an Ar-ion laser and a Claassen filter [20] for the elimination of plasma lines. For the solids, glass melting point capillaries were used as sample containers in the transverse-viewing–transverse-excitation technique. The spectrum of gaseous NF$_3$O was recorded at a pressure of 15 atm using a stainless steel cell with three sapphire windows in a double pass mode. Liquid NF$_3$O was contained in a 4 mm o.d. quartz tube. The spectra were recorded at −120° using a device similar to one previously described [21]. Polarization measurements were carried out according to method VIII listed by Claassen, Selig and Shamir [20].

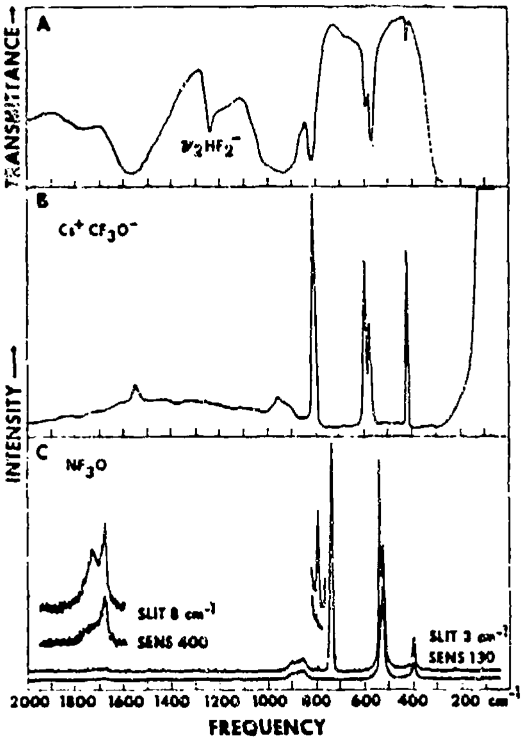


Fig. 1. Trace (A) i.r. spectrum of solid CsOCF$_3$ as AgCl disk; trace (B) Raman spectrum of solid CsOCF$_3$; trace (C) Raman spectrum of liquid NF$_3$O with parallel (upper curve) and perpendicular (lower curve) polarization; the inserts show the weaker bands recorded with increased gain and slit width.

III. RESULTS AND DISCUSSION

Observed spectra

The i.r. and Raman spectrum of solid CsOCF$_3$ and the Raman spectrum of liquid NF$_3$O are shown in Fig. 1. The observed frequencies are listed in Table 1. The Raman spectrum of gaseous NF$_3$O was identical to that recently reported [19] and, hence, is not given. In addition to the fundamentals listed in Table 1, two overtones were observed in the Raman spectra of NF$_3$O. Both of them are polarized and occur in the vicinity of A_1 fundamentals thus allowing an increase in their intensity by Fermi resonance. One of the bands is due to $2\nu_6$ and occurs at 799 cm^{-1} in the liquid and at 796 cm^{-1} in the gas. The other overtone is ascribed to $2\nu_4$ and was observed at 1735 cm^{-1} in the liquid and at 1775 cm^{-1} in the gas. The relatively large frequency shift of $2\nu_4$ between the gas and the liquid is caused by the corresponding shift of ν_4 which in the liquid became relatively broad and had its maximum at about 860 cm^{-1}. The remaining fundamentals of NF$_3$O show only minor frequency shifts when going from the gas phase to the liquid indicating little or no association in the liquid. The fact that ν_5 and ν_3 of NF$_3$O appear more weakly polarized in the gas than in the liquid is due to the sample cell used for the gas. This type of cell allows only qualitative polarization measurements owing to internal reflection from the metal surfaces and owing to the optical activity of the sapphire windows. Since the reassignment of ν_3 and ν_5 of NF$_3$O has recently been discussed in detail [19] no further comment is required.

For CsOCF$_3$, no Raman polarization measurements could be carried out owing to the lack of a suitable solvent. It hydrolyzes in water [14] and is insoluble in CH$_3$CN [15]. In the i.r. spectrum, a medium to weak absorption at 1230 cm^{-1} and a shoulder at 1450 cm^{-1} varied in relative intensity compared to the rest of the spectrum. These bands are due to CsHF$_2$ and represented the only detectable impurity.

Table 1. Vibrational spectrum of $Cs^+CF_3O^-$ compared to that of isoelectronic NF_3O

Obsd freq, cm^{-1}, and intens[a]					Assignment in point group C_{3v}	Approximate description of mode
$Cs^+ CF_3O^-$ solid		NF_3O				
		gas				
IR	Raman	IR[b]	Ra	Liquid Ra		
1560vs, br	1555(0.7)	1691vs	1692(0+)p	1680(0+)	A_1 ν_1	X–C stretch
813s	812(10)	743s	743(10)p	738(10)p	ν_2	sym XF_3 stretch
595ms	597 (7.3)	558sh	542(0.1)p	541(9.3)p	ν_3	δ sym XF_3
960vs, br	960(0.8)br	883vs	884(0.9)dp	860-900(0.5)br, dp	E ν_4	asym XF_3 stretch
574ms	576(4.4)	528s	529(5)dp	528(5.3)dp	ν_5	OXF deformation
423w	422(7.9)	400w	400(0.7)dp	400(1.4)dp	ν_6	δ asym XF_3

(a) uncorrected Raman intensities

(b) data from ref. 5

Assignments

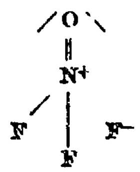
An XY_3Z species of symmetry C_{3v}, such as possibly CF_3O^-, has six fundamentals classified as $3A_1 + 3E$. All six should be active in both the infrared and Raman spectrum. Inspection of Fig. 1 and Table 1 reveals that indeed six bands, active in both the i.r. and Raman spectrum, were observed for $CsOCF_3$. Their frequencies and relative i.r. intensities are similar to those of isoelectronic NF_3O. This similarity, together with the fact that the CF_3O^- salts are isomorphous with the corresponding BF_4^- salts [14], strongly supports the assumption of a pseudo-tetrahedral structure of symmetry C_{3v} for the CF_3O^- anion. Assignments of the six bands to the individual modes (see Table 1) were made by analogy with those of NF_3O and are supported by the following arguments.

Of the six fundamentals, three are stretching and three are deformation vibrations. The three bands occurring above 800 cm^{-1} must be the stretches and those below 600 cm^{-1} must be the deformations. The strong i.r. band at 1560 cm^{-1} has too high a frequency and is too far away from the other two frequencies to be a CF_3 mode. Consequently, it must be the CO stretch. The two remaining bands at 960 and 812 cm^{-1}, respectively, show about the right frequency separation expected for an antisymmetric and a symmetric CF_3 stretching vibration. Based on their relative band widths and Raman intensities, the 960 cm^{-1} band must be the antisymmetric and the 812 cm^{-1} band the symmetric CF_3 stretch.

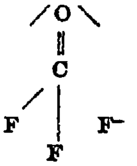
Of the three deformation modes, the antisymmetric CF_3 deformation should have the lowest frequency and be relatively weak in the i.r. and, therefore, is assigned to the 422 cm^{-1} band. The CF_3 rocking and CF_3 umbrella deformation modes were assigned to the 575 and the 596 cm^{-1} band, respectively, based on their relative intensities and by analogy with NF_3O for which these assignments are well established by polarization data.

Conclusion

In spite of the lack of reliable force fields for NF_3O and CF_3O^-, some qualitative statements can be made about the nature of bonding in CF_3O^-. Since the exact bond distances in NF_3O are known from electron-diffraction data [7], it is well established that the NO bond possesses almost double bond character and that the NF bonds are unusually long. This implies very strong contributions from resonance structures such as:

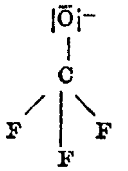


Inspection of Table 1 shows that the frequencies of CF_3O^- are comparable to those of NF_3O. Furthermore, when compared to conventional carbon oxyfluorides containing single bonded oxygen, the CO stretching frequency has increased by about 500 cm^{-1} and the CF_3 stretching frequencies have decreased by about 350 cm^{-1}. These enormous frequency shifts suggest that the bonding in NF_3O is not unique, but also extends to isoelectronic CF_3O^-. Thus, one must invoke also for CF_3O^- strong contributions from resonance structures such as:



(i)

in addition to some contribution from:



(ii)

The predominance of (i) can be rationalized by the high electronegativity of fluorine favoring highly polar bonds and by the strict validity of the octet rule for first row elements. The latter is caused by the high energy required to promote electrons to the 3s level. If these assumptions are valid, an increase in the bond order of the XO bond must be accompanied by a simultaneous decrease in the bond order of the X—F bonds, since the sum of the bond orders cannot surpass four. For higher row elements, the next higher unoccupied electron levels lie much closer and, therefore, the octet can readily be exceeded.

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Novel Onium Salts. Synthesis and Characterization of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$

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The novel oxonium salts $OH_3^+SbF_6$ and $OH_3^+AsF_6^-$ were isolated as well-defined crystalline solids from the H_2O–HF–SbF_5 and the H_2O–HF–AsF_5 system, respectively. These salts are the most stable oxonium salts presently known. It was shown by DSC studies that $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ decompose at about 357 and 193°, respectively. Their ionic nature in both the solid state and polar solvents was established by vibrational and ^{19}F and ^1H NMR spectroscopy. The infrared spectra of these adducts closely resemble those recently attributed to H_2F^+ salts, suggesting that the latter may have been incorrectly identified. Furthermore, the frequencies of the OH_3^+ fundamentals in these salts are very similar to those of isoelectronic NH_3, but significantly different from those previously observed for OH_3^+ in mineral acid monohydrates. This indicates that in the MF_6^- salts the hydrogen bridges are considerably weaker, although similar phenomena are observed for the low-temperature spectra suggesting rigidity of the lattice at low temperature. The assignments for OH_3^+ were examined by force field computations. On the basis of its X-ray powder diffraction pattern, $OH_3^+AsF_6^-$ is cubic with $a = 8.015$ Å, $Z = 4$. From the H_2O–HF–BF_3 system a solid adduct was isolated at low temperature but was not further characterized owing to its thermal instability. A new method for drying HF based on oxonium salts is proposed.

Introduction

During a study of the controlled hydrolysis of $BrF_4^+Sb_2F_{11}^-$ in HF, a stable white solid was obtained in high yields. Elemental analysis of this solid showed that it did not contain detectable amounts of bromine. Its infrared spectrum closely resembled that recently reported[1] by Couzi et al. for H_2F^+. However, attempts to prepare a stable product from HF and SbF_5 alone failed. This agrees with a DTA study[2] of the HF–SbF_5 system which showed no evidence for any high-melting adduct. Surprisingly, the addition of small amounts of water to HF–SbF_5 mixtures produced the same stable solid which, as shown in this paper, was identified as $OH_3^+SbF_6^-$.

A literature search did not reveal any reports on the isolation of $OH_3^+MF_6^-$ salts, in spite of many papers dealing with the relatively unstable mineral acid monohydrates and Commeyras and Olah's proton NMR (singlet at δ 10.25) evidence[3] for the existence of the oxonium ion in SbF_5–$HOSO_2F$ solution. Recently, Bonnet and coworkers studied[4] solutions of SbF_5 in H_2O and HF by DTA and identified the crystalline phases $SbF_5 \cdot 2H_2O$, $4SbF_5 \cdot 5H_2O$, $SbF_5 \cdot H_2O$, $3SbF_5 \cdot 2H_2O$, and $SbF_5 \cdot HF \cdot 2H_2O$. Surprisingly, no evidence for $OH_3^+SbF_6^-$ was reported, although the infrared spectra attributed to $SbF_5 \cdot H_2O$ and $4SbF_5 \cdot 5H_2O$ closely resemble those obtained by us for $OH_3^+SbF_6^-$.

The general interest in oxonium salts and superacid systems,[5,6] in which, unless rigorously dried, these salts are bound to be formed, prompted us to study these simple oxonium salts in more detail. Their unexpected high thermal stability also induced us to study the protonation of other compounds, such as H_2S, HCl, Xe, HNF_2, NF_3, etc. Details on novel salts containing the SH_3^+ and the $NH_2F_2^+$ cations will be reported elsewhere.[7]

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3 and HF) Monel Teflon–FEP vacuum system. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Hydrogen fluoride (The Matheson Co.) was first electrolytically dried[8] followed by treatment with either fluorine or SbF_5. In the latter case, the HF was added to a Teflon–FEP ampoule containing SbF_5. Any water present formed nonvolatile $OH_3^+SbF_6^-$ and the anhydrous HF was pumped off at −40°. Antimony pentafluoride and AsF_5 (Ozark Mahoning Co.) and BF_3 (The Matheson Co.) were purified by distillation and fractional condensation, respectively, prior to their use.

The infrared spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer Model 457 infrared spectrophotometer. The spectra of gases were obtained using Monel cells of 5-cm path length fitted with AgCl windows. Spectra of dry powders at room temperature were recorded as pressed (Wilks minipellet press) disks between AgCl windows. Low-temperature spectra were obtained as dry powders between CsI plates using a technique similar to one previously reported.[9]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[10] for the elimination of plasma lines. Sealed quartz or Teflon–FEP tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded using a previously described[11] device. Polarization measurements were carried out according to method VIII listed by Claassen et al.[10]

Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries (~0.5-mm o.d.).

The ^{19}F and ^1H NMR spectra were recorded at 56.4 and 60 MHz, respectively, on a Varian Model DA60 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique relative to external $CFCl_3$ and TMS, respectively.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used for the determination of the thermal stability of the compounds. The samples were sealed in aluminum pans, and heating rates of 2.5 and 10°/min in N_2 were used.

The H_2O content in the OH_3^+ salts was determined by dissolving a known amount of sample in pyridine and titrating the evolved H_2O with Karl Fischer reagent using a Labindustries Aquametry apparatus. Antimony and arsenic were determined by X-ray fluorescence spectroscopy of basic aqueous solutions.

Preparation of $OH_3^+SbF_6^-$. In a typical experiment, SbF_5 (8.305 mmol) was placed in a Teflon–FEP ampoule and 8 ml of liquid anhydrous HF was added at −196°. The mixture was warmed to 25° to give a homogenous solution. Distilled water (8.30 mmol) was added to the ampoule at −196° and the mixture was warmed to 25°. Removal of all volatile material in vacuo at 25° resulted in 2.116 g of a white solid residue (weight calcd for 8.30 mmol of $OH_3^+SbF_6^-$ 2.115 g). Anal. Calcd for OH_3SbF_6: H_2O, 7.07; Sb, 47.8. Found: H_2O, 6.93; Sb, 48.0.

Preparation of $OH_3^+AsF_6^-$. In a typical experiment, H_2O (5.421 mmol) and anhydrous HF (8 ml of liquid) were combined at −196° in a Teflon–FEP ampoule, followed by warm-up to 25°. Arsenic pentafluoride (5.427 mmol) was added to this mixture at −196° and the contents of the ampoule were allowed to warm slowly to room temperature. Removal of volatile material at 25° in vacuo resulted in 1.128 g of a white solid residue (weight calcd for 5.421 mmol of $OH_3^+AsF_6^-$ 1.127 g). Anal. Calcd for OH_3AsF_6: H_2O, 8.66; As, 36.0. Found: H_2O, 8.26; As, 35.7.

The H_2O–HF–BF_3 System. To a mixture of H_2O (3.66 mmol) and anhydrous HF (10 ml of liquid), prepared as described above, BF_3 (7.4 mmol) was added at −196°. This mixture was kept at −78° for 10 min and then slowly warmed until a clear solution resulted. Removal of volatile material at −70° in vacuo produced a white solid residue melting at around 0° to a colorless liquid having a dissociation pressure of about 4 mm at 22°. The weight of the adduct, after being pumped on at 0° for several minutes, was 376 mg (calcd for 3.66 mmol OH_3BF_4 387 mg).

Results and Discussion

Syntheses. Addition of water to mixtures of HF with the strong Lewis acids SbF_5 and AsF_5 produces stable 1:1:1 adducts in quantitative yield according to

$$HF + H_2O + MF_5 \xrightarrow{HF} H_3O^+MF_6^-$$

The formation of these adducts is not surprising in view of the previous evidence[12-14] showing that in HF solution the following equilibrium exists

$$SbF_5 + 2HF \rightleftarrows H_2F^+SbF_6^-$$

and that the stronger base H_2O can displace[3,15] H_2F^+ with formation of the OH_3^+ cation

$$H_2F^+ + SbF_6^- + H_2O \rightarrow OH_3^+ + SbF_6^- + HF$$

However, in view of the several hundred recent publications dealing with superacid chemistry, the well-known difficulties in obtaining completely anhydrous systems, and the general interest in oxonium salts, we were extremely surprised to find that these stable adducts had not previously been isolated.

It appears that the low-temperature infrared spectra of these adducts have been observed[1] previously by Couzi and coworkers in the course of their study of the binary HF–Lewis acid systems but were mistaken for H_2F^+ salts. Although not impossible, it is highly unlikely that OH_3^+ and H_2F^+ would show such similar vibrational spectra. Furthermore, comparison of the observed frequencies and computed force constants of "H_2F^+" with those of isoelectronic H_2O show poor agreement (H_2O, $f_r = 8.45$, $f_\alpha = 0.76$; "H_2F^+", $f_r = 5.71$, $f_\alpha = 1.36$ mdyn/Å).[1]

The failure of Bonnet et al. to isolate $OH_3^+SbF_6^-$ from the SbF_5–H_2O–HF system[4] may be explained by their unfortunate choice of reaction conditions. They combined H_2O with SbF_5 in the absence of a solvent. This can result in partial hydrolysis of SbF_5 with HF formation, thus making it very difficult to obtain well-defined products.

We have established the 1:1:1 composition of the HF·H_2O·SbF_5 and the HF·H_2O·AsF_5 adducts by the observed material balances, elemental analyses, and vibrational and NMR spectroscopy. With the weaker Lewis acid BF_3, an unstable 1:1:1 adduct is formed at lower temperature. It melts at about 0° to a colorless liquid having a dissociation pressure of about 4 mm at 22°.

The quantitative formation of a stable nonvolatile OH_3^+ salt is an effective way to remove small amounts of water from HF by treating it with a strong Lewis acid. Bismuth pentafluoride, although not used in this study, should be the most convenient drying reagent, since it is nonvolatile at room temperature. Thus, its use would permit the removal of the dry HF from $OH_3^+BiF_6^-$ and the excess of BiF_5 at ambient temperature. This method appears more convenient than previously reported methods, such as pyrolysis of dried $NaHF_2$,[16] electrolytic drying,[8] or fluorine treatment.[17] Furthermore, the stable solid $OH_3^+MF_6^-$ salts could find applications in systems requiring catalytic amounts of strong acids. Owing to their physical properties (see below), these solids should be easier to store, ship, and handle then highly corrosive liquids.

Properties. The $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ salts are white crystalline solids. They are highly soluble in HF and moderately soluble in polar solvents, such as $CH_3SO_2CH_3$. With stronger bases such as pyridine or acetonitrile, water is evolved and the nitrogen atom is protonated. The quantitative displacement of OH_3^+ by pyridine was successfully used for the determination of the H_2O content with Karl Fischer reagent. Evidence for the protonation of acetonitrile was obtained by proton NMR spectroscopy (see below). The oxonium ion is surprisingly inactive as a hydrolyzing agent. In addition to its compatibility with the SbF_6^- and AsF_6^- ions in HF solution, it does not cause BrF_5, BrF_4^+ salts,[7] and NF_4^+ salts[18] to hydrolyze to a significant extent.

Table I. X-Ray Powder Data for $OH_3^+AsF_6^-$ [a]

d_{obsd}, A	d_{calcd}, A	Intens	h	k	l
4.64	4.62	vs	1	1	1
4.01	4.00	vs	2	0	0
2.82	2.83	s	2	2	0
2.420	2.414	w	3	1	1
2.315	2.312	w	2	2	2
1.999	2.002	w	4	0	0
1.833	1.837	w	3	3	1
1.785	1.791	mw	4	2	0
1.636	1.634	m	4	2	2
1.542	1.541	mw	5 3	1 3	1 3
1.414	1.416	vw	4	4	0
1.355	1.353	w	5	3	1
1.336	1.335	w	6 4	0 4	0 2
1.267	1.266	vw	6	2	0

[a] Cubic, $a = 8.015$ A, $V = 514.9$ A^3, $Z = 4$, $\rho_{calcd} = 2.890$ g cm^{-3}, Cu Kα radiation, and Ni filter.

The thermal stability of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ was determined by DSC. The SbF_6^- salt exhibited reversible endotherms at 89 and 209° (probably phase changes), followed by some small irreproducible endotherms from about 230 to 357° and a large irreversible endotherm at 357°. The occurrence of complete decomposition at 357° was also confirmed by the observation of white fumes escaping from the sample cup at this temperature. Heating the salt to 150° under a static vacuum resulted in the buildup of only a little pressure over a period of several hours. The $OH_3^+AsF_6^-$ salt exhibited no endo- or exotherms prior to the onset of its strongly endothermic decomposition at 193° indicating the absence of any phase change between 25 and 193°.

The thermal stability of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ is unusually high, when compared to the previously reported OH_3^+ salts. Most of these salts are stable only at low temperature, and the more stable $OH_3^+CF_3SO_3^-$, $OH_3^+ClO_4^-$, and $OH_3^+CH_3C_6H_4SO_3^-$ melt at 35, 50, and 105°, respectively.[19-21]

X-Ray Powder Diffraction Data. The powder diffraction patterns of $OH_3^+AsF_6^-$ and $OH_3^+SbF_6^-$ are listed in Tables I and II, respectively. The $OH_3^+AsF_6^-$ salt is cubic with $a = 8.015$ Å and $Z = 4$. As previously pointed out,[22] it is very difficult to distinguish from the powder pattern alone for this type of compound whether it has the face-centered cubic $NaSbF_6$ or the primitive cubic $CsPF_6$ structure. The intensities observed for $OH_3^+AsF_6^-$ seem to agree somewhat better with the primitive cubic $CsPF_6$ type. Since the size of the OH_3^+ cation[23] is roughly comparable to that of K^+, Ag^+, or NH_4^+, it is not surprising that $OH_3^+AsF_6^-$ should be isotypic with $Ag^+AsF_6^-$ ($a = 7.74$ Å) and $NH_4^+PF_6^-$ ($a = 7.90$ Å).

The $OH_3^+SbF_6^-$ pattern was indexed for a tetragonal cell with $a = 11.48$ Å, $c = 8.78$ Å, and $Z = 8$. By comparison with the known[22,24] structures of similar MXF_6 compounds, it might be considered as a tetragonally distorted cubic $KSbF_6$ structure. Tetragonal unit cells with $Z = 8$ have previously been reported[25] for $KReF_6$, KWF_6, and $KMoF_6$, although their deviation from a cubic cell is much smaller. This might be explained by the fact that OH_3^+ is not spherical.[23] In addition to the cubic phase ($Z = 8$), a high-temperature tetragonal phase ($Z = 2$) has been reported[22,24] for $AgSbF_6$ and $KSbF_6$ containing one-fourth of the cubic superlattice.

In summary, the structures observed for the $OH_3^+MF_6^-$ salts agree well with those reported[22,24] for related MF_6^- salts. This comparison also suggests the possibility of different phases as was indicated for $OH_3^+SbF_6$ by the DSC data (see above).

Table II. X-Ray Powder Data for $OH_3^+SbF_6^-$ [a]

d_{obsd}, A	d_{calcd}, A	Intens	*h*	*k*	*l*
8.75	8.77	m	0	0	1
4.78	4.80	m	2	0	1
4.38	4.39	s	0	0	2
3.47	3.49	m	2	0	2
3.32	3.34	vs	2	1	2
2.868	2.869	mw	4	0	0
2.785	2.784	m	4	1	0
2.241	2.251	m	5	1	0
2.199	2.194	s	0	0	4
2.053	2.049	mw	4 2	0 0	3 4
2.021	2.017	m	2	1	4
1.901	1.903	mw	3	0	4
1.877	1.877	m	3	1	4
1.779	1.777	mw	6	2	1
1.760	1.756	m	5	4	1
1.680	1.679	mw	6	3	1
1.663		m			
1.595		mw			
1.578		m			
1.515		vw			
1.505		w			
1.401		mw			
1.392		m			
1.347		mw			
1.341		m			
1.258		mw			
1.220		m			
1.187		mw			
1.155		mw			
1.100		mw			
1.075		mw			
1.052		mw			
1.030		mw			
1.010		m			
0.990		m			
0.972		w			
0.963		vw			
0.937		m			
0.922		m			
0.9072		mw			
0.8925		m			
0.8793		m			
0.8663		m			
0.8538		m			
0.8365		vw			
0.8306		m			
0.8251		w			
0.8195		m			
0.8144		w			
0.8091		w			
0.8037		w			
0.7988		m			
0.7890		m			
0.7880		w			
0.7794		m			
0.7786		w			

[a] Tetragonal, $a = 11.48$ A, $c = 8.78$ A, $V = 1157.1$ A^3, $Z = 8$, $\rho_{calcd} = 2.93$ g cm^{-3}, Cu Kα radiation, and Ni filter.

Contrary to $OH_3^+SbF_6^-$, cubic $OH_3^+AsF_6$ did not exhibit a phase change between room temperature and its decomposition point. This is not surprising since $OH_3^+AsF_6^-$ appears to be isotypic with KPF_6 which has a rhombohedral low-temperature and a cubic high-temperature phase.[26]

Nuclear Magnetic Resonance Spectra. The NMR spectra of $OH_3^+SbF_6$ and $OH_3^+AsF_6^-$ were recorded in $CD_3SO_2CD_3$, CH_3CN, and CD_3CN solutions. The ^{19}F NMR spectra of $OH_3^+AsF_6$ in $CD_3SO_2CD_3$ and CH_3CN solution showed a quartet of equal intensity at ϕ 60.9 and 65.4 with $J_{AsF} = 915$ and 930 Hz, respectively, in good agreement with the values previously reported,[27] for octahedral AsF_6. Similarly, the $OH_3^+SbF_6^-$ samples showed a sextet ($J_{^{121}SbF} = 1946$ Hz) and octet ($J_{^{123}SbF} = 1053$ Hz) of equal intensities at ϕ 120.1, characteristic[27,28] of octahedral SbF_6^-. In agreement with the vibrational spectra (see below), no evidence was found for the presence of $MF_5{\cdot}OH_2$[29] or $MF_5{\cdot}NCCH_3$[30,31] molecular adducts in these systems.

The proton NMR spectra of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ in $CD_3SO_2CD_3$ solution showed only a singlet at δ −9.49 and −10.58, respectively. These values agree well with that of δ −10.2 previously attributed[3] to OH_3^+ in superacid solutions. In CH_3CN or CD_3CN solutions, however, the spectra were more complex. The strongest resonances for the SbF_6^- and AsF_6^- salts were observed at δ −10.92 and −11.34, respectively. In addition, a very broad resonance at δ −8.8 and a triplet of equal intensity ($J_{NH} = 53.5$ Hz) at δ −6.3 were observed. The latter is characteristic for NH_4^+.[32] The observation of NH_4^+ together with the fact that the proton resonance in CH_3CN solutions is significantly shifted to lower field, when compared to $CD_3SO_2CD_3$ solutions, indicate that this resonance is due to a $\equiv NH^+$ type species and not to OH_3^+. The CH_3 resonance consisted of a single peak at δ −2.21 indicating rapid exchange between CH_3CN and its protonated form. The ready protonation of CH_3CN in HSO_3F–SbF_5–SO_2 solution has previously been established.[33] The difference between the reported spectrum[33] and our spectrum can be explained by the fact that in one case small amounts of CH_3CN were dissolved in large amounts of acid, whereas in our case small amounts of $OH_3^+SbF_6$ were added to large amounts of CH_3CN. Since the NMR spectrum of OH_3^+ in superacids has previously been reported[3] and agrees with our data for the $CD_3SO_2CD_3$ solution, we have not studied superacid or HF solutions.

Vibrational Spectra. Figures 1 and 2 show the vibrational spectra of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$, respectively. The observed frequencies are listed in Table III. Whereas no difficulty was encountered in obtaining reproducible infrared spectra of $OH_3^+SbF_6^-$ as a dry powder between AgCl disks at room temperature, for $OH_3^+AsF_6^-$ low-temperature conditions were required. At room temperature, the band centered at about 900 cm^{-1} would rapidly become broad and shift to higher frequency (~1020 cm^{-1}). Similarly, the broad band centered at about 3200 cm^{-1} became less symmetric with its maximum being shifted to ~3500 cm^{-1}, and the 1630-cm^{-1} band was shifted to about 1680 cm^{-1}. In the Raman spectra, except for that of $OH_3^+SbF_6^-$ in HF solution, the bands due to OH_3^+ were not observed owing to their very low intensity and broadness.

The anion bands, both in HF and $CD_3SO_2CD_3$ solution, were in excellent agreement with those previously observed for octahedral AsF_6^- [34-36] and SbF_6^-.[35-37] In the room-temperature spectra of the solids, $\nu_2(E_g)$ showed a splitting into two bands which is not uncommon for octahedral MF_6^- ions in solids.[35,37-40] For $OH_3^+SbF_6^-$, the intensities of the infrared bands at about 490 and 570 cm^{-1} varied from sample to sample (see traces A and B of Figure 1). Although one might be tempted to attribute the 490-cm^{-1} band to the presence of some $Sb_2F_{11}^-$ polyanion[35,41-43] or to an OH_3^+ libration mode (see below), we prefer to assign it to SbF_6^- for the following reasons. The $OH_3^+AsF_6^-$ spectra show similar bands and AsF_6^- is unlikely to form stable polyanions,[44] the observed material balances and elemental analyses gave no indication of polyanion formation, and an OH_3^+ libration should be of very low Raman intensity. Whereas in the room-temperature spectra of the solids, $\nu_3(F_{1u})$ and $\nu_1(A_{1g})$ appear as single bands, these bands become doublets in the low-temperature spectra. Furthermore, four relatively sharp bands were observed in the low-temperature infrared spectrum of $OH_3^+AsF_6^-$ (trace B, Figure 2) in the region of $\nu_2(E_g)$ of AsF_6^-.

The most plausible explanation for these additional low-

Table III. Vibrational Spectra of $OH_3{}^+SbF_6{}^-$ and $OH_3{}^+AsF_6{}^-$ and Their Assignments Compared to that of NH_3[a]

		Obsd freq, cm^{-1}, and rel intens[b]									Assignment (point group)	
		$OH_3{}^+SbF_6{}^-$				$OH_3{}^+AsF_6{}^-$						
		Raman						Raman				
		Solid		Soln		Ir, solid		Solid				
NH_3	Ir, solid, 25°	25°	−120°	$CD_3SO_2CD_3$	HF	25°	−196°	25°	−120°	$CD_3SO_2CD_3$, soln	XH_3 (C_{3v})	MF_6 (O_h)
3336	3330 vs, br				3300 (0.2) br, p	3600–2800 vs	3250 sh				$\nu_1(A_1), \nu_3(E)$	
3444	3150 vs, br					vbr	3080 vs					
1626	1615 s				1630 (0.1) br, dp	1630 s, br	1615 s				$\nu_4(E)$	
950	900 s, br					800–1050 s, br	912 s				$\nu_2(A_1)$	
	670 vs, br		674 (10)			720 vs, br	715 vs		715 (10)			$\nu_3(F_{1u})$
		663 (10)						698 (10)				
			640 (5.3)	650 (10)	658 (10) p		676 s		677 (7.4)	680 (10)		$\nu_1(A_{1g})$
	588 sh	590 sh, br	590 (0.3)				586 s					
	(551)[c]	558 (0.8)	559 (1.2)					580 (1) br	566 (4.1)			
				568 (1)	568 (0.9) dp	550 s, br	560 s			573 (0.5)		$\nu_2(E_g)$
	(484)[c]	490 (0.6) br	498 (0.6)				511 s					
		450 sh	450 (0+)					500 (1) br	480 (1)			
							467 s					
						392 s, br	392 vs					
		287 s	288 (0.5)				373 w					
		280 (4.1)	280 (3.4)	274 (3)	273 (2.8) dp		367 w	378 (4)	369 (8)	368 (1.8)		$\nu_4(F_{1u})$
		265 sh	263 (0.4)				361 vw					$\nu_5(F_{2g})$
							255 s				Lattice vib or XH· · ·FM str	

[a] W. S. Benedict and E. K. Plyler, *Can. J. Phys.*, 35, 1235 (1957). [b] Uncorrected Raman intensities. [c] These infrared bands were of variable intensity from sample to sample (see traces A and B of Figure 1), but the relative intensities of their Raman counterparts were similar.

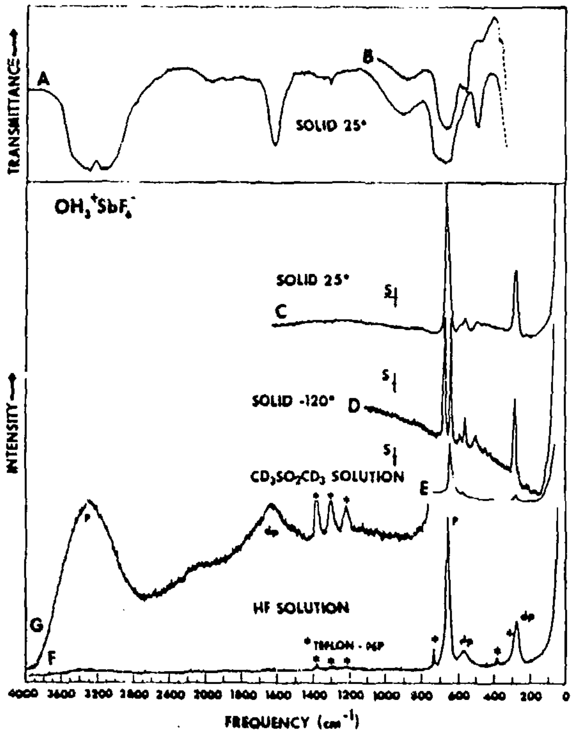

Figure 1. Vibrational spectra of $OH_3^+SbF_6^-$: traces A and B, infrared spectra of two different samples as dry powder between AgCl disks; traces C and D, Raman spectra of the solid contained in a quartz tube at +25 and −120°, respectively; trace E, Raman spectrum of a $CD_3SO_2CD_3$ solution (the broken lines indicate regions obscured by solvent bands); traces F and G, Raman spectra of an HF solution contained in a Teflon–FEP tube at two different recorder voltages. P and dp indicate polarized and depolarized bands, respectively, and S indicates the spectral slit width.

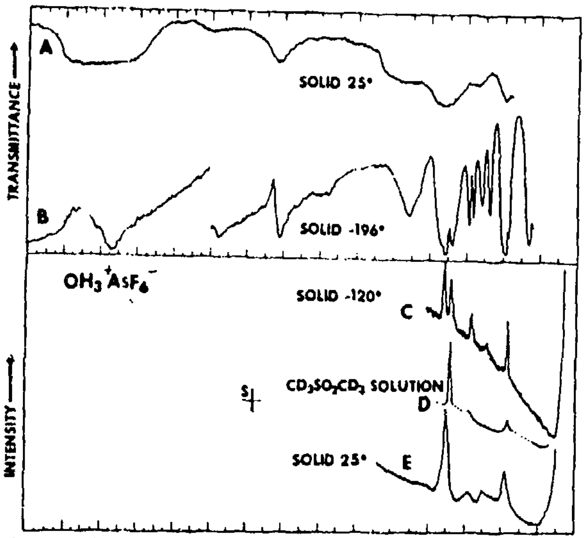

Figure 2. Vibrational spectra of $OH_3^+AsF_6^-$: trace A, infrared spectrum of the solid as a dry powder between AgCl disks at 25°; trace B, infrared spectrum of the solid as a dry powder between CsI disks at −196°; traces C and E, Raman spectra of the solid in a quartz tube recorded at +25 and −120°, respectively; trace D, Raman spectrum of a $CD_3SO_2CD_3$ solution. S indicates the spectral slit width.

temperature splittings is the assumption that at low temperature OH_3^+ and the lattice become rigid. This should result in site symmetry splittings[36] and in a large distortion of the MF_6^- octahedrons owing to cation–anion interaction (H---F bridging), particularly, since the MF_6^- ions are in a field of forces of nonoctahedral symmetry. Similar effects were observed for $OH_3^+ClO_4^-$ by broad-line proton NMR[45,46] and vibrational spectroscopy.[47] However, some of the bands observed in the region of the MF_6^- fundamentals could be of different origin, as was shown[47] by Savoie and Giguere for $OH_3^+NO_3^-$, $OH_3^+ClO_4^-$, and $OH_3^+HSO_4^-$. They established that libration and translation modes of polar OH_3^+ are of relatively high frequency and infrared intensity. Since the OH_3^+ modes are only of very low intensity in the Raman spectrum, the observed Raman bands are very likely due to the anion. However, some of the infrared bands, which have no Raman counterpart, could be due to OH_3^+ libration or translation modes. Spectra of the deuterated species would be helpful to distinguish between these possibilities. In addition, extensive low-temperature vibrational and wide-line NMR spectroscopic studies combined with X-ray and DTA data are desirable to correlate all the observed phenomena. However, this was beyond the scope of the present study.

Assignments for the fundamentals of the OH_3^+ cation were made by comparison with isoelectronic NH_3 (see Table III). Pyramidal XY_3 of symmetry C_{3v} has four fundamentals which are classified as 2 A_1 + 2 E, all being active in both the infrared and Raman spectra. Of these, each symmetry species contains one stretching and one bending mode. The frequencies of the two bending modes are sufficiently separated and present no assignment problem. Of the two stretching modes, the symmetric stretch $\nu_1(A_1)$ is obviously represented by the polarized Raman band at 3300 cm^{-1} observed for $OH_3^+SbF_6^-$ in HF solution. This Raman band has an intense counterpart in the infrared spectrum of the solid. Assuming that no significant frequency shift occurred for ν_1 on going from the solution spectrum to that of the solid, the second intense infrared band in this region (~3150 cm^{-1}) should be due to the antisymmetric stretch $\nu_3(E)$. These assignments are supported by the low-temperature infrared spectrum of $OH_3^+AsF_6^-$ which shows a strong band at about 3080 cm^{-1} with a strong shoulder at about 3250 cm^{-1} in agreement with the higher ir intensity expected[48] for ν_3 in an ideal, rather oblique XY_3 pyramid. The agreement between the frequencies of isoelectronic NH_3 and OH_3^+ is excellent. The only difference in their assignments results from a reversal of ν_1 and ν_3 for OH_3^+. Whereas force field arguments (see below) do not support such a reversal, it must be kept in mind that we are comparing a free molecule with a poorly understood solid exhibiting relatively strong anion–cation coupling.

In our spectra two relatively weak broad infrared bands were frequently observed at about 1950 and 1350 cm^{-1}, respectively. Their relative intensities varied and they cannot readily be assigned to an overtone or combination band. Their origin is at the present not fully understood.

In summary, the vibrational spectra unambiguously establish that the $HF \cdot H_2O \cdot MF_5$ adducts are ionic both in the solid state and in solution and contain octahedral MF_6^- anions and pyramidal OH_3^+ cations, although some of the details of the spectra are still poorly understood. The fundamentals of OH_3^+ in its MF_6^- salts significantly differ from those found for OH_3^+ in mineral acid monohydrates,[21] such as $OH_3^+ClO_4^-$, and resemble more closely those of isoelectronic NH_3. The fact that in $OH_3^+MF_6^-$ the OH stretches have higher and the deformations have lower frequencies than in the mineral acid hydrates strongly indicates that the hydrogen bridging in $OH_3^+MF_6^-$ is significantly weaker, i.e., that these compounds are more ionic.

Force Constants. To support the above assignments, force fields were computed for OH_3^+ (see Table IV) using the vibrational frequency values from this study and the geometry

Table IV. Symmetry and Internal Force Constants[a] of OH_3^+ Compared to Those[b] of NH_3

	OH_3^+					NH_3
Bond angle, deg	110	110	110	110	100	107
Force field	DFF	F_{22} and F_{44} ≡ min	NH_3 TR	$\nu_3 \to \nu_1$ $\nu_1 \to \nu_3$ F_{22} and F_{44} ≡ min	F_{22} and F_{44} ≡ min	GVFF
A_1 $F_{11} = f_r + 2f_{rr}$	6.3369	6.3398	6.3565	5.7783	6.2128	6.4540
$F_{22} = f_\alpha + 2f_{\alpha\alpha}$	0.4296	0.4295	0.4448	0.4295	0.1942	0.4049
$F_{12} = 2f_{r\alpha} + f_{r\alpha}'$	0	0.02395	0.3244	0.02395	0.0183	0.3244
E $F_{33} = f_r - f_{rr}$	5.4213	5.4398	5.4542	5.9696	5.4908	6.4732
$F_{44} = f_\alpha - f_{\alpha\alpha}$	0.5826	0.5817	0.5840	0.5817	0.6752	0.6161
$F_{34} = -f_{r\alpha} + f_{r\alpha}'$	0	−0.0648	−0.1622	−0.0648	−0.0554	−0.1622
f_r	5.7265	5.7398	5.7550	5.9058	5.7315	6.4668
f_{rr}	0.3050	0.3000	0.3008	−0.0638	0.2407	−0.0064
f_α	0.5316	0.5310	0.5376	0.5310	0.5149	0.5457
$f_{\alpha\alpha}$	−0.0510	−0.0507	−0.0464	−0.0507	−0.1603	−0.0704
$f_{r\alpha}$	0	0.0296	0.1622	0.0296	0.0246	0.1622
$f_{r\alpha\alpha}$	0	−0.0352	0	−0.0352	−0.0308	0

[a] All force constants have units of mdyn/Å. Frequency values used: $\nu_1 = 3300$, $\nu_2 = 900$, $\nu_3 = 3150$, and $\nu_4 = 1620$ cm^{-1}, except for column 5 where the frequencies of ν_1 and ν_3 were exchanged. [b] Values from ref 50.

(∠ = 110°, r = 1.01 Å) previously established[23] for the $OH_3^+CH_3C_6H_4SO_3^-$ salt. The force constants were computed by trial and error with the help of a computer to obtain an exact fit between observed and calculated frequencies. Three different force fields were computed to demonstrate that the choice of the force field has little influence on its values for a vibrationally weakly coupled species, such as OH_3^+, in which the central atom is much heavier than the ligands. To demonstrate the small variation in the force constant values, four decimals are listed in Table IV, in spite of the rather large uncertainties in the given force constant values. These are caused by the broadness of the bands and the unknown bond angle of OH_3^+ in its MF_6^- salts. Two of the three force fields used, the diagonal force field and the force field requiring the deformation symmetry force constants to have minimal values, were selected owing to their established[49] usefulness for weakly coupled systems. For the third force field, the off-diagonal symmetry force constants were borrowed from the known[50] general valence force field of isoelectronic NH_3. Since the antisymmetric OH_3^+ stretch has a significantly lower frequency than the symmetric one and since their frequency separation is a function of the bond angle,[51] this might be taken as some evidence for the OH_3^+ bond angle being smaller than that in isoelectronic NH_3. Consequently, we have also computed the three force fields for OH_3^+ assuming a bond angle of 100°. Whereas the stretching force constants show little angle dependence, F_{22} becomes unreasonably small for $\alpha = 100°$, thus arguing against such a small bond angle for OH_3^+. As expected for a weakly coupled species containing only one stretching and one deformation vibration of very different frequency in each symmetry block, the potential energy distribution showed all fundamentals to be highly characteristic. The two high-frequency fundamentals were in all cases pure stretches and the two low-frequency fundamentals were 95–100% deformation modes depending upon the values of the chosen off-diagonal symmetry force constants.

Comparison of the OH_3^+ force fields with that[50] of isoelectronic NH_3 shows good agreement. The only major divergence is found for the stretch–stretch interaction constant f_{rr} which is caused by $\nu_3(E)$ of OH_3^+ having a lower frequency value than $\nu_1(A_1)$. This discrepancy could be eliminated either by reversing their assignment (see Table IV) or by assuming very similar frequency values for them and explaining the observed splitting of the broad band at ~3300 cm^{-1} in the infrared spectrum of $OH_3^+SbF_6^-$ by Fermi resonance between $2\nu_4(A_1 + E + F_2)$ and $\nu_1(A_1)$ or $\nu_3(E)$. Clearly, the force field computations for OH_3^+ and comparison with those for NH_3,[50] PH_3,[50] and SH_3^+ [7] favor $\nu_3 > \nu_1$. However, the experimental data (see above) seem to suggest $\nu_1 > \nu_3$. Obviously, additional experimental data are required to resolve this remaining ambiguity.

Several papers[20,21,52,53] have previously been published dealing with force fields of OH_3^+. Owing to the great variance of the frequencies used, the values reported, for example, for f_r range from 3.93 to 6.31 mdyn/Å. The variance of the frequencies is due partially to the different degree of hydrogen bridging in the different OH_3^+ salts studied[21] and partially to the broadness of the bands rendering their assignments extremely difficult and uncertain.

Conclusion

The novel oxonium salts $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ were synthesized and partially characterized. They possess unusual thermal stability, are easy to prepare, are well defined, appear to be highly ionic and, therefore, should be ideally suited for the study of the oxonium cation.

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Registry No. $OH_3^+SbF_6^-$, 55649-03-1; $OH_3^+AsF_6^-$, 21501-81-5; SbF_5, 7783-70-2; HF, 7664-39-3; H_2O, 7732-18-5; OH_3BF_4, 14219-41-1; BF_3, 7637-07-2; arsenic pentafluoride, 7784-36-3.

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Novel Onium Salts. Synthesis and Characterization of $SH_3^+SbF_6^-$

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The synthesis and properties of $SH_3^+SbF_6^-$, the first known example of a stable salt containing the sulfonium cation, are reported. The SH_3^+ cation was characterized by vibrational spectroscopy and a normal-coordinate analysis was carried out. Attempts to prepare $SH_3^+AsF_6^-$ resulted in the formation of As_2S_5. Protonation of HCl in $HF-SbF_5$ solution yields an unstable white solid, but no evidence was obtained for adduct formation in the $HF-SbF_5-Xe$ system at temperatures as low as −78°.

Introduction

Recent studies[1] in our laboratory showed that the protonation of H_2O in $HF-MF_5$ (M = Sb and As) solutions produces the surprisingly stable oxonium salts $OH_3^+MF_6^-$. This prompted us to investigate the synthesis of other onium salts. In this paper we report on the protonation of H_2S, HCl, and Xe. Results on the protonation of HNF_2 and NF_3 will be given elsewhere.[2]

Whereas a huge number of alkyl- or aryl-substituted sulfonium salts are known, we could not find any literature reports on the isolation of a salt containing the SH_3^+ cation, although Olah and coworkers had observed[3] the SH_3^+ cation at low temperature in $HSO_3F-SbF_5-SO_2$ solution by proton NMR spectroscopy (singlet at δ −6.60). In addition, the formation of gaseous SH_3^+ was studied[5-7] in mass spectrometers (ion–molecule and electron-impact studies). Similarly, the protonation of HCl has been studied only in HSO_3F-SbF_5 solution at low temperature by NMR spectroscopy, but no direct evidence for the formation of a ClH_2^+ cation was reported.[8] For xenon, protonation in $HF-SbF_5$ solution was postulated[9] based on its ability to suppress isotopic hydrogen–deuterium exchange; protonation in ion–molecule reactions has been also reported.[10,11]

Experimental Section

The experimental techniques used in this study were essentially the same as those previously described.[1]

Preparation of $SH_3^+SbF_6^-$. In a typical experiment, SbF_5 (5.38 mmol) and anhydrous HF (10 ml of liquid) were combined at −196° in a Teflon–FEP ampoule. The mixture was warmed to 25° to give a homogenous solution. Hydrogen sulfide (7.10 mmol) was added to the ampoule at −196°. The mixture was warmed first to −78° and then slowly to 25°. During warmup was formed a white solid, which was only partially soluble in the excess of HF. Volatile products were removed at 25° in vacuo, leaving behind 1.452 g of a white, stable solid (weight calcd for 5.38 mmol of $SH_3^+SbF_6^-$ 1.457 g). Anal. Calcd for SH_3SbF_6: Sb, 44.95; S, 11.84. Found: Sb, 44.8; S, 11.9. The $SH_3^+SbF_6^-$ product can be stored at 25° without noticeable decomposition in Teflon or Kel-F containers, but it attacks quartz.

The $HF-AsF_5-H_2S$ System. Anhydrous HF (10 ml of liquid) and AsF_5 (3.54 mmol) were combined at −196° in a Teflon-FEP ampoule. The mixture was warmed to 25° and then recooled to −196°. Hydrogen sulfide (3.54 mmol) was added to the ampoule at −196°. During slow warmup of the mixture to 0° a white to yellow solid formed. The ampoule was recooled to −78° and volatile material was pumped off during warmup to 25° leaving behind 221 mg of a stable yellow solid (weight calcd for 0.708 mmol of As_2S_5 220 mg). Vibrational spectroscopy showed that the solid did not contain bands characteristic for either SH_3^+ (see below) or AsF_6^-. It was insoluble in water but slowly dissolved in boiling concentrated HNO_3. Anal. Calcd for As_2S_5: As, 48.3; S, 51.7. Found: As, 48.5; S, 51.6.

The $HF-SbF_5-HCl$ System. To a homogenized mixture (see above) of SbF_5 (2.57 mmol) and anhydrous HF (5 ml of liquid) in a Teflon–FEP ampoule, HCl (6.81 mmol) was added at −196°. The mixture was warmed to −78° and then cycled several times between −78 and 0°. A white solid was formed upon melting of the starting materials. Volatile material was pumped off at −45°, resulting in 711 mg of an unstable, white solid melting below room temperature to a pale yellow, clear liquid (weight calcd for 2.57 mmol $ClH_2^+SbF_6^-$ 702 mg). The vapor phase above the liquid at 26° was shown by infrared spectroscopy to consist essentially of HF and HCl. The Raman spectrum of the HF solution showed the bands characteristic of SbF_6^- (see below).

The $HF-SbF_5-Xe$ System. To a homogenized (see above) mixture of SbF_5 (3.07 mmol) and anhydrous HF (10 ml of liquid) in a Teflon–FEP ampoule, Xe (7.04 mmol) was added at −196°. The mixture was slowly warmed to 0° and then kept at −78° for 16 hr. No evidence for adduct formation between Xe and $HF-SbF_5$ at −78° was detected, and the xenon starting material was quantitatively

Table I. X-Ray Powder Data for $H_3S^+SbF_6^-$ [a]

d_{obsd}, Å	d_{calcd}, Å	Intens	*hkl*
5.96	5.94	vw	200
5.26	5.26	vs	002
3.94	3.94	vs	202, 300
3.56	3.54	vs	311
3.16	3.16	m	302
2.619	2.623	mw	303, 004
2.456	2.471	w	332
2.257	2.265	m	403
2.176	2.165	ms	502
2.069	2.068	w	105
1.963	1.966	w	503, 404
1.839	1.833	w	315
1.769	1.771	w	630
1.750	1.750	w	006
1.720		w	
1.616		mw	
1.572		w	
1.535		w	
1.484		mw	
1.461		mw	
1.401		w	
1.308		w	
1.251		w	
1.239		w	
1.212		w	

[a] Tetragonal, $a = 11.89$ Å, $c = 10.51$ Å, $V = 1484.0$ Å^3, $Z = 8$, $\rho_{calcd} = 2.43$ g cm^{-3}, Cu K_α radiation, and Ni filter.

recovered from the reaction mixture at −78°.

Results and Discussion

Synthesis and Properties of SH_3^+ Salts. Protonation of H_2S in HF–SbF_5 solution produced the white, stable solid $SH_3^+SbF_6^-$ in quantitative yield according to

$$H_2S + HF + SbF_5 \rightarrow SH_3^+SbF_6^-$$

To our knowledge this is the first reported example of a stable salt containing the sulfonium cation.

According to the DSC data, $SH_3^+SbF_6^-$ starts to decompose at 90° with the onset of an exotherm which rapidly changes into a large endotherm. The salt is moderately soluble in anhydrous HF. Attempts were unsuccessful to dissolve it in organic solvents, such as $CH_3SO_2CH_3$, which were found[1] suitable for $OH_3^+SbF_6^-$. When the solvent was added, gas evolution and the formation of a cinnabar solid (probably Sb_2S_5) and a yellow solution were observed. Attempts to dissolve the sulfonium salt in SbF_5 caused oxidation of SH_3^+ as indicated by gas evolution and the appearance of a strong blue color, similar to that previously reported[12] for polysulfur radical cations. When exposed to atmospheric moisture, the solid turns yellow first and then cinnabar accompanied by the evolution of H_2S. Obviously, H_2S is displaced from its salt by the more basic water. This displacement reaction might be used as a convenient way to generate gaseous H_2S from the storable solid $SH_3^+SbF_6^-$ by the simple addition of water. Vibrational spectroscopy (see below) showed that some samples contained some sulfur in the form of S_8, as was also indicated by their faint yellow color.

The X-ray powder pattern of $SH_3^+SbF_6^-$ is listed in Table I. The tetragonal unit cell with $a = 11.89$ Å, $c = 10.51$ Å, and $Z = 8$ is in good agreement with those found for $OH_3^+SbF_6^-$ and the related $M^+XF_6^-$ salts.[13-15] As expected, $SH_3^+SbF_6^-$ has a larger unit cell and a lower density than $OH_3^+SbF_6^-$ owing to SH_3^+ having a significantly larger radius than OH_3^+.

Attempts to synthesize $SH_3^+AsF_6^-$ from the HF–AsF_5–H_2S system were unsuccessful and resulted in the quantitative conversion of AsF_5 to As_2S_5 according to

$$2AsF_5 + 5H_2S \rightarrow As_2S_5\downarrow + 10HF$$

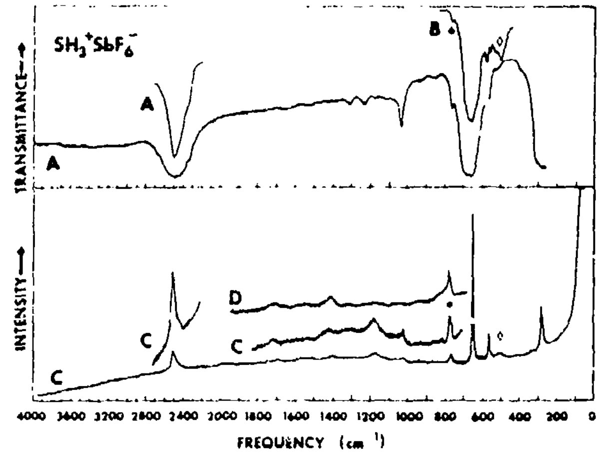

Figure 1. Vibrational spectrum of $SH_3^+SbF_6^-$. For clarity, bands due to sulfur (S_8) were deleted: trace A, infrared spectra of the solid as dry powders between AgBr disks at two different concentrations; part of the intensity of the 270-cm^{-1} band is due to absorption by the thin AgBr windows; trace B, spectrum of a different sample shown to demonstrate the variable relative intensities of the impurity bands marked by an asterisk and a diamond (see text). trace C, Raman spectra of solid $SH_3^+SbF_6^-$ recorded at two different recorder voltages and spectral slit widths of 4 (lower) and 8 cm^{-1} (upper traces); sample container was a quartz tube; trace D, background spectrum recorded after complete decomposition of $SH_3^+SbF_6^-$ had occurred.

This difference in behavior between SbF_5 and AsF_5 is not surprising since it is well known[16] that in the presence of fluoride ions H_2S will precipitate only arsenate, but not antimonate, as the corresponding pentasulfide.

Protonation of HCl and Xe. Since the protonation of H_2O and of the more acidic H_2S had resulted in the formation of novel stable MF_6^- salts, we decided to examine the protonation of the even more acidic species HCl and of Xe. For both, previous studies[8,9] had indicated protonation in solution.

The protonation of HCl in HF–SbF_5 solution produced a white solid product stable at −45° but melting below room temperature with decomposition. From the observed material balance, the composition of the adduct was found to be approximately 1:1:1 and the more volatile decomposition products were shown to be HCl and HF. By analogy with the OH_3^+ and SH_3^+ salts and on the basis of the Raman spectrum of an HF solution showing the presence of SbF_6^-, this adduct is likely to be $ClH_2^+SbF_6^-$. For xenon, no evidence for the formation of a stable adduct was found at temperatures as low as −78°. Our studies indicate that compounds more basic than HCl stand a good chance of forming a reasonably stable protonated SbF_6^- salt. NMR evidence for the existence of such protonated species in superacid solutions at low temperature has already been reported[17] for several species, and the isolation of these and other novel simple protonated cations in form of their stable MF_6^- salts can be predicted. Obviously, the parent species are not limited to nonmetal hydrides but can include many other moieties.

Vibrational Spectrum of $SH_3^+SbF_6^-$. Since $SH_3^+SbF_6^-$ decomposes in organic solvents, such as $CH_3SO_2CH_3$, and its proton NMR spectrum in HSO_3F–SbF_5–SO_2 solution (singlet at δ 6.60)[3] yields little structural information, we have used vibrational spectroscopy to characterize the SH_3^+ cation. The vibrational spectrum of solid $SH_3^+SbF_6^-$ is shown in Figure 1. Attempts to record the Raman spectrum of an HF solution were unsuccessful owing to the moderate solubility of the salt in HF. When exposed to the blue 4880-Å line of an Ar ion laser, the sample tended to decompose rapidly even at −120°. However, this problem could be overcome by defocusing the laser beam. In general, the Raman spectra showed bands[18,19]

Table II. Vibrational Spectrum of $SH_3^+SbF_6^-$ and Its Assignment Compared to That of PH_3[a]

Obsd freq, cm^{-1}, and rel intens[b]			Assignment (point group)	
	$SH_3^+SbF_6^-$ solid			
PH_3	Ir	Raman	XH_3 (C_{3v})	SbF_6^- (O_h)
2328		2520 (1.3)	ν_3(E)	
	2520 vs			
2323		2490 sh	ν_1(A_1)	
	2360 sh		$2\nu_4$(A_1 + E + F_2)	
	1308 w			$\nu_1 + \nu_3$(F_{1u})
	1222 w			$\nu_1 + \nu_2$(E_g)
1122	1180 vw	1180 (0.4)	ν_4(E)	
992	1028 mw	1025 (0.3)	ν_2(A_1)	
	848 vw			$\nu_1 + \nu_4$(F_{1u})
	660 vs			ν_3(F_{1u})
		650 (10)		ν_1(A_{1g})
	569 m	556 (1.6)		ν_2(E_g)
		282 (2.8)		ν_5(F_{2g})
		275 sh		
	270 s			ν_4(F_{1u})

[a] Reference 23. [b] Uncorrected Raman intensities; bands due to decomposition products have not been listed.

due to varying amounts of sulfur (S_8) as was also indicated by the yellowish color of these samples. In addition, the spectra showed a band at 760 cm^{-1} (marked in Figure 1 by an asterisk) which based on literature data[18,19] does not belong to S_8. Decomposition studies showed that, contrary to the $SH_3^+SbF_6^-$ bands, this band was stable toward decomposition in the focused laser beam and, therefore, cannot belong to $SH_3^+SbF_6^-$ (see trace D, Figure 1). The Raman spectrum contains also a weak band at about 500 cm^{-1} (marked by a diamond) which is definitely due to a decomposition product. This band becomes the most intense band in the spectrum, when most of the $SH_3^+SbF_6^-$ has decomposed. The remainder of the spectrum (see Table II) is in excellent agreement with our expectations for ionic $SH_3^+SbF_6^-$ and is discussed below.

The general appearance of the vibrational spectrum of $SH_3^+SbF_6^-$ (see Figure 1) strongly deviates from that[1] of $OH_3^+SbF_6^-$ recorded at room temperature. Contrary to $OH_3^+SbF_6^-$, the bands due to $SH_3^+SbF_6^-$ are sharp and narrow and show little or no splittings indicating for SbF_6^- and SH_3^+ no appreciable deviation from symmetry O_h and C_{3v}, respectively. In particular, the Raman bands due to SbF_6^- are very narrow and exhibit the frequencies and relative intensities expected[20-22] for octahedral SbF_6^-. This indicates that, contrary to $OH_3^+SbF_6^-$, either the cation–anion coupling in $SH_3^+SbF_6^-$ is relatively weak or the crystal lattice becomes rigid at a higher temperature. Since $OH_3^+SbF_6^-$ and $SH_3^+SbF_6^-$ have similar tetragonal unit cells with $Z = 8$ (see above), it is unlikely that crystal effects are the main reason for this pronounced difference. A better explanation for the observed difference is the lower electronegativity of sulfur when compared to oxygen. This should markedly decrease the polarity of the X–H bond and thereby decrease the positive charge on the hydrogen ligands. This in turn should result in a much weaker coulombic interaction between the positively polarized hydrogen ligands of the cation and the negatively polarized fluorine ligands of the anion, hence substantially reducing the cation–anion coupling.

The assignments for the SH_3^+ cation in point group C_{3v} were made by comparison with those[23] of isoelectronic PH_3 (see Table II). Pyramidal XY_3 of symmetry C_{3v} has four fundamentals which are classified as 2 A_1 + 2 E, all being active in both the infrared and the Raman spectra. Of these, each symmetry species contains one stretching and one bending mode. By comparison with PH_3, the two stretching modes of SH_3^+ are expected to have very similar frequencies and, indeed, only one intensive band is observed in the S–H stretching region at 2520 cm^{-1}. Since the symmetric SH_3 stretch should be of much higher Raman intensity than the antisymmetric one, the maximum of the Raman band at 2520 cm^{-1} must be due to ν_1(A_1). This band shows a shoulder at 2490 cm^{-1}, which might represent the antisymmetric stretch ν_3(E). However, we prefer to assume a complete coincidence of ν_1 and ν_3, since ν_3 should be more intense in the infrared spectrum[24] and the infrared band has its maximum at about 2520 cm^{-1}. The weak shoulder observed at 2360 cm^{-1} in the infrared spectrum is due to the overtone $2\nu_4$(A_1 + E + F_2) in Fermi resonance with ν_1 and ν_3.

Of the two deformation modes of SH_3^+, one obviously is represented by the 1028-cm^{-1} infrared band. For the other deformation, we had originally considered the 760-cm^{-1} infrared band. However, a normal-coordinate analysis, carried out with this assignment, resulted in unreasonable force constants. Whereas the stretching force constant in SH_3^+ was larger than in PH_3, the deformation constant was significantly lower. This is not plausible since any H--F bridging possible in such a solid should decrease the value of the stretching and increase the value of the deformation force constant. A careful reexamination of the spectra established that the 760-cm^{-1} band is not part of the $SH_3^+SbF_6^-$ spectrum and that the Raman spectrum exhibits a band of moderate intensity at 1180 cm^{-1}, a frequency value quite reasonable for the missing SH_3^+ deformation. The assignment of this band to ν_4(E) of SH_3^+ is further supported by the observation of its overtone in the infrared spectrum (see above) and the results from a normal-coordinate analysis (see below). Direct observation of ν_4 in the infrared spectrum is complicated by its relatively low infrared intensity and interference by SbF_6^- combination bands. This leaves the 1028-cm^{-1} infrared band for assignment to ν_2(A_1), in excellent agreement with the frequencies[23] of PH_3.

Table III. Symmetry and Internal Force Constants[a] of SH_3^+ Compared to Those of Isoelectronic PH_3

	SH_3^+							PH_3[b]
Bond angle, deg	90	95	95	95	100	105	110	93
Force field	DFF	DFF	F_{22} and F_{44} = min	PH_3 TR	DFF	DFF	DFF	GVFF
A_1 $F_{11} = f_r + 2f_{rr}$	3.6535	3.6730	3.6764	3.6797	3.6930	3.7130	3.7320	3.1222
$F_{22} = f_\alpha + 2f_{\alpha\alpha}$	0.2958	0.3252	0.3252	0.3263	0.3705	0.4472	0.6030	0.2938
$F_{12} = 2f_{r\alpha} + f_{r\alpha}'$	0	0	0.0180	0.0784	0	0	0	0.0784
E $F_{33} = f_r - f_{rr}$	3.6543	3.6445	3.6467	3.6469	3.6350	3.625	3.6158	3.1087
$F_{44} = f_\alpha - f_{\alpha\alpha}$	0.4071	0.3872	0.3873	0.3874	0.3658	0.3426	0.3178	0.3548
$F_{34} = -f_{r\alpha} + f_{r\alpha}'$	0	0	−0.0140	−0.0392	0	0	0	−0.0392
f_r	3.6540	3.6540	3.6566	3.6578	3.6543	3.6543	3.6545	3.1132
f_{rr}	−0.0003	0.0095	0.0099	0.0109	0.0193	0.0293	0.0387	0.0045
f_α	0.3700	0.3665	0.3666	0.3670	0.3674	0.3775	0.4129	0.3345
$f_{\alpha\alpha}$	−0.0371	−0.0207	−0.0207	−0.0204	0.0016	0.0349	0.0951	−0.0203
$f_{r\alpha}$			0.0107	0.0392				0.0392
$f_{r\alpha}'$			−0.0033	0				0

[a] All force constants have units of mdyn/Å. Frequency values used: $\nu_1 = \nu_3 = 2520$, $\nu_2 = 1028$, and $\nu_4 = 1180$ cm^{-1}. [b] Values from ref 23.

Normal-Coordinate Analysis. To support the above assignments for SH_3^+, a normal-coordinate analysis was carried out, the results of which are given in Table III. Since the geometry of SH_3^+ is unknown, we have computed force fields for different bond angles ranging from 90 to 110° (the bond angle in isoelectronic PH_3 is 93.345°).[25] For the bond length in SH_3^+ an estimated value of 1.33 Å was used. The force constants were computed by trial and error with the help of a computer to obtain an exact fit between observed and calculated frequencies. Three different force fields were used to show that for a vibrationally weakly coupled (heavy central atom, light ligands) species, such as SH_3^+, the choice of a particular force field is less important than other variables, such as the bond angle. To demonstrate the small variation in the computed force fields, insignificant decimals are carried in Table III. Of the three different force fields used, the diagonal force field (DFF) and the force field requiring the deformation symmetry force constants to have minimal values were selected for their established[26] usefulness for vibrationally weakly coupled species. The third force field (PH_3,TR) was computed by using the general valence force field (GVFF) off-diagonal symmetry force constants of isoelectronic PH_3 for SH_3^+. As can be seen from Table III, all three force fields yield very similar force constants. Therefore, the given force fields are likely to be good approximations of a GVFF. By comparison with the known bond angles of H_2O, CH_3^+, NH_3, H_2S, and PH_3, a bond angle of about 95° appears to be most likely for SH_3^+, although the choice of the bond angle is not very critical as can be seen from the small variation of the force constants within the most probable bond angle range of 90–100°. As expected for a vibrationally weakly coupled species containing only one stretching and one deformation vibration of very different frequency in each symmetry block, the potential energy distribution showed all fundamentals to be highly characteristic. Thus, ν_1 and ν_3 were 100% pure stretching modes and ν_2 and ν_4 were 97–99% pure deformations. Comparison of the force constants of SH_3^+ with those[23] of PH_3 shows excellent agreement thus supporting the above given assignments for SH_3^+.

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Registry No. $SH_3^+SbF_6^-$, 55590-58-4; SbF_5, 7783-70-2; HF, 7664-39-3; hydrogen sulfide, 7783-06-4; $ClH_2^+SbF_6^-$, 55590-57-3.

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Novel Onium Salts. Synthesis and Characterization of the Difluoroammonium Cation, $NH_2F_2^+$

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The syntheses and properties of $NH_2F_2^+SbF_6^-$ and $NH_2F_2^+AsF_6^-$, the first known examples of difluoroammonium salts, are reported. The $NH_2F_2^+$ cation was characterized by ^{19}F and ^1H NMR and vibrational spectroscopy. At room temperature the $NH_2F_2^+$ salts are metastable and undergo spontaneous exothermic decomposition by HF elimination. Attempts were unsuccessful to prepare either NHF_3^+ salts by protonation of NF_3 at temperatures as low as −78° or fluorine-substituted ammonium salts by direct fluorination of $NH_4^+AsF_6^-$ in HF solution in the temperature range −78 to +25°.

Introduction

Recent studies in our laboratory demonstrated that several novel onium salts can be prepared by protonation of less acidic compounds in HF–MF_5 (M = Sb, As) solutions. Thus, protonation of H_2O and H_2S produced[1,2] the surprisingly stable $OH_3^+MF_6^-$ and $SH_3^+SbF_6^-$ salts, respectively. In this paper, we report on the protonation of HNF_2 and NF_3.

Whereas salts containing the NH_4^+ ion had been described already in the early part of the fourteenth century,[3] fluorine-substituted salts were unknown until 1965. Disproving earlier theoretical computations[4,5] that NF_4^+ salts should be thermodynamically unstable, these salts were synthesized[6,7] in 1965 and shown to be of high thermal stability. Since then, numerous papers dealing with NF_4^+ salts[8-18] and the thermally unstable NF_3^+ radical cation[17] have appeared. Of the mixed $NH_nF_{4-n}^+$ cations, the NH_3F^+ cation has previously been described,[19,20] but no data on the remaining two members in this series, i.e., $NH_2F_2^+$ and NHF_3^+, have been published. This is not surprising, since from comparison with the highly shock-sensitive HNF_2 molecule and its CsF adduct,[21] one might expect these more highly fluorinated mixed ammonium salts to be very susceptible to HF elimination. The adduct formation of HNF_2 with the Lewis acids BF_3, BCl_3, PF_5, and SO_2 has been studied[22] at −196° by infrared spectroscopy, but no evidence was found for ion formation. The thermal stability of these adducts was rather low with (in some cases irreversible) decomposition occurring at about −80°.

Experimental Section

Caution! Difluoramine is highly explosive[21] and protective shielding should be used during handling operations. The compound was always condensed at −142° and the use of a −196° bath should be avoided.[23] In the course of the present study five explosions of both $NH_2F_2^+AsF_6^-$ and $NH_2F_2^+SbF_6^-$ in HF solution occurred, when these solutions were kept between −50 and +25° for extended periods of time. However, the appearance of the ruptured Kel-F or Teflon-FEP containers indicated pressure explosions (probably caused by HF elimination with N_2 formation and by the small ullage above the liquid phase) rather than rapid explosive decomposition. The rate of decomposition of these $NH_2F_2^+$ salt solutions varied strongly from sample to sample, indicating catalysis by trace impurities. The exothermic irreversible decomposition of solid $NH_2F_2^+$ salts appeared to proceed without explosion on a millimolar scale, provided the volume of the container was large enough to avoid overpressurization. When working with such solutions in containers with small ullage, we, therefore, recommend removing the volatile decomposition products by quick pumping at −78° every time before handling the sample.

The experimental techniques used in this study have previously been described.[1] Difluoramine was prepared from difluorourea.[24] Nitrogen trifluoride (99.9%, Rocketdyne) and $NH_4^+HF_2^-$ (Braun Chemical Co.) were used without further purification. Difluoramine was handled in a Pyrex, the other reactants in a Monel Teflon-FEP, vacuum system.

Preparation of $NH_2F_2^+AsF_6^-$. In a typical experiment, dry HF (50 mmol) and AsF_5 (1.74 mmol) were combined at −196° in a passivated (with ClF_3) thin-walled Kel-F capillary. The mixture was shortly warmed to room temperature to obtain a homogenous solution. Difluoramine (2.0 mmol) was added to the ampoule at −142°. The mixture was warmed to −78° and a white solid was formed which was completely soluble in the HF solvent at 20°. Unreacted NHF_2 and HF solvent were removed under dynamic vacuum between −78 and 0°, leaving behind 420 mg of a white solid. This weight is in excellent agreement with that (423 mg) expected for 1.74 mmol of $NH_2F_2^+AsF_6^-$.

For the preparation of the NMR samples, an excess of AsF_5 was used and not pumped off to suppress exchange between the cation and the HF solvent.

Decomposition of $NH_2F_2^+AsF_6^-$. A sample of solid $NH_2F_2^+AsF_6^-$, contained in a Teflon-FEP ampoule, was allowed to warm slowly from −78 to +20°. After about 20 min at 20°, the solid started to melt and spontaneously decomposed with gas and heat evolution (*caution!*). The decomposition products were separated by fractional condensation and identified by infrared spectroscopy or mass spectroscopy. The main constituents were AsF_5, HF, and N_2, in addition to some NF_3 and *trans*-N_2F_2.

Preparation of $NH_2F_2^+SbF_6^-$. In a typical experiment, SbF_5 (1.70 mmol) and dry HF (150 mmol) were combined at −196° in a passivated Teflon-FEP ampoule. The mixture was warmed to 25° to obtain a homogenous solution. Difluoramine (2.02 mmol) was added to the ampoule at −142° and the mixture was warmed to −78°. A white solid formed when the starting materials melted. On warm-up toward 0°, the solid completely dissolved in the excess HF. The unreacted NHF_2 and the HF solvent were pumped off between −45 and 0° leaving behind a white solid residue (499 mg). This weight agrees well with that (493 mg) expected for 1.70 mmol of $NH_2F_2^+SbF_6^-$.

Decomposition of $NH_2F_2^+SbF_6^-$. A sample of $NH_2F_2^+SbF_6^-$ (1.70 mmol), when kept at 25° for about 1 hr, underwent spontaneous exothermic decomposition with melting and gas evolution. The decomposition products, volatile at −78°, consisted of N_2 (0.56 mmol) and NF_3 containing a small amount of *trans*-N_2F_2 (0.58 mmol total). The residue (~410 mg; weight calculated for 1.70 mmol of HF·SbF_5 402 mg) was warmed to 25° under dynamic vacuum. A small amount of white solid stable at 25° was obtained which, based on its infrared spectrum, contained some $N_2F_3^+SbF_6^-$.

NF_3–HF–SbF_5 System. To a homogenized (see above) mixture of SbF_5 (1.93 mmol) and HF (150 mmol) in a Teflon-FEP ampoule was added NF_3 (3.52 mmol) at −196°. The mixture was kept at −78° for 16 hr. No evidence for adduct formation between NF_3 and HF-SbF_5 at −78° was detected, and the NF_3 starting material was recovered from the mixture at −78°.

$NH_4^+AsF_6^-$–HF–F_2 System. Ammonium bifluoride (2.79 mmol) was placed in a Teflon-FEP ampoule and 20 ml of liquid anhydrous HF was added at −78°. To the clear solution was added AsF_5 (3.0 mmol) resulting in the formation of white solid $NH_4^+AsF_6^-$. This solid was only sparingly soluble in HF, even at 25°. The ampoule was pressurized with 1 atm of F_2 at −73° and the contents of the ampoule were agitated for 1 hr at −78°. No pressure decrease (expected for F_2 consumption with HF formation) was observed. The ampoule was kept at each of the temperatures −45, −23, 0, and 25° for 1 hr with agitation, but again no F_2 uptake was observed.

Results and Discussion

Synthesis and Properties. The observed material balances show that protonation of NHF_2 in HF–MF_5 (M = As, Sb) solutions proceeds according to

$$NHF_2 + HF + MF_5 \rightarrow NH_2F_2^+MF_6^-$$

The resulting difluoroammonium salts are white crystalline solids. They are stable at −50° but at room temperature tend to undergo spontaneous exothermic decomposition with melting and gas evolution. In our study, the longest time period during which a solid $NH_2F_2^+$ salt could be kept at room temperature without decomposition was about 0.5 hr. The HF solutions of these salts appear to be reasonably stable at room temperature; however, their stability varied strongly from sample to sample indicating some catalytic effect of by-products or impurities. Precautionary measures for handling these compounds are given in the first paragraph of the Experimental Section.

The main products in the decomposition of these $NH_2F_2^+MF_6^-$ salts are N_2, NF_3, and some *trans*-N_2F_2, in addition to the expected HF and MF_5. The fact that *trans*-N_2F_2 shows little tendency to complex with MF_5 under the given reaction conditions, agrees with previous[25] studies. The observation of only small amounts of *trans*-N_2F_2 but approximately equimolar amounts of N_2 and NF_3 as main products indicates the principal decomposition mode

$$3NH_2F_2^+MF_6^- \rightarrow 3MF_5 + 6HF + N_2 + NF_3$$

The formation of small amounts of *trans*-N_2F_2 might indicate that N_2F_2 is an intermediate in the above decomposition mode; however, previous decomposition studies[21] on N_2F_2 gave no evidence for a disproportionation according to

$$3N_2F_2 \rightarrow 2N_2 + 2NF_3$$

This difference in the decomposition products might be due to the exothermicity of the $NH_2F_2^+MF_6^-$ decomposition causing the formation of excited intermediates. The observed instability of $NH_2F_2^+$ salts toward HF elimination is not surprising. Thus, NHF_2 and its CsF adduct are known[21] to decompose explosively.

The stability of the mixed $NH_nF_{4-n}^+$ fluoroammonium cations decreases with decreasing *n*. Thus, NH_3F^+ is relatively stable,[19,20] $NH_2F_2^+$ is of very marginal stability, and no evidence was found in this study for the existence of a $NHF_3^+SbF_6^-$ salt at temperatures as low as −78°. Since the NH_3F^+ and $NH_2F_2^+$ cations are reasonably stable, particularly in HF solution at low temperatures, the direct fluorination of $NH_4^+AsF_6^-$ by F_2 in HF solution was studied over the temperature range −78 to +25°. However, no fluorination of $NH_4^+AsF_6^-$ was observed under these conditions indicating a significant activation energy for this reaction.

Nuclear Magnetic Resonance Spectra. The ^{19}F and ^1H NMR spectra of $NH_2F_2^+AsF_6^-$ were recorded for HF solutions acidified by AsF_5 to suppress exchange between the cation and the HF solvent. The results are summarized in Table I and compared to the data previously reported for the related species NH_4^+,[1,26] NH_3F^+,[19] NF_4^+,[10,12] and NHF_2.[27] As can be seen, the observed chemical shifts and the hydrogen–fluorine spin–spin coupling constant of $NH_2F_2^+$ are in excellent agreement with those known for the closely related species. Furthermore, the observed multiplicities (1:2:1 triplets) in both the ^1H and the ^{19}F spectra confirm that the species contains two hydrogen and two fluorine atoms. The components of the triplets were relatively broad and their line widths did not significantly decrease with decreasing temperature in the range −30 to −60°. This indicates that the line broadening is due to ^{14}N quadrupole relaxation and not to an exchange process. In addition to the $NH_2F_2^+$ signal, the proton spectrum showed a singlet at δ −8.6 due to HF and the fluorine spectrum exhibited a singlet at φ 173 for rapidly exchanging HF, AsF_6^-, and AsF_5. For a sample of $NH_2F_2^+SbF_6^-$ in unacidified HF, separate signals were observed for the SbF_6^- anion[1,28] and HF at φ 126 and 194.5, respectively.

Table I. ^1H (δ) and ^{19}F (φ) NMR Shifts[a] (ppm) and HF Spin–Spin Coupling Constant (*J*, Hz) of $NH_2F_2^+$ Compared to Those of Closely Related Species

	$NH_4^{+\,b}$	$NH_3F^{+\,c}$	$NH_2F_2^+$	$NF_4^{+\,d}$	$NHF_2{}^e$
δ	−6.3	−10.3 d[f]	−14.2 t		−7.2 t
φ		110.8 q	−11.6 t	−213.5	6 d
J_{HF}		44	34		24

[a] Measured for $NH_2F_2^+AsF_6^-$ in HF solution at −40° relative to external TMS and $CFCl_3$, respectively. [b] References 1 and 26. [c] Reference 19. [d] References 10 and 12. [e] Reference 27. [f] Key: d, doublet; t, triplet; q, quartet.

Vibrational Spectra. The low-temperature infrared and Raman spectra of the solids and the Raman spectra of HF solutions have been recorded for both $NH_2F_2^+AsF_6^-$ and $NH_2F_2^+SbF_6^-$. The observed spectra are shown in Figures 1 and 2, and the observed frequencies and their assignment are listed in Table II. The assignments were made by comparison with those[29] of isoelectronic CH_2F_2. As can be seen from the Raman spectra of the HF solutions, the $NHF_2 \cdot MF_5$ adducts are ionic and exhibit the bands characteristic for octahedral AsF_6^- [30–32] and SbF_6^-.[31–33] In the solid state, site symmetry and crystal field effects, in addition to distortion due to anion–cation interactions,[1] cause a splitting of many bands.[1,31,33–35] In the absence of crystal structural data, no attempt will be made in the following discussion to analyze thoroughly these solid-state effects. An $NH_2F_2^+$ cation of symmetry C_{2v} (see below) already possesses nine fundamentals, the maximum number expected for a five atomic species. Consequently, the cation bands should be affected only by crystal field effects but not by symmetry lowering. Since the assignment of the anion bands (see Table II) is straightforward, we will discuss only that of the cation bands.

An XH_2F_2 species of symmetry C_{2v} possesses nine fundamentals classified as $4\,A_1 + A_2 + 2\,B_1 + 2\,B_2$. All of these should be active in both the infrared and Raman spectra, except for the A_2 mode which should only be Raman active. The Raman spectrum of $NH_2F_2^+AsF_6^-$ in HF solution (Figure 1, traces C, D, E) readily permits the assignment of the three fundamentals involving mainly motions of the NF_2 group, since the relative Raman intensities of the NH_2 modes are very low. After subtraction of the three anion bands, we are left with three reasonably intense bands at 1064, 1039, and 534 cm^{-1}. Of these, the ones at 1064 and 534 cm^{-1} are polarized and, therefore, represent the symmetric NF_2 stretch and the NF_2 scissoring mode of species A_1, respectively. The remaining depolarized Raman band at 1039 cm^{-1} must then be due to

Table II. Vibrational Spectra of $NH_2F_2^+AsF_6^-$ and $NH_2F_2^+SbF_6^-$ Compared to That of CH_2F_2

	Obsd freq (cm^{-1}) and rel intens[b]						Assignment (point group)[c]		
	$NH_2F_2^+AsF_6^-$			$NH_2F_2^+SbF_6^-$					
	Solid		HF soln	Solid		HF soln			
CH_2F_2[a]	Ir	Ra	Ra	Ir	Ra	Ra	XH_2F_2 (C_{2v})	MF_6^- (O_h)	Approx description of mode
3016	2963 mw 2941 mw 2913 m 2885 m 2836 m 2784 m			2980 vw 2935 w 2890 mw 2790 vs 2696 w			$2\nu_7$ and ν_1 or ν_6 + lattice modes ν_6 (B_1)		$\nu_{as}(XH_2)$
2948	2657 s			2637 ms			ν_1 (A_1)		$\nu_{sym}(XH_2)$
1508	1557 s			1543 ms			ν_2 (A_1)		$\delta_{sciss}(XH_2)$
1435	1474 s			1487 ms			ν_8 (B_2)		$\delta_{wag}(XH_2)$
1178	1185 vw			1176 vw			ν_7 (B_1)		$\delta_{rock}(XH_2)$
1113	1073 m 1065 m	1073 sh 1062 (4.5)	1064 (2.7) p	1066 m 1055 sh	1062 (2.3) 1052 (1)	1062 m	ν_3 (A_1)		$\nu_{sym}(XF_2)$
1090	1038 s 1020 w	1041 (3.2)	1039 (0.6) dp	1036 s	1037 (1.9)	1039 w	ν_9 (B_2)		$\nu_{as}(XF_2)$
	720 vw 682 ms			705 vw 680 s				ν_3 (F_{1u})	$\nu_{as}(MF_6)$
		714 (9.6) 674 (10)	683 (10) p	652 m 626 ms 610 mw	671 (10) 639 (8.4)	650 vs		ν_1 (A_{1g})	ν_{sym} in phase (MF_6)
	597 m 547 s	569 (4.9)	570 (0.5) dp	602 mw 550 m	566 (1.9) 539 (0.9)			ν_2 (E_g)	ν_{sym} out of phase (MF_6)
528	532 m	533 (3.1)	534 (0.8) p	528 s	524 (1.3)		ν_4 (A_1)		$\delta_{sciss}(XF_2)$
	414 m 391 vs			360 m 280 vs				ν_4 (F_{1u})	$\delta_{as}(MF_6)$
	376 w 369 w	369 (7.0)	366 (1.4) dp		276 (4.9)			ν_5 (F_{2g})	$\delta_{sym}(MF_6)$
	300 s	290 (1.1) br 216 (0+)			238 (0.4) 103 (2.3)				Lattice vibrations or XH···FM str

[a] Reference 29. [b] Uncorrected Raman intensities. [c] Assignments for the anions bands are made for octahedral symmetry, although in the solid state the actual symmetry is obviously lower.

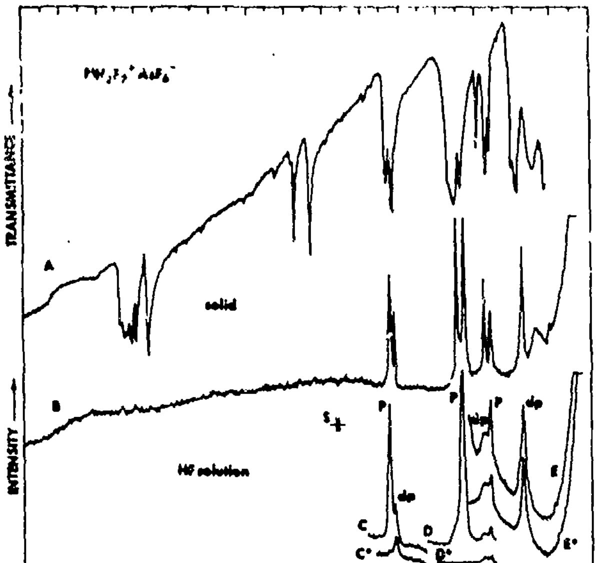

Figure 1. Vibrational spectra of $NH_2F_2^+AsF_6^-$. Trace A: infrared spectrum of the solid as a dry powder between CsI disks, recorded at −196°. Trace B: Raman spectrum of the solid suspended in HF at −70°. Traces C, D, and E: Raman spectrum of an HF solution, recorded at 25° at three different recorder voltages. Traces marked by an asterisk were recorded with the incident polarization perpendicular. P, dp, and S indicate polarized and depolarized bands and spectral slit width, respectively. For the Raman spectra, the 4880-Å exciting line of an Ar ion laser was used, the sample containers being Teflon-FEP or Kel-F tubes.

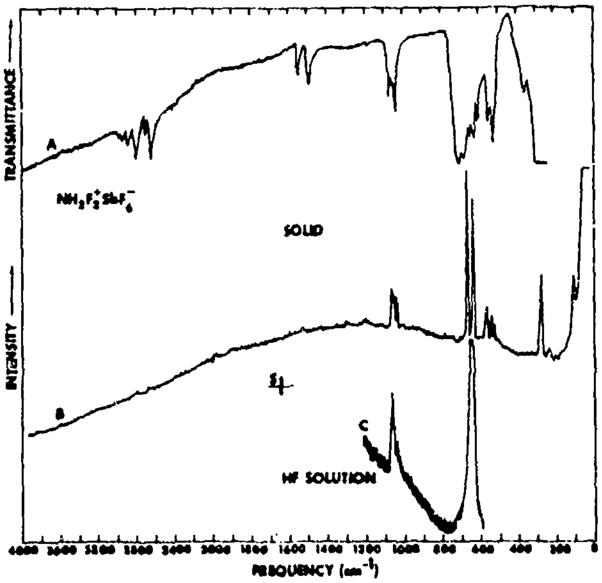

Figure 2. Vibrational spectra of $NH_2F_2^+SbF_6^-$. Trace A: infrared spectrum; bands due to impurities or decomposition products were deleted. Traces B and C: Raman spectra. Recording conditions were identical with those of Figure 1. Trace C is incomplete owing to sudden self-destruction of the sample during the recording of the spectrum.

the antisymmetric NF_2 stretch, ν_9 (B_2).

Identification of the NH_2 modes is possible from the infrared spectra where these modes are expected to be appreciably intense. In the frequency region of the NH_2 stretching modes (2500–3500 cm^{-1}), $NH_2F_2^+SbF_6^-$ exhibits two medium strong bands at 2790 and 2637 cm^{-1} which are assigned, by analogy with CH_2F_2,[29] to the antisymmetric and the symmetric NH_2 stretch, respectively. In addition to these bands, several weaker bands were observed, some of which can be attributed to combination bands (see Table II), probably in Fermi resonance with ν_1 and ν_5. In the infrared spectrum of $NH_2F_2^+AsF_6^-$, the splitting of these bands is even more pronounced. Similar splittings have previously been observed[29] for the CH_2 stretching modes of isoelectronic CH_2F_2. The assignment of these infrared bands to the NH_2 stretching modes is confirmed by the observation of a broad Raman band of very low intensity at about 2800 cm^{-1} for the HF solution of $NH_2F_2^+$-AsF_6^-.

In the region of the NH_2 deformation modes (1700–1100 cm^{-1}) two intense sharp infrared bands were observed at about 1550 and 1480 cm^{-1}, respectively. Based on a comparison of their absolute and relative frequencies with those of CH_2F_2,[29] SiH_2Hal_2,[36] and GeH_2Hal_2,[37] they should represent the scissoring and the wagging deformations, respectively, of the NH_2 group. Comparison of their relative intensities with those of the above dihalohydrides is ambiguous. Whereas in the infrared spectrum of CH_2F_2 the CH_2 scissoring mode is of very low intensity, in the remaining molecules its intensity is similar to that of the wagging mode and very high. Assignment of the 1550- and 1480-cm^{-1} bands of $NH_2F_2^+$ to the NH_2 wagging and the rocking modes, respectively, and of a weak infrared feature at 1655 cm^{-1} to the NH_2 scissoring mode would result in an unreasonably high frequency for the rocking mode and in a too small frequency difference between the wagging and the rocking mode, provided that the NH_2 modes in $NH_2F_2^+$ are not strongly affected by NH···FM bridging between the cations and the anions. Adopting the above assignment of 1550 and 1480 cm^{-1} to the scissoring and wagging mode, respectively, we still have to locate the NH_2 rocking mode. By comparison with the other XH_2F_2 molecules,[29,36,37] we would expect this mode to have a frequency of about 1200 cm^{-1}. The infrared spectra of the $NH_2F_2^+$ salts show indeed a weak band at about 1180 cm^{-1} which is tentatively assigned to the NH_2 rocking mode. However, its relative infrared intensity is unexpectedly low. An alternate assignment for this mode exists by attributing one of the more intense components of the 1050-cm^{-1} band system to it. However, this alternative seems to us less satisfactory for the following reasons. The Raman spectra of the solids show the same splittings. Since the NH_2 modes are of very low intensity in the Raman spectrum (see above), these bands should belong to an NF_2 mode. Furthermore, by comparison with the frequencies of the scissoring and the wagging mode, a frequency of 1070–1020 cm^{-1} for the NH_2 rocking mode appears unreasonably low.

The torsion mode, ν_5 (A_2), should only be Raman active and be of low intensity. This explains our failure to detect this mode for $NH_2F_2^+$.

The spectra of the solid salts show, in addition to the splittings frequently observed[1,31,33-35] for MF_6^- salts, bands in the region 100–300 cm^{-1}. These bands were not observed for the Raman spectrum of $NH_2F_2^+AsF_6^-$ in HF solution and are rather broad. Therefore, they are attributed to lattice modes or cation–anion interaction through XH···FM bridges. Since the spectra of these solids were recorded at temperatures where the lattice is likely to become rigid, the observed phenomena are not surprising. A more detailed discussion of these effects has previously been given for OH_3^+ salts.[1]

The unknown frequency of ν_5 (A_2), the tentative assignment for the NH_2 deformation modes, the uncertainty in the frequencies of ν_6 (B_1) and ν_1 (A_1), and the importance of the off-diagonal terms in the F matrix of the CH_2F_2 general valence force field[29] do not justify a normal-coordinate analysis for $NH_2F_2^+$ at the present time.

Summary

The existence of 1:1:1 adducts between NHF_2, HF, and SbF_5 or AsF_5 was established by the observed material balances. The ionic structures, $NH_2F_2^+MF_6^-$, were established for these adducts by ^1H and ^{19}F NMR and vibrational spectroscopy. Seven or eight of the nine fundamentals, expected for a $NH_2F_2^+$ cation of symmetry C_{2v}, were observed. The nature of the products, resulting from the decomposition of these adducts, was briefly studied. With the exception of NHF_3^+, all of the fluoroammonium ions are now known.

Acknowledgment. The help of Drs. L. Grant, C. Schack, and R. Wilson and the financial support of the Office of Naval Research, Power Branch, is gratefully acknowledged.

Registry No. HF, 7664-39-3; AsF_5, 7784-36-3; NHF_2, 10405-27-3; SbF_5, 7783-70-2; $NH_2F_2^+AsF_6^-$, 56533-30-3; $NH_2F_2^+SbF_6^-$, 56533-31-4.

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SHORT COMMUNICATION

On the PtF_6 - $XeOF_4$ Reaction System

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To Professor George H. Cady on his 70th birthday

Recently, Holloway and Schrobilgen reported [1] that the reaction between KrF^+ salts and $XeOF_4$ does not produce the $XeOF_5^+$ cation, as originally claimed by Bartlett and coworkers [2], but results in the formation of XeF_5^+ and O_2^+ salts. In view of this report and the importance of PtF_6 for the production of high oxidation state compounds [3-8], we wish to communicate results on the PtF_6 - $XeOF_4$ system which show a close relationship between the KrF^+ - $XeOF_4$ [1] and the PtF_6 - $XeOF_4$ reaction system.

The interaction between PtF_6 and $XeOF_4$ was studied in sapphire reactors. When PtF_6 was combined with $XeOF_4$ at -196° and the mixture was allowed to warm to 25°, reaction occurred on melting of the $XeOF_4$. A dark brown solid was formed and its color did not disappear even after keeping the mixture at 25° for 30 hours. Cooling of the mixture to -196° showed the presence of a noncondensible gas which was identified by mass spectroscopy as O_2. Pumping on the mixture at 25° for 24 hours resulted in a mixed, canary yellow-brown solid. The ^{19}F nmr spectrum of the solid dissolved in anhydrous HF consisted at ambient temperature of an AB_4 pattern at $\phi = -227$ and -107 ppm with $J_{FF} = 174$ Hz, characteristic of XeF_5^+ [9,10]. However, the ^{129}Xe satellites, characteristic for xenon compounds, were not observable. This may be due to the presence of paramagnetic species, such as O_2^+ or PtF_5. No signals due to other xenon fluorides were observed. The possibility that the AB_4 pattern might be due to $XeOF_5^+$ was further examined by recording the ^{19}F nmr spectrum in HF of a mixture of the solid reaction product with $XeF_5^+AsF_6^-$. Only one AB_4 set of narrow line width signals was observed. The infrared spectrum of the solid as an AgCl disk showed, in addition to the bands characteristic for PtF_6^- [6,8] and XeF_5^+ [10], a band of medium weak intensity at 939 cm^{-1} indicating the presence of some $XeOF_3^+$ salts [11,12].

The presence of XeF_5^+ and O_2^+ salts in the solid product was confirmed by carrying out a displacement reaction with excess FNO_2 at -80 and 25°. The volatile displacement products consisted of O_2 (identified by mass spectroscopy) and XeF_6 (identified by infrared spectroscopy). The canary yellow solid residue was shown by infrared spectroscopy to be $NO_2^+PtF_6^-$.

When an about tenfold excess of $XeOF_4$ was used for the PtF_6-$XeOF_4$ reaction and the mixture was kept at -30° for several hours before being stored at 25° for four weeks, the percentage of free oxygen evolved had significantly increased in comparison to the above experiment. Furthermore, if the volatile products were removed in vacuo at 0°, the weight gain of the solid product roughly corresponded to that expected for a composition, such as $XeOF_4 \cdot XeF_5^+PtF_6^- + XeOF_3^+PtF_6^-$. Most of the $XeOF_4$ could be removed from the solid by prolonged pumping at 25° and was identified by infrared spectroscopy.

The above results are similar to those found for the KrF^+ - $XeOF_4$ system, i.e. the oxygen in $XeOF_4$ is substituted by fluorine accompanied by the formation of some O_2^+ salts. Furthermore, the solid products seem to form molecular adducts with $XeOF_4$ [1,11,13] which in the case of $XeF_5^+PtF_6^-$ are of only marginal stability at room temperature. The material balances, including the extent of oxygen evolution, are rather complex and depend on the exact reaction conditions. The possibility cannot be ruled out that $XeOF_5^+$ is formed as an unstable intermediate, which readily loses its oxygen. However, the stable reaction product is a XeF_5^+ and not a $XeOF_5^+$ salt.

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CHLORINE OXYFLUORIDES

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I. Introduction

This review is limited to compounds containing both oxygen and fluorine atoms bonded directly to a common chlorine central atom. Therefore, compounds, such as fluorine perchlorate (O_3ClOF), have not been included. Data on O_3ClOF were summarized in a recent review on inorganic hypofluorites (*180*).

The subject of chlorine oxyfluorides* has been reviewed in 1963 by Schmeisser and Brändle (*253*) and in 1969 in "Gmelin's Handbuch der

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* For the sake of clarity, we have not followed a rigid system of nomenclature, such as starting formulas with the central atom followed by the ligands. If, for example, FClO is written as ClOF, an uninformed reader might be induced to think of the compound as a hypofluorite.

Anorganischen Chemie" (*122*). However, both reviews deal only with chloryl fluoride ($FClO_2$) and perchloryl fluoride ($FClO_3$). Since the writing of these reviews, three of the four possible remaining chlorine oxyfluorides i.e., FClO, F_3ClO, and F_3ClO_2, have been characterized, and claims have been made for the synthesis of the fourth one, ClF_5O. Additional information on chlorine oxyfluorides can be found in various monographs and textbooks (*32*, *75*, *77*, *95*, *156*, *169*, *244*) and in particular in "Comprehensive Inorganic Chemistry" in the chapter on the halogens written by Downs and Adams (*84*). A second area of significant recent progress comprises ions derived from chlorine oxyfluorides. Therefore, these are also discussed in detail.

For the present review, the literature cited in *Chemical Abstracts* (Jan. 1965–Dec. 1973) was used in addition to more recent work pub-

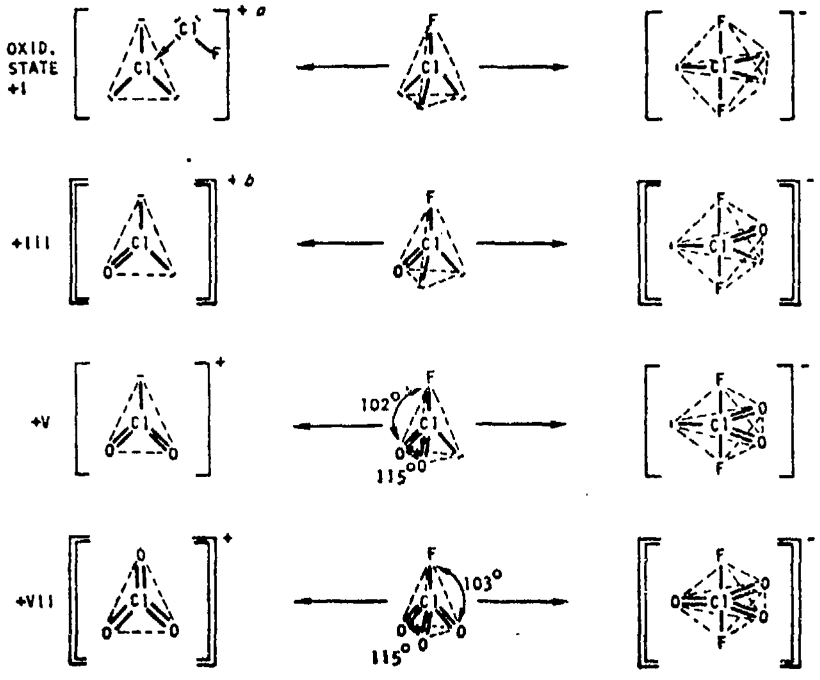


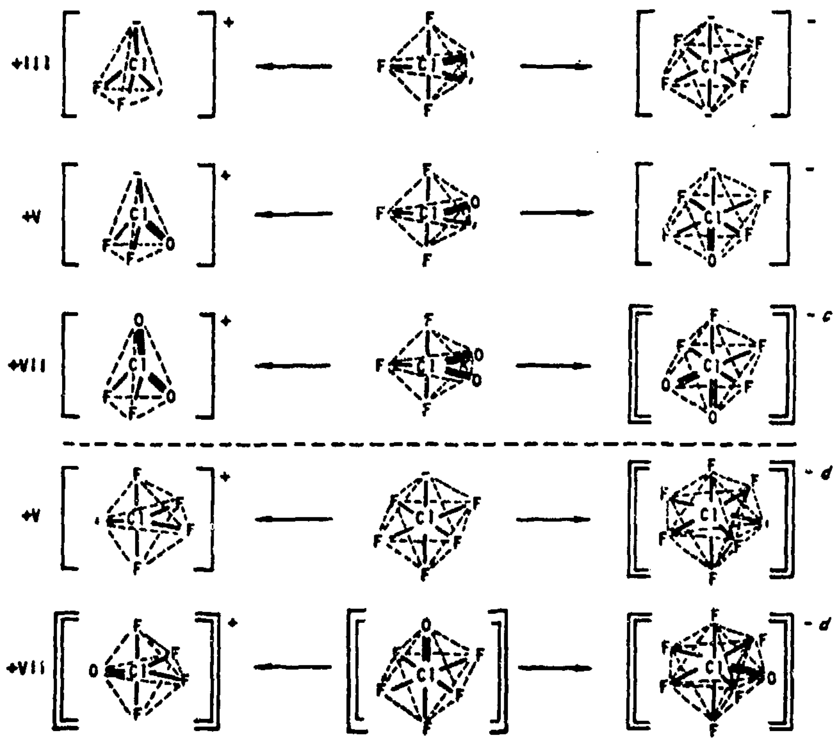
FIG. 1. Geometries of the chlorine oxyfluoride molecules and their ions compared to those of the corresponding chlorine fluorides. [a] Since the Cl^+ cation would possess only an electron sextet, it is stabilized by a ClF molecule to form the Cl_2F^+

lished during 1973 and 1974. For literature before 1965, we have relied mainly on Schmeisser's review (*253*) and Gmelin's handbook (*122*).

In addition to a discussion of the individual compounds, a section was added correlating the physical and chemical properties of the chlorine oxyfluorides with their structure. In the Appendix, full tables of thermodynamic properties are given for each compound, where known.

II. General Aspects

Since most of the physical and chemical properties of the chlorine oxyfluorides can be readily correlated with their molecular structure, we shall discuss briefly some of the more general aspects.



cation. [b] Double brackets indicate yet unknown ions. [c] See text for preference of cis model. [d] These compounds with a coordination number of 7 are unlikely to exist.

A. GEOMETRY

As can be seen from Fig. 1, the structures of all the chlorine oxyfluoride molecules and ions can be derived from those of the corresponding binary chlorine fluorides (*53*) by replacing a free chlorine valence electron pair by a doubly bonded oxygen atom without significant rearrangement of the rest of the molecule.

The only possible exception to this rule could be the yet unknown (*68*) $ClF_4O_2^-$ anion. By comparison with the known structures of the pseudoisoelectronic $IF_4O_2^-$ (*45*, *93*) and $TeF_4O_2^{2-}$ (*260*) anions, the 2 oxygens in $ClF_4O_2^-$ should also be in cis and not in trans position. In these and similar oxyfluoride anions, such as SF_5O^- (*65*) or CF_3O^- (*59*), the negative charge is located mainly on the most electronegative ligands, i.e., fluorine. Furthermore, in pseudo-octahedral species not containing a free valence electron pair on the central atom, such as XF_5O^-, the fluorine trans to the less electronegative ligand appears to be more weakly bonded than the remaining fluorines. This is plausible from molecular orbital arguments. Therefore, for $XF_4O_2^-$ the structure with 2 oxygen atoms trans to 2 fluorines and cis with respect to each other, should favor the resonance structures having the negative charge located on the fluorine ligands.

Since the degree of mutual repulsion decreases in the order, free valence electron pair > double-bonded oxygen > fluorine, the observed bond angles deviate somewhat from those expected for the ideal geometries. Typical examples are $FClO_2$ and $FClO_3$ (Fig. 1).

The structure of radicals and radical ions can also readily be predicted by treating an unpaired electron in the same manner as a free valence

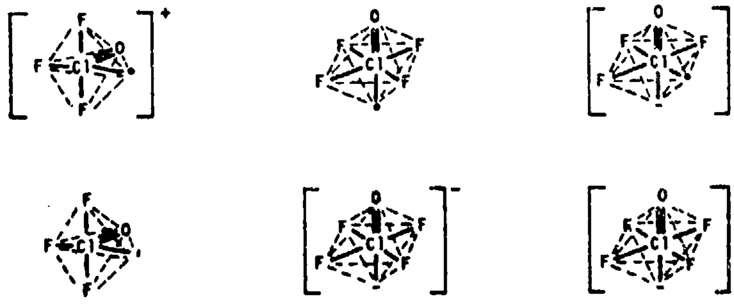


FIG. 2. Structures of the yet unknown ClF_3O^+, ClF_4O, and ClF_3O^- radicals (upper row) predicted by comparison with the known structures (bottom row) of ClF_3O and ClF_4O^-.

electron pair. Therefore, a chlorine oxyfluoride free radical should have the same geometry as the corresponding anion with identical fluorine and oxygen ligands (Fig. 2). Similarly, the structure of a radical cation should be analogous to that of the corresponding molecule having the same ligands. For a radical anion, however, the additional sterically active valence electron will increase the coordination number around the central atom by 1. This should result in a geometry resembling that of the anion containing one F ligand more, but in which one F ligand is replaced by the sterically active free electron. The exact spin distribution would have to be determined experimentally and is not necessarily the same as shown in Fig. 2.

B. LIGAND DISTRIBUTION

As can be seen from Fig. 1, the structures are simple and can be logically predicted if one keeps in mind that free valence electron pairs on the central atom are sterically active and behave as a ligand. For 3, 4, 5, and 6 ligands, always the sterically most favorable arrangements are observed, namely, the triangular plane, tetrahedron, trigonal bipyramid, and the octahedron, respectively (*119*). Based on the information available for halogen oxyfluorides and related compounds such as xenon or chalcogen oxyfluorides the following conclusions concerning the ligand distribution can be reached. In a triangular plane and a tetrahedron all positions are equivalent. In a trigonal bipyramid the two axial positions are occupied by the most electronegative ligands, i.e., F atoms. In octahedrons of the type XF_5A only one arrangement is possible. For XF_4AB, however, the A or B ligands are trans if A and B are either two free electron pairs or one free electron pair and one oxygen ligand. When A and B are 2 O atoms, the cis arrangement appears more favorable (see above). The case of the pentagonal bipyramid is not of practical interest since it appears that the coordination number around a high oxidation state, chlorine central atom is limited to a maximum of 6.

C. RELATIVE BOND STRENGTHS

Unfortunately, exact bond lengths are known only for $FClO_2$ (*220*) and $FClO_3$ (*72*). However, complete vibrational spectra have been published for essentially all of the chlorine oxyfluorides. These can be used for the evaluation of the corresponding force constants. Since the latter are a good measure for the relative strengths of these bonds, their comparison is interesting. As can be seen from Table I, the ClO bonds all

TABLE I

STRETCHING FORCE CONSTANTS OF SOME CHLORINE OXYFLUORIDES

Oxidation state	Compound	f_{ClO} (mdyn/Å)	f_{ClF} (mdyn/Å)			Ref.
			I[a]	II[b]	III[c]	
+VII	$ClF_2O_2^+$	12.1	4.46	—	—	(*69*)
+V	ClF_2O^+	11.20	3.44	—	—	(*58*)
+VII	$FClO_3$	9.4	3.9	—	—	(*174*)
+V	ClF_3O	9.37	3.16	2.34	—	(*55*)
+VII	ClF_3O_2	9.23	3.35	2.70	—	(*57*)
+V	ClF_4O^-	9.13	—	1.79	—	(*56*)
+V	$FClO_2$	9.07	—	—	2.5	(*270*)
+V	ClO_2^+	8.96	—	—	—	(*66*)
+V	$ClF_2O_2^-$	8.3	—	1.6	—	(*54*)
+III	FClO	6.85	—	—	2.59	(*5*)

[a] Mainly covalent bonds.
[b] Mainly semi-ionic 3c–4e bonds
[c] Special case of highly polar $(p—\pi^*)\sigma$ bonds.

possess more or less double-bond character. The variation in the values of the ClO-stretching force constants is mainly due to the combination of several effects. For example, a formal positive charge (i.e., in cations), a high oxidation state of the central atom, and a high number of fluorine ligands tend to increase the ClO-stretching force constant (*57*). In contrast to the ClO bonds, the ClF bond strengths are subject to much

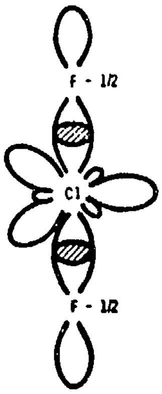


FIG. 3. Schematic bonding in ClF_2^- as explained by a semi-ionic 3c–4e bond model.

larger changes. These strong variations cannot be explained by effects such as listed above for the ClO bonds or by the Gillespie–Nyholm valence shell, electron pair repulsion (VSEPR) theory (*119*) alone. By analogy with the halogen fluorides (*53*), it is necessary to assume contributions from two different kinds of bonding. In addition to the normal covalent bonds possessing a bond order of about 1, the occurrence of semi-ionic 3 center–4 electron bonds (*130*, *232*, *243*) must be invoked. The principle of a semi-ionic 3c–4e bond is demonstrated in Fig. 3. For simplicity, ClF_2^- (*63*) was chosen as an example. Ideally, the two F ligands form two semi-ionic 3c–4e [p—p] σ-bonds with one p electron pair of the chlorine central atom, whereas the free Cl valence electron pairs form an sp^2 hybrid.

Instead of using this semiempirical molecular orbital model, the bonding in ClF_2^- can also adequately be described in the valence-bond representation (*76*) as a resonance hybrid of the following canonical forms: (F—Cl) F^- and F^-(Cl—F). This results in the same average charge distribution as in the molecular orbital model, i.e., $^{-1/2}\text{F-Cl-F}^{-1/2}$. Another and the simplest bond model, proposed by Bilham and Linnett (*29*) for XeF_2 which is pseudoisoelectronic with ClF_2^-, assumes single electron bonds for each X—F bond. It is relatively immaterial, which of these three descriptions is preferred since all of them result in the same charge distribution and a Cl—F bond order of about 0.5.

As can be seen from Table I, these weak ClF bonds occur only when the central atom has a coordination number in excess of 4 and possesses at least one free Cl valence electron pair. In addition to Gillespie's simple VSEPR theory, the following general rule has been proposed by Christe (*53*), which permits the prediction of whether, and how many, semi-ionic bonds are to be formed:

> The free valence electron pairs on the central atom seek high *s*-character; i.e., sp^n hybridization. If the number of ligands is larger than 4 and one or more of them are free valence electron pairs, then as many F ligands form linear semi-ionic 3 center–4 electron bonds as are required to allow the free electron pairs to form an sp^n hybrid with the remaining F ligands. These semi-ionic 3c–4e bonds are considerably weaker and longer than the mainly "covalent" sp^n hybrid bonds.

This rule also holds for the chlorine oxyfluorides as well as for the chlorine fluorides for which it was originally formulated.

An additional effect, however, must be invoked to be able to rationalize fully the experimental data. Inspection of Table I reveals that the ClF-stretching force constants of $FClO_2$ and FClO are significantly lower than expected from the above discussion. In particular, if the known ClF-stretching force constants and bond distances within the pseudo-

TABLE II

COMPARISON OF ClF-STRETCHING FORCE CONSTANTS AND BOND LENGTHS WITHIN THE PSEUDOTETRAHEDRAL SERIES FCl, FClO, $FClO_2$, $FClO_3$

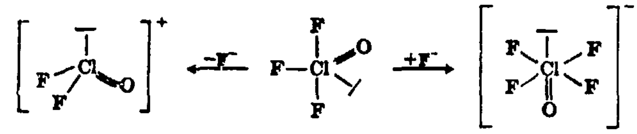
Molecule	f_{ClF} (mdyn/Å)	r_{ClF} (Å)	Ref.
FCl	4.56	1.628	(*122*) (*122*)
FClO	2.59	—	(*5*) —
$FClO_2$	2.5	1.697	(*270*) (*220*)
$FClO_3$	3.9	1.610	(*174*) (*72*)

tetrahedral series FCl, FClO, $FClO_2$, $FClO_3$ are compared (see Fig. 1 and Table II), it becomes obvious that the ClF bonds in FClO and $FClO_2$ are abnormally long and weak. Application of the rules discussed above is of no help in explaining the observed trends. However, if a simple molecular orbital description, similar to that proposed by Spratley and Pimentel (*274*) for FNO and F_2O_2, is used, the data can be rationalized. Molecules FCl, FClO, $FClO_2$, and $FClO_3$ can be thought of as being derived from the combination of an F atom with the Cl, ClO, ClO_2, and ClO_3 radicals, respectively. This hypothetical bond formation involves a 2p electron of the fluorine atom and the unpaired electron of the Cl-containing radical. If according to the example of $(NO)_2$ and $(CN)_2$, given by Spratley and Pimentel (*274*), the unpaired electron occupies an antibonding (π^*) orbital, the resulting bond is very weak. On the other hand, if the unpaired electron occupies a bonding orbital the resulting bond is strong. Since the unpaired electron in Cl and ClO_3 occupies a bonding orbital, the resulting Cl—F bond in FCl and $FClO_3$, respectively, should be strong, whereas those in FClO and $FClO_2$, derived from ClO and ClO_2, respectively, with an antibonding (π^*) electron (*193*), should be weak. These predictions are in excellent agreement with the data of Table II. As a consequence of the high electronegativity of fluorine, most of the electron density in the antibonding (π^*) orbital of ClO or ClO_2 is transferred to the F atom. For FClO and $FClO_2$, this results in a long and highly polar ClF bond with a significant negative charge located on F. Since at the same time electron density is removed from an antibonding orbital of the ClO_x part of the molecule, the bond strength of these ClO bonds is increased. As pointed out by Chi and Andrews (*47*) for ClClO, there is a marked difference in behavior between radicals with a first-row element central atom and those with a second-row element central atom. Owing to their larger size and polarizability, the second-row elements facilitate a charge transfer and the XY_n stretching frequencies usually increase upon combination of XY_n with a halogen radical. For first-row element central atoms, the corresponding frequencies usually show a slight decrease. It should be pointed out, however, that in both cases a highly polar and weak bond of the type $\overset{\delta-}{F}—\overset{\delta+}{X}Y_n$ results, provided the unpaired electron in the XY_n parent radical occupies an antibonding orbital. Supporting evidence for the above postulated charge transfer from XY_n to F was recently given by Parent and Gerry (*220*) for $FClO_2$.

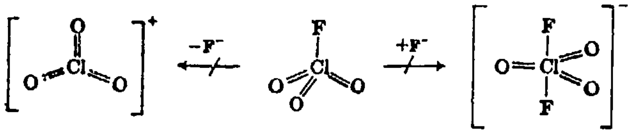
In summary, three types of bonding are invoked to rationalize the remarkable differences in Cl—F bonds encountered for chlorine fluoride oxides. These are (*a*) conventional, mainly covalent bonds, (*b*) weak semi-ionic 3 center–4 electron bonds, and (*c*) weak highly polar ($p—\pi^*$) bonds. It must be kept in mind, however, that all these bond descriptions are idealized extremes, used mainly for didactic reasons. The actual bonds may contain significant contributions from more than one kind of bonding and, as a consequence, there is little black and white, but many shades of gray. Obviously, other bond models can also be used, so long as they adequately account for the experimental data. The steady increase in our knowledge about these compounds is bound to result in significant improvements of these rather empirical and intuitive bond models.

D. Amphoteric Nature, Tendency to Form Adducts, and Reactivity

In many respects the chlorine oxyfluorides resemble the chlorine fluorides. For example, they exhibit little or no self-ionization, but are amphoteric. With strong Lewis acids or bases they can form stable adducts. The tendency to form adducts was found (*64*) not to be so much a function of the relative acidity of the parent chlorine oxyfluoride but rather to depend on the structure of the amphoteric molecule and of that of the anion or the cation formed. The preferred structures are the energetically favored tetrahedron and octahedron. Consequently, a trigonal bipyramidal molecule, such as ClF_3O (*64*), exhibits a pronounced tendency to form either a stable pseudotetrahedral cation or a pseudo-octahedral anion:



On the other hand, tetrahedral $FClO_3$ does not form an adduct with either Lewis acids or bases (*167*, *209*, *224*):



Similarly, the chemical reactivity of these two chlorine oxyfluorides differs vastly: whereas ClF_3O is extremely reactive and cannot be handled even in a well-dried glass vacuum system, $FClO_3$ reacts only slowly with water.

III. Specific Compounds

A. CHLORINE MONOFLUORIDE OXIDE

According to Ruff and Krug (*242*), FClO is formed during hydrolysis of ClF_3 as a solid melting at −70°C to a red liquid which is unstable in the gas phase. However, no conclusive proof for the existence of FClO was given, and it appears that the red color observed may have been due to the presence of chlorine oxides. Heras and co-workers (*137*) have proposed the formation of FClO as an intermediate in the thermal decomposition of $FClO_2$. More recent studies by Bougon and co-workers on the hydrolysis of ClF_3 (*9*, *36*), by Christe on the reaction of ClF_3 with $HONO_3$ (*51*) and on the reaction of ClF_3O with SF_4 (*60*), by Pilipovich *et al.* on the photochemical synthesis of ClF_3O (*228*), and by Schack *et al.* on the reaction chemistry of ClF_3O (*246*) all point to the formation of FClO as an intermediate that is unstable with respect to disproportionation:

$$2FClO \longrightarrow FClO_2 + ClF$$

Attempts to stabilize the FClO formed as an intermediate by complexing with a strong Lewis acid, such as AsF_5 to give $ClO^+AsF_6^-$, were also unsuccessful. Thus the controlled hydrolysis of $ClF_2^+AsF_6^-$ with stoichiometric amounts of H_2O in HF solution resulted only in the formation of $ClO_2^+AsF_6^-$ (*51*). This is not surprising since Lewis acids are known to catalyze such disproportionation reactions.

Recently, Cooper and co-workers (*74*) succeeded in obtaining direct evidence for the existence of free FClO in the gas phase. During a study of the hydrolysis of excess ClF_3 in a flow reactor, a novel species was observed in the infrared spectrum showing a PQR band centered at 1032 cm^{-1}. The species causing this band was found to decompose at ambient

TABLE III

OBSERVED AND CALCULATED FREQUENCIES FOR THE FClO SPECIES[a]

Isotope	Assignment	Obsd. (cm^{-1})	Calcd. (cm^{-1})
$F^{35}Cl^{16}O$	ν_1	1038.0	1038.3
	ν_2	593.5	593.9
	ν_3	315.2	316.0
$F^{37}Cl^{16}O$	ν_1	1029.0	1028.9
	ν_2	587.5	588.4
	ν_3	315.2	313.8
$F^{35}Cl^{18}O$	ν_1	999.2	999.5
	ν_2	593.5	592.6
	ν_3	307.0	308.3
$F^{37}Cl^{18}O$	ν_1	990.1	989.6
	ν_2	587.5	587.1
	ν_3	307.0	306.2

[a] Data from Andrews *et al.* (*5*).

temperature with a half-life of about 25 sec into $FClO_2$ and ClF. If an excess of H_2O was used in the hydrolysis, no FClO but the expected (*9, 36*) ClO_2 was observed as the main product.

The results of Cooper *et al.* were confirmed by a matrix isolation study by Andrews and associates (*5*). The latter authors observed the same species during the photolysis (2200–3600 Å) of argon matrix-isolated ClF and O_3 in the temperature range 4°–15°K. All three fundamentals expected for a bent FClO molecule were observed, and their assignment to FClO was confirmed by the measurement of the ^{18}O and ^{37}Cl isotopic

TABLE IV

FORCE FIELD OF FClO ASSUMING A BOND ANGLE OF 120° AND ALL INTERACTION CONSTANTS TO BE ZERO[a]

$f_{ClO} = 6.85$ mdyn/Å
$f_{ClF} = 2.59$ mdyn/Å
$f_{\alpha} = 0.92$ mdyn Å/rad^2

[a] Data from Andrews *et al.* (*5*).

shifts (Table III) and by force field computations (Table IV). For the force field computation, an FClO bond angle of 120° was assumed. However, on the basis of the increased repulsion from the chlorine free valence electron pairs (see Section II, A), we would expect this angle to be less than the tetrahedral angle of 109°, but larger than that found for ClF_2^+ [103.17° in $ClF_2^+AsF_6^-$ (*181*) and 95.9° in ClF_2^+ SbF_6^- (*88*)]. The small size of the molecule, its high dipole moment, the naturally occurring ^{37}Cl isotope, and its half-life at ambient temperature make it ideally suited for a structure determination by microwave spectroscopy in a flow system.

The force field reported (*5*) for FClO allows some conclusions concerning the strength of the bonds in this molecule. Comparison of the ClO-stretching force constant of FClO with those of the higher oxidation state species listed in Table I makes the FClO value appear surprisingly low. However, when compared to species of similar oxidation state and geometry (Table V), FClO exhibits a value very much in line with our expectations for a ClO double bond. The ClF bond is relatively weak,

TABLE V

COMPARISON OF THE ClO-STRETCHING FORCE CONSTANTS AND BOND ORDERS OF FClO WITH THOSE OF RELATED PSEUDOTETRAHEDRAL SPECIES HAVING A COMPARABLE OXIDATION STATE

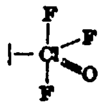
Species	Oxidation state	f_{ClO} (mdyn/Å)	Bond order	Ref.
ClO_2^-	+III	4.26	1.5	(*266*)
FClO	+III	6.85	2	(*5*)
ClO_2	+IV	7.02	2	(*161*)

(I) (II)

indicating that contributions from resonance structures, such as II, are significant as is also the case in the related $FClO_2$ molecule. The high ionicity of the Cl—F bond in these two chlorine fluoride oxides has been discussed above (Section II, C) in terms of a (p—π^*)σ bond.

B. CHLORINE TRIFLUORIDE OXIDE

Chlorine trifluoride oxide,



(III)

was discovered in 1965 at Rocketdyne by Pilipovich *et al.* (*226*, *231*). However, these results were not published until 1972 owing to classification. The same compound was independently discovered in 1970 by Bougon and co-workers (*37*, *39*). A minor modification of Bougon's synthesis by Züchner and Glemser also produced (*300*) ClF_3O. All the data on ClF_3O, except for the short note by Züchner *et al.*, were obtained either at Rocketdyne or at the Centre d'Etudes Nucléaires de Saclay.

Owing to its pseudotrigonal bipyramidal structure with two highly polar Cl—F bonds, ClF_3O possesses only low kinetic stability. This renders it a powerful fluorinating and oxygenating agent requiring the use of metal or Teflon or Kel-F equipment for its handling.

1. *Synthesis*

Several synthetic routes to ClF_3O were developed at Rocketdyne (*226*, *228–231*, *240*). One of these involves the fluorination of Cl_2O at −78°C:

$$2F_2 + Cl_2O \longrightarrow ClF_3O + ClF$$

$$3F_2 + Cl_2O \longrightarrow ClF_3O + ClF_3$$

When no catalyst is used or if KF and NaF are present as catalysts, ClF is the main by-product. When the more basic alkali metal fluorides, RbF and CsF, are used, ClF_3 is the favored coproduct. The formation of ClF_3 rather than ClF is presumably associated with the more ready formation of ClF_2^- intermediates with RbF and CsF. Yields of ClF_3O from Cl_2O are rather variable and may be affected by the particular alkali fluoride present. Yields of over 40% have been consistently obtained and have reached over 80% using either NaF or CsF. Since NaF does not form an adduct with ClF_3O (*64*), stabilization of the product by complex formation does not seem to influence the ClF_3O yields strongly.

Owing to unpredictable explosions experienced with liquid Cl_2O, attempts were made to circumvent the Cl_2O isolation step. For this purpose, the crude Cl_2O, still absorbed on the mercuric salts, was directly fluorinated. Again, ClF_3O was formed, but its yield was too low to make this synthetic route attractive.

The fluorination of solid Cl_2O to ClF_3O proceeded at temperatures as low as −196°C provided the fluorine was suitably activated by methods such as glow discharge. Unactivated fluorine did not interact with Cl_2O at −196°C. The relatively low yield of ClF_3O (1–2%) makes this modification impractical.

The low-temperature fluorination of $NaClO_2$ produced ClF_3O in low yield (*175*, *226*). However, the low yields and poor reproducibility make this route unattractive.

The method (*176*, *226*, *229*) most suitable for the preparation of ClF_3O on a larger scale involves the fluorination of chlorine nitrate at −35°C according to:

$$2F_2 + ClONO_2 \longrightarrow ClF_3O + FNO_2$$

The main advantages of this process are (*a*) less fluorine is required than in the fluorination reactions of Cl_2O yielding ClF_3 as a coproduct, (*b*) the great difference in the volatilities of products FNO_2 and ClF_3O ($\Delta T_{bp} \sim 100°C$) permits an easy separation by fractional condensation, and (*c*) chlorine nitrate can be made more conveniently and, most importantly, does not appear to be hazardous in its handling. Yields of ClF_3O using $ClONO_2$ as a starting material are somewhat higher than those from Cl_2O.

In the fluorination of both Cl_2O and $ClONO_2$, side reactions compete with the actual fluorination step. These are caused by thermal decomposition of the starting materials due to inefficient removal of the heat of reaction. Hence, the rate of the competing reactions is markedly affected by the reaction temperature. At reaction temperatures near or above ambient, the decomposition of the hypochlorite appears to be favored and little or no ClF_3O is formed, resulting in rapid, rather uncontrolled reactions. Apparently, thermal decomposition preceding the fluorination step yields only intermediates incapable of producing ClF_3O. Thus, in order to maximize the desired fluorination reaction, long reaction times at low temperature ($T < 0°C$) are indicated.

A convenient laboratory method for the synthesis of ClF_3O involves UV photolysis of systems containing Cl, F, and oxygen starting materials. At Rocketdyne (*228*, *230*, *240*), ClF_3O was prepared from seven different systems, including a direct synthesis from the elements Cl_2, F_2, and O_2. Bougon *et al.* (*37*, *39*) obtained ClF_3O in high yield from $ClF_3 + OF_2$. The latter synthesis was modified by Züchner *et al.* (*300*) by replacing ClF_3 with ClF_5.

In small-scale operations, ClF_3O can conveniently be purified by complexing it with KF at room temperature. Impurities, such as $FClO_2$, that do not form an adduct under these conditions can be pumped off.

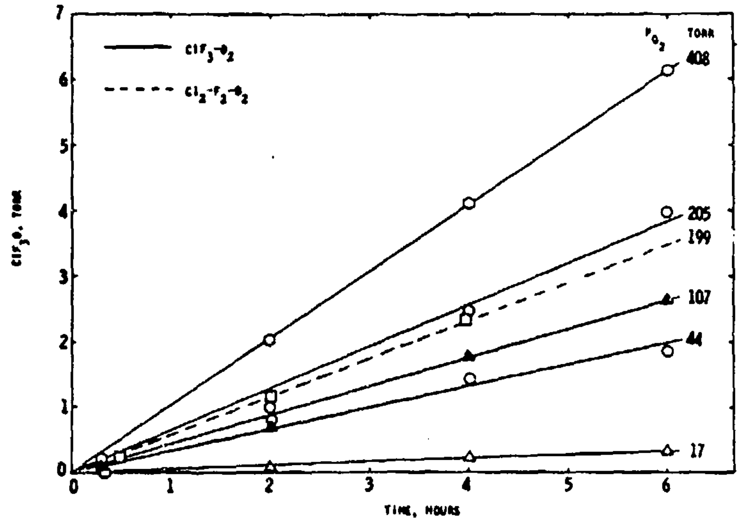


FIG. 4. Chlorine trifluoride oxide formed as a function of time and oxygen partial pressure (P_{ClF_3} = 10 torr).

Pure ClF_3O can be obtained by vacuum pyrolysis at 50° to 70°C, whereas compounds, such as ClF_3, which form a more stable KF adduct remain complexed (*226*).

A detailed kinetic study of the photolyses of the ClF_3—O_2 and of the Cl_2—F_2—O_2 systems was carried out by Axworthy *et al.* (*10*). Contrary to the original report (*228*), the rate of ClF_3O formation was demonstrated to be the same for both systems, to increase with O_2 concentration, and to be independent of irradiation time (Fig. 4). Furthermore, the rate of ClF_3O formation was shown to be proportional to the intensity of the 1847 Å band of the Hg spectrum indicating that the dissociation of O_2 to two ground-state, ^{3}p, oxygen atoms is the primary photochemical process. The following mechanism was proposed which requires the photochemical dissociation of ClF_3 as well:

$$\begin{array}{lcl}
O_2 & \xrightarrow{h\nu\ (1847\ \text{Å})} & O + O \\
ClF_3 & \xrightarrow{h\nu\ (2000\text{–}2500\ \text{Å})} & ClF_2 + F \\
O + ClF_2 & \longrightarrow & ClF_2O \\
ClF_2O + F_2 & \longrightarrow & ClF_3O + F
\end{array}$$

The photolysis of ClF_3 was investigated under similar conditions. A photochemical steady state was quickly achieved, where $[F_2] = [ClF] = \alpha[ClF_3]$, and α has a value of about 1 at low and of about 3 at high pressures. These results together with the known photochemical decomposition of OF_2 (*113*) explain why ClF_3O can be readily generated by the photolysis of so many different starting materials.

2. *Molecular Structure*

Although the exact geometry of ClF_3O has not yet been established, its approximate structure is known from vibrational and ^{19}F NMR spectroscopy. Its UV spectrum has also been reported (*228*).

The ^{19}F NMR spectrum of ClF_3O was studied by several groups. A single signal at $\phi = -262$ (*226*) or -253 (*300*) ppm was reported for liquid ClF_3O. For the gas, a singlet at $\phi = -327$ ppm was observed (*226*).

TABLE VI

VIBRATIONAL SPECTRA OF ClF_3O GAS AND LIQUID AND THEIR ASSIGNMENT IN POINT GROUPS C_s[a]

Observed frequencies (cm^{-1}) and relative intensities					
Gas					
IR	Raman	Solid matrix IR	Liquid Raman	Assignment	Approximate description of mode
1228					
1224 s	1222 (1.5) p	1223 s	1224 (1.0) p	$\nu_1(A')$	$\nu(^{35}Cl{=}O)$
1218					
1213	1211 (0.5) p	1212 m		$\nu_1(A')$	$\nu(^{37}Cl{=}O)$
701	694 (2.6) p	686 s	689 (2.7) p	$\nu_2(A')$	$\nu(^{35}Cl{-}F')$
684	686 sh, p	678 m		$\nu_2(A')$	$\nu(^{37}Cl{-}F')$
676 vs		652 vs		$\nu_7(A'')$	$\nu_{as}(F^{35}ClF)$
666		641 s		$\nu_7(A'')$	$\nu_{as}(F^{37}ClF)$
		499 m		$\nu_8(A'')$	$\delta_{rock}(O^{35}ClF')$
501	500 (1)		497 sh		
		498 sh		$\nu_8(A'')$	$\delta_{rock}(O^{37}ClF')$
491 ms	489 (1)	486 mw		$\nu_3(A')$	$\delta_{sciss}(O^{35}ClF')$
		484 w		$\nu_3(A')$	$\delta_{sciss}(O^{37}ClF')$
481	482 (10) p	478 mw	466 (10)	$\nu_4(A')$	$\nu_s FClF$
412 w	414 (0.2) dp	414 w	405 (0.5) sh	$\nu_9(A'')$	τ
323 313 m	319 (0.1)	323 mw	316 (0.3) p	$\nu_5(A')$	$\delta_s FClF$ out of $F\ddot{Cl}F$ plane $\equiv$ $\delta_{wag} OClF'$
230 mw	224 (0.4) p		227 (1.2) p?	$\nu_6(A')$	$\delta_s FClF$ in $F\ddot{Cl}F$ plane

[a] Data from Christe and Curtis (*55*).

From nuclear relaxation time measurements, Alexandre and Rigny (*3*) were able to determine the chemical shift difference between the equatorial and the 2 axial fluorine atoms as 50 ± 2 ppm. They also obtained a value of 195 Hz for the mean Cl—F coupling constant and values for the exchange time between the fluorine atoms.

Vibrational spectroscopy (*37*, *55*, *300*) provided the best evidence for ClF_3O possessing a pseudotrigonal bipyramidal structure of symmetry C_s, in which 2 fluorines occupy the axial and 1 fluorine, 1 oxygen, and a sterically active free valence electron pair occupy the equatorial positions (see structure III). At Rocketdyne (*55*), a thorough spectroscopic study was carried out including the infrared spectra of gaseous, solid, and matrix-isolated ClF_3O and the Raman spectra of the gas and the liquid.

TABLE VII

INTERNAL FORCE CONSTANTS OF $ClF_3O^{a,b}$

f_D	9.37	f_{rr}	0.26
f_R	3.16	$f_{\beta\beta}$	0.11
f_r	2.34	$f_{\gamma\gamma}$	0.13
f_α	1.84	$f_{r\beta} = -f_{r\beta'}$	0.25
f_β	1.69	$f_{\beta\gamma} = f_{\beta\gamma'}$	0.22
f_γ	1.87		

[a] Data from Christe and Curtis (*55*).

[b] Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch–bend interaction constants in mdyn/radian.

The observed spectra agree well with those reported by the other groups (*37*, *300*), although the latter was incorrectly assigned. The best assignment (*55*) is given in Table VI. A normal coordinate analysis was also carried out for ClF_3O and a modified valence force field was computed (*55*) using the observed ^{35}Cl—^{37}Cl isotopic shifts. Table VII summarizes the internal force constants thus obtained. The geometry of ClF_3O assumed for this computation was $D(ClO) = 1.42$, $R(ClF_{eq}) = 1.62$, and $r(ClF_{ax}) = 1.72$ Å based on the known geometry of ClF_3 and Robinson's correlation between bond length and stretching frequency (*236*, *237*). In the absence of exact structural data, the following ideal bond angle values were assumed: α (OClF′) = 120° and β (OClF) = γ (FClF′) = 90°. However, increased repulsion from the free valence electron pair on chlorine and the double-bonded oxygen should cause some deviations from this ideal structure (see Section II, A).

The force constants of greatest interest are the stretching force constants. The value of 9.37 mdyn/Å obtained for $f_{Cl=O}$ is similar to those computed for $FClO_2$ and ClO_2^+ (see Table I) indicating double-bond character. The value of 2.34 mdyn/Å computed for the axial Cl-F stretching force constant f_r is almost identical with that of 2.34 mdyn/Å, previously calculated (*63*) for ClF_2^-. The corresponding interaction constant, f_{rr}, is also very similar for both species. The relatively low value of f_r in ClF_2^- has previously been interpreted (*63*) in terms of semi-ionic 3 center–4 electron bonds. The same reasoning holds for the axial ClF bonds of ClF_3O. It should be pointed out, however, that in ClF_3O, enhancement of the ionic character of the axial ClF bonds is due to oxygen substitution, whereas in ClF_2^- it is due to the formal negative charge. The value of 3.16 mdyn/Å computed for the equatorial ClF bond of ClF_3O is considerably larger than that of the axial bonds, indicating predominantly covalent bonding. These results are in excellent agreement with a generalized bonding scheme discussed in Section II, C and suggest that the overall bonding in ClF_3O might be described by the following approximation. The bonding of the three equatorial ligands (including the free electron pair on Cl as a ligand and ignoring the second bond of the Cl=O double bond) is mainly due to a sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves mainly one delocalized p-electron pair of the chlorine atom for the formation of a semi-ionic 3 center–4 electron $p\sigma$ bond.

3. *Physical Properties*

Chlorine trifluoride oxide is colorless as a gas or liquid and white in the solid state. Some of its properties are summarized in Table VIII. The vapor pressure of the liquid can be described according to the Rocketdyne study (*226*) by the equation

$$\log P(\mathrm{mm}) = 8.433 - \frac{1680}{T(°\mathrm{K})}$$

or, according to Bougon *et al.* (*31*), by

$$\log P(\mathrm{mm}) = 8.394 - \frac{1655}{T(°\mathrm{K})}$$

Vapor density measurements (*37*, *226*) and mass spectroscopy (*226*, *300*) were used to show that ClF_3O is monomeric in the gas phase. The relatively high boiling point and Trouton constant of ClF_3O imply its association in the liquid phase. More specific evidence about the nature of this association was obtained from the vibrational spectra

TABLE VIII

SOME PROPERTIES OF ClF_3O

Property	Value	Ref.
Melting point	−42° to −44.2°C	(*16*, *37*, *226*)
Boiling point	29° or 27°C	(*37*, *226*)
ΔH_{fusion}	1.975 kcal mole^{-1}	(*16*)
ΔS_{fusion}	8.63 e.u.	(*16*)
ΔH_{vap}	7.7 or 7.57 kcal mole^{-1}	(*37*, *226*)
Trouton constant	25.4 or 25.2 e.u.	(*37*, *226*)
Density(l; 20°C)	1.865 gm ml^{-1}	(*226*)
$\Delta H^0_{f\,298}$(g)	-36.5^a or -35.3^b kcal mole^{-1}	(*15*, *16*, *269*)
$\Delta H^0_{f\,298}$(l)	$-44.1^{a,c}$, $-42.9^{b,c}$, or -38.7^b kcal mole^{-1}	(*16*, *152*, *269*)

[a] Corrected for $\Delta H^0_{f\,HF(g)} = -65.14$ kcal mole^{-1} (*83*).

[b] Corrected for $\Delta H^0_{f\,HF(soln)(75H_2O)} = -77.04$ kcal mole^{-1} (*151*).

[c] Using the $\Delta H^0_{f\,298(g)}$ values of Barberi (*16*) and Sinke (*269*) for the gas and the above listed $\Delta H_{vap} = 7.6$ kcal mole^{-1}.

recorded for the liquid and the solid and from a controlled diffusion experiment carried out for matrix-isolated ClF_3O. It was concluded (*55*) that association appears to involve exclusively the axial fluorine atoms. This finding agrees with the association proposed by Frey *et al.* (*102*) for the structurally related, trigonal bipyramidal molecules SF_4 and ClF_3.

The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation. These properties are given for the range 0–2000°K in the Appendix (Table AI).

4. Chemical Properties

Chlorine trifluoride oxide is stable at ambient temperature and can be stored and handled in well-passivated metal, Teflon, or Kel-F containers without decomposition. Its thermal stability is intermediate between that of ClF_3 and ClF_5. When heated to 280–300°C in a Monel cylinder (*37*, *226*), or to 200°C in a stainless steel cylinder, or to 350°C in a flow system (*226*), ClF_3O decomposes:

$$ClF_3O \longrightarrow ClF_3 + \tfrac{1}{2}O_2$$

It reacts rapidly with glass or quartz and, therefore, cannot be handled in standard glass vacuum systems (*226*). It reacts with numerous materials causing oxidation through both fluorination and oxygenation. With hydrogen-containing species, these reactions may occur at quite low temperature and with hydrocarbon type compounds are generally explosive. However, many chlorine-, fluorine-, or oxygen-substituted compounds, even with lower valent central atoms, react only slowly at ambient temperature, or not at all. Thus, no reaction was observed at room temperature between ClF_3O and chlorine, chlorine fluorides, chlorine oxyfluorides, and the nitrogen fluorides, FNO, FNO_2, NF_3, and N_2F_4 (*246*). However, elevated temperatures or UV photolysis have resulted in appreciable reaction of all compounds examined. With Cl_2 no interaction was detected at 25°C, but at 200°C the following reaction occurred:

$$ClF_3O + Cl_2 \longrightarrow 3ClF + 0.5\,O_2$$

Chlorine monoxide and ClF_3O reacted slowly at room temperature (*246*):

$$ClF_3O + Cl_2O \longrightarrow 2ClF + FClO_2$$

Similarly, $ClOSO_2F$ interacts with ClF_3O (*246*):

$$ClF_3O + 2ClOSO_2F \longrightarrow S_2O_5F_2 + FClO_2 + 2ClF$$

and

$$ClF_3O + ClOSO_2F \longrightarrow SO_2F_2 + FClO_2 + ClF$$

All these reactions can be rationalized in terms of a reduction of ClF_3O to the unstable FClO (see Section III, A) which readily decomposes to $FClO_2$ and ClF. At elevated temperature, $FClO_2$ may decompose further to $ClF + O_2$ (*24*, *137*, *183*).

Several reaction systems were discovered in which, in addition to fluorination, oxygenation also occurred. These include SF_4 (*60*); N_2F_4, HNF_2, and F_2NCFO (*246*, *248*); and MoF_5 (*35*). In the following equations, the end products observed for the SF_4–ClF_3O reaction are underlined:

$$\begin{aligned}
ClF_3O + SF_4 &\xrightarrow[25^\circ]{CsF} \underline{SF_6} + FClO \\
2FClO &\longrightarrow \underline{FClO_2} + ClF \\
SF_4 + ClF &\xrightarrow{CsF} \underline{SF_5Cl} \\
SF_4 + ClF_3O &\longrightarrow \underline{SF_4O} + ClF_3 \\
SF_4 + ClF_3 &\longrightarrow \underline{SF_6} + ClF
\end{aligned}$$

In the MoF_5–ClF_3O system, both MoF_6 and MoF_4O were formed, followed by adduct formation. With N_2F_4, an appreciable reaction rate was observed only above 100°C:

$$ClF_3O + 2N_2F_4 \longrightarrow 3NF_3 + FNO + ClF$$

In addition to these products, small amounts of NF_3O were obtained. The yield of NF_3O from this reaction system could be increased to about 5% when UV irradiation was used. Higher yields of NF_3O (~70%) could be obtained at low temperature from HNF_2 and ClF_3O:

$$ClF_3O + 2HNF_2 \longrightarrow [FClO] + 2HF + 2NF_2^{\cdot}$$

$$2NF_2^{\cdot} + [FClO] \longrightarrow \underline{NF_2Cl} + \underline{NF_3O}$$

with the side reactions,

$$2NF_2^{\cdot} \longrightarrow \underline{N_2F_4}$$

$$2[FClO] \longrightarrow \underline{FClO_2} + ClF$$

$$ClF + HNF_2 \longrightarrow \underline{HF} + \underline{NF_2Cl}$$

The reaction between difluoraminocarbonyl fluoride, F_2NCFO, and ClF_3O yielded again NF_3O and $ClNF_2$ in nearly equimolar amounts. However, the yields were much lower (20% based on ClF_3O consumed) with N_2F_4 being the main N—F containing product.

One reaction was discovered (*246*) in which ClF_3O did not act as an oxidizing but rather as a reducing agent. With the powerful oxidizer PtF_6, it reacted according to

$$ClF_3O + PtF_6 \longrightarrow ClF_2O^+PtF_6^- + 0.5F_2$$

The interaction of ClF_3O with HF, resulting in a fluoride ion abstraction to give the ClF_2O^+ cation (*38*), will be discussed below. With H_2O, an excess of chlorine trifluoride oxide hydrolyzes (*226*) according to

$$ClF_3O + H_2O \longrightarrow FClO_2 + 2HF$$

Mixtures of ClF_3O and ClF_5 (*225*) hold promise as an oxidizer in rocket propulsion.

As discussed in Section II, D, the compound ClF_3O has an energetically unfavorable pseudotrigonal bipyramidal structure. Consequently, it exhibits a pronounced tendency to form adducts with both strong Lewis acids and bases. Adducts containing the ClF_2O^+ cation (see Section III, C) were obtained (*33–35*, *38*, *58*, *64*, *246*, *300*) with the following Lewis acids: BiF_5, SbF_5, AsF_5, PF_5, TaF_5, NbF_5, VF_5, PtF_5, UF_5, MoF_4O, SiF_4, BF_3, and HF. With WF_4O and UF_4O, no stable ionic products were formed (*35*) in spite of the fact that WF_4O is a stronger Lewis acid than MoF_4O. This is caused by the increased tendency of WF_4O to enter the following oxygen–fluorine exchange reaction:

$$ClF_3O + MF_4O \longrightarrow FClO_2 + MF_6 \quad (M = W \text{ or } U)$$

Adducts containing the ClF_4O^- anion (see Section III, D) were prepared (*56, 64, 300*) by reaction of ClF_3O with the Lewis bases CsF, RbF, and KF. With the weaker bases FNO and FNO_2, it does not interact even at −95°C (*64*).

C. DIFLUOROOXYCHLORONIUM(V) CATION

Compounds containing the ClF_2O^+ cation with the following counterions are known: BiF_6^-, SbF_6^-, $Sb_2F_{11}^-$, AsF_6^-, PF_6^-, TaF_6^-, NbF_6^-, VF_6^-, PtF_6^-, UF_6^-, SiF_6^{2-}, BF_4^-, HF_2^-, MoF_5O^-, and $Mo_2F_9O_2^-$ (*33–35, 38, 58, 64, 246, 300*).

1. *Synthesis*

With the exception of the PtF_6^- salt which was prepared from ClF_3O and PtF_6 [(*246*), Section III, B, 4], all the other salts were prepared by direct combination of ClF_3O with the corresponding Lewis acid. When the Lewis acid is a solid at the reaction temperature, or nonvolatile, it is advisable to use either a large excess of ClF_3O or anhydrous HF as a solvent to avoid polyanion formation (*33–35, 64*).

2. *Molecular Structure*

The ionic nature of $ClF_3O\cdot$ Lewis acid adducts was established by vibrational (*33–35, 38, 58, 300*) and ^{19}F NMR (*61*) spectroscopy.

The NMR spectrum of $ClF_2O^+AsF_6^-$ in anhydrous HF showed (*61*) the characteristic quadruplet of AsF_6^- at $\phi = 67.5$ ppm in addition to a single signal due to rapidly exchanging HF and ClF_2O^+. Upon acidification of the HF solvent with AsF_5, a separate signal at $\phi = -272$ ppm was observed for ClF_2O^+ in addition to a single signal due to HF, AsF_6^-, and AsF_5. For $ClF_2O^+PtF_6^-$ in HF the ClF_2O^+ signal was also found at $\phi = -272$ ppm. The observation of a singlet for ClF_2O^+ shows the magnetic equivalence of the 2 fluorine atoms.

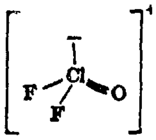
The vibrational spectra were reported (*33–35, 38, 58, 300*) for all of the above-listed ClF_2O^+ salts. In addition to the bands characteristic of the anions, all spectra exhibited bands with frequencies and relative intensities similar to those shown in Table IX. These are characteristic for the ClF_2O^+ cation. The vibrational spectrum of ClF_2O^+ closely resembles that of isoelectronic SF_2O and, therefore, could be readily assigned. The only ambiguity in the assignment existed (*34, 58*) for the two deformation modes occurring in the 380–400 cm^{-1} region. Recent Raman polarization measurements (*34*) have shown that the 400-cm^{-1} band belongs most likely to ν_4 (A′), and the 380-cm^{-1} band to ν_6 (A″).

TABLE IX

Vibrational Spectrum of the ClF_2O^+ Cation

Raman (HF solution) (cm^{-1})	IR (solid) (cm^{-1})	Assignment in point group C_s	Approx. description of mode
1333 (4) 1322 sh } p	1334 s 1323m	ν_1 (A′)	νClO
741 (10) p	734 m	ν_2 (A′)	$\nu_s ClF_2$
715 (1)	694 s	ν_5 (A″)	$\nu_{as} ClF_2$
512 (2) p	512 s	ν_3 (A′)	$\delta_s OClF_2$
404 (2) p	405 m	ν_4 (A′)	$\delta_{sciss} ClF_2$
383 (1)	383 m	ν_6 (A″)	$\delta_{as} OClF_2$

The spectroscopic evidence is consistent with the following structure of symmetry C_s for ClF_2O^+:



(IV)

A normal coordinate analysis was carried out (*58*) for ClF_2O^+ assuming the following geometry: $R_{ClO} = 1.41$ Å; $r_{ClF} = 1.62$ Å, $\beta(OClF) = 108°$; and $\alpha(FClF) = 93°$. A modified valence force field was computed, and the results are given in Table X. As can be seen from Table I, the ClO-

TABLE X

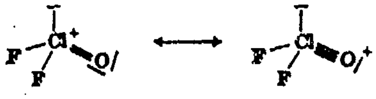
Vibrational Force Constants of ClF_2O^+ [a,b]

f_R	11.20
f_r	3.44
f_β	1.65
f_α	1.78
$f_{\beta\beta}$	0.21
f_{rr}	0'39

[a] Data from Christe *et al.* (*58*).

[b] Stretching constants in mdyn/Å and deformation constants in mdyn Å/radian².

stretching force constant of ClF_2O^+ exhibits a high value, implying that the positive charge in ClF_2O^+ is partially located on the oxygen atom and that contributions from resonance structures, such as VI,



(V) (VI)

are significant. The ClF-stretching force constant of ClF_2O^+ is within the range expected for a predominantly covalent ClF bond (see Table I and discussion in Section II, C).

3. *Properties*

Except for the following salts, the above-listed ClF_2O^+ salts are stable, white, crystalline solids. The UF_6^- salt is blue-green and of marginal stability at ambient temperature. In HF solution or during exposure of the solid to a laser beam, the UF_6^- anion is slowly oxidized by ClF_2O^+ to UF_6 (*33*). For MoF_5 this instability of the pentavalent metal toward oxidation to the hexavalent state is even more pronounced. When ClF_3O and MoF_5 are combined, no stable MoF_6^- salt is formed, but MoF_6 and MoF_4O are the products with the latter being capable of forming stable adducts (*35*). The $ClF_2O^+PtF_6^-$ salt is a canary yellow solid (*246*). The VF_5 and PF_5 adducts exhibit dissociation pressures of 2.5 and 3.5 mm, respectively, at room temperature (*33, 34*). The $(ClF_2O^+)_2\ SiF_6^{2-}$ salt is unstable at room temperature. It reaches a dissociation pressure of 760 mm at 31°C and its dissociation pressure can be represented (*64*) by the equation

$$\log P(\text{mm}) = 11.8018 - \frac{2712.3}{T(^\circ\text{K})}$$

From these data, the heat of dissociation, $\Delta H_d{}^0 = 37.24$ kcal mole^{-1}, and the heat of formation of the solid adduct, $\Delta H^0{}_{f298} = -495.7$ kcal mole^{-1} were obtained. For the latter the literature value was corrected by using the more precise value of -35.9 kcal mole^{-1} for the heat of formation of gaseous ClF_3O (see Table VIII). The adduct melts under its own vapor pressure at 50.5°C (*300*).

The Raman spectrum of a solution of ClF_3O in anhydrous HF shows no bands due to ClF_3O but only those of ClF_2O^+ in agreement with the following ionization scheme (*38*):

$$ClF_3O + HF \longrightarrow ClF_2O^+ + HF_2^-$$

However, no attempts were reported to isolate the neat solid at low temperature and to examine its thermal stability.

The thermal stability of the adducts depends on the strength of the Lewis acids and decreases for the ClF_2O^+ salts in the following order: $SbF_5 > AsF_5 > BF_3 > VF_5 > PF_5 > SiF_4 > HF$ (*33–35*, *38*, *64*). The $ClF_2O^+MoF_5O^-$ salt, when heated in vacuum to 75–80°C or when dissolved in anhydrous HF, is converted to ClF_2O^+, $Mo_2F_9O_2^-$, and ClF_3O. It was shown by Raman spectroscopy that this reaction is reversible. Heating of these compounds to higher temperatures results in decomposition to MoF_4O and ClO_2^+ salts of MoF_4O (*35*).

The X-ray powder patterns were reported for the XF_6^- type (*34*, *64*, *246*) and the BF_4^- (*64*) adduct and were tentatively indexed in the orthorhombic system.

D. TETRAFLUOROOXYCHLORATE(V) ANION

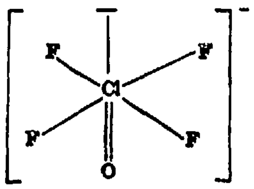
The existence of adducts between ClF_3O and CsF (*56*, *64*, *300*), RbF (*64*), and KF (*64*) has been reported. It was shown (*56*, *300*) by vibrational spectroscopy that these adducts are ionic and contain the ClF_4O^- anion.

1. *Synthesis and Properties*

Chlorine trifluoride oxide was found (*64*) to combine readily with the alkali metal fluorides, CsF, RbF, or KF, at room temperature to form white stable adducts. High conversion to the 1:1 adduct appears to be easiest for CsF. The use of a large excess of ClF_3O, agitation, and extended contact times are conducive to nearly complete conversions. These alkali metal ClF_4O^- salts have found use in the purification of ClF_3O (*226*). The thermal stability of the adducts decreases in the order CsF > RbF > KF. For example, the $KClF_4O$ salt can be decomposed by vacuum pyrolysis at 50–70°C (*226*), whereas a much higher temperature is required for the pyrolysis of $CsClF_4O$.

2. *Molecular Structure*

The ionic nature of these adducts and the structure of the ClF_4O^- anion were established by vibrational spectroscopy (*56*, *300*). It was shown (*56*) that the observed vibrational spectrum (Table XI) is consistent with the following structure of symmetry C_{4v}:



(VII)

TABLE XI

VIBRATIONAL SPECTRA OF $Rb^+ClF_4O^-$ AND $Cs^+ClF_4O^-$ AND THEIR ASSIGNMENT[a]

Observed frequencies (cm^{-1}) and relative intensities				Assignment for XZF_4 in point group C_{4v}	Type of vibration
$Rb^+ClF_4O^-$		$Cs^+ClF_4O^-$			
IR	Raman	IR	Raman		
1216 s	1211 (0.6)	1201 s	1203 (0.6)	A_1 ν_1	ν XZ
462 w	461 (10)	457 w	456 (10)	ν_2	ν_{sym} in-phase XF_4
339 s	[350][b]	339 s	[345][b]	ν_3	δ_{sym} out-of-plane XF_4
	350 (4.3)		345 (4)	B_1 ν_4	ν_{sym} out-of-phase XF_4
				ν_5	δ_{asym} out-of-plane XF_4
283 vw	285 (0.4)	280 vw	283 (0.4)	B_2 ν_6	δ_{sym} in-plane XF_4
600 vs	599 (0.1)	600 vs	594 (0.2)	E ν_7	ν_{asym} XF_4
500	557 (0.4)	560	564 (0.3)		
415 s	416 (1.4)	415 s	416 (1.4)		
394	395 (0.1)	396	397 (0.1)	ν_8	δ ZXF
	213 (0.6)		204 (0.7)	ν_9	δ ym in-plane XF_4

[a] Data from Christe and Curtis (*56*).

[b] Calculated frequency.

A normal coordinate analysis was carried out (*56*) for ClF_4O^- assuming the following geometry: $D(ClO) = 1.42$ Å; $r(ClF) = 1.75$ Å; and all bond angles are 90°. The internal force constants obtained are listed in Table XII. Comparison with the stretching force constants of other chlorine fluorides oxides (see Table I) shows that the ClO bond in ClF_4O^- has full double-bond character, but that the ClF bond is a rather weak semi-ionic 3 center–4 electron bond. This implies that the formal negative charge in ClF_4O^- is distributed almost exclusively over the four fluorine

TABLE XII

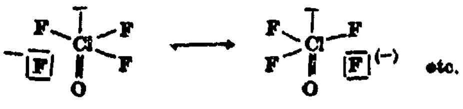
Force Constants of ClF_4O^- [a,b]

f_R	9.13		
f_r	1.79	$f'_{\beta\beta}$	0.29
f_β	1.33	$f'_{\alpha\alpha}$	0.08
f_α	0.61	$f_{r\beta}$	0.15
f_{rr}	0.25	$f''_{r\beta}$	−0.15
f'_{rr}	0.04		

[a] Data from Christe and Curtis (*56*).

[b] Stretching force constants in mdyn/Å and deformation force constants in mdyn Å/radian².

ligands. Resonance structures of the following type can be used to describe this effect:



(VIII) (IX)

E. Chlorine Pentafluoride Oxide

The synthesis of ClF_5O was claimed in 1972 by Züchner and Glemser (*300*) by UV photolysis of a mixture of ClF_5 and OF_2 in a nickel vessel fitted with a sapphire window. Although the authors failed to isolate a pure product, they "identified" ClF_5O in the product mixture by negative-ion mass spectroscopy and ^{19}F NMR spectroscopy. However, the following properties attributed to ClF_5O do not agree with the general trends observed for the remaining chlorine fluorides and oxyfluorides: (*a*) low volatility at −78°C, (*b*) a ^{19}F NMR resonance between −146 and −103 ppm relative to $CFCl_3$, and (*c*) exchange broadening in the NMR spectrum even at −76°C. For ClF_5O, we would expect (*a*) a volatility comparable to that of ClF_5 (*227*) or SF_6 (*279*), (*b*) an averaged ^{19}F NMR chemical shift of about −390 ppm (*61*), and (*c*) the absence of intramolecular exchange owing to chlorine having its maximum coordination number and no free valence electron pair, and owing to the lack of a plausible exchange mechanism.

Attempts to duplicate Züchner and Glemser's experiment (*300*) at Rocketdyne and the Centre d'Etudes Nucleaires de Saclay did not result in any evidence for $\mathrm{ClF_5O}$. In the Rocketdyne study, the progress of the $\mathrm{ClF_5}$–$\mathrm{OF_2}$ photolysis in the temperature range −78° to 30°C, using both unfiltered and Pyrex-filtered UV radiation, was continuously monitored by gas chromatography. At the end of an experiment, the products were also separated by fractional condensation in a Teflon–stainless steel vacuum system and were characterized by vibrational spectroscopy. It was shown that in the $\mathrm{ClF_5}$–$\mathrm{OF_2}$ system, when exposed to unfiltered UV radiation, $\mathrm{ClF_5}$ rapidly decomposes to $\mathrm{ClF_3}$ and $\mathrm{F_2}$ and, therefore, yields only the same products obtainable from the photolysis of $\mathrm{ClF_3}$–$\mathrm{OF_2}$ mixtures, i.e., mainly $\mathrm{ClF_3O}$.

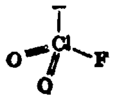
The $^{19}\mathrm{F}$ NMR spectrum observed by Züchner and Glemser (*300*) might be rationalized in terms of a rapidly exchanging mixture of $\mathrm{ClF_3}$ and $\mathrm{ClF_3O}$ as was pointed out to us by Dr. Bougon. To verify this, we have recorded the NMR spectra of $\mathrm{ClF_3}$–$\mathrm{ClF_3O}$ mixtures over the temperature range 40° to −102°C. It was found that mixtures of pure $\mathrm{ClF_3}$ and $\mathrm{ClF_3O}$ yield separate signals for $\mathrm{ClF_3}$ (at about $\phi = -118$ and -10 ppm) and $\mathrm{ClF_3O}$ (at about −269 ppm) over the whole temperature range studied. However, upon addition of about 5 mole% of HF, one single signal is observed for all three species with a chemical shift corresponding to the averaged chemical shifts of the three components. The temperature dependence of these spectra is similar to that reported by Züchner and Glemser (*300*). At 40°C the signal was rather broad, became narrower with decreasing temperature, but broadened below −60°C and shifted to higher field. At −102°C a new and relatively narrow signal appeared significantly shifted upfield. The observed shifts and temperature dependence of these spectra are strongly dependent on the exact composition of the mixture.

The only remaining piece of evidence presented (*300*) for $\mathrm{ClF_5O}$ was the presence of a low-intensity fragment due to $\mathrm{ClF_4O^-}$ in the negative ion mass spectrum of the crude reaction product. However, this fragment might be attributed to a recombination process in the mass spectrometer since a 52% peak was also reported for $\mathrm{F_2^-}$ which can form only by recombination. Furthermore, negative-ion spectra frequently show species of higher mass than that of the parent molecule due to attachment of other atoms or groups (*28*), as was recently also demonstrated for $\mathrm{BrF_5}$, of which the negative-ion spectrum shows a rather intense $\mathrm{BrF_6^-}$ fragment (*194*). In agreement with the preceding NMR interpretation, the observed (*300*) negative-ion mass spectrum is best ascribed to a mixture of $\mathrm{ClF_3O}$, $\mathrm{ClF_3}$, $\mathrm{FClO_2}$, and some $\mathrm{ClF_5}$, with several higher mass peaks and $\mathrm{F_2^-}$ being due to recombination in the spectrometer.

Based on the cited evidence, it appears unlikely that Züchner and Glemser (*300*) had indeed observed $\mathrm{ClF_5O}$.

F. Chloryl Fluoride

Chloryl fluoride,



(X)

was first obtained in 1942 by Schmitz and Schumacher (*256*) by the low-temperature fluorination of ClO_2 with F_2. The compound itself has not been studied very intensively although it is the most frequently encountered reaction product in systems involving reactions of chlorine mono-, tri-, or pentafluorides with oxides or hydroxides. Its structure can be derived from a tetrahedron with a free valence electron pair of chlorine occupying one of the four corners. Compared to $FClO_3$, this structure is less symmetric, kinetically less stable, and contains a highly polar, long $(p-\pi^*)\sigma$ (see Section II, C) bond. Therefore at moderate temperatures, $FClO_2$ is far more reactive than $FClO_3$ in spite of its lower oxidation state.

1. *Synthesis*

In our experience (*70*), $FClO_2$ is most conveniently prepared by combining $NaClO_3$ with an about equimolar amount of ClF_3 at −196°C in a stainless steel cylinder and holding the mixture at room temperature for a day. Chloryl fluoride (bp = −6°C) is thus obtained in high yield and can be separated from the by-products O_2, Cl_2 (bp = −33.8°C), and unreacted ClF_3 (bp = 11.75°C) either by fractional distillation or by repeated fractional condensation through a series of traps maintained at −95°, −112°, and −126°C. This procedure is safe and does not involve the handling of any shock-sensitive materials. It is based on the previous reports by Engelbrecht and Atzwanger (*92*) and Smith and co-workers (*270*) that gaseous ClF_3 reacts with $KClO_3$ to give $FClO_2$ in high yield. The substitution of $KClO_3$ by $NaClO_3$ is significant since the product NaF does not form an adduct with ClF_3, whereas KF does. This decreases by 60% the amount of ClF_3 required for the reaction. By analogy with the known $KClO_3 + BrF_3$ reaction (*296*), the idealized stoichiometry of the above reaction is

$$6\,NaClO_3 + 4ClF_3 \longrightarrow 6NaF + 2Cl_2 + 3O_2 + 6FClO_2$$

The use of larger than stoichiometric amounts of ClF_3 is advisable to avoid the possible formation of shock-sensitive chlorine oxides.

Woolf's original method (*296*) involved the use of $KClO_3$ and BrF_3, according to

$$6KClO_3 + 10BrF_3 \longrightarrow 6KBrF_4 + 2Br_2 + 3O_2 + 6FClO_2$$

Although the yield of $FClO_2$ is high, it is very difficult to obtain pure colorless $FClO_2$ by this method. When $KClO_3$ is replaced by $KClO_4$ (*285*), $FClO_2$ is obtained in 97% yield:

$$3KClO_4 + 5BrF_3 \longrightarrow 3KBrF_4 + Br_2 + 3O_2 + 3FClO_2$$

The product purification problem for this system is analogous to that encountered for the $KClO_3$–BrF_3 system. Direct fluorination of $KClO_3$ with F_2 (*31*, *89*, *92*, *265*) is not synthetically useful for preparing $FClO_2$, since the main product is always $FClO_3$. The interaction of $HOSO_2F$ with $KClO_3$ was reported (*99*) to produce $FClO_2$ in 30% yield. However, a study of this system carried out at Monsanto (*198*) failed to produce $FClO_2$, probably owing to formation of chloryl fluorosulfate.

An alternative route to $FClO_2$ involves the fluorination of chlorine oxides. The resulting $FClO_2$ is usually very pure but the handling of the shock-sensitive chlorine oxides renders these methods unattractive, particularly for the production of larger amounts of material. The original synthesis of $FClO_2$ by Schmitz and Schumacher in 1942 (*256*) involved direct fluorination of ClO_2. When F_2 was added at –80°C to a quartz vessel containing ClO_2, followed by slow warm-up to 20°C, $FClO_2$ was formed in a moderate reaction. The most favorable conditions were a reaction time of 2 min, a reaction temperature of 0°C, and the use of a mixture consisting of 25.6 mm ClO_2, 54.0 mm F_2, and 540.7 mm air. The reaction was found to be homogeneous and bimolecular (*12*). Modifications of this reaction involve passing gaseous F_2 through liquid ClO_2 at –50° to –55°C (*264*) or, preferably, using $CFCl_3$ as a solvent at –78°C (*162*, *254*). Chlorine dioxide can also be fluorinated to $FClO_2$ by passing ClO_2 diluted with N_2 at room temperature over AgF_2 or CoF_3 or by passing ClO_2 through liquid BrF_3 at 30°C (*255*).

The fluorination of chlorine oxides other than ClO_2 also produces $FClO_2$. Thus, $FClO_2$ was obtained in yields of up to 75% by fluorination of Cl_2O_6 with F_2 between 22° and 48°C (*7*, *8*). The high yield of $FClO_2$ coupled with the absence of $FClO_3$ indicates that the primary step is the decomposition of Cl_2O_6 to $2ClO_2 + O_2$ followed by the fluorination of ClO_2 to $FClO_2$. Similarly, the reaction between Cl_2O_6 and FNO_2, when carried out in $CFCl_3$ solution at 0°C, produces $FClO_2$ in addition to $NO_2^+ClO_4^-$ (*255*). Chloryl fluoride is also formed during the fluorination of Cl_2O_6 at –40°C with BrF_3 or BrF_5 (*294*) or with HF (*252*). During thermal decomposition of Cl_2O_7 in the presence of F_2 at 100°–120°C in quartz or Pyrex, $FClO_2$ is formed in addition to $FClO_3$ and ClF (*98*).

The risk of explosions is somewhat reduced in the ClO_2–AgF_2 reaction when the ClO_2 is replaced by the less dangerous Cl_2O. The yield of $FClO_2$ was 35% (*117*, *182*). Similarly, Cl_2O can be fluorinated at −78°C with either ClF (*51*),

$$2Cl_2O + ClF \longrightarrow FClO_2 + 2Cl_2$$

or ClF_3O (*246*),

$$Cl_2O + ClF_3O \longrightarrow FClO_2 + 2ClF$$

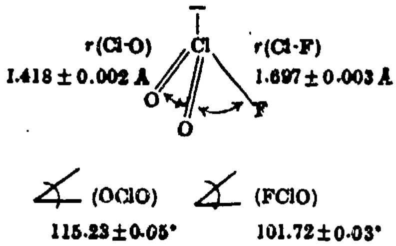
Oxygenation of a chlorine fluoride, if possible, would be more attractive than fluorination of the shock-sensitive chlorine oxides. A process for $FClO_2$ has been claimed by Faust *et al.* (*97*) furnishing $FClO_2$ in about 50% yield by simply heating a mixture of ClF and O_2 to 80°–90°C. However, attempts in our laboratory (*70*) to verify this synthesis failed. It appears, that the $FClO_2$ observed by Faust *et al.* (*97*) in their experiments was due to hydrolysis of ClF (*9*, *36*, *70*).

Numerous reactions have been reported in which $FClO_2$ is formed as a product. Most of these involve the interaction between a chlorine fluoride or oxyfluoride with an oxide or hydroxide. The oxidation state of the chlorine fluoride is not important since +I, +III, and +V compounds all yield $FClO_2$ owing to the tendency of the lower oxyfluorides, such as FClO, to disproportionate. The presence of excess chlorine fluoride is important to avoid formation of chlorine oxides. The following equations are typical examples for these types of reactions:

$$\begin{array}{lll}
5ClF + 2H_2O & \longrightarrow & 4HF + FClO_2 + 2Cl_2 \quad (9, 36) \\
2ClF_3 + 2H_2O & \longrightarrow & 4HF + FClO_2 + ClF \quad (9, 36) \\
ClF_5 + 2H_2O & \longrightarrow & 4HF + FClO_2 \quad (227) \\
ClF_3O + H_2O & \longrightarrow & 2HF + FClO_2 \quad (226) \\
2ClF_3 + 2HONO_2 & \longrightarrow & 2HF + FClO_2 + ClF + 2FNO_2 \quad (51) \\
ClF_5 + 2HONO_2 & \longrightarrow & 2HF + FClO_2 + 2FNO_2 \quad (51) \\
ClF_3O + 2ClOSO_2F & \longrightarrow & \left.\begin{array}{l} S_2O_5F_2 + FClO_2 + 2ClF \\ SO_2F_2 + FClO_2 + ClF \end{array}\right\} \quad (246) \\
ClF_3O + ClOSO_2F & \longrightarrow & \\
2ClF_3 + 3COF_2 & \longrightarrow & 2CF_4 + FClO_2 + CF_3OCl \quad (288) \\
2ClF_3 + UO_2F_2 & \longrightarrow & UF_6 + FClO_2 + ClF \quad (178, 179, 263) \\
6ClF + TeO_2 & \longrightarrow & TeF_5Cl + FClO_2 + 2Cl_2 \quad (168)
\end{array}$$

2. *Molecular Structure*

The exact structure of $FClO_2$ was determined by Parent and Gerry (*219*, *220*) using microwave spectroscopy. The molecule was shown to have C_s symmetry with the following internuclear parameters:



(XI)

Values were also reported for the rotational constants, centrifugal distortion constants, and the chlorine nuclear quadrupole coupling constants of the three isotopic species $^{19}F^{35}Cl^{16}O_2$, $^{19}F^{37}Cl^{16}O_2$, and $^{19}F^{35}Cl^{16}O^{18}O$. The molecular dipole moment was found to be 1.722 ± 0.03 D.

The pyramidal structure of symmetry C_s for $FClO_2$ was also confirmed by vibrational spectroscopy. E. A. Smith *et al.* (*271*) and Arvia and Aymonino (*6*) reported the infrared spectrum of the gas. D. F. Smith *et al.* (*270*) studied the infrared spectrum of the gas, measured the ^{35}Cl–^{37}Cl and ^{16}O–^{18}O isotopic shifts, recorded the Raman spectrum of the liquid, and carried out a normal coordinate analysis. The observed frequencies and their assignment are summarized in Table XIII.

Andrews and co-workers have recently reported (*5*) ^{35}Cl–^{37}Cl and ^{16}O–^{18}O isotopic shifts for the infrared spectrum of argon matrix-isolated $FClO_2$. Tantot (*282*) has studied in his thesis work the infrared and Raman spectra of the gas, the Raman spectrum of the neat liquid and of HF solutions, and the infrared and Raman spectra of the solid.

Force fields for $FClO_2$ were computed by D. F. Smith *et al.* (*270*), Robinson *et al.* (*238*), So and Chau (*272*), and Tantot (*282*). The force fields computed by Smith *et al.* (*270*), So and Chau (*272*), and Tantot (*282*) agree relatively well for the two stretching force constants, suggesting values of about 9.0 and 2.5 mdyn/Å for f_{ClO} and f_{ClF}, respectively. Except for Tantot's computation (*282*) which did not give plausible values for the deformation constants ($f_\alpha > f_\beta$), estimates that significantly deviate from the actual (*220*) geometry of $FClO_2$ were used for these computations. Since the deformation constants are more likely to be angle-dependent, a recomputation using the exact geometry and the observed (*270*) isotopic shifts is desirable.

Mean square amplitudes of vibration were calculated by Baran (*14*) based on the frequencies and estimated geometry reported by Smith *et al.* (*270*). The UV absorption spectrum of $FClO_2$ was studied by Sicre and Schumacher (*264*) and Pilipovich *et al.* (*228*). From a mass spectro-

TABLE XIII

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF $FClO_2$[a]

	Assignment	$F^{35}ClO_2$ (cm^{-1})	$F^{37}ClO_2$ (cm^{-1})	$F^{35}Cl^{18}O_2$ (cm^{-1})	$F^{37}Cl^{18}O_2$ (cm^{-1})	$F^{35}Cl^{16}O^{18}O$ (cm^{-1})	$F^{37}Cl^{16}O^{18}O$ (cm^{-1})
A′	ν_1 sym ClO_2 stretch	1105.8	1098.4	1060.4	1052.6	1080.7	1072.4
	ν_2 ClF stretch	630.2	621.6	624.7	616.0	628.6	618.6
	ν_3 ClO_2 scissor	546.5	543.0	529.0	—	537.8	534.0
	ν_4 FClO bend	401.6	—	—	—	—	—
A″	ν_5 asym ClO_2 stretch	1271.4	1258.6	1229.6	1215.0	1253.6	—
	ν_6 FClO bend	367.0	—	—	—	—	—

[a] Data from Smith *et al.* (*270*).

scopic study of $FClO_3$ (*82*) and using a value of 57 kcal mole^{-1} for the Cl—O bond energy, the electron affinity of $FClO_2$ was estimated to be $\geqslant 2.7$ eV.

The ^{19}F NMR spectrum of liquid $FClO_2$ at −80°C was recorded by Carter *et al.* (*43*) and Christe *et al.* (*61*) and consisted of a single peak at $\phi = -328$ or -315 ppm, respectively. A signal at $\phi = -332$ ppm was tentatively assigned by Alexakos and Cornwell (*2*) to gaseous $FClO_2$.

The weak and highly polar Cl—F bond in FClO can be rationalized in terms of either a $(p—\pi^*)\sigma$ bond (see Section II, C) or a simple valence bond model (*66*) resulting in a resonance hybrid of the following canonical forms: $FClO_2 \leftrightarrow F^- + ClO_2^+$. It has been discussed in detail by Parent and Gerry (*220*), by Carter *et al.* (*43*), and in Section II, C of this review.

3. *Physical Properties*

Chloryl fluoride is colorless as a gas and liquid, and white as a solid. It is stable under normal conditions and some of its physical properties are summarized in Table XIV. Although precise measurements of some of its spectroscopic properties have recently been undertaken (*220, 282*), most of its physical properties are either still unknown or were determined (*256*) at a time when corrosion-resistant metal–Teflon vacuum systems were not yet available. It was shown by vibrational spectroscopy (*282*) that solid $FClO_2$ between −263°C and its melting point exists only in one phase. Neutron diffraction data obtained for this phase at −196°C (*282*) were tentatively indexed based on a monoclinic unit cell with $a = 8.7$, $b = 6.2$, $c = 4.7$ Å, $\beta = 96°$, and $Z = 4$, similar to that of ClF_3.

TABLE XIV

SOME PROPERTIES OF $FClO_2$

Property	Value	Ref.
Melting point	−115° or −123.0° ± 0.4°C	(*15, 16, 256*)
Boiling point	~ −6°C	(*256*)
ΔH_{fusion}	1.440 kcal mole^{-1}	(*15, 16*)
ΔS_{fusion}	9.60 e.u.	(*15, 16*)
ΔH_{vap}	6.2 kcal mole^{-1}	(*256*)
Trouton constant	23.2 e.u.	(*256*)
$\Delta H^0_{f\ 298\ (g)}$	−8.1 ± 2.5 kcal mole$^{-1\ a}$	(*15, 16*)
Dipole moment (g)	1.722 ± 0.03 D	(*220*)

[a] Corrected for $\Delta H^0_{f\ HF(g)} = -65.14$ kcal mole^{-1} (*83*).

Tantot *et al.* (*190*, *282*, *283*) also studied association effects in the liquid phase using vibrational spectroscopy, pulse ^{19}F NMR spectroscopy, and conductometric measurements. They suggest a dipolar dynamic interaction resulting in short-lived associated forms and, possibly, a short-range local order observable on a vibrational but not on an NMR time scale. The specific conductivity of $FClO_2$ in the temperature range −120° to 23°C varies according to Martin and Tantot (*190*) from 1.2 to 3.12 μS cm^{-1} (=10^{-6} $ohm^{-1}cm^{-1}$). The observed conductivity was taken as evidence for self-ionization:

$$2FClO_2 \rightleftharpoons ClO_2^+ + ClO_2F_2^-$$

However, more conclusive evidence is required in view of the reluctance of $FClO_2$ to form $ClO_2F_2^-$ anions (see Section III, F, 4) and of its known reactivity which renders the preparation and handling of very pure $FClO_2$ quite difficult. The vapor pressure of $FClO_2$ as a function of the temperature was measured by Schumacher *et al.* (*8*, *256*), and is listed in Table XV. It can be described by the equation log $P(\text{mm}) = 8.23 - [1412/T(°K)]$. Several thermodynamic properties of $FClO_2$ have been estimated by Rips *et al.* (*235*) by means of correlation increments using only the boiling point of the substance. Whereas the correct boiling point of $FClO_2$ was used, its structure was erroneously assumed to be that of the hypofluorite F—O—Cl=O.

TABLE XV

VAPOR PRESSURES OF CHLORYL FLUORIDE

°C	−78	−65.5	−55	−45.5	−38	−30.2	−23.8	−17.2	−9.7	−6.3
mm of Hg	8.8	25.2	55.9	103.8	161.4	244	338	459	645	740

4. Chemical Properties

Chloryl fluoride is stable at ambient temperature in well-passivated and dry containers. Its thermal decomposition in quartz was studied by Schumacher *et al.* (*24*, *137*). It reaches a measurable rate only above 300°C. The decomposition reaction is monomolecular and its rate is pressure-dependent. The activation energy was calculated to be 45 ± 2 kcal $mole^{-1}$ and the rate constant was determined as $k_\infty = 2.3 \times 10^{13} \times 10^{-45000/4.5T}$ sec^{-1}. The following decomposition mechanism was proposed:

$$\mathrm{FClO_2} \longrightarrow \mathrm{FClO + O}$$
$$\mathrm{O + FClO_2} \longrightarrow \mathrm{FClO + O_2}$$
$$\mathrm{2FClO} \longrightarrow \mathrm{2ClF + O_2}$$

However, based on our present knowledge about FClO (see Section III, A), a more likely decomposition mode for FClO in the above mechanism would be

$$\mathrm{2FClO} \longrightarrow \mathrm{ClF + FClO_2}$$

The thermal decomposition of $FClO_2$ in Monel was studied by Macheteau and Gillardeau (*183*). Decomposition to ClF and O_2 was observed at 100°C (2.5% in 144 hr) and 200°C (10% in 235 hr), but a temperature $>$250°C was required for rate measurements. It was found that the decomposition is of first order and monomolecular at temperatures up to 285°C. At 300°C the reaction becomes second-order. The calculated rate constants and half-life times are summarized in Table XVI. The average activation energy between 250° and 285°C was found to be 23.7 kcal $\mathrm{mole^{-1}}$. The results at temperatures >300°C agree with those reported by Schumacher *et al.* (*137*) for the quartz reactor. Glass is only slowly attacked by $FClO_2$ at room temperature, but traces of HF or H_2O catalyze the reaction (*90*, *265*). Chloryl fluoride reacts with water (*9*, *36*) and anhydrous nitric acid (*51*) according to

TABLE XVI

THERMAL DECOMPOSITION OF $FClO_2$ IN MONEL[a]

Temp. (°C)	Initial press. of $FClO_2$ (mm)	Average rate constant ($\mathrm{sec^{-1}}$)	Half-life
250	52	6.8×10^{-6}	20 hr
250	101	8.5×10^{-6}	22 hr 30 min
270	52	1.8×10^{-5}	10 hr 30 min
285	52	2.8×10^{-5}	6 hr 40 min

[a] Data from Macheteau and Gillardeau (*183*).

$$\mathrm{2FClO_2 + H_2O} \longrightarrow \mathrm{2HF + 2ClO_2 + \tfrac{1}{2}O_2}$$

and

$$\mathrm{2FClO_2 + 2HONO_2} \longrightarrow \mathrm{2HF + 2ClO_2 + N_2O_5 + \tfrac{1}{2}O_2}$$

Both reactions are relatively slow and do not go to completion in several hours at room temperature (*9*, *36*, *51*). In addition, some of the ClO_2

formed can decompose to Cl_2 and O_2 and the nascent oxygen can oxidize $FClO_2$ to $FClO_3$ which is resistant to hydrolysis:

$$FClO_2 + O \longrightarrow FClO_3$$

These results differ from the previous report by Schmeisser and Fink (*255*) that the reaction between $FClO_2$ and $HONO_2$ proceeds at −30°C according to (*46*)

$$2FClO_2 + 2HONO_2 \longrightarrow NO_2ClO_4 + ClO_2 + NO_2 + 2HF$$

The statement made in Gmelin (*122*) and attributed to Bode and Klesper (*31*) that $FClO_2$ hydrolyzes to $FClO_3$ and H_2, is obviously incorrect. Hydrolysis of $FClO_2$ with base (*253*, *264*, *296*) proceeds as follows:

$$FClO_2 + 2OH^- \longrightarrow ClO_3^- + F^- + H_2O$$

Traces of H_2O in $FClO_2$ generate a red-brown color (*256*) which is probably due to ClO_2. With NH_3 it ignites at −78°C and the end products are NH_4Cl and NH_4F (*99*). The observation of a weak band at 1052 cm^{-1} in the Raman spectra of $FClO_2$ in dilute HF solutions in addition to strong bands due to $FClO_2$, was interpreted (*283*) in terms of the equilibrium:

$$HF + FClO_2 \rightleftarrows ClO_2^+ + HF_2^-$$

With HCl, chloryl fluoride reacts (*255*) at −110°C according to

$$HCl + FClO_2 \longrightarrow HF + ClO_2 + \tfrac{1}{2}Cl_2$$

With the stronger reducing agent HBr, it reacts explosively at −110°C (*99*). With $HOSO_2F$, at −78°C (*99*) it forms the stable ClO_2OSO_2F,

$$FClO_2 + HOSO_2F \longrightarrow HF + ClO_2OSO_2F$$

but with $HOSO_2Cl$ at −90°C, only the decomposition products of the analogous ClO_2OSO_2Cl, i.e., SO_3, ClO_2, and Cl_2, are obtained. With anhydrous $HOClO_3$, the following reaction occurs (*87*, *252*):

$$FClO_2 + HOClO_3 \longrightarrow HF + ClO_2OClO_3$$

Sulfur trioxide, at −10°C in $CFCl_3$ solution, undergoes an insertion reaction to yield the orange solid (mp = 27°C) ClO_2OSO_2F (*254*). The same compound was also obtained (*296*) in the absence of a solvent:

$$FClO_2 + SO_3 \longrightarrow ClO_2OSO_2F$$

With the strong reducing agent SO_2, chloryl fluoride reacts explosively at −40°C (*99*). When $FClO_2$ and I_2O_5 are combined at −196°C, then warmed to −50° to −20°C, I_2O_5 is dissolved with formation of O_2, IF_5, ClO_2, Cl_2O_6, and Cl_2O_7 (*294*).

Chloryl fluoride is a fluorinating agent and a moderately strong oxidizer. Thus it can fluorinate AsF_3 to the pentafluoride (*294*):

$$3FClO_2 + AsF_3 \longrightarrow ClO_2^+AsF_6^- + 2ClO_2$$

Sulfur tetrafluoride is oxidized by $FClO_2$ at 50°–300°C to yield a mixture of SF_6, SF_4O, and SF_2O_2 (*4*). Similarly, N_2F_4 is fluorinated at 30°C to give a mixture to NF_3, FNO_2, and FNO (*223*). Uranium tetrafluoride can be oxidized by $FClO_2$ to UF_5 and UF_6, the latter step requiring a reaction temperature between 50° and 150°C (*27*). Metal chlorides are converted by $FClO_2$ into metal fluorides, most of which can form ClO_2^+-containing salts when an excess of $FClO_2$ is used. Typical examples are $SbCl_5$, $SnCl_4$, and $TiCl_4$ which are converted to $ClO_2^+SbF_6^-$, $(ClO_2^+)_2$-SnF_6^{2-}, and $(ClO_2^+)_2TiF_6^{2-}$, respectively. Aluminum trichloride is converted to AlF_3 (*99*, *255*). Oxides, such as I_2O_5 (see above), SiO_2, Sb_2O_5, and B_2O_3 can be converted by $FClO_2$ at −10°C to SiF_4, ClO_2^+-SbF_6^-, and $ClO_2^+BF_4^-$, respectively (*87*). At 50°–100°C, UO_2F_2 reacts only slowly with $FClO_2$, but at 150°C with contact times of 30 min, UF_6, Cl_2, and O_2 are formed (*178*, *179*) according to

$$4FClO_2 + UO_2F_2 \longrightarrow UF_6 + 2Cl_2 + 5O_2$$

Only one reaction was reported in which $FClO_2$ was oxidized from the penta- to the heptavalent state (*49*, *52*, *69*). The powerful oxidizer PtF_6 was required to obtain the following reaction:

$$2FClO_2 + 2PtF_6 \longrightarrow ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^-$$

Chloryl fluoride was converted to ClF_3O by UV-photolysis of systems containing mixtures such as $FClO_2$–F_2, $FClO_2$–ClF, $FClO_2$–ClF_3, and $FClO_2$–ClF_5 (*228*, *240*). These reactions probably do not involve a direct oxygen–fluorine exchange in $FClO_2$, since ClF_3O can be synthesized by the same technique either directly from the three elements or from ClF_3 and oxygen (*228*).

Chloryl fluoride, like most of the other known chlorine fluorides and oxyfluorides, possesses amphoteric character. Owing to its weak and polar $(p—\pi^*)\sigma$ Cl—F bond (see Section II, C), it exhibits a much stronger tendency to form adducts with Lewis acids than with Lewis bases. The adducts with Lewis acids result in salts containing ClO_2^+ cations, and those with bases result in $ClO_2F_2^-$ salts. Both ions are discussed in detail in Sections III, G and H, respectively.

G. CHLORYL CATION

Although the chloryl cation does not contain a ClF bond and, therefore, in a strict sense does not belong to the family of the chlorine fluoride oxides, it was included in this review since it is a true derivative of $FClO_2$.

The existence of $FClO_2$ adducts with BF_3, AsF_5, PF_5, SbF_5, SiF_4, SO_3, and TaF_5 was first reported in 1954 by Schmeisser and Ebenhöch (*87*, *254*) and Woolf (*296*). In 1957, Schmeisser and Fink obtained (*99*, *255*) adducts with TiF_4 and SnF_4. In 1958, Clark and Emeleus described (*73*) the existence of a VF_5 adduct, more recently Christe (*52*) obtained a PtF_6 and IrF_6 adduct, and Yeats and Aubke (*298a*) prepared $ClO_2^+[AsF_5(SO_3F)]^-$ from ClO_2SO_3F and AsF_5.

In a previous review (*253*) the adducts of $FClO_2$ with the stronger Lewis acids, such as AsF_5 or SbF_5, were considered to be ionic and to contain ClO_2^+ cations. However, the corresponding BF_3 and PF_5 adducts were assumed to be molecular adducts. In 1968, Carter *et al.* (*44*) reported evidence for the existence of solvated ClO_2^+ ions in HSO_3F solution. Since then, vibrational spectroscopy has successfully been used to establish the ionic nature of solid $ClO_2^+AsF_6^-$ (*43*, *66*), $ClO_2^+BF_4^-$ (*66*, *155*, *157*), $ClO_2^+SbF_6^- \cdot xSbF_5$ (*42*, *43*, *155*, *157*), $ClO_2^+ClO_4^-$ (*221*), $ClO_2^+PtF_6^-$, and $ClO_2^+IrF_6^-$ (*52*).

1. Syntheses and Properties

Salts containing the ClO_2^+ cation can be prepared either by direct combination of $FClO_2$ with the corresponding perfluorinated Lewis acid with (*254*) or without a solvent (*43*, *66*, *73*, *155*, *209*, *296*), by the interaction of $FClO_2$ with oxides (*87*), chlorides (*99*, *255*), and lower (*294*) or higher (*52*) oxidation state fluorides, or by interaction of the perfluorinated Lewis acid with chlorine oxides (*210*, *247*). The latter reactions, however, produce nonvolatile XF_3O as a by-product:

$$5Cl_2O + 3XF_5 \longrightarrow 2ClO_2^+XF_6^- + XF_3O + 4Cl_2 \quad (X = As, Sb)$$

$$5Cl_2O + 7SbF_5 \longrightarrow 2ClO_2^+Sb_3F_{16}^- + SbF_3O + 4Cl_2$$

$$5ClO_2 + 6SbF_5 \longrightarrow 4ClO_2^+SbF_6^- + 2SbF_3O + \tfrac{1}{2}Cl_2$$

$$5ClO_2 + 14SbF_5 \longrightarrow 4ClO_2^+Sb_3F_{16}^- + 2SbF_3O + \tfrac{1}{2}Cl_2$$

$$Cl_2O_6 + 2SbF_5 \longrightarrow ClO_2^+SbF_6^- + SbF_3O + FClO_2$$

Of the above approaches, the direct combination of $FClO_2$ with the corresponding Lewis acid is generally the most convenient. It yields well-defined products, except for cases, such as SbF_5 (*210*) or TaF_5 (*296*), where polyanion formation is possible. From the $FClO_2$–SbF_5 system, depending on the ratio of the starting materials and the reaction conditions, only $ClO_2^+SbF_6^-$, $ClO_2^+Sb_3F_{16}^-$, or a mixture of the two but no $ClO_2^+Sb_2F_{11}^-$, were obtained (*210*). However, single crystals of

$ClO_2{}^+Sb_2F_{11}{}^-$ have been obtained by Edwards and Sills (*88a*) by the interaction of $ClF_2{}^+SbF_6{}^-$ solutions with glass.

The $FClO_2$ adducts are generally white solids, except for the yellow $PtF_6{}^-$ and $IrF_6{}^-$ salts (*52*) and for $FClO_2 \cdot SO_3$ which was reported to be a red-to-pale yellow low-melting solid (*296*). The properties of the latter compound indicate that in the liquid phase it may exist, by analogy with Cl_2O_6 (*221*), in its covalent form, i.e., O_2ClOSO_2F. The ionicity of chloryl fluorosulfate was also discussed (*298*) in a paper dealing with the liquid range of fluorosulfates. The literature reports on the thermal stability of the $ClO_2{}^+$ salts are rather sketchy. In addition to the data given in Table IV of Schmeisser's review (*253*), stability data were published only for the BF_3 and the SbF_5 adducts. The $FClO_2 \cdot BF_3$ adduct reaches a dissociation pressure of 1 atm at 44.1°C (*66*), whereas $ClO_2{}^+SbF_6{}^-$ (mp = 220–225°C) and $ClO_2{}^+Sb_3F_{16}{}^-$ (mp = 50–53°C) are stable up to 300° and 200°C, respectively (*209*). The $PtF_6{}^-$ and $IrF_6{}^-$ salts of $ClO_2{}^+$ are stable at room temperature (*52*). It should be pointed out that Table IV of Schmeisser (*253*) implies that the thermal stability of the $PF_6{}^-$ salt is higher than that of the $BF_4{}^-$. However, for related cations the reverse is true, and it appears that the data cited might be inaccurate.

X-Ray powder diffraction data have been reported for $ClO_2{}^+AsF_6{}^-$ (*66*) and for $ClO_2{}^+SbF_6{}^-$ and $ClO_2{}^+Sb_3F_{16}{}^-$ (*209*). All the $ClO_2{}^+$ salts react violently with organic compounds and water. With stronger Lewis bases, such as NO, NO_2, $ClNO_2$ (*99, 255*), FNO, and FNO_2 (*51, 68*), the following type of displacement reactions can be carried out:

$$ClO_2{}^+AsF_6{}^- + NO_2 \longrightarrow NO_2{}^+AsF_6{}^- + ClO_2$$

$$ClO_2{}^+AsF_6{}^- + ClNO_2 \longrightarrow NO_2{}^+AsF_6{}^- + ClO_2 + \tfrac{1}{2}Cl_2$$

$$ClO_2{}^+PtF_6{}^- + FNO_2 \longrightarrow NO_2{}^+PtF_6{}^- + FClO_2$$

2. *Molecular Structure*

The $ClO_2{}^+$ cation has been well characterized by vibrational spectroscopy (*42, 43, 66, 155, 157*). Characteristic frequencies and intensities for $ClO_2{}^+$ are summarized in Table XVII. The observed ^{35}Cl–^{37}Cl isotopic shifts were used to calculate the bond angle of $ClO_2{}^+$. It was shown that the cation is sharply bent and that the bond angle approximates 120° (*66, 155*). Force constants were computed as a function of the $ClO_2{}^+$ bond angle (*66, 155*) and the preferred set of constants is included in Table XVII. The value of 8.96 mdyn/Å obtained (*66*) for the ClO-stretching force constant of $ClO_2{}^+$ demonstrates that the ClO bond has double-bond character (see Table I).

TABLE XVII

CHARACTERISTIC FREQUENCIES[a] AND INTERNAL FORCE CONSTANTS[b] OF ClO_2^+

Obsd. freq. (cm^{-1}) and intensities		Assignment in point group C_{2v}		
IR	Raman			
1296.4 m	1296.4 (1)	$\nu_3(B_1)$	ν_{as}	$^{35}ClO_2$
1282.6 mw	—	$\nu_3(B_1)$	ν_{as}	$^{37}ClO_2$
1043.7 mw	1044.4 (10)	$\nu_1(A_1)$	ν_s	$^{35}ClO_2$
1038.3 w	1039.1 (4)	$\nu_1(A_1)$	ν_s	$^{37}ClO_2$
521.0 m	521.3 (3)	$\nu_2(A_1)$	δ	$^{35}ClO_2$
517 sh	—	$\nu_2(A_1)$	δ	$^{37}ClO_2$

$f_r = 8.96 \pm 0.06$ mdyn/Å
$f_{rr} = -0.45 \pm 0.13$ mdyn/Å
$f_{r\alpha} = 0.24 \pm 0.13$ mdyn/Å
$f_\alpha = 0.82 \pm 0.03$ mdyn/Å

[a] Taken for $ClO_2^+AsF_6^-$ from Christe *et al.* (*66*).
[b] Calculated for ∢ OClO = 120°.

These conclusions concerning the structure of ClO_2^+ were recently confirmed by Edwards and Sills (*88a*) who carried out a crystal structure determination for $ClO_2^+Sb_2F_{11}^-$. They found the ClO_2^+ ion to be V-shaped, with an O-Cl-O angle of 122° and a mean Cl-O bond length of 1.31 Å.

H. DIFLUOROCHLORATE(V) ANION

The existence of difluorochlorates of sodium, potassium, and barium was reported in 1965 by Mitra (*195*). However, this claim was met by skepticism since the reported synthesis involved the use of 40% aqueous hydrofluoric acid. In a subsequent paper (*196*), Mitra withdrew his claim. In 1969, Huggins and Fox reported (*141*, *142*) the synthesis of $CsClF_2O_2$ from CsF and $FClO_2$, and a subsequent spectroscopic study by Christe and Curtis showed (*54*) that the vibrational spectrum of the adduct is consistent with a $ClF_2O_2^-$ anion of symmetry C_{2v}.

1. *Synthesis and Properties*

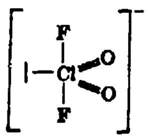
The synthesis of $CsClF_2O_2$ can be readily achieved by the interaction of dry CsF with excess $FClO_2$ at room temperature (*141*, *142*). In the original work (*141, 142*), activated CsF was used which was obtained by vacuum pyrolysis of the CsF–hexafluoroacetone complex. The conversion of CsF to $CsClF_2O_2$ was 87%. When ordinary CsF (dried by fusion in a platinum crucible and powdered) was used (*54*), the conversion of CsF to $CsClF_2O_2$ was 73%.

The $CsClF_2O_2$ adduct is a white solid, stable at 25°C. Vacuum pyrolysis at 80°–100°C yields CsF and $FClO_2$ (*142*), demonstrating that the formation reaction is reversible. It fumes in moist air and reacts explosively with water (*142*). Controlled hydrolysis (*54*) proceeds according to

$$ClF_2O_2^- + H_2O \longrightarrow ClO_2^- + 2HF$$

2. *Structure*

The nature of the $CsClF_2O_2$ adduct was established (*54*) by vibrational spectroscopy. The observed spectra were consistent with a $ClF_2O_2^-$ anion possessing the following structure of symmetry C_{2v}:



(XII)

The observed bands and their assignments are summarized in Table XVIII. A normal coordinate analysis was carried out (*54*) for $ClF_2O_2^-$ assuming the following geometry: $R(ClO) = 1.43$ Å, $r(ClF) = 1.79$ Å, $\alpha(\angle OClO) = 120°$, $\beta(\angle OClF) = 90°$, and $(\angle FClF) = 180°$. The actual bond angles are expected to deviate slightly from this ideal geometry owing to increased repulsion from the free valence electron pair on Cl (see Section II, A). The internal force constants of $ClF_2O_2^-$ are summarized in Table XIX. As can be seen from Table I and the general discussion in Section II, C, the ClO bonds in $ClF_2O_2^-$ have double-bond character and the ClF bonds are as expected, semi-ionic 3 center–4 electron bonds. The polarity of the latter is increased further by the formal negative charge and the high degree of oxygen substitution. The combination of these effects results in the lowest ClF-stretching force constant value found to date for any ClF bond. As demonstrated for several other oxyfluoride anions (see Section III, D), the negative charge in $ClF_2O_2^-$ resides mainly on the ligands having the highest electronegativity, i.e., on the fluorine, and not on the oxygen atoms.

TABLE XVIII

VIBRATIONAL SPECTRUM OF $Cs^+ClF_2O_2^-$ AND ITS ASSIGNMENT[a]

Obsd. freq. (cm^{-1}) and intensities		Assignment for XO_2F_2 in point group C_{2v}	Approx. description of vibration
IR	Raman		
1225 1191 } vs	1221 (0.8)	$\nu_8(B_2)$	$\nu_{as}(XO_2)$
1070 s	1076 (10) 1064 1055	$\nu_1(A_1)$	$\nu_s(XO_2)$
559 m	559 (1.2)	$\nu_2(A_1)$	$\delta_s(XO_2)$
510 vs, br		$\nu_6(B_1)$	$\nu_{as}(XF_2)$
	480 (1), br	$\nu_5(A_2)$?	τ
330–370 m	363 (10)	$\nu_3(A_1)$	$\nu_s(XF_2)$
	337 (8)	$\nu_7(B_1)$, $\nu_9(B_2)$	δ_{rock}, δ_{wag}
	198 (0.7)	$\nu_4(A_1)$	$\delta_s(XF_2)$

[a] Data from Christe and Curtis (*54*).

TABLE XIX

FORCE CONSTANTS OF $ClF_2O_2^-$ [a,b]

f_R	8.3	f_β	1.2
f_{RR}	0.1	$f_{\beta\beta'}$	0.57
f_r	1.6	$f_{\beta\beta}$	0.1
f_{rr}	−0.1	$f_{r\beta} - f_{r\beta'}$	0.3
f_α	1.95		

[a] Data from Christe and Curtis (*54*).

[b] Stretching force constants in mdyn/Å, deformation constants in mdyn Å/radian², and stretch–bend interactions in mdyn/radian.

I. CHLORINE TRIFLUORIDE DIOXIDE

A compound having the empirical composition $(ClF_3O_2)_n$ was reported in 1962 by Streng and Grosse (*128*, *276*, *278*). It was obtained by the interaction of either Cl_2, ClF, or HCl with O_2F_2 between −154°C and −143°C or by UV photolysis of ClF_3 and O_2 mixtures at −78°C. Both methods produced the same product, a violet unstable solid, which irreversibly decomposed above −78°C. In a subsequent study of the infrared and visible spectra of these products, Gardiner and Turner (*108*, *109*) proposed the structure F_2ClOOF for the violet compound. However, both the synthetic and the spectroscopic studies are not convincing and further work is required to establish the composition and structure of this violet species.

A well-defined and characterized compound, having the composition ClF_3O_2 and showing no resemblance to Streng and Grosse's violet compound, was reported in 1972 by Christe (*50*). This work is an excellent example for the perfection of handling techniques for extremely reactive oxidizers. Thus the physical, chemical, and spectroscopic properties of ClF_3O_2 and of its $ClF_2O_2^+$ adducts were determined from a total of 2.2 mmol of material. The fact that ClF_3O_2 as a powerful oxidizer is readily reduced to $FClO_2$ which cannot be removed from ClF_3O_2 by simple fractionation (see below), rendered the handling of this compound puarticlarly difficult.

1. Synthesis and Properties

The synthesis of ClF_3O_2 is best described by the following reaction sequence:

$$2FClO_2 + 2PtF_6 \longrightarrow ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^-$$

Several side reactions compete with this reaction and the yield of $ClF_2O_2^+$ varies greatly with slight changes in the reaction conditions (*52*, *68*). The ClF_3O_2 is then displaced from its $ClF_2O_2^+$ salt according to

$$ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^- + 2FNO_2 \longrightarrow 2NO_2^+PtF_6^- + ClF_3O_2 + FClO_2$$

Chloryl fluoride is slightly less volatile than ClF_3O_2, and, therefore, most of it can be removed from ClF_3O_2 by fractional condensation in a −112°C trap. The remaining $FClO_2$, however, has to be removed by complexing with BF_3:

$$ClF_3O_2 + FClO_2 + 2BF_3 \longrightarrow ClF_2O_2^+BF_4^- + ClO_2^+BF_4^-$$

Since $ClF_2O_2^+BF_4^-$ is stable (*69*) at 20°C, whereas $ClO_2^+BF_4^-$ is not (*66*), the latter can be pumped away at 20°C. The resulting pure $ClF_2O_2^+BF_4^-$ is then treated with an excess of FNO_2 and the evolved ClF_3O_2 and unreacted FNO_2 are readily separated by fractional condensation through a series of −126° and −196°C traps:

$$ClF_2O_2^+BF_4^- + FNO_2 \longrightarrow NO_2^+BF_4^- + ClF_3O_2$$

The overall yield of pure ClF_3O_2 based on the PtF_6 used in step 1 was found to be about 10 mole%.

Pure ClF_3O_2 is colorless as a gas or liquid and white as a solid. Some of its measured (*68*) physical properties are summarized in Table XX. Near its melting point the vapor pressure above liquid ClF_3O_2 was found to be reproducibly lower than expected from the vapor pressure curve given in Table XX. This indicates that close to the melting point some ordering effect occurs in the liquid.

The measured vapor density of ClF_3O_2 indicates that no appreciable association occurs in the gas phase. Its relatively low boiling point and Trouton constant imply little association in the liquid phase. This prediction is confirmed by the vibrational spectra of the liquid and the neat solid which exhibit only minor frequency shifts when compared to the spectra of the gas and the matrix-isolated solid. This finding is somewhat surprising since both ClF_3 (*102*) and ClF_3O (*55*, *226*) show a pronounced tendency to associate in the liquid and solid state through bridges involving the axial fluorine atoms.

TABLE XX

SOME PROPERTIES OF ClF_3O_2[a]

Property	Value
Melting point	−81.2°C
Boiling point	−21.58°C
ΔH_{vap}	5.57 kcal mole^{-1}
Trouton constant	22.13 e.u.
Vapor pressure	$\text{Log } P(\text{mm}) = 7.719 - \dfrac{1217.2}{T\ (°\text{K})}$

[a] Data from Christe and Wilson (*68*).

The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given below assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation. These properties are given for the range 0°–2000°K in the Appendix (Table AII).

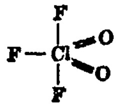
Chlorine trifluoride dioxide resembles chlorine fluorides and oxyfluorides in its corrosive and oxidizing properties. It must be handled in systems consisting of corrosion-resistant metals, Teflon, or sapphire. It appears to be marginally stable in a well-passivated system at ambient temperature. It is a strong oxidative fluorinator as evidenced by its tendency to fluorinate metal surfaces to metal fluorides with $FClO_2$ formation. It reacts explosively with organic materials and care must be taken to avoid such combinations. The hydrolysis of ClF_3O_2 was not quantitatively studied; however, on one occasion a slight leak in an infrared gas cell containing ClF_3O_2 resulted in the formation of $FClO_2$ and HF indicating the following reaction.

$$ClF_3O_2 + H_2O \longrightarrow FClO_2 + 2HF$$

Chlorine trifluoride dioxide forms stable adducts with strong Lewis acids, such as BF_3, AsF_5, or PtF_5 (*49, 68, 69*). These adducts have ionic structures containing the $ClF_2O_2^+$ cation (see Section III, I, 2). The high stability of these adducts can be explained by the change from the energetically unfavorable trigonal-bipyramidal structure of ClF_3O_2 to the more favorable tetrahedral $ClF_2O_2^+$ configuration (see Section II, D). Contrary to ClF_3 (*295*), but by analogy with ClF_3O (*64*), it does not form stable adducts with FNO or FNO_2 at temperatures as low as −78°C. This was demonstrated by the various displacement reactions where ClF_3O_2 and unreacted FNO or FNO_2 could be readily removed from the reactor at −78°C. With the stronger base, CsF, it did not form a stable adduct but decomposed to $FClO_2$ and F_2. However, only relatively small amounts of ClF_3O_2 were available for the complex formation study with CsF, and the possibility of preparing salts such as $Cs^+ClF_4O_2^-$ under more favorable reaction conditions cannot entirely be ruled out.

2. *Molecular Structure*

Vibrational (*57*) and ^{19}F NMR (*68*) spectroscopy were used to establish for ClF_3O_2 the following structure of symmetry C_{2v}, which according to semi-empirical linear combination of atomic orbitals–molecular orbitals (LCAO-MO) self-consistent field (SCF) calculations (*239*) is most stable:



(XIII)

The ^{19}F NMR spectrum of liquid ClF_3O_2 was measured in the temperature range −20° to −80°C. It showed at all temperatures one partially resolved signal centered at −413 ppm below the external standard $CFCl_3$. The observed signal is in excellent agreement with an AB_2 pattern with $J/\nu_0\delta \approx 1.0$ and $J_{FF} = 443$ Hz. The low chemical shift of −413 ppm for ClF_3O_2 is in excellent agreement with a heptavalent chlorine fluoride, and the fluorine–fluorine coupling constant of 443 Hz observed for ClF_3O_2 is similar to that of 421 Hz observed for the structurally related ClF_3 (*61*). Additional support for the above structure was derived from the fact that the B_2 part of the AB_2 pattern occurs downfield from the A part as expected for the axial fluorine atoms in a trigonal bipyramidal arrangement (*120*, *200*).

The infrared spectra of gaseous, solid, and matrix-isolated ClF_3O_2 and the Raman spectra of gaseous and liquid ClF_3O_2 were reported (*57*) and are summarized in Table XXI. The observed data are in excellent agreement with the preceding model (XIII) of symmetry C_{2v}. A normal coordinate analysis was carried out for ClF_3O_2 assuming the following geometry: $D(ClO) = 1.40$ Å, $R(ClF_{eq}) = 1.62$ Å, $r(ClF_{ax}) = 1.72$ Å, $\alpha(OClO) = 130°$, $\beta(F_{eq}ClF_{ax}) = \delta(OClF_{ax}) = 90°$, and $\gamma(OClF_{eq}) = 115°$, based on the observed geometries of ClF_3 and $FClO_3$ and a correlation between ClO bond length and stretching frequency. The deviation of the OClO bond angle from the ideal 120° was estimated by comparison with the known geometries of SF_4O and $FClO_3$. The force constants thus obtained are summarized in Table XXII. The value of the ClO-stretching force constant (9.23 mdyn/Å) is in excellent agreement with that of

TABLE XXI

VIBRATIONAL SPECTRUM OF ClF_3O_2 AND ITS ASSIGNMENT IN POINT GROUP C_{2v}[a]

IR (cm^{-1})	Ra (cm^{-1})	Assignment for ClF_3O_2 in point group C_{2v}		Approx. description of mode
1093 s	1093 (4) p	A_1	ν_1	Sym ClO_2 str
683 m	683 (10) p		ν_2	ClF_{eq} str
519 w	520 (8) p		ν_3	ClO_2 scissor
487 vw	487 (6) p		ν_4	Sym $F_{ax}ClF_{ax}$ str
287 w	285 (1)		ν_5	$F_{ax}ClF_{ax}$ scissor in ClF_3 plane
(417)[b]	402 (0+)	A_2	ν_6	Torsion
695 vs		B_1	ν_7	Antisym $F_{ax}ClF_{ax}$ str
592 s	586 (0+)		ν_8	ClO_2 wag
372 w			ν_9	Antisym $F_{eq}ClF_{ax}$ def in ClF_3 plane
1327 vs	1320 (0+)	B_2	ν_{10}	Antisym ClO_2 str
531 m	530 (1)		ν_{11}	ClO_2 rock
[c]	222 (1)		ν_{12}	$F_{ax}ClF_{ax}$ scissor out of ClF_3 plane

[a] Data from Christe and Curtis (*57*).

[b] Observed only for solid ClF_3O_2.

[c] Below frequency range of spectrometer used.

TABLE XXII

INTERNAL FORCE CONSTANTS OF ClF_3O_2[a,b]

$f_D = 9.23$	$f_{\beta\beta} = 0.09$
$f_R = 3.35$	$f_{r\beta} = f_{r\beta'} = 0.10$
$f_r = 2.70$	$f_{r\delta} = -f_{r\delta'} = 0.25$
$f_\alpha = 1.41$	$f_{D\alpha} = 0.61$
$f_\beta = 1.40$	$f_{\beta\delta} = -f_{\beta\delta'} = -0.16$
$f_\gamma = 1.33$	$f_{\delta\delta} = -f_{\delta\delta'} = -0.34$
$f_\delta = 1.30$	$f_{\delta\delta''} = -0.17$
$f_{DD} = -0.09$	$f_{\gamma\gamma} = -0.30$
$f_{rr} = -0.04$	$f_{R\alpha} = -0.37$

[a] Data from Christe and Curtis (*57*).

[b] Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch-bend interaction constants in mdyn/radian.

9.37 mdyn/Å found for ClF_3O (*55*) and the general valence force field values of 9.07 and 8.96 mdyn/Å reported for $FClO_2$ (*270*) and ClO_2^+, (*66*) respectively. The values of the ClF-stretching force constants are comparable to those previously reported for the related pseudotrigonal bipyramidal molecules ClF_3 (*102*) and ClF_3O (*55*) and are summarized in Table XXIII. In all three molecules, the stretching force constant of the equatorial ClF bond is significantly higher than that of the two axial bonds, although their relative difference decreases with increasing oxidation state of the central atom. The difference in bond strength between equatorial and axial bonds implies significant contributions from semi-ionic 3 center–4 electron bonds to the axial ClF bonds. This bonding scheme has been discussed in detail for the related pseudotrigonal bipyramidal ClF_2^- anion in Section II, C.

TABLE XXIII

ClF STRETCHING FORCE CONSTANTS OF ClF_3O_2 COMPARED TO THOSE OF PSEUDOTRIGONAL BIPYRAMIDAL ClF_3O, ClF_3, ClF_2^-, AND $ClF_2O_2^-$

Compound	f_R (mdyn/Å)	f_r (mdyn/Å)	f_{rr} (mdyn/Å)	$(f_R-f_r)/f_R$	Ref.
ClF_3	4.2	2.7	0.36	0.36	(*102*)
ClF_3O	3.2	2.3	0.26	0.26	(*55*)
ClF_3O_2	3.4	2.7	−0.04	0.19	(*57*)
ClF_2^-	—	2.4	0.17	—	(*63*)
$ClF_2O_2^-$	—	1.6	−0.1	—	(*54*)

Inspection of Table XXIII also reveals that the value of f_r does not depend exclusively on the oxidation state of the central atom. Obviously, formal negative charges (as in the anions) and increasing oxygen substitution facilitate the formation of semi-ionic bonds and, hence, counteract the influence of the oxidation state of the central atom. It is interesting to note that the relative contribution from semi-ionic bonding (see Section II, C) to the axial ClF bonds [$= (f_R - f_r)/f_R$] decreases from ClF_3 to ClF_3O and ClF_3O_2 (see Table XXIII). This can be attributed to the decreasing electron density around the central atom with increasing oxidation state, thus making it more difficult to release electron density to the axial fluorine ligands as required for the formation of semi-ionic bonds.

The bonding in ClF_3O_2 might be described by the following approximation (*53*). The bonding of the three equatorial ligands, ignoring the second bond of the Cl=O double bond, is mainly due to an sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves one delocalized p-electron pair of the chlorine atom for the formation of a semi-ionic 3 center–4 electron pσ bond.

J. DIFLUOROPERCHLORYL CATION

The existence of the $ClO_2F_2^+$ cation in the form of its PtF_6^- salt was reported in 1972 by Christe (*49*). In a subsequent paper (*69*), a full account was given of the synthesis and properties of the PtF_6^-, AsF_6^-, and BF_4^- salts of $ClO_2F_2^+$.

1. Synthesis and Properties

It was found (*52*) that PtF_6 and $FClO_2$, when combined at −196°C and allowed to warm up slowly to 25°C, interacted according to

$$2FClO_2 + 2PtF_6 \longrightarrow ClO_2F_2^+PtF_6^- + ClO_2^+PtF_6^-$$

The yield of $ClO_2F_2^+$ was not 50% as expected from the foregoing equation, but generally about 25% owing to the competing reaction

$$2FClO_2 + 2PtF_6 \longrightarrow 2ClO_2^+PtF_6^- + F_2$$

In some of the experiments, small amounts of $ClF_6^+PtF_6^-$ or ClF_5 and $FClO_3$ were observed, depending on the exact reaction conditions. The formation of some $FClO_3$ is not surprising since it is known that $FClO_2$ readily interacts with nascent oxygen to yield $FClO_3$ (*9, 36, 51*).

Attempts to suppress the competing reaction by changing the reaction conditions (rapid warm-up from −196° to −78°C and completion of the reaction at −78°C) resulted on one occasion in an entirely different course for the reaction:

$$6FClO_2 + 6PtF_6 \longrightarrow 5ClO_2^+PtF_6^- + ClF_6^+PtF_6^- + O_2$$

Further modification of the reaction conditions (rapid warm-up of the $FClO_2$-PtF_6 mixture from −196° to either −78° or 25°C and completion of the reaction at 25°C) did not produce detectable amounts of either $ClO_2F_2^+$ or $ClF_6^+PtF_6^-$, but only $ClO_2^+PtF_6^-$ and ClF_5, F_2, and O_2. This indicates that the nature of the reaction products is more influenced by the warm-up rate of the starting materials from −196° to about −78°C than by the final reaction temperature. Slow warm-up favors the formation of $ClO_2F_2^+$, whereas rapid warm-up yields ClF_6^+ or ClF_5 and F_2 (*52*).

The BF_4^- and AsF_6^- salts were prepared (*69*) as follows:

$$ClO_2^+PtF_6^- + ClO_2F_2^+PtF_6^- + 2FNO_2 \longrightarrow FClO_2 + ClF_3O_2 + 2NO_2^+PtF_6^-$$

Unreacted FNO_2 and some of the $FClO_2$ could be separated from ClF_3O_2 by fractional condensation. The remaining $FClO_2$ was separated from ClF_3O_2 by complexing with BF_3. Since the resulting $ClO_2^+BF_4^-$ has a dissociation pressure (*66*) of 182 mm at 22.1°C while $ClO_2F_2^+BF_4^-$ is stable, the former salt could be readily removed by pumping at 20°C. Conversion of $ClO_2F_2^+BF_4^-$ to the corresponding AsF_6^- salt was accomplished through displacement of BF_4^- by the stronger Lewis acid AsF_5:

$$ClO_2F_2^+BF_4^- + AsF_5 \longrightarrow ClO_2F_2^+AsF_6^- + BF_3$$

All three salts, $ClO_2F_2^+PtF_6^-$, $ClO_2F_2^+AsF_6^-$, and $ClO_2F_2^+BF_4^-$, are solids, stable at 25°C, and react violently with water or organic materials. The PtF_6^- compound is canary yellow, whereas those of AsF_6^- and BF_4^- are white.

The salts dissolve in anhydrous HF without decomposing. They are crystallinic in the solid state, and the X-ray powder diffraction patterns of $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$ have been reported (*69*). The pattern of the former was tentatively indexed on the basis of an orthorhombic unit cell with $a = 5.45$, $b = 7.23$, and $c = 13.00$ Å. Assuming four molecules per unit cell and neglecting contributions from the highly charged central atoms to the volume, a plausible average volume of 16 Å^3 per F or O atom was obtained.

The thermal stability of $ClO_2F_2^+BF_4^-$ is higher than that of $ClO_2^+BF_4^-$ (*66*), $ClF_2^+BF_4^-$ (*259*), or other similar salts. The pronounced tendency of ClF_3O_2 to form stable adducts with Lewis acids is in good agreement with the correlations between the stability of an adduct and the structure of the parent molecule and its ions (see Section II, D). Thus, tetrahedral $ClO_2F_2^+$ (see below) should be energetically much more favorable than trigonal bipyramidal ClF_3O_2.

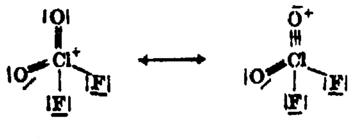
2. *Molecular Structure*

The structure of $ClO_2F_2^+$ salts was established by ^{19}F NMR and vibrational spectroscopy (*69*).

In the ^{19}F NMR spectrum of $ClF_2O_2^+PtF_6^-$ in anhydrous HF, a broad singlet at −310 ppm relative to external $CFCl_3$ was tentatively assigned (*61*) to $ClF_2O_2^+$. Subsequent studies (*69*) of $ClF_2O_2^+BF_4^-$ and $ClF_2O_2^+AsF_6^-$ confirmed the original assignment. The spectrum of $ClF_2O_2^+BF_4^-$ in HF showed a strong temperature dependence. At 30°C it consisted of a single peak at 185 ppm relative to external $CFCl_3$. With decreasing temperature the peak at first became broader and then separated at about 0°C into three signals at −301 ($ClO_2F_2^+$), 146 (BF_4^-), and 194 ppm (HF) which became narrower with further decrease in temperature. The observed peak area ratio of approximately 2:1 for the 146- and −301-ppm signals confirmed their assignment to BF_4^- and $ClO_2F_2^+$, respectively, and proved the ionic nature of the $ClF_3O_2 \cdot BF_3$ adduct in HF solution.

The spectrum of $ClF_2O_2^+AsF_6^-$ in HF (which was acidified with AsF_5) consisted of two resonances at −307 ($ClO_2F_2^+$) and 105 ppm (HF, AsF_5, AsF_6^-), respectively. Rapid exchange among HF, AsF_5, and AsF_6^- preempted the measurement of the $ClO_2F_2^+$ to AsF_6^- peak area ratio (*69*).

The vibrational spectra of the BF_4^-, AsF_6^-, and PtF_6^- salts of $ClO_2F_2^+$ were recorded for both the solids and HF solutions (*69*). It was shown that all three salts are ionic containing, in addition to the anions, a common cation. The vibrational spectrum of this cation closely resembled that of SO_2F_2 indicating a pseudotetrahedral structure of symmetry C_{2v}. The observed frequencies together with the stretching force constants obtained from Cl isotopic shifts are listed in Table XXIV. Inspection of Table I shows that $ClO_2F_2^+$ possesses the highest value known for a ClO-stretching force constant. This is not surprising, since the central atom in $ClO_2F_2^+$ has a high oxidation state (+VII), highly electronegative ligands, and a formal positive charge (cation). The influence of these factors on f_{ClO} was discussed in Section II, C. By analogy with ClF_2O^+ (*58*), the only other known species exhibiting a f_{ClO} value of similar magnitude, contributions from the resonance structure,



(XIV) (XV)

TABLE XXIV

OBSERVED FREQUENCIES, APPROXIMATE DESCRIPTION OF MODES, AND MOST IMPORTANT INTERNAL FORCE CONSTANTS COMPUTED TO FIT THE OBSERVED ^{35}Cl AND ^{37}Cl ISOTOPIC SHIFTS AND ASSUMING TWO DIFFERENT BOND ANGLES OF $ClO_2F_2^+$ [a]

Assignment		Obs. freq. (cm^{-1})	Approx. description of mode
A_1	ν_1	1241	$\nu_{sym}(ClO_2)$
	ν_2	756	$\nu_{sym}(ClF_2)$
	ν_3	514	$\delta_{sym}(ClO_2)$
	ν_4	390	$\delta_{sym}(ClF_2)$
A_2	ν_5	390	τ
B_1	ν_6	1479	$\nu_{asym}(ClO_2)$
	ν_7	530	$\delta_{rock}(ClO_2)$
B_2	ν_8	830	$\nu_{asym}(ClF_2)$
	ν_9	514	$\delta_{rock}(ClF_2)$

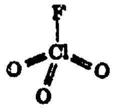
	∠OClO, ∠FClF, deg	
	124, 96	114, 105
f_D (mdyn/Å) (ClO)	12.20	12.04
f_{DD} (mdyn/Å)	−0.46	−0.68
f_R (mdyn/Å) (ClF)	4.40	4.53
f_{RR} (mdyn/Å)	−0.32	0.03

[a] Data from Christe *et al.* (*69*).

might be invoked to explain the high f_{ClO} value. The value of the ClF-stretching force constant (4.46 mdyn/Å) falls within the range expected for a predominantly covalent ClF bond in a cation having a central atom with a +VII oxidation state.

K. PERCHLORYL FLUORIDE

Perchloryl fluoride,



(XVI)

the acyl fluoride of perchloric acid, was first obtained by Bode and Klesper in 1951 (*30*) by the action of F_2 on $KClO_3$ at −40°C, but believed to be ClO_2OF. In 1952 it was prepared by Engelbrecht and Atzwanger (*91*) by electrolysis of $NaClO_4$ in anhydrous HF and was correctly identified. In the mid-fifties it became commercially available from Pennsalt Chemical Corporation and can be purchased in research quantities from Ozark Mahoning Company. Owing to its remarkably low reactivity and high specific impulse (see Section III, K, 5), it received considerable interest as a rocket propellant oxidizer, resulting in a rather thorough study of its properties. Unfortunately, its high vapor pressure (53 atm at $T_c = 95°C$) and coefficient of expansion rendered it inferior to other oxidizer candidates. Owing to its relative inertness (it hydrolyzes only slowly in water), it has found use as a fluorinating agent in organic chemistry. In addition to the general reviews, listed in the Introduction, and brief reviews in Japanese (*205*) and Chinese (*48*), reviews that are devoted exclusively to $FClO_3$ have been published by Pennsalt (*222*), Gall (*106*), and Khutoretskii *et al.* (*158*). The inertness of $FClO_3$ is due to its energetically favorable pseudotetrahedral configuration, its highly covalent and strong Cl—F bond (see Section II, C), and its extremely small dipole moment of 0.023 D. Combined, these properties give it a high kinetic stability in spite of its low thermodynamic stability ($\Delta H^\circ_{f298} = -5.7$ kcal $mole^{-1}$).

1. *Synthesis*

Perchloryl fluoride can be prepared by electrolysis of a saturated solution of $NaClO_4$ in anhydrous HF with a current efficiency of 10% (*91, 92*).

Fluorination of solid $KClO_3$ by F_2 (*30, 31*) produces $FClO_3$, $FClO_2$, ClF, Cl_2O_6, Cl_2, and O_2 (*89, 92*). The yields of $FClO_3$ were about 45% based on the F_2 used (*92*). When the fluorination was carried out below −20°C, yields of $FClO_3$ as high as 60% were obtained (*265*). The fluorination of $NaClO_3$ with F_2 can also be carried out in aqueous solution at 25°–75°C resulting in a 50% yield of $FClO_3$ (*299*; see also *125*). Replacement of F_2 by other fluorinating agents, such as ClF_3, BrF_3, or SbF_5, gives mainly $FClO_2$ and Cl_2 and only low yields of $FClO_3$ (*92*). Purification of crude $FClO_3$ by washing of the products condensible at −196°C with an alkaline $Na_2S_2O_3$ solution produces material containing less than 1.5% of impurities (*92*).

The thermal decomposition of Cl_2O_7 at 100°C in the presence of F_2 produces a mixture of $FClO_3$ and $FClO_2$ in a yield of about 75% (*98*). Similarly, the fluorination of either Cl_2O_6 or Cl_2O_7 with SbF_5 produces $FClO_3$ in high yield (*210*) according to

$$Cl_2O_6 + 2SbF_5 \longrightarrow ClO_2^+SbF_6^- + SbF_3O + FClO_3$$

and

$$Cl_2O_7 + nSbF_5 \longrightarrow SbF_3O\cdot(SbF_5)_{n-1} + 2FClO_3$$

The fluorination of NO_2ClO_4 by ClF_3 at room temperature results in the formation of $FClO_3$ and smaller amounts of $FClO_2$, ClO_2, and $ClNO_2$ (*25*). Perchloryl fluoride is also formed by the interaction of $FClO_2$ with nascent oxygen (*9*, *36*, *51*) and in the reaction of gaseous ClF_3 with UO_2, U_3O_8, and UO_3 (*149*) and with UO_2F_2 (*263*), or by the reaction of $ClF_2^+BiF_6^-$ with metal oxides (*78*). Xenon dioxide tetrafluoride, XeO_2F_4, is capable of oxidizing either ClF_3 or ClF_5 to $FClO_3$ (*143*). Almost quantitative yields of $FClO_3$ and $R_fC{\genfrac{}{}{0pt}{}{\diagup O}{\diagdown F}}$ can be obtained by the alkali metal fluoride-catalyzed decomposition of the corresponding $R_fCF_2OClO_3$ at slightly elevated temperatures (*249*).

The most convenient and commercially attractive methods for preparing $FClO_3$ involve the fluorination of perchlorates. Heating of $KClO_4$ to 70°–120°C in an excess of SbF_5 produces $FClO_3$ in 50% yield (*90*). The yield of $FClO_3$ can be increased to 90% and the reaction temperature can be lowered to 20°–50°C, when a mixture of HF–SbF_5 is used (*292*, *293*). Slightly lower yields were obtained when the HF solvent was replaced by AsF_3, IF_5, or BrF_5.

Most of the commercial processes are based on the use of $HOSO_2F$. This method was proposed in 1956 by Barth-Wehrenalp (*20*). Evolution of $FClO_3$ starts at 50°C and goes to completion at 85°–110°C. The yields of $FClO_3$ vary from 50 to 80% (*20*, *22*, *162*, *163*) and, if necessary, the $HOSO_2F$ can be regenerated (*22*). If desired, the reaction can be carried out in glass apparatus. The influence of certain additives on the yield of $FClO_3$ was studied (*81*). The addition of 5 to 25% of SbF_5 to the $HOSO_2F$ increases the yield of $FClO_3$ to 90% and higher but hinders the regeneration of $HOSO_2F$. The addition of HF–BF_3 increases the $FClO_3$ yield to 85% but requires elevated pressure. Zinc, aluminum, silver, and lead fluorides were found to decrease the yield of $FClO_3$.

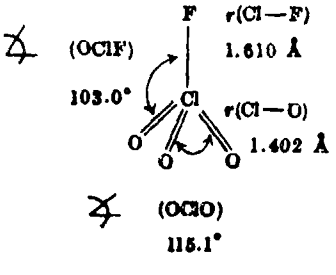
The highest yield of perchloryl fluoride (97%) was achieved with a mixture of fluorosulfonic acid and SbF_5 as fluorinating medium. Potassium, sodium, lithium, magnesium, barium, calcium, and silver perchlorates and perchloric acid itself undergo the reaction. Commercial reagents are used and their additional purification is not necessary; unlike all the previous methods the preparation of perchloryl fluoride by this method can be carried out at room temperature. At high temperature (100°–135°C) the reaction time is 1–10 min in all, which allows the process to be carried out continuously in a packed column. The purity of product obtained after the usual purification reaches 98% and over; air and carbon dioxide are present as trace impurities (*23*).

The exact mechanism of the reaction between ClO_4^- and superacids has as yet not been established, although numerous comments on it were published (*19, 21, 167, 253, 292, 297*). Based on our present understanding of superacid chemistry (*67, 118, 216*) and of the complex formation of $FClO_3$ (see Section III, K, 4), a mechanism involving ClO_3^+ as an intermediate is very unlikely. Furthermore, the high yields of $FClO_3$ (up to 97%) would be surprising in view of the expected instability of ClO_3^+. In our opinion, other mechanisms, such as the one shown, involving protonated perchloric acid (*166*) are more plausible:

$$\begin{array}{lcl}
4HF + 2SbF_5 & \longrightarrow & 2H_2F^+ + 2SbF_6^- \\
2H_2F^+ + ClO_4^- & \longrightarrow & H_2OClO_3^+ + 2HF \\
H_2OClO_3^+ + HF & \longrightarrow & FClO_3 + H_3O^+ \\
\hline
ClO_4^- + 3HF + 2SbF_5 & \longrightarrow & FClO_3 + H_3O^+ + 2SbF_6^-
\end{array}$$

2. *Molecular Structure*

The structural parameters of $FClO_3$ were determined by Clark, Beagley, and Cruickshank (*72*) by gas-phase electron diffraction. The molecule has symmetry C_{3v} and the following bond angles and distances:



(XVII)

Owing to its small dipole moment, $FClO_3$ exhibits only a very weak microwave spectrum (*171, 173*). Since only the $J = 4 \rightarrow 5$, $K = 3$ and the $J = 6 \rightarrow 7$, $K = 3$ and $K = 6$ transitions were observed, a complete structure determination was not possible. However, the estimated geometry and dipole moment are in good agreement with the exact values measured by other methods. Table XXV lists the frequency values and constants that were obtained. The rotational constants, B_0, are in good agreement with the values obtained from the high-resolution infrared spectrum (*184*) of the 549- and 589-cm^{-1} fundamentals.

The dipole moment of $FClO_3$ was determined by dielectric relaxation measurements (*192*) as 0.023 ± 0.003 D and from the $J_{11 \rightarrow 12}$ transition in a resonant cavity at 126196 MHz (*101*) as 0.025 ± 0.003 D. This low dipole moment indicates that the electronegativity of F and the ClO_3 group are comparable, thus resulting in a high degree of covalency for the Cl—F bond.

TABLE XXV

FREQUENCY VALUES AND CONSTANTS FOR PERCHLORYL FLUORIDE

Transitions and constants	$F^{35}ClO_3$ (MHz)	$F^{37}ClO_3$ (MHz)
$J = 4 \rightarrow 5, K = 3$	52585.97 ± 0.05	52560.4 ± 0.3
$J = 6 \rightarrow 7, K = 3$	73619.40 ± 0.05	73583.94 ± 0.05
$J = 6 \rightarrow 7, K = 6$	73618.72 ± 0.05	—
B_0	5258.692 ± 0.005	5256.149 ± 0.005
D_J	0.0014 ± 0.0002	
D_{JK}	0.0018 ± 0.0003	
eq$Q$	−19.2 ± 0.5	−15.4 ± 1.5

The ^{19}F NMR spectrum of $FClO_3$, according to Brownstein (*41*) consists of a partially resolved quartet ($J_{ClF} \sim 310$ Hz) of equal intensity at $\phi = -241.5$ ppm. The lack of rapid quadrupole relaxation indicates a highly symmetric electric field around the central atom in good agreement with the small dipole moment observed for $FClO_3$ (see above). The temperature dependence of the ^{19}F NMR spectrum of $FClO_3$ was studied by Bacon *et al.* (*13*). An expression for the line broadening was derived, and a value of 1.0 kcal mole^{-1} was obtained for the activation energy of molecular reorientation. A value of 278 ± 5 Hz was calculated for $J35_{ClF}$. According to Agahigian *et al.* (*1*), the ^{19}F resonance of $FClO_3$ occurs at $\phi = -287$ ppm, but measurements in our laboratory indicate that this value is inaccurate. A value of $\phi = -252.9 \pm 2$ ppm was found by us for liquid $FClO_3$ at −120°C. The ^{35}Cl and ^{19}F NMR spin-lattice relaxation times and rotational diffusion in liquid $FClO_3$ were measured by Maryott *et al.* (*96*, *191*) using pulse techniques.

The mass spectrum of $FClO_3$ was measured (*82*, *138*, *234*). The vertical ionization potential and the $F—ClO_3$ bond dissociation energy were found to be 13.6 ± 0.2 eV and ~60 kcal $mole^{-1}$, respectively. The average ClO bond dissociation energy and the heat of formation were estimated (*82*) to be 60 and −5.3 kcal $mole^{-1}$, respectively.

The UV absorption spectrum of $FClO_3$ was reported by Sicre and Schumacher (*264*) and Pilipovich *et al.* (*228*).

The vibrational spectrum of $FClO_3$ has been well characterized. The infrared spectrum was thoroughly analyzed by Lide and Mann (*174*) and two of the fundamentals (ν_3 and ν_5) were studied at high resolution by Madden and Benedict (*184*). The Raman spectra of the liquid and of the gas were reported by Powell *et al.* (*233*) and Dunlap *et al.* (*85*) and by Claassen and Appelman (*71*), respectively. The observed fundamentals together with their assignment are summarized in Table XXVI and are in excellent agreement with a molecule of symmetry C_{3v}. The infrared spectrum of $FClO_3$ has also been reported by Engelbrecht *et al.* (*92*), Pennsalt (*222*), Smith *et al.* (*271*), and Karelin *et al.* (*154*). A correlation of ClO-stretching frequencies (*236*) and force constants with bond lengths and bond orders was given by Robinson (*237*); however, his plots and assumptions must be thoroughly updated before being used. Absolute infrared intensities were reported for $FClO_3$ by Kharitonov *et al.* (*157*). Quantum mechanical studies of the atomic, bond, and

TABLE XXVI

VIBRATIONAL SPECTRUM OF GASEOUS $FClO_3$ AND ITS ASSIGNMENT FOR POINT GROUP C_{3v}

		Assignment	Infrared[a] (cm^{-1})	Raman[b] (cm^{-1})
A_1	ν_1	sym ClO_3 stretch	1061 s	1062.8, 1060.9[c] vs, p
	ν_2	ClF stretch	717 s, 707 m	716.8, 706.6 s, p
	ν_3	sym ClO_3 deform.	549 w	548.8 m, p
E	ν_4	asym ClO_3 stretch	1315 vs	1314 w
	ν_5	asym ClO_3 deform.	589 m	573 w
	ν_6	rocking	405 w	414 w

[a] Data from Lide and Mann (*174*).

[b] Data from Claassen and Appelman (*71*).

[c] Splittings are due to ^{35}Cl and ^{37}Cl isotopes.

molecular polarizabilities were carried out by Nagarajan and Redmon (*204*). Numerous force fields (*107*, *140*, *154*, *157*, *201*, *204*, *245*, *273*) were computed for $FClO_3$, but owing to the lack of sufficient experimental data, no unique solution was obtained. Values of about 9.4 and 3.9 mdyn/Å for the ClO- and the ClF-stretching force constants, respectively, appear to us most reasonable. Mean square amplitudes of vibration of $FClO_3$ were calculated by Müller *et al.* (*201*, *203*) and Nagarajan and Redmon (*204*). Müller *et al.* (*201*) have also computed the Coriolis zeta constants for $FClO_3$; however, their values differ significantly from those given by Hoskins (*140*). Molecular reorientation in liquid $FClO_3$ was studied by Sunder and co-workers (*279a*) using Raman spectroscopy.

The high-resolution photoelectron spectrum of $FClO_3$ was studied by DeKock *et al.* (*80*). The results from this study, including *ab initio* SCF MO calculations of the electronic structures, are summarized in Tables XXVII and XXVIII. These calculations indicate considerable participation by 3d orbitals of the Cl atom, although they tend to overestimate the importance of 3d orbitals in bonding by correcting for some inade-

TABLE XXVII

IONIZATION DATA FOR PERCHLORYL FLUORIDE[a,b]

Band No.	Adiabatic i.p. (eV)	Vertical i.p. (eV)	Vibrational spacing (cm^{-1})	Vibrational assignment	Orbital assignment
1	13.04 (1)	—	370 (40)	ν_3 or ν_4	$6b_2$
	13.57 (2)	—	475 (60)	ν_3	$2a_2$
2	14.85 (1)	15.181 (6)	340 (16)	ν_4	$6b_1$
	15.181 (6)	15.307 (6)	1025 (30)	ν_1	$11a_1$
3	16.676 (5)	16.676 (5)	1135 (16)	ν_1	$5b_2$
			805 (30)	ν_2	
			510 (20)	ν_3	
4	18.07 (3)	18.31 (2)	—	—	$5b_1$
5	19.175 (7)	19.390 (4)	850 (30)	ν_2	$4b_2$
			485 (40)	ν_3	
	19.699 (7)	19.807 (7)	855 (30)	ν_2	$9a_1$
			500 (20)	ν_3	
6	—	21.7 (1)	—	—	$4b_1$
7	—	24.2 (1)	—	—	$8a_1$
		Ground state	1269	ν_1	
			848	ν_2	
			544	ν_3	
			384	ν_4	

[a] Data from DeKock *et al.* (*80*).

[b] Standard deviations are given in parentheses after each quantity.

TABLE XXVIII

CALCULATED EIGENVALUES AND PERCENTAGE CHARACTER OF VALENCE MOLECULAR ORBITALS FOR $FClO_3$[a]

Orbital	Eigenvalue (eV)	Atomic character (%)						
		Chlorine orbital			Oxygen orbital		Fluorine orbital	
		3d	3s	3p	2s	2p	2s	2p
$1a_2$	−12.9	—	—	—	—	100	—	—
7e	−14.1	10.5	—	—	—	78.0	—	11.0
$10a_1$	−15.4	12.6	—	1.9	1.1	44.3	—	39.8
6e	−16.0	16.5	—	—	5.3	74.0	—	3.9
5e	−18.6	9.2	—	1.8	1.3	18.7	—	68.9
4e	−21.5	4.3	—	24.8	19.1	38.0	—	13.3
$9a_1$	−23.3	1.1	4.1	34.1	16.8	29.4	2.6	11.4
$8a_1$	−26.2	—	18.2	10.0	34.2	12.3	7.6	17.2
3e	−40.6	2.9	—	24.5	66.7	5.0	—	—
$7a_1$	−43.0	2.4	3.9	8.1	14.0	1.9	68.7	—
$6a_1$	−47.6	—	44.7	—	29.2	6.5	17.5	1.6

[a] Data from DeKock *et al.* (*80*)

quacy in the s and p bases. Results of MO calculations were also reported by Hillier *et al.* (*129*, *139*) and Ionov and Ionova (*146*). The latter authors calculated the electron density distribution in $FClO_3$ as $Q_{Cl} = +0.83$, $Q_O = -0.23$, and $Q_F = -0.14$, using the geometry, the ionization potential of the molecule and of the free atoms, and the orbital exponents of the Slater functions as input data.

X-Ray diffraction data were reported by Tallman *et al.* (*280*, *281*) for solid $FClO_3$ at liquid air temperature. The data were indexed in terms of a tetragonal unit cell with $a = 7.66$ and $c = 5.31$ Å, $Z = 4$, and $d = 2.18$ gm/cm^3. Barberi (*16*, *17*) has shown that solid $FClO_3$ exists between its melting point and −196°C in only one solid phase. Based on entropy calculations, Koehler and Giauque (*160*) suggested that there is a high degree of disorder in the arrangement of the F and O atoms in crystallinic $FClO_3$.

3. *Physical Properties*

Some of the physical properties of $FClO_3$ are summarized in Table XXIX. In the Appendix (Table AIII), the temperature dependence of some of the thermodynamic properties is given (*147*). In addition to these data, the viscosity of gaseous $FClO_3$ between 50 and 150°C was reported

(*218*). Some thermodynamic properties of $FClO_3$ were calculated (*235*) using only the boiling point of the compound and correlation increments.

Perchloryl fluoride is white as a solid and colorless as a liquid and gas. It possesses a characteristic sweetish odor (*92*). Its toxicity is moderate and comparable to that of CH_2CHCN or Cl_2. Tests on mice showed an acute vapor toxicity (LD_{50}) of 630 ppm at 4-hr exposure time. Exposure of monkeys to 40 ppm $FClO_3$ in air for 3 months resulted in enlarged spleens and lungs together with some evidence of red cell destruction (*222*).

The dielectric strength of $FClO_3$ is outstanding and over a broad pressure range is about 30% higher than that of SF_6. During irradiation with ^{60}Co γ-rays, the dielectric strength decreased only by 5% (*46*). The correlation between negative-ion formation and electric breakdown of $FClO_3$ was studied by Hickam and Berg (*138*) by mass spectroscopy. Perchloryl fluoride has been used as an insulator in high-voltage systems.

Perchloryl fluoride was reported (*185*, *195*, *205*, *206*, *222*) to be sparingly soluble (1–3 gm/liter at 1 atm and 25°C) in a wide variety of polar and nonpolar solvents, such as aqueous solutions, alcohols, ketones, esters, ethers, and aromatic and halogenated solvents. However, more recent measurements by Golub *et al.* (*124*) show that these solubilities are substantially (several-fold) higher. When working with larger amounts of $FClO_3$ in organic solvents, all necessary precautions should be taken since mixtures of this kind are potentially explosive. Hammond *et al.* (*132–134*) have extensively studied the extremely weak electron acceptor–donor (ball-plane) interactions between $FClO_3$ and aromatic hydro- and fluorocarbons. Several inorganic acid halides, $HOSO_2F$, PCl_3, $POCl_3$, SO_2Cl_2, $SOCl_2$, $TiCl_4$, and $SiCl_4$ dissolve gaseous $FClO_3$ to the extent of 20–30 gm/liter at 25°C and 1 atm pressure (*106*).

Liquid perchloryl fluoride is a typical nonpolar solvent. Most inorganic and organic salts are insoluble in it. Conversely, most covalent, essentially nonpolar substances, boiling within about 50°C of perchloryl fluoride, are completely miscible, e.g., chlorine, boron trifluoride, sulfur hexafluoride, silicon tetrafluoride, phosgene, nitrous oxide, chlorine trifluoride, chlorofluorocarbons, silicon tetrachloride, sulfuryl chloride, dinitrogen tetroxide, and thionyl chloride (*106*).

Blends of perchloryl fluoride with halogen fluorides are homogeneous and stable. When these are used as storable liquid oxidizers for rocket propulsion, the halogen fluoride usually confers hypergolicity, increased density, and lowered vapor pressure; whereas the perchloryl fluoride provides oxygen needed for efficient combustion of carbon in the fuel or of certain metal additives. The mixtures are thermally stable and their

TABLE XXIX

SOME PHYSICAL PROPERTIES OF $FClO_3$

Property	Value	Ref.
Melting point	−147.75°C	(*92*, ***160***[a])
Boiling point	−46.67°C	(*30*, *92*, ***160***)
T_{crit}	95.17°C	(*92*, *100*, ***148***)
P_{crit}	53.0 atm	(*148*)
Crit. density	0.637 gm cm^{-3}	(***92***, *100*)
Crit. molar volume	161 cm^3	(*92*)
Vapor pressure (for $T = -109°$ to -44°C)	$\text{Log } P(\text{mm}) = -1652.3/T(°K) -8.62625 \log T +0.0046098T +28.44780$	(*92*, *148*, ***160***)
Density of solid (−190°C)	2.19 gm cm^{-3}	(*261*)
Density of liquid (for $T = -142°$ to −39°C)	$\rho(\text{gm cm}^{-3}) = 2.266 - 1.603 \times 10^{-3}T -4.080 \times 10^{-6}T^2(°K)$	(*92*, *100*, ***148***, *222*)
(for $T = 29.9°$ and 53.8°C)	$\rho(\text{gm cm}^{-3}) = 1.390$ and 1.276	(*268*)
Viscosity of liquid (for $T = -77°$ to 54°C)	$\text{Log } \eta = 299\ T^{-1} - 1.755$ (centipoise)	(*222*, ***268***)
Surface tension (for $T = -75.2°$ to −55.6°C)	24.1 to 21.3 dyn cm^{-1}	(*268*)
ΔH_{fusion}	0.9163 kcal mole^{-1}	(*16*, *17*, ***160***)
ΔS_{fusion}	7.12 e.u.	(*16*, *17*)
ΔS_{vap} (−46.67°C)	4.619 kcal mole^{-1}	(*30*, *92*, *148*, ***160***)
Trouton constant	20.395 e.u.	(*30*, *92*, ***160***)
ΔH°_{f298} (g)	−5.7 kcal mole^{-1}	(*15–18*, *82*, *204*, ***291***)
ΔG°_{f298} (g)	11.5 kcal mole^{-1}	(*291*)
S°_{298}	66.65 e.u.	(*147*, *148*, *172*, *208*, ***291***)
$C_{p\ 298}$ (g)	15.517 e.u.	(*147*, ***160***, *204*, *291*)
$C_{p\ 298}$ (l)	27.19 e.u.	(***150***, *160*)
Specific heat ratio, C_p/C_v, gas at 25°C	1.12	(*174*, ***189***)

[a] Bold face reference number indicates reference from which the listed value is quoted.

compatibility with container materials is determined mainly by the halogen fluoride. The density and vapor pressure of perchloryl fluoride-chlorine trifluoride blends have been summarized in tables by Gall (*106*). The miscibility and compatibility of $FClO_3$ at low temperatures was studied by Streng (*277*) for O_2, O_3, O_2F_2, ClF, ClF_3, SF_4, SF_6, CF_3Cl, and C_4H_{10}.

4. *Chemical Properties*

Owing to its pseudotetrahedral configuration, its highly covalent strong Cl—F bond, and low dipole moment, $FClO_3$ possesses high kinetic stability in spite of ΔH_f^0 being only −5.7 and ΔG_f^0 being positive (11.5 kcal mole^{-1}). This is reflected in its high thermal stability and its reluctance to hydrolyze. It is not shock-sensitive and at room temperature is relatively inert. At elevated temperature, however, or under conditions supplying a sufficient amount of activation energy, it is a powerful oxidizer (*211*).

Perchloryl fluoride is thermally stable up to about 400°C. The thermal decomposition of $FClO_3$ in quartz at pressures between 5 and 930 mm and temperatures between 465° and 495°C was studied by Gatti *et al.* (*112*). They found that the decomposition reaction,

$$2FClO_3 \longrightarrow 2ClF + 3O_2$$

is unimolecular and homogeneous with an activation energy of 58.4 ± 2 kcal mole^{-1}. The rate constant at 495.4°C was found to be $k = 9.25 \times 10^{-4}$ sec^{-1} and the following decomposition mechanism was suggested:

$$\begin{aligned} FClO_3 &\longrightarrow FClO_2 + O \\ O + FClO_3 &\longrightarrow FClO_2 + O_2 \\ FClO_2 &\longrightarrow ClF + O_2 \end{aligned}$$

The decomposition kinetics were also calculated by Usmanov and Magarra (*287*) using a dimensionless molecular transfer equation. Perchloryl fluoride can be heated almost to the softening point of glass without explosion (*92*).

Hydrolysis of $FClO_3$ is very slow even at 250°–300°C (*92*). For quantitative hydrolysis, heating of $FClO_3$ with concentrated aqueous hydroxide solution to 300°C in a sealed tube is required:

$$FClO_3 + 2NaOH \longrightarrow NaClO_4 + NaF + H_2O$$

For quantitative analysis, $FClO_3$ can conveniently be reduced at 25°C by an alcoholic solution of KOH resulting in dissolved KF and a precipitate of $KClO_4$ (*222*).

The reaction of $FClO_3$ with metallic sodium or potassium starts only at ~300°C, although it proceeds vigorously (*92*). At room temperature $FClO_3$ is unreactive with a considerable number of gases, liquids, and solids. Again, however, if sufficient activation energy, such as heating to 100°–300°C, is supplied, violent reactions usually occur. With reducing agents, oxides, fluorides, and chlorides are formed. Typical examples are H_2, N_2O, H_2S, SO_2, SCl_2, PCl_3, CaC_2, KCN, NaI, KSCN, $CH_2{=}CCl_2$, and hydrocarbons (*122, 158, 222*). Using dilute mixtures, the H_2S-$FClO_3$ reaction can be controlled and the following products are obtained (*222*):

$$3FClO_3 + 4H_2S \longrightarrow 4SO_2 + 3HF + 3HCl + H_2O$$

In the spectra of H_2S–$FClO_3$ and H_2–$FClO_3$ flames, bands due to S_2, SO_2, OH and to ClO, OH, respectively, were observed (*177*). With HCl at 200°–300°C, the following gas-phase reaction occurs:

$$FClO_3 + 7HCl \longrightarrow HF + 4Cl_2 + 3H_2O$$

Many inorganic ions are oxidized by $FClO_3$ in aqueous solution (*112*). The oxidation rate often depends on the pH of the solution and the temperature. For example: the oxidation of KI in the presence of $NaHCO_3$ is barely detectable; in caustic soda, a slow oxidation occurs; and in 0.1 *M* mineral acid one observes (*92*) quantitative reaction within 4 hr according to

$$FClO_3 + 8I^- + 6H^+ \longrightarrow Cl^- + F^- + 4I_2 + 3H_2O$$

Other ions oxidized by $FClO_3$ include NO_2^-, SO_3^{2-}, and CN^- which are converted to NO_3^-, SO_4^{2-}, and NCO^-, respectively (*106*, *122*, *222*).

Whereas $FClO_3$ is rather inert toward most compounds, including gaseous NH_3, at room temperature it reacts (*92*, *186*, *187*) easily with liquid NH_3 at −78°C or its aqueous solutions:

$$FClO_3 + 3NH_3 \longrightarrow NH_4F + NH_4NHClO_3$$

The reaction is complete in several hours and, in liquid NH_3, it is greatly accelerated by $NaNH_2$ (*186, 187*). From the ammonium perchloryl amide, which could not be isolated in pure form, the corresponding Ag^+, Cs^+, and K^+ salts and K_2NClO_3 and Cs_2NClO_3 have been obtained. These salts, especially when dry, are impact- and friction-sensitive.

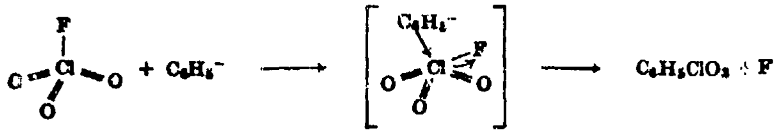
Perchloryl fluoride does not attack glass at moderate temperature, but decomposes at 25°C on contact with activated SiO_2 or Al_2O_3, particularly in the presence of small amounts of H_2O. With other surface-active materials, such as charcoal, ignition may take place. However, there is no reaction at room temperature with synthetic zeolites. It passes freely through a 4 Å molecular sieve, but is completely absorbed by a 5 Å molecular sieve (*188*). Most combustible substances in contact with liquid $FClO_3$ form shock-sensitive explosive compositions. Generally, metal oxides, fluorides, or chlorides do not react with $FClO_3$ at temperatures up to 400°C (*186*). Lalande reported (*164*) that $FClO_3$ oxidizes UF_4 to UF_6. However, a subsequent study by Rude *et al.* (*241*) showed that an intermediate uranium oxyfluoride that disproportionates to UF_6 and UO_2F_2 is formed. Photolysis of mixtures of $FClO_3$ with F_2 or ClF_5 produces ClF_3O (*228, 240*).

Perchloryl fluoride shows no tendency to form adducts with either strong Lewis acids or bases. This behavior has been rationalized in Section II, D. The binary systems of $FClO_3$ with BF_3, PF_5, AsF_5, SbF_5, or SO_3 were studied by Lang (*167*), at Pennsalt (*224*), and by Nikitina and Rosolovskii (*209*). Similarly, at Pennsalt (*224*) no evidence was found for complexing of $FClO_3$ with either CsF or FNO_2.

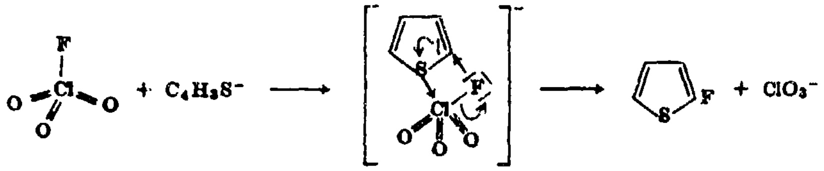
Anhydrous $FClO_3$ does not corrode most of the common metals, but, in the presence of moisture, slow hydrolysis may occur causing corrosion (*40, 122, 127, 222*). The compatibility of various elastomers with 1:1 mixtures of $FClO_3$ and N_2F_4 was studied by Green *et al.* (*126*) and Grigger *et al.* (*127*).

In reactions with organic compounds, $FClO_3$ behaves as either an oxidant or a 1- or 2-center electrophile which, depending on the reaction conditions, can be used for the introduction of either fluorine, a ClO_3 group, or both fluorine and oxygen. A large number of publications have appeared on this subject and have been extensively reviewed by Khutoretskii *et al.* (*158*). Additional general information can be found in Refs. (*106, 122, 169, 262,* and *284*). Since a systematic coverage of this subject is beyond the scope of this review, we give examples only of the most important type of reactions, in addition to references to some of the more recent publications not covered in the previous reviews.

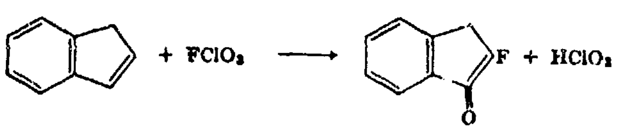
Since $FClO_3$ is highly susceptible to nucleophilic attack at the chlorine atom, it reacts readily with anions. These reactions are relatively well-understood, and Sheppard has proposed (*261*) a general mechanism for these reactions by which the most nucleophilic center in the anion (oxygen or other heteroatom related to carbon) always attacks the chlorine and never the more electronegative fluorine. For localized nucleophiles (such as alkoxides), simple fluoride ion displacement occurs, but, for the mesomeric ions (ambient electrophiles), an intramolecular (cyclic) transfer of F^- can occur in the intermediate to give a C—F bond. The high energy gained by the formation of the C—F bond provides a strong driving force for this fluoride transfer, and fluorine never has to achieve a highly unfavorable energy state with positive charge. This mechanism explains why phenyllithium reacts with $FClO_3$ to give perchloryl benzene, whereas 2-lithiothiophene gives 2-fluorothiophene in high yield (*257*):



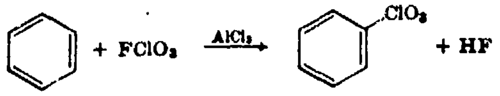
and



Compounds having a cyclic double bond conjugated with an aromatic ring are capable of reacting with $FClO_3$ to give α-fluoroketones. This type of reaction was named oxofluorination and in it $FClO_3$ acts as a 2-center electrophile as shown for indene (*207*):



In the presence of Friedel–Crafts catalysts, such as $AlCl_3$, the $FClO_3$ can be used for introducing a ClO_3 group (perchlorylation) into an aromatic ring (*144*):

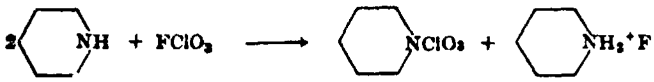


Hydrogenolysis (*258*) of perchloryl aromatic compounds yields ArH and not ArOH, thus confirming the presence of a C—Cl bond. Another useful reaction of $FClO_3$ involves the replacement of the active hydrogens of methylene compounds by fluorine (*145*, *262*, *284*). A typical example is the fluorination of malonic esters:

$$CH_2(COOR)_2 \xrightarrow{+FClO_3} CF_2(COOR)_2$$

Since $FClO_3$ is a very mild fluorinating agent, it has found widespread use for the selective fluorination of compounds such as steroids.

The reaction of cyclic amines with $FClO_3$ is similar to that of $FClO_3$ with NH_3 (see above). For example, the following reaction takes place with piperidine (*110*):



(For additional recent publications dealing with the use of $FClO_3$ as a reagent for the synthesis of organic compounds, see Refs. *94*, *103*, *111*, *114–116*, *153*, *159*, *212*, *213*, *217*, *250*, *286*, *289* and *290*.)

5. *Uses*

The most thoroughly studied application of $FClO_3$ is its use as an oxidant. The spectra of fuel–$FClO_3$ flames were studied (*177*), and the flame speed in mixtures of CH_4 with air and $FClO_3$ was measured (*131*). The H_2–$FClO_3$ flame was found (*251*) to be readily controllable with a low background and useful as an excitation source for flame photometry. For rocket propulsion, the performance of either neat $FClO_3$ or combinations with other oxidizers, such as halogen fluorides (*11*, *26*), was studied and typical performance data (*106*) are given in Table XXX. Small amounts of ClF_3 can be added to neat $FClO_3$ to provide self-ignition. The performance of $FClO_3$ as an oxidizer is similar to that of N_2O_4 (*106*, *136*), and the burning rate of solid propellants is increased by $FClO_3$ (*267*). It has also been proposed to use an acetylene–$FClO_3$ torch

TABLE XXX

PERFORMANCE OF SELECTED STORABLE LIQUID OXIDIZERS FOR ROCKET PROPULSION[a]

Oxidizer	Fuel	Specific impulse[b] (sec)	Density impulse (gm sec/cm^3)
$FClO_3$	UDMH[c]	290	337
ClF_3	UDMH	279	382
65 ClF_3/35 $FClO_3$	UDMH	288	386
$FClO_3$	LiH solid[d]	273	337
ClF_3	LiH solid	288	436
88 ClF_3/12 $FClO_3$	LiH solid	291	433
$FClO_3$	N_2H_4	295	358
ClF_3	N_2H_4	292	436
N_2O_4	N_2H_4	291	354

[a] Data from Gall (*106*).

[b] Pound force × sec/lb mass; shifting equilibrium; pressure ratio 1000:14.7

[c] Unsymmetrical dimethylhydrazine.

[d] LiH, 85%; organic binder, 15%.

for cutting and welding of metals, in the Sterling cycle engine, in high-pressure gas generation for turbine drive, in fuel cells, and in explosives similar to Sprengel liquid O_2–carbon powder combinations (*105*), and as a deodorant in aerosol sprays (*170*). However, the latter application appears very doubtful in view of the substantial toxicity of $FClO_3$ (see above).

The use of $FClO_3$ as a chemical reagent for the introduction of fluorine or a ClO_3 group has been discussed in detail in Section III, K, 4 and is of special value for the synthesis of fluorine-containing steroids. The polymerization of ethylene under a pressure of hundreds of atmospheres and a temperature of about 200°C in the presence of $FClO_3$ has been patented (*135*).

There are patents on the use of $FClO_3$ as a heat transfer medium in refrigeration (*165*) and as an insecticide–fungicide (*123*). Owing to its ability to absorb intensively slow electrons (*138*), $FClO_3$ can be used as a gaseous insulator. Its dielectric properties are superior to those of SF_6, and it hardly deteriorates on exposure to γ-irradiation (*104*).

General information on shipping, handling, safety, etc., of $FClO_3$ can be found in Gall's review (*106*).

L. Chlorine Fluoride Oxide Radicals

Very little is known about chlorine fluoride oxide radicals. Although the formation of the $FClO_3^-$ radical anion in the reaction of $FClO_3$ with nucleophilic agents has been postulated (*286*), it has not been isolated and characterized.

The only well-known species is the $FClO^+$ radical cation. The ESR spectrum of this species was first reported by Olah and Comisarow (*214*, *215*) for both the ClF_3–SbF_5 and the ClF_5–SbF_5 system. However, the spectrum was incorrectly interpreted in terms of a ClF^+ radical cation. Eachus, Slight, and Symons (*86*) suggested that the observed spectrum is due to $FClO^+$ and not to ClF^+. This conclusion was supported by Christe and Muirhead (*62*) who showed that, in the pure ClF_3–SbF_5 and ClF_5–SbF_5 systems, this species could not be observed but was generated by impurities in the starting materials. Additional evidence for this species containing oxygen was obtained by Gillespie and Morton (*121*) who investigated the reaction of ClF and of Cl_2–ClF with the superacid medium HSO_3F–SbF_5–SO_2. It was shown that the addition of H_2O to solutions of $ClF_2^+SbF_6^-$ in SbF_5 strongly enhanced the ESR signal attributed to ClF^+ by Olah and Comisarow. They suggested that the species was due either to $FClO^+$ or $FClO_2^+$, although their attempts to detect ^{17}O hyperfine splitting in a sample treated with enriched water were unsuccessful. The conclusive identification of this species was recently reported by Morton and Preston (*199*). By using ^{17}O substitution techniques, they succeeded in proving that the species contains 1 oxygen atom and is best described as $FClO^+$. This radical cation is characterized by its g value of 2.0059 and the following hyperfine interactions: $a_{17} = 18.0$, $a_{19} = 20.4$, and $a_{35} = 12.9$ G.

During a matrix-isolation infrared study of the F_2–Cl_2O and ClF–O_2 systems, a new species was observed by Andrews *et al.* (*5*) at 733.8 cm^{-1} which was tentatively assigned to the $ClF_2O\cdot$ radical. However, more data are needed for the positive identification of this species.

M. MISCELLANEOUS

The ClO_3F^{2-} anion has been reported by Mitra and Ray (*197*). However, in our opinion their claim is almost certainly incorrect.

A compound of the empirical composition FCl_2O_6 was claimed by DeGuevara (*79*). The following self-explanatory abstract of this patent was found in *Chemical Abstracts* and, we are confident, will be enjoyed by the more knowledgeable readers:

> The title compd. which is claimed to be novel is prepd. by reacting in a hermetically sealed flask 500 ml. 55° Be H_2SO_4, $Ca(OCl)_2$ 5–10, $KClO_2$ 9–20, $KClO_3$ 10–20, and $Mg(ClO_4)_2$ 10–20 g. Cl and a Cl oxide are given off, washed, and collected as a stabilized aq. soln. Simultaneously, F is produced from CaF_2 and H_2SO_4 and washed and dried. The F is passed into the stabilized aq. soln. of FCl_2O_6, which is suitable for use as an antiseptic, preservative, and purifier in the food, wine, perfume, and water industries and as a humectant and bleach for textiles.

IV. Appendix: Tables of Thermodynamic Properties for Some Chlorine Oxyfluorides

TABLE AI

THERMODYNAMIC PROPERTIES FOR ClF_3O GAS[a]

T(°K)	C_p^0 [cal/(mole deg)]	H^0–H_0^0 (kcal/mole)	–(F^0–H_0^0)/T [cal/(mole deg)]	S^0 [cal/(mole deg)]
0	0	0	0	0
100	9.721	0.837	49.255	57.624
200	14.932	2.072	55.613	65.971
298.15	18.593	3.732	60.159	72.675
300	18.646	3.766	60.237	72.790
400	20.875	5.751	64.108	78.486
500	22.260	7.913	67.478	83.305
600	23.160	10.187	70.470	87.448
700	23.771	12.536	73.159	91.067
800	24.200	14.936	75.602	94.271
900	24.512	17.372	77.838	97.141

TABLE AI—*continued*

$T(°K)$	C_p^0 [cal/(mole deg)]	$H^0 - H_0^0$ (kcal/mole)	$-(F° - H_0^0)/T$ [cal/(mole deg)]	S^0 [cal/(mole deg)]
1000	24.744	19.835	79.900	99.736
1100	24.921	22.319	81.813	102.103
1200	25.059	24.818	83.595	104.277
1300	25.168	27.330	85.265	106.288
1400	25.256	29.851	86.834	108.156
1500	25.328	32.380	88.314	109.901
1600	25.387	34.916	89.715	111.538
1700	25.437	37.458	91.044	113.078
1800	25.479	40.003	92.309	114.533
1900	25.514	42.553	93.516	115.912
2000	25.545	45.106	94.668	117.221

[a] Data from Christe and Curtis (*55*).

TABLE AII

THERMODYNAMIC PROPERTIES FOR ClF_3O_2 GAS[a]

$T(°K)$	C_p^0 [cal/(mole deg)]	$H^0 - H_0^0$ (kcal/mole)	$-(F° - H_0^0)/T$ [cal/(mole deg)]	S^0 [cal/(mole deg)]
0	0	0	0	0
100	10.127	0.847	48.967	57.437
200	16.511	2.179	55.516	66.411
298.15	21.256	4.049	60.375	73.956
300	21.327	4.089	60.459	74.088
400	24.384	6.386	64.711	80.675
500	26.362	8.930	68.484	86.344
600	27.685	11.636	71.881	91.275
700	28.599	14.453	74.968	95.615
800	29.251	17.347	77.795	99.479
900	29.727	20.298	80.400	102.953
1000	30.085	23.289	82.816	106.105
1100	30.360	26.312	85.066	108.985
1200	30.574	29.359	87.171	111.637
1300	30.745	32.425	89.148	114.091
1400	30.833	35.507	91.012	116.375
1500	30.995	38.601	92.775	118.509
1600	31.089	41.705	94.447	120.513
1700	31.167	44.818	96.036	122.400
1800	31.233	47.938	97.551	124.183
1900	31.289	51.064	98.997	125.873
2000	31.337	54.196	100.382	127.480

[a] Data from Christe and Curtis (*57*).

TABLE AIII: THERMODYNAMIC PROPERTIES FOR $FClO_3$ GAS[a]

	cal mole^{-1} deg^{-1}			kcal mole^{-1}			
T(°K)	C_p°	S°	$-(F^\circ-H^\circ_{298})T$	$H^\circ-H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K_P
0	0.000	0.000	Infinite	−3.178	−3.034	−3.034	Infinite
100	8.462	54.278	78.032	−2.375	−3.996	1.097	−2.397
200	12.073	61.160	67.968	−1.362	−4.715	6.493	−7.095
298	15.517	66.653	66.653	0.000	−5.120	12.090	−8.861
300	15.573	66.749	66.653	0.029	−5.125	12.196	−8.884
400	18.152	71.602	67.297	1.722	−5.298	18.002	−9.835
500	20.000	75.863	68.593	3.635	−5.312	23.831	−10.416
600	21.319	79.633	70.125	5.704	−5.226	29.653	−10.801
700	22.271	82.994	71.728	7.886	−5.076	35.455	−11.069
800	22.967	86.016	73.328	10.150	−4.884	41.231	−11.263
900	23.487	88.753	74.893	12.474	−4.665	46.983	−11.408
1000	23.883	91.249	76.405	14.843	−4.426	52.710	−11.519
1100	24.189	93.540	77.860	17.248	−4.175	58.410	−11.604
1200	24.430	95.655	79.256	19.679	−3.914	64.090	−11.672
1300	24.624	97.619	80.594	22.132	−3.349	69.746	−11.725
1400	24.780	99.449	81.876	24.602	−3.382	75.380	−11.767
1500	24.909	101.164	83.106	27.087	−3.112	80.998	−11.801
1600	25.016	102.775	84.285	29.584	−2.843	86.596	−11.828
1700	25.105	104.294	85.418	32.090	−2.574	92.179	−11.850
1800	25.181	105.731	86.507	34.604	−2.311	97.744	−11.867
1900	25.246	107.094	87.555	37.125	−2.051	103.297	−11.881
2000	25.301	108.391	88.564	39.653	−1.795	108.833	−11.892
2100	25.349	109.626	89.538	42.185	−1.544	114.359	−11.901
2200	25.391	110.807	90.478	44.723	−1.300	119.871	−11.908
2300	25.428	111.936	91.387	47.264	−1.060	125.374	−11.913
2400	25.461	113.019	92.266	49.808	−0.828	130.868	−11.917
2500	25.489	114.059	93.117	52.356	−0.605	136.347	−11.919
2600	25.515	115.059	93.942	54.906	−0.386	141.823	−11.921
2700	25.538	116.023	94.742	57.458	−0.176	147.289	−11.922

2800	25.558	116.952	95.518	60.013	0.027	152.747	−11.922
2900	25.577	117.849	96.273	62.570	0.223	158.199	−11.922
3000	25.593	118.716	97.007	65.129	0.411	163.641	−11.921
3100	25.608	119.556	97.721	67.689	0.593	169.082	−11.920
3200	25.622	120.369	98.416	70.250	0.767	174.513	−11.918
3300	25.635	121.158	99.093	72.813	0.935	179.937	−11.916
3400	25.646	121.923	99.753	75.377	1.095	185.360	−11.914
3500	25.657	122.667	100.398	77.942	1.249	190.776	−11.912
3600	25.666	123.390	101.026	80.508	1.396	196.192	−11.910
3700	25.675	124.093	101.640	83.075	1.537	201.600	−11.907
3800	25.683	124.778	102.240	85.643	1.673	207.009	−11.905
3900	25.691	125.445	102.827	88.212	1.803	212.404	−11.902
4000	25.698	126.096	103.400	90.782	1.926	217.803	−11.900
4100	25.704	126.730	103.961	93.352	2.043	223.200	−11.897
4200	25.711	127.350	104.511	95.922	2.156	228.592	−11.894
4300	25.716	127.955	105.049	98.494	2.264	233.986	−11.892
4400	25.721	128.546	105.577	101.066	2.366	239.370	−11.889
4500	25.726	129.124	106.093	103.638	2.464	244.755	−11.886
4600	25.731	129.690	106.600	106.211	2.558	250.143	−11.884
4700	25.735	130.243	107.097	108.784	2.646	255.525	−11.881
4800	25.739	130.785	107.585	111.358	2.731	260.904	−11.879
4900	25.743	131.316	108.064	113.932	2.812	266.277	−11.876
5000	25.747	131.836	108.534	116.507	2.889	271.652	−11.873
5100	25.750	132.346	108.996	119.082	2.961	277.029	−11.871
5200	25.753	132.846	109.450	121.657	3.030	282.399	−11.868
5300	25.756	133.336	109.896	124.232	3.097	287.779	−11.866
5400	25.759	132.818	110.335	126.808	3.158	293.140	−11.863
5500	25.762	134.290	110.766	129.384	3.220	298.518	−11.861
5600	25.765	134.755	111.190	131.960	3.274	303.881	−11.859
5700	25.767	135.211	111.608	134.537	3.327	309.248	−11.857
5800	25.769	135.659	112.019	137.114	3.378	314.621	−11.855
5900	25.771	136.099	112.423	139.691	3.425	319.982	−11.852
6000	25.773	136.533	112.821	142.268	3.470	325.349	−11.850

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[a] JANAF Thermochemical Tables (*147*).

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SHORT COMMUNICATION

Some Observations on the Reaction Chemistry of Dioxygenyl Salts and on the Blue and Purple Compounds Believed to be ClF_3O_2

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During our studies of dioxygenyl compounds [1-3] we have also explored the synthetic usefulness of O_2^+ salts for the generation of F atoms at low temperature. Displacement reactions between $O_2^+MF_6^-$ and suitable amphoteric molecules produces free O_2F radicals which can readily decompose to O_2 and atomic F [4] as shown by the following typical example

$$ClF_3O + O_2^+SbF_6^- \rightarrow ClF_2O^+SbF_6^- + O_2F^\cdot$$
$$O_2F^\cdot \rightarrow O_2 + F^\cdot$$

This method of in situ generation of F atoms is superior to uv-photolysis if one of the desired products is unstable towards uv-radiation. Furthermore, O_2^+ salts can readily be synthesized [5,6] in large quantities and, hence, F atoms can be generated in this way more economically and at lower temperatures than by the thermal decomposition of compounds, such as KrF_2. While our study of this method so far has not produced any new high oxidation state compounds, interesting observations were made which provide a better understanding of the nature of the violet and blue unstable compounds, first reported in 1962 by Streng and Grosse [7].

The deep violet compound was obtained [7] by the reaction of O_2F_2 with ClF at -133 to -154°. This compound was a strong oxidizer and was stable at -78°. It was soluble in anhydrous HF at -78° and was not an electrolyte. Its thermal decomposition was suppressed by oxygen. Based on the observed stoichiometry of the overall reaction

$$O_2F_2 + ClF \rightarrow ClF_3 + O_2$$

the violet compound was postulated to have the composition $(ClF_3O_2)_n$. The same material was also obtained by the interaction of O_2F_2 with Cl_2 or HCl or by uv-photolysis of mixtures of ClF_3 and O_2 at -78° [7-9]. The violet compound could be converted into a blue compound by treatment with ClF at -133° or by pumping off the oxygen decomposition product from the violet HF solution at -78° [8]. Similar violet unstable compounds were also observed in the reactions of O_2F_2 with either BrF_3 or SF_4 producing $BrF_5 + O_2$ and $SF_6 + O_2$, respectively [8]. However, no inferences were drawn that the unstable violet intermediate formed in all of these reactions might be identical, and was explained in terms of the compounds ClF_3O_2, BrF_5O_2, and SF_6O_2, respectively [8].

The nature of these violet and blue compounds was studied by Gardiner and Turner [10,11] by infrared and visible spectroscopy. The violet and the blue compound exhibited an infrared absorption at 1535 and 1027 cm^{-1}, respectively, and were interpreted in terms of the peroxides F_2ClOOF and $F_2ClOOClF_2$, respectively [10]. Evidence was also found [11] for the existence of an oxygen pressure dependent equilibrium between the violet and the blue compound

$$\text{violet species} \rightleftharpoons \text{blue species} + O_2$$

In the present study it was found that intensely colored species, exhibiting the same characteristics and thermal stability as Streng's violet and blue compounds, could be obtained for example by the reaction of $O_2^+SbF_6^-$ with ClF, ClF_3, ClF_5, ClF_3O, BrF_5 or HF, the reaction of $O_2^+AsF_6^-$ with $FClO_2$ or HF, and the reaction of $O_2^+GeF_5^-$ with HF. The observed color scheme was similar for all systems. On melting of the amphoteric component an intensely violet colored species, stable below -78° was formed. Frequently, the violet color was concentrated near the surface of the solid O_2^+ salt, whereas the solution had a brownish color. On further warm up the colors changed towards brown and then disappeared with gas evolution. The observed colors also depended to some extent on the melting point of the amphoteric reagent. For example, in the case of ClF_3O which has the highest mp (-42°) of all the compounds studied, the higher reaction starting temperature resulted in the immediate formation of the brown species.

The nature of the reactions was studied by allowing the reactions to go to completion at room temperature, obtaining material balances, and identifying the solid products by vibrational spectroscopy. It was found that lower oxidation state compounds were fluorinated with O_2 evolution as found by Streng [8] for the corresponding O_2F_2 systems. The solids were the MF_6^- salts of the amphoteric fluorides. For the higher oxidation state compounds, a simple displacement reaction accompanied by O_2 and F_2 evolution occurred as shown above for ClF_3O. The only exception to this scheme was HF, which on contact with $O_2^+MF_6^-$ showed initially a violet color. However, on warm up to room temperature a colorless stable solution of $O_2^+MF_6^-$ in HF was obtained, thus demonstrating that HF does not interact with $O_2^+MF_6^-$. The intensity of the initial violet color appeared to vary

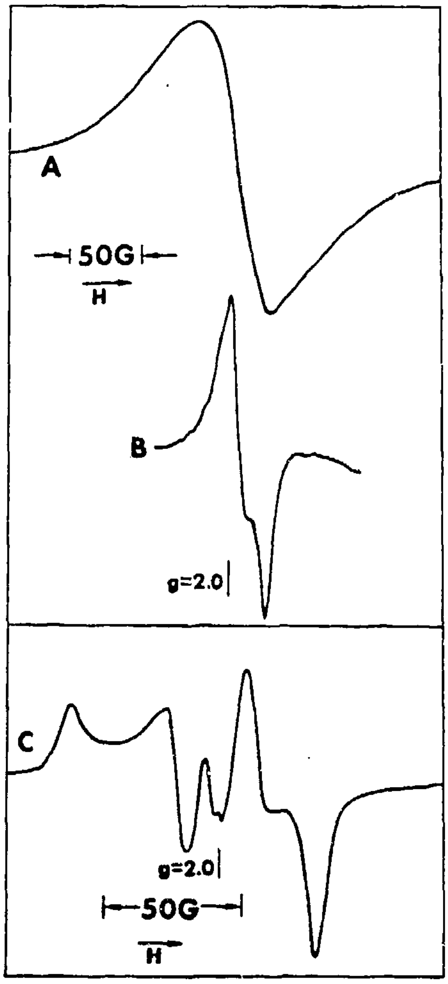

Fig. 1. Typical esr spectra of the colored species produced by the interaction of $O_2^+SbF_6^-$ with amphoteric molecules. Spectrum A: violet species in high concentration at -196° formed in the $O_2^+SbF_6^-$-ClF_3 system. When warmed to -78° and recooled to -196°, the intensity of the signal decreased and its linewidth changed from 53 to 33 G. Spectrum B: light violet species in the $O_2^+SbF_6^-$-BrF_5 system at -196°. Spectrum C: O_2F observed at -150° in the $O_2^+SbF_6^-$-ClF_3O system.

with the degree of dryness of the HF and, therefore, the following reaction is most likely responsible for the initial violet color:

$$O_2^+MF_6^- + HF + H_2O \rightarrow H_3O^+MF_6^- + O_2F$$

The stability of $O_2^+MF_6^-$ in HF solution at room temperature was verified by Raman spectroscopy. The spectrum showed bands at 656, 565, and 273 cm^{-1}, characteristic [12] for octahedral SbF_6^-, and at 1870 cm^{-1}, characteristic [4] for O_2^+.

Since the intense colors observed for the above systems suggest the presence of paramagnetic species, the colored species were generated, then frozen at -196°, and their esr spectra were recorded. It was found that the intense colors are indeed associated with paramagnetic species and, hence, cannot be due to diamagnetic species such as ClF_3O_2, BrF_5O_2 [7-9], ClF_2OOF, or ClF_2OOClF_2 [10,11]. Recently it was also shown that ClF_3O_2, prepared by a different method, is a colorless stable compound [13,14].

Typical esr spectra of the colored species are shown in Figure 1. Spectrum C of Figure 1 is in excellent agreement with the known [15,16] anisotropic esr spectrum of O_2F. Previous studies [15-17] on O_2F have furthermore shown that the observed spectra are extremely sensitive to experimental conditions. Thus, Spectrum A of Figure 1 closely resembles the spectrum ascribed to O_2F in solid O_4F_2 [17]. This establishes the presence of O_2F in the colored species. Whether O_2F is the sole paramagnetic species present in these systems or not, is more difficult to answer. As can be seen from trace B of Figure 1, the appearance of the observed signals can significantly vary. In some cases, the observed widths of the single line signals were as small as 7 G, i.e. much narrower than the fluorine hyperfine splitting of 13 G observed for the isotropic spectrum of O_2F [17]. Furthermore, the observed g values were generally less than 2.0. In no case was direct evidence found for the presence of either a chlorine or multiple fluorine atoms in the paramagnetic species. The narrow line widths and the low g values cannot be explained in terms of O_2F and indicate the presence of another paramagnetic species. In view of the overall information available, plausible candidates for such a species would be $(O_2)_nF$ or less likely $(O_2)_n^+$, where $n \geq 2$.

Another interesting observation was made when recording at ambient temperature the infrared spectra of the solid reaction products containing halogen fluoride MF_6^- salts in addition to some unreacted $O_2^+MF_6^-$. When these samples were pressed as dry powders in silver halide disks,

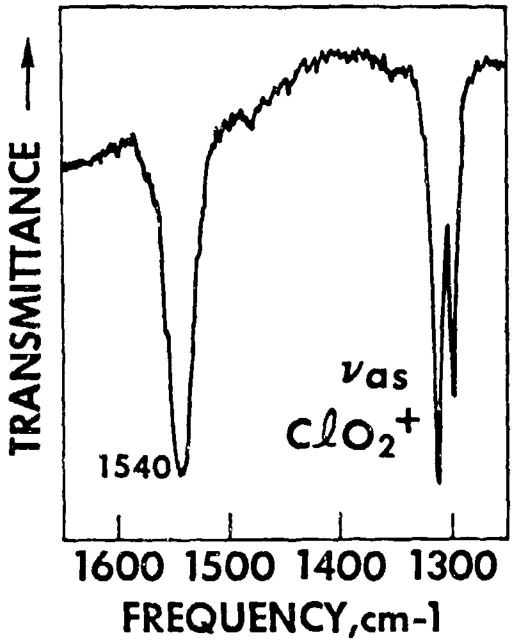

Fig. 2. The 1540 cm^{-1} infrared absorption observed at 25° for the purple species formed when the solid from the FClO$_2$ + O$_2^+$SbF$_6^-$ reaction (ClO$_2^+$SbF$_6^-$ and O$_2^+$SbF$_6^-$) was pressed as a dry powder in an AgCl disk.

the disks initially showed a blue to violet color which usually disappeared within 0.5 to 1 hour. The infrared spectrum (see Figure 2) showed an intense band at 1540 cm^{-1} which decayed with decreasing intensity of the color, while the rest of the spectrum remained unchanged. The frequency of this band is similar to those (1535 and 1527 cm^{-1}) found by Gardiner and Turner [10] at -196° for the violet and the blue species formed in the O_2F_2 + ClF reaction, and to those reported for O_4F_2 (1516 cm^{-1}) [18-21], solid oxygen (1550 cm^{-1}) [22], and O_2F (1494-1500 cm^{-1}) [19,20,23]. For pure O_2^+ salts or halogen fluoride - Lewis acid adducts alone, no evidence for any band in this frequency region or for violet colors was found in pressed silver halide disks. Since matrix isolated and free gaseous species usually have very similar frequencies, the colored species in the silver halide disk is probably not O_2F, but a polyoxygen compound, such as $(O_2)_nF$ or possibly $(O_2)_n^+$.

Unfortunately, the region (550-600 cm^{-1}) expected [19,20,23] for the O-F stretching mode in a species similar to O_2F, was obscured by intense bands due to MF_6^- and the cations formed in the displacement reaction. Attempts were unsuccessful to observe the 1540 cm^{-1} band by placing a

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TITANIUM TETRAPERCHLORATE AND CHROMYL PERCHLORATE

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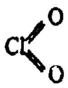
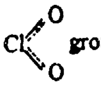
Abstract—Syntheses of titanium tetraperchlorate and chromyl perchlorate are reported using chlorine perchlorate and the respective metal chlorides. These anhydrous metal perchlorates were found to contain bidentate perchlorato ligands.

STUDIES of anhydrous metal perchlorates have been restricted mainly to metals from Groups I and II[1]. Limited studies of transition metal perchlorates have also been reported[2] as well as some work on NO_2^+ and NH_4^+ complex perchlorates[3]. Only more recently have the halogen perchlorates $ClOClO_3$[4] and $BrOClO_3$[5] become available and been shown to be excellent sources of perchlorates[6], $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$, and the novel fluorocarbon perchlorate[7], CF_3OClO_3. As a continuation of the investigation of the chemistry of chlorine perchlorate, its reactions with transition metal chlorides have been examined.

We now report that the action of chlorine perchlorate on titanium tetrachloride and chromyl chloride produced titanium tetraperchlorate and chromyl perchlorate, respectively. The observed stoichiometry for the titanium system was:

$$TiCl_4 + 4ClOClO_3 \rightarrow Ti(ClO_4)_4 + Cl_2.$$

The reaction was carried out at or below −25°, in either Teflon FEP or stainless steel vessels, and without a solvent. Yields of $Ti(ClO_4)_4$ were always 95 per cent or better based on the limiting reagent, $TiCl_4$. The identification of the $Ti(ClO_4)_4$ was based on the overall excellent material balance obtained for the synthesis, elemental analysis, and the i.r. and Raman spectra of the solid. A patent reported[8] the preparation of $Ti(ClO_4)_4$ which involved the reaction of $TiCl_4$ and at least 8-fold amounts of anhydrous perchloric acid. From the data presented, i.e. m.p., analysis and stability, it appears that the $Ti(ClO_4)_4$ described[8] may have been less pure than our samples. For example, it was stated that long term storage required refrigeration to avoid decomposition. Our samples have not degraded during 3 months at ambient temperature. The ClO_4 content reported, 86·4 per cent, significantly differs from the theoretical value of 89·25 per cent. In addition, the reported[8] m.p. of 90–94° is appreciably lower than our value of 101–2°, nor did we note any of the polycrystalline forms that were reported. Thus, it is likely that the present synthesis produces an anhydrous material of higher purity.

The vibrational spectra of $Ti(ClO_4)_4$ were particularly revealing with respect to the nature of the bonding between the titanium central atom and the ClO_4 ligands. The i.r. spectrum in the range 4000–300 cm⁻¹ contained bands at 1300, 1160, 910, 870, 850, 660, 575, 535 and 375 cm⁻¹, all of strong to very strong intensity. These bands are not typical of either an ionic[9] or covalent monodentate[10,11] perchlorate. Instead, they indicate the presence of bidentate perchlorato groups in an approximately tetrahedral arrangement around the titanium. Typical bidentate perchlorate spectra[11] show two pairs of strong i.r. bands at about 1310 and 1170, and 880 and 660 cm⁻¹. These pairs are due to the antisymmetric and symmetric stretching vibrations of the terminal  and the bridging  groups, respectively. They are obviously dominant in the $Ti(ClO_4)_4$ spectrum. Four bidentate ClO_4 groups surrounding Ti lead to a monomeric, coordination number wise saturated configuration which accounts for its observed volatility, i.e. low temperature sublimation.

The thermal stability of $Ti(ClO_4)_4$ was examined in closed bomb tests. After one hour at 115°, the decomposition was incomplete as evidenced by the recovery of less than the theoretical amount of oxygen in the form of O_2 and Cl_2O_7. After 4 hr at 115°, approximately half the oxygen content of the $Ti(ClO_4)_4$ was converted to O_2 and half to Cl_2O_7. The latter was decomposed at 190° in 1·5 hr. Quantitative overall results were obtained for the reaction sequence shown:

$$Ti(ClO_4)_4 \xrightarrow{\Delta} TiO_2 + 2Cl_2O_7 \xrightarrow{\Delta} 2Cl_2 + 7O_2.$$

The observed $O_2:Cl_2$ ratio of 3·54 : 1·00 compared favorably with the theoretical ratio of 3·50 : 1·00. The solid product was identified as titanium dioxide by comparison of its Raman spectrum with that of an authentic sample.

Chromyl perchlorate has been synthesized previously from the reaction of chromyl chloride and chlorine hexoxide[2]. With Cl_2O_4, the observed reaction was:

$$2Cl_2O_4 + CrO_2Cl_2 \rightarrow CrO_2(ClO_4)_2 + 2Cl_2.$$

Chromyl perchlorate is a dark red liquid with less than 1 mm vapor pressure at room temperature. Its high reactivity and low stability precluded successful transfers in the vacuum line. Although AgCl windows were attacked, it was possible to obtain i.r. spectra of the liquid using rapid scanning. Bands were observed at 1305 s, 1240 vs, 1180 s, 1030 s, 980 s, 875 m, 850 m, 735 s, 685 s, 660 s, 580 m, 545 m, 510 w, 435 w and 380 m cm^{-1}. These bands indicate the presence of covalent bidentate perchlorato ligands and of a bent chromyl group. As expected, $CrO_2(ClO_4)_2$ decomposed on heating according to the equation:

$$CrO_2(ClO_4)_2 \xrightarrow{\Delta} CrO_3 + Cl_2 + 3{\cdot}5O_2.$$

The observed $O_2:Cl_2$ ratio was 3·35:1·00 while the CrO_3 was identified by its i.r. spectrum and m.p. Additional studies of metal halides with halogen perchlorates are in progress and will be reported later.

EXPERIMENTAL

Titanium tetrachloride (1·22 mmole) and $ClOClO_3$ (6·01 mmole) were combined at −196° in a 75 ml stainless steel cylinder and then gradually warmed to −25°. After several days, recooling to −196° showed no noncondensable gases were present. The contents of the reactor were separated by fractional condensation in a series of U-traps cooled to −78, −112 and −196°. Nothing was trapped at −78° while the −112° fraction consisted solely of unreacted Cl_2O_4 (1·17 mmole), and the −196° fraction was Cl_2 (4·88 mmole). The pale yellow solid residue left in the reactor weighed 0·525 g. The weight calculated for 1·22 mmole of $Ti(ClO_4)_4$ was 0·544 g and therefore the yield of $Ti(ClO_4)_4$ was 97 per cent. Vacuum sublimation of the $Ti(ClO_4)_4$ was carried out in a Pyrex apparatus at 50–60° using a −78° cold finger. The sublimed material was nearly colorless and had a m.p. with dec. of 101–102°. Almost no residue remained unsublimed (*Anal.* Calcd. for $Ti(ClO_4)_4$: Ti, 10·75; ClO_4, 89·25. Found: Ti, 10·8; ClO_4, 87·9%). A sample of $Ti(ClO_4)_4$ (0·242 mmole) was heated in a stainless steel cylinder for 4 hr at 115° followed by 1·5 hr at 190°. This produced O_2 (1·705 mmole), Cl_2 (0·481 mmole) and a white solid residue of TiO_2 (0·241 mmole).

Chromyl chloride (1·41 mmole) and $ClOClO_3$ (3·16 mmole) were reacted at −45° for several days in a stainless steel cylinder. After separation and identification, the volatile products found were CrO_2F_2 (0·18 mmole), Cl_2 (2·59 mmole) and Cl_2O_4 (0·66 mmole). The $CrO_2(ClO_4)_2$ (1·23 mmole) remained in the cylinder. The CrO_2F_2 probably arose through reaction of CrO_2Cl_2 with the ClF_3 passivated metal surfaces in the reactor and/or vacuum line during transfers (*Anal.* Calcd. for $CrO_2(ClO_4)_2$: ClO_4, 70·3 Found: ClO_4, 69·6%). A sample of $CrO_2(ClO_4)_2$ (0·65 mmole) was pyrolyzed for 15 hr at 110° producing Cl_2 (0·66 mmole), O_2 (2·21 mmole) and CrO_3 (0·65 mmole), m.p. 195–7°, lit. 196°.

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Low-Temperature Ultraviolet Photolysis and Its Application to the Synthesis of Novel and Known NF_4^+ Salts

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Low-temperature uv photolysis was used to synthesize the novel NF_4^+ salts NF_4PF_6 and NF_4GeF_5 and the known salts NF_4BF_4 and NF_4AsF_6. This technique offers the first convenient, simple, and high-yield synthesis for NF_4BF_4. The NF_4PF_6 and NF_4GeF_5 salts were also prepared from NF_4BF_4 by displacement reactions with PF_5 and GeF_4, respectively. Treatment of NF_4GeF_5 with anhydrous HF resulted in its conversion to $(NF_4)_2GeF_6$, and $(NF_4)_2GeF_6$ was quantitatively converted back to NF_4GeF_5 by treatment with an excess of GeF_4. The NF_4^+ salts were characterized by vibrational and ^{19}F NMR spectroscopy and x-ray powder data. A cis-fluorine-bridged polymeric structure is proposed for GeF_5^- in its NF_4^+ salt based on the spectroscopic data, its thermal stability, and lack of reaction with either liquid N_2F_4 or FNO_2. The applicability of low-temperature uv photolysis to other reactant systems was briefly studied. The hydrolysis of NF_4^+ salts was reinvestigated.

Introduction

The synthesis of NF_4^+ salts had been discouraged by the nonexistence of a stable NF_5 parent molecule and theoretical computations[1,2] showing that these salts should be thermodynamically unstable. Once the principle was recognized[3,4] that NF_4^+ salts can be prepared from NF_3, F_2, and a strong Lewis acid in the presence of a suitable activation energy source, various synthetic approaches were discovered.

Low-temperature glow discharge was used for the synthesis of NF_4AsF_6[4,5] and NF_4BF_4.[6,7] High-pressure and thermal activation were employed[8,9] for the synthesis of the thermally very stable $NF_4SbF_6{\cdot}xSbF_5$. The latter method was also applied to the synthesis of NF_4AsF_6, but the reaction rates are low and metal salts are formed[10] as by-products. Low-temperature γ irradiation was used[11] to prepare NF_4BF_4, but it requires special equipment (3-MeV bremsstrahlung) and cannot easily be scaled up. Impure NF_4BF_4 can be prepared by metathesis[12,13] from the readily accessible[9] $NF_4SbF_6{\cdot}xSbF_5$; however, product purification is difficult. A novel method[14] involving uv photolysis was recently reported for the synthesis of NF_4BF_4, NF_4AsF_6, and $NF_4SbF_6{\cdot}xSbF_5$; however, the yields obtained for the BF_4 and the AsF_6^- salt were discouragingly low.

In view of the general interest in NF_4^+ salts and the importance of NF_4BF_4 for chemical HF–DF lasers, we were interested in improved methods for synthesizing pure NF_4^+ salts and in the synthesis of novel salts. The results of this study are summarized in this paper.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in well-passivated (with ClF_3) stainless steel or Monel vacuum lines equipped with Teflon FEP U-traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%) or a Validyne Model DM56A pressure transducer. Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

Arsenic pentafluoride, PF_5, and GeF_4 (Ozark Mahoning), NF_3 and F_2 (Rocketdyne), BF_3 and Kr (Matheson), and OF_2 (Allied Chemical) were purified by fractional condensation prior to their use. The CF_3NF_2 was prepared by uv photolysis of a mixture of $(CF_3CO)_2O$ and N_2F_4.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer as dry powders between AgCl or AgBr windows in the form of pressed disks. The pressing operation was carried out using a Wilks minipellet press. Raman spectra were recorded on a Cary Model 83 double monochromator using the 4880-Å exciting line, a Claassen filter[15] for the elimination of plasma lines, and quartz or Teflon FEP tubes as sample containers. The ^{19}F NMR spectra were recorded at 56.4 MHz on a Varian Model DA-60 high-resolution NMR spectrometer. Chemical shifts were determined by the side-band technique with an accuracy of ±1 ppm relative to the external standard $CFCl_3$. Anhydrous HF[16] was used as a solvent and Teflon FEP tubes (Wilmad Glass Co.) were used as sample containers. The thermal decomposition of NF_4^+ salts was examined with a Perkin-Elmer differential scanning calorimeter (Model DSC-1B) using crimp-seal aluminum pans as sample containers and heating rates of 5°/min at atmospheric pressure. Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with nickel-filtered copper Kα radiation. Quartz capillaries (~0.5-mm o.d.) were used as sample containers.

The low-temperature uv-photolysis reactions were carried out in either a quartz or a stainless steel–sapphire reaction vessel. The quartz reactor had a pan-shaped bottom and a flat top consisting of a 3-in. diameter optical grade quartz window. The vessel had a side arm connected by a Teflon O ring to a Fischer-Porter Teflon valve to facilitate removal of solid reaction products. The depth of the reactor was about 1.5 in. and its volume was 135 ml. The steel–sapphire reactor was constructed from a 3 in. long, 1.75 in. wide (volume 120 ml) 347 stainless steel cylindrical body provided with a 2-in. diameter sapphire flat sealed to the cell body by means of a flange and a Teflon O-ring. A side arm closed by a steel valve was attached to the cell body. The uv source consisted of a 900-W air-cooled high-pressure mercury arc (General Electric Model B-H6) and was positioned 1.5 in. above the flat reactor surface. The bottom of the reactors was kept cold by immersion in liquid N_2. Dry, gaseous N_2 was used as a purge gas to prevent condensation of atmospheric moisture on the flat top of the reactor. As a heat shield a 0.25 in. thick quartz plate was positioned between the uv source and the top of the reactor.

Syntheses of NF_4^+ Salts by Uv Photolysis. In a typical experiment, premixed NF_3 and BF_3 (27 mmol of each) were condensed into the cold (−196 °C) bottom of the pan-shaped quartz reactor. Fluorine (9 mmol) was added and the mixture was photolyzed at −196 °C for 1 h with a 900-W high-pressure Hg arc in the manner described above. After termination of the photolysis, volatile material was pumped out of the reactor during its warm-up to room temperature. The nonvolatile white solid product consisted of NF_4BF_4 (1.0 g) which was shown by vibrational spectroscopy and elemental analysis to contain no detectable impurities.

The uv photolyses of other systems were carried out in the same manner and the results are summarized in Table I.

Syntheses of NF_4^+ Salts by Displacement Reactions without Solvent. In a typical experiment, pure NF_4BF_4 (2.07 mmol) was combined at −196 °C with an excess of PF_5 (40.01 mmol) in a passivated (with ClF_3) 10-ml 316 stainless steel cylinder. The mixture was kept at 25 °C for 64 h. The volatile materials were removed in vacuo and separated by fractional condensation. They consisted of BF_3 (2.05 mmol) and unreacted PF_5 (37.93 mmol). The white solid residue had gained 120 mg in weight. Based on the above material balance, the conversion of NF_4BF_4 to NF_4PF_6 was essentially complete. This was further confirmed by vibrational spectroscopy which showed the solid to be NF_4PF_6 containing no detectable amounts of NF_4BF_4.

A displacement reaction between NF_4BF_4 and GeF_4 was carried out in a similar manner and resulted in a 65 mol % conversion of NF_4BF_4 to NF_4GeF_5. When this step was repeated two more times, the conversion of NF_4BF_4 to NF_4GeF_5 was complete as shown by the observed material balance, the absence of BF_4^- bands in the vibrational spectra, and elemental analysis.

For the elemental analysis, NF_4GeF_5 (0.339 mmol) was hydrolyzed in a Teflon FEP U-trap with 2 ml of distilled water. The formed O_2 (0.114 mmol) was distilled off at −196 °C and the NF_3 (0.336 mmol)

Table I. Comparative Yields of Products Formed by Uv Photolysis[a] at −196 °C

Reactants	Solid Product	Rate of formn of solid, mg/h
NF_3, BF_3, F_2	NF_4BF_4	1000
NF_3, AsF_5, F_2	NF_4AsF_6	1145
NF_3, PF_5, F_2	NF_4PF_6	10
NF_3, GeF_4, F_2	NF_4GeF_5	25
NF_3, SiF_4, F_2		
N_2, AsF_5, F_2		
CF_3NF_2, AsF_5, F_2	AsF_6^- salts of NF_4^+, $N_2F_3^+$, N_2F^+	1051
OF_2, AsF_5, F_2	O_2AsF_6	130

[a] The uv source was a 900-W (GE B-H6) mercury arc without backing mirror. The mole ratio of the reactants was 3:3:1. All reactions were carried out in the pan-shaped quartz reactor with unfiltered radiation and a radiation time of 1 h without reactant surface renewal. For these reasons the given formation rates do not represent maximum attainable values but are given for comparative purposes.

at −126 °C. They were identified by mass and infrared spectroscopy. The aqueous solution was analyzed by x-ray fluorescence for Ge (calcd for NF_4GeF_5, 28.2; found, 28.6) and for hydrolyzable F with an Orion specific ion fluoride electrode (calcd, 44.3; found, 43.7). The presence of H_2O_2 in the hydrolysate was established by its ability to oxidize iodide to free iodine and manganese(II) to manganese(IV) and to reduce MnO_4^-.

Syntheses of NF_4^+ Salts by Displacement Reactions in HF Solution. In a typical experiment pure NF_4BF_4 (2.6 mmol) were placed into a passivated 30-ml Teflon FEP ampule and liquid HF (3 ml) and GeF_4 (3.59 mmol) were added at −196 °C. Upon warm-up of the mixture to room temperature bubbling and foaming was noticed. The contents of the ampule were agitated at 25 °C for several hours on a mechanical shaker. The volatile material was pumped off and based on the observed material balance and spectroscopic and elemental analyses of the solid product, the conversion of NF_4BF_4 to a mixture of NF_4GeF_5 and $(NF_4)_2GeF_6$ was 33 mol %. After repeating this procedure for three more times, the conversion of NF_4BF_4 was 85 mol % and the mole ratio between NF_4GeF_5 and $(NF_4)_2GeF_6$ was about 1.3:1.

Similar exposure of NF_4BF_4 to an excess of PF_5 in HF solution resulted for a single and triple treatment in a conversion of NF_4BF_4 to NF_4PF_6 of 8 and 17 mol %, respectively. However, treatment of NF_4AsF_6 with GeF_4 in HF solution did not produce any detectable amounts of GeF_6^{2-} or GeF_5^- salts.

Interconversion of NF_4GeF_5 and $(NF_4)_2GeF_6$. A sample of pure NF_4GeF_5 was dissolved in a large excess of anhydrous HF in a Teflon FEP ampule. After keeping this solution at 25 °C for 6 h, the volatile products were pumped off at 25 °C. This procedure was repeated three more times and the progress of the reaction was followed by determining the weight change of the solid residue and spectroscopic and elemental analyses of the solid. After the fo[illegible] treatment, the conversion of NF_4GeF_5 to $(NF_4)_2GeF_6$ was [illegible]y complete. Anal. Calcd: Ge, 19.8; NF_3, 38.7; hydrolyzable F, 41.5. Found: Ge, 19.9; NF_3, 38.5; hydrolyzable F, 41.1.

A sample of pure $(NF_4)_2GeF_6$ was treated at 25 °C with a tenfold excess of liquid GeF_4 for 20 h. The unreacted GeF_4 was pumped off at 40 °C. Based on the observed material balance and spectroscopic and elemental analyses of the solid product, the $(NF_4)_2GeF_6$ was quantitatively converted to NF_4GeF_5.

Interaction of NF_4GeF_5 with N_2F_4 and FNO_2. A sample of NF_4GeF_5 was treated at −78 °C for several hours with a large excess of either liquid N_2F_4 or FNO_2. Based on the observed material balances and spectroscopic analyses of the product, very little reaction occurred. The main product was unreacted NF_4GeF_5 containing some GeF_6^{2-} salt.

Results and Discussion

Syntheses of NF_4^+ Salts by Uv Photolysis. The difficulty of synthesizing NF_4^+ salts from NF_3, F_2, and a Lewis acid increases with decreasing strength of the Lewis acid. Whereas the $SbF_6^- \cdot xSbF_5$ salt can readily be prepared using thermal activation[8,9] or room-temperature uv photolysis,[14] these methods are of only marginal feasibility for the AsF_6^- salt and of little or no use for the BF_4^- salt. Since no simple methods existed for the convenient synthesis of the interesting compound $NF_4^+BF_4^-$ in high purity and yield, we have searched for novel synthetic approaches.

It was found that low-temperature uv photolysis is ideally suited for preparing NF_4BF_4. A large number of reaction parameters were studied[17] to maximize the yield. Maximum yields of NF_4BF_4 were obtained close to liquid nitrogen temperature (−196 °C) using unfiltered uv radiation, a short path length to avoid recombination of F atoms to molecular F_2,[14] and periodic addition of fresh starting materials to the uv cell to avoid coating of the surface of the condensed reactants by solid NF_4BF_4. The highest yield of NF_4BF_4 achieved to date in our laboratory with a 900-W mercury arc was in excess of 3 g/h and was achieved with a semiautomated steel–sapphire cell with a vertical cold surface and a periodic feed and product removal system.[18]

Both types of reactors, stainless steel–sapphire and quartz, yield NF_4BF_4 of very high purity showing no detectable impurities, although the quartz reactor is slowly attacked (weight loss of ~1 mg/h of operation) by the F atoms with SiF_4 and O_2^+ formation. However, the possibility of photolytic O_2BF_4 formation[19] does not present a problem since O_2BF_4 is thermally unstable and is removed from NF_4BF_4 by pumping at 25 °C during product workup.

Using estimates for the amount of uv radiation entering the cell (80% for the experiments using a parabolic backing mirror for the uv source) and being absorbed by F_2 (12%), the quantum yield for the formation of NF_4BF_4 at a rate of 3 g/h was calculated to be about 0.015. Since this value is much smaller than unity, it does not provide any experimental proof for a previously suggested[14] gas-phase chain reaction. Since the BF_3 starting material is frozen out as a solid during the reaction, a diffusion-controlled mechanism in the solid (BF_3)–liquid (F_2, NF_3) phase appears more plausible and can account for the low observed quantum yield.

In agreement with our previous report,[14] we found that the rate of NF_4BF_4 formation in the gas phase at room temperature is extremely slow. Contrary to our original statement,[14] we believe that this is not caused by window coating but is due to the low thermal stability[13] of some of the intermediate products.[14] The fact that $NF_4SbF_6 \cdot xSbF_5$ can be readily produced by uv photolysis at room temperature[13] indicates that the stability of these intermediates is influenced by the strength of the Lewis acid used.

The reaction conditions found most suitable for the synthesis of NF_4BF_4 were also tested for the syntheses of the known NF_4AsF_6[3,5,8,9] and the novel PF_6^-, GeF_5^-, SiF_5^-, GeF_6^{2-}, and SiF_6^{2-} salts. The results from these experiments are summarized in Table I and the product formation rates are compared to those obtained for NF_4BF_4 under similar reaction conditions. The NF_4AsF_6 salt can be prepared by our method at a rate comparable to that of NF_4BF_4 and yields a very pure product. This makes low-temperature uv photolysis also the most attractive method presently known for the preparation of high-purity NF_4AsF_6. The novel salts NF_4PF_6 and NF_4GeF_5 were also successfully synthesized by our method although their rate of formation was lower than those of the BF_4^- and AsF_6^- salts. Attempts to synthesize the corresponding SiF_5^- salt were unsuccessful and did not produce any solid stable at −78 °C or above.

Syntheses of Other Salts by Uv Photolysis. Based on our success with NF_4^+ salts, it was interesting to test the applicability of low-temperature uv photolysis to other reactant systems. The results are summarized in Table I.

In the case of CF_3NF_2 no evidence for the formation of the unknown $CF_3NF_3^+$ cation was obtained. Instead, all of the

CF_3NF_2 starting material underwent C–N bond breakage resulting in the formation of a mixture of NF_4^+, $N_2F_3^+$,[20-22] and N_2F^+ [20,23-26] salts. The use of a Vycor (Hanovia 7910)–nickel oxide (Hanovia 9863) filter (transmitting only between 2300 and 4200 Å) to avoid C–N bond breakage did not significantly change the composition of the solid reaction products. Attempts to convert N_2 to either N_2F^+, $N_2F_3^+$, or NF_4^+ salts were unsuccessful.

Photolysis of an OF_2–F_2–AsF_5 mixture gave no evidence for the novel $OF_3^+AsF_6^-$ but produced the known $O_2^+AsF_6^-$.[27] This is not surprising since O_2AsF_6 has previously been prepared by room-temperature uv photolysis[28] or thermal activation[29] of AsF_5 with either OF_2 or $O_2 + F_2$.

The uv photolysis of an equimolar mixture of Kr, F_2, and AsF_5 in the steel–sapphire reactor at −196 °C produced 49 mg/h of an unstable KrF_2–AsF_5 adduct[30,31] which decomposed before it could be transferred out of the reactor for further identification. For NF_4^+ salts the yields in this steel reactor generally were about one-third of those listed in Table I for the quartz reactor. These results are in good agreement with a recent report[32] that KrF_2 can be prepared by uv photolysis of a liquid mixture of Kr and F_2 at −196 °C.

Syntheses of NF_4PF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$ by Displacement Reactions. In view of the relatively slow formation rates of NF_4PF_6 and NF_4GeF_5 during uv photolysis, alternate routes to these salts were sought. Since NF_4BF_4 is more readily available, displacement reactions between NF_4BF_4 and PF_5 or GeF_4 were studied. It was found that essentially pure NF_4PF_6 or NF_4GeF_5 can be obtained by treating NF_4BF_4 with a large excess of liquid PF_5 or GeF_4, respectively, at room temperature. The observed material balances confirm the reactions

$$NF_4BF_4 + PF_5 \rightarrow NF_4PF_6 + BF_3$$

$$NF_4BF_4 + GeF_4 \rightarrow NF_4GeF_5 + BF_3$$

These displacement reactions represent at the present time the most convenient syntheses for larger amounts of NF_4PF_6 and NF_4GeF_5. For NF_4GeF_5, repeated treatment of the NF_4BF_4 starting material with GeF_4 was required to obtain a quantitative conversion.

The usefulness of anhydrous HF as a common solvent in these displacement reactions was studied. The conversions of NF_4BF_4 were found to be lower in HF solution, compared to those in the absence of HF, and even multiple treatments with the HF–Lewis acid mixtures did not result in quantitative conversions. This indicates that HF may act not only as a solvent in these reactions but may participate as a third component in the chemical equilibria involved. Treatment of NF_4AsF_6 with GeF_4 in HF solution did not result in any detectable displacement of AsF_6^-. This shows that, as expected, AsF_5 is a significantly stronger Lewis acid than GeF_4 but that BF_3, PF_5, and GeF_4 are of comparable acid strength.

Another interesting observation was made for the displacement reaction between NF_4BF_4 and GeF_4 in HF. The material balances and the spectroscopic and elemental analyses showed that, in addition to NF_4GeF_5, some $(NF_4)_2GeF_6$ was also formed. This observation suggested the possibility of converting NF_4GeF_5 to $(NF_4)_2GeF_6$ by treatment with HF. Examination of the NF_4GeF_5–HF system indeed revealed that in HF solution NF_4GeF_5 could be quantitatively converted to $(NF_4)_2GeF_6$. The Raman spectra of these solutions (see below) showed the presence of GeF_6^{2-}, indicating a reaction sequence such as

$$2NF_4GeF_5 + 4HF \xrightarrow{HF} 2NF_4^+ + 2GeF_6^{2-} + 2H_2F^+$$

$$2H_2F^+ + GeF_6^{2-} \rightleftarrows 4HF + GeF_4$$

$$2NF_4^+ + GeF_6^{2-} \rightarrow (NF_4)_2GeF_6$$

Removal of the GeF_4 product and repeated treatment with fresh HF were required to obtain a quantitative conversion to $(NF_4)_2GeF_6$ in agreement with the above postulated equilibrium reaction. The above synthesis of $(NF_4)_2GeF_6$ was of particular interest since it afforded the first known example of a NF_4^+ salt containing a multiply charged anion.

Table II. Relative Thermal Stability and Solid-State Transition Temperatures

Sample	Temp of rapid decompn (mp capillary), °C	Temp of reversible endotherm (DSC), °C
NF_4GeF_5[a]	249	129
NF_4PF_6[a]	245	125
NF_4BF_4[b]	330	234
NF_4AsF_6[c]	365	133
$(NF_4)_2GeF_6$	238	*d*

[a] First visual signs of shrinking of sample were observed at about 115 °C. The melting was relatively sharp and was accompanied by gas evolution. [b] Starts to decompose at about 250 °C (thermogram[6]) or [illegible]35 °C (DSC[11]) or 200 °C (slow gas evolution in vacuo[11]). [c] Starts to decompose at about 270 °C (DSC[6]) or 175 °C (slow gas evolution in vacuo[33]). [d] Not recorded.

The postulate that GeF_5^- is in equilibrium with GeF_6^{2-} and GeF_4 was experimentally confirmed. When $(NF_4)_2GeF_6$ was treated with a large excess of liquid GeF_4 at 25 °C, it was quantitatively converted back to NF_4GeF_5. Thus the formation of either NF_4GeF_5 or $(NF_4)_2GeF_6$ or mixtures of both depends on the exact reaction conditions

$$2NF_4GeF_5 \underset{\text{in } GeF_4}{\overset{\text{in HF}}{\rightleftarrows}} (NF_4)_2GeF_6 + GeF_4$$

Since NF_4GeF_5 and $(NF_4)_2GeF_6$ have very different vibrational spectra and x-ray powder patterns (see below), they can be readily distinguished from each other.

In view of the above described tendency of GeF_5^- to interact with HF with GeF_6^{2-} formation, it seemed interesting to examine the reactions of NF_4GeF_5 with other fluoride ion donors. For this purpose, a relatively weak (N_2F_4) and a relatively strong (FNO_2) F^- donor were chosen, and the reactions were studied at −78 °C using a large excess of the donor as the liquid phase. For N_2F_4 no interaction was observed as might be expected from the fact[33] that N_2F_4 and GeF_4 do not form an adduct. However for FNO_2 which is capable of forming a stable GeF_6^{2-} salt, again no complexing was observed. This might be explained either by low solubility of NF_4GeF_5 in FNO_2 or by the probable polymeric nature (see below) of the GeF_5^- anion in NF_4GeF_5 which renders it a rather weak Lewis acid.

Properties of NF_4PF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$. All three compounds are white, crystalline, hygroscopic solids stable at ambient temperature. The thermal stability of the NF_4^+ salts (see Table II) was examined by both DSC in crimped aluminum pans and visual examination in sealed glass melting point capillaries. Whereas DSC was suitable accurately to observe solid-state transitions (see Table II), both methods do not permit the accurate determination of the onset of thermal decomposition. This is caused by the slow decomposition rates of NF_4^+ salts and their suppression by the pressure buildup of the gaseous decomposition products.[34] Consequently, the thermal decomposition of the NF_4^+ salts results in a slow, smooth, and gradual increase of the slope of the DSC curve. For the melting point capillaries, slow gradual shrinkage of the solid can be observed long before rapid decomposition occurs. This behavior also explains the large discrepancies in thermal decomposition temperatures previously reported[6,11] for NF_4BF_4. Obviously, different techniques and experimental conditions can result in vastly different values. As can be seen from Table II, NF_4PF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$ are all

Table III. Crystallographic Data of NF_4^+ Salts[a]

	Unit cell dimensions				Vol per F, Å^3	Calcd density, g/cm^3
	a, Å	c, Å	V, Å^3	Z		
NF_4BF_4	9.944	5.229	517.04	4	16.16	2.27
NF_4PF_6	7.577	5.653	324.53	2	16.23	2.41
NF_4AsF_6[b]	7.70	5.73	339.73	2	16.99	2.72
$(NF_4)_2GeF_6$	10.627	11.114	1255.14	16/3	16.81	2.59

[a] All compounds crystallize in the tetragonal system. [b] Reference 5.

of good thermal stability. The $NF_4Sb_2F_{11}$ salt did not show a solid-state transition but melted at 178 °C. The melt showed a freezing point of 161 °C. The chemical properties of NF_4PF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$ are analogous to those[5,6,9-11] previously reported for other NF_4^+ salts.

Hydrolysis of NF_4^+ Salts. The hydrolysis of NF_4^+ salts was quantitatively studied[9] by Tolberg and co-workers. According to their results the hydrolysis follows the equation

$$NF_4^+ + H_2O \rightarrow NF_3 + H_2F^+ + {}^1/_2O_2$$

This hydrolysis reaction should therefore offer a convenient way to analyze NF_4^+ salts since NF_3 does not hydrolyze in water. A large number of NF_4^+ salts have been analyzed on a routine basis in our laboratory. Whereas quantitative NF_3 evolution was always observed, the amount of oxygen evolved was consistently less than that expected for the above equation. Examination of the hydrolysate showed that the balance of the oxygen was present as H_2O_2, the formation of which can readily be explained by the initial formation of HOF as an unstable[35] intermediate

$$NF_4^+ + OH^- \rightarrow NF_3 + HOF$$

The HOF intermediate can either decompose according to

$$2HOF \rightarrow 2HF + O_2$$

or react in a competing reaction with water according to

$$HOF + HOH \rightarrow HF + HOOH$$

The ratio between H_2O_2 and O_2 varied from experiment to experiment and seemed to depend strongly on the exact reaction conditions.

X-Ray Powder Data. The x-ray powder pattern of NF_4PF_6 is given as supplementary material. The tetragonal unit cell (see Table III) is very similar and, as expected, slightly smaller than that previously reported[5] for NF_4AsF_6. No nonindexable lines were observed for NF_4PF_6 indicating little or no crystalline impurities. Based on the lack of characteristic absences of certain diffraction lines, the most probable space group for NF_4PF_6 is *P*4/*m*.

The powder pattern of NF_4GeF_5 (see supplementary material) was too complex to allow indexing, but the pattern of $(NF_4)_2GeF_6$ (see supplementary material) could be indexed for a tetragonal unit cell (see Table III). The unusual value of $Z = 16/3$ for $(NF_4)_2GeF_6$ requires some comment. Assuming $Z = 5$ would result in an unacceptably high (17.93 Å^3) and $Z = 6$ would result in an unacceptably low (14.94 Å^3) average volume per fluorine atom. By comparison with the known crystal structures of other NF_4^+ salts (see Table III), for $(NF_4)_2GeF_6$ this value should be larger than that (16.16 Å^3) of NF_4BF_4 but smaller than that (16.99 Å^3) of NF_4AsF_6. A plausible value of 16.81 Å^3 can, however, be obtained by assuming a structure derived from that[36] of α-K_2UF_6 but with a tetragonally distorted fourfold unit cell. For α-K_2UF_6 a value of 4/3 was found for Z and explained by assuming a statistical distribution of the anions and cations among the calcium positions of a CaF_2-like structure.

For NF_4BF_4, two different powder patterns have previously been reported. Sinel'nikov and Rosolovskii reported a cubic ($a = 7.53$ Å) structure,[6] whereas Goetschel et al. found[11] a tetragonal unit cell similar to those of the MF_6^- salts. Since both of these and our NF_4BF_4 sample had been prepared under similar conditions at −196 °C, their crystal structures might be expected to be identical. Consequently, we have also recorded the powder pattern of NF_4BF_4 (see supplementary material). Our results closely agreed with those[11] of Goetschel et al. Furthermore, only the tetragonal unit cell results in plausible trends (see Table III) for the density and the average volume per F atom (ignoring contributions from the central atoms).[37] Many of the diffraction lines reported by Sinel'nikov are similar to those reported[38] for NO_2BF_4, a likely impurity in samples prepared by glow-discharge techniques in glass apparatus.[39]

The powder pattern of NF_4BF_4 was indexed[11] by Goetschel et al. on the basis of a tetragonal unit cell with $Z = 2$. However, eight reflections could not be indexed and were tentatively attributed to an impurity. We have also observed these reflections with similar intensities and found that they belong to NF_4BF_4. They can be readily indexed if the volume of the unit cell, proposed by Goetschel, is doubled ($Z = 4$). The questionable diffraction line at $d = 3.126$ Å, reported by Goetschel,[11] was not observed during our study and therefore is attributed to an impurity in Goetschel's sample. The indexing of the NF_4BF_4 powder pattern for $Z = 4$ is given in the supplementary material. The space group *P*4/*nmm* suggested by[11] Goetschel et al. is unlikely since the extinction rule $hk0 = 0$ unless $h + k = 2n$ is not obeyed. Space group *P*4/*m* appears more likely based on the apparent lack of any characteristic absences.

NMR Spectra. The ^{19}F NMR spectra of NF_4PF_6 and $(NF_4)_2GeF_6$ in HF solution showed for NF_4^+ a triplet of equal intensity with $J_{NF} = 230$ Hz at −217.0 and −213.5 ppm, respectively, from external $CFCl_3$, and a common line for the rapidly exchanging solvent and the anions. These values are in excellent agreement with those previously reported for NF_4SbF_6[9] and NF_4AsF_6[40] in HF.

Since NF_4GeF_5 is converted to $(NF_4)_2GeF_6$ by HF and since HF rapidly exchanges with the anion, the NMR spectrum of NF_4GeF_5 was recorded in the inert solvent BrF_5. The spectrum showed in addition to the solvent lines (quintet at ϕ −272 and doublet at ϕ −134) and the characteristic[9,40] NF_4^+ triplet (ϕ −220.1, $J_{NF} = 230$ Hz) a broad unresolved resonance at ϕ 151. Its chemical shift significantly deviates from that (ϕ 123) found[41] for GeF_6^{2-} in H_2O and occurs in the region predicted for GeF_5^-. Attempts to obtain a well-resolved anion spectrum failed owing to the sharp decrease in the solubility of the salt in BrF_5 with decreasing temperature and to the relatively high melting point (−61 °C) of BrF_5. The failure to observe a sharp resonance for the anion might be explained either by a discrete trigonal-bipyramidal GeF_5^- undergoing rapid intramolecular exchange or by a polymeric anion (see below) undergoing rapid intermolecular exchange. Since the BrF_5 signal was well resolved, interaction between BrF_5 and GeF_5^- can be ruled out. The Raman spectrum of this NF_4GeF_5–BrF_5 solution was also recorded. It showed the lines due to NF_4^+ (see below), but unfortunately the solubility of NF_4GeF_5 in BrF_5 is relatively low and the region of the anion bands was masked by strong BrF_5 bands.

Vibrational Spectra. The vibrational spectra of NF_4GeF_5, $(NF_4)_2GeF_6$, NF_4PF_6, and $NF_4Sb_2F_{11}$ are shown in Figures 1–3, respectively. In view of the high purity of our samples and of the resultant good quality of their spectra, the spectra of NF_4AsF_6[10,40] and NF_4BF_4[6,11] are also given for comparison. The observed frequencies and their assignments are summarized in Tables IV–VI. Whereas the assignment of the

Table IV. Vibrational Frequencies[a] and Assignments for Tetrahedral NF_4^+ and BF_4^-

Assignments for NF_4^+, BF_4^- (T_d)	Obsd freq, cm^{-1}, and rel intens[b]														
	NF_4^+													BF_4^-	
	NF_4BF_4		NF_4PF_6		NF_4AsF_6		$NF_4Sb_2F_{11}$		$(NF_4)_2GeF_6$			NF_4GeF_5		NF_4BF_4	
	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Raman, HF soln	Ir	Raman	Ir	Raman
			2380 vw		2380 vw							2380 vw			
$2\nu_3(A_1 + E + F_2) =$ 2320, 2114	2320 vw		2320 w		2320 w		2320 vw		2320 vw			2320 w		2120 vw	
$\nu_1 + \nu_3(F_2) = 2008, 1829$	2000 w		2005 w		2000 w		2010 w		2010 w			2010 w		1830 vw	
$\nu_3 + \nu_4(A_1 + E + F_2) =$ 1769, 1582	1762 vw		1765 w		1762 w		1768 vw		1765 w			1766 w			
$\nu_2 + \nu_3(F_1 + F_2) = 1600, 1407$														1405 vw	
												1465 w			
$\nu_1 + \nu_4(F_2) = 1457, 1297$	1455 w		1457 w		1455 w		1457 w		1462 w			1456 vw		1298 ms	
$2\nu_4(A_1 + E + F_2) =$ 1218, 1050	1222 mw		1221 mw		1222 mw		1221 m		1222 mw			1221 mw			
$\nu_3(F_2)$	1180 sh	1179 (0.6)	1166 vs	1168 (1.5)	1161 vs	1162 (1.0)	1161 vs	1160 (0.2)	1161 vs	1159 (1.2)	1162 (0.4) dp		1168 (0.8)	1120 sh	1130 (0+)
	1162 vs			1150 (0.8)		1151 (0.6)						1160 vs	1159 (0.8)	1057 vs	1055 (0.2)
		1148 (0.6)	1135 vw		1135 vw		1135 w						1149 (0.9)		
$\nu_2 + \nu_4(F_1 + F_2) = 1049, 875$			1056 vw		1052 vw		1049 vw					1055 w		882 vw	
$2\nu_2(A_1 + A_2 + E) = 880, 700$		884 (0+)		880 (0.2)		880 (0+)		879 (0+)		881 (0+)	882 (0.2) p		881 (0+)		
$\nu_1(A_1)$		844 (10)		849 (8.2)		848 (7.3)		848 (2.6)		850 (8.1)	850 (10) p		848 (10)	772 w	772 (3.2)
			611 m		610 sh							613 m	615 (0.8)	525 sh	
$\nu_4(F_2)$	609 s	609 (6.3)		609 (7.4)		609 (5.2)	608 s	608 (1.6)	610 s	609 (10)[c]	609 (3.9) dp	604 m	604 (3.2)		524 (0.4)
			608 m		607 m							593 m	594 (2.6)	522 s	
$\nu_2(E)$		443 (2.6)		441 (2.9)		440 (2.0)		438 (0.5)		441 (3.2)	439 (1.7) dp		440 (2.6)		350 (0.9)
													431 (2.2)		

[a] Unless noted otherwise, the listed spectra are those of the solids. [b] Uncorrected Raman intensities. [c] Coincides with ν_1 of GeF_6^{2-}.

Table V. Vibrational Frequencies and Assignments for Octahedral MF_6 in $(NF_4)_nMF_6$

Assignments for $MF_6(O_h)$	Obsd freq, cm^{-1}, and rel intens[a]						
	NF_4PF_6		NF_4AsF_6		$(NF_4)_2GeF_6$		
	Ir	Raman	Ir	Raman	Ir	Raman	Raman, HF soln
$\nu_1 + \nu_3(F_{1u}) = 1590, 1403$	1590 w		1398 vw				
$\nu_2 + \nu_3(F_{1u} + F_{2u}) = 1413, 1294$	1414 w		1290 vw				
$\nu_1 + \nu_4(F_{1u}) = 1307, 1079$	1308 vw		1080 vvw				
$\nu_2 + \nu_4(F_{1u} + F_{2u}) = 1130, 970$			985 vvw				
	842 vs		720 vs				
$\nu_3(F_{1u})$		838 (1.5)		703 (1.5)	600 vs, br		
	789 w		699 w				
$\nu_1(A_{1g})$	749 w	748 (10)		688 (10)		609 (10)[b]	641 (1.6) p
$\nu_2(E_g)$		571 (0.8)	578 w	578 (1.2)	472 mw	480 (0+) vbr	470 (0+) dp
$\nu_4(F_{1u})$	559 s		396 s		348 vs	350 (0+) br	
	474 vw						
$\nu_5(F_{2g})$		469 (1.2)		369 (3.6)		325 (2.3)	320 (0+) br, dp

[a] Uncorrected Raman intensities; unless noted otherwise, the listed spectra are those of the solids. [b] Contains contribution from $\nu_4(F_2)$ of NF_4^+.

Table VI. Vibrational Frequencies and Assignments for the Anions in NF_4GeF_5 and $NF_4Sb_2F_{11}$

Obsd freq, cm^{-1}, and rel intens			Obsd freq, cm^{-1}, and rel intens		
NF_4GeF_5			$NF_4Sb_2F_{11}$		
Ir	Raman	Assignments for GeF_5^-	Ir	Raman	Assignments for $Sb_2F_{11}^-$
701 vs		Terminal Ge–F str modes	1360 vw		Combination bands
690 sh	689 (1.0)		1295 vw		
673 mw	672 (4.9)		975 vw		
630 vs				764 (0.1)	Sb–F str modes
	578 (1.6)		695 vs		
	490 (0+) br	ν(GeFGe) bridge		689 (3.1)	
474 mw			664 s	678 sh	
386 m				649 (10)	
373 w	373 (0+) br	Def modes		597 sh	
	343 (0+) br		540 w	572 (0+)	
335 m					
	321 (0.8)		497 s		ν(SbFSb) bridge
	281 (1.0)			289 (1.0)	Sb–F def modes
	249 (0.6)			273 (0.7)	
	212 (0.4)			221 (1.8)	
	152 (0.4)			125 (0.4)	Lattice vib

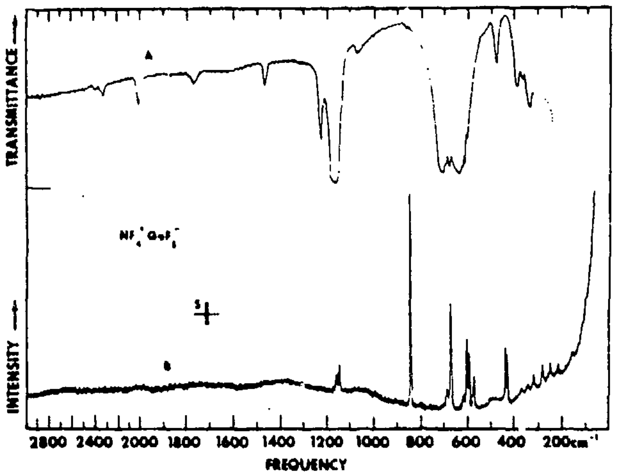

Figure 1. Vibrational spectra of solid NF_4GeF_5: Trace A, infrared spectrum of the dry powder in a silver bromide disk, the absorption below 300 cm^{-1} (broken line) being due to the AgBr windows; trace B, Raman spectrum. S indicating spectral slit width.

four fundamentals expected for tetrahedral NF_4^+ is well established,[10,11,37] the assignment of some combination bands has previously been questioned.[11] Furthermore, it seemed interesting to study the influence of solid-state effects on the vibrational spectra of these highly symmetric octahedral and tetrahedral ions.

Inspection of Figures 1–3 and of Table IV establishes beyond doubt the presence of approximately tetrahedral NF_4^+ ions in these salts. However, for several salts solid-state effects are observed. For the GeF_5^- salt, for example, the degeneracy of the E and the two F_2 modes is completely lifted and a splitting into two and three components, respectively, was observed. This is not surprising since the site symmetry of NF_4^+ in these salts is bound to be lower than T_d. However, since the space groups of the NF_4^+ salts are not firmly established (see above), the assignments for NF_4^+ in Table IV were made assuming symmetry T_d.

Out of the ten possible binary combination bands of NF_4^+ of T_d symmetry seven should be infrared active. Of these, six have been observed in the infrared spectra thus lending further support to the assignment of the fundamentals. In addition, one of the infrared-inactive combination bands was observable at about 880 cm^{-1} in the Raman spectra, probably due to intensity enhancement by Fermi resonance with $\nu_1(A_1)$.

The frequency of $\nu_1(A_1)$ of NF_4^+ varies by several cm^{-1} for the different NF_4^+ salts, and, owing to its narrow line width, this band is well suited to monitor quantitatively by Raman spectroscopy the progress of anion displacement reactions.

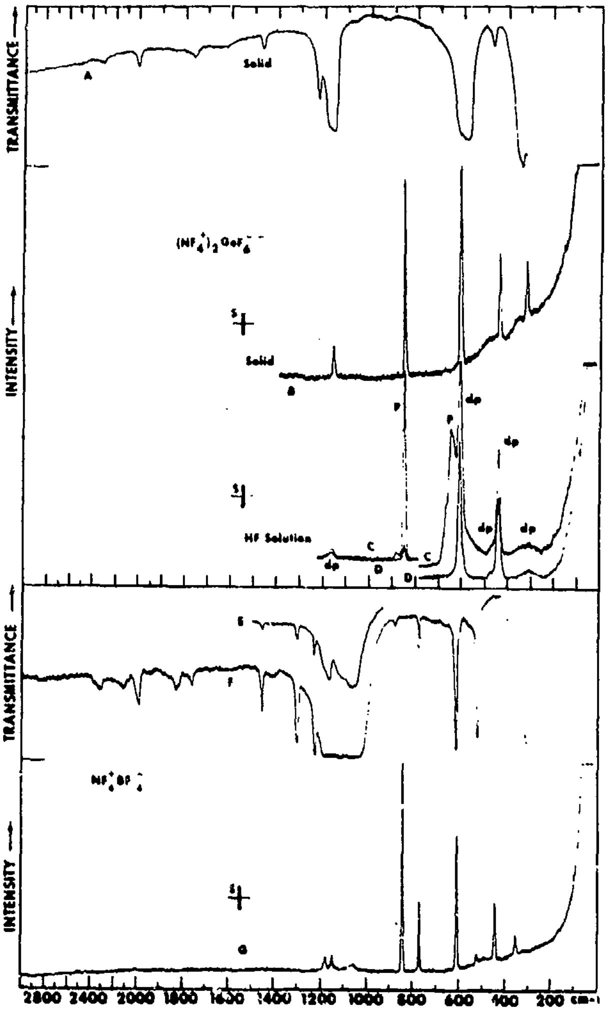

Figure 2. Vibrational spectra of $(NF_4)_2GeF_6$ compared to those of NF_4BF_4: trace A, infrared spectrum of solid $(NF_4)_2GeF_6$ as dry powder in a silver chloride disk; trace B, Raman spectrum of solid $(NF_4)_2GeF_6$; traces C and D, Raman spectra of $(NF_4)_2GeF_6$ in HF solution at two different recorder voltages with incident polarization parallel and perpendicular, respectively [p and dp stand for polarized and depolarized bands, respectively]; traces E and F, infrared spectrum of solid NF_4BF_4 at two different concentrations; trace G, Raman spectrum of solid NF_4BF_4.

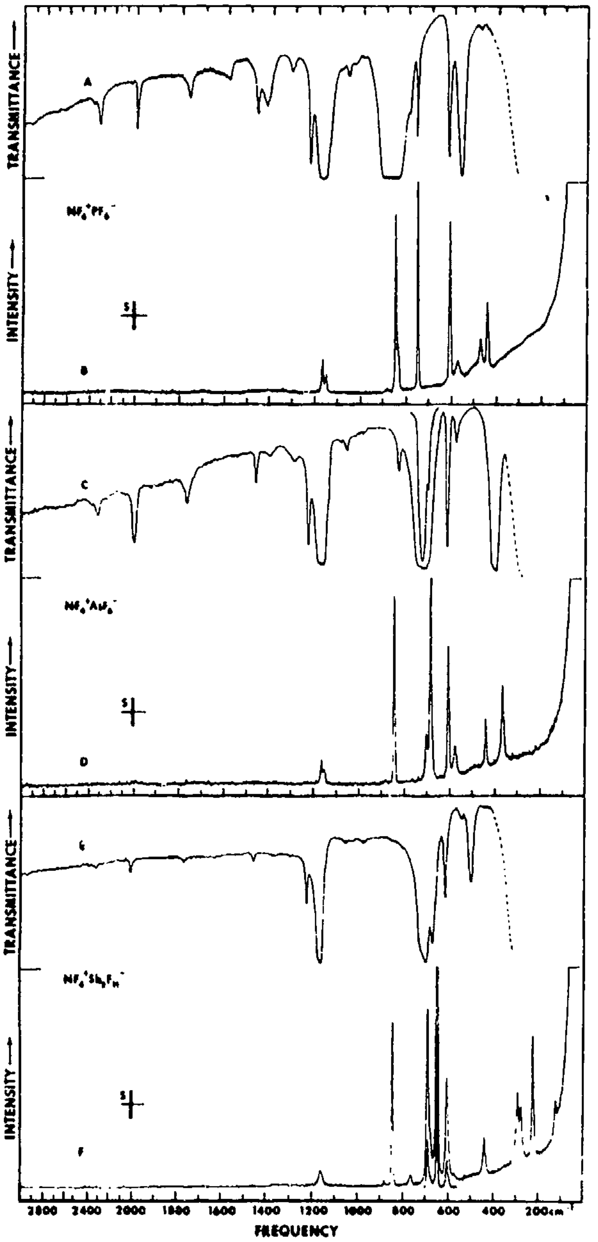

Figure 3. Vibrational spectra of NF_4PF_6, NF_4AsF_6, and $NF_4Sb_2F_{11}$: traces A and B, infrared and Raman spectra, respectively, of solid NF_4PF_6; traces C and D, infrared and Raman spectra, respectively of solid NF_4AsF_6; traces E and F, infrared and Raman (at two different recorder voltages) spectra, respectively, of solid $NF_4Sb_2F_{11}$.

The vibrational spectra of the anions also show solid-state effects. The spectrum of BF_4^- is analogous to that of NF_4^+ and consequently was assigned for point group T_d (see Table IV). The spectra of PF_6^- and AsF_6^- deviate somewhat from the O_h selection rules by showing splittings for the triply degenerate $\nu_3(F_{1u})$ mode and by not strictly following the rule of mutual exclusion. However, the deviations from O_h for these anions are relatively minor and, in the absence of exact knowledge of the space group, assignments (see Table V) were made for O_h. The observed frequencies agree well with those previously reported for other AsF_6^-,[42,43] PF_6^-,[43,44] and GeF_6^{2-} [43,45,46] salts. The spectrum of $Sb_2F_{11}^-$ in $NF_4Sb_2F_{11}$ (see Table VI) is in good agreement with that previously reported[47] for the anion in $O_2^+Sb_2F_{11}^-$, particularly if the pronounced changes observed for the $Sb_2F_{11}^-$ anion in different salts are kept in mind.

Assignments for GeF_5^- in NF_4GeF_5 are more difficult since this anion has not been well characterized. The existence of GeF_5^- salts was postulated[48] by Clark and Dixon and subsequently was established[49] by Wharf and Onyszchuk, who prepared several quaternary alkylammonium and arylarsonium salts. They attributed infrared bands at 690, 652, 343, and 317 cm^{-1} to GeF_5^-. No further data on GeF_5^- could be found in the literature. Recently, $O_2^+GeF_5^-$ was synthesized and its vibrational spectrum was recorded which suggested[50] a polymeric cis-fluorine-bridged structure for GeF_5^-.

Although the general appearance of the GeF_5^- Raman bands in NF_4GeF_5 (see Table VI) is similar to those of GeF_5^- in O_2GeF_5, there are pronounced differences. By analogy with O_2GeF_5, the large number of observed anion bands and the occurrence of bands in the frequency region (450–550 cm^{-1}) expected for fluorine bridge stretching modes rule out the presence of discrete GeF_5^- anions in NF_4GeF_5. The frequencies of the NF_4^+ modes in NF_4GeF_5 are essentially identical with those in NF_4MF_6 salts. Consequently, fluorine bridging of GeF_5^- in NF_4GeF_5 must occur between the anions. Since the addition of an extra fluoride ligand to GeF_5^- results in a pseudooctahedral structure, two kinds of bridging, cis and trans, are possible[51] which should be distinguishable from their vibrational spectra.

For a trans-fluorine-bridged structure, the anion would possess a symmetry center and the four nonbridging fluorines and the central atom would form a square plane. This would result in a highly symmetric structure exhibiting a small number of infrared and Raman bands, which ideally would be mutually exclusive. A typical example for such a trans-fluorine-bridged polymeric XF_5 species is α-BiF_5.[52]

On the other hand, a cis-fluorine-bridged structure would be of lower symmetry and result in a more complex spectrum. The spectra due to the GeF_5^- part of NF_4GeF_5 show a frequency and intensity pattern similar to those observed for NF_4SnF_5[53] and solid TaF_5.[54] Since the structure of solid TaF_5 is known[55] to consist of cyclic cis-fluorine-bridged tetramers, such a cyclic tetramer is also plausible for GeF_5^-. A more detailed discussion of the GeF_5^- spectrum will be given elsewhere.[53] The formation of polymeric anions in NF_4GeF_5 is not surprising in view of the established[51] polymeric nature of CrF_5^{2-}, AlF_5^{2-}, FeF_5^{2-}, and MnF_5^{2-} salts. All of these salts form polymeric chains of MF_6 units with the nature (cis or trans bridges, linear, helical, or ramified) of the chains varying from salt to salt.

Summary

Uv photolysis is a useful and convenient technique for the synthesis of high oxidation state complex fluorides which are difficult to prepare by other methods. Low-temperature conditions may be required if either the final or one of the intermediate products formed by the interaction of the F atoms with the starting materials are thermally unstable. Typical examples are stable $O_2^+AsF_6^-$ which can be prepared at room temperature,[28] unstable $O_2^+BF_4^-$ [13] and $O_2^+GeF_5^-$ [50] which can be prepared at −78 °C, or stable NF_4^+ salts which, depending on the anion, were prepared at either 25 or −196 °C. For the NF_4^+ salts the exact formation mechanism still remains to be established. If the formation of NF_4AsF_6 either by low-temperature uv photolysis or by thermal activation at high pressure[8] involves the same reaction mechanism, reaction kinetics might be more important than the thermal stability of the intermediates.

Three novel NF_4^+ salts, i.e. NF_4PF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$, have been prepared by uv photolysis and displacement reactions and have been characterized. The $(NF_4)_2GeF_6$ salt is the first example of an NF_4^+ salt containing a multiply charged anion. Interesting equilibrium reactions were found which allow the interconversion of GeF_5^-

and GeF_6^{2-} salts. Vibrational spectra indicate that the GeF_5^- anion in NF_4GeF_5 has a cis-fluorine-bridged polymeric structure.

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Registry No. NF_4BF_4, 15640-93-4; NF_4PF_6, 58702-88-8; NF_4AsF_6, 16871-75-3; $NF_4Sb_2F_{11}$, 58702-89-9; $(NF_4)_2GeF_6$, 58702-87-7; NF_4GeF_5, 58702-86-6; NF_3, 7783-54-2; BF_3, 7637-07-2; AsF_5, 7784-36-3; PF_5, 7647-19-0; GeF_4, 7783-58-6; CF_3NF_2, 335-01-3; F_2, 7782-41-4.

Supplementary Material Available: Listings of the observed x-ray powder diffraction patterns of NF_4PF_6, NF_4GeF_5, $(NF_4)_2GeF_6$, and NF_4BF_4 (4 pages). Ordering information is given on any current masthead page.

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Vibrational spectra of the pseudotrigonal bipyramidal tetrafluorides SF_4 and ClF_4^+

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Abstract—The Raman spectra of gaseous, liquid and solid SF_4 have been re-examined. Polarization measurements allow the unambiguous identification of the A_1 modes. The i.r. spectrum of SF_4 isolated in N_2 matrix has been recorded and ^{32}S–^{34}S isotopic shifts have been measured for several fundamentals. The matrix isolation study indicates that the 353 cm^{-1} absorption consists of two fundamentals, thus providing the hitherto missing ninth fundamental of SF_4. Complete assignments are given for SF_4 and are supported by force field and mean amplitudes of vibration computations. The results from the vibrational analysis support an intramolecular Berry-type exchange mechanism for SF_4. Raman polarization data have also been obtained for $ClF_4^+SbF_6^-$ in HF solution and revised assignments and force field values are given for ClF_4^+.

INTRODUCTION

The assignment of the fundamentals of pseudotrigonal bipyramidal tetrafluorides is extremely difficult. Thus, the vibrational spectrum of SF_4, the simplest representative of this type of molecule, is still poorly understood in spite of much recent study. During our study [1] of the structurally similar SF_4O molecule, we realized that the remaining questions concerning the vibrational spectrum of SF_4 had to be settled to give a firm basis for the assignments of the other pseudotrigonal bipyramidal molecules.

The first report on the vibrational spectrum of SF_4 has been published in 1956 by Dodd *et al.* [2]. They reported the Raman spectrum of the liquid and an incomplete i.r. spectrum of the gas. In 1965, Redington and Berney [3] published the i.r. spectrum of solid SF_4 in an argon matrix in the range 1400–400 cm^{-1}. Levin and Berney [4] have carefully studied the complete i.r. spectrum of gaseous SF_4 and have carried out a normal coordinate analysis. The Raman spectrum of gaseous SF_4 and force constants have been reported by Christe and Sawodny [5]. The assignments for SF_4 were revised by Frey *et al.* [6] based on a comparison with the known assignments of related molecules, and by Levin [7] based on the Raman spectrum of solid SF_4 and a CDNO/2 calculation of the i.r. intensities. The i.r. and Raman spectra of solid SF_4 have also been reported by Berney [8] and were interpreted in terms of different crystalline modifications. The far i.r. spectrum of gaseous SF_4 has been studied by Levin and Harris [9] in order to obtain evidence for intramolecular exchange. Finally, Christe *et al.* [10] have recently compared the various proposed assignments and force fields. Review of this extensive work showed that the reported data still did not permit an unambiguous assignment and that all proposed assignments led to inconsistencies. Therefore, we have reexamined the vibrational spectrum of SF_4 to obtain additional experimental data.

Recently, we have also reported [11] the vibrational spectrum and force field of the ClF_4^+ cation which is isoelectronic with SF_4. Since the ClF_4^+ assignments were based on those of SF_4, we have also revised those of ClF_4^+ in the light of our new results for SF_4.

EXPERIMENTAL

Sulfur tetrafluoride (from The Matheson Company) was purified by complexing it with CsF [12]. Only SF_4 forms an adduct with CsF and the unreactive sulfur oxyfluorides were pumped off. Pure SF_4 was recovered by vacuum pyrolysis of the $Cs^+SF_5^-$ residue.

The preparation of $ClF_4{}^+SbF_6{}^-$ and its HF solution have been described previously [11].

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4380 Å exciting line. A Claassen filter was used to eliminate plasma lines [13]. Polarization measurements were carried out by method VIII as described by Claassen *et al.* [13]. For the low-temperature spectra an apparatus was used similar to that described by Miller and Harney [14]. A stainless steel cell with Teflon O-rings and sapphire windows [15] was used to obtain the spectrum of the gas. The sample containers for liquid and solid SF_4 were 3 mm o.d. quartz tubes and those for HF solutions of $ClF_4{}^+SbF_6{}^-$ were Teflon-FEP capillaries. The apparatus, spectrometer, and technique used for the i.r. matrix isolation study have been described previously [16, 17].

RESULTS AND DISCUSSION

Sulfur tetrafluoride. Vibrational spectra and their assignment

The Raman spectra of gaseous, liquid and solid SF_4 and the i.r. spectra of N_2 matrix isolated and solid SF_4 are shown in Figs. 1 and 2, respectively. In this paper, we will limit the discussion of our data to those features which either significantly differ from previous reports or are important for the assignment of the bands.

Of the nine fundamentals expected for SF_4 in point group C_{2v} [4, 5], the assignment of the following modes is well established [7, 10]: A_1, $\nu_1 = 892$, $\nu_2 = 558$; B_1, $\nu_6 = 730$, $\nu_7 = 532$; B_2, $\nu_8 = 867$ cm^{-1}. Identification of the A_1 deformation modes ν_3 and ν_4 should be possible by Raman polarization measurements. Unfortunately, the previous data [2, 5] were ambiguous. The present study shows (see Fig. 1) that the bands at 353 and 228 cm^{-1} are definitely polarized and, therefore, represent ν_3 and ν_4, respectively. This assignment is in agreement with that proposed by Levin [7]. The question concerning the motions corresponding to ν_3 and ν_4 is discussed below.

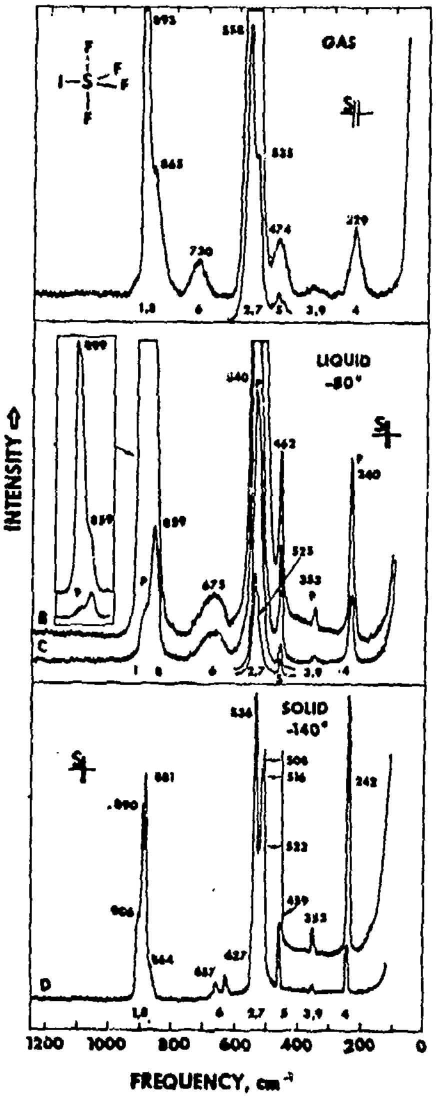

Fig. 1. Raman spectra of SF_4. Traces A, spectrum of the gas at 10 atm pressure recorded at two different recorder voltages. Traces B and C, spectrum of the liquid with the incident polarization perpendicular and parallel, respectively. The insert was recorded at a lower recorder voltage. Traces D, spectrum of the solid recorded at two different recorder voltages. P indicates polarized bands and S the spectral slit-widths. The numbers 1–9 refer to the assignment of the bands to the nine fundamentals of SF_4.

After identification of the 353 and 228 cm^{-1} bands as ν_3 and ν_4, respectively, assignments are still needed for $\nu_5(A_2)$ and $\nu_9(B_2)$. For the gas there is one moderately intense Raman band at 474 cm^{-1} still unassigned. This frequency is too high for ν_9 since a value of 453 cm^{-1} already results in an unreasonably high value of 3.16 mdyn Å radian^{-2} for F_{99} (see Sets V and VI in Tables 1 and 2). Consequently, the 474 cm^{-1} band must represent the torsional mode $\nu_5(A_2)$ which is expected to occur in the frequency range 400–550 cm^{-1}. An extremely weak feature having maxima at 465, 453, 447, 441, 435 and 429 cm^{-1} was observed [4] in the i.r. spectrum of the gas. Since the frequency differences between these and the 474 cm^{-1} Raman band are too large and since $\nu_5(A_2)$ should be i.r. inactive, the i.r. feature is attributed to combination bands, such as $2\nu_4$[7]. A Raman band at about 410 cm^{-1}, that has been reported previously [2, 5] but was questionable [5], was not observed during this study and, therefore, must have been due to an impurity.

Because all observed bands have already been assigned to other fundamentals, it must be assumed that ν_9 coincides with another fundamental. Since a frequency value of 470 cm^{-1} is unreasonably high (see above) for ν_9, only two alternatives, 353 and 228 cm^{-1}, remain. Since $\nu_9(B_2)$ should be reasonably intense in the i.r. spectrum [7], we have carefully examined the i.r. matrix isolation spectrum for evidence of such a coincidence.

As can be seen from trace A' of Fig. 2, the 360 cm^{-1} band is split into two components which are separated by about 3.2 cm^{-1}. This splitting cannot be attributed to the ^{32}S–^{34}S isotopes owing to the high relative intensity of the lower frequency component (natural abundance of ^{34}S is 4.2%). Furthermore, it cannot be due to an associated species or crystal field effects since the remaining bands in the SF_4 spectrum do not show any such splittings. Consequently, these two components are interpreted as the two fundamentals, $\nu_3(A_1)$ and $\nu_9(B_2)$. Since ν_3 should be of higher i.r. intensity than ν_9 [7], the 360 cm^{-1} component is assigned to ν_3 and the 357 cm^{-1} one to ν_9.

The two maxima of the 353 cm^{-1} i.r. absorption of gaseous SF_4 [4] might then be interpreted as the Q branches of the two fundamentals ν_3 and ν_9, although their separation does not preclude their interpretation as a double Q branch of a B-type band [18]. However, it should be kept in mind that the second B-type band at 867 cm^{-1} does not exhibit such a double Q branch and this might also be the case for the ν_9 deformation.

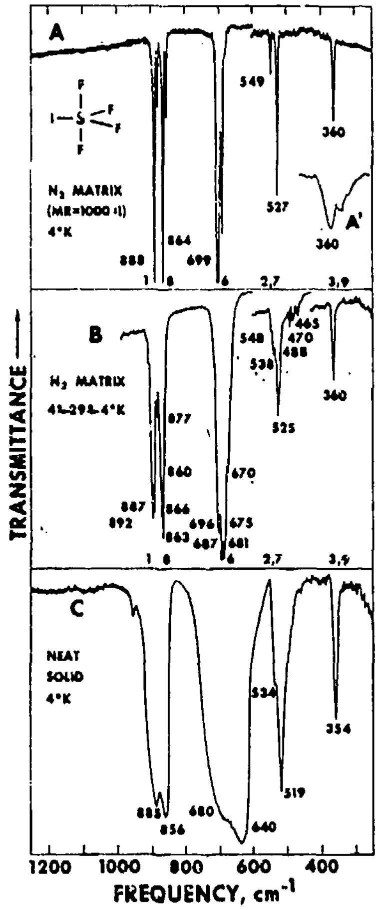

Fig. 2. Infrared Spectra of SF_4. Trace A, spectrum of the N_2 matrix isolated species. Trace A' shows the 360 cm^{-1} band at a tenfold scale expansion under higher resolution conditions. Trace B, sample of trace A after a controlled diffusion experiment. Trace C, neat solid.

Table 1. Assignment of normal modes of SF_4 and ClF_4^+

Species	Approx description of mode	Frequency, cm^{-1}							
		observed		used for SF_4 force field computations					
		SF_4	ClF_4^+	I	II	III	IV	V	VI
A_1 ν_1	$\nu sym XF_2 eq$	892	800	892					
ν_2	$\nu sym XF_2 ax$	558	571	558					
ν_3	$\delta sciss XF_2 eq$ and ax, sym comb	356	385	353	228	353	228	353	228
ν_4	$\delta sciss XF_2 ax$ and eq, asym comb	228	250	228	353	228	353	228	353
A_2 ν_5	XF_2 twist	474	475	470					
B_1 ν_6	$\nu asym XF_2 ax$	730	795	730					
ν_7	$XF_2 eq$ wagging	532	515	532					
B_2 ν_8	$\nu asym XF_2 eq$	867	829	867					
ν_9	$\delta sciss XF_2 ax$ out of plane	350	385	353		228		453	

Table 2. Force constants[a] of SF_4[b,c] and ClF_4^+

	SF_4 I	II	III	IV	V	VI	ClF_4^+
A_1 $F_{11} = f_r + f_{rr}$	5.75	5.71	5.75	5.71	5.75	5.71	4.49
$F_{22} = f_R + f_{RR}$	3.48						3.65
$F_{33} = 0.99 f_\beta + 0.01 f_\gamma - 0.15 f_{\beta\gamma}$	1.07	0.65	1.07	0.65	1.07	0.65	1.38
$F_{44} = 0.004 f_\beta + 0.71 f_\gamma + 0.29 (f_\alpha + f_{\alpha\alpha'} + f_{\alpha\alpha''} + f_{\alpha\alpha'''}) + 0.13 f_{\alpha\beta} + 1.80 f_{\alpha\gamma} + 0.11 f_{\beta\gamma}$	0.40	0.67	0.40	0.67	0.40	0.67	0.50
A_2 $F_{55} = f_\alpha - f_{\alpha\alpha'} - f_{\alpha\alpha''} + f_{\alpha\alpha'''}$	1.93						2.08
B_1 $F_{66} = f_R - f_{RR}$	3.11						3.80
$F_{77} = f_\alpha + f_{\alpha\alpha'} - f_{\alpha\alpha''} - f_{\alpha\alpha'''}$	2.05						1.91
$F_{67} = \sqrt{2} (f_{R\alpha} - f_{R\alpha'})$	0.89						0.89
B_2 $F_{88} = f_r - f_{rr}$	5.26		5.15		5.37		5.07
$F_{99} = f_\alpha - f_{\alpha\alpha'} + f_{\alpha\alpha''} - f_{\alpha\alpha'''}$	1.92		0.81		3.16		2.44
$F_{89} = \sqrt{2} (f_{r\alpha} \cdot f_{r\alpha'})$	0.84		0.50		1.20		0.84
f_r	5.51	5.49	5.45	5.37 5.43	5.56	5.54	4.78
f_R	3.30						3.73
f_{rr}	0.25	0.23	0.30	0.28	0.19	0.17	−0.29
f_{RR}	0.19						−0.08

(a) Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch-bend interaction constants in mdyn/radian.

(b) Preferred set for SF_4 is I (see text).

(c) The given explicit F matrix is for SF_4 and differs somewhat from that of ClF_4^+ owing to the different geometries of the two species. For the explicit F matrix of ClF_4^+ see reference [11].

The Raman spectra showed no evidence for a splitting of the 353 cm^{-1} band. This is not surprising since $\nu_8(B_2)$ is expected to be of much lower Raman intensity than $\nu_3(A_1)$. Therefore, the 353 cm^{-1} Raman band is assumed to be mainly due to $\nu_3(A_1)$, in accord with the polarization measurements.

Additional support for the above assignment of $\nu_8(B_2)$ to the 353 cm^{-1} absorption can be derived from the following considerations: (i) The F_{eq}–F_{ax} mean amplitude of vibration significantly varies with the frequency of ν_9 (see Table 3). Of the two alternatives given for ν_9 (353 and 228 cm^{-1}), only 353 cm^{-1} results in a value falling within the reported [19] uncertainty limits. (ii) We expect F_{99} to have a value similar to those of F_{55} and F_{77} (about 2 mdyn Å radian^{-2}, see Table 2). (iii) For the structurally closely related ClF_3 molecule [6, 20], the in plane and out of plane scissoring modes also coincide and have a frequency value of 328 cm^{-1}, similar to that of 353 cm^{-1} observed for SF_4.

Force field and mean amplitudes of vibration computations

A normal coordinate analysis and a computation of mean amplitudes of vibration were carried out to support the assignments. The results are summarized in Tables 2 to 4. Although the above assignments for SF_4 are well supported, we have computed force fields and mean amplitudes of vibration for both $\nu_3 > \nu_4$ and $\nu_4 > \nu_3$, assuming values of 228, 353 and 453 cm^{-1} for ν_9. This was done to demonstrate that the above assignments are the only set which can satisfactorily account for all the experimental data. The vibrational frequencies used for these computations are listed in Table 1. Slightly better frequency values for ν_3, ν_5 and ν_9 would have

Table 3. Computed[a] (298°K) and observed [19] mean amplitudes (in Å) of vibration of SF_4

	$\langle q^2 \rangle$ calc$^{1/2}$ I	II	III	IV	V	VI	$\langle q^2 \rangle$ obs$^{1/2}$
S–F_{eq}	0.041	0.041	0.041	0.041	0.041	0.041	0.041 ± 0.005
S–F_{ax}	0.048	0.048	0.048	0.048	0.048	0.048	0.047 ± 0.005
F_{eq}–F_{eq}	0.076	0.092	0.076	0.091	0.076	0.091	0.063 ± 0.01
F_{eq}–F_{ax}	0.070	0.073	0.077	0.074	0.068	0.065	0.067 ± 0.005
F_{ax}–F_{ax}	0.061	0.061	0.061	0.061	0.061	0.061	0.059 ± 0.01

(a) Using the force fields of Table 2.

Table 4. Potential energy distribution[a] and eigenvectors for the different force fields of SF_4

Assignment	I, III, V ($\nu_3 > \nu_4$)					II, IV, VI ($\nu_4 > \nu_3$)				
	PED	Eigenvectors				PED	Eigenvectors			
		S_1	S_2	S_3	S_4		S_1	S_2	S_3	S_4
$A_1\ \nu_1$	94 F_{11}	−0.277	−0.015	0.111	0.175	93 F_{11}	−0.277	−0.016	0.108	0.183
ν_2	100 F_{22}	−0.009	0.229	−0.008	−0.011	100 F_{22}	−0.009	0.229	−0.007	−0.012
ν_3	75 F_{33} + 20 F_{44}	0.025	0.005	0.226	0.193	80 F_{33} + 20 F_{44}	0.001	0	0.193	−0.095
ν_4	77 F_{44} + 22 F_{33}	−0.005	−0.001	0.080	−0.242	75 F_{44} + 18 F_{33}	0.029	0.006	0.145	0.290
					ALL SETS, PED					
$A_2\ \nu_5$					100 F_{55}					
$B_1\ \nu_6$					133 F_{66} − 34 F_{67} + 21 F_{77}					
ν_7					93 F_{77}					
	I, II PED		III, IV PED				V, VI PED			
$B_2\ \nu_8$	107 F_{88} − 11 F_{89}		106 F_{88}				109 F_{88} − 16 F_{89}			
ν_9	103 F_{99}		105 F_{99}				102 F_{99}			

(a) Percent contributions. Contributions of less than 10% to the PED are not listed.

been 356, 474 and 350 cm^{-1}, respectively, but the differences are insignificant.

The force fields were computed [21] by trial and error to give an exact fit between observed and calculated frequencies. Sets I to VI are the simplest force fields that duplicated the following ^{32}S–^{34}S isotopic shifts observed in our matrix isolation study: $\Delta\nu_1 = 10.6$, $\Delta\nu_3 \sim 0$, $\Delta\nu_6 = 12.3$, $\Delta\nu_8 = 10.2$ cm^{-1}.

Choice of a force field and identity of the A_1 bending modes

In trigonal bipyramidal pentafluorides generally two acceptable force fields are found [22]. This is caused by the possibility of interchanging the assignments for the in plane axial and equatorial bending modes. For the structurally similar SF_4 molecule, the same problem exists since the assignments of ν_3 and ν_4 in the A_1 block can be interchanged. This results in two different force fields (Sets I, III, V and Sets II, IV, VI, respectively, of Tables 1 and 2). Consequently, a choice of a preferred force field requires a discrimination between the two alternatives.

Further interest was added to this problem by the fact that these molecules can undergo an intramolecular exchange between equatorial and axial ligands [9, 22–26]. This exchange involves a pseudorotational motion of the equatorial and axial fluorine ligands as originally proposed by **Berry** [23]. Therefore, it was desirable to verify the existence of such an exchange for SF_4 by a normal coordinate analysis.

The symmetry coordinates used in our computations for the two A_1 bending modes of SF_4 are $S_3 = -0.074\,\Delta\gamma + 0.997\,\Delta\beta$ and $S_4 = 0.842\,\Delta\gamma + 0.268\,(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) + 0.063\,\Delta\beta$ where α, β and γ are the bond angles between equatorial–axial, equatorial–equatorial, and axial–axial fluorine ligands, respectively. The eigenvectors (*L* matrix) are listed in Table 4. They show that for both assignments, i.e. $\nu_3 > \nu_4$ and $\nu_4 > \nu_3$, the 228 cm^{-1} mode is an antisymmetric and the 356 cm^{-1} mode is a symmetric combination of the symmetry coordinates S_3 and S_4. The main difference between the two assignments is that the relative contributions of equatorial and axial bending to each mode are reversed. For $\nu_3 > \nu_4$, 228 cm^{-1} is mainly axial bending, whereas for $\nu_4 > \nu_3$ it is mainly equatorial bending.

The antisymmetric combination of S_3 and S_4 can be expected to offer the shortest path to a Berry-type exchange. This was experimentally confirmed by Levin's analysis of a hot band progression of the *Q* branch of the 228 cm^{-1} i.r. band [9] and a recent gas phase NMR study [25] which yielded very similar values for the activation energy required for an intra-molecular exchange process. Additional experimental support for 228 and 356 cm^{-1} being antisymmetric and symmetric combinations, respectively, of S_3 and S_4 comes from relative i.r. intensity arguments. The symmetric combination should result in a significantly larger change of the dipole moment and therefore is represented by the more intense 356 cm^{-1} i.r. band.

The evidence presented above establishes the 228 cm^{-1} mode as an anti-symmetric combination of S_3 and S_4 and as the mode involved in a Berry-type exchange, but it does not distinguish between the two alternate assignments, i.e. $\nu_3 > \nu_4$ and $\nu_4 > \nu_3$. However, distinction between these two choices is possible by a comparison between computed and observed [19] mean amplitudes of vibration. As shown in Table 3, only the assignment $\nu_3 > \nu_4$ results in an acceptable value for the $F_{eq} - F_{eq}$ amplitude of vibration and therefore is the preferred assignment. The eigenvectors listed in Table 4 show that ν_3 (356 cm^{-1}) is about an equal mixture of equatorial and axial bending, whereas ν_4 (228 cm^{-1}) involves mainly axial bending. This fact has previously been explained [10] and therefore requires no further comment. It should be kept in mind, however, that in spite of the availability of some $^{32}S - ^{34}S$ isotopic data, the force field used for these computations is still underdetermined. Therefore, the relative contributions to ν_3 and ν_4 from S_3 and S_4 might change somewhat for a general valence force field.

In summary, all nine fundamentals of SF_4 have been observed and their assignment is well supported by Raman polarization and matrix isolation data, and force field and mean amplitudes of vibration computations. The results from the normal coordinate analysis establish the existence of a Berry-type exchange coordinate for SF_4. Our revised assignment (Set I) for SF_4 differs from all previous assignments [2–10] for at least one fundamental.

Comparison of SF_4 *with trigonal bipyramidal* XF_5 *molecules*

Comparison of the above results for SF_4 with those previously reported [22, 27–32] for the structurally related pentafluorides PF_5, VF_5 and AsF_5 indicates significant differences. For the pentafluorides, the higher frequency bending mode was attributed to mainly axial and the lower one to mainly equatorial bending. However, description of these motions in terms of a symmetric and antisymmetric combination of axial and equatorial bending, as discussed above for SF_4 and previously suggested also for the pentafluorides [30], might account for these apparent discrepancies between such similar molecules. The considerably lower force constant values found [27–31] for the Berry-type motion in the pentafluorides, when compared to that of SF_4, might be partially accounted for by the lower activation energies required for intramolecular exchange in these molecules [22, 32, 33].

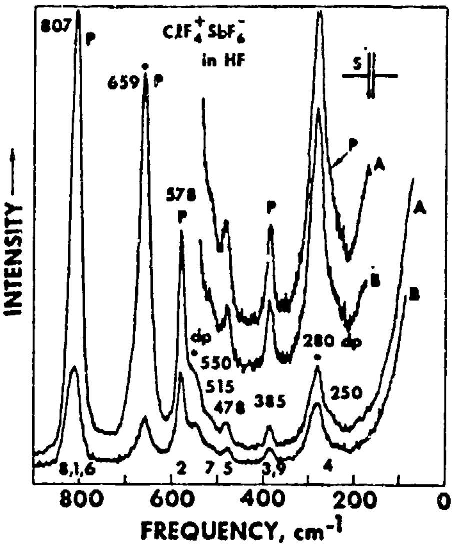

Fig. 3. Raman spectrum of $ClF_4^+SbF_6^-$ in HF solution recorded with the incident polarization perpendicular (traces A) and parallel (traces B). The three bands due to octahedral SbF_6^- are marked by an asterisk.

The ClF_4^+ *cation*

In view of the above results for SF_4, we have also reexamined the Raman spectrum of isoelectronic ClF_4^+. Polarization data were obtained for $ClF_4^+SbF_6^-$ in HF solution (see Fig. 3). Ignoring the bands due to the anion, four polarized bands were observed the frequencies of which are in excellent agreement with those of the four A_1 modes of SF_4. The assignment of the vibrational spectrum of ClF_4^+ (see Table 1) was made by analogy with that of SF_4 using the Raman data from this study and the previously published [11] i.r. data. As can be seen from Figs. 1–3 and Table 1, the vibrational spectra of SF_4 and ClF_4^+ closely resemble each other. This is not surprising since it has previously been shown that the isoelectronic pairs SF_2O–ClF_2O^+ [34], SF_2O_2–$ClF_2O_2^+$ [35], SF_6–ClF_6^+ [36], and SF_5^-–ClF_5 [12] exhibit similar spectra.

The force field of ClF_4^+ was also recomputed (see Table 2) using the frequencies of Table 1 and the geometry assumed earlier [11]. The force field of ClF_4^+ is also underdetermined, and the choice of the off-diagonal symmetry force constants strongly influences the values of the diagonal ones [11]. Consequently, we have chosen for ClF_4^+ a force field similar to that of SF_4 (see above) which has been better defined by the use of ^{32}S–^{34}S isotopic data. In spite of the relatively large uncertainties common [11] to such force fields, comparison of the force constants of SF_4 with those of ClF_4^+ shows the expected trends. In both species, the value of the equatorial stretching force constant f_r is significantly larger than that of the axial one (see Table 2). This implies highly polar axial bonds, as expected for a model containing significant contributions from semi-ionic three-center four-electron *pp σ* bonds [11]. Furthermore, in ClF_4^+ the difference between the axial and the equatorial stretching force constant is smaller than in SF_4. This is caused by the positive charge and the increased oxidation state and electronegativity of the central atom in ClF_4^+, all of which suppress the formation of semi-ionic bonds [37].

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Contribution from Rocketdyne, a Division of Rockwell International, Canoga Park, California 91304, and from the Science Center, Rockwell International, Thousand Oaks, California 91360

Dioxygenyl Pentafluorogermanate(IV), $O_2^+GeF_5^-$

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The novel compound $O_2^+GeF_5^-$ was prepared by uv photolysis of a GeF_4–F_2–O_2 mixture in quartz at -78 °C. The compound is a white crystalline solid and is unstable at 25 °C. It was characterized by infrared, Raman, and ESR spectroscopy. The vibrational spectra indicate for the anions a polymeric cis-fluorine-bridged structure similar to that found for NbF_5. The possibility to convert O_2GeF_5 into $(O_2)_2GeF_6$ by HF treatment at low temperature was briefly studied. For comparison, $(NO)_2GeF_6$ was prepared and characterized by vibrational spectroscopy. The Raman spectrum of solid GeF_4 has also been recorded and longitudinal components were observed for each of the two F_2 modes.

Introduction

The synthesis of $O_2^+PtF_6^-$, the first known example of a dioxygenyl salt, was reported[1] in 1962 by Bartlett and Lohmann. Since then numerous other O_2^+ salts have been synthesized and studied. However, all of the reported[1-16] dioxygenyl salts belong to one of the following three types: $O_2^+MF_6^-$ (M = P, As, Sb, Bi, Pt, Ru, Rh, Pd, or Au), $O_2^+M_2F_{11}^-$ (M = Sb, Bi, Nb, or Ta), or $O_2^+MF_4^-$ (M = B). In view of the interesting physical and chemical properties of these paramagnetic and strongly oxidizing salts, we have studied the possible synthesis of O_2^+ salts containing new types of anions. In this paper we report the synthesis and characterization of $O_2^+GeF_5^-$, the first known representative of the type $O_2^+MF_5^-$. Further interest was added to this study by the fact that the GeF_5^- anion has only recently been discovered.[17] Except for quaternary ammonium salts,[17] no other GeF_5^- salts have been reported and no structural data on GeF_5^- were available.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in a well-passivated (with ClF_3) Monel vacuum line equipped with Teflon FEP U-traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%) or a Validyne Model DM56A pressure transducer. Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

Germanium tetrafluoride (Ozark Mahoning), F_2 (Rocketdyne), and O_2 (research purity, 99.99% minimum, Matheson Gas Products) were used without further purification. Nitrosyl fluoride was prepared from NO and F_2 at -196 °C and purified by fractional condensation.

The infrared spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer Model 457 infrared spectrophotometer. The spectra of gases were obtained using Monel cells of 5-cm path length fitted with AgCl windows. The spectra of solids at room temperature were obtained by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a Wilks minipellet press. The powdered sample was placed between the platelets before starting the pressing operation. The low-temperature spectra were recorded at −196 °C using a cell and transfer technique similar to those previously described.[18] The inner windows of the cell were AgCl or CsI; the outer ones, CsI disks. The instrument was calibrated by comparison with standard calibration points.[19]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[20] for the elimination of plasma lines. Sealed quartz or Teflon FEP tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded using a previously described[21] device. Polarization measurements were carried out according to method VIII listed by Claassen et al.[20]

ESR spectra were recorded as previously described.[15] The ^{19}F NMR spectra were recorded at 56.4 MHz on a Varian Model DA60 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique relative to external $CFCl_3$. Teflon FEP liners (Wilmad Glass Co.) inserted into glass NMR tubes were used as sample containers and anhydrous HF was used as a solvent. Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries (~0.5-mm o.d.)

Synthesis of $O_2^+GeF_5^-$. A 1-l. quartz bulb containing 500 cm^3 of O_2, 250 cm^3 of F_2, and 250 cm^3 of GeF_4 was exposed for 7 days to uv radiation from a high-pressure mercury lamp (Hanovia 616A, 100 W) equipped with a water filter. The condensing tip and the bottom of the reactor were kept at −78 °C. The solid $O_2^+GeF_2^-$ accumulated in the cold section of the reactor which also contained some solid GeF_4. After completion of the photolysis, products volatile at −31 °C were removed in vacuo. The white solid residue (about 500 mg) was transferred, while cold, from the quartz bulb to cold quartz or Teflon FEP tubes in an inert-atmosphere glovebox.

The composition of the solid was determined by allowing weighed samples contained in a Teflon FEP ampule to decompose completely at 25 °C and by separating and measuring the gases noncondensable (O_2 and F_2) and condensable (GeF_4) at −196 °C. The identity of the decomposition products was established by mass and infrared spectroscopy. In a typical experiment, 82 mg of the solid, corresponding to 0.411 mmol of $O_2^+GeF_5^-$ produced upon decomposition 0.63 mmol of $O_2 + F_2$ and 0.42 mmol of GeF_4, thus establishing its composition as O_2GeF_5. The ionic structure of the solid was established by vibrational spectroscopy.

Synthesis of $(NO^+)_2GeF_6^{2-}$. Germanium tetrafluoride (2.17 mmol) and FNO (5.40 mmol) were combined at −196 °C in a passivated Teflon FEP ampule. The mixture was warmed first to −78 °C, then to −45 °C, and then to 25 °C for 30 min. Unreacted FNO (1.05 mmol) was removed by pumping at 25 °C, leaving behind 532 mg of a stable white solid (weight calculated for 2.17 mmol of $(NO)_2GeF_6$ is 535 mg). The ionic structure of the solid was established by vibrational spectroscopy.

Results and Discussion

Synthesis and Properties of $O_2^+GeF_5^-$. Uv photolysis of a mixture of O_2, F_2, and GeF_4 in quartz at −78 °C produces a white crystalline solid according to

$$2O_2 + F_2 + 2GeF_4 \xrightarrow[-78\,°C]{h\nu} 2O_2GeF_5$$

The composition of the solid was established by quantitative thermal decomposition at 25 °C which produces the starting materials. It was found that the decomposition rate is suppressed by a pressure buildup of the gaseous decomposition products. A similar suppression of the decomposition rate of a dioxygenyl salt by the corresponding gaseous Lewis acid has previously been observed[22] for $O_2^+BF_4^-$.

The thermal stability of $O_2^+GeF_5^-$ is similar to that[22] of $O_2^+BF_4^-$. It was stored at −20 °C for over 4 months in either quartz or Teflon FEP containers without noticeable decomposition. It reacts violently with water producing a gas with typical fluorine odor.

$O_2^+GeF_5^-$ is the first example of a dioxygenyl salt of the type $O_2^+MF_5^-$. The relatively good thermal stability of $O_2^+GeF_5^-$ is surprising in view of the fact that GeF_5^- salts are difficult to prepare and that the only known examples possess bulky and strongly stabilizing counterions, such as quaternary ammonium cations.[17] A plausible explanation for the relative stability of GeF_5^- in the presence of a small cation,

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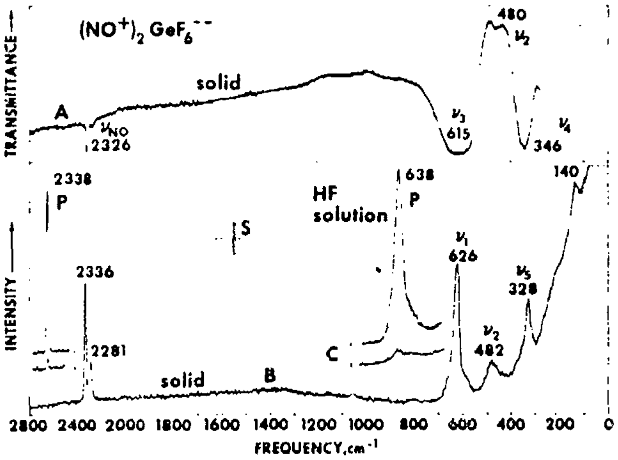

Figure 1. Vibrational spectra of $(NO^+)_2GeF_6^{2-}$ at 25 °C: trace A, infrared spectrum of the dry powder as a AgBr disk; trace B, Raman spectrum of the solid; trace C, Raman spectrum of an HF solution. P indicates polarized bands, and S the spectral slit width.

such as O_2^+, will be given below.

Since a trigonal-bipyramidal GeF_5^- anion would possess an energetically unfavorable structure, it might be possible to convert it to the more favorable and stable octahedral GeF_6^{2-} anion. For NF_4^+ salts, we have found that such a conversion can be achieved by treatment with anhydrous HF. This type of conversion was also studied for $O_2^+GeF_5^-$ as a possible route to $(O_2^+)_2GeF_6^{2-}$ which would be the first known example of a bis(dioxygenyl) salt and should possess very interesting magnetic properties. Unfortunately, the treatment of $O_2^+GeF_5^-$ with HF in the temperature range −78 to −31 °C did not produce any product of sufficient stability and purity to allow its unambiguous identification.

Synthesis, Properties, and Spectra of $(NO^+)_2GeF_6^{2-}$. The knowledge of the vibrational spectra of $(NO^+)_2GeF_6^{2-}$, which should be isostructural with $(O_2^+)_2GeF_6^{2-}$, was desirable to predict the spectrum of GeF_6^{2-} in its hypothetical dioxygenyl salt. The synthesis of $(NO^+)_2GeF_6^{2-}$ by the interaction of either GeO_2 with ClNO and BrF_3[23] or Ge with FNO·3HF[24] has previously been reported but the compound was not characterized. For our study, $(NO^+)_2GeF_6^{2-}$ was prepared in quantitative yield by direct combination of GeF_4 with a slight excess of FNO. It is a white crystalline solid, stable at room temperature.

The vibrational spectrum of $(NO^+)_2GeF_6^{2-}$ is shown in Figure 1. The observed bands and their frequencies agree well with those previously reported for the NO^+ cation[25,26] and the GeF_6^{2-} anion,[27-29] thus confirming the ionic nature of the adduct. The spectra were recorded at 25 and −120 °C but showed no pronounced temperature-dependent order–disorder phenomena caused by reorientational motion of the ions.[14,30,31] The splitting of the NO stretching mode into two bands for the solid disappears in the spectrum of the HF solution (see Figure 1) and, hence, is due to crystal effects. The ^{19}F NMR spectrum of $(NO^+)_2GeF_6^{2-}$ in HF solution was also recorded, but only a single resonance was observed for both GeF_6^{2-} and HF solvent indicating rapid exchange of fluorine.

The x-ray powder diffraction pattern of $(NO^+)_2GeF_6^{2-}$ was also recorded and was tentatively indexed for a hexagonal unit cell with $a = 11.78$ Å, $c = 9.78$ Å, and $Z = 8$; a unit cell apparently related to that of $(NH_4)_2GeF_6$ for which $a = 5.862$ Å, $c = 4.817$ Å, and $Z = 1$ was found.[32] The similarity of the unit cell dimensions per formula unit is not surprising in view of the previous observation[30] that at 25 °C $O_2^+AsF_6^-$ and $OH_3^+AsF_6^-$ possess almost identical unit cells.

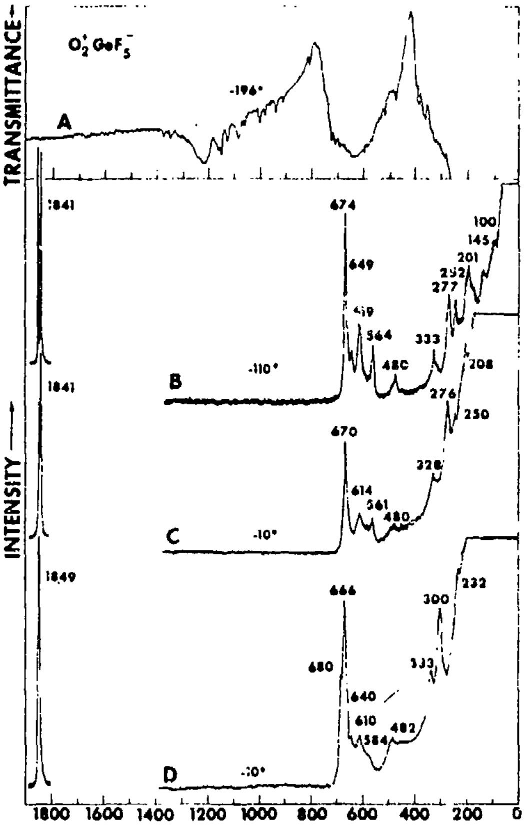

Figure 2. Vibrational spectra of $O_2^+GeF_5^-$: trace A, infrared spectrum of the solid recorded as a dry powder between CsI disks; traces B and C, Raman spectra of a well-aged solid sample; trace D, Raman spectrum of a freshly prepared sample. The spectral slit width used for the recording of the Raman bands in the 1800–1900-cm⁻¹ region was half of that (3 cm⁻¹) used for the recording of the rest of the spectrum at the same gain setting.

Vibrational Spectrum and Structure of $O_2^+GeF_5^-$. The vibrational spectra of $O_2^+GeF_5^-$ are shown in Figures 2 and 3. These spectra are relatively complex and rule out the presence of both GeF_6^{2-} (see above) and solid GeF_4 (see below). Since the Raman spectra show lines between 1840 and 1860 cm⁻¹, characteristic[6,20] for O_2^+, the solid must be ionic and have the composition $O_2^+GeF_5^-$. The Raman spectra were recorded over the temperature range −5 to −130 °C and show a pronounced temperature dependence. At the higher temperatures, the anion bands are broader and fewer in number. By analogy with $O_2^+AsF_6^-$, $O_2^+SbF_6^-$,[14,30,31] and $OH_3^+AsF_6^-$,[31] this might be explained by order–disorder phenomena (see above). Similarly, freshly prepared samples showed a somewhat simpler spectrum (Figure 2, trace D) than well-aged samples.

A closer inspection of the O_2^+ bands in $O_2^+GeF_5^-$ also shows some interesting effects. Whereas a freshly prepared sample showed a single sharp line at 1849 cm⁻¹, the aged samples exhibited two lines at 1841 and 1847–1855 cm⁻¹, respectively. The frequency of the higher energy line and its intensity relative to that of the lower energy decreased with decreasing temperature (see Figure 3). This observation is further evidence for the existence of ordering effects and for a unit cell containing more than one O_2^+ cation.

While the vibrational spectra establish beyond doubt the presence of discrete O_2^+ cations, there is considerable direct and indirect evidence against the presence of discrete GeF_5^- anions, particularly in the well-aged samples. The GeF_5^- anion is isoelectronic with AsF_5 and therefore, should possess a

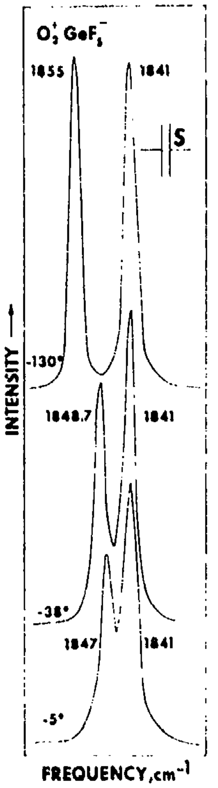

Figure 3. Temperature dependence of the O_2^+ stretching mode in the Raman spectra of $O_2^+GeF_5^-$ recorded with tenfold scale expansion and a spectral slit width of 1.5 cm^{-1}.

trigonal-bipyramidal structure of symmetry D_{3h}. Whereas AsF_5 and PF_5 are highly volatile and on the basis of their vibrational spectra[33,34] are little associated in the liquid and solid state, SbF_5 has a high boiling point and is associated in the gas, liquid, and solid states[35,36] through the formation of cis-fluorine bridges. Since the size of Ge(IV) should be intermediate between those of As(V) and Sb(V), GeF_5^- might very well be polymeric, particularly in an anion-dominated crystal lattice.

Comparison of the Raman spectrum of $O_2^+GeF_5^-$ with those of unassociated PF_5,[33] AsF_5,[34] or SbF_5[35] and associated SbF_5[35] or tetrameric NbF_5[16,36] was found helpful for distinguishing between discrete and polymeric GeF_5^- anions. The observation of at least five Ge–F stretching modes, with one of them (480 cm^{-1}) occurring in the frequency range expected for fluorine-bridged structures, argues against the presence of a discrete GeF_5^- anion. Furthermore, the Raman spectrum of GeF_5^- in $O_2^+GeF_5^-$ closely resembles that[16,36] of solid tetrameric NbF_5, indicating a similar polymeric structure. The crystal structure of solid NbF_5 has been determined by Edwards[37] and its vibrational spectrum was thoroughly analyzed by Beattie and co-workers.[36] Assignments for GeF_5^- on the basis of a cis-fluorine-bridged tetrameric polyanion can therefore be made by analogy with those[36] given by Beattie and co-workers for solid NbF_5. The possibility of a polymeric trans-fluorine-bridged structure for GeF_5^- can be eliminated based on the study of Beattie and co-workers on the vibrational spectrum of trans-fluorine-bridged α-BiF_5 which exhibits a much simpler Raman spectrum.[38]

The infrared spectrum of $O_2^+GeF_5^-$ also supports a polymeric structure for the anion. The 480-cm^{-1} band, indicative of fluorine bridges, was observed and the remaining part of the spectrum is very complex. Although the Raman spectra of the anions in $O_2^+GeF_5^-$ and $NF_4^+GeF_5^-$ [39] are relatively similar, the corresponding infrared spectra are more distinct. This indicates that the structure of polymeric GeF_5^- may be significantly influenced by the nature of the cations.

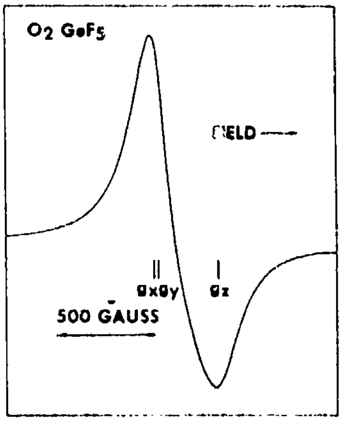

Figure 4. ESR spectrum of $O_2^+GeF_5^-$ recorded at −196 °C.

Additional indirect evidence for a polymeric structure of GeF_5^- in $O_2^+GeF_5^-$ can be derived from the following considerations. (i) The observed thermal stability of $O_2^+GeF_5^-$ would be surprisingly high (see above) for a salt containing discrete GeF_5^- anions. (ii) The GeF_5^- anion shows a strong tendency[17] to add a sixth ligand, such as H_2O or NH_3. Since the O_2^+ cation is quite small, there should be anion–anion contact in the crystal lattice and fluorine bridging appears likely. (iii) The splitting of the O_2^+ stretching mode in the Raman spectrum of $O_2^+GeF_5^-$ indicates a large unit cell containing more than one O_2^+ cation, contrary to $O_2^+MF_6^-$ for which only one very narrow line is observed for the O_2^+ stretch even at low temperatures. (iv) The observed orthorhombic crystal field splitting parameter in the ESR spectrum (see below) is compatible with a structure containing a polyanion. (v) The large number of combination bands observed for $O_2^+GeF_5^-$ in the infrared spectrum indicates many fundamentals and, hence, a rather complex anion.

ESR Spectrum of $O_2^+GeF_5^-$. The ESR spectrum of $O_2^+GeF_5^-$, recorded at −196°, is shown in Figure 4. The peak to peak line width is 283 G. The g factors were determined from computer-simulated spectra[15] as $g_x = 2.00$, $g_y = 1.98$, and $g_z = 1.86$. The natural line width used was Lorentzian with a peak to peak width of about 140 G. The orthorhombic crystal field splitting parameter[15] determined from g_z was 2.7×10^3 cm^{-1}. This value is larger than those reported[12,15] for $O_2^+AsF_6^-$ and $O_2^+BF_4^-$. This larger crystal field could be caused by effects, such as multiple charges or lower symmetry of the anion, and is not surprising in view of the probably polymeric nature of the GeF_5^- anion (see above).

Raman Spectrum of Solid GeF_4. The Raman spectrum of solid GeF_4 was recorded to demonstrate the absence of decomposition products in the spectra of $O_2^+GeF_5^-$. The observed spectrum is shown in Figure 5. It will be briefly discussed since it shows a remarkable deviation from the spectrum expected for a tetrahedral species of symmetry T_d. The observation of six sharp bands instead of the four, expected for T_d, resembles the previous reports for solid SiF_4[40] and CF_4.[41] By analogy with the spectrum of SiF_4 which has been thoroughly analyzed,[40] we assign the additional Raman bands observed for solid GeF_4 to a splitting of the two F_2 modes into longitudinal and transverse components. Longitudinal and transverse waves propagate with different frequencies in cubic or uniaxial crystals with the longitudinal component having the higher frequency.[40] Since the splitting of the F_2 modes into two components might also be explained by lowering of the site symmetry of GeF_4 from T_d to either C_{3v} or C_3, the infrared spectrum of solid GeF_4 was also recorded. However, such a site symmetry lowering seems less likely for the fol-

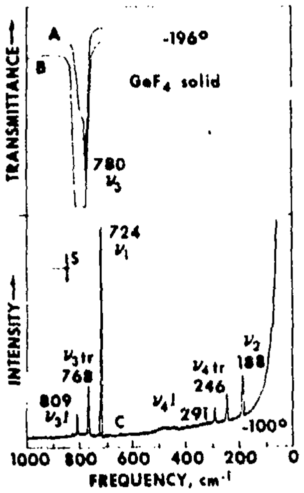

Figure 5. Vibrational spectra of solid GeF_4: traces A and B, infrared spectra recorded at two different concentrations; trace C, Raman spectrum; ℓ and tr indicate the longitudinal and transverse components, respectively, of the F_2 modes.

lowing reasons. (i) No evidence was found in the infrared spectrum for ν_1 which for C_{3v} or C_3 should become infrared active. (ii) The frequency separations between the F_2 components are larger than expected for site symmetry effects. (iii) The infrared spectrum shows only one intense component for ν_3. For C_{3v} or C_3, both components should be infrared active, whereas for a splitting into longitudinal and transverse components only the latter one should be infrared active. A more detailed study of these effects was beyond the scope of this investigation concerned with dioxygenyl salts.

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Registry No. $O_2^+GeF_5^-$, 58672-97-2; $(NO^+)_2GeF_6^{2-}$, 58673-00-0; GeF_4, 7783-58-6.

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VIBRATIONAL SPECTRUM AND FORCE CONSTANTS OF THE XeF_5^+ CATION

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Abstract—The i.r. and Raman spectra of solid $XeF_5^+BF_4^-$ and $XeF_5^+AsF_6^-$ and their Raman and ^{19}F NMR spectra in HF solution were recorded. The observed spectra are consistent with a square-pyramidal XeF_5^+ cation of symmetry C_{4v}. All nine fundamentals were assigned for XeF_5^+ and force constants were computed for the isoelectronic series XeF_5^+, IF_5, TeF_5^- and SbF_5^{2-}.

INTRODUCTION

DURING an investigation of the $XeOF_4$–PtF_6 reaction system[1] the precise knowledge of the vibrational and ^{19}F NMR spectrum of XeF_5^+ was required to allow its distinction from the previously reported[2] $XeOF_3^+$. The latter cation, if indeed existent[1], should belong to the same point group C_{4v} as XeF_5^+ and, therefore, is expected to exhibit similar spectra. Although the crystal structure of several XeF_5^+ salts is known[3–5], only incomplete information on the spectroscopic properties of XeF_5^+ could be found in the literature[2, 6–10]. In this paper we report the i.r. and Raman spectra of solid $XeF_5^+BF_4^-$ and $XeF_5^+AsF_6^-$ and their Raman and ^{19}F spectra in HF solution. Since several assignments for XeF_5^+ were questionable, we have used force field computations for the isoelectronic series XeF_5^+, IF_5, TeF_5^- and SbF_5^{2-} to support our assignments. Force fields for IF_5 and TeF_5^- have previously been computed[11]. However, in the meanwhile the vibrational spectrum of TeF_5^- has been reinvestigated[12, 13] indicating the need for reexamination of our previous[11] assignment for $\nu_4(B_1)$.

EXPERIMENTAL

Apparatus and materials. Volatile materials were manipulated in a well passivated (with ClF_3) Monel-Teflon FEP vacuum system. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0·1 per cent). Solid products were handled in the dry nitrogen atmosphere of a glove box.

I.R. spectra of the solids were recorded on a Perkin Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1} using pressed AgCl pellets[11]. The ^{19}F NMR spectra of HF solutions were recorded on a Varian Model DA60 spectrometer at 56·4 MHz using Teflon FEP sample tubes, $CFCl_3$ as external standard, and the side-band technique. The HF purification and sampling technique has previously been described[14]. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å exciting line. The spectrometer was modified by the addition of a Claassen filter[15] for the elimination of plasma lines. For the solids and HF solutions glass melting point capillaries and FEP NMR sample tubes, respectively, were used in the transverse viewing–transverse excitation mode. Metal masks containing two small holes for entrance and exit of the laser beam and an orthogonal slit-shaped opening for the exit of the scattered light were used for the Teflon tubes to effectively suppress the Teflon bands[16].

Xenon hexafluoride was prepared by the method of Malm[17]. Arsenic pentafluoride (Ozark Mahoning Co.) and BF_3 (The Matheson Co.) were purchased. All volatile materials were purified by fractional condensation prior to their use and their purity was verified by i.r. spectroscopy.

Synthesis of $XeF_5^+BF_4^-$. Boron trifluoride (17·55 mmole) was added in increments at 25° to a Teflon FEP U-trap containing XeF_6 (17·15 mmole). The mixture was kept at 25° for 12 hr. Unreacted BF_3 (0·4 mmole) was pumped off at 0° leaving behind 5·384 g (17·14 mmole) of $XeF_5^+BF_4^-$.

Synthesis of $XeF_5^+AsF_6^-$. Arsenic pentafluoride (3·95 mmole) was added at −196° to a Teflon FEP ampoule containing XeF_6 (1·88 mmole). The mixture was kept at −80° for 20 hr. The volatile material was removed *in vacuo* and consisted of BF_3 (1·86 mmole) and unreacted AsF_5 (2·08 mmole). The white solid residue weighed 783 mg in good agreement with the weight (781 mg) calculated for 1·88 mmole of $XeF_5^+AsF_6^-$.

RESULTS AND DISCUSSIONS

^{19}F NMR *spectra.* The ^{19}F NMR spectra of $XeF_5^+AsF_6^-$ and $XeF_5^+BF_4^-$ in HF solution were measured in the temperature range 20 to −80°. For $XeF_5^+AsF_6^-$, acidification of the HF solution with AsF_5 was required[18] to suppress the exchange rate between XeF_5^+ and the solvent and to allow observation of a separate XeF_5^+ resonance signal. For a AsF_5, $XeF_5^+AsF_6^-$ HF mixture having a mole ratio of 1:1·3:7·6, a sharp AB_4 spectrum in the XeF region was observed at 20° exhibiting the expected ^{129}Xe satellites (see Table 1). In addition a very broad peak at 111 ppm above external $CFCl_3$ was observed for rapidly exchanging HF, AsF_6^- and AsF_5.

For $XeF_5^+BF_4^-$, acidification with BF_3 did not result in a separate XeF_5^+ signal. In neat HF a separate signal was observed for BF_4^- at 148 ppm[19] which at 20° was relatively broad, but became narrow at lower temperature. The HF–XeF_5^+ peak occurred at 20° at 125 ppm and was relatively narrow. With decreasing temperature this resonance became increasingly broader and was shifted upfield (to 170 ppm at −75°), but did not split into separate signals. The upfield shift was caused by partial precipitation of $XeF_5^+BF_4^-$.

The chemical shifts and coupling constants observed for XeF_5^+ in acidified HF are in reasonable agreement with those previously reported for XeF_6 in SbF_5[20] and $HOSO_2F$[21] solution (see Table 1).

Table 1. ^{19}F NMR parameters of XeF_5^+ in acidified HF compared to those in SbF_5[20] and $HOSO_2F$[21] solution

Solvent	Chemical shifts (ppm) A(quintet)	B_4(doublet)	Coupling constants (Hz) J_{FF}	$J_{^{129}XeF^A}$	$J_{^{129}XeF^B}$
$HF(AsF_5)$	−228·4	−110·0	174·1	1433	152·1
SbF_5	−231·7	−108·8	175·7	1512	143·1
$HOSO_2F$			179	1377	170

Vibrational spectra. Figures 1 and 2 show the i.r. and Raman spectra of solid and the Raman spectra in HF solution of $XeF_5^+BF_4^-$ and $XeF_5^+AsF_6^-$, respectively. The observed frequencies are listed in Table 2 and are compared with those reported for isoelectronic IF_5[12, 22, 23].

Schematic line diagrams for the Raman spectrum of solid $XeF_5^+AsF_6^-$ have previously been reported[6, 7], but no assignments were given. The published diagrams[6, 7] and our spectrum agree well for most of the stronger bands. The Raman line diagram of an HF solution of $XeF_5^+AsF_6^-$ has also been published, but significantly deviates from our spectrum and provided no clear evidence for the presence of the AsF_6^- anion[7]. Recently a Raman line diagram for solid $XeF_5^+BF_4^-$ has also been published[2] and been compared to that of IF_5. It agrees well with our spectrum, but owing to the lack of i.r. and solution Raman data the suggested[2] assignment was not well founded and needs revision (see below). Raman spectra of two compounds containing XeF_5^+ in combination with SO_3F^-[10] and PdF_6^{2-}[8] have also been recorded, but again no detailed vibrational analysis was given.

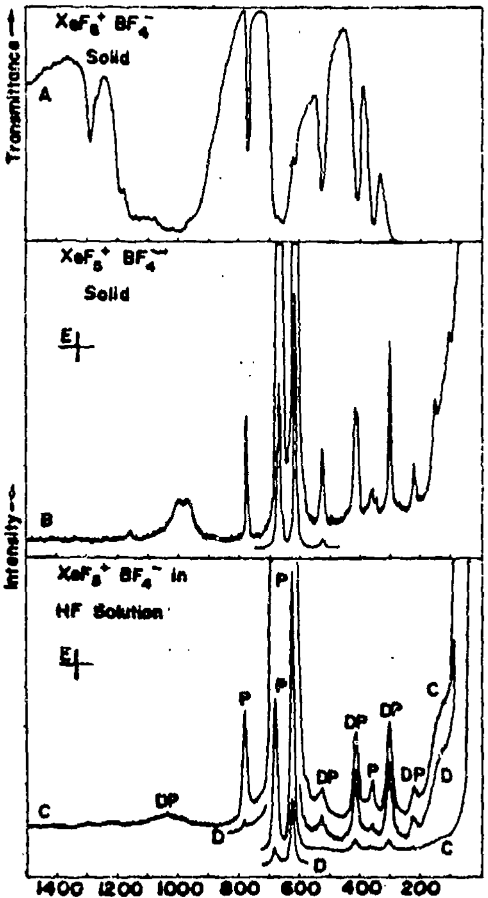

Fig. 1. Vibrational spectra of $XeF_5^+BF_4^-$: A, i.r. spectrum of the solid as AgCl disk; B, Raman spectrum of the solid; C and D, Raman spectrum of the HF solution, incident polarization perpendicular and parallel, respectively; E indicates spectral slit width.

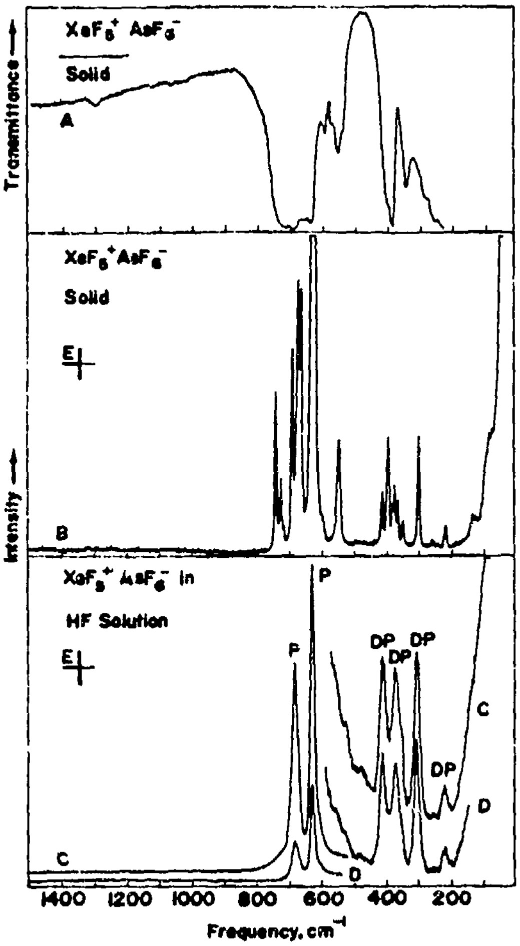

Fig. 2. Vibrational spectra of $XeF_5^+AsF_6^-$.

Inspection of Figs. 1 and 2 and of Table 2 reveals that the vibrational spectra of HF solutions of $XeF_6 \cdot BF_3$ and $XeF_6 \cdot AsF_5$ contain the bands expected[19] for the free BF_4^- and AsF_6^- ions, respectively. The presence of the XeF_5^+ cation in these solutions has been established by ^{19}F NMR spectroscopy (see above). Comparison of the solution spectra with those of the solids shows the presence of the same ions in the solids. For $XeF_5^+BF_4^-$,

Table 2. I.R. and Raman spectra of XeF$_5^+$BF$_4^-$ and XeF$_5^+$AsF$_6^-$ compared to those of IF$_5$

Obsd freq, cm^{-1} and rel. intens.*								Assignment (point group)		
IF$_5$†		XeF$_5^+$BF$_4^-$			XeF$_5^+$AsF$_6^-$			XF$_5$	BF$_4^-$	AsF$_6^-$
I.R.	Raman	I.R.	R		I.R.	R		(C_{4v})	(T_d)	(O_h)
		solid	solid	HF soln	solid	solid	HF soln			
		1289 w			1300 vw			$\nu_2+\nu_7(E)$	$\nu_1+\nu_4(F_2)$	
		1268 vw, sh								
		1192 m, sh				741 (1·6)				
						725 (0·6)				$\nu_3(F_{1u})$
			1159 (0+)							
		950 to		1040(0+) dp					$\nu_3(F_2)$	
		1150 vs, br	997(0·1)			715(0+)				
			969(0·1)		740 to	688(2)				
		773 m	775(0·5)	776(0·5) p					$\nu_1(A_1)$	
					630 vs					
			672 sh							
710 s	710 s, p	672 s, sh	667(6·5)	679(5·4) p		673(2·7)	679(6·3) p	$\nu_1(A_1)$		$\nu_1(A_{1g})$
640 vs	631	652 vs	655 sh			663(2·6)		$\nu_7(E)$		
	616 vs, p	614 w	615(10)	625(10) p		631(10)	625(10) p	$\nu_2(A_1)$		
	604 m			610 sh		600 sh	610 sh	$\nu_4(B_1)$		
		526 m	525(0·3)	525(0·1) dp	595 vw	600 sh			$\nu_4(F_2)$	
		513 w			570 w					
					548 m	545(1)	557(0+) dp			$\nu_2(E_g)$
					537 w					
372 m	372 w	416 m	416(0·4)	410(0·3) dp	408 sh	411(0·5)	408(0·7) dp	$\nu_8(E)$		
		407 m	407(0·4)							
					387 s	394(0·9)				$\nu_4(F_{1u})$
						380(0·1)				
					372 w, sh	375(0·5)	375(0·7) dp			$\nu_5(F_{2g})$
						365(0·4)				
318 m	318 m, p	353 m	359(0·1)	358(0·1) p	345 m	346(0·2)	352 sh	$\nu_3(A_1)$		
			349(0+)						$\nu_2(E)$	
	276 w		299(0·7)	302(0·4) dp		298(1·1)	299(1·0) dp	$\nu_6(B_2)$		
			267(0+)			258(0+)		$\nu_5(B_1)$		
	200 vw		222(0·1)	218(0·1) dp		218(0·2)	217(0·2) dp	$\nu_9(E)$		
			154(0·1)	140 br		130(0·1)		Bands due to lattice vibrations or weak F bridges		
			102(0+)			77(0+)				

*Uncorrected Raman intensities.

†Data from Refs. [12, 22, 23].

the spectra are quite similar. The only deviations from the selection rules for BF_4^- of symmetry T_d are observed in the i.r. spectrum of the solid, where $\nu_1(A_1)$ and $\nu_2(E)$ became i.r. active. This effect is frequently observed for BF_4^- salts in the solid state. It is readily explained by a lower site symmetry and/or crystal field effects. For $XeF_5^+AsF_6^-$, the solid state spectra show little change for the XeF_5^+ bands but pronounced splittings for the AsF_6^- bands. The fact that that in the solid state the spectrum of a highly symmetric ion such as octahedral AsF_6^- is more strongly affected than those of ions of lower symmetry, has previously been discussed in detail[24] for $BrF_2^+SbF_6^-$ and does not rule out predominantly ionic structures. Since the ionic nature of the solid XeF_6·Lewis acid adducts has been established by single crystal X-ray diffraction studies [2–5], we can limit the discussion of the observed spectra to the assignment of the XeF_5^+ bands.

For XeF_5^+ of symmetry C_{4v}, nine fundamental vibrations should be observed. These are classified as $3A_1+2B_1+B_2+3E$. Ideally, all nine modes should be Raman active whereas only the A_1 and E modes should be i.r. active. Of the Raman active modes only those of species A_1 should be polarized.

After subtraction of the anion bands, we are left with three polarized Raman lines at about 680, 625 and 355 cm^{-1}. Based on their frequencies, relative i.r. and Raman intensities, and a comparison with the known spectrum of isoelectronic IF_5 [12, 22, 23], these are assigned to the axial Xe–F stretch, the symmetric XeF_4 stretch, and the umbrella deformation, respectively. The antisymmetric XeF_4 stretch of species E is readily assigned to 652 cm^{-1} based on its high intensity in the i.r. spectrum of $XeF_5^+BF_4^-$. The remaining yet unassigned stretching mode is the symmetric out of phase XeF_4 stretch of species B_1. This mode is i.r. inactive and of relatively low Raman intensity and, therefore, more difficult to assign. It should occur in the region 550–700 cm^{-1}. There are two possible assignments for this mode, i.e. 610 and 672 cm^{-1}, listed in Table 3 as sets A and B, respectively. We strongly prefer set A over set B for the following reasons: (i) a plot of the stretching frequencies within the isoelectronic series XeF_5^+, IF_5, TeF_5^-, SbF_5^{2-} (see Fig. 3 and Table 3) and the force field computations (see below) favor set A, (ii) the shoulder at 672 cm^{-1} in the solid is not observed for the solution spectrum whereas the shoulder at about 610 cm^{-1} is retained.

There are four bands at 410, 300, 261 and 218 cm^{-1} left for assignment to the remaining four yet unassigned deformational modes. Based on its high i.r. intensity, its splitting into two components in the spectrum of solid $XeF_5^+BF_4^-$, and by comparison with IF_5, the 410 cm^{-1} band is assigned to the E mode, ν_8. The $\nu_5(B_1)$ mode involves only a very small change in polarizability and, therefore, should be of very low Raman intensity. For the other members of this series it has not been observed and for XeF_5^+ it is assigned to the very weak Raman line at 261 cm^{-1}. The two remaining bands at 300 and 218 cm^{-1} are assigned to $\nu_6(B_2)$ and $\nu_9(E)$, respectively, by analogy with the well established assignments reported [12] for the remaining members of this isoelectronic series.

For the solids, Raman lines were observed in the vicinity of 100 cm^{-1}. Their frequencies are too low for fundamentals and, therefore, they are attributed to lattice vibrations or weak fluorine bridges. For solid $XeF_5^+BF_4^-$, a Raman line was observed at 154 cm^{-1}. This line is retained in solution although it becomes very broad and shifts to lower frequency. For solid $XeF_5^+AsF_6^-$, a similar Raman band was observed at 130 cm^{-1}. Owing to their relatively large differences in frequency, we feel that these bands do not represent a fundamental of XeF_5^+. A conclusive assignment for these bands cannot be made at the present time.

In summary, the vibrational spectra of $XeF_6 \cdot BF_3$ and $XeF_6 \cdot AsF_5$ are in good agreement with the ionic structures $XeF_5^+BF_4^-$ and $XeF_5^+AsF_6^-$, respectively. Assignments were made for all nine fundamentals of XeF_5^+ in agreement with predictions for a six atomic species of symmetry C_{4v}. Our assignments for XeF_5^+ differ for four modes from those previously cited [2] as unpublished results.

Force constants. The plausibility of our assignments for XeF_5^+ was examined by computation of a modified valence force field and by its comparison with those of isoelectronic IF_5, TeF_5^- and SbF_5^{2-}. The required potential and kinetic energy metrics were computed with a machine method [25] using the geometries shown in Table

Table 3. Comparison of the fundamentals of the isoelectronic series XeF_5^+, IF_5, TeF_5^- and SbF_5^{2-}

Assignment in point group C_{4v}		Approx. description of vibration	Frequencies (cm^{-1})					
			XeF_5^+		IF_5*	TeF_5^-*		SbF_5^{2-}†
			A	*B*		*A*	*B*	
A_1	ν_1	$\nu(XF')$	679		710	624		557
	ν_2	$\nu_s(XF_4)$ in phase	625		616	517		427
	ν_3	$\delta_s(XF_4)$ umbrella	355		318	291		278
B_1	ν_4	$\nu_s(XF_4)$ out of phase	610	672	604	488	579	388
	ν_5	$\delta_{as}(XF_4)$ out of plane	261					
B_2	ν_6	$\delta_s(XF_4)$ in plane	300		276	243		220
E	ν_7	$\nu_{as}(XF_4)$	652		631	479		377
	ν_8	$\delta(F'XF_4)$	410		372	350		307
	ν_9	$\delta_{as}(XF_4)$ in plane	218		200	146		142

*Data from Refs. [12, 22, 23].
†Data from Ref. [12].

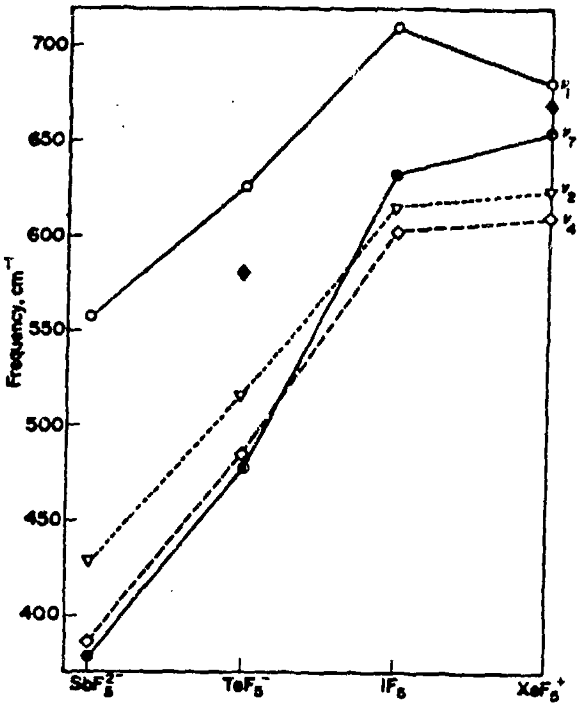

Fig. 3. Plot of the stretching frequencies for the isoelectronic series SbF_5^{2-}, TeF_5^-, IF_5 and XeF_5^+.

4. The force constant definitions used are those of Begun *et al.*[23], except that the deformation coordinates are weighted by unit (1 Å) distance. The force constants were adjusted by trial and error, assuming the simplest possible modified valence force field, to give an exact fit between the observed and computed frequencies. Owing to the heavy central atom, coupling between the diagonal *F* terms should be relatively small and a diagonal force field might be expected to be a reasonable approximation of the general valence force field. When alternate assignments were possible, force fields were computed for both assignments and are included in Table 5 as sets *A* and *B*. The potential energy distribution showed that all vibrations were highly characteristic (88 per cent or higher) except for the A_1 block of XeF_5^+ where the similar frequencies of ν_1 and ν_2 caused considerable mixing of the corresponding symmetry coordinates. However, introduction of a small F_{12} term (sets *A'* and *B'* in Table 5) resulted in highly characteristic vibrations.

Table 4. Assumed molecular parameters for XeF_5^+, IF_5, TeF_5^- and SbF_5^{2-}

	XeF_5^+*	IF_5†	TeF_5^-‡	SbF_5^{2-}§
R, Å (axial)	1·76	1·84	1·86	1·916
r, Å (equatorial)	1·82	1·87	1·95	2·075
β, deg	80·4	81·9	78·8	79·4

*K. Leary, D. H. Templeton, A. Zalkin and N. Bartlett, *Inorg. Chem.* 12, 1726 (1973).

†A. G. Robiette, R. H. Bradley and P. N. Brier, *Chem. Commun.*, 1567 (1971).

‡S. H. Mastin, R. R. Ryan and L. B. Asprey, *Inorg. Chem.* 9, 2100 (1970).

§R. R. Ryan and D. T. Cromer, *Inorg. Chem.* 11, 2322 (1972).

Inspection of Table 5 shows smooth force constant trends within the isoelectronic series XeF_5^+, IF_5, TeF_5^- and SbF_5^{2-}. Of the assignments previously reported[12] for IF_5, TeF_5^- and SbF_5^{2-} only one assignment, ν_4 of TeF_5^-, does not fit the overall picture. The frequency of 569 cm^{-1} assigned[12] to this mode appears too high by about 100 cm^{-1} as can also be seen from Fig. 3. Assignment of either the 492 or 507 cm^{-1} single crystal Raman component[12] to $\nu_4(B_1)$ might resolve this discrepancy and results in a better force field trend and is given as Set *A* in Table 5. The 479 cm^{-1} single crystal Raman band might be then reassigned to the $a_g + b_{2g}$ component of $\nu_7(E)$. Such a reassignment might also account for the high Raman intensity of the 488 powder band which is difficult to explain in terms of the antisymmetric TeF_4 stretch alone, but could be caused by a coincidence of $\nu_4(B_1)$ and $\nu_7(E)$ at 488 cm^{-1}. The 579 cm^{-1} Raman line, which was previously assigned to $\nu_4(B_1)$[12], is very weak and might possibly be due to a combination band such as $\nu_6 + \nu_9 = 588$ or $479 + 95 = 574$.

For XeF_5^+, there was also a question[2] about ν_4 being at 672 or 610 cm^{-1}. As can be seen from Table 5, $\nu_4 = 610$ cm^{-1} (Set *A*) results in an f_{rr} value similar to those found for the other members of this series and makes f_r and f_R more dissimilar in agreement with the observed difference in bond length between equatorial and axial bonds[5].

Table 5 is an excellent example for force constant trends in isoelectronic series containing fluorine ligands. When moving to the right in the periodic system, both the

Table 5. Comparison of the symmetry and internal force constants* of the isoelectronic series XeF_5^+, IF_5, TeF_5^-, SbF_5^{2-} using the assignments of Table 3

		XeF_5^+					TeF_5^-		
		A	$\underline{A}'$	B	B'	IF_5	$\underline{A}$	B	SbF_5^{2-}
A_1	$F_{11} = f_R$	4·35	4·43	4·35	4·43	4·82	3·71		2·93
	$F_{12} = 2f_{Rr}$	0	−0·2†	0	−0·2†	0	0		0
	$F_{22} = f_r + 2f_{rr} + f_{rr'}$	4·38	4·30	4·38	4·30	4·22	2·95		2·01
	$F_{33} = Mf_\beta + (1-M)f_\alpha + 2Mf_{\beta\beta} + Mf_{\beta\beta'} + 2(1-M)f_{\alpha\alpha} + (1-M)f_{\alpha\alpha'} + Nf_{\alpha\beta} + Nf_{\alpha\beta'}$‡	2·90				2·47	2·15		2·23
B_1	$F_{44} = f_r - 2f_{rr} + f_{rr'}$	4·17		5·06		4·08	2·66	3·75	1·68
	$F_{55} = f_\beta - 2f_{\beta\beta} + f_{\beta\beta'}$	2·53				[2·25]§	[1·9]§		[1·9]§
B_2	$F_{66} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha'}$	0·86				0·75	0·65		0·60
E	$F_{77} = f_r - f_{rr'}$	3·65				3·39	1·95		1·16
	$F_{88} = f_\beta - f_{\beta\beta'}$	1·88				1·67	1·57		1·33
	$F_{99} = f_\alpha - f_{\alpha\alpha'}$	0·77				0·67	0·39		0·42
	f_R	4·35	4·43	4·35	4·43	4·82	3·71		2·93
	f_r	3·96	3·94	4·19	4·17	3·77	2·38	2·65	1·50
	$f_{rr'}$	0·05	0·03	−0·17	−0·19	0·04	0·07	−0·20	0·08
	f_{rr}	0·31	0·29	0·54	0·52	0·38	0·43	0·70	0·34
	f_{Rr}	0	−0·1	0	−0·1	0	0		0
	$f_\alpha^¶$	0·77				0·67	0·39		0·42
	f_β	2·36				2·05	1·88		1·77
	$f_{\alpha\alpha}$	−0·05				−0·05	−0·13		−0·09
	$f_{\beta\beta}$	0·15				0·09	0·14		0·15
	$f_{\beta\beta'}$	0·48				0·38	0·31		0·44
	$4f_r + f_R$	20·2				19·9	13·2		8·9
	$f_r : f_R$	0·91	0·89	0·96	0·94	0·78	0·64	0·71	0·51

*Stretching constants are in mdyn/Å and deformation constants in mdyn/Å radian^2; the preferred force constant sets are underlined.

†Interaction term required for the potential energy distribution of ν_1 and ν_2 to be most characteristic, i.e. 100 S_1, and 98% S_2, respectively. For $F_{12} = 0$, the following PED was obtained: $\nu_1 = 74 S_1 + 26 S_2$ and $\nu_2 = 74 S_2 + 26 S_1$.

‡The factors M and N are a function of the bond angles and in alphabetical order have the following numerical values: XeF_5^+, 0·90, 1·19; IF_5, 0·93, 1·03; TeF_5^-, 0·87, 1·33; SbF_5^{2-}, 0·88, 1·28.

§Values estimated from the trends observed for F_{33} and F_{88}.

¶The internal deformation constants were computed assuming $f_{\alpha\beta} = f_{\alpha\beta'} = f_{\alpha\alpha'} = 0$.

oxidation state and the electronegativity of the central atom increase. This results in a decrease of the $X_{\delta+}$–$F_{\delta-}$ bond polarity and an increase of the bond strength and force constants. However, this increase is not linear but levels off towards the sixth or seventh main group for the higher period elements. For the XeF_5^+ series, a second trend can be observed which is reflected by the $f_r : f_R$ ratio. In species containing more than eight valence electrons and at least one free valence electron pair on the central atom, the free valence electron pair seeks as much *s*-character as possible. This results in the formation of linear semi-ionic three center-four electron bond pairs until the free valence electron pair can form an sp^n hybrid with the remaining fluorine ligands[26]. As can be seen from Table 5, the axial bond (f_R) is significantly stronger than the four equatorial ones (f_r) for our series. The formation of the weaker semi-ionic bonds is favored by formal negative charges and increased electronegativity difference between the central atom and the ligand. Thus, SbF_5^{2-} closely approximates the ideal semi-ionic $f_r : f_R$ ratio of 0·5. This ratio increases towards XeF_5^+ for which the equatorial bonds become almost as strong as the axial one. Whereas the force constant data result in a smooth trend, the bond length differences (see Table 4) appear more erratic. This may partially be due to variations in bond distances for the same species depending on the counterion. For example, the equatorial axial bond length differences observed[5] for different XeF_5^+ salts vary from 0·03 to 0·07 Å.

The force constants obtained for this isoelectronic series also serve as a good example for continuous trends within the periodic system. They demonstrate that terms such as semi-ionic or covalent bonds are idealized descriptions of extremes and should be understood as such. In reality, the degree of polarity or ionicity of bonds changes gradually throughout such isoelectronic series resulting in a smooth transition from one type of bonding to the other.

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Fluoride Crystal Structures. Part XXVI.[1] Bis[difluorobromonium(III)] Hexafluorogermanate(IV)

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Crystals of the title compound are monoclinic, space group $P2_1/c$, $a = 5.07(1)$, $b = 13.83(2)$, $c = 6.45(1)$ Å, $\beta = 116.6(3)°$. The structure was solved by the heavy-atom technique and refined by three-dimensional least-squares methods to R 0.087 for 452 visually estimated reflections. The atomic arrangement is consistent with the ionic formulation $[BrF_2]^+{}_2[GeF_6]^{2-}$ but there are strong interactions between the ions through fluorine bridging giving endless chains parallel to the a axis. There is considerable distortion in the octahedral co-ordination of the germanium atom, and the bromine atoms have a distorted square planar co-ordination with two Br–F(terminal) and two Br–F(bridge) distances, means 1.71 and 2.21 Å.

BROMINE trifluoride is amphoteric and can form adducts[2] with strong Lewis acids, such as SbF_5 (ref. 3) or GeF_4.[4] The crystal structure of $BrF_3{\cdot}SbF_5$ has been determined[5] and showed that the adduct is predominantly ionic, although cation–anion interaction occurs through weak fluorine bridges causing distortion of the anion. A controversy existed concerning the structure of the $(BrF_3)_2{\cdot}GeF_4$ adduct. Based on vibrational spectra, Brown and co-workers postulated[4] that it cannot be ionic. Subsequently, Christe and Schack showed[6] that the vibrational spectra do not rule out a predominantly ionic structure containing weak fluorine bridges and/or distorted ions. In view of this controversy and the failure of vibrational spectroscopy to establish unambiguously the nature of $(BrF_3)_2{\cdot}GeF_4$, a crystal structure determination of this adduct appeared most interesting.

EXPERIMENTAL

The preparation of the complex has been described previously.[6] Single crystals were grown by sublimation in a temperature gradient in silica capillaries. The crystals formed as thin plates and most were twinned. One single crystal was sealed in a short length of evacuated silica capillary for the crystallographic investigation. No noticeable decomposition or attack on the silica occurred during data collection.

Crystal Data.—$Br_2F_{10}Ge$, $M = 422$, Monoclinic, $a = 5.07(1)$, $b = 13.83(2)$, $c = 6.45(1)$ Å, $\beta = 116.6(3)°$, $U = 404$ Å^3, $Z = 2$, $D_c = 3.46$, $F(000) = 384$. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences. Cu-K_α ($\lambda = 1.541\,8$ Å) and Mo-K_α ($\lambda = 0.710\,7$ Å, $\mu = 148$ cm^{-1}) radiations; single-crystal precession and Weissenberg photographs.

D_m was not measured but the volume is consistent with $Z = 2$, since with 20 fluorine atoms in the unit cell, the volume per fluorine atom is 20 Å^3, identical with that for $[BrF_2]^+[SbF_6]^-$.

Structure Determination.—Integrated intensities were collected about the a axis (layers 0—4kl) by use of Mo-K_α radiation and a Nonius integrating Weissenberg camera. The relative intensities were measured with a photometer

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of similar design to that described by Jeffery,[7] and structure amplitudes derived for 452 independent reflections by correction for Lorentz and polarization factors.

The structure was solved by conventional Patterson–Fourier techniques, with scattering factors for neutral atoms.[8] Refinement of positional and isotropic temperature parameters, and layer scale factors, was by full-matrix least-squares methods. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimised, initially with unit weights and in the final stages of refinement with $\sqrt{w} = |F_o|/22$ when $|F_o| < 22$ and $\sqrt{w} = 22/|F_o|$ when $|F_o| > 22$. When refinement was almost complete (at R 0.17) an absorption correction was applied, by use of the computer programme ABSCOR, for a crystal, elongated along a with dimensions 0.65 × 0.2 × 0.04 mm. After application of this correction and further cycles of refinement the final R was 0.087. The final parameter shifts were $< 0.1\,\sigma$ and an analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and increasing fractions of $|F_o|$ was satisfactory. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21546 (4 pp., 1 microfiche),* and the final positional parameters and isotropic temperature factors, with their estimated standard deviations, in Table 1. Interatomic distances and angles are given in Table 2.

TABLE 1

Final atomic positional and thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/Å^2$
Ge	0	0	1	2.12(8)
Br	0.3142(5)	0.1357(2)	0.6652(4)	2.34(6)
F(1)	0.0123(38)	0.0350(13)	0.7329(27)	3.03(27)
F(2)	0.7287(41)	0.0953(16)	0.9490(30)	3.86(33)
F(3)	0.2692(38)	0.0839(13)	1.1547(28)	3.38(32)
F(4)	0.5301(40)	0.2143(15)	0.5953(31)	4.48(38)
F(5)	0.0077(41)	0.1782(16)	0.4434(30)	4.13(35)

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances			
Ge–F(1)	1.82(2)	Br–F(4)	1.74(2)
Ge–F(2^{I})	1.83(2)	Br–F(5)	1.69(2)
Ge–F(3)	1.73(2)	Br–F(1)	2.25(2)
F(1) ··· F(3)	2.54(2)	Br–F(2)	2.17(2)
F(1) ··· F(2^{I})	2.54(3)	F(4) ··· F(5)	2.44(3)
F(3) ··· F(2^{I})	2.47(3)	F(1) ··· F(2)	3.37(3)
F(1) ··· F(2^{II})	2.61(3)	F(4) ··· F(2)	2.63(3)
F(1) ··· F(3^{II})	2.49(2)	F(5) ··· F(1)	2.71(3)
F(2) ··· F(3^{II})	2.57(3)		
(*b*) Angles			
F(1)–Ge–F(2^{I})	88.5(8)	F(4)–Br–F(5)	90.7(9)
F(3)–Ge–F(2^{I})	87.7(9)	F(1)–Br–F(2)	99.6(7)
F(1)–Ge–F(3)	91.2(8)	F(1)–Br–F(5)	85.9(8)
Ge–F(1)–Br	131.3(9)	F(2)–Br–F(4)	83.8(8)
Br–F(2)–Ge^{III}	135.4(10)		
(*c*) Contacts < 3.5 Å			
Br ··· F(3)	3.34(2)	F(2) ··· F(3)	3.15(3)
F(1) ··· F(4^{I})	3.32(3)	F(5) ··· F(4^{I})	3.03(3)
Br ··· F(4^{IV})	3.24(2)	F(2) ··· F(4^{IV})	3.11(3)
F(3) ··· F(4^{IV})	3.18(3)	F(4) ··· F(4^{IV})	3.37(1)
Br ··· F(3^{V})	3.28(2)	F(4) ··· F(3^{V})	3.12(2)
F(5) ··· F(3^{V})	3.02(3)	F(5) ··· F(2^{VI})	3.08(2)
F(5) ··· F(2^{VII})	3.44(3)	F(5) ··· F(4^{VII})	2.89(3)

Roman numerals as superscripts refer to atoms in the positions:

I $-1 + x, y, z$
II $-x, -y, 2 - z$
III $1 + x, y, z$
IV $x, \frac{1}{2} - y, \frac{1}{2} + z$
V $x, y, -1 + z$
VI $-1 + x, y, -1 + z$
VII $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$

DISCUSSION

The atomic arrangement is illustrated in Figures 1 and 2. The ionic formulation $[BrF_4]^+_2[GeF_6]^{2-}$ gives the best description for the structure, since it is compatible with the nearest neighbours to the bromine and germanium atoms. Thus, the two fluorine atoms, mean distance 1.71 Å from bromine, and the four fluorines 1.82 and two 1.73 Å from germanium, define the ions, with the next-nearest fluorine atoms to bromine, at a mean distance of 2.21 Å, having a significantly weaker interaction.

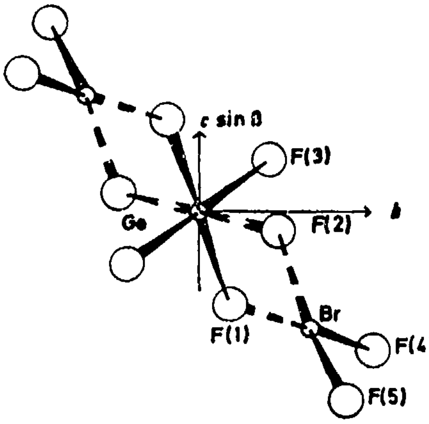

FIGURE 1 The endless chain arrangement shown in projection down [100]

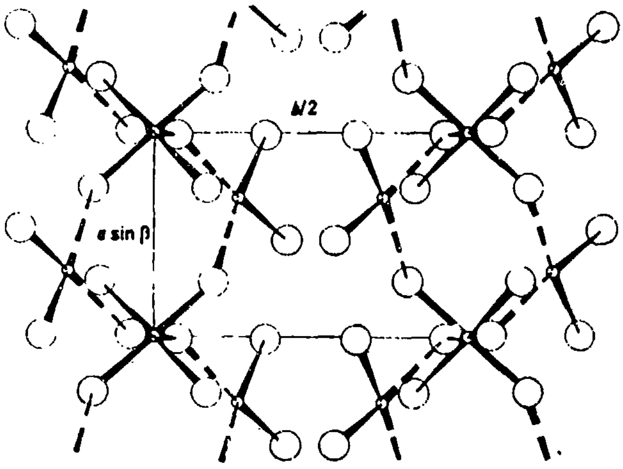

FIGURE 2 Projection of the structure down [001]

The co-ordination around germanium is distorted from octahedral by a lengthening of four coplanar Ge–F bonds involved in bridging to four bromine atoms. The F–Ge–F angles are not significantly different from 90° and the symmetry of the $[GeF_6]$ unit is approximately D_{4h}. This result agrees with the previous conclusions,[4,6] based

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[7] J. W. Jeffery, *J. Sci. Instr.*, 1963, **40**, 494.

[8] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965, p. 202.

on vibrational spectroscopy, that the compound does not contain octahedral $[GeF_6]^{2-}$ ions.

The two Br–F distances in the BrF_2^+ cation are not significantly different. The mean Br–F distance (1.71 Å) and the F–Br–F angle (90.7°) are very similar to the corresponding values (1.69 Å and 93.5°) found for the cation [5] in $[BrF_2]^+[SbF_6]^-$.

Although the ionic formulation gives an approximate description of the structure, the two extra Br–F distances of 2.17 and 2.25 Å, which complete a distorted square-planar fluorine co-ordination around bromine, represent a significant interaction. Thus, there is a contribution to the structure from the covalently bonded fluorine-bridged arrangement. Since Br in $[BrF_2]^+$ possesses two sterically active electron pairs, this cation can be considered to be pseudo-six-co-ordinated.

The long Br–F contacts from pairs of bromine atoms form bridges between separate $[GeF_6]$ units, to give infinite chains running parallel to the *a* axis, as shown in projection in Figures 1 and 2. The ratio of Br–F(bridge) to Br–F(terminal) is 1.29, significantly less than the value of (1.36) for $[BrF_2]^+[SbF_6]^-$,[5] but slightly larger than that (1.27) for $[BrF_4]^+[Sb_2F_{11}]^-$.[9] This indicates that the covalent interaction increases in the order: $[BrF_2]^+[SbF_6]^- < [BrF_2]^+_2[GeF_6]^{2-} \approx [BrF_4]^+[Sb_2F_{11}]^-$. The ratio of the Ge–F(bridge) to Ge–F(terminal) distance (1.05) is very similar to the corresponding Sb–F ratio (1.04) in $[BrF_2]^+[SbF_6]^-$ indicating that the differences in the anion bond lengths are not as good a measure of the strength of the fluorine bridge, and might be influenced by the different number of fluorine bridges involved in the 1 : 1 and 2 : 1 adducts.

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Contribution from Rocketdyne,
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trans-Dihydridotetrafluorophosphate(V) Anion, *trans*-$H_2PF_4^-$

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The novel $H_2PF_4^-$ anion was synthesized in the form of its K^+ and Cs^+ salts. Both compounds are white stable solids decomposing at 266 and 284 °C, respectively. Vibrational and ^{19}F NMR spectroscopy show that the anion has a pseudooctahedral structure with the hydrogen ligands in trans position. All ten active fundamentals expected for symmetry D_{4h} were observed and assigned. A normal-coordinate analysis was carried out and shows that $H_2PF_4^-$ contains highly polar PF bonds.

Introduction

During the synthesis of H_2PF_3 according to the method[1] of Holmes and Storey we observed that the NaF, used for the removal of the HF impurity, formed a labile adduct with H_2PF_3. Whereas numerous alkyl- or aryl-substituted fluorophosphates are known,[2,3] to our knowledge no reports have been published on the existence of the corresponding parent compounds, the hydridofluorophosphates. In view of this and the general interest in fluorine-substituted phosphorus compounds, it seemed interesting to synthesize stable hydridofluorophosphates. For $H_2PF_4^-$ further interest was added by the question of whether the two hydrogen ligands are in cis or in trans position.

Experimental Section

Apparatus and Materials. The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 4251 F4Y). Pressures were measured with a Heise Bourdon tube type gauge (0–1500 mm ±0.1%). Because of the rapid hydrolytic interaction with moisture, all materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. The spectra of solids at room temperature were obtained by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a Wilks minipellet press. The powdered sample was placed between the platelets before starting the pressing operation. The instrument was calibrated by comparison with standard calibration points.[4]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[5] for the elimination of plasma lines. For low-temperature work a Miller Harney device[6] was used. Glass or Teflon FEP capillaries were used as sample tubes in the transverse-viewing, transverse-excitation technique. Polarization measurements were carried out according to method VIII listed by Claassen et al.[5]

The ^{19}F NMR spectra were recorded at 56.4 MHz on a Varian high-resolution NMR spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique with an accuracy of ±1 ppm relative to the external standard $CFCl_3$. Teflon FEP liners (Wilmad Glas Co.) inserted into glass NMR tubes were used as sample containers and CH_3SOCH_3 was used as a solvent.

Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with copper Kα radiation and a nickel filter. Samples were sealed in quartz capillaries (~0.5-mm o.d.).

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used for the determination of the thermal stability of the compounds. The samples were crimp-sealed in aluminum pans, and heating rates of 10°/min were used.

Cesium fluoride and KF were fused in a platinum crucible and powdered in a drybox prior to use. The H_2PF_3 was prepared and purified as previously described.[1]

Synthesis of CsH_2PF_4 and KH_2PF_4. Dry KF (2.27, mmol) was placed into a 10-ml stainless steel cylinder and H_2PF_3 (3.13 mmol) was added at −196 °C. The cylinder was kept at −20 °C for 2 days. Excess H_2PF_3 was removed from the cylinder by pumping for several hours at room temperature. Based on the weight gain of the solid 2.19 mmol of H_2PF_3 was complexed. This corresponded to a 96.5% conversion of the KF to KH_2PF_4. The product was a white powder. Anal. Calcd for KH_2PF_4: K, 26.4; P, 20.9. Found: K, 26.7; P, 20.5.

Similarly, CsF (2.51 mmol) when combined with H_2PF_3 (3.21 mmol) at −20 °C resulted in the uptake of 2.51 mmol of H_2PF_3 corresponding to a 100% conversion of the CsF to CsH_2PF_4. The solid product was slightly off-white. The same results were obtained on combining these materials at room temperature, but the product had a light brown color. Anal. Calcd for CsH_2PF_4: Cs, 54.9; P, 12.8. Found: Cs, 55.0; P, 12.6.

The NaF–H_2PF_3 System. Sodium fluoride also interacted with excess H_2PF_3 at −20 °C although the conversion of NaF to NaH_2PF_4 was considerably lower than that observed for KF and CsF. After 10 days at −20 °C only 35% of the NaF had been converted to NaH_2PF_4. The solid product slowly evolved H_2PF_3 on standing at ambient temperature.

Results and Discussion

Syntheses and Properties. Alkali metal fluorides interact with H_2PF_3 with adduct formation. Whereas NaF forms an adduct unstable at room temperature, both KF and CsF form with excess H_2PF_3 at −20 °C 1:1 adducts in quantitative yield. Both KH_2PF_4 and CsH_2PF_4 are white hygroscopic solids, stable at room temperature and according to DSC data undergo exothermic decomposition at 266 and 284 °C, respectively. Since simple dissociation of the adducts to alkali metal fluorides and H_2PF_3 should be endothermic, the DSC results suggested that the thermal decomposition of these salts involved HF elimination and was probably accompanied by alkali metal bifluoride formation. This was experimentally confirmed when CsH_2PF_4 was subjected to careful vacuum pyrolysis. The volatile decomposition products were trapped at −196 °C and after warm-up to room temperature consisted of HF, PF_3, H_2PF_3, and a pale yellow to orange nonvolatile solid. This solid was extremely reactive and pyrophoric, and upon hydrolysis a gas was evolved exhibiting the characteristic smell of phosphine. A full characterization of this solid was beyond the scope of the present study, but the observed properties strongly suggest an associated species containing PP bonds. The $H_2PF_4^-$ salts are highly soluble in CH_3SOCH_3 and moderately soluble in CH_3CN. Attempts to obtain their x-ray powder diffraction patterns in quartz capillaries were unsuccessful owing to chemical attack of the capillaries. The only patterns observable were those of the corresponding SiF_6^{2-} salts.

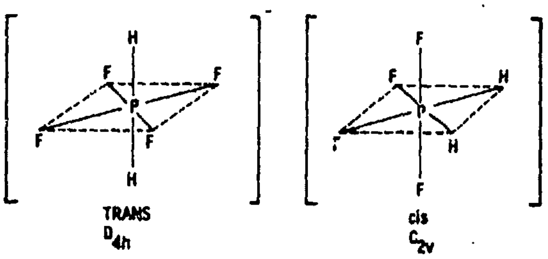

Figure 1. Two possible structural models of $H_2PF_4^-$.

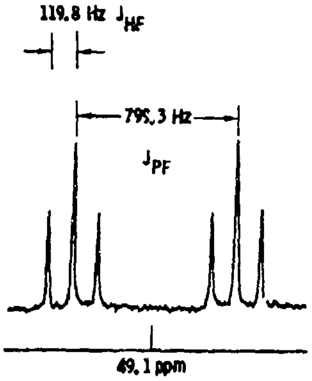

Figure 2. ^{19}F NMR spectrum of $K^+H_2PF_4^-$ in CH_3SOCH_3 solution.

The relatively high thermal stability of these $H_2PF_4^-$ salts and their relative ease of formation are surprising in view of previous reports.[2] Thus, CsF did not form adducts with dialkyltrifluorophosphoranes and the $(CH_3)_2PF_4^-$ anion could only be prepared from $(CH_3)_2PF_3$ and $(CH_3)_3SiN{=}PR_3$. The stability of the resulting salt was attributed to the stabilizing effect of the bulky and resonance-stabilized $[(CH_3)_2P(N{=}PR_3)_2]^+$ cation.

Possible Structures of $H_2PF_4^-$. The hydrogen ligands in $H_2PF_4^-$ could be in either cis or trans position. A priori, it is difficult to predict which of the two isomers is more likely. Whereas in $(CH_3)_2PF_4^-$ and $(CF_3)_2PF_4^-$ the two methyl ligands are trans,[2,3] the oxygen ligands in $IO_2F_4^-$ [7,8] and $TeO_2F_4^{2-}$ [9-11] are cis. For $TeF_4(OH)_2^-$,[11,12] $TeF_4(OCH_3)_2$,[9,13] and $TaF_4Cl_2^-$ [14] both the cis and the trans isomer were observed.

As can be seen from Figure 1, the trans isomer of $H_2PF_4^-$ has higher symmetry than the cis isomer, and therefore, NMR and vibrational spectroscopy should readily distinguish between these two stereoisomers.

^{19}F NMR Spectra. The ^{19}F NMR spectra of KH_2PF_4 and CsH_2PF_4 in CH_3SOCH_3 solution were recorded. They consisted of a well-resolved doublet of triplets (see Figure 2). The observed chemical shifts and coupling constants are listed in Table I.

The trans isomer contains four equivalent fluorine and two equivalent hydrogen atoms. Therefore, the ^{19}F resonance should consist of a doublet of triplets owing to P–F and H–F spin–spin coupling, respectively. For the cis isomer two doublets of triplets would be expected owing to the presence of two nonequivalent pairs of fluorines. The observed spectrum

Table I. ^{19}F NMR Spectral Data for $H_2PF_4^-$ in CH_3SOCH_3 Solution Compared to Those of Related Phosphorus Fluorides

Compd	δ, ppm	J_{PF}, Hz	J_{HF}, Hz
KH_2PF_4	49.1	799.3	119.8
CsH_2PF_4	47.6	798.7	120.8
PF_6^- [a]	73	715	
$(CH_3)_2PF_4^-$ [a]	20.9	856	
HPF_4 [b]	49.6	892	(91)[c]
H_2PF_3 [b]	48.0	860	(80)[c]

[a] Data from ref 2. [b] Data from ref 1; the δ values are the average of rapidly exchanging equatorial and axial fluorines. [c] These values were taken from the proton spectrum; they were not observed in the ^{19}F spectrum owing to the great line width of the signals caused by the rapid exchange of the equatorial and axial fluorine ligands.

agrees with the predictions for the trans isomer and the observed chemical shift and coupling constants agree well with those[1,2] of the related phosphorus fluorides listed in Table I.

Vibrational Spectra. The vibrational spectra of KH_2PF_4 and CsH_2PF_4 provide additional proof for $H_2PF_4^-$ possessing the trans configuration. The observed spectra are shown in Figure 3. The Raman spectra of CsH_2PF_4 were also recorded but are not shown in the figure owing to their similarity to those of KH_2PF_4. The observed frequencies are listed in Table II. Although no laser-induced photodecomposition of the samples was observed at 25 °C using the 4880-Å exciting line, some of the Raman spectra were recorded at lower temperature to improve the resolution of the spectra.

For the trans isomer of symmetry D_{4h} a total of 11 fundamentals are expected. These are classified as 2 A_{1g} + 2 A_{2u} + B_{1g} + B_{2g} + B_{2u} + E_g + 3 E_u. Since the ion has a center of symmetry, the infrared-active bands should be inactive in the Raman spectrum, and vice versa. The B_{2u} mode should be inactive in both the infrared and the Raman spectra. Consequently, we would expect five infrared-active and five Raman-active fundamentals following the principle of mutual exclusion. Of the five Raman-active fundamentals, two should be polarized.

For the cis isomer of symmetry C_{2v} a total of 15 fundamentals are expected which are classified as 6 A_1 + 2 A_2 + 4 B_1 + 3 B_2. Of these, the A_1, B_1, and B_2 modes (total of 13) should be infrared active. All 15 fundamentals should be Raman active and 6 of these should be polarized.

As can be seen from Figure 3 and Table II a total of 10 fundamentals were observed, if we ignore the splittings caused by Fermi resonance (see below). Of these, five are infrared and five are Raman active, and they are mutually exclusive.

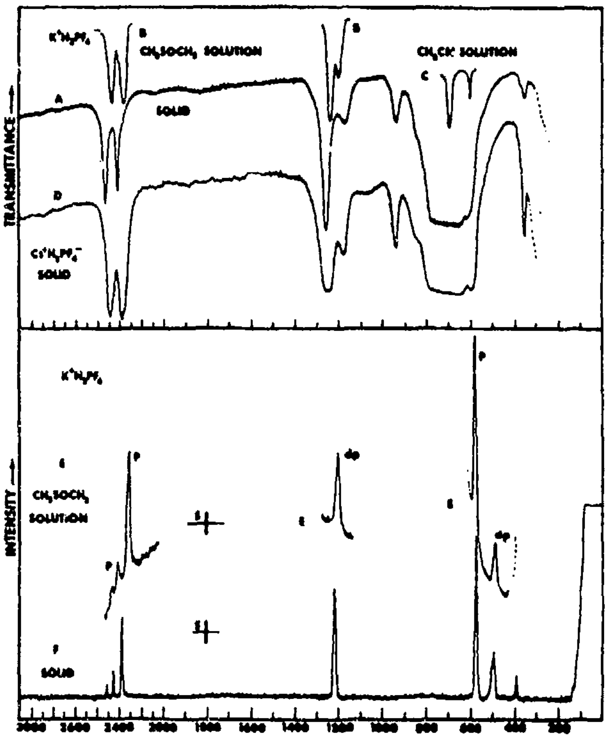

Figure 3. Vibrational spectra of KH_2PF_4 as AgCl disk; the dashed line indicates absorption caused by the window material: traces B and C, solution spectra; trace D, infrared spectrum of solid CsH_2PF_4; trace E, Raman spectrum of KH_2PF_4 in CH_3SOCH_3 solution; p, dp, and S indicate polarized and depolarized bands and spectral slit width, respectively; trace F, Raman spectrum of solid KH_2PF_4 recorded at −90 °C.

Table II. Vibrational Spectra of KH_2PF_4 and CsH_2PF_4 and Their Assignment

Obsd freq, cm^{-1}, and intens[a]								
KH_2PF_4				CsH_2PF_4				
Ir		Raman			Raman			
Solid	$(CH_3)_2SO$ soln	Solid	$(CH_3)_2SO$ soln	Ir Solid	Solid	$(CH_3)_2SO$ soln	Assignment in point group, D_{4h}	Approx description of vib
2518 s }[b]	2467 s }			2495 s }			$\nu_3(A_{2u})$, ν_8 + $\nu_9(A_{1u} + A_{2u} + B_{1u} + B_{2u})$	Antisym PH_2 str
2410 s }	2360 s }			2380 s }				
		2517 (0.7) }	2469 (0.4) p }		2505 (0.9) }	2470 }	$2\nu_9(A_{1g} + A_{2g} + B_{1g} + B_{2g})$	
		2453 (1.5) }	2418 (1.0) p }		2440 (1.5) }	2416 (1) }	$2\nu_8(A_{1g} + A_{2g} + B_{1g} + B_{2g})$	
		2377 (4.9) }	2319 (6.0) p }		2341 (5.1) }	2319 (6) p }	$\nu_1(A_{1g})$	Sym PH_2 str
1253 s }	1236 s }			1251 s }			$\nu_9(E_u)$	δ sciss PH_2
1171 m }	1202 m }			1178 m }			$\nu_5 + \nu_{10}(E_u)$	
		1217 (6.7)	1204 (4.0) dp		1212 (5.9)	1206 (4) dp	$\nu_8(E_g)$	δ wag PH_2
937 m				939 m			$\nu_2 + \nu_{11}(E_u)$	
840 sh				845 sh			$\nu_5 + \nu_{11}(E_u)$	
700 vs, br	701 vs[c,d]			700 vs, br			$\nu_{10}(E_u)$	Antisym PF_4 str
608 s	609 s[d]			610 s			$\nu_4(A_{2u})$	δ umbrella PF_4
		575 (10)	582 (10) p		576 (10)	582 (10) p	$\nu_2(A_{1g})$	Sym in-phase PF_4 str
		495 (2.8)	495 (2.1) dp		496 (2.6)	496 (2) dp	$\nu_5(B_{1g})$	Sym out-of-phase PF_4 str
		394 (1.4)	*c*		397 (1.6)		$\nu_6(B_{2g})$	δ sym in-plane PF_4
355 m				355 m			$\nu_{11}(E_u)$	δ antisym in-plane PF_4

[a] Uncorrected Raman intensities. [b] Braces indicate Fermi resonance. [c] Band obscured by solvent band. [d] Recorded for CH_3CN solution.

Table III. Vibrational Frequencies (cm^{-1}) of the Modes Involving the Square-Planar PF_4 Part of $H_2PF_4^-$ Compared to Those of Similar Molecules and Ions

Approx description of XF_4 mode	PF_4^- [a]	SF_5O^- [b]	$H_2PF_4^-$	ClF_5 [c]	SF_5^- [c]	ClF_4^- [d]	ClF_4O^- [e]
Antisym str	840	785	701	732	590	590	578
Sym in-phase str	735	697	582	538	522	505	456
Sym out-of-phase str	563	541	495	480	435	417	345
Umbrella def	555	506	609	495	466	425	339
Sym in-plane def	462	452	394	375	342	288	283
Antisym in-plane def		325	355	296	241		204

[a] Reference 17. [b] Reference 16. [c] Reference 15. [d] Reference 18. [e] Reference 19.

Furthermore, two of the observed Raman bands are polarized. These data convincingly show that $H_2PF_4^-$ possesses symmetry D_{4h}.

The assignments for $H_2PF_4^-$ (see Table II) were made on the following basis. The two polarized Raman bands must represent the A_{1g} modes with the higher frequency one being the symmetric PH_2 and the lower frequency one being the symmetric in-phase PF_4 stretch. The observation of three Raman bands in the region of the symmetric PH_2 stretch can readily be explained by Fermi resonance between this mode and the combination bands $2\nu_8$ and $2\nu_9$.

The remaining three Raman bands are due to the PH_2 wag, the symmetric out-of-phase PF_4 stretch, and the symmetric in-plane PF_4 deformation, respectively. Their frequencies should decrease in this order and, therefore, their assignment is straightforward.

Of the five infrared-active bands, the antisymmetric PH_2 stretch should have the highest frequency and is assigned to the bands in the 2400-cm^{-1} region. The observed splitting into two bands is caused by Fermi resonance with the combination band $\nu_1 + \nu_9$. The PH_2 scissoring mode should occur at a significantly higher frequency than those of the PF_4 group modes and, hence, is assigned to the strong band at about 1210 cm^{-1}. Again, a splitting is observed owing to Fermi resonance with $\nu_5 + \nu_{10}$.

The remaining three infrared-active modes are the antisymmetric PF_4 stretch, the umbrella PF_4 deformation, and the antisymmetric in-plane PF_4 deformation. The frequencies and the relative intensities of these three fundamentals should decrease in this order. The observed bands are in excellent agreement with these predictions and allow their unambiguous assignment.

In the infrared spectra of the solids the antisymmetric PF_4 stretch results in an extremely broad band, a feature characteristic[8-12] for many square-planar XF_4 groups. In order accurately to locate the band center and to confirm the presence of a single fundamental in this frequency region, solution spectra were recorded. As shown by insert C of Figure 3, the solution spectrum shows a single sharp band at 701 cm^{-1}. The solution spectra also confirm that the splittings observed for the solids for several bands are due to Fermi resonance and are not caused by solid-state effects, since they are also present in the solution spectra. Whereas the solid-state spectra show no significant deviations from the selection rules for point group D_{4h}, significant frequency shifts were observed for several bands on going from the solid state to the solutions. These shifts were most pronounced for fundamentals involving the PH_2 group. Furthermore, the frequency separation of some of the Fermi resonance components in the solution spectra significantly differs from those observed for the solid, thus allowing a somewhat better estimate of the unperturbed frequencies.

Comparison of the frequencies of the modes involving the square-planar PF_4 part of $H_2PF_4^-$ with those of similar square-planar XF_4 groups in related molecules and ions (see Table III),[15-19] shows excellent agreement. The observed frequency trends are as expected for the in-plane modes and confirm the above assignments. The somewhat high-frequency value of the PF_4 umbrella deformation in $H_2PF_4^-$ may be caused by the two axial hydrogen ligands. Since no similar compounds are known, it is impossible to judge whether this frequency increase for the umbrella deformation is characteristic for H_2XF_4 species or not. The frequencies of the PH_2 modes are similar to those observed for other PH compounds, such as PH_3, PH_4^+,[10] H_2PF_3, and HPF_4.[20]

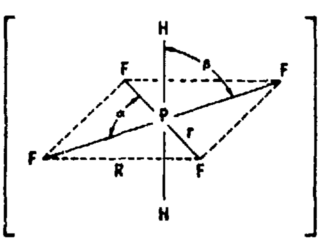

Figure 4. Definition of structural parameters of $H_2PF_4^-$.

Table IV. Symmetry Coordinates[a] for $H_2PF_4^-$

A_{1g}	S_1	$(1/2^{1/2})(\Delta R_1 + \Delta R_2)$
	S_2	$(1/2)(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$
	S_{r1}	$(1/2)(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4)$
	S_{r2}	$(1/8^{1/2})(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6 + \Delta\beta_7 + \Delta\beta_8)$
A_{2u}	S_3	$(1/2^{1/2})(\Delta R_1 - \Delta R_2)$
	S_4	$(1/8^{1/2})(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6 - \Delta\beta_7 - \Delta\beta_8)$
B_{1g}	S_5	$(1/2)(\Delta r_1 - \Delta r_2 + \Delta r_3 + \Delta r_4)$
	S_{r3}	$(1/8^{1/2})(\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4 + \Delta\beta_5 - \Delta\beta_6 + \Delta\beta_7 - \Delta\beta_8)$
B_{2g}	S_6	$(1/2)(\Delta\alpha_1 - \Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4)$
B_{2u}	S_7	$(1/8^{1/2})(\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4 - \Delta\beta_5 + \Delta\beta_6 - \Delta\beta_7 + \Delta\beta_8)$
E_g	$S^x{}_8$	$(1/2)(\Delta\beta_1 - \Delta\beta_3 + \Delta\beta_5 - \Delta\beta_7)$
	$S^y{}_8$	$(1/2)(\Delta\beta_2 - \Delta\beta_4 + \Delta\beta_6 - \Delta\beta_8)$
E_u	$S^x{}_9$	$(1/2)(\Delta\beta_1 - \Delta\beta_3 + \Delta\beta_5 - \Delta\beta_7)$
	$S^x{}_{10}$	$(1/2^{1/2})(\Delta r_1 - \Delta r_3)$
	$S^x{}_{11}$	$(1/2)(\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3 + \Delta\alpha_4)$
	$S^y{}_9$	$(1/2)(\Delta\beta_2 - \Delta\beta_4 + \Delta\beta_6 - \Delta\beta_8)$
	$S^y{}_{10}$	$(1/2^{1/2})(\Delta r_2 - \Delta r_4)$
	$S^y{}_{11}$	$(1/2)(\Delta\alpha_1 + \Delta\alpha_2 - \Delta\alpha_3 - \Delta\alpha_4)$

[a] S_{r1}, S_{r2}, and S_{r3} are the redundant coordinates.

Normal-Coordinate Analysis. A normal-coordinate analysis of $H_2PF_4^-$ was carried out. The definition of the structural parameters is shown in Figure 4. The bond lengths were estimated to be r(PF) = 1.60 Å and R(PH) = 1.40 Å by comparison with similar molecules and ions. All bond angles were assumed to be 90° as required for D_{4h}. The symmetry coordinates used for $H_2PF_4^-$ are given in Table IV. The G matrix and Z transformation were evaluated numerically.[21] The correctness of this transformation was verified by showing that the G matrix and Z transformation were the direct sum of each symmetry block and that the frequencies computed ignoring symmetry were the same after the symmetry transformation was made. Only those F matrix elements regarded as more important were considered and the analytical F matrix is shown in Table V. For the computation of the force constants, the frequency values of the free $H_2PF_4^-$ ion,

Table V. Observed Frequencies (cm^{-1}), Symmetry, Some Internal Force Constants,[a,b] and Potential Energy Distribution[c] of $H_2PF_4^-$

					F		PED	
		Freq			$F_{11,11}$ = Min	$F_{10,11}$ = 0	$F_{11,11}$ = 0	$F_{10,11}$ = 0
A_{1g}	ν_1	2322	F_{11}	$f_R + f_{RR}$	3.201		$100F_{11}$	
	ν_2	582	F_{22}	$f_r + 2f_{rr} + f_{rr}'$	3.790		$100F_{22}$	
A_{2u}	ν_3	2390	F_{33}	$f_R - f_{RR}$	3.174		$100F_{33}$	
	ν_4	609	F_{44}	$f_\beta + f_{\beta\beta} - f_{\beta\beta}' + 2f_{\beta\beta}'' - f_{\beta\beta}''' - 2f_{\beta\beta}''''$	1.615		$100F_{44}$	
B_{1g}	ν_5	495	F_{55}	$f_r - 2f_{rr} + f_{rr}'$	2.742			
B_{2g}	ν_6	394	F_{66}	$f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha}'$	1.112			
B_{2u}	ν_7		F_{77}	$f_\beta + f_{\beta\beta} - f_{\beta\beta}' - 2f_{\beta\beta}'' - f_{\beta\beta}''' + 2f_{\beta\beta}''''$				
E_g	ν_8	1205	F_{88}	$f_\beta - f_{\beta\beta} - f_{\beta\beta}' + f_{\beta\beta}'''$	0.812			
E_u	ν_9	1232	F_{99}	$f_\beta - f_{\beta\beta} + f_{\beta\beta}'$	0.814	0.811	$97F_{99}$	
	ν_{10}	701	$F_{10,10}$	$f_r - f_{rr}'$	2.864	2.153	$107F_{10,10} - 19F_{10,11} + 9F_{11,11}$	$74F_{10,10} + 23F_{11,11}$
	ν_{11}	355	$F_{11,11}$	$f_\alpha - f_{\alpha\alpha}'$	1.176	1.430	$100F_{11,11}$	$23F_{10,10} + 77F_{11,11}$
			$F_{10,11}$	$2^{1/2}f_{r\alpha}$	0.560	0		
			f_R		3.188			
			f_{RR}		0.014			
			f_r		3.065	2.710		
			f_{rr}		0.262			
			f_{rr}'		0.201	0.557		

[a] Stretching constants in mdyn/A, deformation constants in mdyn A/radian^2, and stretch-bend interaction constants in mdyn/radian. [b] f_{rr} and f_{rr}' are the interactions between perpendicular and collinear PF bonds, respectively; $f_{\alpha\alpha}$ and $f_{\alpha\alpha}'$ are the interactions between angles having a common and no common fluorine atom, respectively; $f_{\beta\beta}$, $f_{\beta\beta}'$, $f_{\beta\beta}''$, $f_{\beta\beta}'''$, and $f_{\beta\beta}''''$ are the interactions between angles being coplanar with a common H, coplanar with a common F, perpendicular with a common H, coplanar without a common atom, and perpendicular without a common atom, respectively; $f_{r\alpha}$ is the interaction between a PF stretch and α having a common F. F matrix elements considered less important were omitted. [c] Contributions of less than 5% are not listed.

i.e., the solution values, were used (see Table V), after applying small frequency corrections to the modes disturbed by Fermi resonance.

The computed force constants are shown in Table V. Whereas the values obtained for the B_{1g}, B_{2g}, and E_g block are unique, the remaining blocks are underdetermined. In the A_{1g} block, the G_{12} element equals zero. Therefore, the F_{12} term can be neglected, and F_{11} and F_{22} should be close approximations to a general valence force field. In the A_{2u} block, we have only one stretching and one deformation vibration of very different frequency. Coupling between these two modes is expected to be small and, hence, F_{34} was assumed to be zero. This choice is supported by the potential energy distribution (see Table V) which shows both fundamentals to be 100% characteristic.

For the remaining E_u block, the interaction term $F_{10,11}$ was found to strongly influence the values of $F_{10,10}$ and $F_{11,11}$. Consequently, we have computed F_{99}, $F_{10,10}$, and $F_{11,11}$ as a function of $F_{10,11}$. The important sections of the resulting force constant ellipses are shown in Figure 5. It has previously been shown[22] that the most probable range for F_{xy} is limited by the extremal values F_{yy} and F_{xy} = minimum. These limits suggest uncertainties of about ±0.2 mdyn/Å for f_r and f_{rr} and of about ±0.1 mdyn/Å for f_α. However, the general valence force field is probably closer to the $F_{10,11}$ = mimimum solution and therefore, values such as $f_r = 2.97 \pm 0.10$ and $f_{rr} = 0.36 \pm 0.10$ mdyn/Å seem more realistic.

A summary of the computed force constants and the potential energy distribution are listed in Table V. As can be seen all fundamentals are highly characteristic. The most interesting internal force constants of $H_2PF_4^-$ are the PF and the PH stretching constants since they are a measure for the relative bond strength of these bonds.

The value of the PH stretching force constant f_R (3.19 mdyn/Å) of $H_2PF_4^-$ is in excellent agreement with those of 3.19 and 3.10 mdyn/Å found[10] for PH_4^+ and PH_3, respectively. This indicates that the PH bonds in $H_2PF_4^-$ are highly covalent with a bond order of approximately 1.

Contrary to the PH bonds, the PF stretching force constant f_r (2.97 mdyn/Å) of $H_2PF_4^-$ has a surprisingly low value when compared to those of 4.39 and 5.21 mdyn/Å previously reported for PF_6^- [23] and PF_3,[17] respectively. The low value of f_r in $H_2PF_4^-$ indicates highly polar PF bonds with a bond order closer to 0.5 than to 1. Obviously, the negative charge in $H_2PF_4^-$ resides mainly on the highly electronegative fluorine ligands. A bonding scheme, similar to that previously invoked for the square-planar $HalF_4^-$ anions,[18,24,25] might also be applicable to the square-planar PF_4 part of $H_2PF_4^-$. Both types of anions are structurally closely related. In $HalF_4^-$ the two axial positions are occupied by two free valence electron pairs, whereas in $H_2PF_4^-$ they are occupied by two hydrogen ligands which readily release electron density to the PF_4 part of the anion.

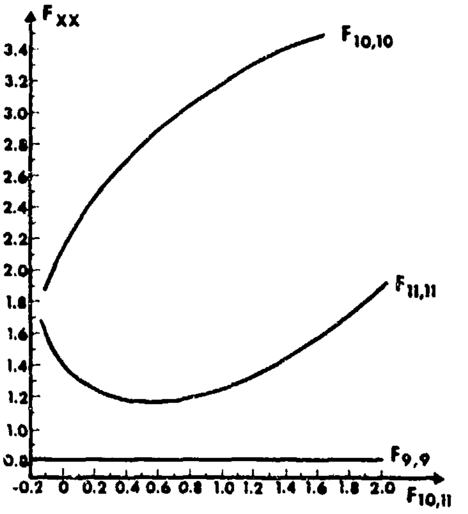

Figure 5. Force constant ellipses for the E_u block of $H_2PF_4^-$. The values of the diagonal symmetry force constants are given as a function of $F_{10,11}$.

General Considerations. The limited number of known examples of pseudooctahedral AF_4X_2 species indicates that the nature of the X ligand determines which stereoisomer is preferred. If X is a free valence electron pair[18,24-26] or a group of low electronegativity, such as H or CH_3,[2] the trans isomer is preferred, but if X is multiply bonded oxygen,[7,11] the cis isomer is preferred. If X is of intermediate electronegativity, such as OH, OCH_3, Cl, Br, etc.,[9,11-14] both the cis and the trans isomers have been observed. An attempt will be made to rationalize these observations.

For X being a free-valence electron pair, the preference for the trans isomer can be explained by the fact the two free-valence electron pairs seek high s character,[27] i.e., form a linear sp hybrid. This results in strong contributions from semiionic three center-four electron bonds[28-30] to the AF_4 part. Since the 3c–4c bonds involve a single p orbital of the central atom for the bonding of two F ligands, the resulting F–A–F group must possess an approximately linear configuration. Since a linear X-A-X and two linear F-A-F groups are possible only for the trans isomer, this should be the preferred configuration.

The trans configuration of $H_2PF_4^-$ can be rationalized by both the 3c–4c bond model and intramolecular attractive forces between the H and the F ligands. The latter rationale is based on the assumption that the negatively polarized fluorine ligands are attracted by the positively polarized hydrogen ligands. In the trans isomer, each H possesses four closest F neighbors, and each F has two closest H neighbors. In the cis isomer, however, each H possesses only three closest F neighbors, and two of the fluorines possess only one closest H neighbor. Therefore, the trans isomer is expected to be energetically favored over the cis isomer.

If X is oxygen, the more electronegative fluorine ligands tend to polarize the X–O bonds. This results in an increased bond order of the X–O bonds according to

$$^{-}\!:\underset{..}{\ddot{O}}-X-F \leftrightarrow \dot{\underset{\cdot}{:}}\!O=X\ F^{-}$$

and

$$\dot{\underset{\cdot}{:}}\!O=X-F \leftrightarrow {}^{+}\!:O\equiv X\ F^{-}$$

and allows the shifting of a formal negative charge from the less electronegative oxygen ligand to the more electronegative fluorine ligand. Molecular orbital following arguments favor this kind of resonance for linear F–A–O groups. However, these are only possible for the cis isomer.

For singly bonded ligands of intermediate electronegativity, such as OH, OCH_3, Cl, Br, etc., both cis and trans isomers have been observed.[9,11-14] This indicates that other factors, such as steric effects or the nature of the formation reaction mechanism, become more important. Consequently, predictions of the expected stereoisomer will be considerably more difficult for these ligands.

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Registry No. KF, 7789-23-3; CsF, 13400-13-0; H_2PF_3, 13659-65-9; KH_2PF_4, 58188-50-4; CsH_2PF_4, 58188-51-5.

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SHORT COMMUNICATION

Improved Syntheses of NF_4BF_4 and NF_4SbF_6

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In view of the importance of NF_4^+ salts for solid propellant NF_3-F_2 gas generators [1], improved syntheses of NF_4BF_4 and NF_4SbF_6 were required.

Two methods have previously been reported for the synthesis of $NF_4SbF_6 \cdot xSbF_5$ involving the use of either high pressure and temperature [2,3] or uv-irradiation [4]. Of these, the thermal method is more convenient for larger scale production. According to Tolberg et al. [2,3] the most favorable reaction conditions are:

$$NF_3 + F_2 + SbF_5 \xrightarrow[\substack{100\text{-}125° \\ 2\ \text{days}}]{3000\ \text{psi}} NF_4Sb_3F_{16}$$

$$NF_4Sb_3F_{16} \xrightarrow[\substack{200° \\ 2\text{-}3\ \text{days}}]{\text{vacuum}} NF_4SbF_6 + 2SbF_5$$

The resulting product contained an appreciable amount of Monel salts and was removed from the reactor by cutting it open with a hacksaw and scraping out the hard clinkered product. Based on recent work done in our laboratory [1], temperatures (250-260°), higher than those reported by Tolberg, are required for the vacuum pyrolysis of $NF_4SbF_6 \cdot xSbF_5$ to NF_4SbF_6 within a reasonable time period.

We have now found that most of the drawbacks of the above procedure can be avoided by directly synthesizing NF_4SbF_6. For this purpose, NF_3, F_2, and SbF_5 in a 2:2:1 mol ratio are heated in a Monel cylinder to 250° for 72 hours. The size of the cylinder is chosen in such manner that at the completion of the reaction the autogenous pressure is about 70 atm. The excess of NF_3 and F_2 is removed under vacuum at room temperature and the desired NF_4SbF_6

product is extracted from the Monel cylinder with anhydrous HF using about 50 ml of liquid HF per 100 g of NF_4SbF_6. Since, contrary to a previous report [3], the formed Monel salt impurities (about 5%) are quite insoluble in anhydrous HF, they can be easily removed from the product by incorporating a porous Teflon filter (Pall Corporation) into the HF solution transfer line. Based on elemental and spectroscopic analyses and the observed material balances, the resulting product was shown to be essentially pure NF_4SbF_6.

Several methods have previously been reported for the synthesis of NF_4BF_4. This salt can be prepared either directly from NF_3, F_2, and BF_3 using glow discharge [5,6], bremsstrahlung [7] or ultraviolet radiation [4,8], or indirectly from NF_4SbF_6 using a metathetical process [3,9]. Of these, the metathetical process is most amenable to the larger scale production of NF_4BF_4 utilizing existing technology. The original metathetical NF_4BF_4 process [3] involved the following steps:

$$CsF + HF \xrightarrow{HF} CsHF_2$$

$$NF_4SbF_6 + CsHF_2 \xrightarrow{HF} CsSbF_6\downarrow + NF_4HF_2$$

$$NF_4HF_2 + BF_3 \xrightarrow{HF} NF_4BF_4 + HF$$

Since the crude product, thus obtained, contained much $CsSbF_6$, its NF_4BF_4 content was increased by extraction with BrF_5. The use of BrF_5 resulted in the following side reaction:

$$NF_4BF_4 + CsSbF_6 \xrightarrow{BrF_5} CsBF_4\downarrow + NF_4SbF_6$$

The composition of the final product was reported [3] to be: 91.5% NF_4BF_4 and 8.5% NF_4SbF_6. In addition to the requirement of BrF_5 as a recrystallization solvent, this process suffers from the following disadvantage. Highly concentrated solutions of NF_4HF_2 in HF are unstable decomposing to NF_3, F_2, and HF. This can cause a pressure build up in the metathesis apparatus which in turn can render filtration steps more difficult.

This process was somewhat improved upon [9] by substituting CsF by AgF. This modification eliminated the BrF_5 extraction step and resulted in a product of the composition (mol %): NF_4BF_4 (89), $NF_4Sb_2F_{11}$ (7.9), $AgBF_4$ (3.1). However, the process still involved the handling of concentrated NF_4HF_2 solutions. Furthermore, the cost of silver salts is rather high and therefore requires their recycling in high yields.

We have now found that NF_4BF_4 of at least 97 mol % purity can be prepared by a simpler process using anhydrous HF at different temperatures as the only solvent. Furthermore, we have shown that the purity of the NF_4BF_4

can be raised to above 99 mol % by a single recrystallization from BrF_5. The cesium content in both products was shown to be less than 0.1 mol %, the principal impurity being NF_4SbF_6.

Our improved process consists of the following steps:

$$CsBF_4 + 1.1\ NF_4SbF_6 \xrightarrow[-78^\circ\ \text{filtr.}]{HF} CsSbF_6\downarrow + NF_4BF_4 + 0.1\ NF_4SbF_6$$

$$NF_4BF_4 + 0.1\ NF_4SbF_6 \xrightarrow[25^\circ]{\text{recryst. from HF}} \underset{(97\ \text{m}\ \%)}{NF_4BF_4\downarrow} + \text{mother liquor}$$

$$NF_4BF_4 \xrightarrow[25^\circ]{\text{recryst. from } BrF_5} \underset{(99+\ \text{m}\ \%)}{NF_4BF_4\downarrow} + \text{mother liquor}$$

The important features of our process are:

(i) The use of $CsBF_4$ instead of $CsHF_2$ eliminates one step and avoids the complications caused by NF_4HF_2.

(ii) The use of a 10 mol % excess of NF_4SbF_6 decreases the solubility of $CsSbF_6$ by the common ion effect.

(iii) Carrying out the $CsSbF_6$ filtration step at -78° decreases the SbF_6^- concentration since the solubilities of SbF_6^- salts in anhydrous HF decrease with decreasing temperature much more rapidly than those of BF_4^- salts. Furthermore, the amount of NF_4BF_4, retained in the $CsSbF_6$ filter cake by absorption of a certain volume of mother liquor, is minimized owing to the decreased solubilities.

(iv) Since NF_4BF_4 and NF_4SbF_6 have comparable solubilities in HF at room temperature, the 10% excess of NF_4SbF_6 used in the $CsSbF_6$ precipitation step can be removed as mother liquor by recrystallization from HF at room temperature. Unfortunately, the solubilities in HF at room temperature are so high that a significant percentage of the mother liquor is retained by the NF_4BF_4 precipitate. This problem can be minimized by using for this recrystallization a solvent in which these NF_4^+ salts are less souble. Thus, a single recrystallization from BrF_5 raised the product purity above the 99 mol % level. Other suitable solvents could be used to replace BrF_5 in this step. The mother liquors of the recrystallization steps can be easily recycled into the $CsSbF_6$ precipitation step, thus avoiding the loss of any NF_4^+ values.

In summary, the combination of the two improved processes for the syntheses of NF_4SbF_6 and NF_4BF_4, respectively, results in a relatively simple and economical process for the production of NF_4BF_4 in a purity of about 97 mol %. Furthermore, it was demonstrated for the first time that high purity (99+ mol %) NF_4BF_4 can be prepared by metathesis.

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Synthesis and Characterization of NF_4BiF_6 and Some Properties of NF_4SbF_6

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Perfluoroammonium salts are known[1] of the following anions: PF_6^-, AsF_6^-, SbF_6^-, $SbF_6 \cdot nSbF_5^-$, BF_4^-, GeF_5^-, and GeF_6^{2-}. Very recently, the synthesis and chemistry of NF_4^+ salts have received considerable attention owing to their potential for solid propellant NF_3–F_2 gas generators for chemical DF lasers. The concept of such a gas generator was conceived[2] and to a large extent developed at Rocketdyne. Originally, the fluorine gas generators were aimed at the direct generation of F atoms by burning a highly overoxidized grain, consisting mainly of an NF_4^+ salt, with a small amount of fuel, such as Teflon powder, according to

$$NF_4MF_6 + (CF_2)_n \rightarrow CF_4 + NF_3 + MF_5 + Q$$

$$NF_4MF_6 \xrightarrow{+Q} NF_3 + F_2 + MF_5$$

$$2NF_3 + F_2 \xrightarrow{+Q} N_2 + 8F\cdot$$

The heat of reaction (Q) generated in such a system is sufficient to pyrolyze the remaining NF_4MF_6 and to dissociate most of the NF_3 and F_2 to F atoms. For an NF_3–F_2 gas generator, the underlying principle is quite similar, except for keeping the burning temperature lower since dissociation of NF_3 and F_2 to F atoms is not required.

In view of the above developments, we were interested in the synthesis of new NF_4^+ salts and in the characterization of new and known NF_4^+ salts. In this paper, we report on the synthesis of the new salt NF_4BiF_6 and on some properties of the known NF_4SbF_6. Since these two salts can be readily prepared in high yields, they are important starting materials for the syntheses of other NF_4^+ salts used in NF_3–F_2 gas generator compositions.

Experimental Section

Materials and Apparatus. The equipment and handling procedures used in this work were identical with those[1] recently described. The NF_4BF_4 starting material was prepared by low-temperature UV photolysis[1] and did not contain any detectable impurities. The α-BiF_5 was purchased from Ozark Mahoning Co. and did not contain any impurities detectable by Raman spectroscopy. The $NF_4Sb_2F_{11}$ was prepared as described.[3]

Synthesis of NF_4BiF_6 by Displacement Reaction without Solvent. Pure NF_4BF_4 (10.1 mmol) and α-BiF_5 (10.1 mmol) were powdered, mixed, and placed in a prepassivated (with ClF_3) 95-mL Monel cylinder. The cylinder was heated to 180 °C for 1.5 h. Products, volatile at 20 °C, were removed by pumping and separated by fractional condensation. They consisted of 7.8 mmol of BF_3 in addition to a small amount of material noncondensable at −196 °C. The amount of BF_3 evolution was confirmed by the weight loss of the solid-containing cylinder. The conversion of NF_4BF_4 to NF_4BiF_6 was further confirmed by Raman spectroscopy of the solid. The solid was removed from the cylinder, finely powdered, returned to the cylinder, and heated to 175 °C for an additional 18 h. This resulted in the evolution of an additional 2.3 mmol of BF_3, in excellent agreement with the observed weight loss. The complete conversion of NF_4BF_4 to NF_4BiF_6 was confirmed by infrared and Raman spectroscopy and elemental analysis. Anal. Calcd for NF_4BiF_6: NF_3, 17.15; BiF_3, 64.49. Found: NF_3, 16.9; BiF_3, 60.0 An explanation for the low BiF_3 value is given below.

Synthesis of NF_4BiF_6 by Displacement Reaction in HF. Dry HF (5 mL of liquid) was added at −78 °C to a Teflon–FEP ampule containing NF_4BF_4 and BiF_5 (9.9 mmol of each). The mixture was agitated at 20 °C for several hours and gas evolution was observed. The volatile products were pumped off at 20 °C and the HF treatment was repeated. After removal of the volatile products from the second HF treatment, 4.075 g of a white, stable solid (weight calculated for 9.9 mmol of NF_4BiF_6 4.089 g) was left behind which was shown by infrared and Raman spectroscopy to be identical with the analyzed product obtained from the above described thermal displacement reaction.

Direct Synthesis of $NF_4BiF_6 \cdot nBiF_5$. In a typical experiment, a mixture of NF_3 (238 mmol), F_2 (238 mmol), and BiF_5 (10.06 mmol) in a prepassivated 95-mL Monel cylinder was heated for 30 h to 175 °C under an autogenous pressure of 167 atm. Unreacted NF_3 and F_2 (~463 mmol total) were pumped off at 20 °C leaving behind 3.75 g of a white, stable solid (weight calculated for 6.29 mmol of $NF_4BiF_6 \cdot 0.6BiF_5$ 3.745 g). Anal. Calcd for $NF_4BiF_6 \cdot 0.6BiF_5$: NF_3, 11.92; BiF_3, 71.60. Found: NF_3, 11.9; BiF_3, 69.00.

Pyrolysis of $NF_4BiF_6 \cdot nBiF_5$. A sample (3.29 mmol) of $NF_4BiF_6 \cdot 1.46BiF_5$, prepared as described above expept for using a significantly shorter reaction time, was subjected to vacuum pyrolysis at 280 °C for 1.5 h. The white crystalline residue (1.13 g) was identified by vibrational spectroscopy and its x-ray diffraction powder pattern to be mainly NF_4BiF_6 (weight calculated for 3.29 mmol of NF_4BiF_6 1.36 g) corresponding to a yield of 83%.

Synthesis of NF_4SbF_6. The thermal reaction[4] of NF_3–F_2–SbF_5 at 115 °C, followed by vacuum pyrolysis at 200 °C, produces[3] a product of the approximate composition $NF_4Sb_2F_{11}$. This product can be converted to NF_4SbF_6 by vacuum pyrolysis at higher temperature; however, this SbF_5 removal is accompanied by a competing reaction, i.e., the thermal decomposition of some of the desired NF_4SbF_6. Pyrolysis at 250–260 °C for 1–1.5 h under dynamic vacuum resulted in complete conversion to NF_4SbF_6. Measurement of the NF_3 evolved during this pyrolysis showed that less than 3% of the NF_4SbF_6 had undergone decomposition. When the pyrolysis was carried out at 275–300 °C, even for relatively short periods of time, significantly higher losses of NF_4SbF_6 due to thermal decomposition occurred.

In a typical experiment, $NF_4Sb_2F_{11}$ (31.0 mmol) in a 95-mL Monel cylinder was pyrolyzed under dynamic vacuum at 255 °C for 80 min. The evolved SbF_5 was condensed in a Teflon-FEP U-trap kept at −196 °C. The white solid residue consisted of 30.4 mmol of NF_4SbF_6 (98 mol % yield based on NF_4^+). Anal. Calcd for NF_4SbF_6: NF_3, 21.80; Sb, 37.38. Found: NF_3, 21.72; Sb, 37.41; Ni, 0.08; Cu, 0.03.

Elemental Analyses. For the elemental analyses, a weighed amount (several mmol) of the NF_4^+ salt was placed in the bottom of a Teflon-FEP U-trap, which was closed off by valves. The trap was cooled to −196 °C and several milliliters of distilled water was frozen out in the upper section of the U-trap. The frozen water was shaken down into the cold bottom section of the U-tube and the ice and the NF_4^+ salt were mixed while being cold. This mixing procedure was found important to avoid violent reactions between solid NF_4^+ salts and isolated droplets of liquid water, which sometimes were encountered when thawing the ice in the upper part of the tube and allowing the liquid water to run down onto the NF_4^+ salt. The mixture of ice and NF_4^+ salt was warmed to 20 °C for 30 min. Upon melting of the ice, gas evolution occurred. The contents of the trap were cooled and the evolved O_2 and NF_3 were distilled off at −196 and −126 °C, respectively, and were measured volumetrically. For NF_4SbF_6, the aqueous hydrolysate was analyzed for Sb by x-ray fluorescence spectroscopy. For the BiF_5 salts, a white, water-insoluble precipitate formed on hydrolysis. This precipitate was filtered off at 0 °C, washed with a small amount of cold, distilled water, dried at 103 °C, and weighed. It was identified by its x-ray powder diffraction pattern[4] and by electron microprobe x-ray analysis as BiF_3. Anal. Calcd for BiF_3: Bi, 78.57; F, 21.43; O, 0. Found: Bi, 78.6; F, 21.3; O, 0. Although 93–97% of the BiF_3 could be isolated in this manner, the solubility of BiF_3, particularly in the presence of HF, is not low enough[5] to permit a quantitative precipitation of BiF_3.

Results and Discussion

Syntheses. The new NF_4^+ salt NF_4BiF_6 was prepared either from NF_4BF_4 and BiF_5 by the displacement reaction

$$NF_4BF_4 + BiF_5 \rightarrow NF_4BiF_6 + BF_3$$

or directly by the elevated temperature–pressure method[6] followed by vacuum pyrolysis

$$NF_3 + F_2 + (n + 1)BiF_5 \xrightarrow{175\,°C} NF_4BiF_6 \cdot nBiF_5$$

$$NF_4BiF_6 \cdot nBiF_5 \xrightarrow{280\,°C} NF_4BiF_6 + nBiF_5$$

The displacement reaction can be carried out either at 25 °C in HF solution or in the absence of a solvent at elevated temperature.

The synthesis of NF_4BiF_6 is more difficult than that of NF_4SbF_6 owing to the fact that at ambient temperature α-BiF_5 is a nonvolatile, polymeric, trans-fluorine-bridged solid. Consequently, temperatures above the melting point (151.4 °C) of BiF_5 are required for both the displacement reaction and the elevated temperature–pressure method. Since removal of excess BiF_5 is inconvenient, the displacement reactions are best carried out with stoichiometric amounts of starting materials. As for SbF_5,[6] the direct synthesis of the perfluoroammonium perfluorobismuthate salt at elevated temperature and pressure tends to produce polyanions (mainly $Bi_2F_{11}^-$).[7] The feasibility of converting these salts to NF_4BiF_6 by vacuum pyrolysis was demonstrated, but no effort was made to maximize the reaction conditions.

The pyrolysis of $NF_4Sb_2F_{11}$ to NF_4SbF_6 and SbF_5 was briefly investigated, when we discovered that the reaction conditions (200 °C) previously recommended[8] for the pyrolysis were not suitable for obtaining pure NF_4SbF_6. In our experience, a significantly higher pyrolysis temperature of about 250 °C was required for the production of essentially pure NF_4SbF_6. At this temperature, little or no decomposition of the NF_4SbF_6 itself took place. On the basis of the results obtained in our laboratory, the thermal reaction between approximately equimolar amounts of NF_3, F_2, and SbF_5 at temperatures ranging from 115 to 200 °C and autogenous pressures of about 200 atm produces a product of the composition $NF_4SbF_6 \cdot nSbF_5$ with n ranging from 2.1 to 3.2 depending on the exact reaction conditions. Vacuum pyrolysis of these products at 200 °C reduces n to a level ranging from 0.8 to 1.1. Pyrolysis at 260 °C reduces the value of n to zero.

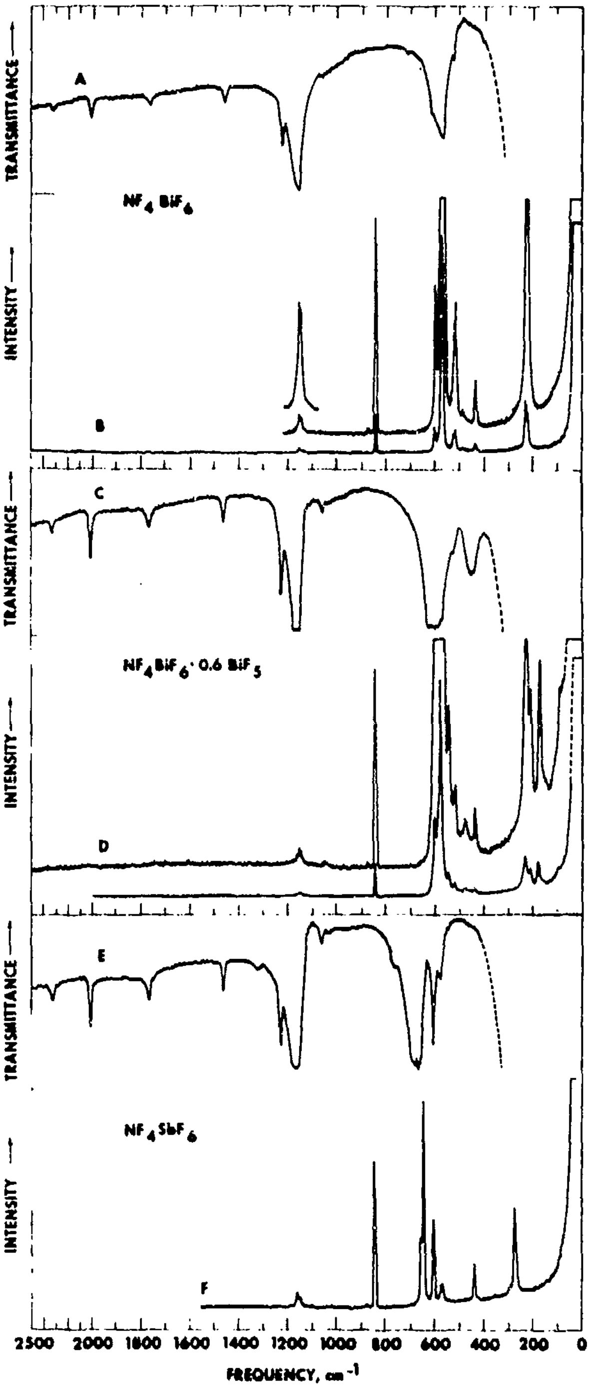

Figure 1. Vibrational spectra of NF_4BiF_6, $NF_4BiF_6 \cdot 0.6BiF_5$, and NF_4SbF_6: traces A, C, and E, infrared spectra of the solids in silver chloride disks, the absorptions below 300 cm^{-1} (broken lines) being due to the AgCl windows; traces B, D, and F, Raman spectra of the solids recorded at different sensitivities, the spectral slit width used at the lower sensitivity levels being 2 cm^{-1}.

Properties. The composition of the NF_4^+ salts was established by both the observed material balances and elemental analyses. The NF_4BiF_6 salt is a white crystalline solid melting in a sealed glass capillary at about 341 °C. The x-ray powder diffraction pattern of the sample prepared by pyrolysis of

Table I. Crystallographic Data of NF_4SbF_6 and NF_4BiF_6 Compared to Those of NF_4PF_6 and NF_4AsF_6

	Tetragonal unit cell dimensions					
	a, A	c, A	V, A^3	Z	Vol/F, A^3	Calcd density, g/cm^3
NF_4PF_6[a]	7.577	5.653	324.53	2	16.23	2.41
NF_4AsF_6[b]	7.70	5.73	339.73	2	16.99	2.72
NF_4SbF_6	7.903	5.806	362.63	2	18.13	2.98
NF_4BiF_6	8.006	5.821	373.10	2	18.66	3.68

[a] Reference 1. [b] Reference 7.

$NF_4BiF_6 \cdot nBiF_5$ is given as supplementary material. It could readily be indexed for a tetragonal unit cell, analogous to those of NF_4PF_6,[1] NF_4AsF_6,[9] and NF_4SbF_6 (see Table I). Several weak lines of variable intensity could not be indexed for a tetragonal unit cell, and corresponding lines had not been observed for the other isotypic NF_4MF_6 salts. Consequently, these extra lines are attributed to impurities, such as polyanion salts, and have not been included in the listing.

The NF_4SbF_6 salt melts at about 318 °C. Its x-ray powder diffraction pattern is given as supplementary material. All of the observed lines could be indexed for a tetragonal unit cell, analogous to those observed for the other NF_4MF_6 salts (see Table I). As expected, the unit cell dimensions and calculated densities increase in the order $PF_6^- < AsF_6^- < SbF_6^- < BiF_6^-$.

The hydrolyses of NF_4SbF_6 and NF_4BiF_6 showed a distinct difference as far as the amount of oxygen evolution is concerned. The NF_4SbF_6 behaved as the previously studied[1] NF_4^+ salts and generated O_2 according to

$$NF_4^+ + H_2O \rightarrow NF_3 + H_2F^+ + {}^1/_2O_2$$

This reaction, however, is not quantitative owing to a competing reaction[1] involving the formation of some H_2O_2. Thus, for NF_4SbF_6, only 0.45 mol of O_2 was observed per mole of NF_3. For NF_4BiF_6, however, 0.86 mol of O_2 was obtained per mole of NF_3. Furthermore, no evidence for the formation of brown Bi_2O_5 (generated when BiF_5 is hydrolyzed) was observed, but white BiF_3 was precipitated. This oxidation of H_2O by BiF_6^- according to

$$BiF_6^- + H_2O \rightarrow BiF_3\downarrow + HF_2^- + HF + {}^1/_2O_2$$

can account for the additional O_2 evolution, which by analogy[1] with NF_4^+ might not be quantitative owing to the formation of some H_2O_2.

The oxygen evolution during the hydrolysis of the closely related O_2^+ salts has recently been studied.[10] In agreement with our findings for NF_4^+ salts, the observed O_2 evolution was generally lower than the calculated values. However, for O_2BiF_6, no evidence for the reduction of pentavalent bismuth was reported. Furthermore, the given explanation, i.e., that the low observed O_2 values are due to samples which had undergone partial decomposition according to

$$2O_2MF_6 \rightarrow O_2M_2F_{11} + O_2 + {}^1/_2F_2$$

cannot account for the low O_2 value found for salts, such as O_2AsF_6, which contain a volatile Lewis acid and do not form a stable $M_2F_{11}^-$ anion. Therefore, some of the conclusions, such as "*all* dioxygenyl salts prepared so far are intrinsically unstable at room temperature", which are based on the low observed oxygen values, are open to question. Obviously, competing side reactions, such as those observed for the NF_4^+ salts, might play an important role and give rise to low oxygen values.

Vibrational Spectra. The vibrational spectra of NF_4BiF_6, $NF_4BiF_6 \cdot 0.6BiF_5$, and NF_4SbF_6 are shown in Figure 1. The

Table II. Vibrational Spectra of Solid NF_4BiF_6, $NF_4BiF_6 \cdot 0.6BiF_5$, and NF_4SbF_6

Obsd freq, cm^{-1}, and rel intens[a]						Assignments (point group)		
NF_4BiF_6		$NF_4BiF_6 \cdot 0.6BiF_5$		NF_4SbF_6				
IR	Raman	IR	Raman	IR	Raman	NF_4^+ (T_d)	MF_6^- (O_h)	$M_2F_{11}^-$
2320 vw		2320 vw		2320 vw		$2\nu_3$ ($A_1 + E + F_2$)		
2010 w		2010 w		2010 w		$\nu_1 + \nu_3$ (F_2)		
1768 vw		1768 vw		1768 vw		$\nu_3 + \nu_4$ ($A_1 + E + F_2$)		
1462 vw		1462 vw		1460 vw		$\nu_1 + \nu_4$ (F_2)		
1228 mw		1228 mw		1227 mw		$2\nu_4$ ($A_1 + E + F_2$)		
1175 sh				1177 sh				
1160 vs	1159 (0.15)	1160 vs	1156 (0.13)	1162 vs	1160 (0.6)	ν_3 (F_2)		
1145 sh	1150 sh	1145 sh		1145 sh	1150 (0.2)			
				1323 vw			$\nu_1 + \nu_3$ (F_{1u})	
1056 vw		1056 vw		1056 vw		$\nu_2 + \nu_4$ ($F_1 + F_2$)		
	878 (0+)		875 (0+)		878 (0.2)	$2\nu_2$ ($A_1 + A_2 + E$)		
	844 (1.8)		844 (1.5)		843 (7.0)	ν_1 (A_1)		
				763 vw			$\nu_2 + \nu_4$ ($F_{1u} + F_{2u}$)	
730 vw							$\nu_2 + \nu_4$ ($F_{1u} + F_{2u}$)	
		600 vs	602 (2)					BiF str
		618 m						
610 m	608 (1)			609 m	604 (3.9)	ν_4 (F_2)		
			602 (2)					
	580 (10)		580 (10)		648 (10)		ν_1 (A_{1g})	
				675 vs				
576 vs		575 sh		665 vs			ν_3 (F_{1u})	
				655 sh	655 (1)			
			548 (0.5)					BiF str
529 w	529 sh	531 sh		576 w				
	521 (0.8)		521 (0.25)		569 (0.9)		ν_2 (E_g)	
			475 (0.13)					
		452 m						BiFBi str
	438 (0.35)		436 (0.25)		437 (1.5)	ν_2 (E)		
	228 (2.1)		230 (1.4)		275 (3.8)		ν_5 (F_{2g})	
			211 (0.4)					
			175 (0.9)					Def
			150 sh					
	115 (0+) br		95 (0.1)			Lattice vib		

[a] Uncorrected Raman intensities.

observed frequencies and their assignments are summarized in Table II. The spectra are in excellent agreement with those previously reported for the NF_4^+ cation[1] and the BiF_6^- [7,11,12] and SbF_6^- [7,12-15] anions, thus confirming the ionic nature of these adducts. By analogy with the previously studied[1] NF_4^+ salts, the degeneracy of some of the modes is lifted and crystal field splittings are observed. For example, the antisymmetric NF_4^+ stretching mode ν_3 (F_2) is split into three components, and the ν_3 (F_{1u}) and the ν_2 (E_g) modes of SbF_6^- show a splitting into three and two components, respectively. The presence of polyanions, such as $Bi_2F_{11}^-$,[7] in the $NF_4BiF_6 \cdot nBiF_5$ adducts is apparent from the appearance of a medium intense infrared band at 452 cm^{-1}, which is attributed to the stretching mode of the Bi–F–Bi bridge. Furthermore, additional bands were observed in the region of the BiF stretching and deformation modes. The maximum of the most intense BiF stretching infrared band was found to vary somewhat from sample to sample and varied from 575 to 605 cm^{-1}. In addition, some of the pyrolysis products showed weak infrared bands at 475 and 400 cm^{-1}. A comparison of the spectra of NF_4BiF_6 and $NF_4BiF_6 \cdot nBiF_5$ with those of NF_4SbF_6 and $NF_4Sb_2F_{11}$[1] shows a similar pattern for both when going from MF_6^- to $M_2F_{11}^-$.

Summary

The new NF_4^+ salt NF_4BiF_6 was prepared by the reaction between equimolar amounts of NF_4BF_4 and BiF_5 either at 180 °C without solvent or at 20 °C in HF solution. A salt of the composition $NF_4BiF_6 \cdot nBiF_5$ ($n = 0.6$–1.5) was prepared directly from NF_3, F_2, and BiF_5 at elevated temperature and pressure. It was converted to NF_4BiF_6 by vacuum pyrolysis at 280 °C. The salts were characterized by elemental analyses and vibrational spectroscopy, and their hydrolyses were studied. The pyrolysis of $NF_4SbF_6 \cdot nSbF_5$ to NF_4SbF_6 was briefly investigated, and the vibrational spectrum and x-ray powder pattern of NF_4SbF_6 are reported.

Acknowledgment. We are indebted to Dr. L. R. Grant for helpful discussions and to the Office of Naval Research for financial support.

Registry No. NF_4BiF_6, 61587-71-1; NF_4SbF_6, 16871-76-4; α-BiF_5, 7787-62-4; $NF_4Sb_2F_{11}$, 58702-89-9.

Supplementary Material Available: Tables III and IV, listing the observed x-ray powder diffraction patterns of NF_4BiF_6 and NF_4SbF_6 (2 pages). Ordering information is given on any current masthead page.

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Contribution from Rocketdyne, A Division of Rockwell International,
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Synthesis and Characterization of $(NF_4)_2SnF_6$ and NF_4SnF_5

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The novel NF_4^+ salt $(NF_4)_2SnF_6$ was prepared by metathesis between Cs_2SnF_6 and NF_4SbF_6 in HF solution. It is a white solid, stable to above 200 °C. Based on its x-ray powder data, it crystallizes in the tetragonal system and is isotypic with $(NF_4)_2GeF_6$. Its composition was established by elemental analysis, and the presence of tetrahedral NF_4^+ and octahedral SnF_6^{2-} ions in the solid state and in BrF_5 solution was demonstrated by vibrational and ^{19}F NMR spectroscopy, respectively. The salt NF_4SnF_5 was obtained in quantitative yield from the displacement reaction between equimolar amounts of NF_4BF_4 and SnF_4 in HF solution. When a large excess of NF_4BF_4 was used, the main product was again NF_4SnF_5 and only a small amount of $(NF_4)_2SnF_6$ was formed. The NF_4SnF_5 salt was characterized by elemental analysis, vibrational and ^{19}F NMR spectroscopy, and x-ray powder data. The vibrational spectra of the solid and the ^{19}F NMR spectra of BrF_5 solutions show that SnF_5^- possesses a polymeric structure of cis-fluorine-bridged SnF_6 octahedra, analogous to that observed for GeF_5^- in NF_4GeF_5. The potential of $(NF_4)_2SnF_6$ for a "self-clinkering" NF_3–F_2 gas generator is briefly discussed.

Introduction

Perfluoroammonium salts are of significant interest owing to their potential for solid propellant NF_3–F_2 gas generators for chemical HF-DF lasers.[1] Salts are known of the following anions: PF_6^-, AsF_6^-, SbF_6^-, $SbF_6^-\cdot nSbF_5$, BiF_6^-, $BiF_6^-\cdot nBiF_5$, BF_4^-, GeF_5^-, and GeF_6^{2-}.[1,2] All of these salts are derived from Lewis acids which are volatile and either completely or at least partially monomeric at temperatures below the thermal decomposition temperature of their NF_4^+ salts. Since these volatile Lewis acids are undesirable for NF_3–F_2 gas generators, they must be removed by complexing (clinker formation) with a strong Lewis base, such as KF. Since the addition of a clinker-forming component degrades the performance of an NF_3–F_2 gas generator, the synthesis of NF_4^+ salts, derived from nonvolatile Lewis acids, became very desirable. However, this objective presented a synthetic challenge, since nonvolatile Lewis acids are highly polymeric and already possess favorable high coordination numbers. Consequently, these polymeric compounds are quite unreactive and do not behave like strong Lewis acids, thus rendering a direct synthesis[3] from NF_3, F_2, and the Lewis acid impossible. In this paper we report the synthesis of NF_4^+ salts derived from SnF_4, a doubly trans-fluorine-bridged polymer[4,5] subliming at 704 °C, using metathetical[6,7] and displacement[1,2] reactions.

Experimental Section

Materials and Apparatus. The equipment and handling procedures used in this work were identical with those recently described.[1,2] The NF_4BF_4[1] and NF_4SbF_6[2] starting materials were prepared as previously reported. The SnF_4 (Ozark Mahoning) and $SnCl_4$ (Baker) were used as received. The NF_3 and F_2 were prepared at Rocketdyne, the HF (Matheson) was dried as previously described,[8] and the BrF_5 (Matheson) was purified by fractional condensation prior to use. The CsF was fused in a platinum crucible and powdered in the drybox.

Synthesis of Cs_2SnF_6. Dry CsF (10.45 mmol) and $SnCl_4$ (5.22 mmol) were combined in a passivated Teflon FEP ampule. Anhydrous HF (10 mL of liquid) was added, and the mixture was agitated at 20 °C for several hours until HCl evolution had ceased and a clear solution was obtained. The volatile materials were pumped off at 50 °C. The white solid residue (2.604 g; weight calculated for 5.22 mmol of Cs_2SnF_6 2.600 g) was shown by infrared and Raman spectroscopy[9,10] and its x-ray diffraction powder pattern[11] to be of excellent purity.

If SnF_4 is readily available, the following synthesis of Cs_2SnF_6 was found to be somewhat more convenient. A mixture of CsF and SnF_4 (2:1 mole ratio) was fused in a covered platinum crucible until a clear melt was obtained. Alternately, CsF and SnF_4 (2:1 mole ratio) were agitated in anhydrous HF until a clear solution was obtained (SnF_4 is only very sparingly soluble in HF). In both cases the resulting products were shown by spectroscopic techniques to be undistinguishable from that obtained by the above method.

Synthesis of $(NF_4)_2SnF_6$. The small-scale metathetical reactions were carried out in the apparatus depicted in Figure 1. It consisted of three Teflon FEP U-traps interconnected by Monel unions (Swagelok) and closed off at both ends by a Monel valve. The union between trap II and trap III contained a Teflon filter (porous Teflon sheet, $^1/_{16}$-in. thickness from Russel Assoc. Inc.) and was held in place by a press fit. The passivated apparatus was taken to the drybox and Cs_2SnF_6 and NF_4SbF_6 (in a 1:2 mole ratio) were placed into traps I and II, respectively. The apparatus was connected to the vacuum line through flexible corrugated Teflon FEP tubing. Anhydrous HF, in an amount sufficient to just dissolve the starting materials, was added to traps I and II. Trap I was flexed to allow the Cs_2SnF_6 solution to run into trap II containing the NF_4SbF_6 solution. Upon contact of the two solutions, copious amounts of a white precipitate ($CsSbF_6$) formed. The contents of trap II were agitated for several minutes to obtain good mixing. Then the apparatus was inverted to allow the solution to run onto the filter. To generate a pressure differential across the filter, trap III was cooled to −80 °C. After completion of the filtration step, trap III was warmed to ambient temperature and the HF solvent was pumped off. The solid residue on top of the filter consisted mainly of $CsSbF_6$, whereas the solid collected in trap III was mainly the desired $(NF_4)_2SnF_6$.

The following example gives a typical product distribution obtainable with the above procedure and apparatus: starting materials NF_4SbF_6 (9.72 mmol), Cs_2SnF_6 (4.86 mmol); weight of solid on filter 4.24 g; weight of solid in trap III 1.36 g (weight calculated for 4.86 mmol of $(NF_4)_2SnF_6$ 2.01 g). Anal. Calcd for solid from trap III, a mixture of 82.8% $(NF_4)_2SnF_6$, 12.9% NF_4SbF_6, and 4.3% $CsSbF_6$: NF_3, 31.72; Sn, 24.60; Sb, 5.24; Cs, 1.43. Found: NF_3, 31.5; Sn, 25.1; Sb, 5.9; Cs, 1.3.

Synthesis of NF_4SnF_5. A mixture of NF_4BF_4 and SnF_4 (9.82 mmol each) was placed into a passivated Teflon–FEP ampule containing a Teflon-coated magnetic stirring bar. Anhydrous HF (10 mL of

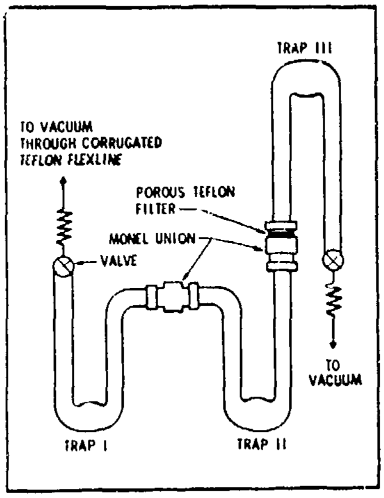

Figure 1. Apparatus for small-scale metathetical reactions consisting of three interconnected Teflon–FEP U-traps.

liquid) was added at −78 °C, and the resulting suspension was stirred at 25 °C for 2 h. The volatile material was pumped off at 35 °C leaving behind a white stable solid which, on the basis of its weight (3.094 g) and Raman spectrum, consisted of 83 mol % NF_4SnF_5 and 17 mol % unreacted starting materials. The HF treatment was repeated (again for 2 h) and the nonvolatile residue (2.980 g; weight calculated for 9.82 mmol of NF_4SnF_5 2.982 g) was shown by infrared, Raman, and ^{19}F NMR spectroscopy to be essentially pure NF_4SnF_5. Anal. Calcd for NF_4SnF_5: NF_3, 23.38; Sn, 39.08. Found: NF_3, 23.6; Sn, 38.7.

When a mixture of NF_4BF_4 and SnF_4 in a mole ratio of 2:1 was treated eight times, as described above, with liquid HF for a total of 35 days, the resulting nonvolatile residue consisted mainly of NF_4SnF_5, unreacted NF_4BF_4, and a small amount of $(NF_4)_2SnF_6$.

Results and Discussion

Syntheses. As pointed out in the Introduction, SnF_4 is polymeric with Sn being hexacoordinated. Consequently, solid SnF_4 does not act as a strong Lewis acid. This was experimentally confirmed by demonstrating that mixtures of NF_3, F_2, and SnF_4, when heated to temperatures of up to 300 °C at autogenous pressures of about 150 atm, did not show any evidence for NF_4^+ formation.

Since a direct synthesis of an NF_4^+ salt derived from SnF_4 was not possible, we have studied metathetical and displacement reactions. Because it has previously been shown[12] that SnF_6^{2-} salts are stable in anhydrous HF, the metathetical and displacement reactions were carried out in this solvent. On the basis of the reported solubilities of $CsSbF_6$ (5.6 g/100 g of HF),[6] NF_4SbF_6 (280 g/100 g of HF),[6] and Cs_2SnF_6 (~250 g/100 g of HF)[12] and the predicted high solubility of $(NF_4)_2SnF_6$ (the analogous $(NF_4)_2GeF_6$ is very soluble in HF),[2] the metathetical reaction

$$2NF_4SbF_6 + Cs_2SnF_6 \xrightarrow{\text{HF soln}} 2CsSbF_6\downarrow + (NF_4)_2SnF_6$$

should be capable of producing $(NF_4)_2SnF_6$ in a purity of about 93 mol %. The soundness of these predictions was experimentally verified. A product was obtained which based on its elemental analysis had the following composition (mol %): $(NF_4)_2SnF_6$, 82.8; NF_4SbF_6, 12.9; $CsSbF_6$, 4.3. Whereas the amount of $CsSbF_6$ found in the product approximates that predicted, the presence of about 13% NF_4SbF_6 indicates the loss of some Cs_2SnF_6. This was probably caused by the hold up of some of the Cs_2SnF_6 solution in trap I (see Figure 1) during its transfer to trap II. It should be possible to eliminate most of the NF_4SbF_6 from the product either by minimizing the relative loss of Cs_2SnF_6 during transfer by scaling up the reaction or by recrystallization of the product. However, both approaches were beyond the scope of the present study.

Whereas SnF_4 is quite insoluble in anhydrous HF (contrary to a previous literature report[13]), it dissolves reasonably fast in HF solutions containing an excess of an alkali metal fluoride with formation of the corresponding alkali metal SnF_6^{2-} salt. SnF_4 has also been reported to act as a relatively strong acid in HF solution.[13] Furthermore, GeF_4 is capable of displacing BF_4^- in NF_4BF_4,[2] and the strength of a Lewis acid generally increases within a group of the periodic system with increasing atomic weight of the central atom. Consequently, SnF_4 in HF might be expected to also be capable of displacing BF_4^- in NF_4BF_4.

When equimolar mixtures of NF_4BF_4 and SnF_4 were stirred in anhydrous HF, the following quantitative reaction occurred

$$NF_4BF_4 + SnF_4 \xrightarrow{\text{HF}} NF_4SnF_5 + BF_3$$

However, BF_3 interacts with HF and the above reaction appears to be an equilibrium reaction. Consequently, it was found advantageous to pump off the volatile products and to repeat the HF treatment at least once to obtain complete conversion to NF_4SnF_5. No evidence for SnF_6^{2-} formation was observed under these conditions. The quantitative formation of SnF_5^- was surprising, since for the alkali metal fluoride–SnF_4 systems exclusive SnF_6^{2-} formation was observed during our study. We could not find any previous literature reports on SnF_5^-, except for a recent low-temperature ^{19}F NMR study by Dean[14] which demonstrated the presence of polyanions in SO_2 solutions of mixtures of SnF_6^{2-} and SnF_4.

The possibility of preparing $(NF_4)_2SnF_6$ from a 2:1 mixture of NF_4BF_4 and SnF_4 was examined. However, even after eight HF treatments for a total of 35 days only a small amount of SnF_6^{2-} had formed. The main products were NF_4SnF_5 and unreacted NF_4BF_4. These results indicate that the Lewis acid strength of SnF_5^- in HF is insufficient to displace most of the BF_4^- from its NF_4^+ salt and that, in agreement with Dean's observation for SO_2 solutions,[14] the equilibrium is shifted far to the right.

$$SnF_6^{2-} + SnF_4 \rightleftarrows 2SnF_5^-$$

Properties. Both salts, $(NF_4)_2SnF_6$ and NF_4SnF_5, are white, stable, crystallinic, moisture-sensitive solids. As previously pointed out,[2] the onset of thermal decomposition is difficult to define for NF_4^+ salts owing to the absence of a sharp decomposition point. For the SnF_4 salts, one of the decomposition products is nonvolatile solid SnF_4 and, therefore, no melting point could be observed. Visual observation for $(NF_4)_2SnF_6$ in sealed glass capillaries indicated the first signs of decomposition at about 240 °C. The occurrence of decomposition in this temperature range was confirmed by a DSC study which showed the onset of an irreversible endotherm at about 225 °C which was accompanied by F_2 evolution. Furthermore, sealed glass capillaries, when heated above 300 °C, exploded due to pressure buildup from the gaseous decomposition products. For NF_4SnF_5 in a sealed glass capillary, slight shrinkage of the solid was observed at about 120 °C. The DSC curve did not show any evidence for a sharp change in slope up to a temperature of about 270 °C, where a large exotherm started. It should be kept in mind, however, that for powerful oxidizers, such as NF_4^+ salts, exotherms can be caused by reaction of the oxidizer with the aluminum sample container.

The hydrolysis of $(NF_4)_2SnF_6$ and NF_4SnF_5 proceeds, as previously established for other NF_4^+ salts,[2,15] with quantitative NF_3 evolution. This reaction was also used for the elemental analyses. In anhydrous HF, the $(NF_4)_2SnF_6$ salt is highly soluble, whereas NF_4SnF_5 is of moderate solubility. Both salts are also soluble in BrF_5; however the solubilities are considerably lower than those in HF.

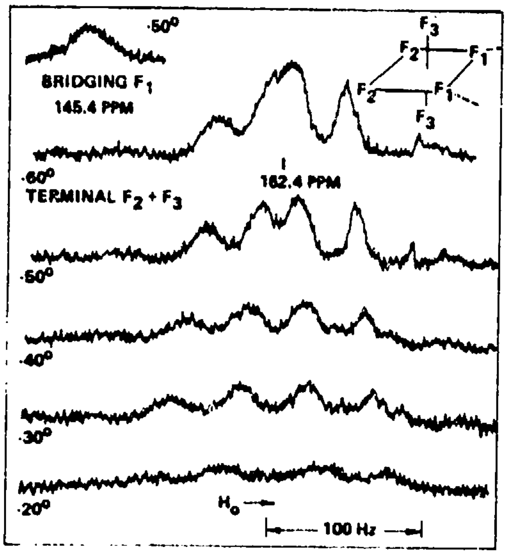

Figure 2. Temperature dependence of the ^{19}F NMR spectrum of the $(SnF_5)_n^{n-}$ part of NF_4SnF_5 in BrF_5 solution, recorded at 56.4 MHz using $CFCl_3$ as external standard.

X-Ray Powder Data. The powder pattern of $(NF_4)_2SnF_6$ is given as supplementary material. The observed pattern, after correction for several weak lines due to the presence of the metathesis by-products NF_4SbF_6[1] and $CsSbF_6$,[16] is very similar to that[2] of $(NF_4)_2GeF_6$, indicating that the two compounds are isotypic. The pattern was indexed for a tetragonal unit cell, and the resulting crystallographic parameters of $(NF_4)_2SnF_6$ are compared in Table I with those of other NF_4^+ salts. As can be seen, the agreement is excellent. Since $(NF_4)_2GeF_6$ has been prepared in high purity and is well characterized,[2] the x-ray powder data establish beyond doubt that the major crystalline product from the NF_4SbF_6 + Cs_2SnF_6 metathesis is indeed $(NF_4)_2SnF_6$.

Table I. Crystallographic Data of $(NF_4)_2SnF_6$ Compared to Those of Other NF_4^+ Salts

	Tetragonal unit cell dimensions					Calcd den-sity, g/cm³
	a, Å	c, Å	V, Å³	Z	Vol/F, Å³	
NF_4PF_6[a]	7.577	5.653	324.53	2	16.23	2.41
NF_4AsF_6[a]	7.70	5.73	339.73	2	16.99	2.72
NF_4SbF_6[a]	7.903	5.806	362.63	2	18.13	2.98
NF_4BiF_6[a]	8.006	5.821	373.10	2	18.66	3.68
NF_4BF_4[b]	9.944	5.229	517.04	4	16.16	2.27
$(NF_4)_2GeF_6$[b]	10.627	11.114	1255.14	$^{16}/_{3}$	16.81	2.59
$(NF_4)_2SnF_6$	10.828	11.406	1337.35	$^{16}/_{3}$	17.91	2.73

[a] Reference 1. [b] Reference 2.

The powder pattern of NF_4SnF_5 was also recorded and is given as supplementary material. It did not contain any lines which could be attributed to either NF_4BF_4,[2] SnF_4, or

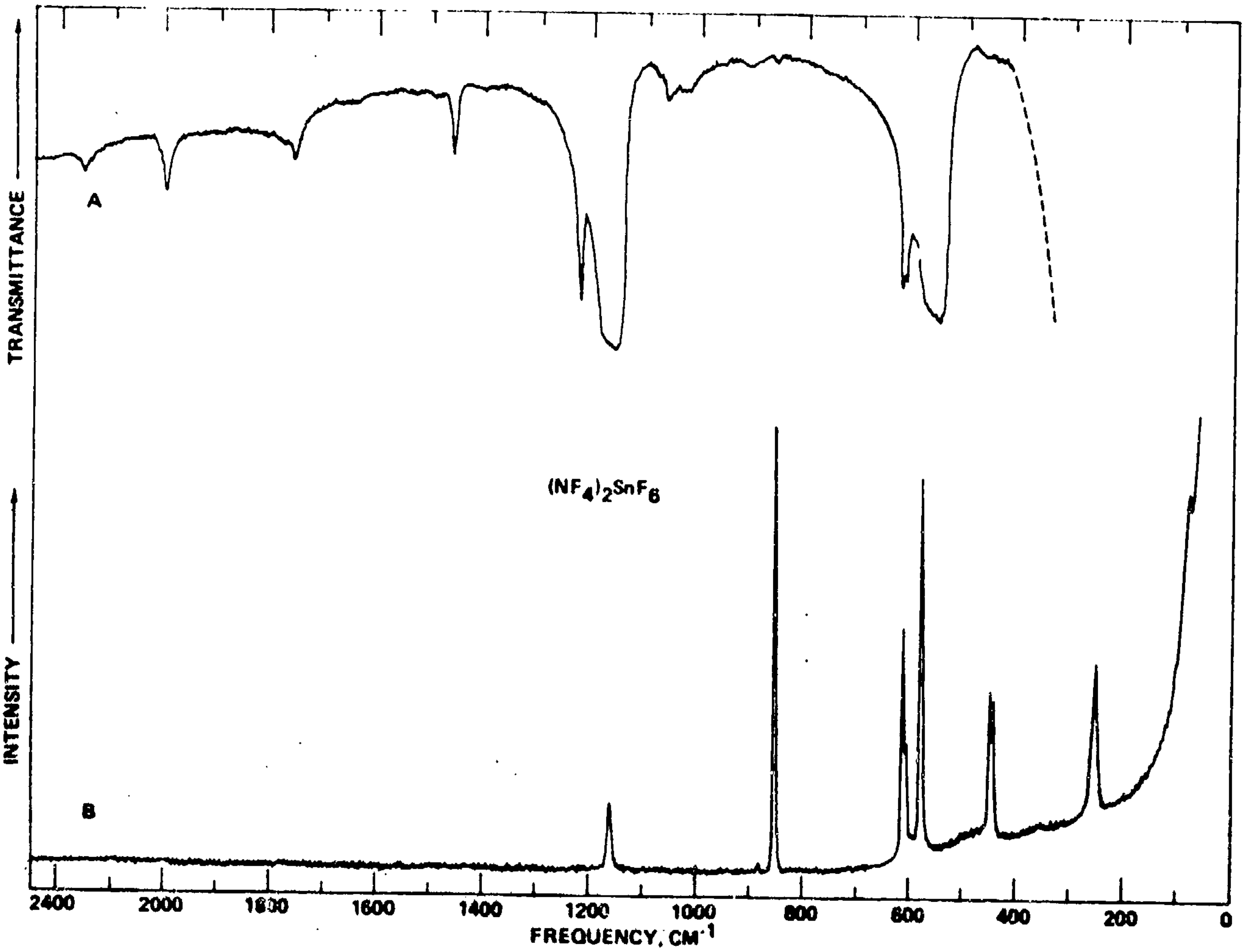

Figure 3. Vibrational spectra of solid $(NF_4)_2SnF_6$: trace A, infrared spectrum of the dry powder in a silver chloride disk, the absorption below 400 cm^{-1} (broken line) being due to the AgCl windows; trace B, Raman spectrum recorded at a spectral slit width of 3 cm^{-1}. Weak bands due to SbF_6^- were deleted from the spectra.

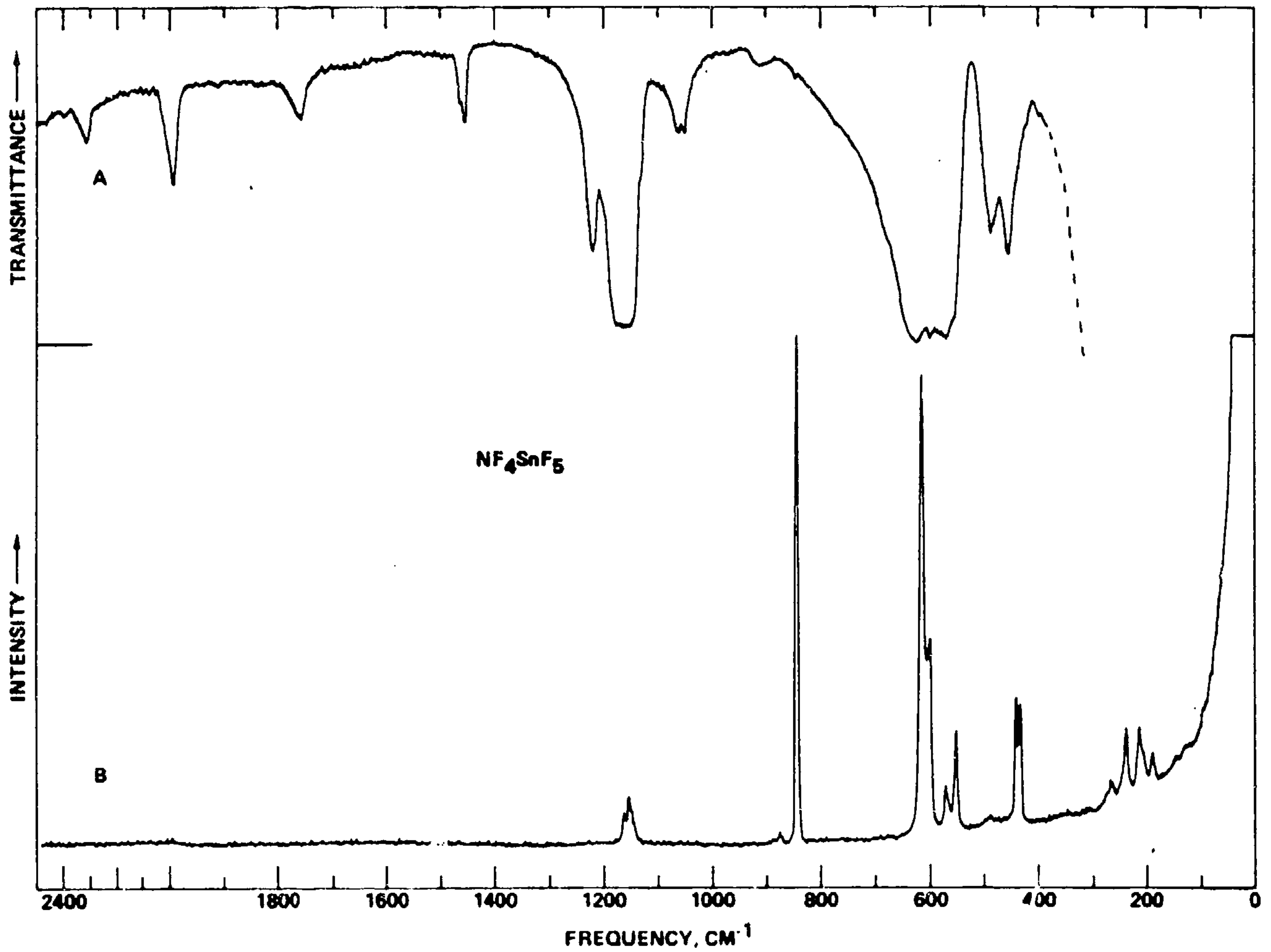

Figure 4. Vibrational spectra of solid NF_4SnF_5, recorded under the same conditions as those of Figure 3.

$(NF_4)_2SnF_6$. Reliable indexing of the pattern was not possible owing to the large number of observed lines, but it somewhat resembles that previously observed[2] for NF_4GeF_5.

NMR Spectra. The ^{19}F NMR spectra were recorded for both $(NF_4)_2SnF_6$ and NF_4SnF_5 in BrF_5 solution. In spite of its higher melting point (−60.5 °C) and lower solubilities, this solvent was preferred over HF, because it was found difficult[2] to suppress rapid fluoride exchange between HF and the anions. In BrF_5 solution, no such problems were encountered. Well-resolved spectra were observed for both the NF_4^+ cation and the corresponding anions, in addition to the sharp quintet (ϕ −272) and doublet (ϕ −136) with $J_{FF} = 74.7$ Hz characteristic for BrF_5.[2,17] For both the $(NF_4)_2SnF_6$ and the NF_4SnF_5 solution a triplet of equal intensity with ϕ −220, $J_{NF} = 229.6$ Hz, and a line width at half-height of about 5 Hz was observed which is characteristic for tetrahedral NF_4^+.[2,15,18] The $(NF_4)_2SnF_6$ solution showed in addition to these resonances a narrow singlet at ϕ 149 with the appropriate $^{117/119}Sn$ satellites (average $J_{SnF} = 1549$ Hz). These values are in good agreement with those previously reported[14,19] for octahedral SnF_6^{2-} in different solvents. This assignment was further confirmed by recording the spectrum of Cs_2SnF_6 in BrF_5 solution.

Two resonances were observed for SnF_5^- of NF_4SnF_5 at ϕ 145.4 and 162.4, respectively, with an area ratio of 1:4. At −20 °C the resonances consisted of broad lines, but at lower temperatures the ϕ 162.4 signal showed splittings. These splittings exhibited a pronounced temperature dependence (see Figure 2). The observed spectrum can be interpreted by comparison with the data previously reported[14] by Dean for $(SnF_5)_n^{n-}$ in SO_2 solution. For this ion, Dean observed a singlet at 140.4 ppm and two approximately 1:2:1 triplets at 154.2 and 158.1 ppm, respectively, with area ratios of 1:2:2. The lower field triplet was broader than the higher field triplet and the coupling constant was 58 Hz. These data unambiguously showed[14] that $(SnF_5)_n^{n-}$ must have a polymeric structure consisting of cis-fluorine-bridged SnF_6 octahedrons. Our data for $(SnF_5)_n^{n-}$ in NF_4SnF_5 are quite similar with the only exception that the difference in chemical shift between the two triplets has decreased and decreases further with decreasing temperature. Thus the resonance at 164.2 ppm (area 4) can be interpreted as an A_2B_2 system strongly distorted by second-order effects.[20] The singlet at 145.4 ppm (area 1) must then be due to the bridging fluorines. The 4:1 area ratio results from the fact that only the two bridging fluorines are shared by two octahedrons. As found by Dean, the coupling between the axial and the terminal equatorial fluorines is much larger (about 40–60 Hz) than that between the terminal and the bridging fluorines. Furthermore, the lower field half of the 162.4-ppm resonance shows a greater line width than the upper half, indicating weak, but differing, coupling between the bridging and the two types of terminal fluorines.

Our observations for NF_4SnF_5 are in excellent agreement with the data of Dean[14] and demonstrate the polymeric cis-fluorine-bridged nature of SnF_5^-. However, we are less confident than Dean that, in $(SnF_5)_n^{n-}$, *n* equals 2. Higher values of *n* can certainly not be excluded and *n* might vary within and from sample to sample, as indicated by varying

Table II. Vibrational Spectra of Solid $(NF_4)_2SnF_6$ Compared to Those of Cs_2SnF_6

Obsd freq, cm^{-1}, and rel intens[a]				Assignments (point group)	
$(NF_4)_2SnF_6$		Cs_2SnF_6			
IR	Raman	IR	Raman	NF_4^+ (T_d)	SnF_6^{2-} (O_h)
2310 vw				$2\nu_3$ ($A_1 + E + F_2$)	
2005 vw				$\nu_1 + \nu_3$ (F_2)	
1764 vw				$\nu_3 + \nu_4$ ($A_1 + E + F_2$)	
1463 vw				$\nu_1 + \nu_4$ (F_2)	
1224 mw				$2\nu_4$ ($A_1 + E + F_2$)	
1160 vs	1158 (1.5)			ν_3 (F_2)	
1132 vw, sh					$\nu_1 + \nu_3$ (F_{1u})
1059 vw				$\nu_2 + \nu_4$ ($F_1 + F_2$)	
1026 vw					$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$)
	881 (0.1)			$2\nu_2$ ($A_1 + A_2 + E$)	
854 vvw	853 (10)			ν_1 (A_1)	
613 mw	613 (5.0)			$\}\ \nu_4(F_2)$	
605 mw	607 (1.5)				
	579 (8.3)		573 (10)		ν_1 (A_{1g})
550 vs		555 vs			ν_3 (F_{1u})
	470 (0+) br		460 (1.2)		ν_2 (E_g)
	449 (3.1)			$\}\ \nu_2$ (E)	
	442 (2.9)				
	251 (3.3)		249 (4.5)		ν_5 (F_{2g})
	84 (0.3)			Lattice vib	

[a] Uncorrected Raman intensities

Table III. Vibrational Spectra of Solid NF_4SnF_5 Compared to Those of NF_4GeF_5

Obsd freq, cm^{-1}, and rel intens[a]				Assignments[c] (point group)	
NF_4SnF_5		NF_4GeF_5[b]			
IR	Raman	IR	Raman	NF_4^+ (T_d)	$(MF_5)_4^{4-}$
		2380 vw		$\}\ 2\nu_3$ ($A_1 + E + F_2$)	
2320 w		2320 w			
2000 w		2010 w		$\nu_1 + \nu_3$ (F_2)	
1760 w		1766 w		$\nu_3 + \nu_4$ ($A_1 + E + F_2$)	
1464 vw		1465 w		$\}\ \nu_1 + \nu_4$ (F_2)	
1456 w		1456 vw			
1222 mw		1221 mw		$2\nu_4$ ($A_1 + E + F_2$)	
	1168 (0.4)		1168 (0.8)	$\}\ \nu_3$ (F_2)	
1165 vs	1159 (0.8)	1160 vs	1159 (0.8)		
	1150 sh		1149 (0.9)		
1134 w, sh					
1061 w		1055 w		$\}\ \nu_2 + \nu_4$ ($F_1 + F_2$)	
1048 w					
	881 (0.2)		881 (0+)	$2\nu_2$ ($A_1 + A_2 + E$)	
850 vw	851 (10)		848 (10)	ν_1 (A_1)	
635 vs		701 vs			$\nu_{as}(MF_2)_{ax}$ (ν_{22}) + $\nu_{as}(MF_2)_{eq}$ (ν_{25})
		690 sh	689 (1.0)		$\nu_{as}(MF_2)_{ax}$ (ν_{17}) + $\nu_{sym}(MF_2)_{eq}$ (ν_7)
	622 (9.2)	673 mw	672 (4.9)		$\nu_{sym}(MF_2)_{eq}$ (ν_1)
		613 m	615 (0.8)	$\}\ \nu_4$ (F_2)	
605 mw	606 (3.3)	604 m	604 (3.2)		
		593 m	594 (2.6)		
575 vs		630 vs			$\nu_{as}(MF_2)_{eq}$ (ν_{16})
	574 (0.5)				$\nu_{as}(MF_2)_{eq}$ (ν_{11})
559 w, sh	558 (2.0)		578 (1.6)		$\nu_{sym}(MF_2)_{ax}$ (ν_2)
490 m	490 (0+)		490 (0+)		$\nu_{sym}(MFM)_{bridge}$ (ν_9)
458 m		474 mw			$\nu_{as}(MFM)_{bridge}$ (ν_{28})
	448 (2.5)		440 (2.6)	$\}\ \nu_2$ (E)	
	440 (2.3)		431 (2.2)		
		386 m			
		373 w	373 (0+) br		Def modes
			343 (0+) br		
		335 m			
	272 (0.6)		321 (0.8)		
	247 (1.4)		281 (1.0)		
	222 (1.1)		249 (0.6)		
	197 (0.6)		212 (0.4)		
	154 (0+)				
	135 (0.2)		152 (0.4)		

[a] Uncorrected Raman intensities. [b] Data from ref 2. [c] Assignments for $(MF_5)_4^{4-}$ were made by analogy with the data of ref 25.

solubilities observed for different samples during this study. Attempts were unsuccessful to observe the spectrum of a 1:1 mole ratio mixture of Cs_2SnF_6 and SnF_4 in BrF_5 solution owing to its low solubility. Only a signal due to SnF_6^{2-} was observed.

Vibrational Spectra. The infrared and Raman spectra of $(NF_4)_2SnF_6$ and NF_4SnF_5 were recorded and are shown in Figures 3 and 4, respectively. The observed frequencies and their assignments are listed in Tables II and III. Comparison with the known spectra[1,2] of other NF_4^+ salts clearly demonstrates the presence of tetrahedral NF_4^+ cations, and the bands due to NF_4^+ can be easily assigned. The observation of small splittings for the degenerate modes of NF_4^+ and the observation of the ideally infrared-inactive $\nu_1(A_1)$ mode as a very weak band in the infrared spectra indicate that the site symmetry of NF_4^+ in these solids is lower than T_d. This is not surprising in view of the above given x-ray powder data and has previously been also observed[1,2] for other NF_4^+ salts.

The assignments for the anion bands in $(NF_4)_2SnF_6$ are also straightforward. The vibrational spectra of octahedral SnF_6^{2-} are well-known[19,21-24] and establish the presence of SnF_6^{2-} in $(NF_4)_2SnF_6$ (see Table II).

The anion spectrum in NF_4SnF_5 shows a pattern very similar to that of the anion in NF_4GeF_5. Furthermore, the general appearance of these anion spectra closely resembles the spectrum previously reported[25] for solid TaF_5. The structure of the latter has been established by x-ray diffraction data[26] as a cis-fluorine-bridged tetramer. Consequently, the observed vibrational spectra indicate a value of 4 for n in these $(MF_5)_n^{n-}$ polyanions. A thorough vibrational analysis has been carried out[25] for tetrameric NbF_5 and TaF_5 by Beattie and co-workers. Using their data, we have made tentative assignments for the stretching modes of SnF_5^- and GeF_5^- based on tetrameric anions, which are given in Table III. The assumption of a low degree of polymerization, such as a cyclic tetramer, for the anions in these NF_4MF_5 salts is not unreasonable in view of their appreciable solubility in solvents, such as HF or BrF_5. However, a crystal structure determination is desirable to confirm the above conclusions.

Summary

The successful syntheses of NF_4SnF_5 and $(NF_4)_2SnF_6$ demonstrate the possibility of preparing NF_4^+ salts derived from nonvolatile and unreactive polymeric Lewis acids. Such salts are important for solid propellant NF_3–F_2 gas generators for chemical HF–DF lasers, because they do not require the addition of a clinker-forming reagent. The synthesis of NF_4SnF_5 was achieved by depolymerizing SnF_4 in anhydrous HF and displacing BF_4^- from NF_4BF_4 as BF_3 gas. For the synthesis of $(NF_4)_2SnF_6$ a metathetical process was required. Both NF_4^+ salts were characterized by material balance, elemental analysis, infrared, Raman, and ^{19}F NMR spectroscopy, x-ray powder diffraction data, and DSC. Whereas $(NF_4)_2SnF_6$ contains monomeric SnF_6^{2-} anions, NF_4SnF_5 contains polymeric, cis-fluorine-bridged, hexacoordinated anions. The vibrational spectra indicate that in solid NF_4SnF_5 the anion is probably present as a cyclic tetramer.

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Registry No. $(NF_4)_2SnF_6$, 61587-66-4; $(NF_4)_4(SnF_5)_4$, 61587-68-6; NF_4SnF_5, 61587-75-5; Cs_2SnF_6, 16919-25-8; SnF_4, 7783-62-2.

Supplementary Material Available: Tables IV and V, showing x-ray powder data (2 pages). Ordering information is given on any current masthead page.

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Vibrational spectrum and normal coordinate analysis of SF_5Br

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Abstract—The i.r. spectrum of gaseous and the Raman spectrum of liquid SF_5Br are reported. Ten out of 11 fundamentals expected for symmetry C_{4v} were observed and assigned. A normal coordinate analysis was carried out and thermodynamic properties in the range 0–2000 K were computed.

INTRODUCTION

Whereas the vibrational spectra and force fields of SF_5Cl [1–3], SeF_5Cl [4], and TeF_5Cl [5] have been well characterized, similar data on the corresponding bromine compounds are lacking. Since SF_5Br is an important intermediate for the synthesis of SF_5 substituted compounds, a thorough characterization of this molecule was desired. In this paper, we report its vibrational spectrum and the results of a normal coordinate analysis.

EXPERIMENTAL

The SF_5Br was prepared by the interaction of BrF with SF_4 in the presence of CsF in a stainless steel reactor at 90° for 24 hr. The reaction products were separated by repeated fractional condensation through a series of traps maintained at −95 and −112°. The SF_5Br was retained in the −112° trap. It was found difficult to obtain a colorless product, free of traces of Br_2, owing to its tendency to decompose to S_2F_{10} and Br_2 under the influence of light.

The i.r. spectra were recorded at Rocketdyne on both a Perkin–Elmer Model 457 and a Beckman Model 4250 spectrophotometer, calibrated by comparison with standard calibration points [6]. Stainless steel cells of 5 and 10-cm path length fitted with AgCl or high density polyethylene windows (seasoned with ClF_3) were used as sample containers. The Raman spectrum of liquid SF_5Br was recorded at UC Berkeley on a Spex Model 1400 double monochromator, using the 6764 Å exciting line for a Kr ion laser and quartz capillaries as sample containers.

RESULTS AND DISCUSSION

Vibrational spectra of SF_5Br.

The i.r. spectrum of SF_5Br is shown in Fig. 1. Three very weak bands at 945, 820 and 545 cm^{-1} were deleted from the figure, since their relative intensities varied from sample to sample and bands of similar frequencies have previously been reported [7] for S_2F_{10}, the photolytic decomposition product of SF_5Br. The frequencies observed for the i.r. spectrum of the gas and the Raman spectrum of the liquid, together with their assignments for point group C_{4v}, are given in Table 1. The agreement between the frequencies of the gas and the liquid is good indicating very little or no association in the liquid phase.

Since SF_5Br can be considered as a monosubstituted derivative of octahedral SF_6, it should belong to point group C_{4v}. The 11 fundamentals of SF_5Br of symmetry C_{4v} can be classified as $4A_1+2B_1+B_2+4E$. Of these, all 11 modes should be Raman active, whereas only the A_1 and E modes should be i.r. active. Of the Raman lines, only the four A_1 modes should be polarized.

The observed spectrum agrees with these predictions. The assignment of the bands to the individual modes was done by analogy with the known spectra of closely related SF_5Cl [1–3], SeF_5Cl [4], and SF_5O^- [8] (see Table 2) and, therefore, requires only little discussion. For SF_5Cl the revised assignment [4] was used. The frequencies of SF_5Br, which mainly involve motions of the SF_5 part of the molecule, deviate by less than 24 cm^{-1} from those previously reported for SF_5Cl [1–3]. The vibrations involving mainly an S—Br motion show the expected pronounced mass effect. The frequency of

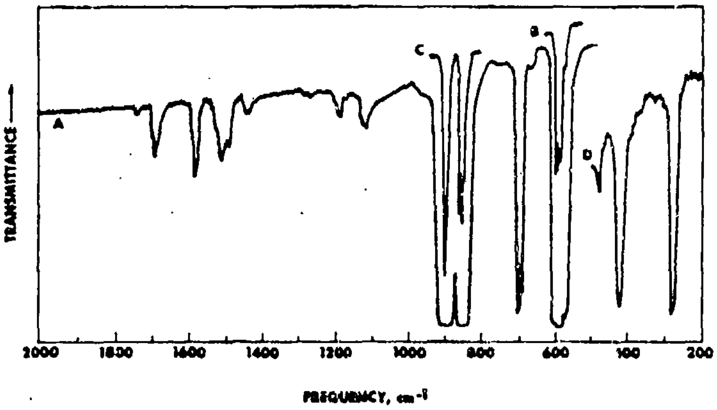

Fig. 1. Infrared spectrum of gaseous SF_5Br. Traces *A*, *B* and *C*, 100, 4.5 and 1 mm, respectively, in a 5 cm pathlength cell with AgCl windows; trace *D*, 700 mm in a 10 cm pathlength cell with polyethylene windows.

275 cm^{-1} assigned to the S–Br stretch in SF_5Br is in good agreement with the value of 305 cm^{-1} found for this mode in $BrSO_2F$ [9].

The above assignments are further supported by the observed i.r. band contours (PQR structure for the A_1 modes), the Raman polarization data, and the fact that all the observed combination bands (see Table 1) can be assigned without violation of the C_{4v} selection rules. The failure to detect ν_6 in the Raman spectrum is no surprise since for this type of molecules this mode is generally of very low intensity and also was not observed for the related molecules SF_5Cl [1–3] and SeF_5Cl [5]. By analogy with SF_5Cl [3], ν_{11} of SF_5Br is of very low intensity in the i.r. spectrum, but is readily observed in the Raman spectrum.

Table 1. Vibrational spectra of SF_5Br and their assignment in point group C_{4v}

Obsd freq, cm^{-1}, and intensity*		
Infrared gas	Raman liquid	Assignment
1745 vw		$\nu_1+\nu_8=1743\ (E)$
1696 w		$2\nu_1=1698\ (A_1)$
1588 w		$\nu_2+\nu_8=1586\ (E)$
1540 vw		$\nu_1+\nu_2=1541\ (A_1)$
1514 w		$\nu_5+\nu_8=1514\ (E)$
1489 vw		$\nu_3+\nu_8=1485\ (E)$
1443 vw		$\nu_1+\nu_3=1440\ (A_1)$
1280 vw		$\nu_2+\nu_3=1283\ (A_1)$
1268 vw		$\nu_1+\nu_{10}=1267\ (E)$ or $\nu_2+\nu_9=1267\ (E)$
1193 vw		$\nu_5+\nu_9=1195\ (E)$
1175 vvw		$2\nu_3=1182\ (A_1)$
1120 vw		$\nu_1+\nu_4=1120\ (A_1)$
894 vs	898 (0.2) dp	$\nu_8\ (E)$
849 vs, P, Q, R	848 (0.02) p	$\nu_1\ (A_1)$
692 m, P, Q, R	691 (7.6) p	$\nu_2\ (A_1)$
	620 (0.3) dp	$\nu_5\ (B_1)$
591 m, P, Q, R	586 (0.2) p	$\nu_3\ (A_1)$
575 m	575 (0.02) dp	$\nu_9\ (E)$
	500 (0.2) dp	$\nu_7\ (B_2)$
477 vw		$\nu_2-\nu_{11}=470\ (E)$
418 mw	419 (0.4) dp	$\nu_{10}\ (E)$
271 mw	272 (10) p	$\nu_4\ (A_1)$
	222 (0.6) dp	$\nu_{11}\ (E)$

* Uncorrected Raman intensities.

Table 2. Vibrational spectrum of SF_5Br compared to those of SF_5Cl, SF_5O^- and SeF_5Cl

Obsd freq, cm^{-1}, and intensity									
SF_5Br		SF_5Cl [1–4]		SF_5O^- [8]		SeF_5Cl [4]		Assignment in point group C_{4v}	Approximate description of vibration
i.r. gas	Ra liquid	i.r. gas	Ra liquid	i.r.	Ra	i.r. gas	Ra liquid		
849 vs	848 (0.02) p	855 vs	833 (0.2) p	735 vs	722 (0.2)	729 ms	721 (1.8) p	A_1 ν_1	ν (XF)
692 m	691 (7.6) p	707 s	704 (3) p	697 m	697 (10)	654 w	656 (10) p	ν_2	ν sym (XF_4)
591 m	586 (0.2) p	602 s	603 (0.2) p	506 s	506 (1)	440 vs	443 (2.2) p	ν_3	δ sym out of plane (XF_4)
271 mw	272 (10) p	402 s	403 (10) p	1154 vs	1153 (1)	384 mw	385 (8.5) p	ν_4	ν (XY)
	620 (0.3) dp		625 (0.7) dp		541 (3.3)		636 (0.6) dp	B_1 ν_5	ν sym out of phase (XF_4)
					472 (0.2)			ν_6	δ asym out of plane (XF_4)
	500 (0.2) dp		505 (0.2) dp		452 (0.9)		380 dp	B_2 ν_7	δ sym in plane (XF_4)
894 vs	898 (0.2) dp	909 vs	927 (0.2) dp	785 vs	780 (0.1)	745 vs	745 (0.3) dp	E ν_8	ν asym (XF_4)
575 m	575 (0.02) dp	579 mw	584 (0.1) dp	530 sh	530 (2)	421 s	424 (0.4) dp	ν_9	δ (FXF_4)
418 mw	419 (0.4) dp	441 m	442 (0.8) dp	325 mw		334 m	336 (1.2) dp	ν_{10}	δ asym in plane (XF_4)
	222 (0.6) dp	287 vw	271 (0.6) dp	606 s	607 (2.2)		213 (1.4) dp	ν_{11}	δ (YXF_4)

Force constants

A normal-coordinate analysis was carried out to aid the spectral assignment. The kinetic and potential energy metrics were computed by a machine method [10], assuming the following geometry and coordinate definitions: $R_{SF'} = r_{SF} = 1.60$ Å, $D_{SBr} = 2.27$ Å [11], $\alpha = \angle FSF = 90°$, $\beta = \angle F'SF = 90°$ and $\gamma = \angle BrSF = 90°$, where F' refers to the axial (unique) fluorine ligand. The symmetry coordinates used were identical with those previously reported [12] for IF_5O. The deformation coordinates were weighted by unit (1 Å) distance.

The force constants were calculated by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies using the simplest possible modified valence force field. Unique force constants could not be computed since the general valence force field has 24 symmetry force constants and there are only 11 frequencies. It was found that in both the A_1 and E block off-diagonal force constants are required to fit the observed frequencies. In the A_1 block, the F_{12}, F_{23} and F_{24} terms may be neglected [13] since their corresponding G matrix elements are zero. In the E block, however, all G matrix elements are nonzero. Based on our experience with related molecules, the most plausible interaction constants were selected and their values were kept as small as possible. Additional criteria for selecting the off-diagonal F terms were a plausible potential energy distribution and the condition to make $F_{11} = f_R \approx f_r$. The resulting force constants are listed in Tables 3 and 4. Uncertainty estimates are difficult to make

Table 3. Symmetry force constants of SF_5Br*

A_1 ν_1	849	$F_{11} = f_R$	= 4.50
ν_2	692	$F_{22} = f_r + 2f_{rr} + f_{rr}'$	= 5.36
ν_3	591	$F_{33} = \frac{1}{2}(f_\beta + 2f_{\beta\beta} + f_{\beta\beta}' + f_\gamma + 2f_{\gamma\gamma} + f_{\gamma\gamma}'$ $- 2f_{\beta\gamma} + 4f_{\beta\gamma}' - 2f_{\beta\gamma}'')$	= 2.35
ν_4	271	$F_{44} = f_D$	= 2.23
		$F_{13} = \sqrt{2}(f_{R\beta} - f_{R\gamma})$	= 0.48
		$F_{14} = f_{RD}$	= 0.67
		$F_{34} = \sqrt{2}(f_{D\beta} - f_{D\gamma})$	= −0.30
B_1 ν_5	620	$F_{55} = f_r - 2f_{rr} + f_{rr}'$	= 4.30
ν_6	[470]†	$F_{66} = \frac{1}{2}(f_\beta - 2f_{\beta\beta} + f_{\beta\beta}' + f_\gamma - 2f_{\gamma\gamma} + f_{\gamma\gamma}'$ $- 2f_{\beta\gamma} + 4f_{\beta\gamma}' - 2f_{\beta\gamma}'')$	= 3.16
B_2 ν_7	500	$F_{77} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha}'$	= 1.79
E ν_8	894	$F_{88} = f_r - f_{rr}'$	= 3.74
ν_9	575	$F_{99} = f_\beta - f_{\beta\beta}'$	= 2.62
ν_{10}	418	$F_{1010} = f_\alpha - f_{\alpha\alpha}'$	= 1.90
ν_{11}	222	$F_{1111} = f_\gamma - f_{\gamma\gamma}'$	= 1.26
		$F_{89} = f_{r\beta} - f_{r\beta}''$	= 0.66
		$F_{811} = f_{r\gamma} - f_{r\gamma}''$	= 0.45

* Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch–bend interaction constants in mdyn/radian.
† estimated value.

Table 4. Internal force constants of SF_5Br*†

$f_R = 4.50$
$f_D = 2.23$
$f_r = 4.285$
$f_{rr} = 0.265$
$f_{rr}' = 0.545$
$f_{RD} = 0.67$
$f_\alpha = 1.955$
$f_{\alpha\alpha} = -f_{\alpha\alpha}' = 0.055$
$f_\beta = 3.216$
$f_{\beta\beta} = -0.277$
$f_{\beta\beta}' = 0.596$
$f_\gamma = 1.479$
$f_{\gamma\gamma} = -0.128$
$f_{\gamma\gamma}' = 0.219$
$f_{R\beta} = 0.34$
$f_{D\gamma} = 0.212$
$f_{r\beta} = -f_{r\beta}'' = 0.33$
$f_{r\gamma} = -f_{r\gamma}'' = 0.225$

* Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian², and stretch–bend interaction constants in mdyn/radian.

† Only the values of the stretching force constants can be uniquely determined from the symmetry force constants; for the computation of the remaining constants, the following assumptions were made:

$$f_{\beta\gamma} = f_{\beta\gamma}' = f_{\beta\gamma}'' = f_{R\gamma} = f_{D\beta} = 0, \quad f_{r\beta} = -f_{r\beta}'',$$
$$f_{r\gamma} = -f_{r\gamma}'', \text{ and } \frac{f_\beta}{f_\gamma} = \frac{f_{\beta\beta}}{f_{\gamma\gamma}} = \frac{f_{\beta\beta}'}{f_{\gamma\gamma}'}$$

owing to the underdetermined nature of the force field. However, numerical experiments and comparisons with related molecules (see Table 5) indicate that the listed principal force constants might be expected to be a reasonable approximation of the general valence force field values.

Comparison of the SF_5Br stretching force constants with those of SF_6 [14], SF_5Cl [5, 15], SF_5O^- [8] and SeF_5Cl [4] (see Table 5) shows the expected trends. The SF stretching force constant values decrease in the order: $SF_6 > SF_5Cl > SF_5Br > SF_5O^-$. This may be explained [4] by the decreasing electronegativity from F towards Br and the formal negative charge in SF_5O^- which all tend to release electron density to the remaining fluorine—ligands. This results in an increased polarity ($S^{\delta+}-F^{\delta-}$) of these S—F bonds and, consequently, a lowering of the SF stretching force constants. The stretch–stretch interaction constants also show continuous trends, although it is difficult to rationalize why in SF_6 (for which a GVFF is known [14]) the value of f_{rr}' becomes smaller than that of f_{rr}. Generally, the interaction between linear bonds (f_{rr}') is larger than that between bonds at right angles (f_{rr}).

Table 5. Stretching force constants (in mdyn/Å) of SF_5Br compared to those of SF_5O^-, SF_5Cl, SF_6, SeF_5Cl and SeF_6

	SF_6 [14]	SF_5Cl [15]	SF_5Cl [5]	SF_5Br	SF_5O^- [8]	SeF_6*	SeF_5Cl [4]
f_R	5.26	4.83	4.62	4.50	3.75	5.01	4.42
f_D		2.94	2.75	2.23	6.46		2.75
f_r		4.51	4.59	4.29	3.60		4.31
f_{rr}	0.341	0.30	0.26	0.27	0.54	0.12	0.07
f_{rr}'	0.002	0.47	0.35	0.55	0.75	0.14	0.35
f_{RD}		0.44	0.4	0.67	0.66		

* Abramowitz and I. W. Levin, *Inorg. Chem.*, **6**, 538 (1967).

The potential energy distribution [16] for SF_5Br is given in Table 6. As can be seen, most fundamentals are reasonably characteristic, thus supporting the above assignments. The mixing of the axial SF stretch (ν_1) with the equatorial SF_4 umbrella

Table 6. Potential energy distribution for SF_5Br*

A_1	ν_1	849	$72F_{11}+54F_{33}+11F_{44}-18F_{13}-12F_{14}$
	ν_2	692	$100F_{22}$
	ν_3	591	$36F_{11}+46F_{33}+12F_{13}$
	ν_4	271	$92F_{44}$
B_1	ν_5	620	$100F_{55}$
	ν_6	470	$100F_{66}$
B_2	ν_7	500	$100F_{77}$
E	ν_8	894	$85F_{88}+14F_{99}+19F_{10,10}-14F_{89}$
	ν_9	575	$78F_{99}+11F_{89}$
	ν_{10}	418	$14F_{88}+71F_{10,10}$
	ν_{11}	222	$93F_{11,11}$

* Per cent contributions. Contributions of less than 10% to the PED are not listed.

Table 7. Computed thermodynamic properties of SF_5Br*

T, K	$C_p°$	H°−H°o	−(F°−H°o)/T	S°
0	0	0	0	0
100	9.916	0.844	51.584	60.020
200	15.763	2.121	58.033	68.637
298.15	20.527	3.918	62.744	75.883
300	20.598	3.956	62.825	76.010
400	23.619	6.179	66.938	82.386
500	25.459	8.640	70.590	87.870
600	26.619	11.248	73.875	92.622
700	27.382	13.951	76.857	96.787
800	27.909	16.717	79.583	100.480
900	28.284	19.528	82.092	103.790
1000	28.559	22.371	84.414	106.785
1100	28.767	25.237	86.574	109.517
1200	28.928	28.122	88.592	112.027
1300	29.054	31.022	90.485	114.348
1400	29.155	33.932	92.267	116.505
1500	29.238	36.852	93.951	118.519
1600	29.305	39.779	95.546	120.408
1700	29.362	42.713	97.061	122.187
1800	29.409	45.651	98.504	123.866
1900	29.450	48.594	99.881	125.457
2000	29.484	51.541	101.198	126.969

* Units for $C_p°$, S°, and F° are calories, moles, and degrees Kelvin; for H° units are kilocalories and moles.

deformation (ν_3) is no surprise in view of their similar motions and frequencies.

Thermodynamic properties

The thermodynamic properties of SF_5Br were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation [17]. These properties are given for the range 0–2000 K in Table 7.

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Contribution from Rocketdyne,
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Synthesis and Characterization of $(NF_4)_2TiF_6$ and of Higher NF_4^+ and Cs^+ Poly(perfluorotitanate(IV)) Salts

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Metathesis between Cs_2TiF_6 and NF_4SbF_6 in HF solution was used to prepare the novel perfluoroammonium salt $(NF_4)_2TiF_6$. The compound is a white crystalline solid, stable to about 200 °C. It was characterized by elemental analysis and infrared, Raman, and ^{19}F NMR spectroscopy. X-ray powder data show that the compound (tetragonal, $a = 10.715$ Å, $c = 11.114$ Å) is isotypic with $(NF_4)_2GeF_6$ and $(NF_4)_2SnF_6$. Thermal or HF solution displacement reactions between NF_4BF_4 and TiF_4 produced the polyperfluorotitanate(IV) salts $NF_4Ti_2F_9$ and $NF_4Ti_3F_{13}$. Heating of NF_3, F_2, and TiF_4 to 190 °C at an autogenous pressure of 160 atm produced a salt of the approximate composition $NF_4Ti_6F_{25}$. For comparison, TiF_4 and the salts Cs_2TiF_6, $Cs_2Ti_2F_{10}$, and $CsTi_2F_9$ were synthesized and characterized by vibrational spectroscopy.

Introduction

Although the nonexistence of an NF_5 parent molecule and the high ionization potentials of NF_3 and fluorine made the original synthesis of NF_4^+ salts difficult,[1] their surprisingly high thermal stability permits the syntheses of salts of relatively weak Lewis acids. Thus, the preparation of stable NF_4^+ salts[2,3] containing GeF_5^-, GeF_6^{2-}, SnF_5^-, and SnF_6^{2-} anions has been recently reported. Since NF_4^+ salts are of significant interest for solid propellant NF_3–F_2 gas generators[4] for chemical HF–DF lasers, the synthesis of novel higher performing NF_4^+ salts is desirable. In this paper, we report on the syntheses and properties of NF_4^+ salts derived from TiF_4.

Experimental Section

Materials and Apparatus. The equipment and handling procedures used in this work were identical with those previously described.[2-4] The CsF was fused in a platinum crucible and powdered in the drybox. The NF_3 and F_2 were prepared at Rocketdyne, the HF (Matheson) was dried as previously described,[5] and the BrF_5 (Matheson) was purified by fractional condensation prior to use. Pure NF_4BF_4 was prepared from NF_3, F_2, and BF_3 by uv photolysis[2] at −196 °C and the NF_4SbF_6 was synthesized as previously described.[4] A 10 year old sample of commercial TiF_4 (Allied) had undergone partial hydrolysis but was converted back to pure TiF_4 by fluorinating it in a Monel cylinder for 2 days at 250 °C with F_2 at 70 atm. Both, treated and untreated, samples of TiF_4 were used in the displacement reactions with NF_4BF_4. In some cases the course of the reactions was influenced by the choice of the TiF_4.

Synthesis of Cs_2TiF_6. Dry CsF (40.3 mmol) and TiF_4 (20.15 mmol) were combined in a passivated Teflon FEP ampule. Anhydrous HF (3 ml of liquid) was added at −78 °C. The mixture was warmed to 24 °C and stirred for 1 h until all solid material had dissolved. The volatile materials were pumped off at 70 °C for 2 h. The white solid residue (8.621 g; weight calcd for 20.15 mmol of Cs_2TiF_6 8.619 g) was shown by infrared and Raman spectroscopy to be Cs_2TiF_6 of excellent purity. The products obtained from both untreated and prefluorinated TiF_4 were undistinguishable. The solubility of Cs_2TiF_6 in anhydrous HF at 24 °C was found to be about 4 g/g of HF.

Synthesis of $Cs_2Ti_2F_{10}$. This salt was synthesized from equimolar amounts of Cs_2TiF_6 and prefluorinated TiF_4 either by heating in a Monel cylinder to 180 °C for 7 days or by stirring the mixture in liquid anhydrous HF for 4 days at 25 °C and pumping off the volatile material at 50 °C for 3 h. The observed weights closely corresponded to those expected for $Cs_2Ti_2F_{10}$. Vibrational spectroscopy showed only small amounts of TiF_6^{2-} and $Ti_2F_9^-$ for the product of the thermal reaction and of TiF_4, $Ti_2F_9^-$, TiF_6^{2-}, and a higher polyanion (Raman band at 778 cm^{-1}) for the HF reaction.

Synthesis of $CsTi_2F_9$. This salt was prepared as described above for $Cs_2Ti_2F_{10}$, except for using Cs_2TiF_6 and TiF_4 in a 1:3 mole ratio. Vibrational spectroscopy showed that the product from the HF reaction contained mainly $Ti_2F_9^-$ with traces of TiF_4 and $Ti_2F_{10}^{2-}$ being present. The product from the thermal reaction was a mixture of approximately $4TiF_4$, $4CsTi_2F_9$, and $2Cs_2Ti_2F_{10}$.

Table I. Results from the Displacement Reactions between NF_4BF_4 and TiF_4

Reactants (mol)	Reaction conditions	Products (mol)
NF_4BF_4 (6), untreated TiF_4 (6)	HF, 24 °C, 18 h	$NF_4Ti_2F_9$ (4), NF_4BF_4 (4)
NF_4BF_4 (6), untreated TiF_4 (12)	HF, 24 °C, 72 h	$NF_4Ti_2F_9$ (6)
NF_4BF_4 (6), prefluor TiF_4 (6)	HF, 24 °C, 138 h	$NF_4Ti_3F_{13}$ (~2), NF_4BF_4 (~4), small amt of $NF_4Ti_2F_9$
NF_4BF_4 (6), prefluor TiF_4 (12)	HF, 24 °C, 96 h	$NF_4Ti_3F_{13}$ (4), NF_4BF_4 (2)
NF_4BF_4 (6), untreated TiF_4 (6)	190 °C, 18 h	$NF_4Ti_2F_9$ (~3), NF_3 (~3), BF_3 (~6), small amt of NF_4BF_4 and $NF_4Ti_3F_{13}$
NF_4BF_4 (6), untreated TiF_4 (6)	160 °C, 60 h	$NF_4Ti_3F_{13}$ (2), NF_4BF_4 (1.4), NF_3 (2.6), BF_3 (4.6)
NF_4BF_4 (6), prefluor TiF_4 (6)	170 °C, 20 h	$NF_4Ti_2F_9$ (3), NF_4BF_4 (3), BF_3 (3)
NF_4BF_4 (6), prefluor TiF_4 (12)	170 °C, 20 h	$NF_4Ti_2F_9$ (3.6), $NF_4Ti_3F_{13}$ (1.6), BF_3 (5.4), NF_4BF_4 (0.6)
NF_4BF_4 (6), prefluor TiF_4 (12)	170 °C, 192 h	$NF_4Ti_2F_9$ (6), BF_3 (6)

The synthesis of higher polyperfluorotitanate(IV) anions was attempted by heating a 1:5 mole ratio mixture of Cs_2TiF_6 and TiF_4 to 180 °C for 7 days. Vibrational spectroscopy, however, showed the presence of only $Ti_2F_{10}^{2-}$, $Ti_2F_9^-$, and unreacted TiF_4.

Synthesis of $(NF_4)_2TiF_6$. The metathetical synthesis of $(NF_4)_2TiF_6$ from saturated HF solutions of NF_4SbF_6 (10.00 mmol) and Cs_2TiF_6 (5.00 mmol) was carried out in the apparatus previously described[3] for the synthesis of $(NF_4)_2SnF_6$. After combination of the solutions of the two starting materials at room temperature and formation of a $CsSbF_6$ precipitate, the mixture was cooled to 78 °C and filtered. The volatile materials were pumped off at 50 °C for 1 hr. The filter cake (3.85 g) was shown by its x-ray powder diffraction pattern and vibrational spectroscopy to be mainly $CsSbF_6$ containing, due to the hold up of some mother liquid, a small amount of $(NF_4)_2TiF_6$. The filtrate residue (1.55 g; weight calcd for 5 mmol of $(NF_4)_2TiF_6$ 1 71 g) had the following composition (mol %): $(NF_4)_2TiF_6$, 88.5; $CsSbF_6$, 11.5. Found: NF_3, 36.3; Ti, 12.21; Sb, 4.11; Cs, 4.4. Calcd for a mixture of 88.5% $(NF_4)_2TiF_6$ and 11.5% $CsSbF_6$: NF_3, 36.43; Ti, 12.29; Sb, 4.06; Cs, 4.43. Based on the observed Raman spectrum, the composition of the filtrate residue was estimated to be 90% $(NF_4)_2TiF_6$ and 10% $CsSbF_6$, in good agreement with the above elemental analysis.

Displacement Reactions between NF_4BF_4 and TiF_4. These displacement reactions were carried out either in HF solution at room temperature or by heating the starting materials in the absence of a solvent in a Monel cylinder. For the HF solution reactions, the solid starting materials (6 mmol of NF_4BF_4 in each experiment) were placed in a passivated Teflon FEP ampule and 15 ml of liquid anhydrous HF was added. The mixture was stirred with a Teflon-coated magnetic stirring bar at room temperature for a given time period. The volatile products were pumped off at 50 °C for 3 h and the composition of the solid residue was determined by elemental and spectroscopic analyses and from the observed material balances.

The thermal displacement reactions were carried out in a prepassivated 90-ml Monel cylinder which was heated in an electric oven for a specified time period. The volatile products were separated by fractional condensation in a vacuum line, measured by *PVT*, and identified by infrared spectroscopy. The solid residues were weighed and characterized by elemental and spectroscopic analyses. The results of these experiments are summarized in Table I.

Direct Synthesis of NF_4^+ Poly(perfluorotitanates(IV)). Prefluorinated TiF_4 (11.3 mmol), NF_3 (200 mmol), and F_2 (200 mmol) were heated in a passivated 90-ml Monel cylinder to various temperatures for different time periods. After each heating cycle, the volatile products were temporarily removed and the progress of the reaction was followed by determining the weight gain of the solid and recording its vibrational spectra. Heating to 200 °C for 3 days resulted in a weight gain of 8 mg and the vibrational spectra showed mainly unreacted TiF_4 in addition to a small amount of NF_4^+ and a poly(perfluorotitanate(IV)) anion (probably $Ti_6F_{25}^-$; see below) having its strongest Raman line at 784 cm^{-1}. During the next two heating cycles (190–195 °C for 14 days and 180 °C for 35 days) the solid gained 149 and 41 mg, respectively. The vibrational spectra did not show any evidence of unreacted TiF_4, and the relative intensities of the bands due to NF_4^+ had significantly increased. Furthermore, the 784-cm^{-1} Raman line had become by far the most intense Raman line. Additional heating to 230 °C for 3 days did not result in significant changes in either the weight or the vibrational spectra of the solid. On the basis of the observed weight increase and the lack of spectroscopic evidence for the presence of lower poly(perfluorotitanate(IV)) anions, the solid product appears to have the approximate composition $NF_4Ti_6F_{25}$ (calcd weight increase 205 mg; obsd weight increase 198 mg).

Results and Discussion

Syntheses of NF_4^+ Salts. Perfluoroammonium salts of TiF_4 were prepared by the following methods.

(1) **Metathesis:**

$$Cs_2TiF_6 + 2NF_4SbF_6 \xrightarrow{\text{HF soln}} 2CsSbF_6\downarrow + (NF_4)_2TiF_6$$

The yield of $(NF_4)_2TiF_6$ in this reaction is practically quantitative, except for material losses caused by the retention of a certain amount of mother liquor by the filter cake. The purity of the material obtained in this manner was approximately 88.5 mol %, the remainder being $CsSbF_6$.

(2) **Direct Synthesis from NF_3, F_2, and TiF_4:**

$$NF_3 + F_2 + 6TiF_4 \xrightarrow[\text{160 atm}]{\text{190 °C}} NF_4Ti_6F_{25}$$

Heating of TiF_4 with a large excess of NF_3 and F_2 to 180–195 °C for 50 days under an autogenous pressure of about 160 atm produced a solid of the approximate composition $NF_4Ti_6F_{25}$. Significant increases or decreases of the reaction temperature resulted in lower conversions of NF_3 to NF_4^+.

(3) **Displacement Reactions:**

$$NF_4BF_4 + nTiF_4 \rightarrow NF_4TiF_5\cdot(n-1)TiF_4 + BF_3$$

These reactions were carried out either in anhydrous HF solution at room temperature or by heating the solid starting materials in a Monel cylinder to 160–190 °C. The composition of the products was influenced by both the reaction conditions and the choice of the TiF_4 starting material (see Table I). For the HF solution displacement reactions, the use of prefluorinated TiF_4 (see below) resulted in the following approximate stoichiometry, independent of the mole ratio of the starting materials

$$NF_4BF_4 + 3TiF_4 \xrightarrow{\text{HF, 24 °C}} NF_4Ti_3F_{13} + BF_3$$

When untreated TiF_4 was used, the reaction stoichiometry changed from 1:3 to 1:2, again independent of the mole ratio of the starting materials

$$NF_4BF_4 + 2TiF_4 \xrightarrow{\text{HF, 24 °C}} NF_4Ti_2F_9 + BF_3$$

In the thermal displacement reactions, the use of prefluorinated TiF_4 at 170 °C resulted in a clean 1:2 reaction between NF_4BF_4 and TiF_4 according to

$$NF_4BF_4 + 2TiF_4 \xrightarrow{\text{170 °C}} NF_4Ti_2F_9 + BF_3$$

When an excess of NF_4BF_4 was used, the reaction was complete in 20 h, producing a mixture of $NF_4Ti_2F_9$ and unreacted NF_4BF_4. When we used a 1:2 mole ratio of NF_4BF_4 and TiF_4, however, longer heating periods were required to avoid the formation of some $NF_4Ti_3F_{13}$ as a by-product.

With untreated TiF_4, some of the NF_4^+ salt was used up for the fluorination of the partially hydrolyzed TiF_4; however, the main product formed at 190 °C was again $NF_4Ti_2F_9$. When the reaction temperature was lowered to 160 °C, the main product was $NF_4Ti_3F_{13}$.

The above results are not surprising in view of our present understanding of NF_4^+ chemistry. It appears that the nature of the Lewis acid determines the possible synthetic routes toward their NF_4^+ salts. If a sufficiently strong Lewis acid is monomeric at the reaction temperature, a direct synthesis from NF_3, F_2, and the Lewis acid is possible. The initial step in this direct synthesis is the generation of F atoms[1] from F_2 by either discharge,[6,7] radiation,[1,2,8] or heating.[4,9] These F atoms then react with the monomeric Lewis acid to form a Lewis acid–F· radical,[10] a species which might be capable[1,11] of supplying the energy (ionization potential of NF_3 minus the energy released by the formation of the ion pair) required for the oxidation of NF_3 to NF_3^+. The latter cation can then be readily fluorinated by either F· or F_2 to NF_4^+. A typical example for this scheme is the low-temperature UV photolysis of the NF_3–F_2–BF_3 system[1,2,10]

$$F_2 \xrightarrow{h\nu} 2F\cdot$$

$$F\cdot + BF_3 \rightarrow BF_4\cdot$$

$$BF_4\cdot + NF_3 \rightarrow NF_3^+BF_4^-$$

$$NF_3^+BF_4^- + F \rightarrow NF_4^+BF_4^-$$

On the other hand, if the Lewis acid is polymeric at temperatures above the thermal decomposition point of its NF_4^+ salt, indirect synthetic methods must be used. A typical example is SnF_4 (sublimation point 704 °C), where metathesis

$$Cs_2SnF_6 + 2NF_4SbF_6 \xrightarrow{\text{HF soln}} 2CsSbF_6\downarrow + (NF_4)_2SnF_6$$

and the displacement reaction

$$2NF_4BF_4 + 2SnF_4 \xrightarrow{\text{HF soln}} (NF_4)_2Sn_2F_{10} + 2BF_3$$

have successfully been applied[3] to the syntheses of its NF_4^+ salts.

The physical properties of TiF_4 (polymeric solid at room temperature with a vapor pressure of 1 atm at 284 °C) are intermediate between those of BF_3 (bp −101 °C) or GeF_4 (1 atm vapor pressure at −36 °C) and SnF_4 (bp 705 °C). Consequently, the successful, although slow, direct thermal synthesis of an NF_4^+ salt of TiF_4 and the pronounced tendency of TiF_4 to form polyanions are not unexpected. However, the actual composition of the polyanions was surprising. Whereas both GeF_4 and SnF_4 in their displacement reactions[2,3] with NF_4BF_4 form exclusively the $Ge_2F_{10}^{2-}$ and $Sn_2F_{10}^{2-}$ anions, respectively, no evidence was obtained for the formation of $Ti_2F_{10}^{2-}$ in the corresponding reactions of TiF_4. Instead, only the polymeric anions $Ti_2F_9^-$ and $Ti_3F_{11}^-$ were observed. Since TiF_6^{2-} is known[12] to associate with TiF_5^- or TiF_4 to form $Ti_2F_{11}^{3-}$ and $Ti_2F_{10}^{2-}$, respectively, the failure to observe the two latter anions in the NF_4BF_4–TiF_4 displacement reactions suggests that TiF_6^{2-} is not formed as an intermediate in appreciable quantities. Furthermore, the absence of observable amounts of $Ti_2F_{10}^{2-}$ indicates either that TiF_5^- preferentially associates with TiF_4 rather than with itself or that the smallest TiF_4 units present which will accept a fluoride ion are dimers. Unfortunately, the structures both of solid TiF_4 and of the species present in its HF solutions are unknown. Consequently, it is at present inappropriate to rationalize the different behavior of TiF_4 and of the two main-group tetrafluorides.

The fact that the displacement reaction in HF solution resulted for untreated TiF_4 in a lower polyanion ($Ti_2F_9^-$) than for prefluorinated TiF_4, is consistent with previous reports[13] on the solubility of TiF_4 in HF. Thus TiF_4 is only sparingly soluble in anhydrous HF, but its solubility is significantly increased by the addition of a Lewis base, such as an alkali metal fluoride or water. Apparently, the base, i.e., F^- ions, helps to depolymerize the TiF_4. Since the untreated TiF_4 was partially hydrolyzed, it probably generated upon addition to the HF solution some H_2O, which in the presence of HF and TiF_4 would be protonated to yield OH_3^+ and a polytitanate anion. No chemical interaction between OH_3^+ and NF_4^+ is expected, since it has previously been demonstrated that $OH_3^+SbF_6^-$ and $NF_4^+SbF_6^-$ can coexist in HF solution.[14]

A previous study[13] on the relative strength of fluoro acids in HF solution had placed BF_3, SnF_4, and TiF_4 in categories 2, 3, and 5, respectively, where the acid strength decreased with increasing category number. The results from our studies, i.e., the fact that both SnF_4 and TiF_4 are capable of quantitatively displacing BF_4^- from NF_4BF_4 in HF solution, indicate that this acid classification is not generally valid.

Syntheses of Cs Salts. For the characterization of the poly(perfluorotitanate(IV)) anions in their NF_4^+ salts, a better knowledge of these anions was required. Very little information on poly(perfluorotitanate(IV)) has previously been published. Except for a recent DSC study on $NOTiF_5$, which was shown to decompose at 225 °C to $NOTi_2F_9$ and FNO,[15] the only detailed study on poly(perfluorotitanates) was carried out by Dean.[12] Studying the TiF_4–$(Pr_2NH_2)_2TiF_6$ system in SO_2 solution by ^{19}F NMR spectroscopy, he established the presence of the $Ti_2F_{11}^{3-}$, $Ti_2F_{10}^{2-}$, and $Ti_2F_9^-$ anions, in addition to other unidentified polymeric anions.

Our study in anhydrous HF as a solvent showed that pure Cs_2TiF_6 is formed from stoichiometric amounts of CsF and either untreated or prefluorinated TiF_4

$$2CsF + TiF_4 \xrightarrow{\text{HF}} Cs_2TiF_6$$

The compound $Cs_2Ti_2F_{10}$ can be produced from an equimolar mixture of Cs_2TiF_6 and TiF_4 by either HF treatment at room temperature or heating of the solids to 180 °C

$$Cs_2TiF_6 + TiF_4 \xrightarrow[\text{HF, 25 °C}]{\text{180 °C or}} Cs_2Ti_2F_{10}$$

Vibrational spectroscopy showed only traces of TiF_4, TiF_6^{2-}, and $Ti_2F_9^-$, indicating that under these conditions $Ti_2F_{10}^{2-}$ is clearly the favored species.

When the mole ratio of Cs_2TiF_6 to TiF_4 was changed to 1:3, the reaction in HF solution produced almost exclusively $Ti_2F_9^-$ according to

$$Cs_2TiF_6 + 3TiF_4 \xrightarrow{\text{HF, 25 °C}} 2CsTi_2F_9$$

Only traces of TiF_4 and $Ti_2F_{10}^{2-}$ were present. The thermal reaction, however, produced a mixture of approximately $4TiF_4$, $4CsTi_2F_9$, and $2Cs_2Ti_2F_{10}$.

A further increase of the TiF_4 ratio in the thermal reactions did not produce any evidence for the formation of polyanions higher than $Ti_2F_9^-$ but resulted in unreacted TiF_4. The HF solution study was not extended beyond the 1:3 Cs_2TiF_6:TiF_4 mole ratio.

Properties. The most interesting one of the novel salts prepared during this study is $(NF_4)_2TiF_6$, since it has the highest usable fluorine content of any presently known NF_4^+ salt. All the NF_4^+ perfluorotitanates(IV) are white crystalline solids. Based on observations of their thermal decompositions in sealed glass capillaries and on the results of the direct thermal synthesis and of the thermal displacement reactions, these NF_4^+ salts are stable to at least 200°. By analogy with the other known NF_4^+ salts, it is difficult to obtain meaningful decomposition temperatures from either melting point determinations or DSC data.[2,3] All salts are hygroscopic and hydrolyze in water with quantitative NF_3 and less than quantitative O_2 evolution, in agreement with previous findings.[2] The hydrolysate shows the yellow color characteristic for titanyl salts. The $(NF_4)_2TiF_6$ salt is highly soluble in HF and moderately soluble in BrF_5. For the polyanion salts, the

Table II. X-Ray Powder Data for $(NF_4)_2TiF_6$[a]

d_{obsd}	d_{calcd}	Intens	*hkl*
6.23	6.26	vw	111
5.57	5.56	vs	002
4.93	4.93	w	102
3.49	3.50	s	103
3.39	3.39	s	310
2.94	2.93	ms	213
2.782	2.778	m	004
2.465	2.463	w	331
2.315	2.318	mw	323
2.201	2.200	s	422
2.100	2.101	w	510
1.990	1.990	vw	520 502
1.892	1.894	m	440
1.789	1.789	mw	600 442
1.663	1.664	mw	226
1.641	1.644	mw	306

[a] Tetragonal; $a = 10.715$ A, $c = 11.114$ A; Cu Kα radiation; Ni filter.

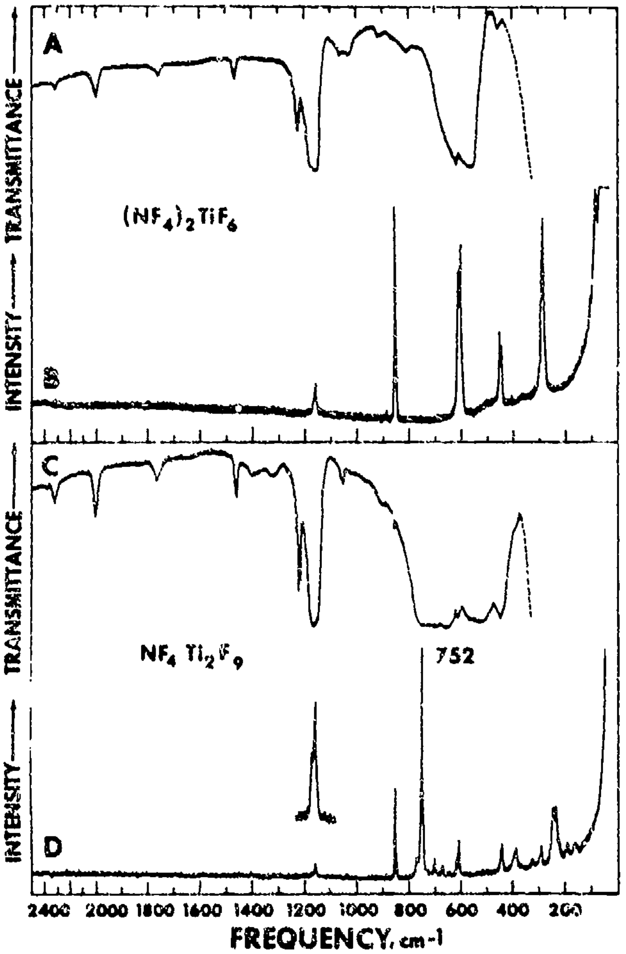


Figure 1. Vibrational spectra of solid $(NF_4)_2TiF_6$ and $NF_4Ti_2F_9$: traces A and B, infrared and Raman spectra of $(NF_4)_2TiF_6$, respectively; traces C and D, corresponding spectra of $NF_4Ti_2F_9$, prepared by the thermal (170 °C) displacement reaction between NF_4BF_4 and TiF_4 (1:2). The absorptions below 400 cm^{-1} in the infrared spectra (broken lines) are due to the AgCl windows. Weak bands, due to impurities, were deleted from the spectra. Raman spectra were recorded with a spectral slit width of 3 cm^{-1}. The insert was recorded at a higher recorder gain.

solubility decreases with increasing anion size.

The Cs^+ salts are also stable, white, crystallinic solids. The Cs_2TiF_6 salt is very soluble in HF (about 4 g/g of HF), but the solubility sharply decreases for the polyanion salts. The hydrolysis of the cesium poly(perfluorotitanates(IV)) was followed by Raman spectroscopy. The spectra obtained for the solid phase in equilibrium with the aqueous phase showed that the bands due to TiF_4 and the higher polyanion impurities disappeared first, accompanied by a simultaneous growth of the TiF_6^{2-} bands. The aqueous phase showed TiF_6^{2-} as the main constituent.

Table III. Crystallographic Data of $(NF_4)_2TiF_6$ Compared to Those of Other NF_4^+ Salts

	Tetragonal unit cell dimensions					
	a, A	*c*, A	*V*, A^3	*Z*	Vol/F, A^3	Calcd density, g/cm^3
NF_4PF_6[a]	7.577	5.653	324.53	2	16.23	2.41
NF_4AsF_6[b]	7.70	5.73	339.73	2	16.99	2.72
NF_4SbF_6[c]	7.903	5.806	362.63	2	18.13	2.98
NF_4BiF_6[c]	8.006	5.821	373.10	2	18.66	3.68
NF_4BF_4[a]	9.944	5.229	517.04	4	16.16	2.27
$(NF_4)_2GeF_6$[a]	10.627	11.114	1255.14	$^{16}/_3$	16.81	2.59
$(NF_4)_2SnF_6$[d]	10.828	11.406	1337.35	$^{16}/_3$	17.91	2.73
$(NF_4)_2TiF_6$	10.715	11.114	1276.01	$^{16}/_3$	17.09	2.37

[a] Reference 2. [b] Reference 6. [c] Reference 4. [d] Reference 3.

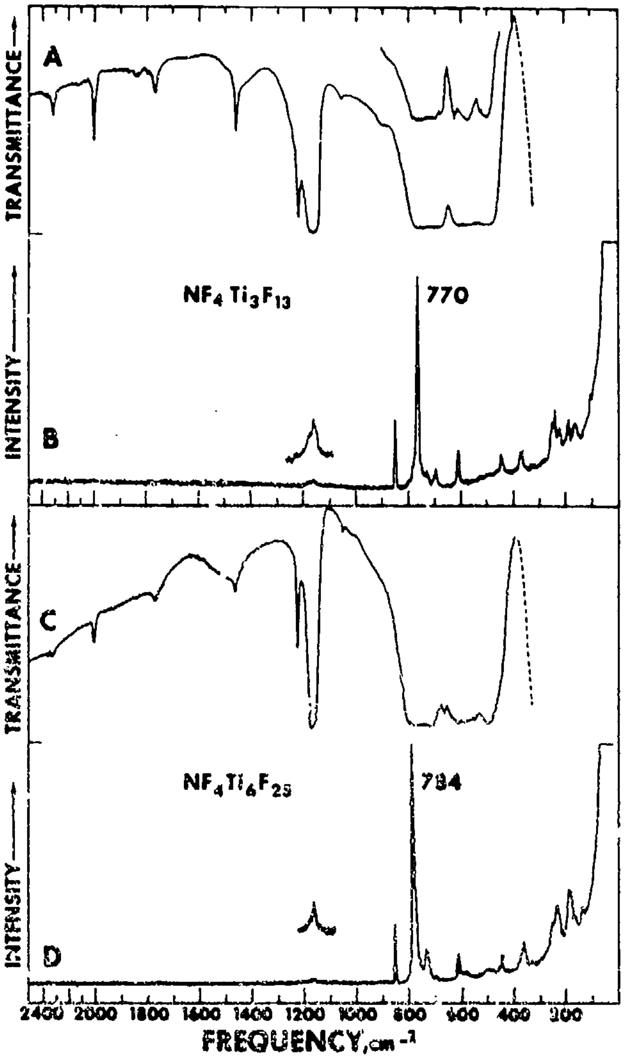


Figure 2. Vibrational spectra of solid $NF_4Ti_3F_{13}$ and $NF_4Ti_6F_{25}$, recorded under the same conditions as those of Figure 1. The samples of $NF_4Ti_3F_{13}$ and $NF_4Ti_6F_{25}$ were prepared by the displacement reaction between NF_4BF_4 and prefluorinated TiF_4 in HF and by direct synthesis from NF_3, F_2, and TiF_4 at 190 °C, respectively.

Table IV. Vibrational Spectra of Solid $(NF_4)_2TiF_6$ Compared to Those of Cs_2TiF_6

Obsd freq (cm^{-1}) and rel intens[a]				Assignments (point group)	
$(NF_4)_2TiF_6$		Cs_2TiF_6			
IR	Raman	IR	Raman	NF_4^+ (T_d)	TiF_6^{2-} (O_h)[b]
2340 sh				$2\nu_3$ ($A_1 + E + F_2$)	
2320 vw					
2003 w				$\nu_1 + \nu_3$ (F_2)	
1780 sh				$\nu_3 + \nu_4$ ($A_1 + E + F_2$)	
1760 vw					
1463 w				$\nu_1 + \nu_4$ (F_2)	
1219 mw				$2\nu_4$ ($A_1 + E + F_2$)	
1160 vs	1158 (1.4)			ν_3 (F_2)	
1132 sh, vw					
1060 vw				$\nu_2 + \nu_4$ ($F_1 + F_2$)	
1021 w					
910 vw					$\nu_1 + \nu_4$ (F_{1u})
	883 (0.1)			$2\nu_2$ ($A_1 + A_2 + E$)	
850 sh, vw	853 (10)			ν_1 (A_1)	
804 w					
611 mw	612 (5)			ν_4 (F_2)	
	607 sh				
	601 (8.0)		599 (10)		ν_1 (A_{1g})
563 vs		562 vs			ν_3 (F_{1u})
452 vw	450 (3.3)			ν_2 (E)	
	442 (2.6)				
	289 (8.2)		284 (9.8)		ν_5 (F_{2g})
	107 (0+)		84 (1.2)	Lattice vib	
	86 (2)		68 (3.2)		
			56 (1.7)		

[a] Uncorrected Raman intensities. [b] The site symmetry of TiF_6^{2-} in Cs_2TiF_6 is D_{3d}, but for simplicity and in view of the unknown site symmetry of TiF_6^{2-} in $(NF_4)_2TiF_6$, the assignments for TiF_6^{2-} were made for the point group (O_h) of the free ion.

Table V. Vibrational Spectra of Solid $CsTi_2F_9$, $NF_4Ti_2F_9$, $NF_4Ti_3F_{13}$, and $NF_4Ti_6F_{25}$

Obsd freq (cm^{-1}) and rel intens[a]								Assignments for NF_4^+ in point group T_d
$CsTi_2F_9$		$NF_4Ti_2F_9$		$NF_4Ti_3F_{13}$		$NF_4Ti_6F_{25}$		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
				2360 sh		2350 sh		$2\nu_3$ ($A_1 + E + F_2$)
		2320 vw		2320 vw		2320 vw		
		2004 w		2002 w		2002 w		$\nu_1 + \nu_3$ (F_2)
		1765 vw		1766 vw		1768 vw		$\nu_3 + \nu_4$ ($A_1 + E + F_2$)
		1458 w		1458 w		1457 w		$\nu_1 + \nu_4$ (F_2)
		1400 vw						
		1322 vw						
		1223 vw		1220 mw		1220 mw		$2\nu_4$ ($A_1 + E + F_2$)
		1216 w						
		1164 vs	1169 (0.2)	1166 vs	1175 sh	1165 vw	1165 (0.1)	ν_3 (F_2)
			1158 (0.5)		1160 (0.2)			
		1054 vw		1055 vw		1051 vw		$\nu_2 + \nu_4$ ($F_1 + F_2$)
		904 vw		905 sh				
		853 vw	851 (3.8)		851 (3.2)		851 (2.4)	ν_1 (A_1)
725 vs, br	752 (10)	725 vs, br	752 (10)	760 vs, br	770 (10)	765 vs	784 (10)	
	701 (0.7)		702 (0.7)		731 (0.3)		735 (1.2)	
650 vs	670 (0.4)	650 vs	670 (0.5)	702 vs		712 vs		
	645 (0+)		645 (0+)		696 (0.8)		698 (0.1)	
				675 s		661 s		
		615 s	615 (0.5)	615 s	611 (1.6)	610 s	611 (0.9)	ν_4 (F_2)
		608 s	608 (1.6)					
530 vs, br		530 vs, br		578 vs		585 vs	588 (0+)	
446 vs		446 vs		502 vs		492 vs	500 (0+)	
			444 (0.5)		446 (0.9)		445 (0.7)	ν_2 (E)
			439 (1.1)					
390 sh	388 (0.9)	390 sh	389 (0.9)		371 (1.0)		363 (1.0)	
	327 (0.3)		326 (0.3)		252 (0.5)		251 sh	
	290 (0.8)		290 (0.9)		241 (2.0)		242 (1.5)	
	247 (2.4)		247 (2.4)		223 (0.5)		223 sh	
	238 (2.4)		237 (2.4)		190 (1.0)		188 (1.7)	
	225 sh		225 sh		168 (0.8)		165 sh	
	192 (0.5)		192 (0.5)				139 (0.4)	
	162 (0.4)		162 (0.4)					

[a] Uncorrected Raman intensities.

X-Ray Powder Data. The powder pattern of $(NF_4)_2TiF_6$ is listed in Table II. After correction for weak lines due to $CsSbF_6$ and NF_4SbF_6, all observed lines could be indexed for a tetragonal unit cell. The resulting crystallographic parameters are compared in Table III to those of similar NF_4^+ salts. The similarity of the patterns of $(NF_4)_2TiF_6$, (N-

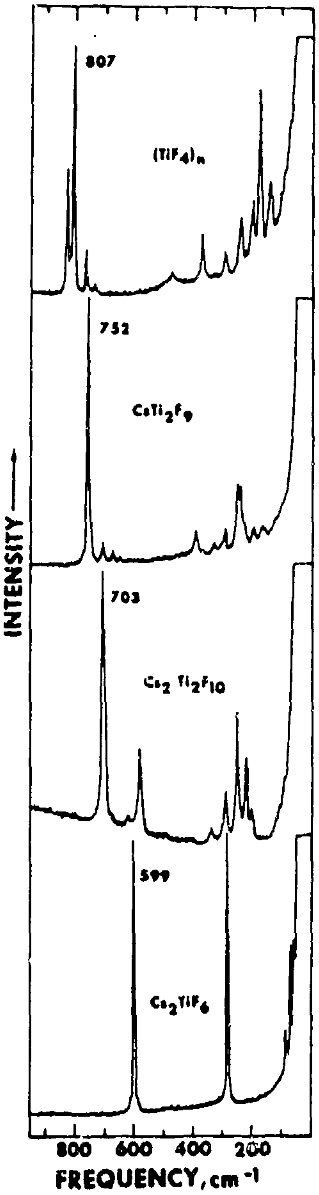


Figure 3. Raman spectra of solid Cs_2TiF_6, $Cs_2Ti_2F_{10}$, $CsTi_2F_9$, and prefluorinated TiF_4.

$F_4)_2SnF_6$,[3] and $(NF_4)_2GeF_6$[2] indicates that the three compounds are isotypic.

NMR Spectra. Since in HF solution rapid exchange between the solvent and the anion prevents observation of well-resolved anion spectra, the ^{19}F NMR spectrum of $(NF_4)_2TiF_6$ was recorded in BrF_5 solution. In addition to the solvent lines,[2] the spectrum showed the characteristic[9,16] triplet (ϕ −220.8, J_{NF} = 229 Hz) for NF_4^+ and the characteristic[12,17] TiF_6^{2-} signal at ϕ −81.7. The solubility of the NF_4^+ polytitanate salts in BrF_5 was too low to permit the observation of useful spectra. Since the ^{19}F NMR spectra of $Ti_2F_{11}^{3-}$, $Ti_2F_{10}^{2-}$, and $Ti_2F_9^-$ in SO_2 solution have previously been studied and assigned in detail by Dean,[12] no further work in this direction was undertaken.

Vibrational Spectra. The infrared and Raman spectrum of solid $(NF_4)_2TiF_6$ is shown in Figure 1. The observed frequencies are listed in Table IV. Comparison with the previously reported[2,4,8,16,18] spectra of other NF_4^+ salts demonstrates beyond doubt the presence of the NF_4^+ cation. The remaining bands are due to the anion and are in excellent agreement with those previously reported for TiF_6^{2-} in

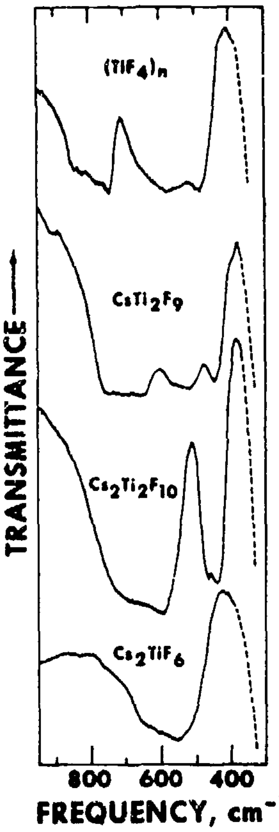


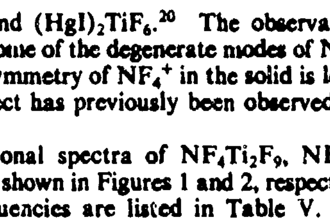
Figure 4. Infrared spectra of solid Cs_2TiF_6, $Cs_2Ti_2F_{10}$, $CsTi_2F_9$, and prefluorinated TiF_4 as dry powders in AgCl disks.

Cs_2TiF_6[17,19] and $(HgI)_2TiF_6$.[20] The observation of small splittings for some of the degenerate modes of NF_4^+ indicates that the site symmetry of NF_4^+ in the solid is lower than T_d. The same effect has previously been observed[3] for isotypic $(NF_4)_2SnF_6$.

The vibrational spectra of $NF_4Ti_2F_9$, $NF_4Ti_3F_{13}$, and $NF_4Ti_6F_{25}$ are shown in Figures 1 and 2, respectively, and the observed frequencies are listed in Table V. Again, the presence of NF_4^+ is clearly established.

For a better characterization of the anion bands, the vibrational spectra of several cesium salts and of solid TiF_4 were also recorded (see Figures 3 and 4, and Tables IV–VI). Since Cs_2TiF_6 can be prepared in high purity and since higher polytitanate impurities preferentially underwent hydrolysis, no problems were encountered with defining the principal bands belonging to each anion. The single most useful band for the identification of a poly(perfluorotitanate(IV)) anion is the symmetric, in-phase, terminal TiF stretching mode. This mode results in a narrow and very intense Raman band, the frequencies of which have been denoted in Figures 1–3. As can be seen, the frequency of this band increases with increasing TiF_4 content and decreasing negative charge of the anion, i.e., $TiF_6^{2-} < Ti_2F_{10}^{2-} < Ti_2F_9^- < Ti_3F_{13}^- < Ti_6F_{25}^- < (TiF_4)_n$.

The structure of $Ti_2F_{10}^{2-}$ (I) has been established[12] by ^{19}F



I

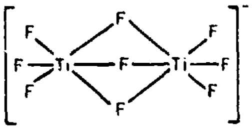
NMR spectroscopy as the cis fluorine-bridged dimer and a

Table VI. Vibrational Spectra of Solid $Cs_2Ti_2F_{10}$ and Prefluorinated TiF_4

$Cs_2Ti_2F_{10}$			TiF_4	
Obsd freq (cm^{-1}) and rel intens[a]		Assignments[b] for point group D_{2h}	Obsd freq and rel intens[a]	
IR	Raman		IR	Raman
	703 (10)	ν_1 (A_g)		829 (5.0)
		ν_{17} (B_{2g})		817 (0.4)
	620 (0.2)	ν_9 (B_{1g})	840–730 vs, br	807 (10)
	577 (3)	ν_2 (A_g)		761 (1.7)
		ν_{13} (B_{1u})		731 (0.4)
		ν_{24} (B_{3u})	580 vs, br	
730–600 vs, br		ν_{20} (B_{2u})	481 vs	
		ν_{27} (B_{3u})		471 (0.5)
468 m		ν_{28} (B_{3u})		370 (1.7)
441 s		ν_{21} (B_{2u})		291 (0.9)
	335 (0.5)	ν_{18} (B_{2g})		239 (1.8)
		ν_{11} (B_{1g})		221 (0+)
	284 (1.7)	ν_4 (Ag)		201 (2.0)
	248 (4.8)	ν_{14} (B_{3g})		179 (6.1)
	218 (2.8)	ν_5 (Ag)		140 (2.0)
	199 (0.8)	ν_{12} (B_{1g})		99 (0+)
				87 (0+)
				70 (0+)

[a] Uncorrected Raman intensities. [b] Using the symmetry coordinates of ref 21.

thorough vibrational analysis has previously been carried[21,22] out for the isostructural molecule Nb_2Cl_{10}. Consequently, sufficient information was available to allow some tentative assignments for $Ti_2F_{10}^{2-}$. These assignments are summarized in Table VI and are based on the symmetry coordinates defined for Nb_2Cl_{10} by Beattie and co-workers.[21] No attempts were made to assign the spectra of the remaining poly(perfluorotitanate(IV)) anions and TiF_4 itself, although some data are available for $Ti_2F_9^-$. Dean suggested[12] on the basis of ^{19}F NMR data for $Ti_2F_9^-$ the triply fluorine-bridged structure II



II

and Beattie has analyzed[21] the vibrational spectrum of the isostructural $Tl_2Cl_9^{3-}$ anion. Our spectra of prefluorinated TiF_4 (see Figures 3 and 4) significantly differ from those of untreated TiF_4 and those[23-25] previously reported in the literature.

Summary

The synthesis of NF_4^+ salts has successfully been extended to a subgroup element. The results of this study show that TiF_4 can act as a much stronger Lewis acid than predicted on the basis of previous literature data.[13] Thus, stable NF_4^+ salts derived from TiF_4 can be prepared either directly or indirectly. Of all the presently known NF_4^+ salts, $(NF_4)_2TiF_6$ contains the highest percentage of usable fluorine.

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Registry No. $(NF_4)_2TiF_6$, 61128-92-5; Cs_2TiF_6, 16919-28-1; $CsTi_2F_9$, 61128-93-6; $NF_4Ti_2F_9$, 61128-94-7; $NF_4Ti_3F_{13}$, 61267-52-5; $NF_4Ti_6F_{25}$, 61303-83-1; $Cs_2Ti_2F_{10}$, 61128-95-8; NF_4BF_4, 15640-93-1; CsF, 13400-13-0; TiF_4, 7783-63-3; NF_3, 7783-54-2; F_2, 7782-41-4.

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Vibrational spectra of thionyl tetrafluoride, SF_4O

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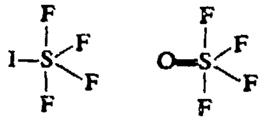
Abstract—The i.r. spectra of gaseous, solid, and matrix-isolated SF_4O and the Raman spectra of gaseous, liquid and solid SF_4O are reported. It is shown that several bands previously attributed to SF_4O belong to impurities, and 8 of the 12 fundamentals of SF_4O were reassigned. A normal coordinate analysis was carried out and indicates for SF_4O a structural model with significantly longer axial than equatorial S—F bonds, in disagreement with Gundersen and Hedberg's favored Model *A*. Thermodynamic properties are also reported for SF_4O.

INTRODUCTION

During a study of the vibrational spectra of SF_4 [1], we became also interested in those of SF_4O. The molecular structures of these two molecules [2–6] are closely related and can both be derived from a trigonal bipyramid. The main difference between them is that in SF_4 one of the equatorial positions is occupied by a sterically active free valence electron pair, whereas in SF_4O it is occupied by a doubly bonded oxygen atom.



A closer examination of the available literature data [7–9] on the vibrational spectra of SF_4O revealed many discrepancies and indicated the need for a thorough reinvestigation. Our experimental data, which are reported in this paper, showed that several bands, previously attributed [7–9] to SF_4O, actually belong to impurities, and resulted in the reassignment of 8 of the 12 fundamentals of SF_4O.

EXPERIMENTAL

Pure SF_4O was prepared by vacuum pyrolysis of $CsSF_5O$ [10]. The complexing of crude SF_4O with CsF [10] was found necessary in order to completely remove any SO_2F_2 present. The latter does not form a stable adduct with CsF and can therefore be readily removed from $CsSF_5O$ by pumping.

Volatile compounds were manipulated in a well passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves.

The i.r. spectra were recorded on a Perkin–Elmer Model 457 spectrophotometer in the range of 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard gas calibration points [11]. The gas cells were made of stainless steel with path lengths of either 5 or 10 cm. The windows were made of either AgCl, AgBr, or high density polyethylene seasoned by ClF_3. The apparatus, materials, and technique used for the matrix-isolation study have previously been described [12, 13].

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å exciting line. A Claassen filter was used to eliminate plasma lines [14]. Polarization measurements were carried out by method VIII as described by Claassen *et al.* [14]. For the low-temperature spectra an apparatus was used similar to that described by Miller and Harney [15]. A stainless steel cell with Teflon O-rings and sapphire windows [16] was used to obtain the spectrum of the gas. The sample containers for liquid and solid SF_4O were either 3 mm o.d. quartz tubes or Teflon–FEP capillaries used in the transverse excitation-transverse viewing mode.

The ^{19}F NMR spectra were recorded at 56.4 MHz on a Varian Model DA-60 high resolution NMR spectrometer, equipped with a variable temperature probe. Chemical shifts were determined by the side-band technique relative to the external standard $CFCl_3$. Teflon FEP tubes (Wilmad Glass Co.) were used as sample containers. Samples of neat SF_4O, of SF_4O over NaF (for removal of any HF possibly present), and of SF_4O–$FClO_3$ mixtures (1:3 mole ratio) over NaF showed only a single signal for SF_4O over the entire liquid range (mp of $FClO_3$ –147.75°C).

RESULTS AND DISCUSSION

Vibrational spectra. Figure 1 shows the i.r. spectra of gaseous, solid and N_2-matrix-isolated SF_4O. Figure 2 shows the Raman spectra of gaseous, liquid, and solid SF_4O. For the liquid phase, some variation in the spectra was observed. The spectra generally observed over a fairly wide temperature range are shown by traces *D–F* in Fig. 2. During one occasion, however, a spectrum was observed at −80°C which more closely resembled that of gaseous SF_4O. It is shown as trace *G* in Fig. 2. Attempts to reproduce the spectrum with the same or other samples were unsuccessful, and the reason for its deviation could not be established. Figure 3 shows the most intense i.r. bands of gaseous and matrix-isolated SF_4O at higher resolution

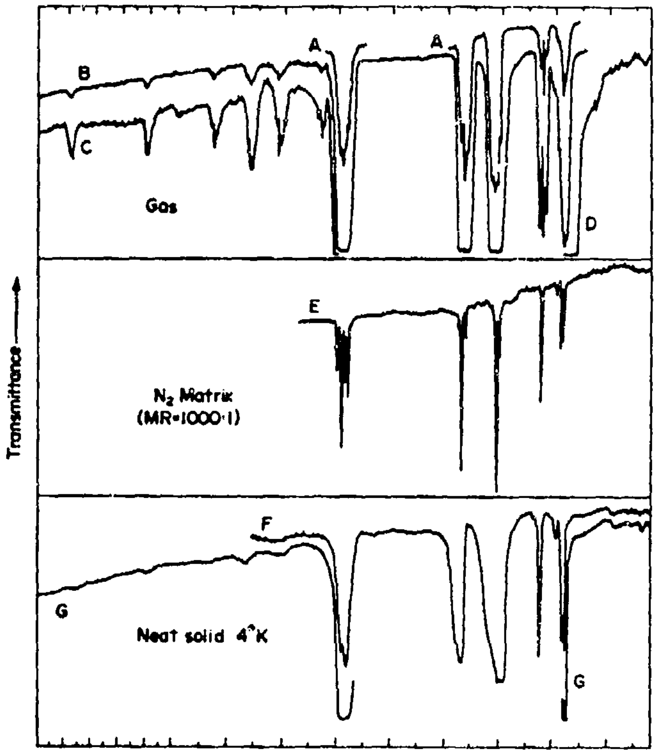


Fig. 1. Infrared spectra of SF_4O. Traces A–D, spectra of the gas at different pressures in a 5-cm path length cell. Trace *A*, 10 mm (AgBr windows); trace *B*, 75 mm (AgCl windows); trace *C*, 500 mm (AgBr windows); trace *D*, 1500 mm (polyethylene windows). Trace *E*, spectrum of SF_4O in a N_2 matrix (mole ratio 1:1000) at 4 K. Traces *F* and *G*, spectra of neat solid SF_4O at two different sample thicknesses at 4 K (CsI windows).

and scale expansion, allowing some conclusions about the band contours and the determination of the ^{32}S—^{34}S isotopic shifts. The observed frequencies are listed in Table 1.

Comparison of the spectra of the gas, the liquid, and the solid shows only minor frequency shifts, indicating little association in the liquid and solid phase. This is in good agreement with its relatively low boiling point (−35.1°C) and Trouton constant (21.9) [7] and with the observations made for the similar molecule ClF_3O_2 [17].

The trigonal-bipyramidal structure of SF_4O has been established by electron diffraction [3–5] and microwave [6] studies. However, four different models of symmetry C_{2v} were found [5] which were all in excellent agreement with the experimental electron diffraction data. No distinction between the four models was possible, but fortunately all of them are very similar as far as the vibrational assignments are concerned. Consequently, knowledge of the exact model is not necessary for making the assignments for SF_4O.

The 12 fundamentals expected for an XY_4Z molecule of symmetry C_{2v} can be classified as $5A_1+A_2+3B_1+3B_2$. All of these should be active in both the i.r. and Raman spectra, except for the A_2 mode which should be only Raman active.

Assignment of the stretching modes. The assignment of the stretching modes of SF_4O is relatively easy. There are three stretching modes in species A_1, i.e., the S═O stretch and the symmetric axial SF_2 and the symmetric equatorial SF_2 stretch. Of these, the SO double bond stretch, ν_1, should have the highest frequency, should result in an intense i.r. and a polarized Raman band, and should occur above 1000 cm^{-1}. Obviously, this fundamental must be assigned to the bands in the 1350–1390 cm^{-1} region. The splitting into four components in the matrix-isolation spectrum and the complex band contour in the i.r. spectrum of the gas are

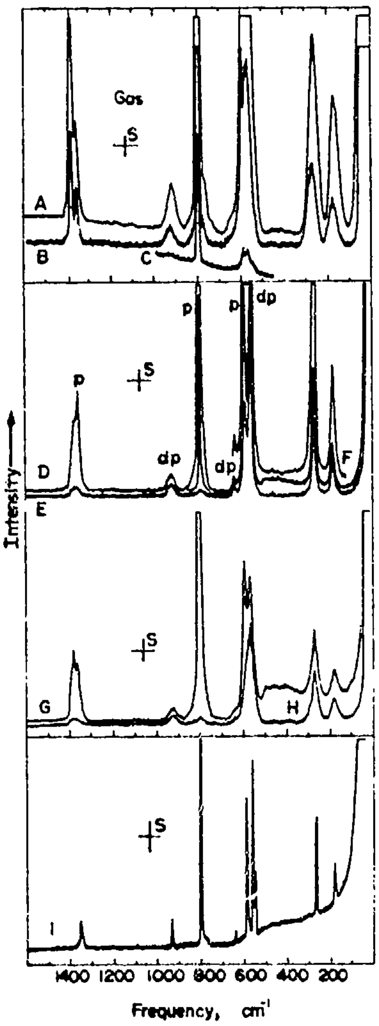


Fig. 2. Raman spectra of SF$_4$O. Traces A–C, spectra of the gas at 10 atm pressure in a stainless steel cell with sapphire windows recorded at three different sensitivities. Traces *D* and *E*, characteristic spectrum of the liquid in a quartz capillary at −80° with the incident polarization perpendicular and parallel, respectively. The broad band between 300 and 500 cm^{-1} is mainly due to quartz, as shown by trace *F* which was recorded for a sample contained in a Teflon–FEP capillary. Traces *G* and *H*, irreproducible spectrum of the liquid in a quartz capillary at −80° with the incident polarization perpendicular and parallel, respectively. Trace I, spectrum of solid SF$_4$O in a quartz tube at −130°C.

caused by Fermi resonance between ν_1 and several A_1 combination bands (see Table 1).

The symmetric equatorial SF$_2$ and axial SF$_2$ stretching modes ν_2 and ν_3 should give rise to two strong polarized Raman bands in the frequency range 500–1000 cm^{-1}. Since the equatorial SF$_2$ group is strongly bent, its symmetric stretching mode should result in an intense i.r. band, whereas for the almost linear axial SF$_2$ group the symmetric stretch should be of low i.r. intensity. Furthermore, by comparison with similar pseudo-trigonal bipyramidal molecules [1, 17], the symmetric equatorial stretch should have a significantly higher frequency than the axial one. Accordingly, the symmetric equatorial SF$_2$ and the symmetric axial SF$_2$ stretching modes are readily assigned to the bands at about 796 and 588 cm^{-1}, respectively. For the observation of ν_2 and ν_3 in the i.r. spectra, the matrix isolation data (see Fig. 3) were helpful since ν_2 almost coincides with ν_7 (B_1), and ν_3 occurs in the vicinity of two i.r. bands of higher intensity.

There are two antisymmetric SF$_2$ stretching modes, the equatorial one, ν_{10} (B_2), and the axial one, $\nu_7\,(B_1)$. Both should occur in the frequency range 700–1000 cm^{-1} and be very intense in the i.r. spectrum. In the Raman spectra, ν_{10} should be considerably more intense than ν_7 because of the large difference in the equatorial and axial SF$_2$ bond angles. Consequently, $\nu_{10}\,(B_2)$ and $\nu_7\,(B_1)$ can be assigned with confidence to the bands at about 926 and 819 cm^{-1}, respectively. The i.r. band contour of ν_7 (see Fig. 3) is complicated by $\nu_2\,(A_1)$ which has a similar frequency (see above) and by Fermi resonance with $\nu_5+\nu_8\,(B_1)$.

Assignment of the deformation modes. The assignment of the remaining bands to the seven deformation modes is more difficult, since only five intense bands (at about 639, 567, 560, 265 and 174 cm^{-1}) were observed with the possibility of a sixth weak fundamental at about 455 cm^{-1}. A similar situation was encountered for SF$_4$ [1]. It is very difficult to decide if the lack of observation of a fundamental is caused either by its low intensity or by a coincidence of two fundamentals. Tentative assignments for the SF$_4$O deformation modes can be made based on the following arguments.

The 639 cm^{-1} band has too high a frequency for an SF$_2$ deformation and, therefore, should be due to the S=O wagging mode, $\nu_8\,(B_1)$. Additional support for this assignment comes from the i.r. gas phase band contour which is similar to $\nu_7\,(B_1)$ (see Fig. 3). Furthermore, there is some evidence in the i.r. spectrum of the gas for Fermi resonance between $\nu_7\,(B_1)$ and the 174 + 639 cm^{-1} combination band. Since the 174 cm^{-1} band belongs to species A_1 (see below), the 639 cm^{-1} mode must belong to species B_1.

The lowest frequency mode (174 cm^{-1}) should be the one involved in an intramolecular Berry-type

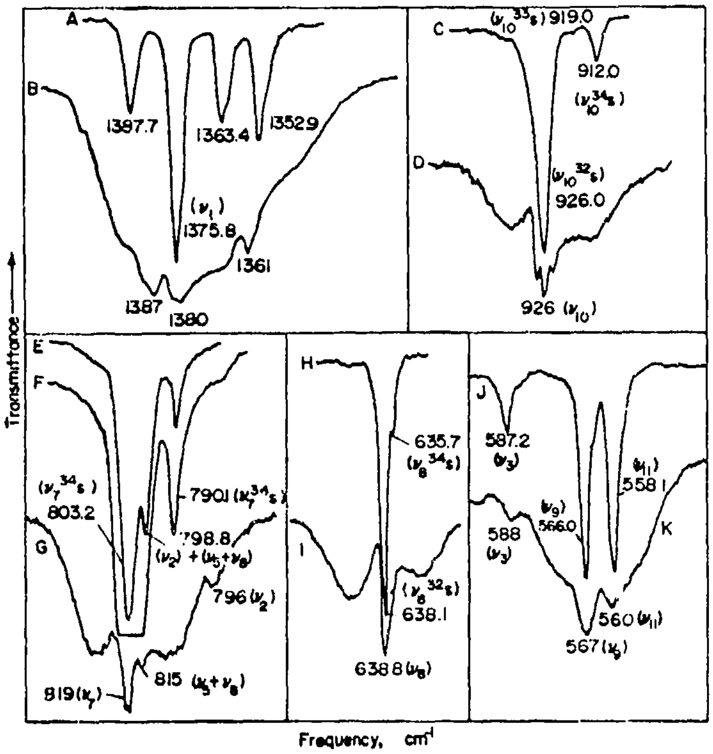


Fig. 3. Principal i.r. bands of gaseous and N_2-matrix-isolated SF_4O recorded at tenfold scale expansion under higher resolution conditions. The frequency scale of the gas and matrix spectra have been slightly shifted relative to each other to allow better comparison.

exchange mechanism [1]. Consequently, the 174 cm^{-1} Raman band is assigned to $\nu_5 (A_1)$ by analogy with SF_4 [1]. The relative ease of intramolecular exchange in SF_4O was confirmed by our failure to observe separate ^{19}F NMR signals for the equatorial and axial fluorines in SF_4O at temperatures as low as −145°C. Polarization measurements on the liquid provided no direct evidence for the 174 cm^{-1} fundamental being polarized. Similarly, all the other deformation modes also had a depolarization ratio of 0.75. However, a polarized combination band (588 + 174) in Fermi resonance with $\nu_2 (A_1)$ was observed. Since the 588 cm^{-1} band has been established (see above) as an A_1 mode, the 174 cm^{-1} band must also belong to species A_1.

By comparison with the closely related PF_5 [18] and SF_4 [1] molecules, the equatorial SF_2 wagging deformation $\nu_9 (B_2)$ of SF_4O should be of high Raman and of medium i.r. intensity and have a frequency between 500 and 600 cm^{-1}. It is therefore assigned to the higher frequency component of the two bands observed in the 550–570 cm^{-1} region.

Ignoring for the time being the A_2 torsional mode, we still need assignments for the antisymmetric equatorial OSF_2 in plane deformation $\nu_{11} (B_2)$, the equatorial SF_2 scissoring mode $\nu_4 (A_1)$, and the axial SF_2 out of plane scissoring mode $\nu_{12} (B_2)$. The following bands are still unassigned: (i) a band at about 560 cm^{-1} of medium intensity in both the i.r. and Raman spectrum; (ii) a band at about 270 cm^{-1} of medium strong Raman and of low i.r. intensity; (iii) a band at about 450 cm^{-1} of low intensity in both the i.r. and Raman spectrum. By comparison with the known spectrum of planar OCF_2 [19], ν_{11} of SF_4O is expected to have a higher frequency and Raman intensity than ν_4. Furthermore, the frequency of $\nu_{12} (B_2)$ should be lower than those of ν_{11} and ν_4 and by comparison with other similar molecules [1, 17, 18, 20] might be expected to be either degenerate with or close to that of the in plane axial SF_2 scissoring mode ν_5 (174 cm^{-1}). Consequently, the 560 cm^{-1} band of SF_4O should be due to $\nu_{11} (B_2)$.

For the assignment of the 270 cm^{-1} band of SF_4O, two alternatives remain, $\nu_4 (A_1)$ and $\nu_{12} (B_2)$.

We prefer its assignment to $\nu_{12}(B_2)$ for the following reasons: (i) its relatively low frequency value is more in line with our expectations for ν_{12} (see above); (ii) its relative i.r. and Raman intensities do not correspond well to those observed for the CF_2 scissoring in planar OCF_2 [19]; (iii) for ClF_3O_2 two intense low-frequency Raman bands were observed [17] at 222 and 285 cm^{-1}, respectively, which resemble those at 185 and 268 cm^{-1} observed for SF_4O. Therefore, these two Raman bands should belong to a structural element common to both ClF_3O_2 and SF_4O. Since ClF_3O_2 contains only one equatorial F atom [17, 21], this common structural element must be the axial FXF group, and the two modes should be due to the axial in plane and out of plane scissoring modes. The assignments previously made [17] for these two modes in ClF_3O_2 should be reversed.

All the observed bands are now assigned, except for a very weak i.r. and Raman band at about 450 cm^{-1}. This band could either be due to the still unassigned $\nu_4(A_1)$ fundamental or the $174+265=439$ cm^{-1} combination band. Its assignment to the $\nu_5(A_2)$ torsional mode is unlikely based on its activity in the i.r. spectrum of gaseous SF_4O. Since the observed frequency (~ 450 cm^{-1}) does not agree too well with that of 439 cm^{-1}, calculated for $\nu_3+\nu_{12}$, we tentatively assign the 450 cm^{-1} band to $\nu_4(A_1)$. However, the relatively low i.r. intensity of the 450 cm^{-1} band is disturbing for this assignment, and the possibility cannot be ruled out that $\nu_4(A_1)$ might occur in the 560 cm^{-1} region, but is difficult to detect owing to the presence of three other nearby fundamentals.

Except for the A_2 torsional mode, all fundamentals of SF_4O have thus been assigned. The assignments for all stretching modes and most of the deformations can be considered firm. The A_2 torsional mode which should be only Raman active could not be positively identified. It is expected to occur in the region 400–550 cm^{-1} in which several extremely weak and therefore questionable Raman features were observed.

Combination bands. A further point in support of the above assignments are the combination bands. All observed combination bands could be assigned (see Table 1) without violation of the selection rules for C_{2v} ($B_1+B_2=A_2$ and $A_1+A_2=A_2$ combinations are i.r. forbidden). Furthermore, for cases involving Fermi resonance, the corresponding fundamentals and combination bands belonged always to the same symmetry species.

Band contours. The i.r. gas phase band contours were also examined. Based on the published microwave data ($A=0.13663$, $B=0.11204$, $C=0.10808$ cm^{-1}) [6], the band contours of SF_4O should approximate those of set 39 in the tables of UEDA and SHIMANOUCHI [22]. Since the B and C values are quite similar, the B and C type bands should be similar under our resolution conditions, and the A type bands should show a narrower Q branch. Since the A axis (smallest moment of inertia) obviously must lie in the direction of the F_{ax}—S—F_{ax} bonds, the B_1 modes should exhibit a narrower Q branch. The observed band contours of ν_7 and ν_8 (see Fig. 3) agree well with this prediction. The largest moment of inertia should be along the S=O axis. Therefore, the A_1 modes should exhibit C type band contours, and the B_2 modes should show a B type contour with a double Q branch. Based on these arguments, we prefer to attribute the complex structure observed for the Q branch of the 926 cm^{-1} $\nu_{10}(B_2)$ band to hot bands. Unfortunately, most of the band contours observed for SF_4O are complicated by effects, such as coincidence of several fundamentals, Fermi resonance, ^{32}S—^{34}S isotopic splittings, and possibly hot bands. The only band having a relatively undisturbed contour is $\nu_8(B_1)$ at 639 cm^{-1}.

Isotopic splittings. The natural abundances of the sulfur isotopes are: $^{32}S=95.06$, $^{33}S=0.74$ and $^{34}S=4.18\%$. For some of the fundamentals splittings due to these isotopes were observed in the matrix isolation i.r. spectra and are listed in Table 1 and Fig. 3.

Comparison with related molecules. A comparison of the assignments for SF_4O to those previously made for the related molecules SF_4 [1], ClF_3 [20], and ClF_3O_2 [17] is given in Table 2. For ClF_3 and ClF_3O_2 only the modes associated with the F_{ax}—Cl—F_{ax} group are listed to avoid confusion. The general agreement is relatively good, if the following points are kept in mind: (i) In the chlorine fluorides, the central atom is more electronegative than oxygen. Consequently, oxygen addition results in an electron release to chlorine and weakens the Cl—F bonds by increasing their polarity. For sulfur fluorides, the effect is reverse because oxygen is more electronegative than the sulfur atom. (ii) In SF_4O, coupling between ν_1 and ν_2 increases their frequency difference and results in a frequency value for ν_2 which is surprisingly low by comparison with that found for SF_4.

As can be seen from Table 2, the problems associated with the assignment of the deformation modes in these pseudo-trigonal bipyramidal molecules are not trivial and more information is required before these assignments should be

Table 1. Vibrational spectra of SF_4O and their assignment in point group C_{2v}

Obsd freq, cm^{-1}, and intensity*							Assignment†	
Infrared			Raman					
Gas	Matrix Isolated	Solid Neat	Gas‡	Liquid A§	Liquid B**	Solid		
2740 vw		2720 vw					2×1380 = 2760	$2\nu_1(A_1)$
2188 vw		2180 vw					1380+819 = 2199	$\nu_1+\nu_7(B_1)$
							1380+796 = 2176	$\nu_1+\nu_2(A_1)$
1852 vw							2×926 = 1852	$2\nu_{10}(A_1)$
1716 vw		1725 vw					796+926 = 1722	$\nu_2+\nu_{10}(B_2)$
1619 vw		1600 vw					796+819 = 1615	$\nu_2+\nu_7(B_1)$
1600 vw							2×796 = 1492	$2\nu_2(A_1)$
1459 vw							819+639 = 1458	$\nu_7+\nu_8(A_1)$
1387 vs	1387.7 m						819+566 = 1385	$\nu_7+\nu_9(A_1)$
1380 vs	1375.8 s	1378 ms	1380(0.7) p	1376(0.7) p	1370 sh p	1353(0.6)		$\nu_1(A_1)$
	1363.4 m						796+588 = 1384	$\nu_2+\nu_3(A_1)$
1361 vs		1359 s	1357(0.3) p	1359(0.5) p	1358(0.6) p			
	1352.9 ms						174+639+566 = 1379	$\nu_5+\nu_8+\nu_9(A_1)$
	1339.7 w						174+925+265 = 1365	$\nu_5+\nu_{10}+\nu_{12}(A_1)$
							2×588+174 = 1350	$2\nu_3+\nu_5(A_1)$
926 s	926.0 s	929 s	924(0.2)	925(0.2) dp	930(0.1) dp	934(0.5)		$\nu_{10}(^{32}S)(B_2)$
	919.0 w							$\nu_{10}(^{33}S)(B_2)$
	912.0 mw							$\nu_{10}(^{34}S)(B_2)$
819 vs	803.2 vs	820– vs	815 sh					$\nu_7(^{32}S)(B_1)$
815 m	798.8 m	780 vs					174+639 = 813	$\nu_5+\nu_8(B_1)$
	790.1 m							$\nu_7(^{34}S)(B_1)$
796 m	798.8 mw	798 mw	795(10) p	797(10) p	799(10) p	799(10)		$\nu_2(A_1)$
			766(0.1)	772 sh, p	774 sh, p	777(0.2)	588+174 = 762	$\nu_3+\nu_5(A_1)$
638.8 ms	638.1 ms	636 ms	640 sh	639(0.05) dp	639(0.06) dp	638(0.2)		$\nu_8(^{32}S)(B_1)$
	635.7 w							$\nu_8(^{34}S)(B_1)$
588 mw	587.2 mw	588 mw	587(1.7) p	588(1.7) p	583(1.4) p	588(2.4)		$\nu_3(A_1)$
567 ms	566.0 ms	562 ms	566(1.7)	561(1.8) dp	559(1.4) dp	560(3.0)		$\nu_9(B_1)$
560 ms	558.1 ms	554 ms				551(1.0)		$\nu_{11}(B_2)$
447 vvw			455(0+)		460(0+)		174+265 = 439	$\nu_5+\nu_{12}(B_2)$ or $\nu_4(A_1)$
270 vw		270 vw	265(0.7)	268(0.9) dp	268(0.7) dp	269(1.5)		$\nu_{12}(B_2)$
			174(0.4)	179(0.4) dp	185(0.3) dp	184(0.6)		$\nu_5(A_1)$

* Uncorrected Raman intensities representing the relative peak height; the relative peak widths and, hence, the relative peak heights change for the different phases.

† The assignments for some of the deformation modes are tentative.

‡ Only qualitative polarization measurements could be obtained for the gas, owing to the optical activity of the sapphire windows of the gas cell.

§ Spectrum of trace *G* of Fig. 2.

** Spectrum of traces *D*–*F* of Fig. 2.

Table 2. Vibrational spectra of SF_4O compared to those of SF_4, ClF_3 and ClF_3O_2

ClF_3 [20]		ClF_3O_2 [17]		SF_4 [1]		SF_4O		Assignment for SF_4O in point group C_{2v}	Approx. description of mode for SF_4O
i.r.	Ra	i.r.	Ra	i.r.	Ra	i.r.	Ra		
						1380 vs	1380(0.7) p	$A_1\,\nu_1$	S═O stretch
				892 s	893(9.2) p	796 m	795(10) p	ν_2	sym equat SF_2 stretch
530 m	529 vs,p	487 vw	487(6) p	558 m	558(10) p	588 mw	587(1.7) p	ν_3	sym axial SF_2 stretch
				353	356(0+)	447 vvw	455(0+)	ν_4	equat SF_2 scissor
328	329 w, p		222(1)	226 w	229(1.0)		174(0.4)	ν_5	axial SF_2 scissor in $F_{ax}SO$ plane
					474(0.7)			$A_2\,\nu_6$	torsion
702 vs		695 vs		728 vs	730(0.5)	819 vs	815 sh	$B_1\,\nu_7$	antisym axial SF_2 stretch
						639 ms	640 sh	ν_8	S═O wagging
				532 ms	535(3.5)	567 ms	566(1.7)	ν_9	equat SF_2 wagging
				867 s	865 sh	926 s	924(0.2)	$B_2\,\nu_{10}$	antisym equat SF_2 stretch
				353 ms	356(0+)	{560 ms	566	ν_{11}	equat SF_2 rocking
328 s	329 w	287 w	285(1)			270 vw	265(0.7)	ν_{12}	axial SF_2 scissor out of $F_{ax}SO$ plane

considered as being well established. A large number of suitable molecules, such as SF_4, SF_4O, ClF_3, ClF_3O, ClF_3O_2, PF_5, PF_4X and PF_3X_2, are available and are ideally suited for a systematic study. Unfortunately, such a systematic study is beyond the scope of the present investigation.

Force constants. A normal coordinate analysis was carried out for SF_4O to support the above assignments. The potential and kinetic energy metrics were computed by a machine method [23]. The geometry used for the computation was model D of GUNDERSEN and HEDBERG [5] since it agrees best with the microwave data [6]. The symmetry coordinates used were analogous to those previously given for ClF_3O_2 [17], except for exchanging the equatorial oxygen atoms for fluorines and vice versa (see Fig. 4). As in that work, the redundant coordinate in the A_1 block was found from the numerical B matrix, and the deformation coordinates were made orthogonal to the redundancy by the Gram-Schmidt process. The bending coordinates were weighted by unit (1 Å) distance. The G matrix and Z transformation were found numerically by the computer and, hence, only the coefficients for the more important force constants are given in Table 3.

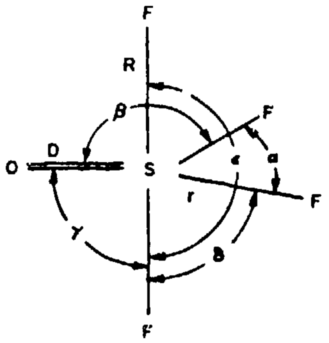


Fig. 4. Definition of internal coordinates.

The force constants were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. The observed ^{32}S—^{34}S isotopic shifts were used as additional constraints (see Table 3). For example, for the A_1 block a diagonal valence force field (DVFF) results in an isotopic shift of 17.4 cm^{-1} for ν_1 and an unreasonably (see below) low value of 11.05 mdyn/Å for the SO stretching force constant. Based on intensity arguments, ν_1 (^{34}S) is best ascribed to the shoulder on the 1363.4 cm^{-1} band (see trace A of Fig. 3) indicating an isotopic shift of 15 cm^{-1} for ν_1. With this constraint, a force field (MVFF I) is obtained which results in a more plausible value for F_1; (see below) and a more characteristic potential energy distribution (see Table 3).

For the B_1 block two solutions were found (see Table 3) which were capable of duplicating the observed isotopic shifts. Their main difference is the sign of f_{RR}. Since a value of 0.28 mdyn/Å for f_{RR} agrees much better with the values found for related molecules (see Table 4), we prefer set I of Table 3 over set II, although the PED of set II is more characteristic. Strong mixing of the modes in B_1 would not be surprising in view of their similar frequencies and their ease of coupling. An exact duplication of the observed matrix isolation isotopic shifts could be achieved by using for ν_7 the observed matrix isolation frequency value (803 cm^{-1}) in place of the gas phase value (819 cm^{-1}). The resulting force field was almost identical to MVFF I (see Table 3) and, therefore, is

Table 3. Observed frequencies (cm^{-1}), symmetry force constants,* computed and observed ^{32}S—^{34}S isotopic shifts (cm^{-1}), and potential energy distribution† for SF_4O

		Frequency		MVFF I F	MVFF I ΔνCOMP	MVFF I ΔνOBSD	MVFF I PED	DVFF F	DVFF ΔνCOMP	DVFF PED
A_1	ν_1	1380	$F_{11} = f_D$	11.990	14.8	~15	$100F_{11}$	11.05	17.4	$89F_{11}$
	ν_2	796	$F_{22} = f_r + f_{rr}$	5.951	2.4		$100F_{22}$	5.98	1.8	$88F_{22} + 10F_{11}$
	ν_3	588	$F_{33} = f_R + f_{RR}$	3.825	0.1		$98F_{33}$	3.83	0.1	$99F_{33}$
	ν_4	450	$F_{44} = 0.32(2f_\alpha + f_\beta) + 0.15(2f_\epsilon + f_\gamma)$	1.440	1.6		$100F_{44}$	1.45	1.0	$94F_{44}$
	ν_5	174	$F_{55} = 0.24(2f_\alpha + f_\beta) + 0.16f_\delta + 0.27(2f_\epsilon + f_\gamma)$	0.1486	0.7		$96F_{55}$	0.1475	0.8	$97F_{55}$
			$F_{12} = \sqrt{2}f_{Dr}$	1.1						
			$F_{24} = 0.56(2f_{r\alpha} - f_{r\beta} - f_{r\beta'}) + 0.24(f_{r\gamma} - f_{r\gamma'})$	−0.7						
A_2	ν_6	400	$F_{66} = f_\delta - f_{\delta\delta} - f_{\delta\delta'} + f_{\delta\delta''}$	1.279	0		$100F_{66}$			
		475		1.803						
		550		2.417					MVFF II	
B_1	ν_7	819	$F_{77} = f_R - f_{RR}$	3.26	13.4	13.1	$63F_{77} + 64F_{88} + 10F_{99} - 13F_{78} - 17F_{79}$	4.303	13.0	$124F_{77} + 10F_{88} + 18F_{99}$ $- 23F_{78} - 28F_{79}$
	ν_8	639	$F_{88} = f_\gamma - f_{\gamma\gamma}$	2.77	2.4	2.4	$41F_{77} + 25F_{88} + 48F_{99} - 31F_{79}$	2.359	1.8	$104F_{88}$
	ν_9	566	$F_{99} = f_\delta - f_{\delta\delta} + f_{\delta\delta'} - f_{\delta\delta''}$	2.63	1.0	1–2	$12F_{77} + 15F_{88} + 60F_{99} + 18F_{79}$	2.470	1.9	$94F_{99}$
			$F_{78} = f_{R\gamma} - f_{R\gamma'}$	0.31				1.02		
			$F_{79} = \sqrt{2}(f_{R\delta} - f_{R\delta'})$	1.01				0.95		
			$F_{89} = \sqrt{2}(f_{\gamma\delta} - f_{\gamma\delta'})$	−0.37				−0.15		
B_2	ν_{10}	926	$F_{10,10} = f_r - f_{rr}$	5.415	14.0	14.0	$103F_{10,10} + 11F_{11,11} - 18F_{10,11}$			
	ν_{11}	560	$F_{11,11} = f_\beta - f_{\beta\beta}$	1.459	2.7		$91F_{11,11}$			
	ν_{12}	265	$F_{12,12} = f_\delta - f_{\delta\delta} - f_{\delta\delta'} - f_{\delta\delta''}$	1.023	0.6		$94F_{12,12}$			
			$F_{10,11} = f_{r\beta} - f_{r\beta'}$	0.75						
MATRIX FREQUENCIES										
B_1	ν_7	803	F_{77}	3.24	13.1	13.1	$66F_{77} + 64F_{88} + 10F_{99} - 15F_{78} - 18F_{79}$			
	ν_8	638	F_{88}	2.70	2.4	2.4	$41F_{77} + 26F_{88} + 47F_{99} - 31F_{79} + 9F_{89}$			
	ν_9	566	F_{99}	2.62	1.1	1–2	$11F_{77} + 15F_{88} + 62F_{62} + 18F_{79}$			
			F_{78}	0.35						
			F_{79}	1.02						
			F_{89}	−0.36						

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* Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch-bend interaction constants in mdyn/radian.

† Percent contributions. Contributions of less than 9% to the PED are not listed.

Table 4. Stretching force constants (mdyn/Å) of SF_4O compared to those of similar molecules

	SF_6[24]	SF_4O	SF_2O_2[25]	SO_3[26]	SF_4[1]	SF_2O[27]	SO_2[28]	SF_2[29]	SO[30]	ClF_3O_2[17]	$FClO_3$[31]	ClF_3O[32]	$FClO_2$[33]	ClF_3[34]	FClO[35]
$f_{x=0}$		11.99	11.63	10.61		11.22	10.42		8.12	9.23	9.4	9.37	9.07		6.85
f_r(eq)	5.26	5.68	5.29		5.51	4.07		4.78		3.35	3.9	3.16	2.53	4.19	2.59
f_R(ax)		3.54			3.30					2.70		2.34		2.70	
f_{rr}	0.34	0.27	0.26		0.25	0.35		0.39							
f_{RR}		0.28			0.19					−0.04		0.26			0.35

Table 5. Thermodynamic properties of SF_4O

T, K	Cp°, cal/mol	H°−H$_0$°, kcal/mol	−(F°−h$_0$°)/T, cal/(mol deg)	S°, cal/(mol deg)
0	0	0	0	0
100	10.185	0.861	50.332	58.946
200	15.546	2.138	56.890	67.580
298.15	20.314	3.910	61.611	74.726
300	20.388	3.948	61.692	74.852
400	23.683	6.163	65.794	81.202
500	25.849	8.647	69.442	86.736
600	27.301	11.309	72.737	91.585
700	28.303	14.092	75.742	95.873
800	29.016	16.960	78.502	99.702
900	29.538	19.889	81.052	103.151
1000	29.929	22.863	83.421	106.285
1100	30.229	25.872	85.632	109.152
1200	30.463	28.907	87.703	111.792
1300	30.650	31.963	89.651	114.238
1400	30.800	35.036	91.490	116.516
1500	30.923	38.122	93.230	118.645
1600	31.025	41.220	94.882	120.644
1700	31.110	44.327	96.453	122.527
1800	31.182	47.441	97.951	124.308
1900	31.243	50.563	99.383	125.995
2000	31.296	53.690	100.754	127.599
2100	31.341	56.821	102.069	129.127
2200	31.381	59.958	103.333	130.586
2300	31.415	63.097	104.548	131.982
2400	31.446	66.241	105.719	133.320
2500	31.473	69.386	106.849	134.604
2600	31.497	72.535	107.941	135.839
2700	31.518	75.686	108.996	137.028
2800	31.538	78.839	110.018	138.174
2900	31.555	81.993	111.008	139.281
3000	31.571	85.150	111.968	140.351
3100	31.585	88.307	112.901	141.387
3200	31.598	91.466	113.807	142.390
3300	31.609	94.627	114.688	143.362
3400	31.620	97.788	115.545	144.306
3500	31.630	100.951	116.380	145.223
3600	31.639	104.114	117.193	146.114
3700	31.647	107.279	117.987	146.981
3800	31.655	110.444	118.761	147.825
3900	31.662	113.609	119.517	148.647
4000	31.669	116.776	120.255	149.449
4100	31.675	119.943	120.977	150.231
4200	31.680	123.111	121.682	150.995
4300	31.686	126.279	122.373	151.740
4400	31.691	129.448	123.049	152.469
4500	31.695	132.617	123.710	153.181
4600	31.699	135.787	124.359	153.878
4700	31.704	138.957	124.994	154.559
4800	31.707	142.128	125.617	155.227
4900	31.711	145.299	126.228	155.881
5000	31.714	148.470	126.827	156.521
5100	31.717	151.642	127.416	157.149
5200	31.720	154.813	127.993	157.765
5300	31.723	157.986	128.561	158.370
5400	31.726	161.158	129.118	158.963
5500	31.728	164.331	129.666	159545
5600	31.731	167.504	130.205	160.116
5700	31.733	170.677	130.735	160.678
5800	21.735	173.850	131.256	161.230
5900	31.737	177.024	131.768	161.772
6000	31.739	180.198	132.273	162.306

not separately listed. Contrary to the findings for the B_1 block, the potential energy distribution for the A_1 and B_2 blocks is highly characteristic.

A comparison of the stretching force constants of SF_4O with those previously reported for similar molecules [24–35] is given in Table 4 and shows the expected trends. The equatorial SF bonds in SF_4O are significantly stronger than the axial ones (even if MVFF II is chosen), thus supporting our choice of an electron diffraction data model [5] in which $r\text{SF}_{eq}$ is significantly shorter than $r\text{SF}_{ax}$. By analogy with the other related pseudotrigonal-bipyramidal sulfur or chlorine fluorides or oxyfluorides, the bonding in SF_4O might be described by the following model. The bonding of the three equatorial ligands, ignoring the second bond of the S═O double bond, is mainly due to an sp^2 hybrid, whereas the bonding of the two axial SF bonds involves one delocalized p-electron pair of the sulfur atom for the formation of a semi-ionic three-center four-electron $p\sigma$ bond [36–38]. The incorrectness of the assignments previously made [9] by Cleveland and coworkers is also reflected by their force field which resulted in significantly stronger axial ($f_R = 5.54$ mdyn/Å) than equatorial ($f_r = 4.40$ mdyn/Å) SF bonds, contrary to the electron diffraction data [3–5].

The S—O stretching force constant increases with both increasing oxidation state of the central atom and increasing fluorine substitution. The equatorial S—F stretching force constants also tend to increase for the same sulfur oxidation state with increasing fluorine substitution, except for $SF_4O \rightarrow SF_6$. Provided the given force constants differences are meaningful, the latter effect might be explained by the higher s-character of the equatorial SF bonds in SF_4O (sp^2) when compared to those in SF_4 (sp^3d^2). Comparison between the stretching force constants of SF_4O and SF_4 shows good agreement, the slight increase from SF_4 to SF_4O being attributable to the increase of the sulfur oxidation state.

Thermodynamic properties. In view of the absence of thermodynamic data for SF_4O in the literature and of their interest for chemical lasers, we have computed thermodynamic properties for SF_4O (see Table 5). The molecular geometry and frequencies from the above force field computation were adopted assuming $\nu_4 = 475\ \text{cm}^{-1}$ and an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation [39]. It should be kept in mind, however, that the frequencies of two fundamentals (ν_4 and ν_6) are uncertain and that the sum of the frequencies may therefore be in error by as much as 200 cm^{-1}.

SUMMARY

The vibrational spectra of pure SF_4O have been recorded. Out of the 12 fundamentals expected for symmetry C_{2v}, 10 have been observed and the previous assignments [9] were revised for 8 of the fundamentals. As for SF_4, the assignments for the A_1 equatorial SF_2 scissoring and the A_2 torsional mode present difficulties. A systematic study of the vibrational spectra of the presently known pseudotrigonal bipyramidal fluorides and oxyfluorides is desirable to support the assignments for the deformation modes. The results of a normal coordinate analysis indicate that the proposed assignments for SF_4O are plausible. The stretching force constants of SF_4O are in good agreement with those found for SF_4 and similar molecules. The large difference in the values of the equatorial and the axial SF_2 stretching force constants indicates that model D (or possibly C) of Gundersen and Hedberg [5] are more probable than their preferred model A.

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SHORT COMMUNICATION

A Simple Method for the Purification of Fluorine

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A simple method for the purification of fluorine gas is described. With the exception of nitrogen and argon, all impurities usually present in commercial fluorine can be readily removed by 1) conversion of O_2 to nonvolatile O_2^+ salts, and 2) a 70 to 63°K trap-to-trap distillation.

Commercial fluorine gas contains 1-2% of impurities, primarily O_2, N_2 and HF with trace amounts of Ar, CO_2, CF_4, C_2F_6, C_3F_8, COF_2, NF_3, OF_2, SiF_4, SF_6, SO_2F_2, and others [1-5]. For most preparative purposes the O_2 content of fluorine does not interfere with the desired reactions, and the purification of F_2 can be limited to the removal of HF by a NaF scrubber. For example, a nearly quantitative synthesis of IrF_6 is possible by heating Ir metal in an atmosphere of 20% F_2 and 80% O_2 [6]. However, there are applications, where oxygen free fluorine is needed. A typical example is the HF-DF chemical laser. It is known [7,8] that molecular oxygen acts as an inhibitor for the chain branching reaction of H_2 and F_2. In addition, the presence of O_2 causes the formation of water which is a very strong deactivator for vibrationally excited HF or DF [9]. In order to obtain meaningful baseline data, oxygen free fluorine is required. Furthermore, in the syntheses of the very expensive platinum metal hexafluorides RuF_6, RhF_6, and PtF_6 the yield of the products is decreased by the formation of the undesired and volatile [10] $O_2^+MF_6^-$ salts. Similarly, in the syntheses of ReF_7 and OsF_6 the presence of O_2 results in the formation of the corresponding oxide pentafluorides. Other applications requiring high purity fluorine include calorimetry [1], and spectroscopic [11, 12] and analytical [3] studies.

Previously described methods for the purification of fluorine involved either low-temperature distillation [2-4], low-temperature uv-photolysis [13], or the pyrolysis of K_2NiF_6 in the presence of KF [4]. These methods have the following shortcomings. The low-temperature distillations require rather complex and expensive equipment which is beyond the reach of most laboratories. The low-temperature uv-photolysis involves the irradiation of liquid fluorine in a glass apparatus to convert O_2 to the less volatile O_2F_2, followed by a distillation at 90°K. This method is not suitable for scale-up, and the handling of larger amounts of liquid fluorine in a glass apparatus presents a potential hazard. The pyrolysis of K_2NiF_6-KF mixtures is somewhat cumbersome, because the bulk of the material and not the impurity must be converted to a nonvolatile compound. In this paper, we describe an alternate method which we have found to be more convenient than those previously reported.

(1) Removal of Oxygen

We have found that the well known [14-16] reaction

$$O_2 + F_2 + nSbF_5 \xrightarrow{\Delta E} O_2^+SbF_6^- \cdot (n-1)SbF_5$$

is ideally suited for the removal of oxygen impurities from fluorine. Either heating [14] or uv-photolysis [15] can be used for activation of the reaction. Of these two activation energy sources, thermal activation is preferred owing to its scalability and simplicity.

In a typical example, crude F_2 (17 g, 500 mmol) [17] and SbF_5 (2.1 g, 10 mmol) [18] in a 1.2 ℓ Monel reactor were heated for 2 h to 460°K. The vessel was cooled to 90°K and the F_2 was distilled into a container kept at 77°K. The excess of unreacted SbF_5 was removed from the Monel vessel by pumping at room temperature. The vessel was opened in a dry box and contained 1.1 g of a white solid which was identified by its vibrational spectra [16] as $O_2^+Sb_2F_{11}^-$. The above procedure was repeated with pretreated F_2. In this case, no evidence for the formation of any O_2^+ salt was obtained and the reaction vessel showed clean inner surfaces. It can therefore be assumed that the oxygen was quantitatively removed by a single heating cycle.

(2) Removal of Trace Impurities

It is known that impurities which have no measurable vapor pressure at 90°K can be removed from F_2 by a 90 to 77°K trap-to-trap distillation. For the removal of the more volatile impurities CF_4, NF_3, and OF_2, however, lower temperatures are required. In our experience, a 70 to 63°K trap-to-trap distillation can be carried out with relative ease and removes all remaining impurities, except for N_2 and Ar which usually do not interfere with most applications. Since the amount of N_2 present in commercial F_2 can vary strongly depending on the batch and supplier, no meaningful number can be quoted for the overall purity of the F_2 obtained by our method. The temperature of 63°K (nitrogen slush bath) is easily obtained by either pumping on liquid N_2 or by passing a stream of helium, precooled to 77°K, through liquid N_2. The temperature of 70°K is obtained either by passing He through liquid N_2 or by allowing a 63°K trap to gradually warm towards 70°K. The purity of F_2 after two 70 to 63°K trap-to-trap distillations was tested by recording its infrared spectrum as a solid [12] at 12°K. No detectable impurities were observed. The absence of impurities volatile at 70°K but nonvolatile at 63°K in the purified fluorine was established by mass spectroscopy.

Thus, a 70 to 63°K trap-to-trap distillation combined with the O_2 scavenging method using SbF_5 provides a convenient purification method for fluorine.

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Synthesis and Characterization of $(NF_4)_2NiF_6$

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The NF_4^+ cation has successfully been coupled with the energetic NiF_6^{2-} anion in the form of the stable $(NF_4)_2NiF_6$ salt. The salt was prepared from Cs_2NiF_6 and NF_4SbF_6 by metathesis in HF. It was characterized by elemental analysis, vibrational spectroscopy, and its x-ray powder diffraction pattern. Its hydrolysis and thermal decomposition were studied.

Introduction

A large number of strongly oxidizing complex fluoro cations and anions are known. However, their potential application as energetic oxidizers had been handicapped by the fact that they formed stable salts only with nonenergetic counterions. The recent syntheses[1-3] of several stable NF_4^+ salts, derived from relatively weak Lewis acids, indicated that the NF_4^+ cation might possess the necessary stability required for its successful combination with energetic anions.

In this paper we report the synthesis and properties of $(NF_4)_2NiF_6$ which, to our knowledge, is the first known example of a stable salt containing both a strongly oxidizing complex fluoro cation and anion. The NiF_6^{2-} anion is well-known[4-19] and is a strong oxidizer owing to the fact that the parent molecule NiF_4 is unstable and decomposes to lower nickel fluorides and elemental fluorine.[17,18]

Experimental Section

Materials and Apparatus. The equipment and handling procedures used in this work were identical with those previously described.[2,3] The NF_4SbF_6 was prepared as previously[20] reported. The HF (Matheson) was dried by F_2 treatment[21] and was stored over K_2NiF_6 (Ozark Mahoning) prior to use. The Cs_2NiF_6 was prepared by heating a finely ground 2:1 molar mixture of dried CsF and $NiCl_2$ (Alfa) with 15 mol of F_2/mol of $NiCl_2$ in a nickel cylinder to 250 °C for 16 h. The volatile products were pumped off at room temperature. The solid product was finely powdered in the drybox and the fluorination step was repeated as described above. The weight and the vibrational spectra of the resulting crimson red solid were in excellent agreement with those expected[9,15,16] for Cs_2NiF_6.

In the infrared spectrum of Cs_2NiF_6 several relatively intense previously unreported combination bands (cm^{-1}) were observed. These were $\nu_1 + \nu_3$ (1205 w, 1187 mw), $\nu_2 + \nu_3$ (1164 mw, 1144 m), $\nu_3 + \nu_5$ (954 sh, 936 w), $\nu_1 + \nu_4$ (884 vw), and $\nu_2 + \nu_4$ (842 vw). From these combination bands a splitting of ν_1 into two components with frequencies of 660 and 641 cm^{-1} can be deduced. The observed frequencies (cm^{-1}) and relative intensities of the fundamentals were as follows: infrared, ν_3 (645 vs, br), ν_4 (331 s); Raman, ν_1 [545 (10)], ν_2 [503 (7.5)], ν_5 [294 (4)].

Synthesis of $(NF_4)_2NiF_6$. In the glovebox a mixture of Cs_2NiF_6 (13.50 mmol) and NF_4SbF_6 (27.94 mmol) was placed in a $^3/_4$-in. o.d. Teflon FEP U-trap which was connected through a 180 °C coupling to a second U-trap. This coupling contained a porous Teflon filter (Pall Corp.). The free ends of both U-traps were closed off by valves. Both valves were connected through flexible, corrugated Teflon FEP tubing to a vacuum manifold. Dry HF (10 mL of liquid) was added at −78 °C to the trap containing the reactants. The mixture was warmed to 25 °C and stirred with a Teflon-coated magnetic stirring bar for 30 min. The U-tube and filter coupling were cooled to −78 °C and the trap was inverted. The receiving trap was also cooled to −78 °C and the solution above the filter was pressurized by 2 atm of dry nitrogen to accelerate the filtration. After completion of the filtration, the HF solvent was removed by pumping for 12 h at 25 °C. The filter cake consisted of 10.15 g of a light brown solid (weight calcd for 27.0 mmol of $CsSbF_6$ 9.95 g) which was identified by analysis and vibrational spectroscopy as mainly $CsSbF_6$ containing a small amount of NF_4^+ and NiF_6^{2-} salts. The filtrate residue consisted of 4.36 g of a deep red solid (weight calcd for 13.5 mmol of $(NF_4)_2NiF_6$ 4.76 g) which on the basis of elemental and spectroscopic analyses had the following composition (wt %): $(NF_4)_2NiF_6$, 82.35; NF_4SbF_6, 13.98; $CsSbF_6$, 3.56. Anal. Calcd: Ni, 13.71; Sb, 6.40; Cs, 1.28; NF_3, 36.20. Found: Ni, 13.70; Sb, 6.44; Cs, 1.31; NF_3, 36.19. The method for purifying this material by recrystallization from anhydrous HF at ambient temperature has previously been described[20] for NF_4BF_4.

Hydrolysis of $(NF_4)_2NiF_6$. *Caution!* The reaction of $(NF_4)_2NiF_6$ with water is very violent and can result in explosions. About 5 mL of distilled water was frozen out at −196 °C in the upper section of a Teflon FEP U-trap containing about 1 mmol of $(NF_4)_2NiF_6$. The frozen water was knocked down into the bottom section of the tube containing the sample and the ice and sample were mixed by agitation at low temperature. After good mixing was achieved, the mixture was carefully warmed toward room temperature and as soon as interaction was noticeable, the mixture was chilled again by liquid N_2. This procedure was repeated until the color of the sample had completely changed from red to the green color characteristic for divalent nickel. The products volatile at −78 °C consisted of O_2, NF_3, and OF_2. The oxygen was separated from the NF_3 and OF_2 at −210 °C, and the NF_3:OF_2 ratio was determined by infrared spectroscopy. The hydrolysate was analyzed for Ni, Cs, Sb by both x-ray fluorescence and atomic absorption spectroscopy. The mole ratio of O_2 to OF_2 was found to vary somewhat from experiment to experiment, but approached 2:1 with the total amount being close to that expected for the reduction of N(+V) and Ni(+IV) to N(+III) and Ni(+II), respectively. Control experiments on the hydrolysis of Cs_2NiF_6 under indentical conditions resulted in the evolution of O_2 only in amounts corresponding to the reduction of Ni(+IV) to Ni(+II).

Pyrolysis of $(NF_4)_2NiF_6$. A sample of $(NF_4)_2NiF_6$ (296 mg) was placed into a prepassivated (with ClF_3, followed by F_2 at 130 °C) $^1/_4$-in. o.d. stainless steel U-tube (volume 10.46 cm^3) closed off on both ends by Hoke valves (3132M25). One side of the U was connected to a pressure transducer (Validyne, Model AP10) and the other side to the vacuum line. The U-tube was kept at a constant temperature with an oil bath and the pressure build-up was measured as a function of time. Periodic evacuation of the system revealed that the decomposition rate was not influenced by the pressure of the gaseous decomposition products. The decomposition rates of $(NF_4)_2NiF_6$ were determined over the temperature range 80–128 °C. All measurements were carried out on one sample starting at the lowest temperature. At the highest temperature (128 °C), an exhaustive pyrolysis of the remaining undecomposed 82% of the original sample was carried out until gas evolution practically ceased. The evolved gas was shown by infrared and mass spectroscopy to be a mixture of NF_3 and F_2 in a mole ratio of about 2:3. On the basis of its weight loss and vibrational spectrum, the solid residue from the exhaustive pyrolysis was shown to consist of the thermally more stable NF_4SbF_6 and $CsSbF_6$ impurities and the previously described[9,17] nonstoichiometric brown nickel fluoride $NiF_{2.x}$.

The thermal decomposition was also visually followed by heating a sample of $(NF_4)_2NiF_6$ in a sealed glass capillary. At 130 °C the color of the sample changed from dark red to brown ($NiF_{2.x}$) which at higher temperatures changed to gray. Vibrational spectra of the final decomposition product and those obtained from the yellow pyrolysis product of Cs_2NiF_6 showed that in both cases the main product was NiF_2 (Raman, 520 vs, 425 s; IR, 520 sh, 425 s, br).

Results and Discussion

Synthesis and Properties. Since the NiF_6^{2-} anion is stable in anhydrous HF solution,[9,12,17] the synthesis of $(NF_4)_2NiF_6$ by metathesis appeared feasible. Both NF_4SbF_6 and Cs_2NiF_6 are highly soluble in HF, whereas $CsSbF_6$ is of relatively low solubility, particularly at lower temperature. Consequently, the following reaction was used to prepare $(NF_4)_2NiF_6$:

$$2NF_4SbF_6 + Cs_2NiF_6 \xrightarrow[-78\ °C\ \text{filtr}]{HF} 2CsSbF_6\downarrow + (NF_4)_2NiF_6$$

Table I. X-Ray Powder Data for $(NF_4)_2NiF_6$[a]

d(obsd), Å	*d*(calcd), Å	Intens	*hkl*
5.46	5.49	vs	002
3.42	3.45	ms	103
3.31	3.31	s	310
2.880	2.878	ms	213
2.742	2.738	mw	004
2.407	2.405	mw	331
2.150	2.150	s	422
1.954	1.954	w	502 432
1.846	1.849	m	440

[a] Tetragonal; $a = 10.457$ Å, $c = 10.953$ Å; Cu Kα radiation, Ni filter.

Table II. Crystallographic Data of $(NF_4)_2NiF_6$ Compared to Those of Other $(NF_4)_2MF_6$ Salts[a]

	Tetragonal unit cell dimensions				
	a, Å	*c*, Å	*V*, Å³	Vol/F, Å³	Calcd density, g/cm³
$(NF_4)_2TiF_6$[b]	10.715	11.114	1276.0	17.09	2.37
$(NF_4)_2NiF_6$	10.457	10.953	1197.7	16.04	2.61
$(NF_4)_2GeF_6$[c]	10.627	11.114	1255.1	16.81	2.59
$(NF_4)_2SnF_6$[d]	10.828	11.406	1337.4	17.91	2.73

[a] For all compounds $Z = {}^{16}/_{3}$. [b] Reference 1. [c] Reference 3. [d] Reference 2.

The optimization of a NF_4SbF_6–cesium salt based metathetical process and the possible product purification have previously been discussed in detail for the corresponding NF_4BF_4 process[20] and hence are not being reiterated.

The resulting $(NF_4)_2NiF_6$ is a deep red hygroscopic solid, stable at room temperature. In the absence of fuels, the compound is not shock sensitive. It crystallizes in the tetragonal system (see Table I) and is isotypic with the other known $(NF_4)_2MF_6$ (M = Ge, Sn, Ti)[1-3] salts (see Table II). As expected, the size of the unit cell decreases from $(NF_4)_2TiF_6$ to $(NF_4)_2NiF_6$ owing to the transition metal contraction and then increases again when going from Ni to the main-group elements.

The vibrational spectra of $(NF_4)_2NiF_6$ are shown in Figure 1 and the observed frequencies and their assignments are summarized in Table III. The observed frequencies and intensities are in excellent agreement with those previously reported for other NF_4^+ salts[1-3] and K_2NiF_6[9,15] and Cs_2NiF_6 (see Experimental Section), thus establishing the ionic nature of $(NF_4)_2NiF_6$.

Thermal Decomposition. The thermal decomposition of $(NF_4)_2NiF_6$ was investigated by DSC and visual observation of samples sealed in glass melting point capillaries. The DSC curves of samples sealed in aluminum pans indicated the onset of very slow endothermic decomposition between 110 to 120 °C, which increased with increasing temperture and became rapid between 200 and 210 °C. The fact that $(NF_4)_2NiF_6$ undergoes appreciable decomposition well below 200 °C was confirmed by visual observation of samples sealed in glass melting point capillaries. Heating to 130 °C resulted in the formation of the brown nonstoichiometric NiF_{2-x}[9,17] (see Experimental Section). As previously discussed,[1-3] these data are only qualitative.

Since the thermal stability of a powerful oxidizer, such as $(NF_4)_2NiF_6$, is of great practical importance, its rate of decomposition was quantitatively studied by total pressure measurements over the temperature range 80–128 °C. The decomposition follows the equation

$$(NF_4)_2NiF_6 \rightarrow 2NF_3 + (3 - x/2)F_2 + NiF_{2-x}$$

The decomposition rate was found to be independent of the gas pressure, as expected for an irreversible reaction involving the decomposition of the thermodynamically unstable NiF_4 to NiF_{2-x}. Owing to the limited amount of sample available, all measurements were carried out on the same sample. From 80 to 110 °C the decomposition rates were measured only for low α (fraction of material decomposed) values. At 128 °C an exhaustive decomposition was carried out for the α range 0.18–1. Plots of α as a function of time *t* resulted in straight lines for the α range 0–0.18 from 80 to 110 °C and for α = 0.18–0.6 at 128 °C. From these straight lines, rate constants, *k*, were calculated for each temperature (see Table IV). An Arrhenius plot of log *k* vs. $1/T$ resulted in a straight line. The fact that this plot included the data points obtained for both low and high α values strongly suggests that the decomposition rates are independent of α at $\alpha < 0.6$. From the Arrhenius plot, the following expressions can be derived for the specific reaction rate constant (s^{-1}) and activation energy of the $(NF_4)_2NiF_6$ decomposition

$$k = 4.840 \times 10^{14} e^{-35161/RT(K)}$$

$$\Delta H_a = 35.161 \text{ kcal/mol}$$

A detailed study of the exact decomposition mechanism was beyond the scope of this study. However, the failure to observe significant sigmoid character for the decomposition curves indicates that the decomposition is not autocatalytic. Furthermore, the fact that the decomposition rates were independent of α over a large range of α suggests that the decomposition occurs at active sites and that the number of these sites is fixed.[22] In view of the experimental limitations (only one sample was used and the sample contained impurities, although these were more stable than the compound of interest), the above kinetic data will have to be verified in a more

Table III. Vibrational Spectra of Solid $(NF_4)_2NiF_6$

Obsd freq, cm⁻¹, and rel intens[a]		Assignments (point group)[b]	
IR	Raman	NF_4^+ (T_d)	NiF_6^{2-} (O_h)
2301 vw		$2\nu_3$ ($A_1 + E + F_2$)	
1998 w		$\nu_1 + \nu_3$ (F_2)	
1756 vw		$\nu_3 + \nu_4$ ($A_1 + E + F_2$)	
1460 vw		$\nu_1 + \nu_4$ (F_2)	
1218 m		$2\nu_4$ ($A_1 + E + F_2$)	
1156 vs	1157 (0.1)	ν_3 (F_2)	
1055 vw		$\nu_2 + \nu_4$ ($F_1 + F_2$)	
854 vw	854 (1)	ν_1 (A_1)	
648 vs			ν_3 (F_{1u})
609 m 604 sh	609 (0.5)	ν_4 (F_2)	
556 vw	555 (10)		ν_1 (A_{1g})
512 vw	512 (7)		ν_2 (E_g)
	457 (0.5) 454 (0.5)	ν_2 (E)	
443 vw			
332 mw			ν_4 (F_{1u})
	307 (1.5) 298 (4)		ν_5 (F_{2g})
	90 (0.1) 60 (0+)	Lattice vib	

[a] Uncorrected Raman intensities. [b] The actual site symmetries of NF_4^+ and NiF_6^{2-} in this salt are probably lower than T_d and O_h, respectively, as indicated by the large unit cell ($Z = {}^{16}/_{3}$) and the observed slight deviations from the selection rules and the lifting of the degeneracy for some of the modes; however, since the actual site symmetries are unknown, the assignments are given for the idealized point groups.

Table IV. Rate Constants Observed for the Thermal Decompositon of $(NF_4)_2NiF_6$

T, °C	*k*, s⁻¹	*T*, °C	*k*, s⁻¹
80	8.279×10^{-8}	110	4.197×10^{-6}
90	2.739×10^{-7}	128	3.012×10^{-5}
99	1.165×10^{-6}		

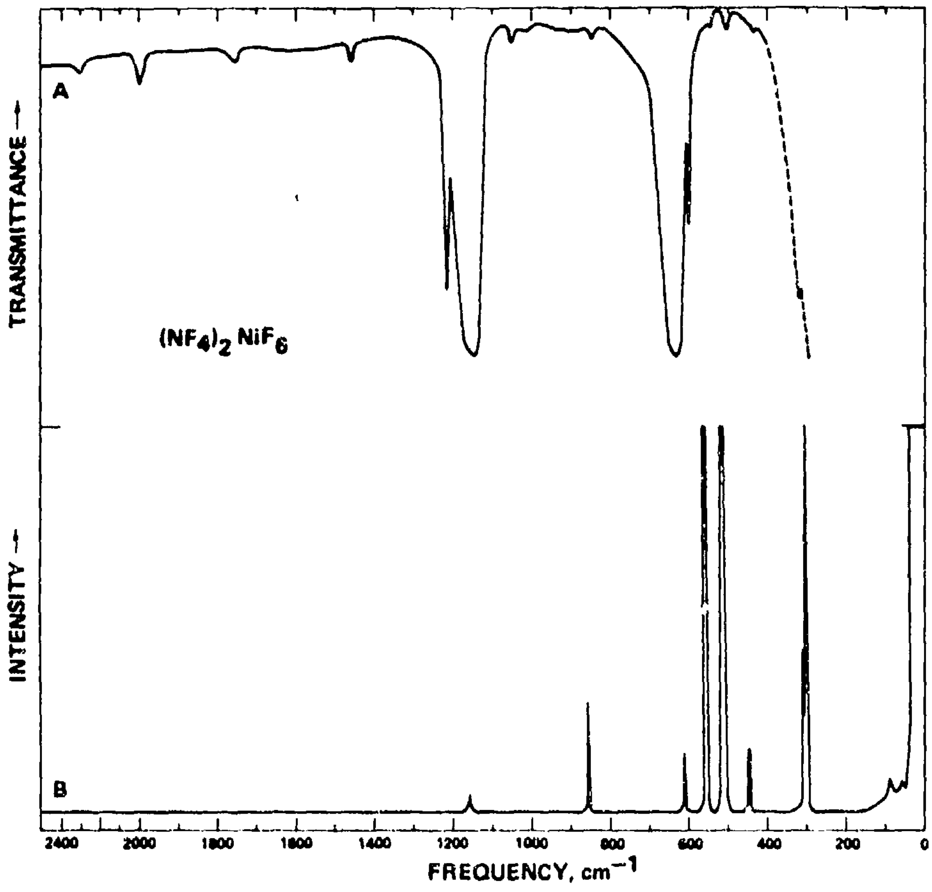

Figure 1. Vibrational spectra of solid $(NF_4)_2NiF_6$: trace A, infrared spectrum of the dry powder in a silver chloride disk, the absorption below 400 cm^{-1} (broken line) being due to the AgCl windows; trace B, Raman spectrum, recorded on a Cary Model 83 using the 6471-Å line of a Kr ion laser and a spectral slit width of 2 cm^{-1}.

detailed study on pure $(NF_4)_2NiF_6$.

The thermal decomposition of $(NF_4)_2NiF_6$ differs strongly from that previously reported[23] for NF_4AsF_6. Contrary to our findings for $(NF_4)_2NiF_6$, the decomposition of NF_4AsF_6 was found to be pressure dependent indicating the equilibrium

$$NF_3 + F_2 + AsF_5 \rightleftharpoons NF_4AsF_6$$

Because of the irreversibility of the $(NF_4)_2NiF_6$ decomposition, the heat of dissociation and thereby the heat of formation of solid $(NF_4)_2NiF_6$ cannot be computed. However, in view of its importance for performance calculations, the heat of formation of solid $(NF_4)_2NiF_6$ was estimated to be about −230 kcal/mol based on the sequence (where all values are in kcal/mol)

$$\begin{array}{lll} & & \\ (NF_4)_2NiF_6(s) & \xrightarrow{106} 2\overset{62.8}{NF_3(g)} + 2F_2(g) + & \overset{(60)}{NiF_4(g)} \\ & & \big\downarrow -20 \\ & & NiF_2(g) + F_2(g) \\ & & \big\downarrow -79.4 \\ & & NiF_2(s) \\ & & -159.5 \end{array}$$

The values for the heat of formation[24] and heat of sublimation[25] of solid NiF_2 and for the heat of formation of gaseous NF_3[26] are literature values. The heats of decomposition of gaseous NiF_4 and solid $(NF_4)_2NiF_6$ are estimates. The latter estimate[27] is based on the known[28] value of −34.6 kcal/mol of the reaction $NF_4BF_4(s) \rightarrow NF_3(g) + F_2(g) + BF_3(g)$. A value for the heat of formation of $(NF_4)_2NiF_6$ being slightly more negative than −222 kcal/mol ($\Delta H_f^\circ(NiF_2(s)) + 2\Delta H_f^\circ(NF_3(g))$) is supported by our DSC measurements which showed the decomposition of $(NF_4)_2NiF_6$ to be mildly endothermic.

Hydrolysis. The hydrolysis of $(NF_4)_2NiF_6$ can be described approximately by the equation

$$2(NF_4)_2NiF_6 + 5H_2O \rightarrow 4NF_3 + 10HF + 2O_2 + OF_2 + 2NiF_2$$

Whereas the NF_3 evolution and formation of +II Ni were quantitative, the ratio of O_2:OF_2 varied from experiment to experiment. The observation of significant amounts of OF_2 was quite unexpected since neither NF_4^+ nor NiF_6^{2-} alone produces OF_2 during hydrolysis. This was verified by studying the hydrolysis of Cs_2NiF_6 which, in agreement with a previous report,[9] produced only O_2 according to

$$2NiF_6^{2-} + 2H_2O \rightarrow 4HF_2^- + 2NiF_2 + O_2$$

The hydrolyses of NF_4^+ salts containing nonoxidizing anions have been studied previously. Although O_2 evolution had not always been quantitative, H_2O_2 and not OF_2 had been the only observed by-product.[3] It thus appears that the combination of NF_4^+ and NiF_6^{2-} is required to produce significant amounts of OF_2. A plausible explanation for the formation of OF_2 is the fluorination of HOF, a likely intermediate in the rapid hydrolysis of NF_4^+,[3] by the hydrolytically more stable NiF_6^{2-} according to

$$NF_4^+ + 2HOH \rightarrow FOH + H_3O^+ + NF_3$$

$$FOH + NiF_6^{2-} \rightarrow FOF + HF + NiF_4^{2-}$$

Summary

The successful synthesis of $(NF_4)_2NiF_6$ is significant since, to our knowledge, it is the first combination of a strongly oxidizing complex fluoro cation with a strongly oxidizing complex fluoro anion in the form of a stable salt. Its potential as an oxidizer and an ingredient for a solid propellant NF_3–F_2 gas generator[2,29,30] for chemical HF–DF lasers becomes evident from the following comparison. On thermal decomposition, 1 cm^3 of solid $(NF_4)_2NiF_6$ is capable of producing 12% more useful fluorine values, i.e., in the form of F_2 and NF_3, than liquid F_2 at −187 °C. Furthermore, $(NF_4)_2NiF_6$ is a stable solid at ambient temperature which can be safely stored without requiring cryogenic cooling. The physical and spectroscopic properties of $(NF_4)_4NiF_6$ are in excellent agreement with those predicted for a solid containing NF_4^+ and NiF_6^{2} ions. The only unexpected property was the observation of significant amounts of OF_2 during hydrolysis.

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Registry No. $(NF_4)_2NiF_6$, 63105-40-8; Cs_2NiF_6, 17218-49-4; NF_4SbF_6, 16871-76-4; NiF_2, 10028-18-9.

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ON THE SYNTHESES AND PROPERTIES OF SOME HEXAFLUOROBISMUTHATE (V) SALTS AND THEIR USE IN THE METATHETICAL SYNTHESIS OF NF_4^+ SALTS

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SUMMARY

The salts $LiBiF_6$, $NaBiF_6$, $KBiF_6$, $CsBiF_6$ and NF_4BiF_6 were prepared and characterized. Differences in the observed numbers and relative intensities of some of the Raman bands of these salts are explained by crystal effects. Solubilities of these salts in anhydrous HF at -78° were determined and compared to those of the corresponding SbF_6^- salts. It was shown that, contrary to a previous report, $CsBiF_6$ does not exhibit any unusual properties such as forming a mushy volatile HF adduct. The potential of NF_4BiF_6 based metathetical processes for the production of other NF_4^+ salts was evaluated. The novel $H_3O^+BiF_6^-$ salt was prepared and characterized. The usefulness of BiF_5 for water removal from HF is briefly discussed.

INTRODUCTION

In the course of our work on oxonium salts [1] and metathetical NF_4^+ salt processes [2-6], we became interested in pentavalent bismuth compounds as possible replacements for the corresponding antimony compounds. For example, the use of the less volatile BiF_5 has been proposed [1], but has never been tested, as an alternative to SbF_5

for removal of small amounts of water from HF. Because NF_4BiF_6 has become readily accessible by direct thermal synthesis from NF_3, F_2, and BiF_5 [7], it holds potential as a starting material in metathetical processes for the production of other less accessible NF_4^+ salts. However, its usefulness in such a process depends on the relative solubilities of its salts in a suitable solvent, such as anhydrous HF. Although BiF_6^- salts have been known [8] since 1950, only a small number of papers [7, 9-18] dealing with BiF_6^- salts have been reported since then, and some of the reported data are very much open to question. For example, Surles and coworkers reported [13] that HF formed a stable adduct with $CsBiF_6$ and that this adduct readily sublimed on heating. Consequently, a more systematic study of BiF_6^- salts was necessary in order to be able to properly evaluate the potential of BiF_6^- salts in the above applications.

EXPERIMENTAL

Materials and Apparatus

The apparatus, handling procedures, and the method used for the HF drying have previously been described [1,6]. Bismuth pentafluoride (Ozark Mahoning Co.) did not contain any detectable impurities and was used as received. Antimony pentafluoride (Ozark Mahoning Co.) was distilled prior to use. Lithium fluoride (Baker, A. R.) and NaF (MCB, Reagent grade) were used as received. Potassium fluoride (Allied, Reagent grade) and CsF (KBI) were dried by fusion in a platinum crucible and powdered in the drybox. The syntheses of NF_4BiF_6 [7] and NF_4SbF_6 [4] have previously been described. Except for $NaBF_4$ which was obtained from H_3BO_3 and Na_2CO_3 in concentrated aqueous HF solution, all the alkali metal tetrafluoroborates were prepared by introducing a slight excess of gaseous BF_3 into stirred solutions of the corresponding alkali metal fluorides in anhydrous HF at 20°, followed by removal of the volatile products.

Syntheses of BiF_6^- and SbF_6^- Salts

For the syntheses of the alkali metal hexafluorobismuthates, equimolar amounts of finely powdered alkali metal fluoride and BiF_5 were heated in a Monel cylinder for several days to 280° under 2 atm of F_2. The vibrational spectra of the resulting products showed no evidence for the presence of either unreacted BiF_5 [19] or polybismuthate salts [7]. When these reactions were carried out at 150°, however, the products contained some polybismuthate salts. The alkali metal hexafluoroantimonates were prepared in a similar manner by heating equimolar mixtures of SbF_5 and the corresponding alkali metal fluoride in a F_2 atmosphere to 280°. Again, vibrational spectra of the solid products showed no evidence for the presence of polyantimonates.

Spectra

Infrared spectra of solids were recorded as dry powders between pressed AgCl or AgBr disks on a Perkin Elmer Model 283 spectrometer. Raman spectra were recorded in glass melting point, quartz or Kel-F capillaries on a Cary Model 83 spectrophotometer using the 4880Å exciting line of an Argon ion laser. Debye-Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with nickel filtered copper Kα radiation and quartz capillaries as sample containers. The thermal decomposition of salts was examined with a Perkin Elmer differential scanning calorimeter (Model DSC-1B) using crimp-sealed aluminum pans as sample containers and a heating rate of 2.5°/min at atmospheric pressure.

Solubility Measurements

Solubilities of the salts in anhydrous HF at -78° were measured in an apparatus similar to that previously described [6] for metathetical reactions, except for eliminating trap I. Saturated solutions were prepared at -78° and separated from excess undissolved salt by filtration at -78°. The HF solvent was pumped off at ambient temperature, and the amount of HF used and of the solid residues obtained after HF removal were determined by weighing.

Metathetical Reactions

Metathetical reactions between NF_4BiF_6 or NF_4SbF_6 and different alkali metal tetrafluoroborates in anhydrous HF solution were carried out as previously described [4,6].

Synthesis of H_3OBiF_6

Bismuth pentafluoride (10.08 mmol) was transferred in the glove box into a passivated (with ClF_3) Teflon FEP ampule containing a Teflon coated magnetic stirring bar. Anhydrous HF (10.12 g) which had been stored over BiF_5 was condensed into the ampule at -196°. The mixture was warmed to room temperature, and the Raman spectrum of the resulting clear solution was recorded. It showed bands similar, but not identical, to those expected for either BiF_6^- (see below) or solid BiF_5 [16, 19]. The ampule was cooled to -196°, and distilled H_2O (10 mmol) was syringed into the ampule. On warm up to ambient temperature, a copius white precipitate was formed. The mixture was stirred for ten hours at 25°. The Raman spectrum of the clear solution above the white solid precipitate showed the bands characteristic for BiF_6^- (see below). Removal of the HF solvent in a dynamic vacuum at -45° resulted in the formation of a white solid (3.469g, weight calcd for 10.08 mmol of H_3OBiF_6 = 3.447g) which was identified by Raman and infrared spectroscopy as $H_3O^+BiF_6^-$. This solid was stable at ambient temperature only under an HF pressure of about 20mm. On evacuation of the ampule, the white solid would immediately turn dark brown. When the valve of the ampule was closed to allow the pressure to build up again, the white color of the sample was restored. Complete decomposition of H_3OBiF_6 in a dynamic vacuum at 35° for 3 days resulted in a light cream colored solid. Based on its weight, physical properties (nonhygroscopic, insoluble in H_2O and aqueous HCl, sublimination at the softening point of glass), and elemental analysis (found: Bi, 77.2; F, 23.3; O, 0.2; calcd for BiF_3: Bi, 78.57, F, 21.43; O, 0) this solid appeared to be mainly BiF_3. The vibrational spectra of the solid decomposition product did not show any evidence for the presence of either H_3O^+ or BiF_6^-.

RESULTS AND DISCUSSION

Syntheses and Properties of Hexafluorobismuthates

The alkali metal hexafluorobismuthates were prepared from equimolar amounts of BiF_5 and the corresponding alkali metal fluoride by heating to 280° in a Monel cylinder. Fluorine was added to the cylinder to suppress possible decomposition of BiF_5 to BiF_3 and F_2. This synthesis is similar to that [9] previously reported, except for using a significantly higher temperature. Using the previously reported [9] temperature conditions (85-150°), the product always contained some polybismuthate salt. For the syntheses of the alkali metal hexafluoroantimonates, similar reaction conditions were required to suppress the formation of polyantimonates.

The rather unusual properties previously reported [13] for $CsBiF_6$ could not be confirmed. Thus, $CsBiF_6$ was quantitatively recovered from HF solutions by pumping at ambient temperature, without any evidence for the formation of a stable $CsBiF_6 \cdot xHF$ adduct. Furthermore, no evidence was found for sublimation without decomposition for either HF treated or untreated $CsBiF_6$. DSC data obtained for $CsBiF_6$ showed a small reversible endotherm at 190°, attributed to a phase change, and the onset of a large endotherm at 308°, attributed to decomposition. Thermal decomposition of $CsBiF_6$ around 300° was confirmed by visual observation of samples sealed in melting point capillaries. At this temperature, sublimation of BiF_5 to the colder parts of the capillary occurred. For comparison, DSC data were also recorded for $CsSbF_6$. They showed a small reversible endotherm (phase change) at 187° and the onset of endothermic decomposition at 296°. These data show that the thermal stabilities of $CsSbF_6$ and $CsBiF_6$ are similar, with the bismuth salt being slightly more stable.

The vibrational spectra of the alkali metal hexafluorobismuthates were also recorded and showed some remarkable differences (see Figure 1). Particularly, the Raman active deformation mode exhibited different numbers of bands and intensity ratios. In order to determine whether the observed splittings were caused by the simultaneous presence of more than one crystal modification, the Debye-Scherrer powder patterns of these compounds were recorded. In excellent agreement with a previous report [10], it was found that $LiBiF_6$ and $NaBiF_6$ were rhombohedral ($LiSbF_6$ type), $KBiF_6$ was cubic (low-temperature α-modification), and $CsBiF_6$ was rhombohedral ($KOsF_6$ type). No evidence was found for the presence of other modifications in either the thermally prepared (280°) or the HF recrystallized (-78°) samples. The observed splittings can be readily explained, however, by solid state effects. In the rhombohedral compounds (space group $R\bar{3}-C_{3i}^{2}$, Nr. 148, 1 molecule per Bravais cell [10]), the site symmetry of BiF_6^- is C_{3i}.

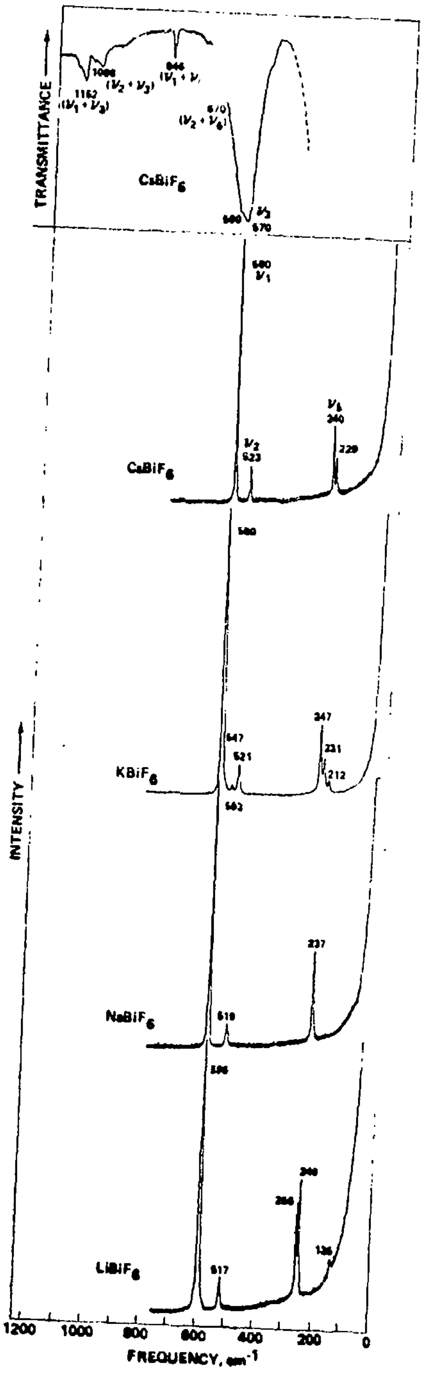

Figure 1.

Infrared spectrum of $CsBiF_6$ and Raman spectra of $CsBiF_6$, $KBiF_6$, $NaBiF_6$, and $LiBiF_6$. The infrared spectrum was recorded as a dry powder between pressed AgCl disks. The broken line is due to absorption by the window material.

TABLE I.

Correlation Table for Isolated BiF_6^- of Point Group O_h and for Site Symmetry C_{3i}

O_h	C_{3i}
A_{1g}	A_g
E_g	E_g
F_{2g}	$A_g + E_g$
F_{1u}	$A_u + E_u$
F_{2u}	$A_u + E_u$

Therefore, from Table I only the F_{2g} mode in the Raman and the F_{1u} modes in the infrared are expected to be split into two components. For cubic $KBiF_6$ (space group Ia3, Nr. 206) the site symmetry of BiF_6^- is again C_{3i}, but since the Bravais cell contains four molecules, factor group splitting can further cause the doubly degenerate E_g modes to split into two components. These predictions are in good agreement with our observations (see Figure 1), except for $NaBiF_6$ which exhibits only one Raman band in the BiF_6^- deformation region. This lack of splitting for $NaBiF_6$ is attributed to a coincidence of the frequencies of the A_g and the E_g components of ν_5. This is plausible since the weaker (probably the E_g) component has a higher frequency in $LiBiF_6$ and a lower frequency in $CsBiF_6$ than the more intense (probably the A_g) component. The frequency separation of the two components in $NaBiF_6$ must be rather small since, even at a spectral slit width of 1 cm^{-1}, we could not resolve the band into two components.

The infrared spectrum of $CsBiF_6$ (see Figure 1) shows a very intense and broad band for the antisymmetric BiF_6^- stretching mode ν_3 (F_{1u}) at 570 cm^{-1}. It exhibits a pronounced shoulder at 590 cm^{-1} which probably represents the second component of ν_3 predicted for C_{3i} symmetry (see Table 1). In addition, several infrared allowed combination bands were observed (see Figure 1). From these, the frequencies of the two remaining deformation modes can be derived as: $\nu_4(F_{1u}) = 277$ and $\nu_6(F_{2u}) = 147$ cm^{-1}. It should be noted that the combination bands involving ν_3 show splittings of about 20 cm^{-1}, analogous to that exhibited by ν_3 itself. This lends further support to the above assignments.

The previously reported [16] Raman spectrum of $NOBiF_6$ exhibits the same splittings and intensity pattern as α-$KBiF_6$, indicating that the two compounds are probably isotypic. Of the six frequency values reported by Bougon and coworkers [14] for BiF_6^-, ν_4 and ν_5 appear too low and should be revised. In agreement with a previous report [7], it was found that infrared spectroscopy is well suited for the detection of polybismuthate impurities in BiF_6^- salts. The polyanions result in an intense infrared band at around 440 cm^{-1}.

Solubility Measurements

The metathetical production of NF_4^+ salts is based on the following principle. A readily available and highly soluble NF_4^+ salt, such as NF_4SbF_6, is reacted in a suitable solvent, such as anhydrous HF, with an alkali metal salt containing the desired anion. If the alkali metal is chosen in such a manner that the starting materials and the desired NF_4^+ salt product are highly soluble and the resulting alkali metal SbF_6^- salt, for example, is of very low solubility, the following general equilibrium, where X=Sb, can be shifted far to the right hand side:

$$MY + NF_4XF_6 \xrightarrow{HF} MXF_6\downarrow + NF_4Y$$

The principle has been demonstrated for salts where Y = BF_4^- [2-4], SnF_6^{2-} [6], TiF_6^{2-} [5], and NiF_6^{2-} [20]. Prior to now, X had always been Sb; but the case where X could be Bi had not been tested. Since NF_4BiF_6 has recently become readily available by direct synthesis [7], and since an extrapolation of crude solubility data, previously measured [2] for alkali metal XF_6^- salts (X=As, Sb) in HF at room temperature, indicated that $LiBiF_6$ might possess the lowest solubility of any MXF_6 salt, quantitative solubility data for MXF_6 salts in anhydrous HF were desired. These data should allow to determine whether a BiF_6^- based process would offer any significant advantages over one based on SbF_6^-.

The solubilities of NF_4^+ and of several alkali metal BiF_6^- and SbF_6^- salts were measured in anhydrous HF at -78°. The low temperature was chosen based on our past experience [4]. The results of our measurements are summarized in Table II. As can be seen, the measured solubilities clearly favor a process based on a cesium rather than a lithium salt. Furthermore, the solubility of $CsBiF_6$ is only slightly lower than that of $CsSbF_6$, thus not compensating for the significantly lower solubility of the NF_4BiF_6 starting material in HF and its less favorable formation rate [7], compared to those of NF_4SbF_6 [4]. Consequently, based on all the presently available experimental data, a $CsSbF_6$ based process appears to be the most attractive method for the metathetical preparation of other NF_4^+ salts.

TABLE II

Solubilities of Various BiF_6^- and SbF_6^- Salts in Anhydrous HF at -78°

Anion / Cation	SbF_6^-		BiF_6^-	
	a	b	a	b
NF_4^+	259.0	0.7951	173.1	0.4191
Li^+	9.21	0.0379	11.9	0.0361
Na^+	7.48	0.0289	25.6	0.0740
K^+	c	c	20.2	0.0558
Cs^+	1.80	0.00488	1.71	0.00373

a) in mg of solute per g of HF

b) in mole of solute per 1000g of HF

c) not measured

Metathetical NF_4BF_4 Production

Since in the metathetical production of NF_4BF_4 highly concentrated HF solutions are used, the activity coefficients of the ions are expected to differ significantly from those of the more dilute solutions of the solubility measurements. Consequently, the knowledge of solubility data is insufficient to predict accurately the product composition obtainable from metathetical experiments.

Metathetical NF_4BF_4 production runs using different MBF_4 and NF_4XF_6 salts in HF were carried out. Typical results from such experiments are shown in Table III. As can be seen, the data of Tables II and III are only in qualitative, but not quantitative, agreement. As expected, the solubilities of the alkali metal hexafluoro-antimonates and bismuthates are much higher in the concentrated solutions of the metathetical runs. Furthermore, Table III shows that a cesium salt-based process results in the best product purity. The extremely low yield of NF_4BF_4 for the KBF_4 - NF_4SbF_6 system is caused by KBF_4 being less soluble in HF than $KSbF_6$. Keeping the difference in the stoichiometry of the used starting materials in mind, (see footnote of Table III) the results obtained for the $LiBF_4$ - NF_4SbF_6 and the $LiBF_4$ - NF_4BiF_6 system are roughly comparable.

TABLE III.

Comparison of the Composition of the Crude Products Obtained by the Metatheses of NF_4^+ Salts with Different Alkali Metal Tetrafluoroborates in HF at -78°

System[a]	Composition of Product (weight %)		
	NF_4BF_4	NF_4XF_6	MXF_6
$LiBF_4$ - NF_4SbF_6	81.7	8.4	9.9
$LiBF_4$ - NF_4BiF_6	86.7	5.9	7.4
$NaBF_4$ - NF_4SbF_6	68.3	12.6	19.1
KBF_4 - NF_4SbF_6	15.3	79.6	5.1
$CsBF_4$ - NF_4SbF_6	85.4	13.3	1.3

(a) A 5 mole % excess of the NF_4^+ salt was used in all runs, except for the $LiBF_4$ - NF_4BiF_6 system, where approximately stoichiometric amounts of starting materials were used.

Oxonium Hexafluorobismuthate

Our interest in the possible existence of $H_3O^+BiF_6^-$ was twofold. The salt has previously been proposed [1] as a potential candidate for the removal of traces of water from HF. Furthermore, its possible formation in wet HF solutions of BiF_5 might interfere with metathetical experiments, or result in undesired by-products, particularly when BiF_6^- salts are prepared from BiF_5 and alkali metal fluorides in HF solution [13].

It was found that, contrary to a previous literature report [13], BiF_5 is quite soluble in anhydrous HF and has a solubility in excess of 300 mg of BiF_5 per g of HF at 22°. The Raman spectrum of this solution (Figure 2, trace A) significantly differs in the deformation region from those of the BiF_6^- anion in HF solution (Figure 2, trace B) and of solid BiF_5 [16, 19], but is not unreasonable for an associated hexacoordinated bismuth fluoride.

On addition of water to this solution a copious white precipitate formed. The formation of this less soluble solid in the presence of small amounts of water could explain the previous report [13] on the low solubility of BiF_5 in supposedly anhydrous HF. The Raman spectrum (Figure 2, trace B) of the HF solution above the white solid showed one polarized (591 cm^{-1}) and two depolarized bands (520 and 220 cm^{-1}), in agreement with our expectations for octahedral BiF_6^-. These frequency values are similar to those observed for the alkali metal BiF_6^- salts in the solid state (see above). The Raman spectrum of the precipitate was also recorded and was similar to that of the liquid phase. These observations show that water addition converts HF dissolved BiF_5 into a BiF_6^- salt.

Further identification of the formed precipitate was achieved by pumping off the HF solvent at -45°. Based on the observed material balance and vibrational spectra, the following reaction occurred

$$H_2O + HF + BiF_5 \longrightarrow H_3O^+BiF_6^-$$

The Raman spectra of the solid product (Figure 2, traces C) showed the presence of the bands characteristic for BiF_6^- (see above) and H_3O^+ [1]. The presence of these ions was further confirmed by infrared spectroscopy at -196° which showed a strong band at 3240 cm^{-1} with a shoulder at 3000 cm^{-1} due to H_3O^+ stretching and a very intense

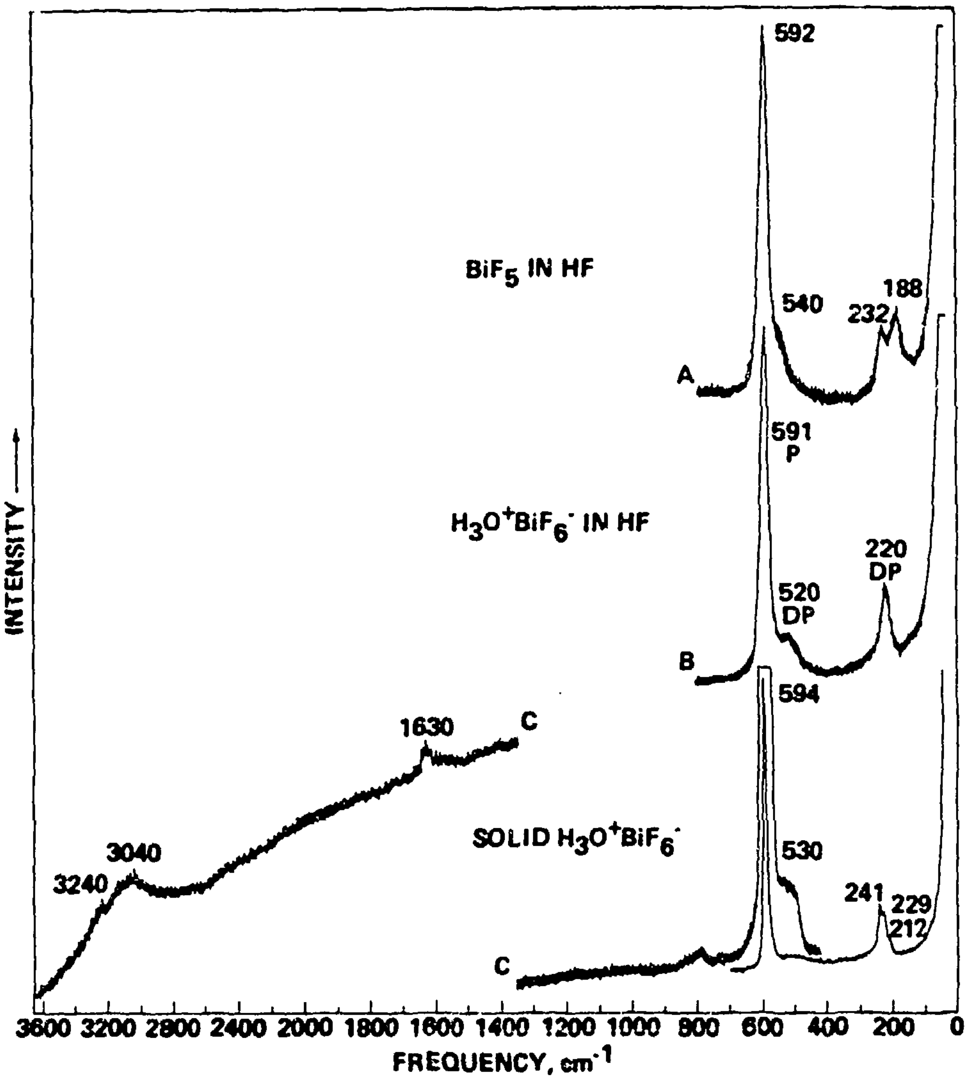

Figure 2. Raman spectra of a 1 molar solution of BiF_5 in HF (trace A), a saturated solution of H_3OBiF_6 in HF (trace B), and of solid H_3OBiF_6 (trace C). All spectra were recorded at room temperature. P and DP indicates polarized and depolarized lines, respectively.

broad band with maxima at 598, 566 and 538 cm^{-1} due to BiF_6^- stretching. The splittings for the BiF_6^- stretching mode is not surprising since at the low temperature rotational motions of the ions in the crystal lattice are frozen out [1] causing symmetry lowering due to strong anion-cation interactions. The same temperature effect was observed for the Raman spectra. At -100°, the 594 cm^{-1} band was observed to split into the following bands: 595 vs, 586 s, 574 mw, 562 w, 555 sh.

An interesting behavior was observed for solid H_3OBiF_6. At ambient temperature, H_3OBiF_6 appears to be stable only under an HF pressure of about 20 torr.When the HF is pumped off, the compound turns instantly dark brown indicating hydrolysis of BiF_5 [9]. When the HF pressure is restored, the solid turns white again. The nature of the decomposition product was established by allowing a sample of H_3OBiF_6 to completely decompose in a dynamic vacuum for 3 days at 35°. The solid residue was found to be mainly BiF_3, as expected from the known [9] hydrolysis of BiF_5. Based on these observations, it appears that H_3OBiF_6 first undergoes a reversible dissociation according to

$$H_3OBiF_6 \rightleftharpoons H_2O + HF + BiF_5$$

followed by the irreversible hydrolysis

$$BiF_5 + H_2O \longrightarrow BiF_3 + 2HF + 1/2O_2$$

with the first step being strongly suppressed by HF.

Although the thermal stability of H_3OBiF_6 appears to be lower than that [1] of H_3OSbF_6, the following reaction cycle might offer a convenient method for drying HF:

$$BiF_5 + H_2O + HF \longrightarrow H_3OBiF_6$$

$$H_3OBiF_6 \longrightarrow BiF_3 + 3HF + 1/2O_2$$

$$\underline{BiF_3 + F_2 \longrightarrow BiF_5}$$

$$H_2O + F_2 \longrightarrow 2HF + 1/2O_2$$

The advantage of this cycle over one using SbF_5 would be that BiF_5 is a nonvolatile solid which is easier to handle. As shown by the above equations, the proposed cycle amounts to a fluorination of water to yield HF and oxygen. Although this objective can also be achieved by a direct treatment of wet HF with high pressure fluorine with agitation [1], the proposed cycle could offer practical advantages. For example, in the proposed cycle the fluorination step could be limited to a relatively small amount of BiF_3 instead of treating the bulk of the HF with a large excess of high pressure fluorine which has to be recovered.

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SHORT COMMUNICATION

On the Synthesis of the $N_2F_5^+$ Cation. A Critical Comment on the Paper by Toy and Stringham.

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Toy and Stringham recently reported [1] the synthesis of $N_2F_5^+(CF_3)_3CO^-$, a salt containing the novel pentafluorohydrazinium cation. This cation would be of significant academic and practical interest [2] since it would constitute the first known example of a substituted NF_4^+ cation, i.e. an NF_4^+ cation in which a fluorine ligand is replaced by an NF_2 group. According to the authors of [1], $N_2F_5^+(CF_3)_3CO^-$ was formed in a very unusual reaction involving the transfer of a fluorine cation from $(CF_3)_3COF$ to N_2F_4 according to:

$$(CF_3)_3COF \longrightarrow (CF_3)_3CO^- + F^+ \xrightarrow{+N_2F_4} N_2F_5^+(CF_3)_3CO^-$$

Since such a heterolytic fission [3] of $(CF_3)_3COF$ with F^+ formation is unlikely, the reported [1] synthetic and spectroscopic evidence for $N_2F_5^+(CF_3)_3CO^-$ was critically reviewed. The following points indicate that the reported white solid is not $N_2F_5^+(CF_3)_3CO^-$, but most likely the known [4] compound $(NO^+)_2SiF_6^{2-}$.

(1) The reference, cited by the authors of [1] for the known existence of $N_2F_5^+$, is Sheppard and Sharts' book on Organic Fluorine Chemistry (Benjamin, New York 1969, page 328). Although this book lists the reaction of N_2F_4 with AsF_5 to yield $N_2F_5^+AsF_6^-$, this is clearly a typographical error. Examination of the original reference [5] shows that the product from this reaction is $N_2F_3^+AsF_6^-$, in agreement with other previous reports [6,7], and unpublished results from this laboratory.

(2) It was also reported [1] that the white solid was formed only in a Pyrex vessel, but not in a copper vessel. The slow reaction proceeded with the formation of a brown gas. This is charcteristic of the well known [8] attack of glass by nitrogen fluorides to form $(NO)_2SiF_6$ as the principal product. The observed [1] weight of the solid product (50% yield based presumably on the molecular weight of $N_2F_5^+(CF_3)_3CO^-$) is in fair agreement with that expected for a high yield formation of $(NO)_2SiF_6$ according to:

$$N_2F_4 + 2(CF_3)_3COF \longrightarrow 2NF_3 + (CF_3)_3COOC(CF_3)_3$$

$$2NF_3 + SiO_2 \longrightarrow (NO)_2SiF_6$$

Unfortunately, no elemental analysis was reported for the white solid, and its identification was based only on infrared, mass, and ^{19}F nmr spectroscopy.

(3) For the infrared spectrum of the solid, pressed as a NaCl disk, the following absorptions were reported [1]: 1450 (s), 1233 (s), 809 (vs), 730 (vs), and 480 (s) cm^{-1}. These bands do not agree with expectations for either a tertiary perfluorobutoxy group [9,10] or a nitrogen fluoride cation [2, 7, 11]. However, the bands at 730 and 480 cm^{-1} are in excellent agreement with those of the SiF_6^{2-} anion [12]. The bands at 1450 and 1233 cm^{-1} are characteristic [12] for the HF_2^- anion, which could readily form from $(NO)_2SiF_6$ and NaCl in the presence of moisture. No infrared data were reported for the higher frequency range which would allow a positive identification of the NO^+ cation.

(4) For the mass spectrum only 4 mass peaks were reported [1] at 104, 85, 71 and 52 m/e. The peaks at 104 and 85 were assigned to $N_2F_4^+$ and $N_2F_3^+$, respectively, but since N_2 has the same mass as Si, they can equally well be assigned to SiF_4^+ and SiF_3^+. Based on their observed relative abundances of 2 and 100, respectively, we prefer their assignment to SiF_4 [13], which is the product expected for the thermal dissociation of a SiF_6^{2-} salt. It is important to note that no fragments due to $(CF_3)_3CO^-$ could be detected [1] for the white solid.

(5) The ^{19}F nmr spectrum of an HF solution of the product showed at room temperature only one exchange broadened resonance at ϕ=204 due to HF. On cooling to -80°C a singlet at ϕ=149 appeared which was assigned [1] to the $(CF_3)_3CO^-$ anion. However, for a tertiary perfluorobutoxy group a resonance around ϕ=70 should be expected [9, 10]. Furthermore, we cannot envision a mechanism which could provide for a rapid fluorine exchange between the covalent CF_3 groups and the HF solvent. On the other hand, the observed chemical shift and exchange characteristics are in line with expectations for a silicon fluoride. Unpublished work in this laboratory has shown that the SiF_6^{2-} anion is unstable in HF solution undergoing solvolysis according to $SiF_6^{2-} + 2HF \rightleftharpoons SiF_4 + 2HF_2^-$. The chemical shifts reported for SiF_4 in CCl_4 and SiF_6^{2-} in H_2O are ϕ=160 and 126, respectively, and acid was found to catalyze fluorine exchange between SiF_6^{2-} and F^- [14].

In summary, all the experimental data available for the reported [1] white solid are consistent with a hexafluorosilicate salt, such as $(NO)_2SiF_6$, but cannot be reconciled with the proposed composition $N_2F_5^+(CF_3)_3CO^-$.

Very recently, Stringham and Toy have also claimed [15] the synthesis of $N_2F_5^+BF_4^-$ by the photolytic reaction of N_2F_4 and BF_3 in the presence of fluorine below -100°C. Based on our experience, these reaction conditions are not likely to produce an $N_2F_5^+$ salt. Generally, compounds containing-NF_2 groups readily undergo fluorination to NF_3 during photolysis, followed by formation of NF_4^+ salts [16]. If the reaction is carried out in glass, formation of FNO is also possible, which can result in the formation of $NO^+BF_4^-$. Unpublished work in this laboratory has also shown that N_2F_4 does not form a stable adduct with BF_3 at temperatures as low as -78°C. At -78°C, an equimolar mixture of N_2F_4 and BF_3 is still liquid and can be transferred quantitatively from trap to trap. Therefore, the only solid products expected from the photolysis of N_2F_4-F_2-BF_3 mixtures in glass are NF_4BF_4 and BF_4^- salts of NO^+ or NO_2^+.

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Electron Spin Resonance Evidence for the Formation of the NF_3^+ Radical Cation as an Intermediate in the Syntheses of NF_4^+ Salts by Low-Temperature Ultraviolet Photolysis

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The mechanism of the formation of NF_4^+ salts is of significant practical and theoretical interest. From a practical point of view, a better understanding of this mechanism would permit optimization of the reaction conditions for the direct syntheses of NF_4^+ salts, such as NF_4BF_4, NF_4PF_6, or NF_4GeF_5.[1] From a theoretical point of view, the formation of the NF_4^+ cation is intriguing[2] because its parent molecule NF_5 does not exist as a stable species. Since under the conditions used for most of the syntheses of NF_4^+ salts an F^+ cation should be extremely difficult, if not impossible, to prepare by chemical means, the following mechanism has previously been proposed[2] for the formation of NF_4AsF_6:

$$F_2 \xrightarrow{\Delta E} 2F\cdot \tag{1}$$

$$F\cdot + AsF_5 \rightarrow AsF_6\cdot \tag{2}$$

$$AsF_6\cdot + NF_3 \rightarrow \dot{N}F_3^+AsF_6^- \tag{3}$$

$$\dot{N}F_3^+AsF_6^- + F_2 \rightarrow NF_4^+AsF_6^- + F\cdot \tag{4}$$

In good agreement with the known experimental facts,[2] this mechanism requires only a moderate activation energy ($D°(F_2) = 36.8$ kcal mol^{-1}).[3] The two critical intermediates are the $AsF_6\cdot$ radical and the $\dot{N}F_3^+$ radical cation. Whereas the $AsF_6\cdot$ radical is unknown, the $\dot{N}F_3^+$ radical cation was shown[4] to form during γ irradiation of NF_4^+ salts at −196 °C. Although this observation of the $\dot{N}F_3^+$ cation demonstrated its possible existence at low temperature, it remained to be shown that the $\dot{N}F_3^+$ radical cation is indeed formed as an intermediate in the syntheses of NF_4^+ salts. We have now succeeded in observing experimentally the $\dot{N}F_3^+$ radical cation by ESR spectroscopy as an intermediate in the low-temperature UV photolyses of both the NF_3–F_2–AsF_5 and the NF_3–F_2–BF_3 systems. The results and implications derived from the observations are given in this paper.

Experimental Section

Binary and ternary mixtures of the starting materials were prepared for both the NF_3–F_2–BF_3 and the NF_3–F_2–AsF_5 systems in a stainless-steel Teflon FEP vacuum system. The sample tubes consisted of flamed-out quartz tubes of 4-mm o.d., 30-cm long, with a ballast volume of about 150 mL attached at the top. The starting materials were condensed into these tubes at −210 °C and the tubes were flame sealed. The NF_3 (Rocketdyne) was used without further purification, F_2 (Rocketdyne) was passed through a NaF scrubber for HF removal, and BF_3 (Matheson) and AsF_5 (Ozark Mahoning) were purified by fractional condensation prior to use. About 300 cm^3 of gas mixture was used for each sample tube in the following mole ratios: NF_3:F_2 = 1:10; BF_3:F_2 = 1:10; AsF_5:F_2 = 1:10; NF_3:BF_3 = 1:1; NF_3:AsF_5 = 1:1; NF_3:F_2:BF_3 = 1:4:1 and 1:2:1; NF_3:F_2:AsF_5 = 1:4:1.

The ESR spectra were recorded as previously described.[5,6] Variable-temperature control over the temperature range 4–300 K was achieved with an Air Products liquid-helium-transfer refrigerator, Model LTD110. For the photolyses, an Oriel Model 6240 arc lamp with a 200-W Hg lamp was used. In some of the experiments, the starting materials were condensed at −196 °C into the tip of the ESR tube and were irradiated for 10–30 min while inserted in a liquid-nitrogen-filled unsilvered Dewar. The ESR tube was then quickly transferred to the precooled ESR spectrometer. In other experiments, the sample tubes were irradiated at various temperatures inside the ESR cavity.

Results and Discussion

UV photolysis of both the NF_3–F_2–AsF_5 and the NF_3–F_2–BF_3 systems produced an intensely violet species which exhibited the ESR signal shown in Figure 1, traces A and B. Comparison with the previously published[4] anisotropic spectrum of the $\dot{N}F_3^+$ cation (trace C, Figure 1) establishes beyond doubt the presence of $\dot{N}F_3^+$ in our samples. The spectra are assigned on the basis of anisotropic hyperfine coupling to three fluorine atoms ($I = {}^1/_2$) and approximately isotropic hyperfine coupling to one nitrogen atom ($I = 1$). The g matrix is isotropic to within the line width. The spectra thus appear as a quartet of triplets as shown in Figure 1. The broader line widths observed in the spectra of UV-irradiated NF_3–F_2–AsF_5 and NF_3–F_2–BF_3 mixtures than in γ-irradiated NF_4SbF_6 may be the result of exchange or of dipolar interactions of materials on the surfaces of the solid components of the mixtures.

The observation of identical signals for both the BF_3- and the AsF_5-containing system proves that the signal must be due to a species not containing boron or arsenic. By carrying out irradiation experiments of the sample within the ESR cavity at −196 °C, it was shown that the signal strength increased during irradiation but did not decrease when the lamp was turned off. The thermal stability of the signal in the absence of UV radiation depended on the strength of the Lewis acid used. For the stronger Lewis acid AsF_5, the signal did not change significantly up to about −105 °C, whereas for BF_3 decomposition started at about −155 °C. When the sample tubes were warmed to ambient temperature, they contained white stable solids which were identified by Raman spectroscopy as NF_4AsF_6 and NF_4BF_4, respectively.[1,7,8] Irradiation of all possible binary mixtures, i.e., NF_3–F_2, Lewis acid–F_2, and NF_3–Lewis acid, under comparable conditions did not produce any ESR signal attributable to $\dot{N}F_3^+$.

A positive identification of the proposed $AsF_6\cdot$ or $BF_4\cdot$ radical intermediates was not possible in the above experi-

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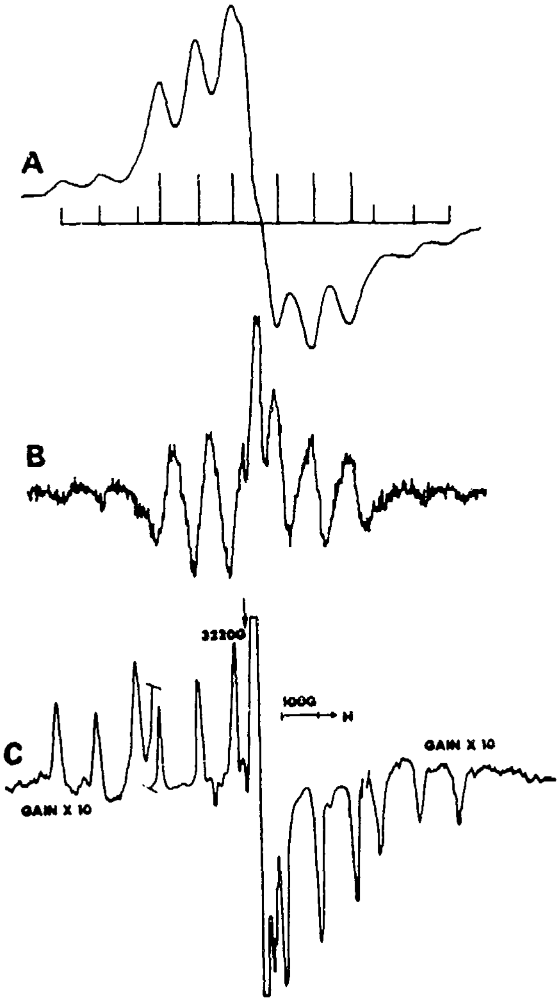

Figure 1. ESR spectra of the $\dot{N}F_3^+$ radical cation obtained by UV photolysis of NF_3–F_2–BF_3 at −196 °C: trace A, first derivative; trace B, second derivative. For comparison, the known[4] first-derivative spectrum of $\dot{N}F_3^+$ obtained by γ irradiation of polycrystalline NF_4SbF_6 at −196 °C is given as trace C.

ments. The observation of hyperfine splittings for the free $AsF_6\cdot$ or $BF_4\cdot$ radical at temperatures above several Kelvins is not likely because they would be in orbitally degenerate states which could cause rapid spin relaxation resulting in a strongly temperature-dependent line width. Furthermore, if we assume the existence of an $AsF_6\cdot$ or $BF_4\cdot$ radical in an ionic lattice, rapid electron exchange between the radicals and the corresponding anions is possible which would destroy hyperfine structure. The line width of the resulting signal would depend on the rate of exchange. Finally, in our experiments we were dealing with polymeric solid AsF_5 or BF_3 phases which on combination with a fluorine radical are not likely to result in an isolated $AsF_6\cdot$ or $BF_4\cdot$ radical. In our experiments, several ESR signals were observed in addition to $\dot{N}F_3^+$. However, in the absence of observable hyperfine structure we prefer not to make any assignments.

On the basis of our results, the following conclusions can be reached concerning the formation mechanism of NF_4^+ salts. (i) The $\dot{N}F_3^+$ radical cation is indeed an important intermediate. (ii) The requirement of UV activation and of both F_2 and a Lewis acid for the synthesis of $\dot{N}F_3^+$ is in agreement with steps 1 and 2 of the given mechanism. (iii) The strength of the Lewis acid determines the thermal stability and lifetime of the intermediate $\dot{N}F_3^+$ salt formed. This can account for the low-temperature conditions required for the synthesis of the NF_4^+ salts of weaker Lewis acids. (iv) In the absence of UV irradiation, the $\dot{N}F_3^+$ salts do not spontaneously react with the large excess of liquid F_2 present. This indicates that in the absence of an activation energy source the thermodynamically feasible[2] chain-propagation step $\dot{N}F_3^+AsF_6^- + F_2 \rightarrow NF_4^+AsF_6^- + F\cdot$ does not play an important role. Possibly, the conversion of $\dot{N}F_3^+AsF_6^-$ to $NF_4^+AsF_6^-$ may require $F\cdot$ atoms according to

$$\dot{N}F_3^+AsF_6^- + F\cdot \rightarrow NF_4^+AsF_6^- \qquad (5)$$

Since the intermediate $\dot{N}F_3^+$ salt is an ionic solid, its reaction with a fluorine atom might well be a heterogeneous diffusion-controlled reaction and step 5 might be the rate-determining step in the mechanism. It was shown that at temperatures above −196 °C, where a given $\dot{N}F_3^+$ salt is still stable in the absence of light, UV irradiation causes a rapid decay of the $\dot{N}F_3^+$ ESR signal. However, it was not possible to distinguish whether this decay was caused by photodecomposition of the intermediate $\dot{N}F_3^+$ salt or by the reaction of the latter with the generated F atoms according to step 5.

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Registry No. $\dot{N}F_3^+$, 54384-83-7; NF_4AsF_6, 16871-75-3; NF_4BF_4, 15640-93-4.

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Vibrational Spectra and Force Fields of the Tetrafluorooxohalate(V) Anions ClF_4O^-, BrF_4O^-, and IF_4O^-

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Improved syntheses are described for BrF_4O^- and IF_4O^- salts, and their vibrational spectra are reported. The spectra of $CsBrF_4O$ are simpler than those previously reported for $KBrF_4O$ and thus allow more reliable assignments. For comparison, the low-temperature Raman spectrum of $CsClF_4O$ has also been recorded. Normal-coordinate analyses have been carried out for the ClF_4O^-, BrF_4O^-, and IF_4O^- anions and are compared to those of the structurally related $HalF_4^-$ anions and $HalF_5$ molecules and those of XeF_4, XeF_4O, and XeF_5^+.

Introduction

The existence of $KBrF_4O$, a salt containing a novel bromine oxyfluoride anion, has recently been reported both by Bougon and co-workers[1] and by Gillespie and Spekkens.[2] It was obtained either by the reaction[1] of $KBrO_3$ with a large excess of BrF_5 at 80 °C in the presence of F_2 or by the reaction[2] of $KBrF_6$ with $KBrO_3$ in CH_3CN solution. Both methods have drawbacks. Although Bougon's method[1] can yield a pure product, the course of the reaction is difficult to control and frequently $KBrF_4$ is obtained as the only product (see below). Gillespie's method[2] produces a mixture of $KBrF_2O_2$ and $KBrF_4O$ which must be separated by numerous extractions with CH_3CN. In view of these difficulties, an improved synthetic method for the synthesis of BrF_4O^- was desirable.

Although the crystal structure of $CsIF_4O$ has been reported,[3] only a small amount of the material had been obtained accidentally during unsuccessful attempts to crystallize $CsIF_6$ from CH_3CN solution. Furthermore, products containing mixtures of MIF_4O and MIF_2O_2 salts have been prepared[4] by the interaction of MIO_3 or MIO_2F_2 with IF_5 or by the controlled hydrolysis of MIF_6 in CH_3CN. However, no suitable method for the preparation of pure MIF_4O has previously been reported.

The vibrational spectra of these $HalF_4O^-$ anions were also of interest. For IF_4O^- only spectra of mixtures of IF_4O^- and $IF_2O_2^-$ salts were known,[4] and for $KBrF_4O$ the previously reported[1,2] Raman spectra exhibited more bands than permitted for an isolated six-atom species. Interionic dynamic coupling was suggested[1] to account for the large number of bands observed for $KBrF_4O$. However, in view of their similar relative intensities, the bands occurring in the 530–390-cm^{-1} region could not be reliably assigned.

In this paper we report improved syntheses for BrF_4O^- and IF_4O^- salts and their vibrational spectra which allow more reliable assignments for these ions. These assignments are supported by normal-coordinate analyses of 12 structurally closely related species.

Experimental Section

Materials. Bromine pentafluoride (Matheson Co.) was treated with 35 atm of F_2 at 200 °C for 24 h prior to its use. Fluorine (Rocketdyne) was passed through a NaF scrubber for removal of HF. The alkali metal perbromates[5] and $CsClF_4O$[6] were prepared as previously described. Potassium bromate (Baker AR) was used as received. Iodine pentafluoride was purified by distillation and I_2O_5 was prepared from I_2 and HNO_3. The KF was dried by fusion in a platinum crucible.

Apparatus. Volatile materials were manipulated in a well-passivated (with ClF_3 and BrF_5) 304 stainless-steel vacuum line equipped with Teflon FEP U-traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

Infrared spectra were recorded on Perkin-Elmer Model 283 and 577 spectrophotometers. For gases a Monel cell with AgCl windows was used. The spectrum of $CsBrF_4O$ was recorded as a dry powder between AgBr windows in the form of a pressed disk. The pressing operation was carried out using a Wilks minipellet press. The spectrum of KIF_4O was recorded as a Nujol mull between CsI windows. Raman spectra were recorded on Cary Model 82 and 83 spectrometers using the 4880-Å exciting line, a Claassen filter[7] for the elimination of plasma lines, and melting-point capillaries or Kel-F tubes as sample containers. For the low-temperature spectra a previously described[8] device was used.

Synthesis of KIF_4O. A mixture of KF and I_2O_5 in a mole ratio of 5:1 was treated with a large excess of IF_5 for 1 h at 25 °C. Volatile products were pumped off, first at 25 °C and then at 100 °C. The white crystalline residue was identified by elemental and spectroscopic analyses as KIF_4O. Anal. Calcd for KIF_4O: K, 15.2; I, 49.2. Found: K, 15.1; I, 49.0.

Syntheses of BrF_4O^- Salts. In a typical experiment, $CsBrO_4$ (2.044 mmol) was placed into a sapphire reaction tube ($^1/_2$ in. o.d. × 12 in. length, Tyco) which contained a Teflon-coated magnetic stirring bar and was attached to a valve through a Swagelok compression fitting using a Teflon front ferrule and a steel back ferrule. Bromine pentafluoride (14.1 mmol) and F_2 (2.4 mmol) were added at −78 °C. The mixture was stirred at 25 °C for 30 h and then cooled to −196 °C. The products volatile at −196 °C were pumped off and those volatile at 25 °C were separated by fractional condensation through a series of traps kept at −64, −95, and −196 °C, respectively. On the basis of their infrared and Raman spectra, they consisted of $FBrO_2$, BrF_5, and $FBrO_3$, respectively. On the basis of its infrared and Raman spectrum, the white solid residue (623 mg) consisted of $CsBrF_4O$ (weight calculated for 2.044 mmol of $CsBrF_4O$ was 623 mg). Similar results were obtained when the reaction was carried out at 70 °C. However, if the reaction was carried in the absence of F_2, the conversion of $CsBrO_4$ to $CsBrF_4O$ was very low, even after prolonged heating to 80 °C. The influence of HF on this reaction was also studied. The addition of 5 mol % (based on $MBrO_4$) HF did not produce significant amounts of BrF_4O^- in the reaction of $CsBrO_4$ with BrF_5 in the absence of F_2 at 25–50 °C.

For the $KBrO_4$–BrF_5–F_2 reaction system, when studied in the same manner as described above for $CsBrO_4$, higher reaction temperatures were required. For example, at 45 °C for 19 h, essentially all of the $KBrO_4$ starting material was recovered unchanged. Heating of the starting materials to 80 °C for 95 h resulted in a conversion of $KBrO_4$ to $KBrF_4O$ of about 70%.

A sample of $KBrF_4O$ was also prepared from $KBrO_3$ and BrF_5 by closely following the procedure published[1] by Bougon. However, when the reaction conditions or the scale of the reaction were slightly modified, several experiments produced $KBrF_4$ in almost quantitative yield, even when the BrF_5 was prefluorinated with 35 atm of F_2 at 200 °C. No evidence was found for the formation of significant amounts of $FBrO_3$ in these reactions.

The $CsClF_4O$–ClF_3 System. A weighed sample of $CsClF_4O$ in a tenfold excess of ClF_3 was stirred for 24 h at 25 °C. The volatile products were pumped off and consisted of unreacted ClF_3 and ClF_3O. On the basis of its weight and vibrational spectra,[9] the white solid

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residue consisted exclusively of $CsClF_4$.

Results and Discussion

Synthesis of XF_4O^- Salts. The reaction of I_2O_5 with a large excess of IF_5 in the presence of a stoichiometric amount of KF affords essentially pure KIF_4O in a one-step reaction according to

$$I_2O_5 + 3IF_5 + 5KF \rightarrow 5KIF_4O$$

This synthesis is based on the previous report[10] of Aynsley et al. that the reaction of I_2O_5 with IF_5 produces IF_3O.

The KIF_4O prepared in this manner is a white, crystalline solid. It is stable up to about 200 °C and hydrolyzes according to

$$KIF_4O + 2H_2O \rightarrow KIO_3 + 4HF$$

Attempts to synthesize K_2IF_5O by changing the $KF:I_2O_5$ ratio in the above synthesis were unsuccessful. On the basis of its vibrational spectra, the resulting product was shown to be $KIF_4O{\cdot}KF$.

For the synthesis of BrF_4O^- salts, the reactions of $MBrO_4$ with F_2 in BrF_5 solution were found to be most reproducible. Whereas $CsBrO_4$ is fluorinated even at ambient temperature, the reaction of $KBrO_4$ requires heating to about 80 °C. Although the formation of BrF_4O^- salts in these reactions was shown to be reproducible and quantitative, the amount of the volatile by-products $FBrO_2$ and $FBrO_3$ varied and was never sufficient to account for all of the missing oxygen. The remaining oxygen was probably in the form of O_2 which was pumped off at −196 °C together with the unreacted F_2. Furthermore, it is remarkable that under the given conditions the reactions did not proceed in the absence of F_2. This implies that F_2 participates in these reactions and does not merely serve the purpose of suppressing a possible reduction of BrF_5 to BrF_3, as was previously suggested[3] for the bromate–BrF_5 system. It was also shown that, contrary to a previous report on the $KBrO_3$–BrF_5 system, the addition of small amounts of HF did not significantly catalyze the $CsBrO_4$–BrF_5 reaction between 20 and 50 °C.

Although the reaction of $KBrO_3$ with BrF_5 to form $KBrF_4O$ which was previously reported[1] by Bougon and co-workers was successfully duplicated in our laboratory, it was difficult to accomplish. Frequently, quantitative conversion to $KBrF_4$ was obtained. Since the BrF_5 used in our experiments had been thoroughly prefluorinated with F_2 at 200 °C, it could not have contained sufficient BrF_3 for a quantitative displacement reaction, such as

$$KBrF_4O + BrF_3 \rightarrow KBrF_4 + BrF_3O$$

That such a displacement reaction of $HalF_4O^-$ by $HalF_3$ can indeed proceed quantitatively was demonstrated in this study for the system

$$CsClF_4O + ClF_3 \rightarrow CsClF_4 + ClF_3O$$

In view of the possibility of such a displacement reaction and the known[11] thermal instability of BrF_3O, the presence of a small amount of BrF_3 might be sufficient to catalyze the decomposition of BrF_4O^- to BrF_4^- according to

$$\begin{tikzcd}[column sep=small] BrF_4O^- + & BrF_3 \arrow[r] & BrF_4^- + BrF_3O \arrow[dl, "\Delta T"] \\ & BrF_3 + {}^1/_2O_2 \arrow[u] & \end{tikzcd}$$

Our finding that BrF_4^- can be readily formed in this system confirms the original report[12] by Schmeisser and Pammer but is inconsistent with the recent report[2] of Gillespie and Spekkens.

From a mechanistic point of view, the reactions of BrF_5 with BrO_3^- or BrO_4^- are very interesting since they involve an oxygen–fluorine exchange. On the basis of the observed quantitative yields of BrF_4O^-, a free-radical mechanism involving the addition of oxygen atoms to bromine fluorides is extremely unlikely. Furthermore, the increased reactivity of the thermally more stable $CsBrO_4$ relative to that of $KBrO_4$ suggests an alkali metal salt catalyzed reaction. A mechanism involving the addition of BrF_5 or BrF_6^- across a Br=O double bond of BrO_4^- or BrO_3^- followed by $FBrO_3$ or $FBrO_2$ elimination with BrF_4O^- formation appears plausible but requires additional experimental support.

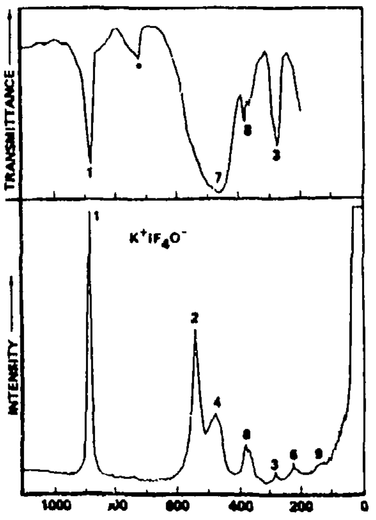

Figure 1. Vibrational spectra of KIF_4O: upper trace, infrared spectrum of a Nujol mull between CsI windows; lower trace, Raman spectrum. The band marked by an asterisk is due to Nujol. The numbers 1–9 designate the assignments to the corresponding fundamentals.

Vibrational Spectra. Vibrational spectra were recorded for KIF_4O, $CsBrF_4O$, $KBrF_4O$, and $CsClF_4O$. The spectra of KIF_4O (see Figure 1 and Table I) are in fair agreement with those[4] previously assigned to the MIF_4O part of MIO_2F_2–MIF_4O mixtures, except for the relative intensities of the 280- and 365-cm⁻¹ infrared bands. This discrepancy is caused by the fact[4] that $IO_2F_2^-$ possesses a strong infrared band at 360 cm⁻¹.

The vibrational spectra of $CsBrF_4O$ are shown in Figure 2. The spectra of $KBrF_4O$ were in excellent agreement with those[1,2] previously reported and, hence, are not reiterated. Surprisingly, the vibrational spectra of $CsBrF_4O$ significantly differed from those of $KBrF_4O$. Since in the $HalF_4$ stretching frequency region the room-temperature Raman spectrum of $CsBrF_4O$ was more similar to that[13] of $CsClF_4O$ than to that[1,2] of $KBrF_4O$, we have also reexamined the Raman spectrum of $CsClF_4O$ (see Figure 3).

By analogy with the previous report[2] on $KBrF_4O$, it was found that cooling of the samples resulted in much better resolved Raman spectra. The observed frequencies of $CsBrF_4O$ and $CsClF_4O$ are summarized in Table I. Attempts to obtain the Raman spectrum of $CsBrF_4O$ in anhydrous HF solution failed owing to the displacement reaction

$$CsBrF_4O + HF \rightarrow CsHF_2 + BrF_3O$$

The observed spectrum was in excellent agreement with that recently reported[11] for BrF_3O.

The previously reported[1,2] Raman spectra of $KBrF_4O$ are very complex and contain more bands than expected for an isolated six-atom species. Furthermore, the relative intensities of many bands are too similar to allow conclusive assignments. In view of these complications and in the absence of additional structural data on BrF_4O^-, the proposed[1,2] C_{4v} structure for BrF_4O^- had to be considered tentative, although very likely.

Table I. Vibrational Spectra of KIF_4O, $CsBrF_4O$, and $CsClF_4O$ and Assignments for $CsBrF_4O$: Observed Frequencies (cm^{-1}) and Relative Intensities[a]

KIF_4O		$CsBrF_4O$			$CsClF_4O$	
			Raman		Raman	
IR	Raman	IR	25 °C	−120 °C	25 °C	−120 °C
885 s	887 (10)	934 vs	931 (4.8)	929 (5.5) ν_1	1223 (0.3)	1228 (0.4)
540 sh	540 (5.8)		500 (10)	499 (10) ν_2	1213 sh	1215 sh
480 vs				482 (2.9) ν_7	1200 (0.6)	1202 (0.7)
	478 (2.3)	570–460 vs	472 (4.4)	471 (4.2) ν_7	1189 (0.2)	1191 (0.4)
383 m	381 (1.3)		444 (3)	444 (3.2) ν_7		1182 sh
366 mw	368 (1)			421 (5.9) ν_8		605 (0.2)
279 ms	283 (0.3)		413 (6.8)	417 (7.9) ν_4	585 (0.6)	588 (0.9)
	224 (0.5)	399 }	400 sh	401 (2.7) ν_6	556 (0.3)	559 (0.5)
	140 (0+)	389 } m		390 (1.5) ν_8	465 sh	470 (5)
		301 vs	299 (1.5)	303 (1.6) ν_3	455 (10)	459 (9)
				291 (0.2) ν_3		452 (10)
		240 sh	236 (1.7)	234 (2.1) ν_6		435 (0.3)
			218 sh	225 sh ν_6		419 sh
			202 (0+)	205 (0.2) ν_5	412 (2.4)	414 (3.5)
			178 (0.5)	179 (0.5) ν_9	395 sh	395 (1.2)
				164 (0.2) ν_9		370 sh
				80	353 (5.5)	358 (6.6)
				62		345 (5)
					335 sh	334 (3.7)
						320 sh
						290 sh
					276 (0.5)	278 (0.6)
						258 (0.2)
						215 sh
						200 sh
					196 (1.0)	194 (1)
						185 sh
					82	89
					70	73

[a] Uncorrected Raman intensities (peak heights).

Table II. Comparison of the Frequencies (cm^{-1}) of the Fundamental Vibrations of the $HalF_4O^-$ Anions with Those of Similar Molecules and Ions

Approx description of mode for XF_4Y in point group C_{4v}			ClF_4O^-	ClF_4^-	ClF_5	BrF_4O^-	BrF_4^-	BrF_5	IF_4^-	IF_4O^-	IF_5	XeF_4	XeF_4O	XeF_5^+
A_1	ν_1	$\nu(XY)$	1203		708	930		682		887	710		926	679
	ν_2	$\nu_{sym}(XF_4)$	456	505	539	500	523	587	522	537	616	543	576	625
	ν_3	δ_{sym}(out-of-plane XF_4)	339	425	495	302	317	369	271	279	318	291	294	355
B_1	ν_4	ν_{sym}(out-of-phase XF_4)	356	417	480	417	449	535	455	480	604	502	527	610
	ν_5	δ_{asym}(out-of-plane XF_4)				205								261
B_2	ν_6	δ_{sym}(in-plane XF_4)	278	288	375	235	246	312	195	219	276	235	233	300
E	ν_7	$\nu_{asym}(XF_4)$	578	590	725	505	478	644	448	482	631	586	608	652
	ν_8	$\delta(YXF_4)$	414		484	395		415		374	372		361	410
	ν_9	δ_{asym}(in-plane XF_4)	194		299	179	[183]	237		140	200		161	218

Consequently, a detailed analysis of the simpler $CsBrF_4O$ spectrum and its comparison with those of ClF_4O^- and IF_4O^- were expected to provide additional support for the proposed C_{4v} model.

Assignments for BrF_4O^-. For an isolated BrF_4O^- anion of symmetry C_{4v} nine fundamental vibrations should be observed. These are classified as 3 A_1 + 2 B_1 + B_2 + 3 E. All nine modes should be Raman active, whereas only the A_1 and E modes should be infrared active. For a solid salt, such as $CsBrF_4O$, the actual site symmetry of the anions is expected to be lower than C_{4v}. This symmetry lowering can cause a splitting of the E modes into their degenerate components and violations of the above given selection rules. Furthermore, if the unit cell contains more than one anion, the number of internal modes can increase by a factor Z, where Z is the number of anions per unit cell. On the basis of tentative unit-cell dimensions reported[1] by Bougon for $KBrF_4O$, Z is estimated to be about 32. Assuming that $CsBrF_4O$ has a similar crystal structure, each mode could be split into many components. However, only a much lower number of bands are usually observed since these correlation splittings are relatively small and usually do not exceed 1–2% of the mode frequency.

Assignments for BrF_4O^- can be made by comparison with the known vibrational spectra of the structurally related species ClF_4O^-,[13] ClF_4^-,[9] ClF_5,[14-17] BrF_4^-,[18] BrF_5,[14,16] IF_4^-,[19] IF_5,[14,16] XeF_4,[19,20] XeF_4O,[14] and XeF_5^+.[21] All of these species are pseudooctahedral with an approximately square-planar XF_4 group. A summary of the frequencies of their fundamental vibrations is given in Table II.

On the basis of its high frequency and relative intensity, the Br=O stretching mode ν_1 (A_1) must be assigned to the band at 930 cm^{-1}. Of the remaining bands, the symmetric in-phase BrF_4 stretching mode ν_2 (A_1) should be the most intense Raman band and by comparison with the known assignments for ClF_4^-, ClF_4O^-, BrF_4^-, IF_4^-, and IF_4O^- should have a frequency in the vicinity of about 500 cm^{-1}. It therefore must be assigned to the Raman band at 500 cm^{-1}. The symmetric out-of-phase BrF_4 stretching mode ν_4 (B_1) should be the second most intense Raman band and, by comparison with the known frequencies of the closely related BrF_4^- anion (see Table II), is predicted to occur about 80 cm^{-1} below ν_2 (A_1). Conse-

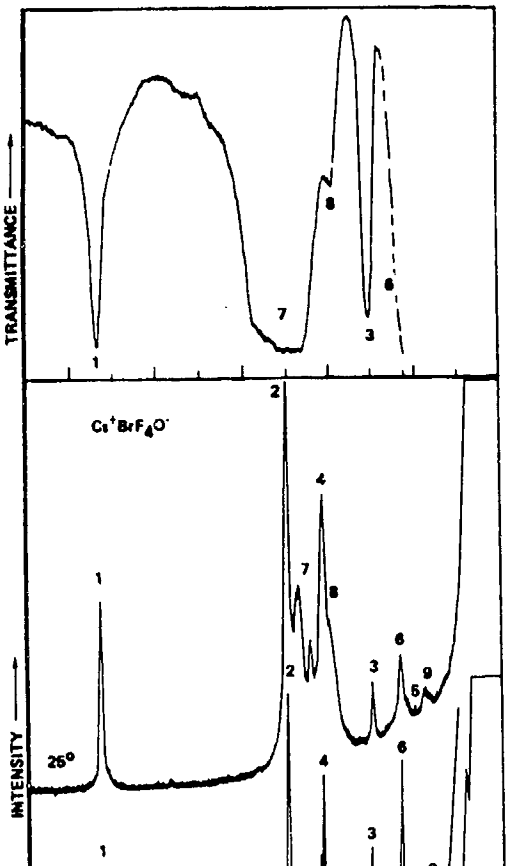

Figure 2. Vibrational spectra of $CsBrF_4O$: upper trace, infrared spectrum of the dry powder in an AgBr disk, the broken line indicating absorption due to the window material; lower traces, Raman spectra recorded at different temperatures and gain settings with a spectral slit width of 2 cm^{-1}.

quently, this mode must be assigned to the band at about 417 cm^{-1}. The last stretching mode, the antisymmetric BrF_4 stretch, ν_7 (E), is expected to result in a very strong and broad infrared band in the 450–550-cm^{-1} frequency region. Such an infrared band has been observed (see Figure 2) and is consequently assigned to ν_7. In the Raman spectrum, there are three bands at 482, 471, and 444 cm^{-1}, respectively, which are assigned to the degenerate ν_7 (E) mode for the following reasons. Their frequencies are too high for a deformation mode and differ by too much from those of the nondegenerate ν_2 and ν_4 modes in order to be accounted for by correlation splittings of the latter. The splitting of ν_7 into three components can be explained by Fermi resonance (see below).

The assignments for the BrF_4O^- deformation modes can be made by comparison with those of BrF_5 and BrF_4^-. In this type of molecule, the umbrella deformation mode ν_3 (A_1) always results in a very intense infrared band and, consequently, is assigned to the strong infrared band at 301 cm^{-1}. Then the 236- and 178-cm^{-1} bands must be due to the symmetric and the antisymmetric in-plane XF_4 deformation modes, ν_6 (B_2) and ν_9 (E), respectively, with ν_6 (see Table II) always having the higher frequency. The $OBrF_4$ deformation mode ν_8 (E) is assigned to the remaining Raman bands at 421, 401, and 390 cm^{-1} which show the expected counterparts of medium intensity in the infrared spectrum. The last yet unassigned deformation mode is the antisymmetric out-of-plane XF_4 deformation ν_5 (B_1). This mode is expected to be of very low intensity and usually is not observed for similar species. Of the compounds listed in Table II, it has only been observed for XeF_5^+ at 261 cm^{-1}. Since the related ν_3 (A_1) mode of XeF_5^+ exhibits a frequency higher by 53 cm^{-1} than that of ν_3 of BrF_4O^-, the frequency of ν_5 of BrF_4O^- might be expected to occur around 210 cm^{-1}. A careful inspection of the Raman spectrum of $CsBrF_4O$ shows indeed a very weak band at 205 cm^{-1} which is therefore assigned to ν_5 (B_1) of BrF_4O^-. The two bands at 80 and 62 cm^{-1}, respectively, observed in the Raman spectrum of $CsBrF_4O$ occur at too low a frequency for internal BrF_4O^- vibrations and must be assigned to lattice modes.

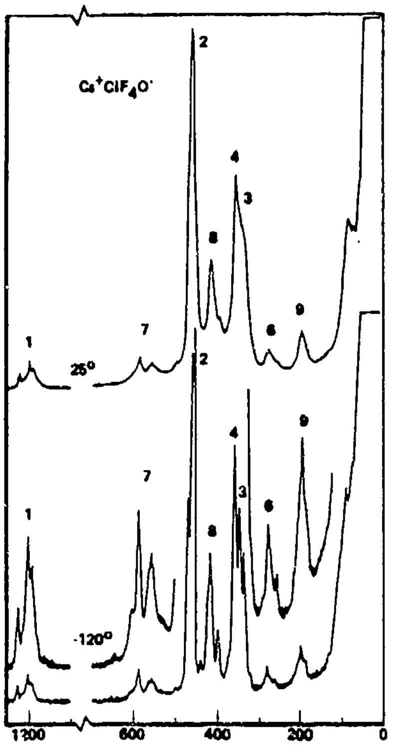

Figure 3. Raman spectra of $CsClF_4O$ recorded at different temperatures and gain settings with a spectral slit width of 2 cm^{-1}.

The splittings, best observed in the low-temperature Raman spectrum of $CsBrF_4O$, can be readily accounted for by assuming a splitting into two components for each of the three doubly degenerate E modes. The additional splittings observed for ν_7 and ν_8 can be readily explained by Fermi resonance of ν_7 and ν_8 with the E mode combination bands ($\nu_3 + \nu_9$) and ($\nu_6 + \nu_9$), respectively. Similarly the splitting observed for ν_3 might be explained by Fermi resonance with a combination band of a lower frequency mode and a lattice vibration. Since bromine contains two naturally occurring isotopes (^{79}Br and ^{81}Br) in almost equal abundance, we have computed the approximate isotopic splittings to be expected for BrF_4O^-. In all cases the computed isotopic splittings were considerably smaller than those observed and the relative intensities did not exhibit the correct 1:1 ratio. Consequently, the observed splittings cannot be attributed to the bromine isotopes.

The assignments proposed for $CsBrF_4O$ are summarized in Tables I and II. When compared to those of the related

Table III. Assumed Molecular Parameters for ClF_4O^-, BrF_4O^-, and IF_4O^-

Parameter	ClF_4O^-	BrF_4O^-	IF_4O^-
R, A (ax)	1.42	1.56	1.72
r, A (eq)	1.75	1.88	1.965
β, deg (<OXF)	90	90	90
α, deg (<FXF)	90	90	90

compounds of Table II, these assignments for BrF_4O^- result in very satisfactory frequency trends. Additional support for the assignments comes from the results of a normal-coordinate analysis (see below).

On the basis of the above assignments for $CsBrF_4O$, the previously reported[1,2] vibrational spectrum of $KBrF_4O$ can be reassigned in the following manner (cm^{-1}): 930 (ν_1); 529 (ν_2); 506, 486, 481, 459 (ν_7); 434 (ν_4); 421, 409, 399 (ν_8); 314 (ν_3); 248, 239 (ν_6); 196, 184, 161 (ν_9).

Assignments for ClF_4O^- and IF_4O^-. The assignments previously proposed[13] for ClF_4O^- have been confirmed by this study. In view of the low-temperature splittings observed for BrF_4O^-, we have examined the low-temperature Raman spectrum of $CsClF_4O$ for similar effects. In general, the assignments for chlorine fluorides are more difficult than those of the corresponding bromine and iodine compounds. This is caused by a well-documented[22] overlap of the frequency ranges of the stretching and the deformation modes. This frequently results in coincidences of fundamental vibrations and, if they belong to the same symmetry species, in their mixing.

Although the room-temperature Raman spectra of $CsBrF_4O$ (see Figure 2) and $CsClF_4O$ (see Figure 3) in the $HalF_4$ stretching frequencies region appear at first glance to be quite analogous, this first impression is somewhat misleading. For ClF_4O^-, the antisymmetric ClF_4 stretching mode ν_7 has a frequency considerably higher than those of the two symmetric stretching modes ν_2 and ν_4, whereas for BrF_4O^- the frequency of ν_7 falls between those of ν_2 and ν_4. Therefore, for ClF_4O^- the bands belonging to ν_7 are well isolated and can be assigned with confidence. The remaining assignment of the ClF_4O^- spectrum has previously been discussed in detail[13] and, therefore, is not reiterated.

For IF_4O^-, the assignments[4] proposed by Milne and Moffett have been adopted, except for ν_9 (E). This mode results in a very weak and broad Raman band. On the basis of frequency correlations with related molecules and force constant arguments, a frequency of about 140 cm^{-1} appears more plausible than the value of 124 cm^{-1} previously proposed.[4]

Table II lists the frequencies of 12 species containing an approximately square-planar XF_4 group. The given assignments are all consistent with each other, thus rendering any gross misassignments for any of these species highly unlikely. The trends observed within this group of 12 species will be discussed in terms of their force constants (see below) rather than in terms of their frequencies since the frequencies of some of the modes are strongly influenced by the mass of the central atom.

Force Constants. The plausibility of the above assignments for the XF_4O^- anions was examined by computations of modified valence force fields and by their comparison with those of the structurally related XF_4 and XF_5 species. The required potential and kinetic energy metrics were computed by a machine method[23] using the geometries listed in Table III. For BrF_4O^- and ClF_4O^- the exact geometries are unknown and therefore idealized bond angles of 90° were assumed. The bond lengths of BrF_4O^- were estimated by comparison with those known for the related species BrF_4^-,[24] BrF_5,[25] and BrO_4^-.[26] For ClF_4O^- the previous estimates[13] were adopted. For IF_4O^- the exact geometry is known.[3] Since the observed OIF bond angle of 89° is very close to the 90° estimates used for ClF_4O^- and BrF_4O^- and since the OXeF bond angle in $XeOF_4$ was found to be larger than 90° (91.8°),[27] we have also used a 90° bond angle for IF_4O^-. This simplifies the computations and makes the resulting force fields more comparable. The force constant definitions used are those[14] of Begun et al. Literature values, for which the deformation coordinates had been weighted by unit (1 Å) distance, were converted back to unweighted values to allow a better comparison. The force constants were adjusted by trial and error, assuming the simplest possible modified valence force field, to give an exact fit between the observed and computed frequencies. The potential energy distribution showed that for the XF_4O^- anions all of the vibrations were highly characteristic (99–100%), except for the E block. However, introduction of small F_{78} terms resulted in the E-block vibrations also becoming highly characteristic (91% or higher). The resulting force fields are summarized in Table IV.

As can be seen from Table IV, the force constants are all very reasonable. A few very minor deviations can be readily explained. For example, f_{rr} of BrF_4^- appears somewhat high. This is caused by using for the antisymmetric stretching mode the relatively low frequency value of 478 cm^{-1} observed for the solution spectrum.[19] For the solid, the band due to this vibration is extremely broad[18] with its band center being closer

Table IV. Comparison of the Symmetry and Internal Force Constants[a] of 12 Species Containing an Approximately Square-Planar XF_4 Group Using the Assignments and Frequency Values of Table II

		ClF_4O^-	$ClF_4^{-\,b}$	$ClF_5^{\,c}$	BrF_4O^-	$BrF_4^{-\,b}$	$BrF_5^{\,c}$	$IF_4^{-\,b}$	IF_4O^-	$IF_5^{\,c}$	$XeF_4^{\,b}$	$XeF_4O^{\,d}$	$XeF_5^{+\,e}$
A_1	$F_{11} = f_R$	9.38		3.51	6.70		4.02		6.56	4.82		7.08	4.35
	$F_{22} = f_r + 2f_{rr} + f_{rr}'$	2.33	2.853	3.24	2.80	3.06	3.81	3.052	3.23	4.22	3.302	3.60	4.38
	$F_{33} = f_\beta + 2f_{\beta\beta} + f_{\beta\beta}'$	0.415	0.630	1.20	0.470	0.577	0.805	0.514	0.575	0.72	0.597	0.601	0.875
B_1	$F_{44} = f_r - 2f_{rr} + f_{rr}'$	1.38	1.946	2.59	1.95	2.258	3.21	2.319	2.58	4.08	2.822	3.11	4.17
	$F_{55} = f_\beta - 2f_{\beta\beta} + f_{\beta\beta}'$				0.682								0.764
B_2	$F_{66} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha}'$	0.216	0.232	0.389	0.154	0.169	0.271	0.106	0.134	0.217	0.155	0.152	0.260
E	$F_{77} = f_r - f_{rr}'$	1.81	1.86	2.43	1.91	1.794	2.97	1.755	2.01	3.39	3.048	3.16	3.65
	$F_{88} = f_\beta - f_{\beta\beta}'$	0.494		0.772	0.386		0.635		0.444	0.526		0.418	0.595
	$F_{99} = f_\alpha - f_{\alpha\alpha}'$	0.157		0.382	0.142	0.143	0.249		0.091	0.192		0.122	0.232
	$F_{78} = f_{r\beta} - f_{r\beta}'$	0.246		0.185	0.128				0.087				
f_R		9.38		3.51	6.70		4.02		6.56	4.82		7.08	4.35
f_r		1.838	2.13	2.674	2.142	2.227	3.24	2.221	2.458	3.77	3.055	3.258	3.968
f_{rr}		0.238	0.23	0.161	0.213	0.20	0.15	0.183	0.163	0.035	0.120	0.123	0.053
f_{rr}'		0.028	0.27	0.244	0.232	0.433	0.27	0.466	0.447	0.38	0.007	0.098	0.318
$f_\alpha^{\,f}$		0.187	~0.2	0.385	0.148	0.156	0.260	~0.1	0.113	0.205	~0.13	0.137	0.246
$f_\beta^{\,g}$		0.46	~0.6	0.98	0.428	~0.5	0.720	~0.46	0.510	0.623	~0.49	0.509	0.735

[a] All values in mdyn/A. [b] Data from ref 19. [c] Data from ref 16. [d] Data from ref 14. [e] Data from ref 21; values of f_{rr} and f_{rr}' in Table V of ref 21 should be exchanged. [f] Assuming $f_{\alpha\alpha} = 0$. [g] Assuming $f_{\beta\beta} = 0$.

to 500 cm^{-1}. If this higher frequency value is chosen, f_{rr} of BrF_4^- becomes more similar to those of BrF_4O^- and BrF_5. Similarly for the lighter central atoms, the off-diagonal symmetry force constants in the E block become more important, thus increasing the uncertainties in these numbers which were obtained from underdetermined force fields.

General Trends. Inspection of Table IV reveals the following trends. Whereas the values of the XF stretching force constants either are similar (within the XF_4^- series) or increase in the direction Cl < Br < I (for XF_4O^- and XF_5), the XO stretching force constant in ClF_4O^- is much higher than those in both BrF_4O and IF_4O^-. Since the values of the XO force constants within the ClO_4^-, BrO_4^-, IO_4^- series (8.24, 6.05, 5.90 mdyn/Å)[28] exhibit the same trend, this seems to reflect a general characteristic of XO bonds. In the XO_4^- series, the central X atom does not possess any free valence electron pair or fluorine ligands, and therefore no special resonance or bonding effects should be invoked. The bond-weakening effect of a formal negative charge in the anions and the bond-strengthening effect of a positive charge in the cations are as expected. The negative charge increases the $X^{\delta+}—F^{\delta-}$ polarity of the XF_4 bonds, thus weakening them. The reverse is true for a positive charge. This effect can also account for most of the observed increase in the force constants when going from an iodine species to the corresponding isoelectronic xenon species which differ by one formal charge.

A comparison of the XF_4^-–XF_4O^- pairs for each halogen shows that for X being chlorine, an oxygen substituent releases electron density to the more electronegative ClF_4 group, thus increasing the polarity of the ClF_4 bonds and decreasing the Cl–F stretching force constant. For X being bromine, there is little change in the X–F stretching force constant indicating comparable electronegativities for oxygen and the BrF_4 group. For X being iodine, oxygen becomes more electronegative than the IF_4 group, thus withdrawing electron density from IF_4 and increasing the covalency of the IF_4 bonds.

The XF_4 deformation constants f_α show the expected trend. With decreasing size of the central atom, the mutual repulsion among the ligands increases and the bonds become more difficult to deform. The FXO angle deformation constant, f_β, does not appear to change significantly when going from chlorine to iodine. However, for a given halogen atom, f_β appears to follow the same trends exhibited by the corresponding XF_4 stretching force constants, f_r.

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Registry No. $CsClF_4O$, 39018-38-7; $CsBrF_4O$, 65391-03-9; KIF_4O, 59654-71-6; KF, 7789-23-3; I_2O_5, 12029-98-0; IF_5, 7783-66-6; $CsBrO_4$, 33259-95-9; BrF_5, 7789-30-2; F_2, 7782-41-4; $KBrF_4O$, 60995-34-8; ClF_3, 7790-91-2; $CsClF_4$, 15321-04-7; ClF_5, 13637-63-3; BrF_4^-, 19702-38-6; IF_4^-, 19702-40-0; XeF_4, 13709-61-0; XeF_4O, 13774-85-1; XeF_5^+, 42879-72-1.

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Bromine Trifluoride Oxide. Vibrational Spectrum, Force Constants, and Thermodynamic Properties

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The infrared spectra of gaseous, solid, and matrix-isolated BrF_3O and the Raman spectra of solid and liquid BrF_3O and of its HF and $FClO_3$ solutions are reported. Nine fundamental vibrations were observed, and some $^{79}Br-^{81}Br$ isotopic shifts were measured in Ne, Ar, and N_2 matrices. These data support a pseudo-trigonal-bipyramidal structure of symmetry C_s with two fluorine atoms at the apexes and one fluorine, one oxygen, and one localized free electron pair at the remaining corners. A modified valence force field was computed using the isotopic data. The results show that the equatorial Br–F bond (f_R = 3.51 mdyn/Å) is significantly stronger than the two axial Br–F bonds (f_r = 2.93 mdyn/Å) and that the bond order of the Br–O bond is close to 2 (f_D = 7.68 mdyn/Å). The vibrational and ^{19}F NMR spectra show that in the liquid and solid state BrF_3O is associated through the axial fluorine atoms. Thermodynamic properties were computed for BrF_3O in the range 0–2000 K.

Introduction

The synthesis of the novel bromine oxyfluoride BrF_3O has recently been reported[1] by Bougon and Bui Huy. On the basis of incomplete vibrational spectra, a structure of symmetry C_s was proposed[1] for BrF_3O. In this paper, the results of a detailed investigation and analysis of the vibrational and ^{19}F NMR spectra of this interesting compound are given which confirm the previously proposed structure.

Experimental Section

Bromine trifluoride oxide was prepared, as previously described,[1] from $KBrF_4O$ and O_2AsF_6 by a displacement reaction in BrF_5. The starting materials $KBrF_4O$ and O_2AsF_6 were obtained by literature methods.[2,3] The vacuum lines, spectrometers, instruments, and sampling techniques used at C.E.N have previously been described.[4,5]

At Rocketdyne, the BrF_3O was prepared in a passivated sapphire reactor which was connected through a small-volume Teflon FEP U-trap to a stainless steel Teflon FEP vacuum system. The crude BrF_3O was collected in this U-trap by fractional condensation at −20 °C and was further purified by briefly pumping off the more volatile components at 0°. The U-trap was incorporated into the matrix-isolation apparatus so that the diluent gas could be swept through the trap into the matrix-isolation inlet system. The length and diameter of the matrix inlet tube were kept at a minimum to avoid decomposition of the BrF_3O. The molar ratio of diluent to sample was controlled by the temperature and hereby the vapor pressure of BrF_3O in the U-trap. In order to avoid extensive decomposition of BrF_3O, rapid deposition rates were required. The matrix-isolation experiments were carried out at 3.6 K using CsI windows and an apparatus previously described.[6,7] A Perkin-Elmer Model 283 spectrometer was used which was calibrated by comparison with standard gas calibration points.[8,9] The reported frequencies and isotopic shifts are believed to be accurate to ±1 and ±0.1 cm^{-1}, respectively.

The recording of infrared spectra of gaseous BrF_3O was found difficult due to rapid attack of the AgCl or AgBr windows. Since the attack of the AgBr windows was very rapid, they were protected by a 1 mm thick polyethylene sheet. To ensure that the observed bands were indeed belonging to BrF_3O, the cell was periodically evacuated and refilled with fresh BrF_3O. One of the decomposition products found in the infrared cell was BrF_3.

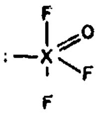
The concentrated solution of BrF_3O in HF was obtained by dissolving a sample of $CsBrF_4O$ in a thin-walled 6 mm o.d. Kel-F capillary in anhydrous HF. When the HF was added, the following displacement reaction occured in quantitative yield:[10]

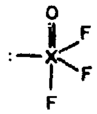
$$CsBrF_4O + HF \rightarrow CsHF_2 + BrF_3O$$

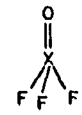
The Raman spectra of this solution were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line. A Claassen filter was used to eliminate plasma lines.[11] Polarization measurements were carried out by method VIII as described by Claassen et al.[11]

Results and Discussion

As previously discussed[12] in detail for ClF_3O, a monomeric halogen trifluoride oxide molecule theoretically could possess one of the following three structures:


I (C_s)


II (C_s)


III (C_{3v})

It has previously been shown[12] that ClF_3O has structure I, and the same arguments also hold for BrF_3O. Thus, the observed number of fundamental vibrations, the Br isotopic shifts, the infrared gas band contours, and relative band intensities and frequencies all rule out structures II and III. The following paragraphs can, therefore, be limited to a discussion of the experimental data in terms of structure I.

Infrared Spectrum of the Gas. Figure 1 shows the infrared spectrum of gaseous BrF_3O. Due to the low vapor pressure and low thermal stability of BrF_3O, only the five most intense infrared bands were observed in the gas phase. Figure 2 shows the band contours of four of these bands with scale expansion under higher resolution conditions. From the estimated (see below) geometry of BrF_3O, the three rotational constants were computed to be A = 0.189, B = 0.119, and C = 0.086 cm^{-1}. On the basis of these values, the infrared band contours of BrF_3O should be intermediate between those of sets 25 and 24 in the tables of Ueda and Shimanouchi.[13] The band at 601 cm^{-1} shows a P–R branch separation of about 17 cm^{-1} (see Figure 2), in excellent agreement with the 17 cm^{-1} estimate[13] for an A-type band. This confirms the assignment of this band to the antisymmetric axial F–Br–F stretching mode, ν_7 (A″). For this mode, the change of dipole moment occurs along the axis with the smallest moment of inertia. The second band for which a well-defined band contour was observed is the Br–O stretching mode, ν_1 (A′), at 995 cm^{-1}. This band does not exhibit well-defined P and R branches, as expected[13] for a blend of the B and C type.

Infrared Spectra of Matrix-Isolated BrF_3O. Due to the limited availability of gas-phase data and the tendency of BrF_3O to associate in the liquid and solid state (see below), it was important to obtain matrix-isolation spectra. Furthermore, these spectra were expected to yield information about the nature of the association of BrF_3O. Since for the closely related BrF_3[14] and $FBrO_2$[15] molecules pronounced and unpredictable matrix effects and splittings were observed, the spectra of BrF_3O were recorded in three different matrix materials, i.e., Ne, Ar, and N_2. A survey scan of BrF_3O in N_2 is shown in Figure 3, trace A. Spectra of BrF_3O in Ne, Ar, and N_2, recorded with scale expansion and under high resolution conditions, are given in Figures 4–7, together with the observed frequencies. As can be seen, the matrix data confirm the presence of the five bands observed in the gas-

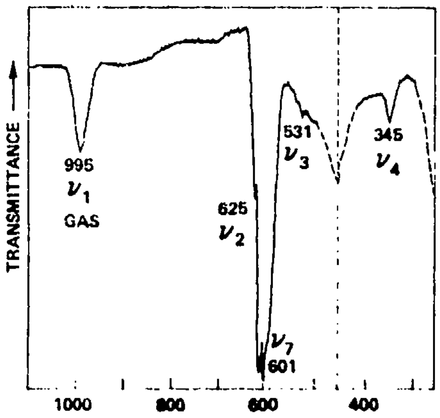


Figure 1. Infrared spectrum of gaseous BrF_3O at 5 mm pressure. The window material used above 450 cm^{-1} was AgCl and below 450 cm^{-1} was AgBr protected by a 1 mm thick polyethylene sheet. The broken lines indicate absorption due to the window material.

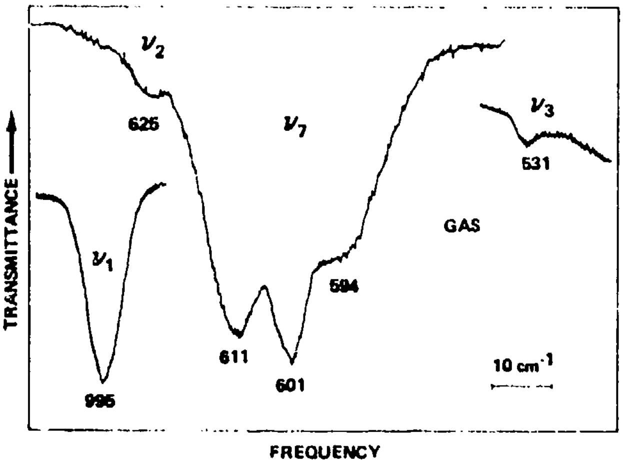


Figure 2. Infrared band contours recorded for gaseous BrF_3O with 10-fold scale expansion under higher resolution conditions.

phase spectra. Two additional fundamental vibrations were observed at about 400 and 250 cm^{-1}, in agreement with the Raman data (see below). By analogy with previous reports[14,16] on matrix-isolated BrF_3, the BrF_3O spectra exhibited pronounced matrix frequency shifts and splittings. As for BrF_3[14] and $FBrO_2$,[15] a Ne matrix was found to give for most bands the simplest spectrum and the frequency values closest to those observed for the gas phase.

The matrix spectra exhibit, in addition to site and bromine isotopic splittings (see below), bands due to associated BrF_3O. Most of these are marked by a P in Figures 4–7. Their assignment to associated BrF_3O was confirmed by variation of the matrix ratio, controlled-diffusion experiments, and the recording of the spectrum of neat solid BrF_3O at 3.6 K (see trace B of Figure 3). Their interpretation will be discussed later.

Reliable determination of the bromine isotopic shifts (bromine has two natural isotopes, ^{79}Br and ^{81}Br, of about equal abundance) was important for the assignments and force field computations. Whereas matrix splittings depend on the matrix material, the isotopic splittings should be matrix independent and be observable in all three matrix materials.

In a Ne matrix, monomeric BrF_3O appears to occupy only one matrix site, as evidenced by the observation of a single isotopic doublet for ν_1, ν_2, and ν_7 (see Figures 4–7). The splittings observed for ν_3, ν_8, and ν_5 in Ne are too large for bromine isotopes and also were not observed for the Ar and N_2 matrices which contained much less associated BrF_3O. Consequently, one of the two bands in each of these pairs is attributed to associated BrF_3O.

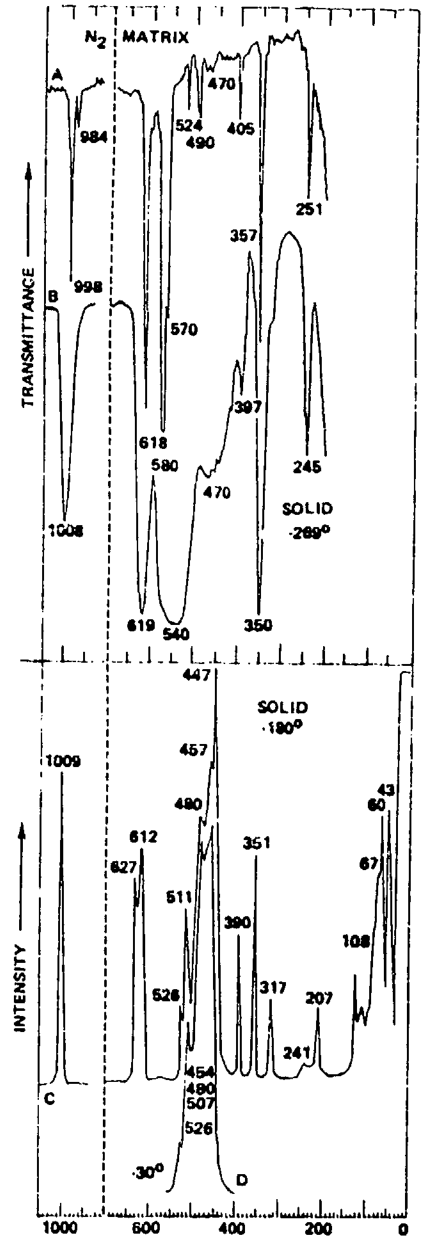


Figure 3. Vibrational spectra of solid BrF_3O: trace A, infrared spectrum of BrF_3O in a N_2 matrix (MR ~ 1000:1), recorded at 3.6 K using CsI windows; trace B, infrared spectrum of neat BrF_3O, recorded at 3.6 K using CsI windows; traces C and D, Raman spectra of neat BrF_3O, recorded at −180 and −30 °C, respectively. The parts of the −30 °C spectrum, not shown in this figure, closely resembled those of trace C.

In Ar or N_2 matrices, monomeric BrF_3O occupies at least two different matrix sites. When the site symmetry splittings are of the same magnitude as the bromine isotopic splittings, the two central lines will coincide and the bands can have the appearance of a triplet with a more intense central component. Typical examples for such apparent triplets are the bands at about 580 cm^{-1} in Ar and at about 998 and 618 cm^{-1} in N_2. The observed and computed ^{79}Br–^{81}Br isotopic shifts will be given and discussed in the force field section. The doublet at 985.6 and 982.9 cm^{-1}, observed for the N_2 matrix (see Figure 4, lower trace), exhibits a splitting (2.7 cm^{-1}) too large for

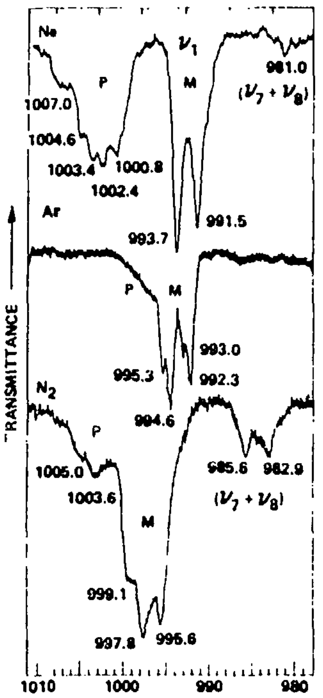


Figure 4. Infrared spectra of matrix-isolated BrF_3O (ν_1 region), recorded at 3.6 K with 20-fold scale expansion under higher resolution conditions. The upper, middle, and lower traces were recorded for Ne, Ar, and N_2 matrices, respectively. (MR ~ 1000:1). Bands due to monomeric and to associated BrF_3O are marked by M and P, respectively.

either ν_1 (2.25 cm^{-1}) or an N_2 site splitting but has about the right frequency separation (2.9 cm^{-1}) for the bromine isotopes in the combination band ($\nu_7 + \nu_8$) and, therefore, is assigned in this manner.

Raman Spectra. Raman spectra of BrF_3O were recorded for the solid at −180 and −30 °C (Figure 3, traces C and D), for the liquid at 20 °C, and for HF solutions at high and low concentrations (Figure 8, traces A, B, and C). The spectra of the solid, liquid, and HF solutions agree well with each other, except for the symmetric axial F–Br–F stretching mode, ν_3 (A′), which, due to association effects (see below), shows varying degrees of splitting and frequency shifts to lower frequencies. The infrared spectra (see above) had shown seven of the nine fundamental vibrations, expected[12] for BrF_3O of symmetry C_s. The remaining two fundamental vibrations are readily identified from the Raman spectra and have frequencies of about 200 and 330 cm^{-1}. Polarization measurements were carried out for the concentrated HF solution (traces B, Figure 8) and show the number of polarized and depolarized bands expected for model I (6 A′ + 3 A″).

Assignments. Assignment of the nine fundamental vibrations observed for BrF_3O is straightforward. By analogy with ClF_3O,[12] model I of symmetry C_s should possess 6 A′ and 3 A″ modes, all being infrared and Raman active. In the Raman spectrum, only the A′ modes should be polarized. The experimental observations are in agreement with these predictions.

Of the six fundamental vibrations in species A′, three should be stretching modes involving the Br═O, the equatorial Br–F, and the axial F–Br–F bonds, respectively. The Br═O stretching mode should have a significantly higher frequency than the Br–F modes and, therefore, is assigned to the band at about 1000 cm^{-1}. The equatorial Br–F stretching mode should have a higher frequency and infrared intensity and a significantly larger ^{79}Br–^{81}Br isotopic splitting than the symmetric axial F–Br–F stretch. Consequently, these two modes are assigned to the bands at 625 and 531 cm^{-1}, respectively.

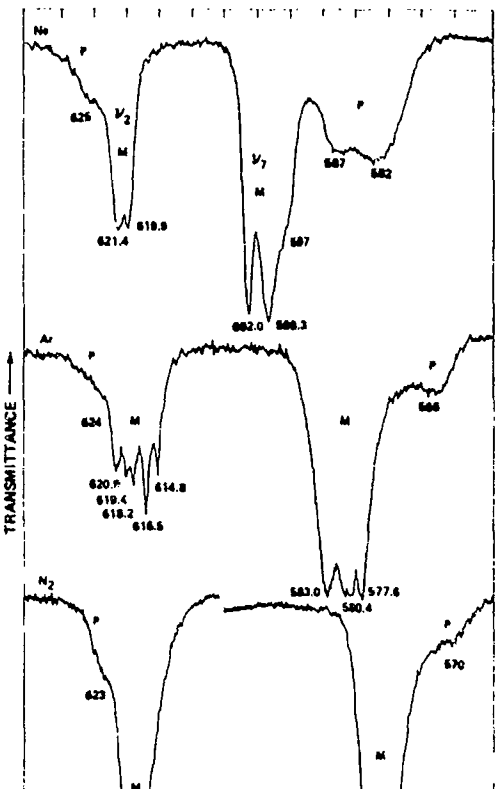


Figure 5. Infrared spectra of matrix-isolated BrF_3O (ν_4 and ν_5 region). The ν_2 band in N_2 matrix was recorded for a thicker sample.

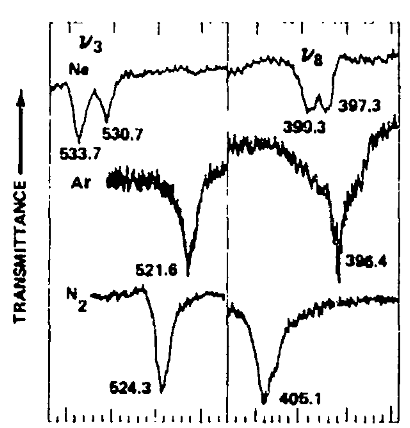
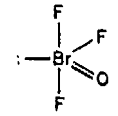
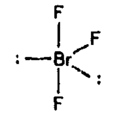
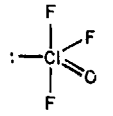
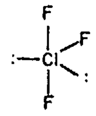


Figure 6. Infrared spectra of matrix-isolated BrF_3O (ν_7 and ν_8 region).

For the assignment of the three A′ deformation modes, three polarized Raman bands at about 350, 240, and 200 cm^{-1} are available. The three deformation modes can be approximately described as an equatorial F–Br–O scissoring motion and as two axial F–Br–F bending motions. Since only one of these three involves the doubly bonded oxygen ligand, it should have the highest frequency and is assigned to the 350-cm^{-1} fun-

Table I. Vibrational Spectra[a] of BrF_3O Compared to Those of BrF_3,[b] ClF_3O,[c] and ClF_3[b]

Obsd freq, cm^{-1} (rel intens[d])									
								Ascign for XF_3O in point group	Approx
IR	R[g]	IR	R	IR	R	IR	R	C_s	description of mode
995 s	1008 s, p			1224 s	1222 (1.5) p			A′ ν_1	$\nu(X{=}O)$
625 s	619 vs, p	675 s	675 s, p	692 s	694 (2.6) p	751 s	752 s, p	ν_2	$\nu(XF_{eq})$
531 mw	502 vs, p	552 w	552 vs, p	481 m	482 (10) p	530 m	529 vs, p	ν_3	$\nu_{sym}(F_{ax}XF_{ax})$
345 ms	350 m, p			491 ms	489 (1)			ν_4	$\delta_{sciss}(OXF_{eq})$
240 m[e]	235 w	242		318 m	319 (0.1)	328		ν_5	$\delta_{sciss}(F_{ax}XF_{ax})$ out of FXF plane
	198 mw, p	242	233 w, p	230 mw	224 (0.4) p	328	329 w, p	ν_6	$\delta_{sciss}(F_{ax}XF_{ax})$ in FXF plane
601 vs		614 vs	612 vvw	676 vs		702 vs		A″ ν_7	$\nu_{as}(F_{ax}XF_{ax})$
397 mw[f]	394 mw, dp	350 vw		501 m	500 (1)	442 w	431 w, dp	ν_8	$\delta_{wag}(OXF_{eq})$
	330 sh, dp			412 w	414 (0.2) dp			ν_9	$\tau(OXF_{eq})$

[a] All frequencies are gas-phase values except as noted. [b] Data from ref 17. [c] Data from ref 12. [d] Uncorrected Raman intensities. [e] Ne matrix value. [f] Neat solid. [g] Concentrated HF solution.

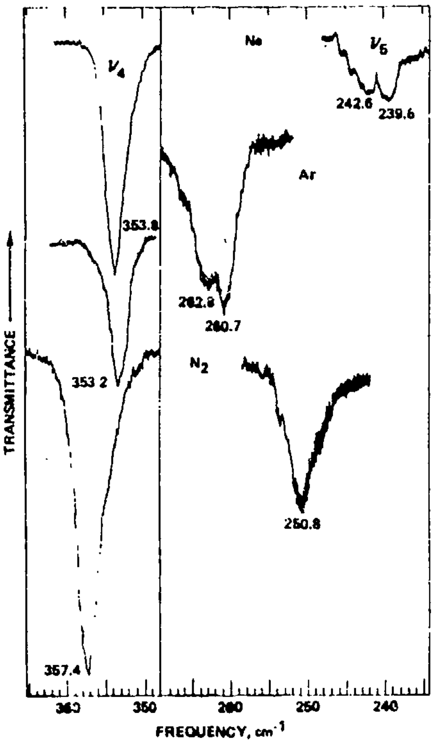


Figure 7. Infrared spectra of matrix-isolated BrF_3O (ν_4 and ν_5 region). The ν_4 and ν_5 bands in N_2 and the ν_5 band in Ar were recorded for a thicker sample.

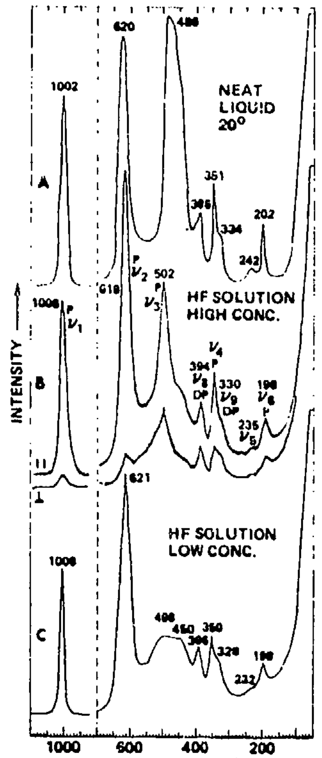


Figure 8. Raman spectra of liquid BrF_3O: trace A, neat liquid; traces B, concentrated HF solution with the incident polarization parallel and perpendicular; P and DP indicate polarized and depolarized bands, respectively; trace C, dilute HF solution.

damental. The two remaining fundamentals belong to the two axial F–Br–F bending modes. Since they are highly mixed (see below), their identity will be discussed in the force constant section.

There are three fundamental vibrations in species A″ with frequencies of about 600, 390, and 330 cm^{-1} available for assignment to the antisymmetric axial F–Br–F stretch and the equatorial F–Br–O wagging and torsion motions. On the basis of its high frequency, large ^{79}Br–^{81}Br isotopic splitting, and high infrared and low Raman intensity, the 600-cm^{-1} fundamental must be assigned to the antisymmetric axial F–Br–F stretching mode. Assignments for the two remaining deformation modes are made on the basis of their relative infrared intensities. The torsional mode should be of much lower intensity than the wagging mode and is, therefore, assigned to the 330-cm^{-1} fundamental. This leaves the 390-cm^{-1} fundamental for assignment to the wagging mode. The bands observed below 130 cm^{-1} in the Raman spectrum of solid BrF_3O have frequencies too low for internal modes and also were not observed for either the liquid or HF solutions. Consequently, they are assigned to lattice vibrations.

The above assignments are summarized in Table I and compared to those previously reported for ClF_3O[12] and BrF_3.[14,16,17] As can be seen, the agreement is excellent, thus lending additional support to our assignments. The decrease in the frequencies of the Hal–F stretching vibrations on oxygen addition is caused by the following effect. These halogen fluorides are more electronegative than oxygen. Consequently,

Table II. Observed Frequencies, Symmetry Force Constants,[a] Computed and Observed ^{79}Br–^{81}Br Isotopic Shifts, and Potential Energy Distribution[b] for BrF_3O

		Freq, cm^{-1}	Symmetry force constants		Isotopic shifts, cm^{-1}		PED
					$\Delta\nu_{comp}$	$\Delta\nu_{obsd}$	
A′	ν_1	995	$F_{11} = f_D$	7.68	2.28	2.25	99 F_{11}
	ν_2	625	$F_{22} = f_R$	3.51	1.54	1.5	97 F_{22}
	ν_3	531	$F_{33} = f_r + f_{rr}$	3.16	0		100 F_{33}
	ν_4	345	$F_{44} = f_\alpha$	1.21	1.01		93 F_{44}
	ν_5	236	$F_{55} = f_\beta + f_{\beta\beta'}$	1.70	0.54		91 F_{55} − 63 F_{56} + 70 F_{66}
	ν_6	201	$F_{66} = f_\gamma + f_{\gamma\gamma'}$	1.62	0.30		45 F_{66} + 25 F_{56} + 24 F_{55}
			$F_{56} = f_{\beta\gamma'} + f_{\beta\gamma''}$	0.65			
A″	ν_7	601	$F_{77} = f_r - f_{rr}$	2.70	2.68	2.7	98 F_{77}
	ν_8	394	$F_{88} = f_\beta - f_{\beta\beta'}$	1.23	0.23		98 F_{88}
	ν_9	330	$F_{99} = f_\gamma - f_{\gamma\gamma'}$	1.15	0.21		96 F_{99}
			$F_{78} = f_{r\beta} - f_{r\beta'}$	0.2			

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad^2, and stretch-bend interaction constants in mdyn/rad. [b] Percent contributions. Contributions of less than 9% to the PED are not listed.

Table III. Stretching Force Constants (mdyn/Å) of BrF_3O Compared to Those of Similar Molecules

	BrO_3^-[a]	BrO_4^-[b]	BrF_4O^-[c]	$FBrO_2$[d]	BrF_3O	BrF_3[e]	BrF_5[f]	ClF_3O[g]	ClO_4^-[b]	ClF_3[h]
f_D(XO)	5.28	6.05	6.70	6.98	7.68			9.37	8.24	
f_R(XF′)					3.51	4.07	4.02	3.16		4.19
f_r(XF)			2.14	2.75	2.93	3.10	3.24	2.34		2.70
f_{rr}			0.21		0.23	0.31	0.15	0.26		0.36

[a] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie", Springer-Verlag, West Berlin, 1966. [b] Reference 22. [c] Reference 10. [d] K. O. Christe, E. C. Curtis, and E. Jacob, unpublished results. [e] Reference 16. [f] K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, 11, 1679 (1972). [g] Reference 12. [h] Reference 14.

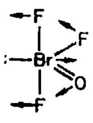
an added oxygen ligand releases electron density to the rest of the molecule. This increases the $F^{\delta-}$–$Hal^{\delta+}$ polarity of these bonds and thereby weakens them.

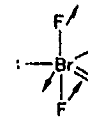
Force Constants. A normal-coordinate analysis was carried out for BrF_3O to support the above assignments. The potential and kinetic energy metrics were computed by a machine method.[18] The geometry assumed for this computation was $D(Br–O) = 1.56$ Å, $R(Br–F') = 1.72$ Å, $r(Br–F) = 1.81$ Å, $\alpha(O–Br–F') = 120°$, $\beta(O–Br–F) = \gamma\ (F'–Br–F) = 90°$, based on the observed[19] geometry for BrF_3 and an extrapolation between Br–O bond length and stretching frequency, similar to that[20] used for Cl–O bonds, using the data published for BrO_4^-[21,22] and $FBrO_3$.[23,24] In the absence of structural data for BrF_3O, we assumed an idealized geometry with 90 and 120° bond angles. However, on the basis of the known increase in mutual repulsion within the series F < O < free electron pair, the true geometry of BrF_3O is expected to show a F′–Br–O bond angle of less than 120° and a slightly bent axial F–Br–F group. The latter prediction is also supported by the observation of the symmetric axial BrF_2 stretching mode as a weak band in the infrared spectrum of gaseous BrF_3O. The symmetry coordinates used for BrF_3O were identical with those previously given[12] for ClF_3O, except for interchanging S_3 and S_4. The bending coordinates were weighted by unit (1 Å) distance.

The force constants were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. The observed ^{79}Br–^{81}Br isotopic shifts were used as additional constraints, and the most simple force field was chosen which exactly duplicated these shifts. The computed force constants are listed in Table II. Uncertainty estimates are difficult to make. However, numerical experiments indicate that the uncertainties in the valence force constants should not exceed 0.1 mdyn/Å.

As can be seen from Table II, the observed frequencies and isotopic shifts can be accurately duplicated by a force field which, except for F_{56} and F_{78}, is diagonal. In the A″ block, a small value was required for F_{78} in order to be able to fit the isotopic shift observed for ν_7. The introduction of a nonzero value for F_{78} also resulted in the PED becoming significantly more characteristic. In the A′ block, a relatively large value was required for F_{56} in order to be able to fit ν_5 and ν_6. However, the remaining fundamentals were little influenced by the value of F_{56}.

The potential energy distribution (see Table II) shows that all fundamentals are highly characteristic, except for ν_5 and ν_6 which correspond to approximately equal mixtures of F_{55} and F_{66}. More information on the nature of ν_5 and ν_6 can be obtained from the eigenvector matrix **L**. Its important elements for ν_5 and ν_6 are as follows: ν_5, $-0.006S_4$, $0.133S_5$, $-0.119S_6$; ν_6, $-0.034S_4$, $0.057S_5$, $0.081S_6$. By analogy with ClF_3O[12], ν_6 and ν_5 correspond to a symmetric and an antisymmetric combination, respectively, of the symmetry coordinates S_6 and S_5. As shown by the stick diagram


ν_6


ν_5

ν_6 can be visualized as a symmetric bending motion of the two axial fluorine atoms in a plane containing the linear F–Br–F group and the free valence electron pair of bromine. The ν_5 fundamental can be considered as the corresponding bending motion perpendicular to this plane. As shown by the stick diagram, ν_6 also contains a significant contribution from the equatorial scissoring coordinate S_4.

The force constants of greatest interest are the stretching force constants since they are a direct measure for the strength and covalent character of the various bonds. A comparison of the stretching force constants of BrF_3O with those of similar molecules and ions is given in Table III. As can be seen, the value of the Br–O stretching force constant is in good agreement with our expectations for a BrO double bond. The general trend of the Br–O stretching force constants listed in Table III is similar to that observed for chlorine oxyfluorides.[25] The force constant increases with increasing fluorine substitution, oxidation state, and formal charge of the central atom. Consequently, it is not surprising that BrF_3O exhibits the highest f_D value of the listed compounds. The only presently known bromine oxyfluoride expected to have a higher

Table IV. ^{19}F NMR Spectra[a] of Neat BrF_3O and of BrF_3O in $FClO_3$ Solution

	Temp, °C				
	+10	−10	−20	−30	−40
Neat liquid	−165.2				
2.3 M soln	−165.2	−163.2	−161.4	−160.8	−160.2
2.5 × 10^{-2} M soln		−169.7	−169.5	−168.9	−167.2

[a] Chemical shifts in ppm. $CFCl_3$ was used as an external standard.

Table V. Thermodynamic Properties for BrF_3O

T, K	$C_p°$, kcal mol^{-1} deg^{-1}	$H° - H_0°$, kcal mol^{-1}	$-(F° - H_0°)/T$, kcal mol^{-1} deg^{-1}	$S°$, cal mol^{-1} deg^{-1}
0	0	0	0	0
100	10.871	0.872	30.788	59.512
200	16.448	2.255	37.595	68.868
298.15	19.830	4.050	62.543	76.127
300	19.878	4.087	62.627	76.250
400	21.852	6.182	66.809	82.264
500	23.032	8.431	70.416	87.278
600	23.775	10.774	73.591	91.548
700	24.265	13.178	76.427	95.252
800	24.603	15.622	78.988	98.516
900	24.845	18.095	81.322	101.428
1000	25.023	20.589	83.466	104.055
1100	25.157	23.098	85.448	106.447
1200	25.261	25.619	87.291	108.641
1300	25.343	28.150	89.012	110.666
1400	25.409	30.688	90.627	112.547
1500	25.462	33.231	92.147	114.301
1600	25.506	35.780	93.584	115.946
1700	25.543	38.332	94.945	117.494
1800	25.574	40.888	96.239	118.955
1900	25.600	43.447	97.471	120.338
2000	25.623	46.008	98.648	121.652

f_D value is the BrF_2O^+ cation w[illegible] has a Br–O stretching frequency of about 1050 cm^{-1}.[26-]

The Br–F stretching force constants of BrF_3O are similar to those of BrF_3, although somewhat lower due to the electron density releasing effect of the oxygen substituent (see above). The difference between the equatorial and the axial Br–F stretching force constant of BrF_3O is significantly larger than their estimated uncertainties (see above). This indicates that the equatorial Br–F bond is significantly stronger than the two axial ones. The same effect has previously been observed for ClF_3O and was explained[12] by significant contributions from semiionic three-center four-electron pσ bonds[29-31] to the axial bonds.

NMR Data. ^{19}F NMR spectra were recorded for the neat liquid at +10 °C and for $FClO_3$ solutions of two different concentrations in the temperature range +10 to −40 °C (see Table IV). By analogy with ClF_3O,[25,32,33] only a single line signal was observed. However, it has been shown[34] by relaxation time measurements that ClF_3O contains two different kinds of fluorines with a chemical shift separation of 50 ppm. The observation of a single line signal was attributed to rapid exchange.[34] Consequently, the observation of a single line signal for BrF_3O might be explained in a similar manner and should not be used as an argument against the above proposed model of symmetry C_s.

The signal observed for BrF_3O was shifted to higher field with both decreasing temperature and increasing concentration. Both trends indicate that the resonance for associated BrF_3O (see below) occurs upfield from that of monomeric BrF_3O.

Association in the Liquid and Solid Phase. The physical properties of BrF_3O, i.e., its relatively high melting and boiling point and low vapor pressure, indicate association in the liquid and solid phase. This was experimentally confirmed by vibrational and NMR spectroscopy. By analogy with the findings for the similar pseudo-trigonal-bipyramidal molecules BrF_3, SF_4, ClF_3,[14,35] and ClF_3O,[12] it can be shown that condensed BrF_3O is associated through fluorine bridges. The bromine atom achieves pseudohexacoordination by accepting an axial fluorine atom of another BrF_3O molecule as a fourth equatorial ligand.

As expected[12] for this type of association, the axial F–Br–F stretching frequencies are shifted to significantly lower frequencies, whereas the Br–O and the equatorial Br–F stretch are only little affected. Thus, the Raman spectra of the neat liquid and of HF solutions of BrF_3O (see Figure 8) show that the band due to the symmetric axial F–Br–F stretching mode has decreased in frequency by 30–80 cm^{-1} and has become very broad. The Raman spectrum of a 2 × 10^{-2} M solution of BrF_3O in $FClO_3$ at −10 °C has also been recorded. However, in this relatively unpolar solvent, the monomer concentration is high, as evidenced by ν_{sym}(F–Br–F) having a frequency of 527 cm^{-1}. For the Br–O and the equatorial Br–F stretching mode, frequencies of 996 and 619 cm^{-1}, respectively, were observed which are also close to those of the corresponding gas-phase values.

For neat solid BrF_3O (see Figure 3, traces B–D) association predominates, as expected.[12] For the symmetric F–Br–F stretching mode, only a weak Raman band occurred in the monomer region at 526 cm^{-1}, but a series of bands was observed at 511, 480, 457, and 447 cm^{-1} with increasing relative intensities which show infrared counterparts of medium intensities. Furthermore, the infrared frequency of the antisymmetric F–Br–F stretching mode has decreased by about 60 cm^{-1}, relative to the gas-phase value.

The above conclusions were further corroborated by the results from the matrix-isolation study. In addition to the bands due to monomeric BrF_3O, new bands were observed, particularly in the Ne spectra. These new bands had frequencies similar to those of neat solid BrF_3O and, therefore, are assigned to associated BrF_3O. In agreement with previous findings[12] for ClF_3O, the bands due to associated BrF_3O were observed on the high-frequency sides of ν(Br=O) and ν(Br–F') and the low-frequency side of ν_{as}(F–Br–F) (see Figures 4 and 5 and the bands marked by P). For ν_{sym}(F–Br–F), the bands due to associated BrF_3O at 490 and 470 cm^{-1} (trace A, Figure 3) exhibited a large shift to lower frequencies and were more intense than that of the corresponding monomer band at 524 cm^{-1}. The higher intensities of the 490- and 470-cm^{-1} bands do not imply the presence of more associated than monomeric BrF_3O but are mainly due to a larger change of dipole moment involved in these modes. The ratio of monomer to oligomer can better be judged from the relative intensities of bands, such as ν(BrO), which do not participate in the bridge formation. In Figure 3, trace A, the appropriate bands are 998 cm^{-1} (monomer) and the shoulder on its high-frequency side (oligomer).

It should be noted that the spectra of neat liquid or solid BrF_3O did not show any evidence for bands due to BrF_2O^+[26-28] or BrF_4O^-.[2,10,36] This rules out extensive self-ionization according to $2BrF_3O \rightleftarrows BrF_2O^+BrF_4O^-$.

Additional support for the proposed association stems from the ^{19}F NMR spectra of BrF_3O which by analogy with those[26,34] of ClF_3O show an upfield shift with increasing concentration and decreasing temperature, conditions which favor association. For ClF_3O, the axial fluorine signal is observed[34] at higher field than that due to the equatorial fluorine. Since the axial fluorine bond is weaker than the equatorial one, an upfield shift is indicative of bond weakening, i.e., association.

Thermodynamic Properties. The thermodynamic properties of BrF_3O were computed with the molecular geometry given above and the vibrational frequencies of Table II, assuming an ideal gas at 1 atm and using the harmonic-oscillator–rigid-rotor approximation.[37] These properties are given for the range 0–2000 K in Table V.

Conclusion. Except for the ^{19}F NMR data, which in the absence of relaxation time measurements[34] are inconclusive, all of the data observed for BrF_3O are in excellent agreement with the predictions made for model I of symmetry C_s. Whereas gaseous, matrix-isolated, and $FClO_3$-dissolved BrF_3O is mainly monomeric, liquid, solid, and HF-dissolved BrF_3O shows pronounced association involving bridging through the axial fluorine atoms.[38]

Acknowledgment. K.O.C. is indebted to Mr. R. D. Wilson for experimental help, to Drs. L. R. Grant, C. J. Schack, and W. W. Wilson for helpful discussions, and to the Office of Naval Research, Power Branch, for financial support. R.B. is grateful to Mr. T. Bui Huy for experimental contributions.

Registry No. BrF_3O, 61519-37-7.

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Reactions of Electropositive Chlorine Compounds with Fluorocarbons

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Abstract. The reactions of simple chlorine containing compounds of the general composition XCl are reviewed and discussed. The compounds included for review are ClF, R_fOCl, SF_5OCl, CF_3OOCl, SF_5OOCl, $ClOSO_2F$, $ClOClO_3$ and $ClONO_2$. It is concluded that most of the known reaction chemistry of electropositive chlorine compounds can be rationalized in terms of either addition of Cl–X across multiple bonds or oxidative addition to atoms, such as iodine or sulfur in their lower oxidation states. The observed variety of final reaction products can be explained by a multitude of secondary reactions which can involve either eliminations, further additions or degradations. The observed reactions are easily moderated and controlled and only seldom is no reaction encountered.

INTRODUCTION

This review is concerned with the reactions of simple chlorine containing compounds of the general composition XCl in which the chlorine atom has electropositive character. The $X^{\delta-}$–$Cl^{\delta+}$ polarization of the XCl bonds arises from the combination of chlorine with a group of higher electronegativity. The compounds included for review are ClF, R_fOCl, SF_5OCl, CF_3OOCl, SF_5OOCl, $ClOSO_2F$, $ClOClO_3$, and $ClONO_2$. Except for chlorine monofluoride and chlorine nitrate, these compounds have all been discovered within the last 15 years. Nevertheless during this relatively short period an extensive reaction chemistry has developed involving both inorganic and organic compounds. In particular, the incorporation of positive chlorine species in fluorocarbons and their reactions with fluorocarbons are often unique. This review was written because this area of investigation is most interesting and fruitful and since it has not previously been reviewed.

By virtue of the combination of chlorine with a highly electronegative substituent, all of these materials are medium to strong oxidizing agents. As a consequence of this, care in their handling and use is mandatory. On the other hand, it is this enhanced reactivity which promotes and makes interesting their reactions with the "inert" fluorocarbons.

CHLORINE MONOFLUORIDE

Synthesis and Properties

Chlorine monofluoride was first prepared in 1928 by Ruff and Ascher[1] by a thermal reaction of the elements. Because this reaction can be difficult to control, the alternate method of Schmitz and Schumacher[2] is commonly used to obtain ClF.

$$Cl_2 + ClF_3 \xrightarrow{\Delta} 3\ ClF$$

Recent detailed descriptions of this method are available for either flow[3] or static[4] conditions as well as flow conditions for the reaction of the elements.[5] The low mp (−156°C) and bp (−100°C) of ClF facilitate its manipulation in vacuum systems and permit contact and mixing under moderating effect of low temperature. Extensive reviews[6-8] have been published on the physical properties and general chemistry of ClF and other interhalogen fluorides.

Musgrave[9] has described early reactions of halogen fluorides with organic materials. Others[10-13] have touched on the subject but have been more concerned with systems leading to the addition of the elements of XF (X = Cl, Br, I) to organic substrates. The reagents used in the latter reactions are generally not the interhalogen fluorides themselves but rather mixtures of X and F sources such as N-halosuccinimide and HF. The reactions of ClF surveyed in these monographs attest to its oxidizing character and vigorous nature.

Based on the observed reaction chemistry and the common acceptance of fluorine as the most electronegative element, it was a consensus that the direction of the polarization in chlorine monofluoride is $Cl^{\delta+}$–$F^{\delta-}$. Recently, however, this concept was disputed by Ewing et al.[14] who, based on Zeeman effect measurements, concluded that the sign of the electric dipole in the molecule should be $Cl^{\delta-}$–$F^{\delta+}$. Shortly after this report, Hartree–Fock calculation by Greene[15] and ESCA results of Carroll and Thomas[16] were published which supported the classical electropositive chlorine concept for ClF. At about the same time, some of the original authors of the Zeeman investigation reexamined[17] their results. While no error in the experimental data was found it was concluded that the marginal nature of the Zeeman dipole measurements was insufficient to prove the direction of the dipole, and that the measurement should be repeated under higher resolution conditions. The ESCA experiments fulfill this need and it is safe to say that the polarity in ClF is as expected. The reactions of ClF with fluorocarbons which reflect this polarity, are divided by type and summarized in the following paragraphs.

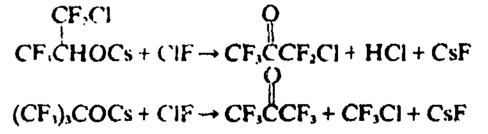
Chlorination

Reactions of ClF which have most often been used to attain chlorination of a substrate are those involving alkali metal salts, –OH, and –CH functions. In the case of salts the formation of the alkali metal fluoride provides an effective driving force for the reaction. This method provided the first synthesis of the perfluoroalkyl hypochlorites CF_3OCl[18] and $(CF_3)_3COCl$.[19]

$$KOCF_3 + ClF \xrightarrow{-78°C} KF + CF_3OCl$$

Assurance that only the salt and not its decomposition products, COF_2 and KF, reacted, was achieved by conducting the above reaction at a temperure of –78°C at which no decomposition of the $KOCF_3$ starting material is possible. The class of R_fOCl compounds, which are themselves positive chlorine species, will be discussed in detail later.

Cesium salts obtained as by-products in fluorocarbon ester reactions were identified by treatment with ClF.[20]



$$CF_3CH(CF_2Cl)OCs + ClF \rightarrow CF_3C(O)CF_2Cl + HCl + CsF$$

$$(CF_3)_3COCs + ClF \rightarrow CF_3C(O)CF_3 + CF_3Cl + CsF$$

Here one would have expected an alkyl hypochlorite to form. That it was not observed might be due to lack of controlled reaction conditions causing decomposition of the hypochlorites to the products shown. A simple chlorination was noted[20] for the trifluoromethyl sulfinate salt.

$$CF_3SO_2Cs + ClF \rightarrow CF_3SO_2Cl + CsF$$

Another effective driving force resulting in chlorination is the formation of HF. Several –OH compounds have thereby been converted to the corresponding hypochlorites.[20]

$$ROH + ClF \xrightarrow{25°C} ROCl + HF$$

$$R = (CF_3)_3C\text{-},\ (CF_3)_2CH\text{-},\ (CF_3)_2CCH_3\text{-},\ CF_3CH_2\text{-}$$

However, perfluoropinacol gave only degradation products while *t*-butyl alcohol reacted explosively. From the successful cases it was concluded that one CF_3 group in the α position is all that is necessary to allow preparation of the hypochlorite from the alcohol. Peroxy hydrogens can also be substituted by chlorine using ClF.[21]

$$CF_3OOH + ClF \xrightarrow{111°C} CF_3OOCl + HF$$

No O–O bond cleavage was observed and thus no CF_3OCl formed. The reported stability of the compound at 25° has not been experienced by others[22] although it is sufficiently stable to be synthetically useful as will be shown later. Quite recently DesMarteau[23] has utilized this reaction path to prepare and isolate for the first time, perfluoroacyl hypochlorites.

$$R_fCO_2H + ClF \xrightarrow{} R_fCO_2Cl + HF$$

$$R_f = CF_3,\ C_3F_7$$

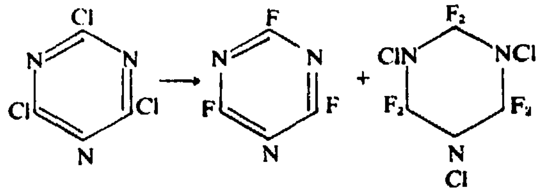
As expected the compounds have low thermal stability. In addition they are explosive. Displacement of hydrogen from carbon need not occur if a more reactive site is available in the substrate as in the case of the alcohols described above. Lacking the presence of a more reactive group, however, stepwise substitution of H by Cl can occur.[24]

$$CF_3SCH_2CH_2SCF_3 + ClF \rightarrow CF_3SCHClCH_2SCF_3 + CF_3SCCl_2CH_2SCF_3 + HF$$

In this relatively uncontrolled experiment, one and two chlorines were substituted onto the same carbon indicating a preferential reactivity. This specificity is further demonstrated by the fact that the sulfur is not affected even though sulfur is often attacked and oxidized by ClF in similar compounds.[24] Aromatic hydrocarbons have been studied by Gambaretto and Napoli.[5] Using stoichiometric quantities, monochloro substitution products were obtained in all cases with yields ranging from 60–80%. Benzene gave chlorobenzene, and toluene produced 2- and 4-chlorotoluene in a 2:1 ratio. Styrene reacted primarily via ClF addition to the olefin side chain, but this was succeeded by limited substitution in the *para* position only. These aromatic chlorinations are indicative of a directed electrophilic attack. In these instances as in others, carefully selected reaction conditions, such as solvents, diluents, and low temperature, resulted in controlled specific chlorine substitution reactions. Furthermore, in all the preceding examples ClF reacted exclusively as a positive chlorine material.

Fluorination

Non-oxidative fluorination. Relatively few cases have been reported in which ClF acts simply as a fluorine substituting agent. One process involving fluorination as a significant pathway is the conversion of cyanuric chloride to the fluoride.[25]

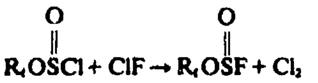


I II

Pure ClF produced 43% I and 17% II, while pure ClF_3 gave only I but in the same yield. Presumably the nitrogen lone pairs increase the negative character of the ring chlorine thus facilitating its combination with $Cl^{\delta+}$ and replacement with fluorine. Perhaps a more plausible explanation for the above reaction is the stepwise addition of ClF across a C=N double bond, followed by Cl_2 elimination. Product II could then be obtained from I by a repeated ClF addition. The analogous reactions were observed for the addition of ClF to nitriles. Although not exclusively a fluorination process, the action of ClF on tetrachlorobutadiene has been shown[26] to be partially of that nature.

$$ClCH{=}CClCCl{=}CHCl \xrightarrow{ClF} ClCF_2CFClCFClCF_2Cl\ (15\%\ I) + Cl_2CFCFClCFClCFCl_2\ (25\%\ II) + C_4F_5Cl_5\ (50\%\ III)$$

Most probably ClF addition to the double bonds occurred, followed by HF or HCl elimination, followed by further ClF addition. As a net result, fluorination, chlorination, and chlorofluorination all occurred, but the former was dominant. For comparison, ClF_3 gave similar products but the amounts of II and III were reversed as would be anticipated in view of its higher fluorine values. The displacement of chlorine from fluoroalkyl chlorosulfites to furnish the fluorosulfite has been reported.[27]



$$R_fOS(O)Cl + ClF \rightarrow R_fOS(O)F + Cl_2$$

$$R_f = CF_3CH_2\text{-},\ (CF_3)_2CH\text{-},\ (CF_3)_2CCH_3\text{-}$$

This halogen exchange could not be effected by NaF or KF even at 120°C. Side reactions were not encountered and the fluoroalkyl fluorosulfites were found to have very good thermal stability. All of the foregoing reactions are examples for the replacement of chlorine by fluorine.

Oxidative fluorination. During studies on lower valent sulfur and nitrogen containing fluorocarbons, Shreeve and coworkers have made very skillful use of ClF reactions. Some of their early work has been summarized.[28] Basically, it has been shown that ClF is capable of effecting stepwise oxidation of S(II) to S(IV) and S(VI) without large amounts of C–S bond cleavage. Generally, this is achieved through careful reaction temperature control, but sometimes the nature of substituents on sulfur is the dominant factor in determining the final oxidation state of sulfur in the product. Although these are multistep fluorination reactions and probably involve intermediate S–Cl moieties, these have not been observed until the S (VI) stage is attained as in R_fSF_4Cl.

The first report[29] of this kind of fluorination used a -78°C reaction temperature which resulted in exclusive conversion of S(II) to S(IV).

$$R_fSR_f' + 2\ ClF \rightarrow R_fSF_2R_f'$$

$$R_f = CF_3- \qquad R_f' = CF_3-,\ CF_3CF_2-,\ CF_3CF_2CF_2-$$

Yields were greater than 90% and no C–S bond breakage was noted. In contrast, when conventional fluorinating agents (AgF_2, CoF_3, F_2) were employed, only C–S scission and degradation products were obtained. The use of ClF at higher temperatures resulted in additional oxidation[30,31] furnishing S(VI) derivatives. However, these reactions were now accompanied by significant amounts of C–S bond cleavage.

$$CF_3SCF_3 + ClF \rightarrow CF_3SF_4CF_3\ (48\%) + CF_3SF_4Cl\ (25\%)$$

$$CF_3SCF_2CF_3 + ClF \rightarrow CF_3SF_4CF_2CF_3\ (13\%) + CF_3SF_4Cl\ (13\%) + CF_3CF_2SF_4Cl\ (31\%)$$

Interestingly, these S(VI) compounds with pseudooctahedral geometry were found by NMR to be mixtures of *cis* and *trans* isomers. These reactions yielded the first examples of the *cis* isomers, since previously published electrochemical methods[32] provide only the *trans* isomer. Also, if the substrate for the ClF reaction does not belong to the R_fSR_f type but has one R_f replaced by –Cl, -SCF_3,[31] or R[33,34] then again only the *trans* isomer is formed.

$$R_fSCl + ClF \rightarrow R_fSF_4Cl\ (55\%)$$

$$R_f = CF_3-,\ C_2F_5-,\ n\text{-}C_3F_7-,\ n\text{-}C_4F_9-$$

$$R_fSSR_f + ClF \rightarrow R_fSF_4Cl\ (25\text{–}75\%)$$

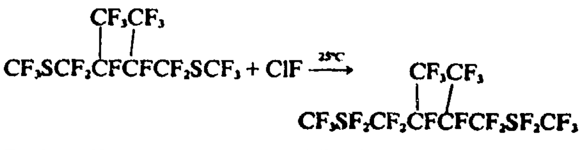
$$R_f = CF_3-,\ C_2F_5-$$

$$CF_3SR + ClF \rightarrow CF_3SF_4R\ (70\%)$$

$$R = CH_3-,\ C_2H_5-$$

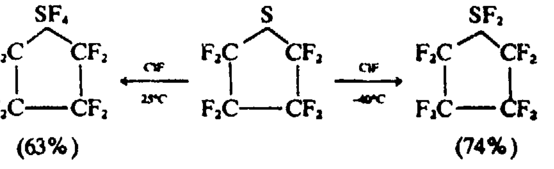
$$CF_3SCH_2SCF_3 + ClF \rightarrow CF_3SF_4CH_2SF_4CF_3\ (30\%) + CF_3SF_4CH_2F\ (15\%)$$

For the R_fSCl and R_fSSR_f cases there were observed varying amounts of R_fSF_5 products formed by the displacement of Cl by F in R_fSF_4Cl. While in the R_fSR_f–ClF reaction the intermediate S(IV) products could be isolated, R_fSR and ClF were found to give hexavalent sulfur only, even at low temperaure and with less than stoichiometric amounts of ClF. Thus the presence of the alkyl group promotes considerably the ease of oxidation of the sulfur central atom by this electrophilic reagent. Somewhat at variance with these results are the findings of Haran and Sharp[34] that are shown by the equation:

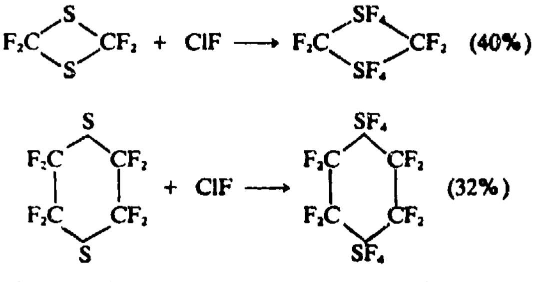


$$CF_3SCF_2CF(CF_3)CF(CF_3)CF_2SCF_3 + ClF \xrightarrow{25°C} CF_3SF_2CF_2CF(CF_3)CF(CF_3)CF_2SF_2CF_3$$

Both sulfur atoms were oxidized but only to S(IV) despite excess quantities of ClF being present. In addition, the reluctance of the sulfur to participate in this reaction is reflected by the fact that 75% of the starting material remained unreacted. Apparently there is an increasing tendency to resist oxidation as the bulkiness of the fluoroalkyl part of the molecule increases. More examples are needed to verify this trend. Cyclic perfluoroalkyl sulfides are also capable of stepwise oxidative fluorination with chlorine monofluoride.[35]



Again only temperature control is required to produce either an S(IV) fluoride or an S(VI) fluoride in good yield. Similar results were obtained for the room temperature reaction of perfluoro-1,3-dithietane and perfluoro-1,4-dithietane.[35]

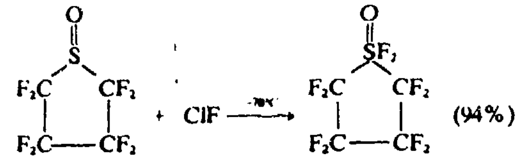


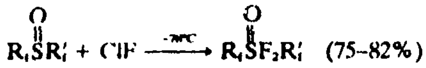
Unfortunately no low temperature experiments were carried out with the dithietanes, but it is to be expected that at lower temperature the sulfur (IV) fluoride analogs of these compounds could be prepared. Once more, it should be noted that in all the fluorination reactions examined involving cyclic or acyclic disulfides, the only products isolated were those in which both sulfur atoms are in the same oxidation state, S(IV) or S(VI). This is characteristic for ClF since other oxidizing agents are capable of forming molecules containing sulfur in two different oxidation states. In particular, *m*-chloroperbenzoic acid has exhibited selectivity in its oxidizing action.[34]

$$CF_3SCH_2SCF_3 + 2\ ClC_6H_4CO_3H \xrightarrow{25°C} CF_3SCH_2S(O)CF_3\ (99\%)$$

$$CF_3SCH_2SCF_3 + \text{excess I} \xrightarrow{25°C} CF_3SCH_2S(O)CF_3\ (80\%) + CF_3SCH_2SO_2CF_3\ (20\%)$$

Of the available sulfur atoms only one reacts giving a sulfoxide or a sulfone. This reagent does not oxidize bis-perfluoroalkyl sulfides. Sulfoxides are susceptible to oxidative fluorination and several examples have been reported.[35,36]



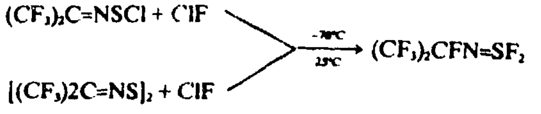


$$R_f\overset{O}{\overset{\|}{S}}R_f' + ClF \xrightarrow{-78°C} R_f\overset{O}{\overset{\|}{S}}F_2R_f' \quad (75\text{–}82\%)$$

$R_f = CF_3–, C_2F_5–$ $R_f' = CF_3–, C_2F_5–$

Obviously, the fluorination of the sulfoxides is a very facile process as reflected by the low temperature conditions employed and the high yields realized. In fact, higher temperatures lead to C–S bond breaking. It appears that doubly bonded oxygen on sulfur compared to two fluorines enhances appreciably the oxidation from S(IV) to S(VI) by providing increased electron density at the sulfur. This parallels the results for electron donating alkyl substituents on sulfur.[36]

The identification and characterization of the various sulfur (II), (IV), and (VI) fluorides and oxyfluorides is generally quite precise. This is due to the ^{19}F-NMR chemical shifts characteristic for the various species containing sulfur in different oxidation states. The application of this important tool to these systems has been summarized by Shreeve.[28] A final instance of oxidative fluorination of fluorocarbons via ClF has been described for chloro(hexafluoroisopropylidenimino)sulfur(II) and bis(hexafluoroisopropylidenimino)disulfide.[37]



In each case sulfur (II) is oxidized to sulfur (IV) fluoride by what is effectively a 1,3 addition of fluorine accompanied by a double bond shift and the cleavage of either an S–Cl or S–S linkage. Many other fluorinating agents (e.g. NF_3O, AgF_2, CsF, but not KF) also gave the same fluorination product from the corresponding sulfenyl chloride. Once more, electron donating groups bonded to sulfur are seen to promote oxidative fluorination.

Chlorfluorination

Addition. Saturation of multiple bonds by the addition of ClF represents the most common usage of ClF. Usable multiple bond systems include: C=C, C=O, C=S, S=N, C=N, and C≡N. Some of these reactions require catalysis but most do not. Normally a directed polar addition occurs in high yield but exceptions to this rule are also known. In this section we will be concerned only with simple additions. Systems that also undergo fluorination or extensive bond cleavage will be discussed separately. The use of solvents and cooling permits good conversion of ethylene derivatives to the corresponding ClF adducts without attack on hydrogen.[5]

$$ClCH{=}CH_2 \xrightarrow{ClF} ClFCHCH_2Cl \quad (72\%)$$

$$ClCH{=}CHCl \longrightarrow ClFCHCHCl_2 \quad (75\%)$$

$$\phi CH{=}CH_2 \longrightarrow \phi FCHCH_2Cl \quad (80\%)$$

Markovnikov addition was observed in each case. With butadiene a variety of chlorine fluoride additions ensued[5] attributed to a 1,2-Markovnikov addition as a first step followed by an only partially directed second addition.

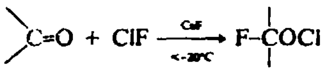
$$CH_2{=}CHCH{=}CH_2 \xrightarrow{ClF} ClCH_2CHFCH{=}CH_2 \xrightarrow{ClF}$$

$$ClCH_2CHFCHClCH_2F\ (69\%) +$$

$$ClCH_2CHFCHFCH_2Cl\ (31\%)$$

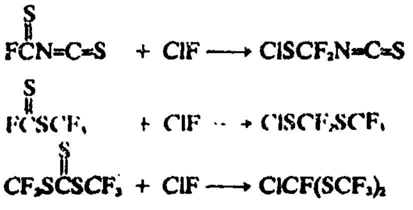
The intermediate is an allylic type olefin and reactions of other allyl substrates were shown also to give mixed Markovnikov and anti-Markovnikov ClF addition products. Calculated electronegativity values for R in the $RCH{=}CH_2$ compounds were used by Gambaretto and Napoli to explain the various observed proportions of the different adducts. Boguslovskaya, et al.[38] also carried out a study of ClF additions to R–allyl type compounds, correlating the nature of R– with the direction of addition. In all cases mixed adducts were found but in varying amounts. Moldavskii et al.,[39] as part of a study on perfluoropropene reactivity, showed that ClF forms exclusively $i\text{–}C_3F_7Cl$, the Markovnikov predicted product, in greater than 90% yield. Thus with the exception of allylic precursors, the reported ClF additions are overwhelmingly directed electrophilic additions.

Carbonyl groups are not affected by ClF alone. However, in the presence of Lewis bases, such as CsF, they are attacked readily to generate fluorocarbon hypochlorites.



This mode of addition was discovered at nearly the same time by three groups.[18,40-42] The French workers' efforts[42] were limited to CF_3OCl which was first found by them as a secondary product in the reaction of COF_2 and ClF_3 on alumina. Compounds prepared by the base catalysis[18,40,41] were: CF_3OCl, C_2F_5OCl, $i\text{–}C_3F_7OCl$, $ClCF_2CF(CF_3)OCl$, and $ClO(CF_2)_3OCl$. The intermediacy of R_fO^- species is established in these systems and is wholly analogous to the preceding discovery[43] of base catalyzed fluorination of carbonyls to give R_fOF products. The induced polarity of the C=O bond together with the fixed dipole of ClF allows only a directed addition to give FC–OCl. In fact, the same net addition was also reported by Fox and coworkers[44] when strong Lewis acids, such as HF, BF_3, or AsF_5, were present. It was postulated that acid catalysis promoted hypochlorite formation through interaction of the acid with ClF thereby increasing the ClF polarity and reactivity toward carbonyl groups. However, polarization of the carbonyl bond according to $^{\delta+}C\text{–}\underline{\bar{O}}^{\delta-}| \rightarrow AsF_5$ cannot be ruled out as an alternative explanation. The interesting chemistry of these hypochlorites will be discussed later.

Thiocarbonyl groups would appear to be ideal candidates for additions of ClF. However, only one report of such interaction has appeared,[45] the reported reactions being:



$$F\overset{S}{\overset{\|}{C}}N{=}C{=}S + ClF \longrightarrow ClSCF_2N{=}C{=}S$$

$$F\overset{S}{\overset{\|}{C}}SCF_3 + ClF \longrightarrow ClSCF_2SCF_3$$

$$CF_3S\overset{S}{\overset{\|}{C}}SCF_3 + ClF \longrightarrow ClCF(SCF_3)_2$$

Catalysts were not required to convert the thiocarbonyl to a sulfenyl chloride. Also, sulfide links and other unsaturation in the starting materials were unaffected by the ClF. Polar additions of ClF to S(VI)=N bonds have been studied by Yu and Shreeve.[46]

$$CF_3SF_4{=}NCF_3 + ClF \rightarrow CF_3SF_4NClCF_3$$

Cesium fluoride may be used to promote this addition, but is not essential. When the double bond involves tetravalent sulfur and nitrogen, ClF causes cleavage (see below). Numerous compounds containing C=N linkages have been investigated with respect to ClF additions. Without exception, these additions are polar and result in saturation of the C=N bond without its rupture. For example, fluorinated isocyanates react as shown:[47]

$$R_fN{=}C{=}O + ClF \longrightarrow R_fNClCFO \quad (60\text{–}90\%)$$

$$R_f = CF_3\text{–},\ CF_3CO\text{–},\ FCO\text{–},\ Cl\text{–}$$

These products are generated at room temperature or below and have typical chloramine reactivity, i.e. with HCl, chlorine is eliminated and the amine formed. Other positive chlorine species, such as Cl_2O and CF_3OCl, are unreactive toward the isocyanates.

Fluorocarbon imines have been extensively studied by Shreeve and coworkers. Acylimines,[48] haloimines,[49] and alkylimines[50, 51] all add ClF without C–N bond cleavage.

$$R_f\overset{\overset{\large O}{\|}}{C}N{=}C(CF_3)_2 + ClF \xrightarrow{80°C} R_f\overset{\overset{\large O}{\|}}{C}NClCF(CF_3)_2 \quad (75\text{–}99\%)$$

$$R_f = CF_3\text{–},\ C_2F_5\text{–}$$

$$XN{=}CR'R + ClF \xrightarrow{-20°C} XNClCFR'R \quad (60\text{–}80\%)$$

$$R = CF_3\text{–}, Cl, F \quad R' = CF_3\text{–}, Cl, F \quad X = Cl, F, \text{–}N{=}CRR'$$

The directed polar additions found do not usually require the presence of a catalyst, such as CsF, to take place unless the imino carbon is peralkylated. Then a catalyst may be necessary. If the product chloroamine also has a chlorine bound to the adjacent carbon it can be dechlorinated readily to give a new imine.

$$ClCF{=}NF \xrightarrow{ClF} ClCF_2NFCl \xrightarrow{-Cl_2}$$

$$CF_2{=}NF \xrightarrow{ClF} CF_3NFCl \not\longrightarrow -Cl_2$$

Typical alkylimine systems are shown in the equation.

$$RN{=}CR'R'' + ClF \longrightarrow RNClCFR'R'' \quad (70\text{–}95\%)$$

$$R = CF_3\text{–}, (CF_3)_2CF\text{–} \qquad R' = CF_3\text{–}, F\text{–} \qquad R'' = CF_3\text{–}$$

An example[44] of an imine which even under stringent conditions does not react without a catalyst with ClF is illustrated.

$$\nleftarrow CF_3SF_4N{=}CFCF_3 + ClF \xrightarrow[25°C]{CsF} CF_3SF_4NClCF_2CF_3 \quad (100\%)$$

It is also noteworthy that the SF_4–N bond is retained under these conditions while certain SF_4–C or SF_4–Cl substrates[11] are subject to significant fluorinative cleavage under milder conditions. Previously, the simultaneous fluorination and clorofluorination of cyanuric chloride with ClF[25] had been described. More recently, it has been demonstrated[52] that cyanuric fluoride is an excellent precursor to the same chlorofluorination product.

$$(FCN)_3 + 3\,ClF \longrightarrow (F_2CNCl)_3 \quad (90\%)$$

Quite unexpectedly this triazacyclohexane was found to serve as a mild fluorinating agent in several cases, being reduced to $(FCN)_3$ and Cl_2. It is very rare that C–F bonds function as active fluorine sources. In addition to the many C=N additions cited above it is also well established that nitriles can add ClF.[53]

$$R_fCN + 2ClF \longrightarrow R_fCF_2NCl_2 \quad (65\text{–}76\%)$$

$$R_f = CF_3\text{–}, C_2F_5\text{–}, ClCF_2\text{–}, \text{–}CF_2\text{–}$$

These additions were carried out in the temperature range of 0 to −78°C and no mono ClF adduct could be detected, even when less than a stoichiometric amount of ClF was used. This is caused by the fact that this intermediate imine, –CF=NCl, is more reactive toward ClF than the nitrile itself. Cyanogen chloride behaves similarly, but the chloroamine spontaneously dechlorinates.[54]

$$ClN \xrightarrow{ClF} ClCF_2NCl_2 \xrightarrow[\Delta,\ \text{fast}]{25°C,\ \text{slow}} Cl_2 + CF_2{=}NCl$$

In contrast to this is the thermolysis[53] of the R_fNCl_2 compounds which require a higher temperature, 200°C, and results in of formation fo the azo compounds $R_fN{=}NR_f$.

Addition and fluorination. In the addition reactions of ClF occasionally fluorination was also observed and could not be precluded. These limited cases generally involve imino-type unsaturation.[51]

$$\overset{\text{no CsF}}{\nleftarrow} CF_3CCl_2N{=}C(CF_3)_2 + ClF \xrightarrow{CsF} CF_3CF_2NClCF(CF_3)_2$$

This product is the result of a series of ClF additions and Cl_2 eliminations promoted by CsF. One of the corresponding intermediates has been isolated for the related imine.

$$CF_3CCl{=}NCF(CF_3)_2 \xrightarrow[\text{no CsF}]{ClF} CF_3CF{=}NCF(CF_3)_2$$

$$CF_3CCl{=}NCF(CF_3)_2 \xrightarrow[CsF]{ClF} CF_3CF_2NClCF(CF_3)_2$$

Thus the ability to lose Cl_2 from >CCl–NCl– groups plays a dominant role in these cases. Less easily explained is the following azine–ClF reaction.[49]

$$(CF_3)_2C{=}N\text{–}N{=}C(CF_3)_2 \xrightarrow[\text{no CsF}]{ClF} (CF_3)_2CFN{=}NCCl(CF_3)_2$$

$$(CF_3)_2C{=}N\text{–}N{=}C(CF_3)_2 \xrightarrow[CsF]{ClF} (CF_3)_2CFN{=}NCCl(CF_3)_2 + (CF_3)_2CFN{=}NCF(CF_3)_2$$

Without CsF, a 1,4-chlorine fluoride addition occurs whereas with CsF a displacement of Cl by F is also encountered. The yield of the latter reaction varied but could not be completely supressed. Furthermore, CsF and ClF could not be made to give the fluorinated products using the 1,4-ClF adduct as a starting material.

Cleavage of bonds. While the preceding ClF addition schemes involved little or no bond breaking, there are numerous systems in which bond cleavage is the main result of the action of ClF. For example, treatment of KSCN at −30°C gives a variety of products, but none of these retains an S–C bond.[35]

$$KSCN + ClF \longrightarrow SF_5Cl,\ CF_3NCl_2,\ SF_6,\ CF_3N{=}NCF_3$$

In like manner, sulfinyl amines do not generate any N–S derivatives.[36,37]

$$RN{=}S{=}O + ClF \rightarrow RNCl_2 + SOF_2$$

$$R = CF_3–,\ FSO_2–$$

When ClNSO is subjected to ClF, nitrogen trichloride is a likely intermediate, although it was not isolated.[38]

$$ClNSO \xrightarrow{ClF} NCl_3 + SOF_2 \longrightarrow 1.5\ Cl_2 + 0.5\ N_2$$

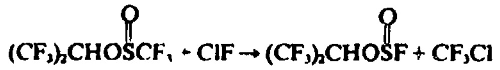
It was always observed that S(IV)–N bonds did not survive the action of ClF. This also appears to hold true for iminosulfur difluorides.[36]

$$R_fN{=}SF_2 + ClF \rightarrow R_fNCl_2 + SF_4$$

$$R_f = FCO–,\ CF_3CO–,\ CF_3–,\ i\text{–}C_3F_7–,\ F_2SNCF_2CF_2–$$

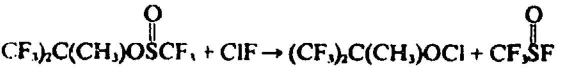
Efforts failed to isolate a mono adduct retaining the N–S linkage.

In the discussion of sulfide–ClF reactions, the important bond cleavage reactions of R_fSSR_f and R_fSR_f have been mentioned. Sulfinyl esters show at least two different bond breaking paths:[20]



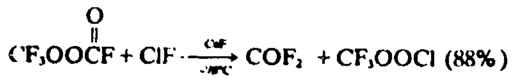
$$(CF_3)_2CHO\overset{O}{\overset{\|}{S}}CF_3 + ClF \rightarrow (CF_3)_2CHO\overset{O}{\overset{\|}{S}}F + CF_3Cl$$

and



$$(CF_3)_2C(CH_3)O\overset{O}{\overset{\|}{S}}CF_3 + ClF \rightarrow (CF_3)_2C(CH_3)OCl + CF_3\overset{O}{\overset{\|}{S}}F$$

Because this particular process was not studied in much detail, it is not possible to define the conditions favoring either an S–O bond breakage to furnish an hypochlorite or an S–C bond fission to produce a sulfinyl fluoride. A synthetically useful C–O cleavage reaction brought about by ClF was reported for fluorocarbonyl trifluormethyl peroxide.[22]



$$CF_3OO\overset{O}{\overset{\|}{C}}F + ClF \xrightarrow[-20°C]{CsF} COF_2 + CF_3OOCl\ (88\%)$$

This procedure simplifies the synthesis of CF_3OOCl by elimination of the previously required intermediate step of hydrolyzing CF_3OOCFO to CF_3OOH.

Summary. It is evident from the above discussion that ClF has recently been successfully exploited in a variety of fluorocarbon reactions. The high reactivity of ClF under a wide range of conditions generally results in good to excellent yields of specific products. Quite often these are unattainable by other means. It is likely that similar judicious applications of ClF to other yet unexplored cases will provide interesting and useful results.

R_fOCl/SF_5OCl

The close relationship between the fluorocarbon hypochlorites and pentafluorosulfur hypochlorite permits a joint discussion of their chemistry.

Syntheses and Properties

The earliest reported syntheses of R_fOCl were base catalyzed ClF additions to carbonyl functions.[18,41] Although not widely tested, Cl_2O was also used as a positive chlorine source to prepare the trifluoromethyl derivative.[41]

$$COF_2 + Cl_2O \xrightarrow[-20°C]{CsF} CF_3OCl + [CsOCl]$$

The base catalyzed chlorofluorination process was also applied to thionyl tetrafluoride.[41,39]

$$SOF_4 + ClF \xrightarrow[-20°C]{CsF} SF_5OCl$$

This is directly related to Ruff and Lustig's fluorination procedure[40] for the synthesis of SF_5OF. Soon after the original reports, acid catalysis was shown to be effective in this hypochlorite formation.[44] Subsequently, the reaction of ClF and certain alcohols opened yet another route to fluorocarbon hypochlorites.[19] All of these R_fOCl syntheses have been described in the preceding ClF reactions sections. Fluorocarbon hypochlorites and SF_5OCl are colorless liquids and gases. Volatility is related to molecular weight and is consistent with typical covalent fluorocarbons. For example, CF_3OCl has a bp of −46°C and SF_5OCl has a bp of 9°C. The thermal stability of the simpler compounds decreases rapidly from that of CF_3OCl in the following order: $CF_3OCl \gg C_2F_5OCl > i\text{–}C_3F_7OCl \sim SF_5OCl$. When an α fluorine is not present as in the ROH derived hypochlorites,[19] $(CF_3)_3COCl$, $CH_3C(CF_3)_2OCl$, $(CF_3)_2CHOCl$, etc.; then they are reported to be stable to at least 80°C. The hypochlorites are all susceptible to hydrolysis which is one of the major problems in utilizing them.

Reactions

General. The R_fOCl and SF_5OCl chemistry encompasses both radical and polar reactions. As part of the characterization of these compounds, the influence of UV photolysis was examined.

$$2\ CF_3OCl \xrightarrow{h\nu} CF_3OOCF_3 + Cl_2$$

$$2\ SF_5OCl \xrightarrow{h\nu} SF_5OOSF_5 + Cl_2$$

The high yields (90%)[18,41] of these peroxide forming processes render them useful for preparing these compounds. For CF_3OCl the photolysis has been studied under matrix conditions.[42] Longer chain R_fOCl with α fluorines give only degradation products attributed to rapid decomposition of the R_fCF_2O radicals. When the alkoxy radicals are stabilized by some special structural feature, then again peroxides can be obtained via photolysis.[43]

$$CH_3C(CF_3)_2OCl \xrightarrow[quartz]{h\nu} CH_3C(CF_3)_2OOC(CF_3)_2CH_3\ (90\%)$$

$$(CF_3)_3COCl \xrightarrow[h\nu,\ quartz]{-30°C} (CF_3)_3COOC(CF_3)_3\ (30\%)$$

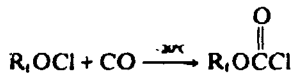
Other radical combinations are also known,[18,39] e.g. with NF_2 to produce CF_3ONF_2 and SF_5ONF_2. A reaction directly associated with the positive chlorine nature of the hypochlorites is the increased tendency to combine with negative chlorine. Seppelt has exploited this property as illustrated.[44,45]

$$CF_3OCl + HCl \xrightarrow[\text{solv}]{120^\circ C} CF_3OH + Cl_2$$

$$SF_5OCl + HCl \xrightarrow{-95^\circ C} SF_5OH + Cl_2$$

Trifluoromethyl alcohol is the first example of an isolated primary perfluoroalcohol. These have always been considered as nonexistent owing to their ready loss of HF. The thermal stability of CF_3OH is greater than that of SF_5OH (dec at −20° vs. −60°C) even though the former's decomposition is thermodynamically more favored. This has been explained in terms of the longer intramolecular H -F distances in CF_3OH compared to that in SF_5OH.

Oxidation. Spontaneous insertion of carbon monoxide into the OCl bond of these hypochlorites occurs in a near quantitative manner.[66] This is formally an oxidation of the carbon.



$$R_fOCl + CO \xrightarrow{-30^\circ C} R_fOC(O)Cl$$

$R_f = CF_3-, C_2F_5-, i\text{-}C_3F_7-, SF_5, (CF_3)_3C-, (CF_3)_2CH-$, etc.

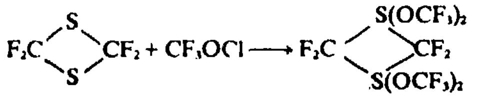
Hypofluorites undergo this reaction only with activation, while the best known alkyl hypochlorite, $(CH_3)_3COCl$, does not react with CO to 80°C. Fluorocarbon hypochlorites add directly to SO_2 at room temperature or below.[19,66] Excellent yields of the corresponding chlorosulfate are obtained by inserting the sulfur of the SO_2 molecule into the OCl bond.

$$R_fOCl + SO_2 \longrightarrow R_fOSO_2Cl$$

$R_f = CF_3-,\ i\text{-}C_3F_7-,\ (CF_3)_3C-,\ (CF_3)_2CH-,\ CH_3C(CF_3)_2-,\ CF_3CH_2-$

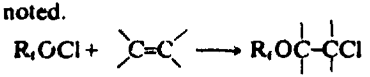
This represents a formal oxidation of S(IV) to S(VI). Under the influence of UV light CF_3OCl has been found to oxidize bis(trifluoromethyl)sulfide and tetrafluoro-1,3-dithietane.[67]

$$CF_3SCF_3 + CF_3OCl \xrightarrow[20\,h]{UV} (CF_3)_2S(OCF_3)_2$$



However, the duration of the described experiment seems incompatible with CF_3OCl being the active agent in this oxidation of S(II) to S(IV). Thus, CF_3OCl under UV irradiation decomposes rapidly to CF_3OOCF_3 and Cl_2. Therefore, unless the oxidation of S(II) to S(IV) occurs quickly it would appear that CF_3OOCF_3 alone, or assisted by Cl_2, must be the oxidizing agent.

Addition. The addition of R_fOCl to olefins has been investigated by several groups.[30,68,69] Rapid reaction was generally noted.



$$R_fOCl + \ \rangle C{=}C\langle \ \longrightarrow R_fO\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}Cl$$

$R_f = CF_3-$ Olefin = $CF_2{=}CF_2$, $CH_2{=}CH_2$, $CF_2{=}CFCl$, $CH_2{=}CHCl$, $CF_2{=}CH_2$, $CF_3CF{=}CF_2$, $CF_3OCH{=}CH_2$, $CFCl{=}CFCl$

$R_f = i\text{-}C_3F_7-$ Olefin = $CF_2{=}CF_2$

$R_f = (CF_3)_3C-$ Olefin = $CF_2{=}CF_2$, $CH_2{=}CH_2$

$R_f = SF_5-$ Olefin = $CF_2{=}CF_2$, $CH_2{=}CH_2$

Except for $CF_2{=}CFCl$, $CF_3CF{=}CF_2$, and $CF_3OCH{=}CH_2$ one product only was formed in these directed additions. That product was the one predicted on the basis of the chlorine from R_fOCl adding to the most electronegative carbon of the C=C bond. Where total direction was not possible the ratio of isomers obtained (if reported) was:

$$6\ CF_3OCFClCF_2Cl : 5\ CF_3OCF_2CFCl_2$$

and

$$7\ CF_3OCF_2CFClCF_3 : 3\ ClCF_2CF(OCF_3)CF_3$$

If the addition was allowed to proceed without moderation, some evidence for dimers and oils was noted,[68] thus indicating that R_fOCl is capable of inducing radical chain processes. The high yields (90%) and facile, yet controllable reactions experienced with these systems are contrary to those found for similar CF_3OF[70] and SF_5OF[71] additions which are extremely difficult to control. As would be expected the fluorocarbon ether products, especially the perhalofluorinated ones have outstanding thermal stability.[69] Additional 1:1 adducts of olefins and both CF_3OCl and SF_5OCl have been made and a comparison of their properties is being conducted.[72] Because of their desirable properties, these adducts should be a fertile area for investigation. Of all the olefins examined,[69] only $CF_3CF{=}CFCF_3$ failed to react along with the butyne, $CF_3C{\equiv}CCF_3$. One additional report on the addition of CF_3OCl to a double bond has appeared.[73]

$$C_2F_5N{=}CF_2 + CF_3OCl \rightarrow [C_2F_5NClCF_2OCF_3] \rightarrow C_2F_5NClCF_3 + COF_2$$

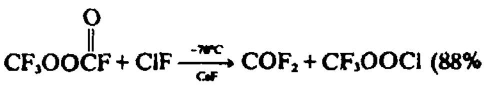
Decomposition of the adduct is surprising. By way of comparison, CF_3OF participates in this reaction only at 250°C and then only to form the fluorinated product, $C_2F_5NFCF_3$.

CF_3OOCl/SF_5OOCl

Syntheses and Properties

Chloroperoxytrifluoromethane has been prepared by two methods.

$$CF_3OOH + ClF \xrightarrow{-111^\circ C} HF + CF_3OOCl\ (95\%)$$

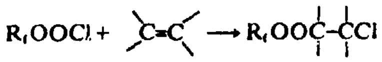


$$CF_3OOC(O)F + ClF \xrightarrow[CsF]{-78^\circ C} COF_2 + CF_3OOCl\ (88\%)$$

The former method[21] was used for the original synthesis of the compound and gives a purer product. The second route[22] pesumably proceeds via formation of CF_3OOCF_2OCl which decomposes eliminating COF_2 to furnish CF_3OOCl. Some dispute as to the stability of this pale yellow liquid (bp −20°) has arisen. While Ratcliffe, et al.[21] claimed that the compound was stable for prolonged periods at 25°C, Walker and DesMarteau reported only a few hours half life at that temperature.[22] Recently, the molecular structures of CF_3OOCl and the related CF_3OOH and CF_3OOF have been determined using gas phase electron diffraction.[74] For the chloro compound, steric CF_3–Cl interactions occur giving rise to two distinct conformers. The synthesis of SF_5OOCl was accomplished[75] by reactions analogous to those cited above for CF_3OOCl. The starting materials have been reported; SF_5OOH[76] and SF_5OOCFO.[77] Pentafluorosulfur peroxypochlorite was obtained in 70% yield from the hydroperoxide and in 90% yield from the fluoroacylperoxide. It is a straw-yellow liquid with an extrapolated boiling point of 26.4°C but it decomposes rapidly at 22°C.

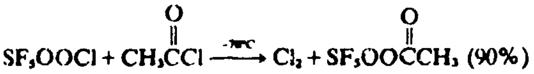
Reactions

The primary reaction mode of these R_fOOCl compounds is the rupture of the terminal hypochlorite bond. Both CF_3OOCl[22] and SF_5OOCl[76] add readily to olefins below 0°C to form peroxides.



$R_f = CF_3-$, SF_5- Olefin = C_2H_4, C_2F_4, C_2F_3Cl. CF_2CH_2, CF_2CCl_2, CFHCHCl, *cis*-CFHCFH

Yields vary and are usually higher for the CF_3-compound. Normally, where isomers are possible, only one product is formed in agreement with a directed, electrophilic addition. Smaller quantities of R_fO ethers are also obtained. The R_fO ether products are believed[76] to arise from reaction of R_fOCl, a decomposition product of R_fOOCl, with the olefins. The fluorocarbon peroxides that are formed are colorless liquids, stable at 22°C. Perfluoro-2-butyne did not react with CF_3OOCl and neither CF_3OOCl nor SF_5OOCl reacted with perfluoropropene or perfluorocyclopentene. Earlier,[21] it was shown that, unlike R_fOCl type materials, the R_fOOCl moieties do not insert CO or SO_2 into the O–Cl bond. Peroxyesters can be prepared from SF_5OOCl (and SF_5OOH) via acyl halide reactions[77] as shown by the following example:



$$SF_5OOCl + CH_3\overset{\overset{\displaystyle O}{\|}}{C}Cl \xrightarrow{-78°C} Cl_2 + SF_5OO\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \ (90\%)$$

This peroxyester is an ambient temperature stable compound, as are others prepared from SF_5OOH. Clearly, these chloroperoxides behave as positive chlorine species and are useful for the synthesis of many new peroxy derivatives.

CHLORINE FLUOROSULFATE

Synthesis and Properties

Chlorine fluorosulfate was first prepared[78] by Gilbreath and Cady according to:

$$Cl_2 + S_2O_6F_2 \xrightarrow{125°C} 2\ ClOSO_2F \ (100\%)$$

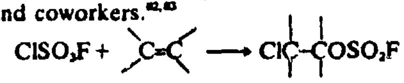
More recently, a more convenient procedure was developed[80,81] using the readily available SO_3 as a starting material.

$$ClF + SO_3 \longrightarrow ClOSO_2F \ (98\%)$$

Chlorine fluorosulfate is a pale yellow liquid (bp 43°C) which on standing or handling becomes red presumably due to the formation of some ClO_2SO_3F. It is stable at room temperature and has been stored in stainless steel for more than a year without significant decomposition. Nonetheless, it is an extremely reactive material with a host of substrates.

Reactions

Addition. At the time of its discovery, $ClOSO_2F$ (or $ClSO_3F$) was shown to add to olefinic double bonds, i.e. $CF_2{=}CF_2$.[79] Since then, these and similar reactions of $ClSO_3F$ have been studied by Moldavskii[38] and mainly by Fokin and coworkers.[82,83]



Olefins = C_2F_4, CFClCFCl, C_2F_3Cl, C_3F_6, $(CF_3)_2C{=}CF_2$, C_2Cl_4

Except for C_2F_3Cl where two isomers were noted, only one product was obtained following Markovnikov's rule. The order of reactivity with $ClSO_3F$ was: $C_2F_4 <$ $CFCl{=}CFCl \sim CF_2{=}CFCl < CF_3CF{=}CF_2 < (CF_3)_2C{=}CF_2$. Although this order of reactivity is similar to that observed for nucleophilic reagents, it was speculated[82] that the high electrophilicity of $ClSO_3F$ and the formation of isomers with C_2F_3Cl are in keeping with an electrophilic mechanism. Numerous other double bonds are also attacked by $ClSO_3F$. For example imines react at low temperature.[73,84]

$$C_2F_5N{=}CF_2 + ClSO_3F \xrightarrow{-78°C} C_2F_5NClCF_2OSO_2F$$

$$FN{=}C(NF_2)_2 + ClSO_3F \xrightarrow{-78°C} FNClC(NF_2)_2OSO_2F$$

In contrast HSO_3F must be heated to react with $C_2F_5N{=}CF_2$ and $S_2O_6F_2$ does not react at all.[73] These N–chloro compounds are stable at ambient temperature and are the only products, as expected for a directed polar addition.

Fluorinated isocyanates add $ClSO_3F$ according to:[47]

$$R_fN{=}C{=}O + ClSO_3F \longrightarrow R_fNCl\overset{\overset{\displaystyle O}{\|}}{C}OSO_2F \xrightarrow[-SO_3]{80°C} R_fNCl\overset{\overset{\displaystyle O}{\|}}{C}F$$

$R_f = CF_3-$, F–

Chlorine monofluoride adducts were similarly prepared[47] but other positive chlorine containing molecules, such as Cl_2O, CF_3OCl, ClNCO, and $ClNSF_2$, did not react. For ClNSO, the $ClSO_3F$ additions[38] were also analogous to those of ClF.

$$2\ ClN{=}S{=}O + 4\ ClSO_3F \longrightarrow 3\ Cl_2 + N_2 + 2\ SO(OSO_2F)_2$$

Only 2:1 addition was possible, and the intermediate NCl_3 decomposed to the elements. Most unusual is the ease with which $ClSO_3F$ adds to hexafluorobenzene below 20°C to give 1:1, 2:1, and 3:1 adducts depending on the stoichiometry employed.[85]

$$C_6F_6 + ClSO_3F \longrightarrow C_6F_6Cl(OSO_2F) + C_6F_6Cl_2(OSO_2F)_2 + C_6F_6Cl_3(OSO_2F)_3$$

Peroxydisulfuryl difluoride behaves similarly. Both compounds give a *para*-adduct in the 1:1 addition, as demonstrated by hydrolysis to 4-chloropentafluoro-2, 5-cyclohexadiene-one and fluoranil, respectively. These benzene adducts have good thermal stability and are high boiling liquids. Further details on their properties are lacking. The triple bond of nitrile groups also adds $ClSO_3F$ in a 1:1 manner.[86]

$$FC(NO_2)_2CN + ClSO_3F \rightarrow FC(NO_2)_2C(OSO_2F){=}NCl$$

If a cyano salt is involved, both chlorination and addition occur.

$$MC(NO_2)_2CN + 2\ ClSO_3F \rightarrow MSO_3F + ClC(NO_2)_2C(OSO_2F){=}NCl$$

It should be remembered that –C≡N and ClF reacted only in a 1:2 stoichiometry.[53]

Substitution. Fokin and coworkers investigated the replacement of chlorine and iodine by fluorosulfate in selected fluorocarbon halides using $ClSO_3F$.[87]

$$CFCl_2CFCl_2 + ClSO_3F \xrightarrow{40°C} CFCl_2CFClOSO_3F$$

$$CF_2ClCFCl_2 + ClSO_3F \xrightarrow{50^{\circ}C} CF_2ClCFClOSO_2F \ (84\%)$$

$$2\ CF_2Cl_2 + 3\ ClSO_3F \xrightarrow{80^{\circ}C} CF_2Cl(OSO_2F)\ (37\%) + CF_2(OSO_2F)_2\ (29\%)$$

$$CF_3I + ClSO_3F \xrightarrow{20^{\circ}C} CF_3OSO_2F \ (83\%)$$

Catalysis by HSO_3F was found to be necessary for these reactions to proceed. In general, facile stepwise substitution of chlorine in $-CFCl_2$ groups was observed. However, the method seemed restricted inasmuch as $CF_3CFClCF_2Cl$ was reported to be unreactive up to 100°C. Nevertheless in our experience[illegible] the Cl in $-CF_2Cl$ groups can be replaced as shown by:

$$ClCF_2CF_2Cl + ClSO_3F \xrightarrow{110^{\circ}C} ClCF_2CF_2OSO_2F \ (90\%)$$

The terminal Cl in $CF_3CFClCF_2Cl$ has also been replaced by $-SO_3F$ using $ClSO_3F$ and a small amount of Br_2 as a catalyst.[illegible] Bromo compounds, as expected, react more readily and some typical examples are:

$$C_2F_5Br + ClSO_3F \xrightarrow{25^{\circ}C} C_2F_5OSO_2F \ (96\%)$$

$$BrCF_2CF_2CF_2Br + ClSO_3F \xrightarrow{25^{\circ}C} CF_2(CF_2OSO_2F)_2 \ (50\%)$$

In none of these cases was the presence of HSO_3F necessary to attain the desired reaction. Acid salts and acids interact with $ClSO_3F$ in an expected manner, but the isolation of the unusual CF_3CO_2Cl intermediate was surprising.[illegible]

$$CF_3CO_2H + ClSO_3F \longrightarrow CF_3CO_2Cl \longrightarrow CF_3Cl + CO_2$$

As already mentioned above, the same compound has only recently been reported by DesMarteau[23] using ClF as the source of positive chlorine.

CHLORINE PERCHLORATE

Synthesis and Properties

Chlorine perchlorate is easily prepared by the action of $ClSO_3F$ on certain perchlorate salts.[illegible]

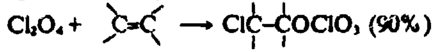
$$MClO_4 + ClSO_3F \xrightarrow{<-20^{\circ}C} MSO_3F + ClOClO_3 \ (90\%)$$

$$M = Cs^+, NO_2^+$$

Chlorine monofluoride has been used in place of $ClSO_3F$ but yields were very low and unreliable. Chlorine perchlorate ($ClOClO_3$ or Cl_2O_4) is a pale yellow liquid (extrapolated bp 44.5°C) with only limited stability at room temperature. It and nearly all of its covalent derivatives are shock sensitive. Consequently, they should always be treated with the respect appropriate for potential explosives. As a member of the class of compounds known as chlorine oxides, it is unusual because it is the only one containing chlorine in two different oxidation states, i.e. (+I) and (+VII).

Reactions

When examined with fluorocarbon olefins, reaction occurred rapidly at low temperature in a 1:1 mole ratio providing colorless liquid products.[illegible]



C_2F_4, C_2F_3Cl, CFClCFCl, C_3F_6, $CF_2{=}CFCF{=}CF_2$

The terminal Cl–O bond of $ClOClO_3$ was always cleaved during these reactions. The mono-adduct of perfluorobutadiene decomposed explosively and spontaneously at ambient temperature. All the other compounds exhibit good to excellent (100°C) thermal stability. Only one isomer was noted in all cases. For C_3F_6, this was the Markovnikov predicted product, $CF_3CFClCF_2OClO_3$, while for C_2F_3Cl it was the anti-Markovnikov compound, $ClCF_2CFCl(OClO_3)$. This is unexplained and different from $ClSO_3F$[81] and SF_5OOCl[75] which gave a mixture of isomers, and from CF_3OOCl[22] which gave only the expected $Cl_2CFCF_2OOCF_3$. Aromatic fluorocarbons add Cl_2O_4 at low temperature,[illegible] much as they do $ClSO_3F$,[illegible] confirming the close relationship of these two hypochlorites. Some minor differences, however, appear to occur since a 1:2, but not a 1:3, addition product is formed.

$$C_6F_6 + 2\ Cl_2O_4 \longrightarrow C_6F_6Cl_2(OClO_3)_2$$

$$C_6F_5Cl + 2\ Cl_2O_4 \longrightarrow C_6F_5Cl_3(OClO_3)_2$$

Both products are cyclohexenes and, based on NMR, only one isomer is obtained in each case. They are colorless, viscous liquids. With C_6F_5Br a more complex reaction was observed entailing addition and ring opening. The exact nature of the product has not been determined. Various fluorocarbon halides have been found to react with Cl_2O_4 resulting in a displacement of the halide by a perchlorate group.[91] In saturated fluorocarbon chlorides, primary and secondary chlorines in either mono or dichloro groups did not react. Trichlorofluoromethane did react, but gave COFCl and Cl_2O_7 as primary products. Bromine compounds were more susceptible to attack, as shown.

$$BrCF_2CF_2Br + Cl_2O_4 \xrightarrow{-25^{\circ}C} BrCF_2CF_2OClO_3 \ (11\%)$$

$$CF_3CFBrCF_2Br + Cl_2O_4 \xrightarrow{0^{\circ}C} CF_3CFBrCF_2OClO_3 \ (45\%)$$

$$(CFBrCF_2Br)_2 + Cl_2O_4 \xrightarrow{-25^{\circ}C} (CFBrCF_2OClO_3)_2 \ (90\%)$$

Geminal bromines, when substituted, led to decomposition products. If the bromine is on carbon adjacent to a perfluorogroup, no substitution ensued. Fluorocarbon iodides reacted vigorously with Cl_2O_4 as shown.

$$2\ R_fI + 4\ Cl_2O_4 \rightarrow (R_f)_2I^+I(ClO_4)_4^- \longrightarrow 2\ R_fOClO_3 + 2\ [IClO_4]$$

$$R_f = CF_3-, C_2F_5-, i\text{-}C_3F_7-, ICF_2CF_2-, C_6F_5-$$

With $C_7F_{15}I$, $i\text{-}C_3F_7I$, and C_6F_5I the intermediate salt was isolated and characterized.[91] Thermal decomposition of the heptane salt afforded $C_7F_{15}OClO_3$, but the isopropyl and the aromatic compounds exploded before they could give the simple covalent perchlorate. These conversions of R_fI to R_fOClO_3 were high yield processes. The only other known route to fluorocarbon perchlorates, which does not involve the halogen perchlorates, is the reaction of alcohols and alkoxides with Cl_2O_7, wherein the products normally were not isolated.[illegible]

CHLORINE NITRATE

Synthesis and Properties

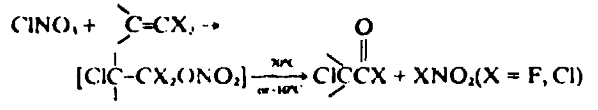
Originally chlorine nitrate was prepared from either Cl_2O or ClO_2 with NO_2 or N_2O_5.[illegible] To avoid the use of the hazardous chlorine oxides, the following alternate synthesis was developed.[illegible]

$$ClF + HNO_3 \xrightarrow{-20^\circ C} HF + ClNO_3\ (90\%)$$

Commercial anhydrous nitric acid may be used. The formed $ClNO_3$ ($ClONO_2$) is a pale yellow liquid (bp 23°C) which undergoes slow decomposition at ambient temperatures, but which may be stored indefinitely at −40°C or lower.

Reactions

Only one report on the addition of $ClNO_3$ to unsaturated fluorocarbons has appeared.[illegible]



The vigorous reaction of $ClNO_3$ with these olefins necessitated dilution with solvents. When two halogens were on the nitrate carbon, the illustrated low temperature decomposition occurred. This instability has discouraged further work on fluorocarbon nitrates.

As part of a study on halogen nitrates,[7] the system CF_3I–$ClNO_3$ was examined with the following results.

$$CF_3I + 2\ ClNO_3 \xrightarrow{-45^\circ C} Cl_2 + CF_3I(ONO_2)_2 \xrightarrow{25^\circ C}$$
$$COF_2,\ CF_3I,\ N_2O_5,\ \text{etc.}$$

Thus, as with Cl_2O_4, an intermediate oxidized iodo derivative is generated first. Unlike the perchlorate case however, this does not decompose to a stable R_fNO_3, but degrades as shown. Naumann and coworkers have studied these processes more carefully,[illegible] isolating the $CF_3I(ONO_2)_2$ intermediate and obtaining still another intermediate which they did not isolate.

$$CF_3I + ClNO_3 \rightarrow CF_3ICl(ONO_2) \xrightarrow{<-20^\circ C} CF_3I(ONO_2)_2$$

A thorough, controlled decomposition scheme was worked out for the dinitrato moiety above −20°C involving intermediates, such as CF_3IO and CF_3IO_2. The overall decomposition equation is:

$$10\ CF_3I(NO_3)_2 \rightarrow 5\ CF_3I + 5\ COF_2 + 10\ N_2O_5 + I_2 + IF_5 + I_2O_5$$

Raman spectroscopic characterization of $CF_3I(NO_3)_2$, $C_2F_5I(NO_3)_2$, and related compounds has been reported.[illegible] Even though $ClNO_3$ has been available for a number of years, it has not been extensively investigated with respect to fluorocarbons. This might be explained by the apparent instability of the products.

SUMMARY

Most of the known reaction chemistry of electropositive chlorine compounds can be rationalized in terms of either addition of Cl–X across multiple bonds or oxidative addition to atoms, such as iodine or sulfur in their lower oxidation states. The observed variety of the final reaction products can be explained by a multitude of secondary reactions which can involve either eliminations, further additions, or degradations. The observed reactions are easily moderated and controlled, and only rarely was no reaction encountered. The $Cl^{\delta+}$–$X^{\delta-}$ polarity of the Cl–X bond in these compounds was demonstrated by the "directed" nature of many of the reactions. The strong electrophilic character of these compounds was also evident. Because of the great reactivity of these compounds and the limited amount of work done so far in this area, there are many opportunities for future fruitful research.

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Bromyl Fluoride. Vibrational Spectra, Force Field, and Thermodynamic Properties

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Infrared spectra are reported for $FBr^{18}O_2$ in the gas phase and for $FBr^{16}O_2$ in Ne, N_2, and Ar matrices at 3.6 K. Isotopic shifts were measured for $^{79}Br-^{81}Br$ and $^{16}O-^{18}O$ and were used for the computation of a valence force field. Thermodynamic properties were computed for $FBrO_2$ and $FClO_2$ in the range 0–2000 K.

Introduction

Bromyl fluoride was first synthesized by Schmeisser and Pammer[1,2] in 1955. Because of its low thermal stability and high reactivity, this compound had been only poorly characterized and was not further studied until 1975. In 1975, Gillespie and Spekkens published[3] the Raman spectra of solid and liquid $FBrO_2$ and proposed a monomeric pyramidal structure, similar to that[4] of $FClO_2$. Using Raman frequencies reported[3] for liquid $FBrO_2$, Baran calculated[5] a modified valence force field and mean amplitudes of vibration for $FBrO_2$, assuming all bond angles to be 108°. Very recently, Jacob succeeded[6] in obtaining good gas-phase infrared spectra for $FBrO_2$ in spite of the fact that gaseous $FBrO_2$ possesses a half-life of only 30 min at 15 °C. He also prepared a sample of $FBr^{18}O_2$ and reported preliminary infrared data for the gas and for the neat and the argon matrix isolated solid. Although the oxygen isotopic shifts were measured, no $^{79}Br-^{81}Br$ isotopic shifts were given.[24]

In this paper, we report higher resolution spectra and oxygen and bromine isotopic shifts for gaseous and for Ne, N_2, and Ar matrix isolated $FBrO_2$. In view of the interest[3,5] in the nature of bonding in $FBrO_2$, a new force field computation appeared warranted, particularly since the previously used[5] frequencies significantly differ from those of gaseous $FBrO_2$ and since the previously assumed[5] geometry of $FBrO_2$ was only a crude estimate. Furthermore, the availability of both oxygen and bromine isotopic shifts offered a unique opportunity to test the value of such additional data for the refinement of force fields for compounds, such as bromine oxyfluorides.

Experimental Section

The samples of $FBrO_2$ used for recording the gas-phase spectra were prepared, as previously described,[6] by low-temperature cocondensation of BrF_5 and H_2O. The infrared spectra of gaseous $FBrO_2$ were recorded at 15 °C on a Perkin-Elmer Model 325 spectrophotometer in the range 4000–290 cm^{-1} using a nickel cell with AgBr windows attached to an external mirror system (optical path length 110 cm).

The samples of $FBrO_2$ used for the matrix isolation study were obtained as a byproduct during a spectroscopic study[7] of BrF_3O. The spectrometer and handling have been previously described.[7]

Results and Discussion

Infrared Spectra of Gaseous $FBrO_2$. A survey infrared spectrum of gaseous $FBr^{18}O_2$ is shown in Figure 1. The corresponding spectrum of $FBr^{16}O_2$ has previously been re-

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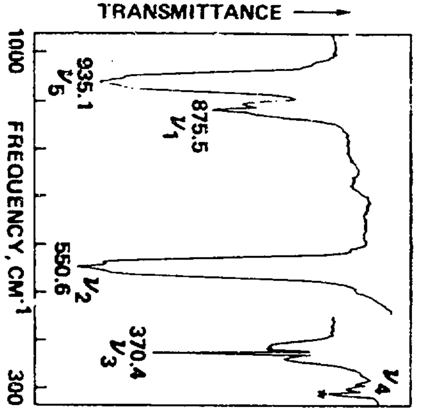


Figure 1. Survey infrared spectrum of gaseous $FBr^{18}O_2$ recorded at 15 °C in a nickel cell equipped with AgBr windows with an optical path length of 110 cm^{-1}. The band marked by an asterisk in due to HF.

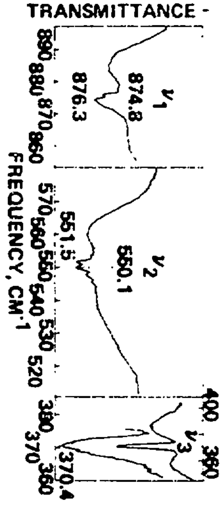


Figure 2. Band contours of ν_1, ν_2, and ν_3 of gaseous $FBr^{18}O_2$ recorded under higher resolution conditions with scale expansion. For ν_1 and ν_2 the frequencies of the ^{79}Br and ^{81}Br Q-branch centers are marked. For ν_3, only the unresolved Q branch is shown at the same scale as that used for ν_1 and ν_2. The complete band envelope is shown at a 2.5× compressed scale.

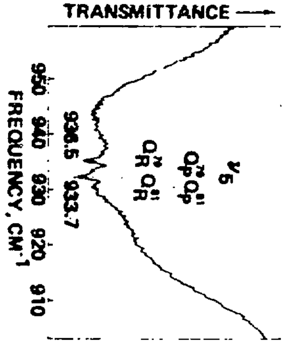


Figure 3. Band contour of ν_5 of gaseous $FBr^{18}O_2$ showing the double Q branches for both bromine isotopes.

ported.[6] Figures 2 and 3 show the band contours of each band recorded under higher resolution conditions and scale expansion.

The observed gas-phase frequencies of $FBrO_2$ are compared in Table I to those[3,6] previously reported for the liquid and the solid. As can be seen from Table I, the gas-phase frequencies significantly deviate from those of liquid and solid $FBrO_2$, indicating some degree of association in the condensed phases. The BrF stretching mode, ν_2 (A′), exhibits the most pronounced frequency change (−62 cm^{-1}) on going from the gas to the solid, whereas the mean frequency change of the two BrO_2 stretching modes, ν_1 (A′) and ν_5 (A″), is only −17 cm^{-1}. This indicates that association takes place mainly through the fluorine ligands. Preferential association through fluorine ligands has previously also been demonstrated[7] for BrF_3O.

Infrared Spectra of Matrix-isolated $FBrO_2$. In order to obtain unambiguous bromine isotopic shifts (bromine contains two naturally occurring isotopes, ^{79}Br and ^{81}Br, of almost equal

Table I. Vibrational Spectra of $FBrO_2$

assignment in point group C_s	obsd freq, cm^{-1}, and rel intens															anharmonic isotopic shifts, cm^{-1}	
	Infrared												Raman[b]				
	gas				matrix isolated						solid[a] (−87 °C)						
					Ne		N_2		Ar								
	$F^{79}Br$-$^{16}O_2$	$F^{81}Br$-$^{16}O_2$	$F^{79}Br$-$^{18}O_2$	$F^{81}Br$-$^{18}O_2$	$F^{79}Br$-$^{16}O_2$	$F^{81}Br$-$^{16}O_2$	$F^{79}Br$-$^{16}O_2$	$F^{81}Br$-$^{16}O_2$	$F^{79}Br$-$^{16}O_2$	$F^{81}Br$-$^{16}O_2$	F-$^{79,81}Br$-$^{16}O_2$	F-$^{79,81}Br$-$^{18}O_2$	solid −75 °C $F^{79,81}Br^{16}O_2$	liquid −10 °C $F^{79,81}Br^{16}O_2$	BrF_5 soln room temp $F^{79,81}Br^{16}O_2$	$\Delta_{^{16}O^{18}O}$	$\Delta_{^{79}Br^{81}Br}$
A′ ν_1	921.0	919.5	876.3	874.8	921.6	920.1	922.3	920.8	914.8	913.3	918 vs	867	908 (100)	908 (100) p	916 (100) p	44.7	1.5
ν_2	551.9	550.4	551.5	550.1	546.2	544.8	535.7	534.3	537.0	535.6	490 vs, br	486	524 sh 496 (25) 487 sh	506 (36) p		0.4	1.4
ν_3	385.8		370.4		386.8		391.2		384.0		387 ms	369	400 sh 386 (10)	394 (14) p		15.4	
ν_4	~310		~296								305 mw	290	305 (20) 294 sh	305 (21) p		~14	
A″ ν_5	978.9	976.2	936.5	933.7	976.2	973.6	971.2	968.6	967.2	965.6	947 vs, br	902	963 (5) 940 (20)	953 (14) dp	962 (8) dp	42.4	2.7
ν_6											276 271 mw	260	267 (15)	271 (16) dp			

[a] Data from ref 6. [b] Data from ref 3.

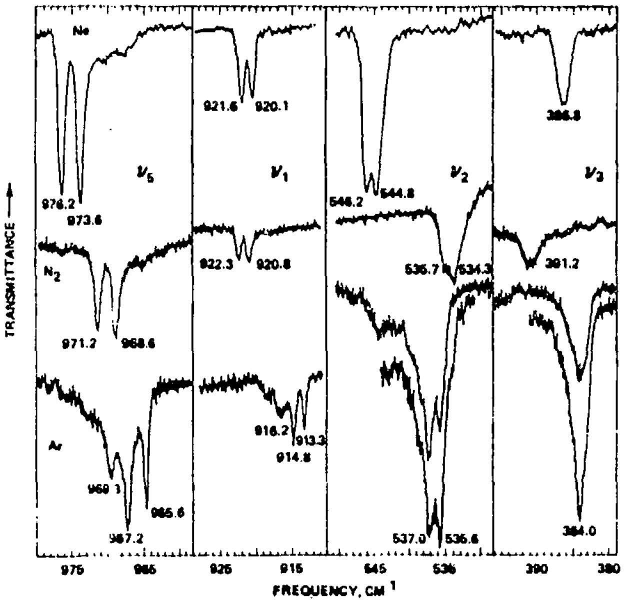


Figure 4. Infrared spectra of Ne, N_2, and Ar matrix isolated $FBr^{16}O_2$, recorded at 3.6 K with 20-fold scale expansion under higher resolution conditions using CsI windows and a mole ratio of ~1000:1.

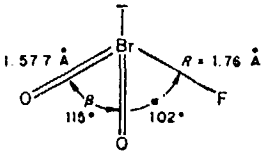
abundance) for $FBrO_2$, the infrared spectra of matrix-isolated $FBr^{16}O_2$ were recorded at 3.6 K. Since, for the related BrF_3O[7] and BrF_3[8] molecules, pronounced and unpredictable matrix effects and splittings were observed, the spectra of $FBrO_2$ were recorded in three different matrix materials, i.e., Ne, N_2, and Ar. The observed spectra, recorded under higher resolution conditions with 20-fold scale expansion, are shown in Figure 4. The observed frequencies are listed in Table I. By analogy with previous reports on matrix-isolated BrF_3[8,9] and BrF_3O,[7] the $FBrO_2$ spectra exhibited pronounced matrix frequency shifts. As for BrF_3[8] and BrF_3O,[7] a Ne matrix was found to give the best results and frequency values very close to those found for the gas phase (see Table I). Association effects were most pronounced in the Ar matrix.

Assignments and Determination of Isotopic Shifts. The assignments for $FBrO_2$ in point group C_s are straightforward and are well supported by Raman polarization data,[3] by ^{18}O isotopic shifts,[6] and by comparison with the spectra of the closely related $FClO_2$[10] and SeO_2F^-[3] species. They are listed in Table I and require no further comment.

For the determination of the ^{16}O–^{18}O isotopic shifts in $FBrO_2$, the gas-phase anharmonic infrared frequencies listed in Table I were used. However for compounds exhibiting such large isotopic shifts, anharmonicity corrections of these shifts are important for force field calculations. Unfortunately, no experimental data are available for $FBrO_2$ to permit reliable anharmonicity corrections. However for RuO_4, which possesses a central atom of a mass similar to that of Br and exhibits comparable ^{16}O–^{18}O isotopic shifts, anharmonicity corrections were estimated[11] to be about 1.4 and 0.5 cm^{-1} for the ^{16}O–^{18}O isotopic shifts of the ν_3 stretching and the ν_4 deformation modes, respectively. Assuming similar correction values for $FBrO_2$, the magnitude of the expected anharmonicity corrections obviously is significantly larger than the 0.1 cm^{-1} uncertainty in the values of the observed anharmonic frequencies. Therefore, we have treated the observed anharmonic oxygen isotopic shifts in the following normal-coordinate analysis as the lower limit and have used 1.6 and 1.0 cm^{-1} larger shifts as the upper limits for the stretching modes ν_1 and ν_5 and the deformation mode ν_3, respectively. As will be shown, the force field analysis supports this choice.

For the bromine isotopic shifts, anharmonicity corrections are much less of a problem due to the smallness (0–3 cm^{-1}) of these shifts. Therefore, possible anharmonicity corrections for these shifts should not exceed the measured uncertainties (±0.1 cm^{-1}) of these shifts. The best values for the isotopic shifts are listed in the last two columns of Table I. The agreement between the bromine isotopic shifts observed for gaseous $FBrO_2$ and those observed for the matrix-isolated species is generally good if one takes into consideration that the Q-branch band contours of ν_1 and ν_2 are distorted on the P-branch side by hot bands and that for ν_5 a double Q branch is observed for each bromine isotope.

Force Field Computations. A normal-coordinate analysis was carried out for $FBrO_2$ to obtain more reliable force constants for this interesting molecule and to examine the usefulness of isotopic shifts for such an analysis. The potential and kinetic energy matrices were computed by a machine method.[12] The geometry



was assumed for this computation, based on the known geometries of $FBrO_3$,[13] $FClO_3$,[14] and $FClO_2$[4] and an extrapolation between BrO bond length and stretching frequency, similar to that[15] used for ClO bonds, using the data published for BrO_4^-[16,17] and $FBrO_3$.[13,18] This geometry appears more likely than that ($\alpha = \beta = 108°$, $r = 1.63$ Å) chosen[5] by Baran for his computation. The symmetry coordinates used for $FBrO_2$ were identical with those previously given[10] for $FClO_2$, except for the correction of the obvious typographical error in the factor of S_4. The bending coordinates were weighted by unit (1 Å) distance.

The force constants were adjusted by trial and error with the aid of a computer to give an exact (0.1 cm^{-1}) fit between all observed and computed frequencies. The observed ^{79}Br–^{81}Br and ^{16}O–^{18}O isotopic shifts were used as additional constraints. We will first discuss our choice of a force field for the A″ block since it contains only one stretching and one deformation mode.

The force constants of F_{55} and F_{66} were computed as a function of F_{56}. The resulting curves are shown in Figure 5. We have also computed the bromine and oxygen isotopic shifts over the same range of F_{56} and have plotted their values in Figure 5. The observed isotopic shifts, $\Delta_{Br_{\nu_5}}$ ± 0.1 cm^{-1} and $\Delta_{O_{\nu_5}}$ ± 1.6 cm^{-1} (see above discussion of anharmonicity corrections), were used to define the probable range of the force constants. The values thus obtained are given in Figure 5 and Table II. Figure 5 demonstrates the importance of the anharmonicity corrections for $\Delta_{O_{\nu_5}}$, i.e., a better overlap with the $\Delta_{Br_{\nu_5}}$ force field constraint, as previously demonstrated[19] by McDowell and Goldblatt for OsO_4. Furthermore, it shows that the preferred force field closely corresponds to F_{66} being a minimum, a condition previously shown[19,20] to be a good approximation to the general valence force field values for similar weakly coupled systems.

For the A′ block of $FBrO_2$ the problem of defining a preferred force field is more difficult since this block contains two stretching and two deformation modes. Numerical experiments showed that only three of the six off-diagonal symmetry force constants were essential for fitting the isotopic data. These three off-diagonal constants were F_{13}, F_{24}, and F_{34}, with F_{13} and F_{34} being more important then F_{24}. This result is in good agreement with the previous findings[10] for the related $FClO_2$ molecule and is not surprising in view of

Table II. Observed Frequencies for $F^{79}Br^{16}O_2$, Symmetry Force Constants,[a] Computed and Observed $^{16}O-^{18}O$ and $^{79}Br-^{81}Br$ Isotopic Shifts, and Potential Energy Distribution[b]

assignment in point group C_s	approx description of mode	freq, cm⁻¹	symmetry force constants		isotopic shifts, cm⁻¹ calcd Δ_O	calcd Δ_{Br}	obsd Δ_O	obsd Δ_{Br}	PED
A′ ν_1	$\nu_{sym}(BrO_2)$	921.0	$F_{11} = f_r + f_{rr}$	6.931 ± 0.095	45.23	1.56	44.7	1.5	96 F_{11}
ν_2	$\nu(BrF)$	551.9	$F_{22} = f_R$	2.750 ± 0.04	0.31	1.40	0.4	1.4	99 F_{22}
ν_3	$\delta_{scis}(BrO_2)$	385.8	$F_{33} = f_\beta$	1.453 ± 0.08	15.65	1.12	15.4		76 F_{33}, 16 F_{34}
ν_4	$\delta_{sym}(FBrO_2)$	310	$F_{44} = f_\alpha + f_{\alpha\alpha}$	1.487 ± 0.08	11.74	0.52			103 F_{44}, 37 F_{33}, −41 F_{34}
			$F_{13} = f_{r\beta}$	−0.40 ± 0.19					
			$F_{24} = f_{R\alpha}$	0.095 ± 0.09					
			$F_{34} = f_{\alpha\beta}$	0.49 ± 0.07					
A″ ν_5	$\nu_{asym}(BrO_2)$	978.9	$F_{55} = f_r - f_{rr}$	7.037 ± 0.06	43.28	2.70	42.4	2.7	100 F_{55}
ν_6	$\delta_{asym}(FBrO_2)$	273	$F_{66} = f_\alpha - f_{\alpha\alpha}$	0.762 ± 0.004	7.21	0.33			100 F_{66}
			$F_{56} = f_{r\alpha} - f_{r\alpha}'$	0.14 ± 0.22					

[a] Stretching constants in mdyn/A, deformation constants in mdyn A/rad², and stretch-bend interaction constants in mdyn/rad. [b] Percent contributions. Contributions of less than 9% to the PED are not listed.

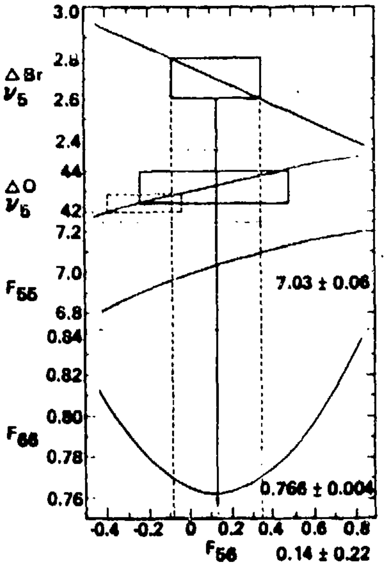


Figure 5. Force constant display of the A″ block of $FBrO_2$ using the observed bromine (2.7 ± 0.1 cm⁻¹) and oxygen (42.4 ± 1.6 cm⁻¹) isotopic shifts as constraints. F_{55}, F_{66}, and F_{56} have units of mdyn/Å, mdyn Å/rad², and mdyn/rad, respectively. The rectangle of $\Delta_{O,5}$ marked by broken lines represents the observed anharmonic oxygen shift of ν_5 ± 0.4 cm⁻¹, whereas the solid rectangle assumes the observed anharmonic oxygen shift as the lower limit and a 1.6 cm⁻¹ higher value, for anharmonicity corrected, as the upper limit. The broken and the solid vertical lines indicate the plausible force constant ranges and the preferred force field, respectively.

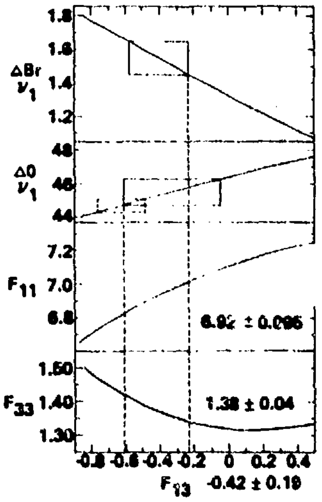


Figure 6. Force constant display of the A′ block. All off-diagonal constants were set to zero, except for F_{13}. Only those diagonal constants are shown which were significantly influenced by changes in the interaction constant F_{13}. For additional explanation see caption of Figure 5.

the fact that G_{13}, G_{24}, and G_{34} are the major off-diagonal G matrix terms in the A′ block. It was also shown that the variation of F_{13}, F_{24}, and F_{34} strongly influenced only the corresponding diagonal terms. This relative independence of the interaction constants permitted us to examine each of them separately. The results of these computations were again summarized in graphical form and are presented in Figures 6–8. In this manner, the values of F_{13}, F_{24}, and F_{34}, required to duplicate all of the observed isotopic data, were determined. These three interaction constants were then combined in a single force field, and a satisfactory fit of the isotopic data could be achieved with only minor adjustments. The resulting force field is given in Table II. The computed oxygen shifts were intentionally kept slightly larger than those observed to leave some room for any future anharmonicity corrections.

Figures 6 and 7, dealing with the stretch–bend interaction constants F_{13} and F_{24}, respectively, are analogous to Figure 5, which has been discussed above in detail for the A″ block, and therefore do not require any further comment. Figure 8 shows the dependence of the two diagonal bending constants F_{33} and F_{44} on the bend–bend interaction constant F_{34}. In order to be able to fit the observed oxygen shift of ν_3, either a rather large positive or a small negative value is required for F_{34}. Of these two possibilities, the former is preferred, since it results in more plausible force constants. For F_{34} = 0.2, the potential energy distribution (PED) is essentially 100% characteristic (F_{44} = minimum), whereas, for the extreme values of F_{34}, ν_3 and ν_4 become about even mixtures of F_{33} and

Table III. Internal Force Constants[a] of $FBrO_2$ Compared to Those Previously Reported

	this work	ref 5	b
f_r	6.984 ± 0.08	6.76	6.78
f_R	2.750 ± 0.04	2.25	2.24
f_{rr}	−0.05 ± 0.08	0	0.14
f_α	1.125 ± 0.04	1.090	1.066
f_β	1.453 ± 0.08	1.664	1.485
$f_{\alpha\alpha}$	0.363 ± 0.04	0.344	0.288
$f_{\alpha\beta}$	0.49 ± 0.07	0.01	
$f_{R\alpha}$	0.095 ± 0.09	0.034	
$f_{r\alpha}$	−0.07 ± 0.11	0	
$f_{r\alpha}'$	+0.07 ± 0.11	0	

[a] Units are identical with those of Table II. [b] R. Bougon, P. Joubert, and G. Tantot, *J. Chem. Phys.*, 66, 1562 (1977).

Table IV. Stretching Force Constants (mdyn/A) of $FBrO_2$ Compared to Those of Other Bromine Compounds

	BrO_3^- [a]	BrO_4^- [b]	$BrF_2O_2^-$ [k]	BrF_4O^- [c]	BrF_4^- [d]	$FBrO_2$	$FBrO_2$ [e]	BrF_3O [f]	BrF	BrF_3 [g]	BrF_5 [h]	BrF_2^+ [i]	BrF_6^+ [j]
f_r(BrO)	5.28	6.05	6.32	6.70		6.98	6.92	7.68					
f_R(BrF)			1.63	2.14	2.23	2.75		2.93		3.10	3.24		
f_R'(BrF)							3.22	3.51	4.07	4.07	4.02	4.60	4.90

[a] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie", Springer-Verlag, Berlin, 1966. [b] Reference 17. [c] K. O. Christe, R. D. Wilson, E. C. Curtis, W. Kuhlmann, and W. Sawodny, *Inorg. Chem.*, 17, 533 (1978). [d] K. O. Christe and D. Naumann, *ibid.*, 12, 59 (1973). [e] Reference 13. [f] K. O. Christe, E. C. Curtis, and R. Bougon, *Inorg. Chem.*, 17, 533 (1978). [g] Reference 9. [h] K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, 11, 1679 (1972). [i] K. O. Christe and C. J. Schack, *ibid.*, 9, 2296 (1970). [j] K. O. Christe and R. D. Wilson, *ibid.*, 14, 694 (1975). [k] R. Bougon, P. Joubert, and G. Tantot, *J. Chem. Phys.*, 66, 1562 (1977).

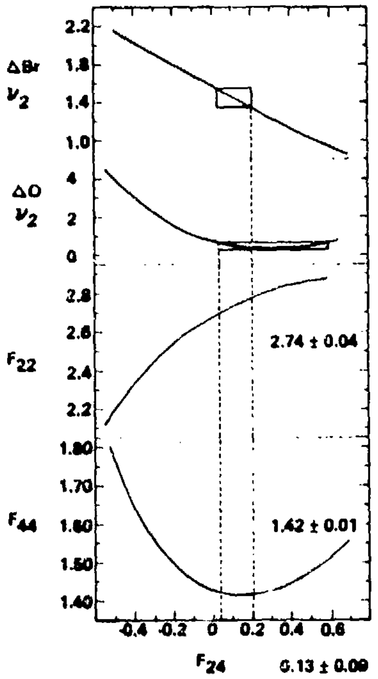


Figure 7. Force constant display of the A′ block showing the dependence of F_{22} and F_{44} on F_{24}. For additional explanation see captions of Figures 5 and 6.

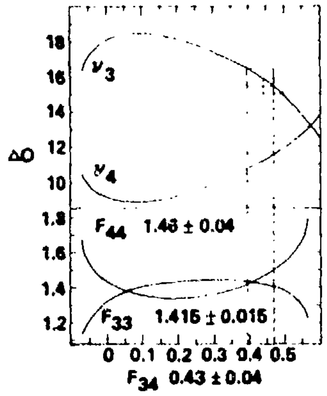


Figure 8. Force constant display of the A′ block showing the dependence of F_{33} and F_{44} on F_{34}.

F_{44}. The moderate amount of mixing obtained for ν_3 and ν_4 in our preferred force field (see Table II) is not surprising in view of their similar frequencies and motions involved. The remainder of the PED (see Table II) is highly characteristic and supports the approximate description of the modes given in Table II.

A comparison of the internal force constants of $FBrO_2$ with those previously reported is given in Table III. As can be seen, our force field significantly differs, particularly for f_R and $f_{\alpha\beta}$.

Table V. Thermodynamic Properties for $F^{79}Br^{16}O_2$

T, K	$C_p°$, cal/(mol deg)	$(H°_T - H°_0)$, kcal/mol	$-(F°_T - H°_0)/T$, cal/(mol deg)	$S°_T$, eu
0	0	0	0	0
100	9.493	0.831	48.749	57.059
200	12.831	1.957	54.945	64.732
298.15	15.033	3.332	59.119	70.295
300	15.066	3.360	59.188	70.388
400	16.527	4.945	62.576	74.938
500	17.467	6.648	65.438	78.734
600	18.082	8.427	67.931	81.977
700	18.498	10.258	70.144	84.797
800	18.789	12.123	72.134	87.288
900	18.998	14.013	73.944	89.513
1000	19.154	15.921	75.603	91.523
1100	19.272	17.842	77.134	93.355
1200	19.363	19.774	78.557	95.036
1300	19.436	21.714	79.885	96.589
1400	19.494	23.661	81.130	98.031
1500	19.541	25.613	82.303	99.378
1600	19.580	27.569	83.410	100.640
1700	19.613	29.529	84.458	101.828
1800	19.640	31.491	85.455	102.950
1900	19.664	33.456	86.404	104.013
2000	19.684	35.424	87.310	105.022

Our results show that the BrF bond in $FBrO_2$ is significantly stronger than previously assumed.[1,5]

Comparison with Similar Compounds and Bonding in $FBrO_2$. A comparison of the $FBrO_2$ stretching force constants with those of other bromine oxides, fluorides, and oxyfluorides is given in Table IV. The BrF stretching force constants are separated into two groups. The low f_R force constants observed for $BrF_2O_2^-$, BrF_4O^-, BrF_4^-, and some of the bonds in BrF_3 and BrF_5 can be attributed to significant contributions from semiionic, three-center, four-electron bonding while it is assumed that the bonds belonging to the f_R' group are largely covalent. The spread within each group is caused by secondary effects, such as formal charge (anion, neutral molecule, or cation), degree of fluorine substitution, and oxidation state of the central atom. These effects have previously been discussed[21,22] at length for the corresponding chlorine compounds and appear to be also applicable to the bromine compounds of Table IV, although for the latter they are somewhat less pronounced. This is caused by the fact that the larger bromine central atoms are more polarizable than chlorine, thereby causing the two types of bonds to become less distinct.

As far as $FBrO_2$ is concerned, it can be seen from Table IV that its stretching force constants do not fit too well the general trends of Table IV, and it is therefore placed between these two groups. A similar anomaly has previously been noted for $FClO_2$ and was explained by a weak highly polar $(p-\pi^*)\sigma$ bond.[22] The same explanation, i.e., bonding between a 2p electron of F and an antibonding π^* orbital of the BrO_2 radical, can be invoked for $FBrO_2$.

Thermodynamic Properties. The thermodynamic properties of $F^{79}Br^{16}O_2$ were computed with the molecular geometry

Table VI. Thermodynamic Properties of $F^{35}Cl^{16}O_2$

T, K	$C_p°$, cal/(mol deg)	$(H°_T - H°_0)$, kcal/mol	$-(F°_T - H°_0)/T$, cal/(mol deg)	$S°_T$, eu
0	0	0	0	0
100	8.507	0.805	46.851	54.898
200	11.267	1.790	52.666	61.618
298.15	13.509	3.012	56.456	66.559
300	13.545	3.037	56.519	66.643
400	15.167	4.478	59.581	70.775
500	16.318	6.055	62.180	74.291
600	17.134	7.730	64.459	77.342
700	17.718	9.474	66.495	80.030
800	18.143	11.268	68.339	82.425
900	18.459	13.099	70.026	84.581
1000	18.699	14.958	71.581	86.539
1100	18.884	16.837	73.023	88.330
1200	19.030	18.733	74.368	89.979
1300	19.147	20.642	75.629	91.507
1400	19.241	22.562	76.814	92.930
1500	19.318	24.490	77.934	94.260
1600	19.382	26.425	78.993	95.509
1700	19.436	28.366	80.000	96.686
1800	19.481	30.312	80.958	97.798
1900	19.520	32.262	81.872	98.852
2000	19.554	34.216	82.747	99.854

given above and the vibrational frequencies of Table II, assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator, rigid-rotor approximation.[23] These properties are given for the range 0–2000 K in Table V. Since no thermodynamic data had previously been reported for $FClO_2$, we have also computed these properties for $F^{35}Cl^{16}O_2$ (see Table VI) using the previously published frequencies[10] and geometry.[4]

Conclusion

A force field has been computed for $FBrO_2$ using gas-phase frequency values and bromine and oxygen isotopic shifts. It was shown that the most important force constants, f_{BrO} and f_{BrF}, can be determined with an accuracy of about 0.08 and 0.04 mdyn/Å, respectively. The importance of anharmonicity corrections for the oxygen shifts was demonstrated. In the absence of such anharmonicity corrections, the bromine isotopic shifts are more useful for defining the force field because of the smaller anharmonicity corrections required. The BrF bond in $FBrO_2$ (2.75 mdyn/Å) is considerably stronger than previously assumed (2.25 mdyn/Å)[5] but is still somewhat weaker than predicted by comparison with related bromine compounds. This weakening effect might be explained by assuming a polar σ bond between a 2p electron of F and an antibonding π^* orbital of the BrO_2 radical.

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Registry No. $F^{79}Br^{16}O_2$, 67452-70-4; $F^{35}Cl^{16}O_2$, 35880-03-6; $FBrO_2$, 22585-64-4; $FBr^{18}O_2$, 64544-65-6; ^{18}O, 14797-71-8; ^{79}Br, 14336-94-8; ^{81}Br, 14380-59-7.

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Chemistry and Structure of $N_2F_3^+$ Salts

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The novel $N_2F_3^+$ salt $N_2F_3SbF_6$ was prepared from N_2F_4 and SbF_5 in anhydrous HF solution. A metathetical reaction between $N_2F_3SbF_6$ and Cs_2SnF_6 in HF produced N_2F_4 and the novel salt $N_2F_3SnF_5$. It was shown that N_2F_4 and BF_3 do not form a stable adduct at temperatures as low as −78 °C. The vibrational and ^{19}F NMR spectra of the $N_2F_3^+$ cation were reexamined. All the experimental data are consistent with a planar structure of symmetry C_s for $N_2F_3^+$. The previously reported vibrational assignments, made on the basis of a nonplanar structure of symmetry C_1, are revised for six fundamental frequencies.

Introduction

The first report on the formation of a stable adduct between N_2F_4 and a Lewis acid was published[1] in 1965 by Ruff. He showed[1,2] that SbF_5, when treated with an excess of N_2F_4 in AsF_3 solution, produced, depending on the pressure of N_2F_4, either the 1:2 adduct $N_2F_4 \cdot 2SbF_5$ or the 1:3 adduct $N_2F_4 \cdot 3SbF_5$. On the basis of the observed ^{19}F NMR spectrum and an incomplete infrared spectrum, he assigned to $N_2F_4 \cdot 2SbF_5$ the ionic structure $N_2F_3^+Sb_2F_{11}^-$ with hindered rotation around the N–N bond in $N_2F_3^+$. In 1967, Young and Moy published[3] the syntheses of adducts between N_2F_4 and AsF_5. At −78 °C and ambient temperature, the AsF_5:N_2F_4 combination ratios were reported to be 2.3 and 1.3 ± 0.2, respectively. In addition to an incomplete infrared spectrum and an unresolved ^{19}F NMR spectrum, the strongest lines of an X-ray powder diffraction pattern were given which was indexed on the basis of a cubic unit cell with $a = 10.8$ Å. In the same year, Lawless published[4] a better resolved infrared spectrum of $N_2F_3AsF_6$, but no assignments were offered. In 1970, Qureshi and Aubke published[5] a paper dealing with the infrared and Raman spectra of solid $N_2F_3AsF_6$ and $N_2F_3Sb_2F_{11}$. With the exception of the N–N torsional mode, they observed and tentatively assigned all fundamental vibrations of $N_2F_3^+$ proposing a nonplanar structure of symmetry C_1.

Since $N_2F_3^+$ salts are of interest as burning aids in solid propellant NF_3–F_2 gas generator formulations,[6] we have studied (i) the synthesis of $N_2F_3SbF_6$, (ii) the possibility of converting $N_2F_3SbF_6$ into "self-clinkering"[7] $N_2F_3^+$ salts by metathetical reactions,[8] and (iii) the vibrational spectra and structure of the $N_2F_3^+$ cation. The results of this study are summarized in this paper.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in a well-passivated (with ClF_3) Monel vacuum line equipped with Teflon-FEP U-traps and diaphragm valves. Pressures were measured with either a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%) or a Validyne Model DM 56A pressure transducer. Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

Arsenic pentafluoride and SbF_5 (Ozark Mahoning), N_2F_4 (Air Products), and BF_3 and SO_2 (Matheson) were purified by fractional condensation prior to use. The BrF_5 (Matheson) was treated with F_2 at 200 °C and then purified by fractional condensation. HF was dried as previously described.[9] The SnF_4 (Ozark Mahoning) was used as received. The preparation of Cs_2SnF_6 has previously been described.[7]

The infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as dry powders pressed between AgBr or AgCl disks in a Wilks minipellet press. Raman spectra were recorded on a Cary Model 83 spectrometer using the 4880-Å exciting line and a Claassen filter[10] for the elimination of plasma lines. Polarization measurements for HF solutions in thin-walled KelF capillaries were carried out by method VIII, as described[10] by Claassen et al. The ^{19}F NMR spectra were recorded on a Varian Model EM 390 spectrometer at 84.6 MHz using Teflon–FEP sample tubes (Wilmad Glass Co.) and $CFCl_3$ as an external standard. Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with nickel-filtered copper Kα radiation.

Synthesis of $N_2F_3SbF_6$. A Teflon ampule, containing a Teflon-coated magnetic stirring bar and equipped with a stainless steel valve, was loaded with 14.4 mmol of SbF_5 in a glovebox and attached to the vacuum line. Then 2 mL of anhydrous HF was condensed into the ampule at −78 °C. While the mixture was stirred and warmed to ambient temperature, the system was pressurized with N_2F_4 (~1 atm). A gradual decrease in the pressure was noted due to uptake of N_2F_4. Periodic cycling to below 0 °C seemed to increase the rate of N_2F_4 uptake. After several hours the unreacted N_2F_4 and HF solvent were pumped off at 40 °C until constant weight was achieved. The observed weight gain corresponded to the reaction of 12.1 mmol of N_2F_4. When the reaction was repeated on a larger scale with 8 mL of HF for 3 days, it was found that 74.0 mmol of SbF_5 reacted with 73.5 mmol of N_2F_4 to give 23.66 g of $N_2F_3SbF_6$ (weight of $N_2F_3SbF_6$ calculated for 74.0 mmol of SbF_5: 23.74 g), which was characterized by ^{19}F NMR and vibrational spectroscopy.

Synthesis of $N_2F_3AsF_6$. A 30-mL stainless steel cylinder was loaded at −196 °C with 22.8 mmol of AsF_5 and 26.8 mmol of N_2F_4. In a prechilled but empty Dewar, the cylinder was allowed to warm slowly from −196 °C to room temperature. Unreacted N_2F_4 (4.0 mmol) was recovered by pumping at ambient temperature. The weight (6.25 g) of the resulting white solid was in excellent agreement with that (6.25 g) calculated for 22.8 mmol of $N_2F_3AsF_6$. The compound, when prepared in this manner, always was slightly tacky, but hard. It was characterized by ^{19}F NMR and vibrational spectroscopy.

The N_2F_4–BF_3 Systems. Equimolar amounts of N_2F_4 and BF_3, when combined at −78 °C in a Teflon–FEP ampule, did not form a solid. The liquid could be distilled at −78 °C to a colder trap without leaving any solid residue behind.

The N_2F_4–SnF_4 System. A suspension of SnF_4 (4.68 mmol) in 4 mL of liquid HF in a Teflon–FEP ampule was pressurized with N_2F_4 (12.7 mmol) to a pressure of 900 mm. The mixture was stirred for 5 days at room temperature. On the basis of its vibrational spectra and chemical analysis, the white solid residue obtained upon removal of all material volatile at 25 °C did not contain any $N_2F_3^+$.

Synthesis of $N_2F_3SnF_5$. Solid $N_2F_3SbF_6$ (6.48 mmol) and Cs_2SnF_6 (3.24 mmol) were placed in a previously described Teflon–FEP apparatus, and approximately 2 mL of anhydrous HF was added. After the system was stirred and shaken vigorously for 30 min at room temperature, some of the HF was removed under vacuum and the mixture was cooled to −78 °C. The solid and liquid phases were separated by pressure filtration, and the volatile products were removed by pumping at 25 °C for 15 h. The volatile material was separated by fractional condensation and consisted of the HF solvent and N_2F_4 (3.2 mmol). The filtrate residue (0.3 g) was shown by vibrational spectroscopy to contain the $N_2F_3^+$ and $(SnF_5^-)_n$ ions[1-5,7] as the main components, in addition to a small amount of SbF_6^-. The filter cake consisted mainly of $CsSbF_6$ with lesser amounts of $N_2F_3SnF_5$.

Attempts were unsuccessful to suppress N_2F_4 evolution in the above reaction by carrying out the entire metathesis at −78 °C. Again N_2F_4 evolution and $N_2F_3SnF_5$ formation were observed.

Results and Discussion

Synthesis. For the metathetical synthesis of $N_2F_3^+$ salts using the $CsSbF_6$ process,[8] $N_2F_3SbF_6$ was needed as a starting material. Although Ruff had studied[1,2] the interaction of N_2F_4 with SbF_5 in a solvent, such as AsF_3, he had obtained only the polyantimonates $N_2F_3Sb_2F_{11}$ and $N_2F_3Sb_3F_{16}$. We found that, if this reaction is carried out in HF solution using excess N_2F_4 at a pressure of about 1 atm, $N_2F_3SbF_6$ can be obtained in quantitative yield and excellent purity according to

$$N_2F_4 + SbF_5 \xrightarrow[\text{room temp}]{\text{HF soln}} N_2F_3SbF_6$$

Similarly, no difficulty was encountered in preparing a well-defined 1:1 adduct between N_2F_4 and AsF_5. In this case, no solvent was required and the yield was quantitative:

$$N_2F_4 + AsF_5 \xrightarrow{25\ °C} N_2F_3AsF_6$$

According to a previous report[3] by Young and Moy on the same system, the averaged composition of their adduct was $N_2F_4 \cdot 1.33AsF_5$ and, in the presence of HF as a solvent, the yield was only about 65%.

Boron trifluoride, which is a weaker Lewis acid than SbF_5 and AsF_5, does not form a stable adduct with N_2F_4 at temperatures as low as −78 °C. Our attempts also failed to directly synthesize an $N_2F_3^+$ salt derived from SnF_4 by treatment of a SnF_4–HF suspension with N_2F_4. No N_2F_4 uptake occurred. This lack of reactivity cannot be due to insufficient acid strength of SnF_4 since metathesis in HF yields stable $N_2F_3SnF_5$ (see below). A more plausible explanation is that N_2F_4 is not a strong enough Lewis base to depolymerize SnF_4.

Since the direct synthesis of an adduct between N_2F_4 and SnF_4 was not possible, a metathetical reaction between $N_2F_3SbF_6$ and Cs_2SnF_6 was carried out in HF solution. The following reaction occurred:

$$2N_2F_3SbF_6 + Cs_2SnF_6 \xrightarrow[-78\ °C\ \text{filtration}]{\text{HF soln}} 2CsSbF_6\downarrow + N_2F_3SnF_5 + N_2F_4$$

The $N_2F_3SnF_5$ salt is a white solid, stable at room temperature. It is considerably more soluble in HF than $CsSbF_6$, thus making the metathesis possible. Attempts were unsuccessful to prepare $(N_2F_3)_2SnF_6$ by modification of the above reaction

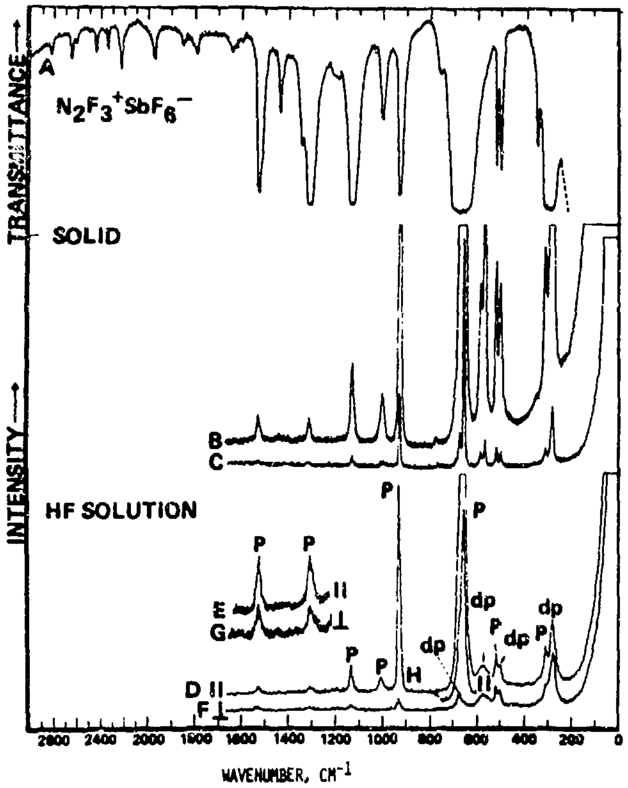
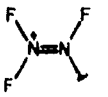


Figure 1. Vibrational spectra of $N_2F_3SbF_6$: trace A, infrared spectrum of the solid as an AgBr disk, the broken line being due to absorption by the window material; traces B and C, Raman spectrum of the solid recorded at two different recorder voltages with spectral slit widths of 3 and 8 cm^{-1}, respectively; traces D–H, Raman spectra of an HF solution recorded at different recorder voltages and spectral slit widths (5 and 8 cm^{-1}) with incident polarization parallel and perpendicular (p and dp stand for polarized and depolarized bands, respectively).

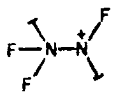
conditions. This was somewhat unexpected in view of the fact that previously no difficulty was encountered in the preparation of the analogous $(NF_4)_2SnF_6$ salt from NF_4SbF_6 and Cs_2SnF_6 under similar reaction conditions.[7] It should be remembered, however, that the favored reaction product from the displacement reaction between NF_4BF_4 and SnF_4 in HF was NF_4SnF_5 and not $(NF_4)_2SnF_6$.[7] These results indicate that the reaction chemistry of SnF_4 and its anions in HF is rather complex and hard to predict without exact knowledge of the corresponding solvation and lattice energies of the possible products.

Vibrational Spectra. Figures 1–3 show the vibrational spectra of $N_2F_3SbF_6$, $N_2F_3AsF_6$, and $N_2F_3SnF_5$, respectively. The observed frequencies are listed in Tables I and II. The vibrational spectra of SbF_6^-,[5,6,11,12] AsF_6^-,[5,11,13,14] and $(SnF_5^-)_n$[7] are well-known and can be assigned without difficulty (see Tables I and II). The remaining bands should be due to the $N_2F_3^+$ cation.

The $N_2F_3^+$ cation could possess either a planar structure of symmetry C_s (I) or a nonplanar structure of symmetry C_1



I (C_s)



II (C_1)

caused by significant contributions from resonance structure II. The assignments previously made[5] by Qureshi and Aubke for $N_2F_3^+$ were based on symmetry C_1, although structure II is energetically considerably less favorable than I (one nitrogen possesses only six valence electrons) and is in poor agreement with the published NMR data[1,2] which show hindered rotation around the N–N bond up to at least 120 °C. Symmetry C_1 had previously been chosen[4] because the highest Raman frequency observed for either solid $N_2F_3AsF_6$ or $N_2F_3Sb_2F_{11}$ occurred at about 1310 cm^{-1}. Since this frequency is considerably lower than expected[15,16] for an N═N bond, significant contributions from II were assumed.[5]

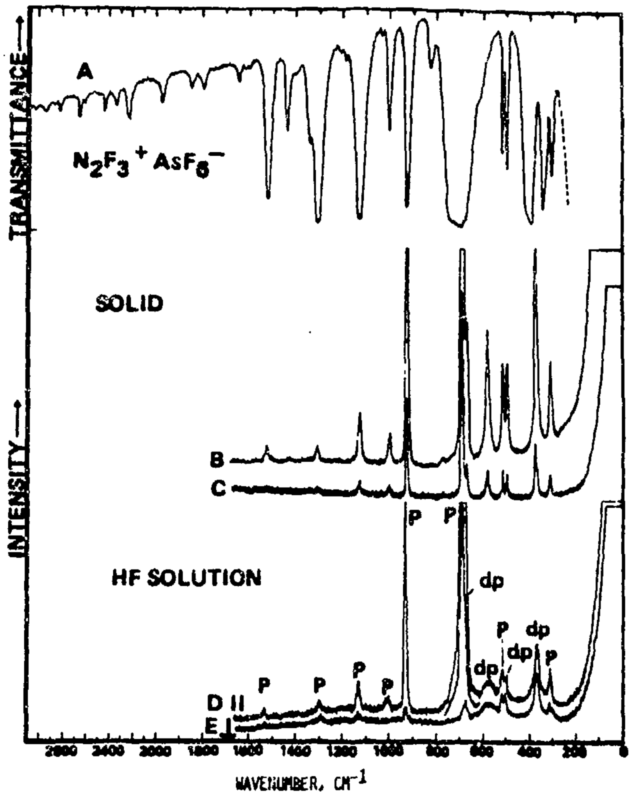


Figure 2. Vibrational spectra of $N_2F_3AsF_6$. For explanation, see caption of Figure 1.

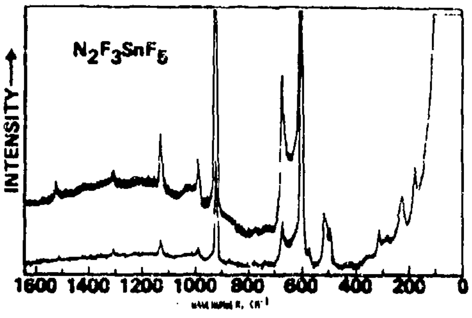


Figure 3. Raman spectrum of solid $N_2F_3SnF_5$ recorded at two different recorder voltages.

As can be seen from Figures 1–3, the highest Raman band observed for all three $N_2F_3^+$ salts occurs at about 1520 cm^{-1}, thus confirming the original assignment[1-3] of the strong 1520-cm^{-1} infrared band to the N═N stretching mode and eliminating the basis for Qureshi and Aubke's reassignment.[5] The previous failure to observe the 1520-cm^{-1} Raman band can be explained by its relatively low intensity and the low signal to noise ratio in the reported spectrum.[5]

Having established the identity of the N═N stretching mode, we can now proceed to test if the rest of the $N_2F_3^+$ spectrum is consistent with symmetry C_s. For $N_2F_3^+$ of C_s symmetry a total of nine fundamental vibrations is expected of which six belong to species A′ and three belong to A″. An approximate description of these nine modes is given in Table

Table I. Vibrational Spectra of $N_2F_3AsF_6$ and $N_2F_3SbF_6$

assignments for $N_2F_3^+$ in point group C_s	obsd freq, cm^{-1}, and rel intens[a]						assignments for MF_6^- in point group O_h
	$N_2F_3SbF_6$			$N_2F_3AsF_6$			
	solid		HF soln Raman	solid		HF soln Raman	
	IR	Raman		IR	Raman		
$\nu_1 + \nu_2$ (A′) = 2829	2825 vw			2820 vw			
$\nu_1 + \nu_3$ (A′) = 2649	2647 vw			2643 vw			
$2\nu_2$ (A′) = 2614	2608 vvw			2605 vvw			
$\nu_1 + \nu_4$ (A′) = 2447	2443 vw			2440 vw			
$\nu_2 + 2\nu_5$ (A′) = 2339	2343 vw			2340 vw			
$\nu_2 + \nu_4$ (A′) = 2232	2227 w			2223 w			
$\nu_3 + \nu_4$ (A′) = 2052	2050 sh						
$\nu_2 + \nu_7$ (A″) = 1978	1976 w			1970 w			
$2\nu_4$ (A′) = 1850	1850 vw			1846 vw			
$\nu_3 + \nu_7$ (A″) = 1798	1796 vw			1795 vw			
$\nu_3 + \nu_5$ (A′) = 1643	1642 vw			1639 vw			
$\nu_2 + \nu_6$ (A′) = 1617	1619 sh			1617 vvw			
$\nu_4 + \nu_7$ (A″) = 1596	1599 vvw			1596 vvw			
ν_1 (A′)	1522 s	1522 (0.1)	1522 (0.1) p	1519 s	1520 (0.2)	1524 (0.2) p	
$\nu_3 + \nu_6$ (A′) = 1437	1436 m	1424 (0+)	1435 (0+)	1432 m	1430 (0+)		
				1390 vw			$\nu_1 + \nu_3$ (F_{1u})
$2\nu_7$ (A′) = 1342	1343 m			1340 m			
ν_2 (A′)	1310 vs	1307 (0.1)	1306 (0.1) p	1307 vs	1305 (0.2)	1300 (0.2) p	
$\nu_5 + 2\nu_9$ (A′) = 1204	1210 vw			1206 vw			$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$)
$\nu_5 + \nu_7$ (A″) = 1187	1189 vw			1186 vw			
ν_3 (A′)	1127 vs	1124 (0.4)	1127 (0.6) p	1128 vw	1127 (0.6)	1128 (0.7) p	
$2\nu_5$ (A′) = 1032	1033 vvw			1032 vvw			
$2\nu_8$ (A′) = 994	998 m	997 (0.2)	1000 (0.25) p	996 m	997 (0.3)	1001 (0.3) p	
ν_4 (A′)	925 s	924 (3.2)	927 (6.1) p	923 s	925 (4.7)	929 (5.9) p	
	755 mw			826 mw			$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)
	670 vs			699 vs			ν_3 (F_{1u})
ν_7 (A″)		670 (0.9)	671 (0.8) dp		671 (0.9)	671 (0.8) dp	
		656 (10)	655 (10 p		690 (10)	689 (10) p	ν_1 (A_{1g})
				620 sh			$\nu_5 + \nu_6$ ($A_{1u} + E_u + F_{1u} + F_{2u}$)
		582 (0.4) }	575 (0.4) dp		581 (1.3)	575 (0.4) dp	ν_2 (E_g)
		566 (1.1) }					
ν_5 (A′)	515 ms	514 (0.8)	518 (1.0) p	515 ms	516 (1.2)	516 (0.9) p	
ν_8 (A″)	497 ms	496 (0.5)	499 (0.6) dp	496 ms	497 (1.1)	498 (0.5) dp	
ν_9 (A″)	345 m	348 (0+)		343 ms			
ν_6 (A′)		310 (0.5)	310 (0.6) p		310 (0.9)	310 (1.0) p	
	290 vs			392 s			ν_4 (F_{1u})
		280 (2.4)	280 (2.3) dp		374 (3.6)	371 (2.0) dp	ν_5 (F_{2g})

[a] Uncorrected Raman intensities.

Table II. Vibrational Spectra of Solid $N_2F_3SnF_5$

obsd freq, cm^{-1}, and rel intens		assignment	
IR	Raman	$N_2F_3^+$ (C_s)	$(SnF_5^-)_n$
1518 s	1519 (0.1)	ν_1 (A′)	
1428 m		$\nu_3 + \nu_6$ (A′)	
1341 m		$2\nu_7$ (A′)	
1304 vs	1304 (0.1)	ν_2 (A′)	
1126 vs	1127 (0.5)	ν_3 (A′)	
986 m	988 (0.4)	$2\nu_8$ (A′)	
921 vs	921 (3.9)	ν_4 (A′)	
	670 (1.1)	ν_7 (A′)	
635 } s, br 610 }	604 (10)		} str modes
	572 (0.3)		
	512 (2)	ν_5 (A′)	
490–450 m, br	492 (1)	ν_8 (A″)	bridge str
	310 (0.8)	ν_6 (A′)	
	228 (1.3)		} def modes
	179 (1.1)		

Table III. Fundamental Frequencies (cm^{-1}) of $N_2F_3^+$ and Their Assignment in Point Group C_s

freq	assignment		approx description of mode
1522	A′	ν_1	N=N str
1307		ν_2	asym NF_2 str
1127		ν_3	NF′ str
925		ν_4	sym NF_2 str
516		ν_5	δ(sym NF_2) in plane
310		ν_6	δ($FNNF_2$) in plane
671	A″	ν_7	δ(asym $FNNF_2$) out of plane
497		ν_8	δ(sym $FNNF_2$) out of plane
344		ν_9	N=N torsion

III. All nine modes should be infrared and Raman active, with a possible exception being the torsional mode ν_9 which is expected to be of very low Raman intensity. The three A″ modes should result in depolarized Raman bands.

As can be seen from Table III, three NF stretching modes are expected all belonging to species A′ and occurring in the frequency range 900–1300 cm^{-1}. There are three very intense infrared bands in this region (see Figures 1 and 2), all of which have Raman counterparts. Of the three predicted NF stretching modes, the symmetric NF_2 stretch (ν_4) is expected to have the highest Raman intensity and the lowest depolarization ratio and, therefore, is assigned to the band at about 925 cm^{-1}. The reverse should hold true for the antisymmetric NF_2 stretching mode ν_2 which, therefore, is assigned to the band at about 1310 cm^{-1}. This leaves the assignment of the band at about 1127 cm^{-1} to the unique NF stretching mode ν_3, the frequency of which is similar to that of the NF stretch in N_2F^+.[17]

For the assignment of the five deformation modes, the following five frequencies are available: 671, 516, 497, 344, and 310 cm^{-1}. Of these, the 516- and 310-cm^{-1} bands are clearly polarized in the Raman spectra and therefore must represent the two remaining A′ modes. By comparison with

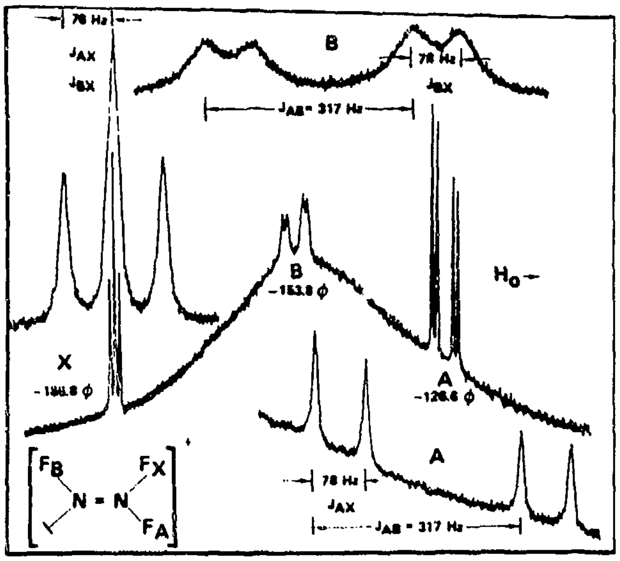


Figure 4. ^{19}F, NMR spectrum of $N_2F_3AsF_6$ in BrF_5 solution, recorded at −78 °C and 84.6 MHz using $CFCl_3$ as external standard. The very broad background signal is due to rapidly exchanging BrF_5 and AsF_6^-. The inserts show the A, B, and X signals, all recorded with tenfold scale expansion, but different recorder gain settings.

the known frequencies of the NF_2[18] and CF_2[19] radicals, the 516-cm^{-1} band is assigned to the NF_2 scissoring mode ν_5, leaving the 310-cm^{-1} band for the unique FNN in-plane deformation mode ν_6.

Of the remaining three fundamental frequencies, the 671- and 497-cm^{-1} ones exhibit reasonably intense depolarized Raman bands, whereas the 344-cm^{-1} one has been observed only in one Raman spectrum (Figure 1, trace B) as an extremely weak band. In the infrared spectra, the 344-cm^{-1} fundamental is of medium intensity. These intensity relations indentify the 344-cm^{-1} band as the N=N torsional mode. Of the two remaining frequencies, the 671-cm^{-1} fundamental is assigned to the antisymmetic and the 497-cm^{-1} fundamental to the symmetric $FNNF_2$ out-of-plane deformation. This assignment is based on that[20] of the related C_2F_4 molecule. Numerous combination bands were observed in the infrared spectra. Their assignment is given in Table I.

In summary, the vibrational spectra of the $N_2F_3^+$ ion are entirely consistent with our predictions for a planar model of symmetry C_s. All nine fundamentals were observed, with six of them being polarized and two of them being depolarized in the Raman spectra. As expected, the torsional mode is of very low Raman intensity. The double-bond character of the NN bond in $N_2F_3^+$ is confirmed by the high frequencies of the NN stretching and the torsional mode.

NMR Spectra. The ^{19}F NMR spectra of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ were recorded at 84.6 MHz in SO_2, BrF_5, SbF_5, and HF solution. The HF solvent was acidified with either AsF_5 or SbF_5 to suppress exchange between the solvent and the cation.[20,22] In HF, BrF_5, and SbF_5 solutions, exchange between the anions and the solvent was observed; however, in SO_2 solution separate signals were observed for AsF_6^- at φ 57 and SbF_6^- at φ 111 with the appropriate area ratios.

For $N_2F_3^+$, a typical ABX pattern with an area ratio of 1:1:1 was observed at about φ −127, −154, and −187, respectively. The chemical shifts of these signals exhibited only little solvent and temperature dependence. Even at 150 °C (SbF_5 solution), no averaging of the NF resonances was noticeable, indicating strongly hindered rotation about the N–N axis, as expected for a N=N. These findings are in excellent agreement with the previous report by Ruff for $N_2F_3Sb_2F_{11}$ in SO_2 solution and the melt.

Our low-temperature spectra (−70 to −90 °C) in either BrF_5 (see Figure 4) or acidified HF solutions were much better resolved than those obtainable for the SO_2 solution and thus permitted a more accurate determination of the three coupling constants. The A signal consisted of a sharp doublet of doublets with J_{AB} = 317 Hz, J_{AX} = 78 Hz, and a line width of about 8 Hz. The B signal was again a doublet of doublets with J_{AB} = 317 HZ and J_{BX} ≈ 78 Hz, but with significantly broader lines (line width of about 60 Hz). The X signal was a sharp 1:2:1 (J = 78 Hz) triplet indicating very similar values of J_{AX} and J_{BX}. Our observed coupling constants significantly differ from those (J_{AB} = 379 Hz, J_{AX} = 81 Hz, J_{BX} = 45 Hz) previously reported[2] for a poorly resolved spectrum.

Assignment of ABX to the three fluorines in $N_2F_3^+$ can be made based on the following arguments. The two nitrogen atoms in $N_2F_3^+$ are not equivalent. The one possessing only one fluorine ligand is centered in an electrically less symmetric field thus making ^{14}N quadrupole relaxation more effective and causing line broadening. Consequently, the broadened B signal is assigned to the unique fluorine. Since for the related FN=NF, CF_2=NF, and substituted fluoroethylenes the cis coupling constants were found to be always significantly smaller than the trans ones,[23] A (J_{AB} = 317 Hz) should be trans and X (J_{BX} = 78 Hz) should be cis with respect to B. The resulting structure is shown in Figure 4. The observed coupling constants are similar to those observed for cis FN=NF (J = 99 Hz) and trans FN=NF (J = 322 Hz).[23]

X-ray Powder Data. The X-ray powder patterns of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ are given as supplementary material. Young and Moy have reported[3] the three strongest lines for $N_2F_3AsF_6$ and stated that the pattern can be indexed for a cubic unit cell with a = 10.8 Å. Although our data confirm the three previously reported lines,[3] our observed pattern cannot be indexed based on the previously given unit-cell dimensions. In view of the nonspherical geometry of $N_2F_3^+$, a relatively small cubic unit cell would be very surprising for $N_2F_3AsF_6$.

Acknowledgment. We are indebted to Drs. L. R. Grant and W. W. Wilson for helpful discussions and to Mr. R. D. Wilson for experimental help. This work was supported in part by the Office of Naval Research and the U.S. Army Research Office.

Registry No. $N_2F_3SbF_6$, 67328-70-5; $N_2F_3SnF_5$, 67328-71-6; $N_2F_3AsF_6$, 12254-91-0; N_2F_4, 10036-47-2; SbF_5, 7783-70-2.

Supplementary Material Available: Table IV, listing the observed X-ray powder diffraction patterns of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ (1 page). Ordering information is given on any current masthead page.

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Electron Spin Resonance Spectra of the $^{14}NF_3^{+\cdot}$ and $^{15}NF_3^{+\cdot}$ Radical Cations

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The ESR spectra of the $^{14}NF_3^{+\cdot}$ and $^{15}NF_3^{+\cdot}$ radical cations were observed over the temperature range 15–340 K. The radical cations were generated either by γ irradiation of NF_4^+ salts or by low-temperature UV photolysis of NF_3–F_2–Lewis acid mixtures. For $NF_3^{+\cdot}$, two different types of spectra were observed. At the lower temperatures, a highly anisotropic spectrum was obtained which is attributed to a rigid radical. At the higher temperatures, a more isotropic spectrum was observed which is attributed to $NF_3^{+\cdot}$ of axial symmetry. An analysis of the observed spectra was carried out and was supported by computer simulations and the observed ^{15}N isotopic data. It was found that the previously reported value of the isotropic fluorine hyperfine splitting is incorrect. The resulting spin density distributions indicate that $NF_3^{+\cdot}$ is pyramidal but that within the isoelectronic series $BF_3^{-\cdot}$, $CF_3\cdot$, $NF_3^{+\cdot}$ the planarity of the radicals increases from $BF_3^{-\cdot}$ toward $NF_3^{+\cdot}$.

Introduction

Radicals and radical ions formed from first-row elements have been the subject of numerous studies. These species provide experimental data by which molecular orbital models can be tested and also define limits within which the properties of isoelectronic species can be predicted. Electron spin resonance (ESR) provides a useful technique for studying the structure of these radicals[1] since the spin distribution in s and p orbitals can be determined from hyperfine splittings (hfs) and limits can often be set on the energies of excited states through the g factors.[1,2]

This study was prompted by the following observations: (i) During a recent study[3] of the synthesis of NF_4^+ salts, ESR spectra were obtained which were substantially different from those previously reported.[4] The radicals exhibiting these spectra were stable up to 250 K, depending upon the particular anion. The ESR spectra recorded at these higher temperatures could not be reconciled with the parameters previously given by Mishra et al.[4] (ii) On the basis of the known isotropic fluorine hyperfine splittings (a_F(iso)) of isoelectronic $BF_3^{-\cdot}$ (17.8 mT)[5] and CF_3 (14.35 mT),[6-10] the value of 16.7 mT previously reported[4] of $NF_3^{+\cdot}$ appeared to be much too high if a monotonic trend in the values for a_F(iso) is assumed for the isoelectronic series. Since the values of the hyperfine splittings can be used to determine the structure of these radicals, a reexamination of the previously given[4] analysis of the ESR spectra seemed necessary. For this purpose, it was also found necessary to study the isotopically labeled $^{15}NF_3^{+\cdot}$ to permit unambiguous assignment of the nitrogen hfs.

In this paper we report the ESR spectra of $^{14}NF_3^{+\cdot}$ and $^{15}NF_3^{+\cdot}$, including a study of their temperature dependencies and a revised analysis of the hyperfine splittings.

Experimental Section

Synthesis of $^{15}NF_4^+$ Salts. The low-temperature UV photolysis experiments of NF_3–F_2–Lewis acid mixtures were carried out in quartz containers as previously described.[3] The $^{15}NF_3$ used in some of these experiments was prepared by glow discharge of $^{15}N_2$ (99% ^{15}N, Stohler Isotope Chemicals) and F_2 (Rocketdyne) mixtures according to the method of Maya.[11] The samples of NF_4BF_4 and NF_4AsF_6 used for the ^{60}Co γ-irradiation experiments were prepared by low-temperature UV photolysis in a quartz reactor using a previously described[12] method. The samples of NF_4^+ antimonates were prepared by heating mixtures of NF_3, F_2, and SbF_5 at elevated pressures in a Monel cylinder.[13] These salts were recrystallized from anhydrous HF to remove residual Monel salt impurities.

γ Irradiation. NF_4^+ salts were transferred in a dry nitrogen atmosphere into 4-mm o.d. quartz tubes (J. F. Scanlon Co., Solvang, Calif.) which were flame-sealed under vacuum. Typically, samples of 100 mg of $^{14}NF_4^+$ salts were used while only 15-mg samples of $^{15}NF_4^+$ salts were available. Samples were exposed to ^{60}Co γ irradiation at 77 K, using a flux rate of 4×10^5 R h^{-1}. Samples of the $^{14}NF_4^+$ salts were exposed between 15 and 24 h, while the sample of the $^{15}NF_4^+$ salt was exposed for 40 h. Samples were annealed in dry ice (195 K) prior to recording their ESR signals. The $NF_3^{+\cdot}$ signal intensity did not decrease even when the samples were stored at 195 K for several months.

UV Experiments. The conditions used for the UV photolyses have previously been described.[3]

ESR Spectra. ESR spectra were recorded using a computer-controlled ESR spectrometer previously described.[14] The spectrometer operated at 9.303 GHz with a TE_{104} rectangular dual cavity and an LTD-3-110 (Air Products) Helitran temperature controller. A 15-in. magnet was used with the spectrometer. Signal averaging combined with programs for smoothing spectra and removal of background signals was used to record weak spectra. Intense spectra were recorded using standard dual cavity techniques. The magnetic field standard was Mn^{2+}.[15] Values of the magnetic parameters were $a_{Mn} = 8.673 \pm 0.003$ mT (1 T = 10^4 Oe) and $g = 2.00095 \pm 0.00005$.[16] Field positions were computed to third order. Spectra were recorded between 15 and 340 K.

Simulations of ESR Spectra. Simulations of the ESR spectra of powders were carried out using a program developed by White and Belford based on the method of Pilbrow and Winfield[17] and modified by Chasteen.[18] The program computes second-order shifts of one nucleus and permits the hyperfine axis of that nucleus to be nonparallel to the remainder of the hyperfine axes. It also allows anisotropic line widths to be used in the calculation. The program was further modified in our laboratory to include second-order splittings from one equivalent set of nuclei.

Results

ESR Spectra. During a recent ESR study[3] of the UV photolysis of mixtures of NF_3, F_2, and BF_3 or AsF_5, spectra similar to that shown in Figure 1a were observed at ca. 77 K. However, as shown in Figure 1 of ref 3, these spectra were very poorly resolved. These spectra, which were attributed to a immobile $NF_3^{+\cdot}$ radical cation in a matrix, are expected to exhibit unique features (singularities) which correspond to the orientation of the threefold symmetry axis of the radical along directions parallel and perpendicular to the applied magnetic field. However, only the parallel component of the spectrum is clearly identifiable.

Upon warming of the UV-photolyzed mixture, the spectra began to change. The thermal stability of the observed ESR signals strongly depended upon the Lewis acid used. For AsF_5 the ESR signal became more intense about 130 K and appeared to be more isotropic. At 180 K, the signal started to lose intensity, and it decayed rapidly at 230 K. This loss of signal intensity can be attributed to the disappearance of the condensed AsF_5 phase. However, a relatively weak residual signal remained above 230 K which can be attributed to $NF_3^{+\cdot}$ trapped in the solid NF_4AsF_6 formed during the UV photolysis. For the more volatile BF_3, the change from the anisotropic low-temperature spectrum to the more isotropic higher temperature one occurred at about 117 K. At 140 K, the

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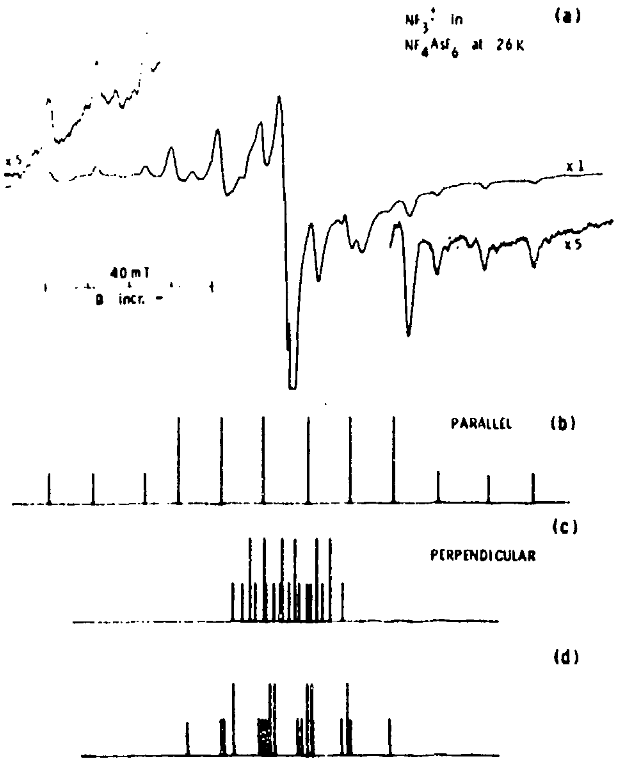

Figure 1. (a) ESR spectrum of $^{14}NF_3^{+}\cdot$ at 26 K in NF_4AsF_6 γ irradiated at 77 K after annealing at 195 K. (b) Stick plots of the line positions to first order, assuming parallel F-atom tensors with the C_{3v} axis of the radical aligned parallel to the applied field. (c) Stick plot to second order of the line positions of the radical with its C_{3v} axis perpendicular to the applied field (our analysis). (d) Stick plot to second order under conditions of (c) using the previously reported assignment. See discussion of (c) and (d) in text.

$NF_3^{+}\cdot$ signal was completely lost. Although the more isotropic spectra observed for the NF_3–F_2–AsF_5 and NF_3–F_2–BF_3 systems exhibited broad lines, it became evident that they could not be interpreted in terms of the parameters previously assigned to $NF_3^{+}\cdot$.

In order to resolve these disparities, the temperature dependence of the ESR spectra of the γ-irradiated salts of NF_4^{+} was investigated. Salts used in this study were NF_4BF_4, NF_4AsF_6, NF_4SbF_6, and $NF_4SbF_6 \cdot 0.8SbF_5$, all of which gave similar spectra after γ irradiation at 77 K, followed by annealing at 195 K in solid CO_2. Contrary to Mishra,[4] no problem was encountered in generating $NF_3^{+}\cdot$ by γ irradiation of NF_4BF_4. Prior to annealing, residual signals were observed on either side of the $NF_3^{+}\cdot$ resonance, in addition to an intense sharp line at $g = 2$. The origin of these signals, which may have been due to the anion,[4] was not investigated. The annealed samples exhibited different spectra at high and low temperatures. The low-temperature spectrum, observed between 10 and 140 K, was similar to that previously attributed to $NF_3^{+}\cdot$,[4] and is shown in Figure 1 for irradiated NF_4AsF_6 at 26 K. Other salts gave similar spectra, except that the lines exhibited a shoulder to the high field side of the main resonance. The line width of the spectrum increased slightly with longer irradiation times but was independent of temperature. Reducing the amount of $NF_3^{+}\cdot$ by warming the sample resulted in a narrower line. These observations suggest that dipolar interactions occurred between nearby defect sites. There is one difference between our spectra and that observed by Mishra et al.;[4] even in the more dilute solutions, we were unable to resolve some of the features which were attributed to the alignment of the C_{3v} axis of the radical perpendicular to the magnetic field. We did, however, observe shoulders at these positions.

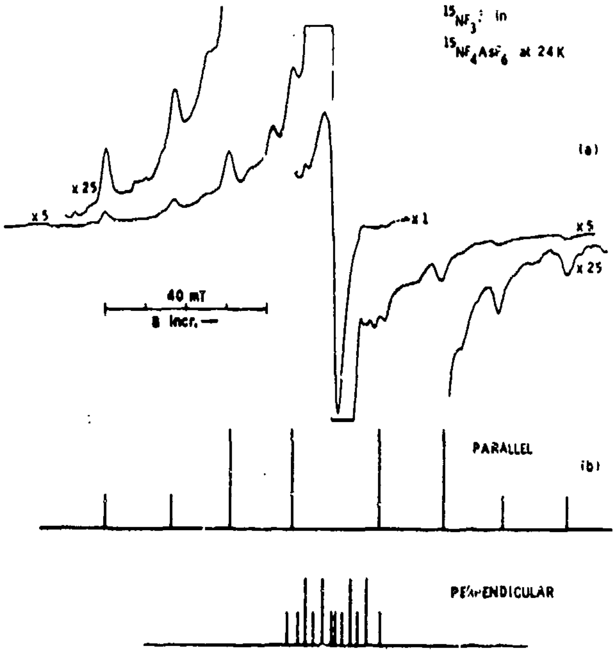

Figure 2. (a) ESR spectrum of $^{15}NF_3^{+}\cdot$ at 24 K in $^{15}NF_4AsF_6$ γ irradiated at 77 K after annealing at 195 K. (b) Stick plots of the line positions for the C_{3v} axis of the radical aligned parallel and perpendicular to the applied field, assuming parallel fluorine hfs tensors.

As the temperature of the arsenate and antimonate salts is increased to the range 140 and 235 K, the low-temperature spectrum collapses and then forms a sharper one with a narrower span. This spectrum is independent of temperature between 240 and 340 K, where decomposition begins, and is shown in Figure 3 for irradiated NF_4AsF_6 at 240 K. The lifetime of the species at room temperature is about 2 weeks but decreases to about 10 min at 340 K. Similar spectra were observed for the irradiated borate salts between about 270 and 320 K.

In order to be certain that the spectra reported here are due to $NF_3^{+}\cdot$, isotopically pure $^{15}NF_4AsF_6$ and $^{15}NF_4BF_4$ were prepared. The signal observed for the irradiated salts exhibited the same temperature dependence as those obtained for $^{14}NF_4^{+}$ salts. However, since only ca. 15 mg of $^{15}NF_4^{+}$ salts was prepared, longer irradiation times had to be used resulting in slightly broadened lines. The low-temperature spectrum of $^{15}NF_3^{+}\cdot$ in $^{15}NF_4AsF_6$ is shown in Figure 2, where the ^{14}N triplets are replaced by ^{15}N doublets. The high-temperature $^{15}NF_3^{+}\cdot$ spectrum is shown in Figure 4 and is analogous to the high-temperature $^{14}NF_3^{+}\cdot$ spectrum.

Discussion

Low-Temperature Spectra of $^{14}NF_3^{+}\cdot$. Several unusual features become apparent upon close inspection of the $NF_3^{+}\cdot$ spectra at low temperatures. Most significantly, the distinct, intense features of the spectra must be assigned to the radical with its threefold symmetry (C_{3v}) axis aligned parallel to the applied magnetic field. Generally, however, the most intense features of the spectra of axially symmetric radicals in powders are assigned to the orientation in which the symmetry axis is perpendicular to the applied field.[18-20] Since no such features are observed here, it is clear that this spectrum cannot be treated in the conventional manner used for axial or nearly axial symmetry.

A second feature is that the positions of the lines in the spectrum that correspond to the ∥ orientation do not fall into the positions calculated from the hyperfine splittings (hfs)

Table I. Hyperfine Splittings[a] of $^{14}NF_3^+$ and $^{15}NF_3^+$ at High and Low Temperatures

	$^{14}NF_3^+$		$^{15}NF_3^+$	
	26 K	240 K	24 K	240 K
$a_F(\parallel)$	30.8[c]	2.00 ± 0.25	30.6[c]	2.40 ± 0.25
$a_F(\perp)$	(−)3.3[c]	12.48 ± 0.05	(−)3.8[c]	11.97 ± 0.05
$a_N(\parallel)$	11.49 ± 0.20	8.70 ± 0.25	−16.08 ± 0.20	−12.20 ± 0.25[c]
$a_N(\perp)$	7.8 ± 0.5	9.36 ± 0.05	−10.6 ± 1.0	−13.03 ± 0.05[c]
a_F(iso)	8.1	8.99 ± 0.14	7.7	8.78 ± 0.14
a_N(iso)	9.0	9.14 ± 0.14	−12.4	−12.75 ± 0.14
$g(\parallel)$	2.003 ± 0.002	2.0073 ± 0.0010	2.003 ± 0.002	2.0079 ± 0.0012
$g(\perp)$	2.006 ± 0.002	2.0040 ± 0.0007	2.005 ± 0.002	2.0047 ± 0.0007
g(iso)	2.005 ± 0.002	2.0051 ± 0.0007	2.005 ± 0.002	2.0058 ± 0.0009

[a] Hyperfine splittings are in mT (1 mT = 10 Oe). [b] The sign of the ^{14}N hfs is assumed to be positive; thus ^{15}N hfs are negative by virtue of their nuclear moments. [c] These are effective values based on supposed axial symmetry for individual tensors; $a_F(z)$ = 30.8 mT and $a_F(x) = a_F(y) \sim 3.3$ mT (see text).

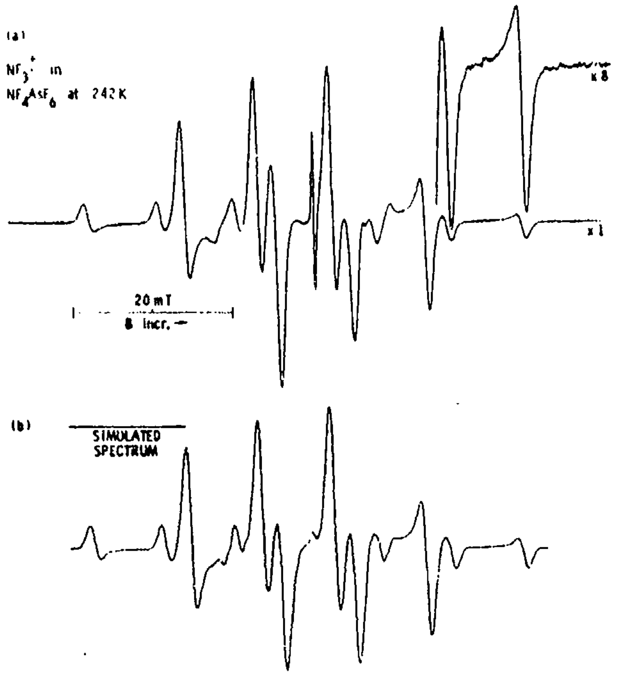

Figure 3. (a) ESR spectra of $^{14}NF_3^{+}\cdot$ at 242 K in NF_4AsF_6 γ irradiated at 77 K. (b) Computer simulation of spectrum assuming axial symmetry and the parameters given in Table I.

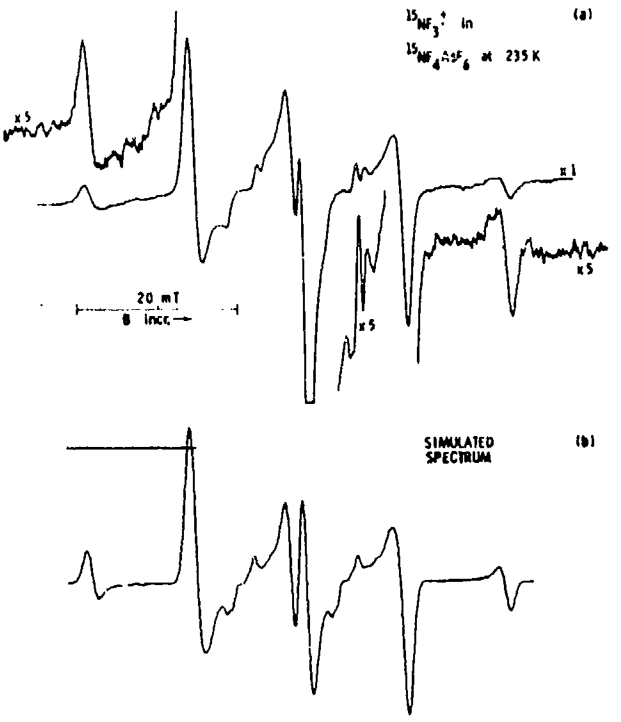

Figure 4. (a) ESR spectra of $^{15}NF_3^{+}\cdot$ at 235 K in $^{15}NF_4AsF_6$ γ irradiated at 77 K. (b) Computer simulation of spectrum assuming axial symmetry and parameters given in Table I.

which are given in Table I. These values are calculated from the extrema of the spectrum. For a system which exhibits a large hfs with axial symmetry, the field positions in which the unique axis is parallel to the magnetic field, $H_{I,M_I}(\parallel)$, is given by eq 1 to second order,[21] where $g(\parallel)$, $g(\perp)$, $a(\parallel)$, and $a(\perp)$

$$H_{I,M_I}(\parallel) = H_0(\parallel) - a(\parallel)M_I - \frac{a(\perp)^2[g(\perp)/g(\parallel)]^2}{2[H_0(\parallel) - a(\parallel)M_I]}[I(I+1) - M_I^2] \quad (1)$$

are the parallel and perpendicular g factors and hfs, respectively, $H_0(\parallel)$ is given by $h\nu/g(\parallel)\mu_B$, I is the total nuclear spin, and M_I is the component of spin parallel to the magnetic field. The analogous equation for $H_{I,M_I}(\perp)$ is given by eq 2,[21]

$$H_{I,M_I}(\perp) = H_0(\perp) - a(\perp)M_I - \frac{a(\perp)^2 + a(\parallel)^2[g(\parallel)/g(\perp)]^2}{4[H_0(\perp) - a(\perp)M_I]}[I(I+1) - M_I^2] \quad (2)$$

where $H_0(\perp)$ is given by $h\nu/g(\perp)\mu_B$. Field positions are plotted on the same field axis under the spectrum in Figure 1b, for the molecule oriented ∥ and ⊥ to the field. Second-order shifts are only significant for $NF_3^{+}\cdot$ when the field is ⊥ to the C_{3v} axis of the radical. Note that for the ∥ orientation, while the lines corresponding to $M_I(F) = +^3/_2$ and $-^3/_2$ agree with the calculated positions, the lines corresponding to $M_I(F) = +^1/_2$ and $-^1/_2$ are shifted away from the center of the spectrum.

A final complication in the interpretation of this spectrum is that there are several extra lines present which cannot be explained in the conventional analysis assuming axial symmetry. Similar features were observed in spectra of $CF_3\cdot$ which were explained[9,10] by the fact that, while the hyperfine tensors of each of the fluorine atoms are equivalent, they are not mutually parallel. This causes the axial component of the tensor to be at an angle of 18° with respect to the C_{3v} symmetry axis.[9] As a result, singularities in the spectrum appear which correspond to orientations of the radical with respect to the applied field which are other than parallel or perpendicular.

In the spectrum of $CF_3\cdot$, there are sets of lines which correspond to either the parallel or the perpendicular orientation. However, these do not occur in the positions expected from the values of the hfs. Because $a_F(\parallel) > a_F(\perp)$, the lines $|M_I(F)| = {}^3/_2$ which correspond to parallel alignment are shifted closer to the center of the spectrum, while those of

$|M_I(F)| = {}^1/_2$ are shifted away from the center. Shifts in opposite directions occur for the lines which correspond to the perpendicular orientation. The effective value, $a_F(\|)$, is then given by eq 3, where $a_x = a_y$ and a_z are the principal values of the hyperfine tensor.

$$a_F^2(\|) = a_z^2 \cos^2 \alpha + a_x^2 \sin^2 \alpha \qquad (3)$$

The spectrum of $NF_3^{+}\cdot$ is more complicated because of the added anisotropy of the ^{14}N hfs. Here the nitrogen hyperfine tensor will determine the positions of the singularities of the spectrum. As a result, the treatment given by Maruani et al.[9,10] for $CF_3\cdot$ needs to be modified. We report here, effective values for the hyperfine tensor, determined from the extrema of the spectra. In units of mT, $a_F(\|) = 30.8$, $a_F(\perp) = 3.3$, $a_N(\|) = 11.49$, and $a_N(\perp) = 7.8$. In contrast, Mishra et al.[4] report $a_F(\|) = 30.0$, $a_F(\perp) = 10.0$, $a_N(\|) = 11.5$, and $a_N(\perp) = 9.0$. The stick plot representing this analysis is shown in Figure 1b,c for the parallel and perpendicular orientations, respectively. The analysis of the parallel orientation is in agreement with the previous[4] assignment; however, there is substantial difference between our analysis of the perpendicular orientation and the previous one,[4] shown in Figure 1d. The analysis of the perpendicular components depends upon which features are selected. Since these features are buried within the spectrum and since extra lines appear, this assignment is indeed difficult. However, because of the large value of $a_F(\|)$, there are downfield shifts of 1–5 mT due to second-order effects. Therefore, the features corresponding to the perpendicular orientation are those which are asymmetric with respect to the center of the spectrum, after allowing for the second-order splittings of the $|M_I(F)| = {}^1/_2$ lines. Furthermore, the features that we have selected are consistent with the analyses of high-temperature spectra as well as those derived from the $^{15}NF_3^{+}\cdot$ spectra.

Low-Temperature Spectra of $^{15}NF_3^{+}$. In order to confirm the analysis of the $^{14}NF_3^{+}\cdot$ spectra, samples of isotopically pure $^{15}NF_4^{+}$ salts were prepared. Since only 15 mg of sample was available, long irradiation times were used to get a sufficiently strong signal. This resulted in some line broadening. Nevertheless, because the spectra are less complicated, some features of the $\perp$ orientation can be observed. The result of the analysis is given in Table I. Within experimental error, the fluorine hfs are equivalent for $^{14}NF_3^{+}\cdot$ and $^{15}NF_3^{+}\cdot$, while their nitrogen hfs are in the ratio of their nuclear magnetogyric ratios (−1.403). The observed spectrum and a stick-plot of the analysis are shown in Figure 2. Note also that the spectrum exhibits anomalies similar to those discussed for $^{14}NF_3^{+}\cdot$.

High-Temperature Spectra of $^{14}NF_3^{+}\cdot$. The high-temperature spectrum of $^{14}NF_3^{+}\cdot$ shown in Figure 3 can be interpreted in terms of an axially symmetric radical containing three nuclei of $I = {}^1/_2$ and one nucleus of $I = 1$. A unique feature of this spectrum is that the hfs for the parallel orientation are smaller than those of the $\perp$ orientation. However, as discussed earlier, the features representing the $\perp$ orientation are considerably stronger than those of the $\|$ orientation. As a result, the features of the parallel orientation in the middle of the spectra are masked, and they can only be determined by computer simulation. For $^{14}NF_3^{+}\cdot$ in NF_4AsF_6, the spectrum is interpreted in terms of a nitrogen nucleus ($I = 1$) and three equivalent fluorine nuclei ($I = {}^1/_2$). The hyperfine splittings are, in mT, $a_N(\perp) = 9.36$, $a_N(\|) = 8.70$, $a_F(\perp) = 12.48$, and $a_F(\|) = 2.00$. These values are independent of temperature between 235 and 340 K.

High-Temperature Spectra of $^{15}NF_3^{+}\cdot$. In order to confirm the assignment of the $^{14}NF_3^{+}\cdot$ spectra, spectra of a γ-irradiated sample of $^{15}NF_4AsF_6$ were obtained (Figure 4). These spectra can be analyzed in terms of one ^{15}N atom ($I = {}^1/_2$) and three equivalent ^{19}F atoms ($I = {}^1/_2$). The hyperfine splittings are given in Table I. The $^{15}NF_3^{+}\cdot$-containing samples exhibited the same thermal stability as the $^{14}NF_3^{+}\cdot$-containing samples described above.

Comparison of High- and Low-Temperature Spectra. The g factors and hyperfine splittings of the different $NF_3^{+}\cdot$ ESR spectra are given in Table I. That they are all due to $NF_3^{+}\cdot$ is established by the following observations: spectra of the irradiated ^{14}N and ^{15}N salts contain nuclei of the correct spins and numbers; fluorine atom hfs of $^{14}NF_3^{+}\cdot$ and $^{15}NF_3^{+}\cdot$ are equal at high and low temperatures, respectively, while the respective N-atom hfs are in the correct ratio of their nuclear moments; high-temperature spectra reversibly change into the low-temperature spectra, which are less intense; computed values of the isotropic hfs are the same in high- and low-temperature spectra, provided that the sign of $a_F(\perp)$ at low temperature is taken as negative.

The reason for the difference between the high-temperature and the low-temperature spectra is probably due to temperature-dependent rotation of $NF_3^{+}\cdot$ about a single axis. Spectra of $CF_3\cdot$ in a 1:30 CF_3I/Kr matrix change from one characteristic of a stationary radical to one characteristic of a freely rotating radical, as the temperature is increased from 4.2 to 35 K.[10] Examples in which similar changes occur between 77 and 300 K include $NH_3^{+}\cdot$ and $ND_3^{+}\cdot$ in their respective ammonium perchlorates[22] and $PF_5^{-}\cdot$ in KPF_6.[23,24] The averaging processes for $NH_3^{+}\cdot$ and $ND_3^{+}\cdot$,[22] as well as $PF_5^{-}\cdot$,[24] were attributed to rotations of these radical ions.

As the temperature of the $NF_3^{+}\cdot$-containing samples is increased, the spectra change between two different anisotropies. At low temperatures, the spectra are indicative of motionless $NF_3^{+}\cdot$, while at high temperatures, the spectra are indicative of uniaxial rotation. Most likely, this rotation occurs about an axis close to that of its minimum moment of inertia and is probably accompanied by some libration. Preliminary X-ray studies[26] on NF_4BF_4 show that the lattice is tetragonal, which may provide a preferential direction for rotation of the smaller $NF_3^{+}\cdot$ cation. Since this radical should be in its minimum energy configuration, significant deviations from the energetically favored pyramidal structure are extremely unlikely. Also, there are no phase changes of the lattice between 100 K and room temperature as indicated by Raman spectroscopy.[25] Inversion of the radical about the nitrogen would be expected to result in more nearly complete averaging.

Supporting evidence for rotation of $NF_3^{+}\cdot$ is provided by the fact that the $a_F(\perp)$ values observed for $^{14}NF_3^{+}\cdot$ and $^{15}NF_3^{+}\cdot$ are not identical. Since $NF_3^{+}\cdot$ has a pyramidal structure (see below), the moments of inertia of $^{14}NF_3^{+}\cdot$ and $^{15}NF_3^{+}\cdot$ must be different. This causes their rotational axes to be different, resulting in different $a_F(\perp)$ values.

UV-photolyzed mixtures of NF_3, BF_3, and Lewis acid at low temperatures exhibited spectra which were similar to that of Figure 1, except that the lines were broader. The line width increased slightly with longer photolysis, while the intensity increased. The higher temperature spectra (see for example Figure 5) can be interpreted in terms of the hyperfine parameters of the $NF_3^{+}\cdot$ spectra observed for the γ-irradiated salts (see Figure 3), although the line widths are quite different. For the photolyzed samples, the transition between the low and higher temperature spectra occurred at much lower temperatures than the γ-irradiated salts and the thermal stability of the radical depended upon the volatility of the Lewis acid used (see Results section). This suggests that these radicals are associated with solid AsF_5 or BF_3. The weaker residual signals observed after complete evaporation of the NF_3–F_2–Lewis acid condensed phases are similar to those in the γ-irradiated $NF_4^{+}\cdot$ salts. This suggests that they are due to $NF_3^{+}\cdot$ trapped in small amounts of $NF_4^{+}\cdot$ salts formed during the photolysis.

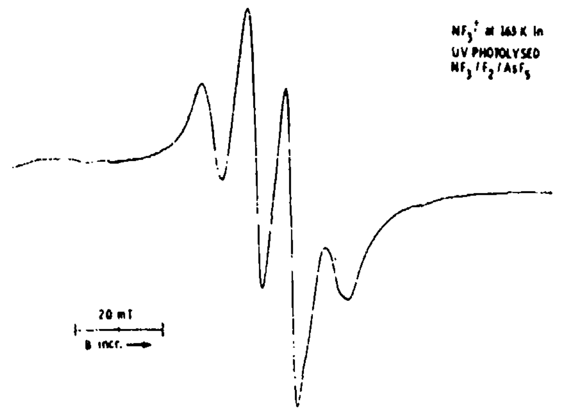

Figure 5. ESR spectrum of the $NF_3^{+}\cdot$ radial at 163 K produced by UV photolysis of a mixture of NF_3–F_2–AsF_5 (1:4:1) at 77 K. Comparison with Figure 1a shows that the six intense lines of the spectra are broadened into four overlapping lines, with the wings not resolved.

Table II. Comparison of Hyperfine Couplings of Radicals XF_3 Used in Table III

	$^{14}NF_3^{+}\cdot$[a]	$^{12}CF_3\cdot$ and $^{13}CF_3\cdot$	$^{11}BF_3^{-}\cdot$[b]	$^{14}NF_2O\cdot$[c]
$a_X(\perp)$	7.8[d]	24.7[f]		
$a_X(\parallel)$	11.49[d]	31.8[f]		
$a_F(\perp)$	(−)3.3[d]	8.4[g]		
$a_F(\parallel)$	30.8[d]	26.4[g]		
a_F(iso)	8.98[e]	14.25[h]	17.8	14.34
a_X(iso)	9.14[e]	27.15[h]	15.3	9.39
g(iso)	2.0051[e]	2.0031[h]	2.0021	2.0058

[a] This work. [b] Reference 5. [c] References 27 and 28. [d] Taken from low-temperature spectra. [e] Taken from high-temperature spectra. [f] Reference 29. [g] Reference 9. [h] Reference 6.

Table III. Spin Densities on the Central Atom and Fluorine Atoms of $NF^{+}\cdot$ Compared to Those of Related Radicals

radical	$\rho_X^{s}(X)$	$\rho_X^{p}(X)$	ρ_F^{s}	g(iso)
$BF_3^{-}\cdot$	0.212		0.0104	2.0021
$CF_3\cdot$	0.245	0.717	0.0084	2.0029
$NF_3^{+}\cdot$	0.166	0.687	0.0053	2.0051
$NF_2O\cdot$	0.170		0.0084	2.0058
$NF_2\cdot$	0.030	0.956	0.0052	2.0044

[a] Spin densities calculated from the data in Table II, assuming that atomic isotropic hyperfine couplings a° in mT are 72.1 for B, 111.0 for C, 55.0 for N, and 17100 for F, and the atomic anisotropic couplings b° are 3.24 for C and 1.71 for N. (See ref 30.)

Structures of $NF_3^{+}\cdot$. ESR data for $NF_3^{+}\cdot$ and isoelectronic species are compared in Table II. Since the tensors of the fluorine hfs need not be exactly axially symmetric, we averaged those in the $CF_3\cdot$ radical[9] to yield an effective value to be compared with that of $NF_3^{+}\cdot$. The spin densities on the s and p orbitals, ρ_i^{s} and ρ_i^{p}, respectively, of the central atom, given in Table III, were calculated by eq 4 and 5, where a_i and b_i

$$\rho_i^{s} = a_i(\mathrm{iso})/a_i^{\circ} \tag{4}$$

$$\rho_i^{p} = (a_i(\parallel) - a_i(\mathrm{iso}))/2b_i^{\circ} \tag{5}$$

are the isotropic and anisotropic hfs of an electron in the s and p orbitals of atom i, and a_i(iso) is the calculated isotropic hfs. For $BF_3^{-}\cdot$, no experimental anisotropic hfs were available, and values calculated from ref 31 had to be used.

The values of ρ_N^{s} for $NF_3^{+}\cdot$ and $NF_2O\cdot$ are nearly the same, as expected from the isoelectronic character of the $\ddot{F}$: and $\ddot{O}$: substituents. Although the ρ^{s} values for the series $NF_3^{+}\cdot$, $CF_3\cdot$, and $BF_3\cdot$ do not follow a monotonic trend, without a measured value for the anistropic boron hfs, the hybridization cannot be accurately determined. The value of ρ^{p}/ρ^{s} for $CF_3\cdot$ is 2.9, while that of $NF_3^{+}\cdot$ is 4.1. This suggests that the free electron in $NF_3^{+}\cdot$ has more p character than that in $CF_3\cdot$. This in turn suggests that the hybridization of the XF bonds in $CF_3\cdot$ is nearly sp^3 but that in $NF_3^{+}\cdot$ is between sp^3 and sp^2. This in turn indicates that $NF_3^{+}\cdot$ is more planar than $CF_3\cdot$ in contrast to the conclusion of Mishra et al.[4] This is further supported by the fact that the observed anisotropy in the fluorine hfs is greater for $NF_3^{+}\cdot$ than for $CF_3\cdot$. Recent theoretical calculations[31] based on the isotropic hfs of $BF_3^{-}\cdot$, $CF_3\cdot$, and $NF_3^{+}\cdot$ also indicate that the planarity increases from $BF_3^{-}\cdot$ toward $NF_3^{+}\cdot$.

The same conclusions are reached if the values of a_i° and b_i° reported by Hurd and Coodin[32] are used. These values are approximately 15% larger than those used here, so that smaller spin densities are computed. Although these absolute values appear more realistic, they leave the ratios of ρ^{p}/ρ^{s} unchanged.

The spin densities of $NF_3^{+}\cdot$ and $NF_2\cdot$ are also compared in Table III. The spin density distribution for $NF_2\cdot$ is calculated from the ESR data of Kasai and Whipple,[33] and the data are consistent with the isotropic data of Farmer et al.[35] Values in mT are $a_N(\parallel) = 4.9$, $a_N(\perp) = 0.0$, $a_F(\parallel) = 21.2$, and $a_F(\perp) = -16.9$. In $NF_2\cdot$, the unpaired electron is primarily in a p orbital so that there is no delocalization of the unpaired electron into the orbital of the lone pair on nitrogen. Thus, the structure of this radical is surprisingly different from that of $NF_3^{+}\cdot$.

Work is underway to analyze, in detail, the hyperfine splittings of the $NF_3^{+}\cdot$ radical and determine the angle α between the nitrogen and fluorine hyperfine tensors. In the $CF_3\cdot$ radical, α was found to be 17.8°.[9,10] Edlund et al.[35] reported that the direction of the hfs was not perpendicular to the C–F bond, but at an angle of 54° to it. A precise analysis of the low-temperature spectrum of $NF_3^{+}\cdot$ may substantiate the above conclusions. Since the $NF_3^{+}\cdot$ radical is slightly more planar, α for $NF_3^{+}\cdot$ may be different from that of $CF_3\cdot$.

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ON THE FORMATION AND DECOMPOSITION MECHANISM OF NF_4^+ SALTS

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Received . . . .

Abstract

The thermal decompositions of NF_4BF_4 and NF_4AsF_6 were studied in a sapphire reactor at different temperatures by total pressure measurements. It was found that the rates, previously reported by Solomon and coworkers for NF_4AsF_6, significantly differ from those of the present investigation, although both studies result in a 3/2 reaction order. From the temperature dependence of the observed decomposition rates, the following values were obtained for the global activation energies, $E_{NF_4BF_4} = 36.6 \pm 0.8$ kcal mol^{-1} and $E_{NF_4AsF_6} = 44.7 \pm 4.2$ kcal mol^{-1}. The suppression of the decomposition rates by the NF_3, F_2 and BF_3 or AsF_5 was measured. A critical evaluation of all experimental data available on the NF_4^+ salt formation and decomposition suggests the following reversible reaction mechanism

$$F_2 \rightleftharpoons 2\dot{F}$$

$$\dot{F} + NF_3 \rightleftharpoons \dot{N}F_4$$

$$\dot{N}F_4 + AsF_5 \rightleftharpoons \dot{N}F_3^+AsF_6^-$$

$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftharpoons NF_4^+AsF_6^-$$

A Born-Haber cycle was calculated for NF_4BF_4 and shows that the global decomposition activation energy and the heat of the formation reaction are identical within experimental errors and that the second step of the above mechanism is approximately thermochemically neutral. The rate of the thermal formation of NF_4SbF_6 at 250°C was also studied.

Introduction

The formation and decomposition reactions of NF_4^+ salts are of significant theoretical and practical interest. From a theoretical point of view, the question arises whether $\dot{N}F_4$ or NF_5 are produced as unstable intermediates. These would be highly unusual because first row elements generally do not form hypervalent molecules. From a practical point of view, a better knowledge of the formation and the decomposition mechanism is necessary in order to improve on existing synthetic methods.

Several mechanisms have previously been postulated for the formation of NF_4^+ salts. In 1966, Christe and coworkers suggested in their original reports[1,2] on the synthesis of NF_4AsF_6 by low-temperature glow-discharge that either NF_3^+ or F^+ (or F_2^+) are generated in the discharge. These radical cations could then react with either F_2 or NF_3 to yield NF_4^+. In 1972, Solomon and coworkers reported[3] the results from a kinetic study of the thermal decomposition of NF_4AsF_6 in Monel. Based on total pressure measurements, they concluded that the decomposition involved the equilibrium dissociation step

$$NF_4AsF_6 \rightleftharpoons NF_5 + AsF_5$$

followed by irreversible decomposition of the unstable NF_5 according to:

$$NF_5 \longrightarrow NF_3 + F_2$$

The latter step was taken to be a 3/2-order reaction. From the temperature dependence of the kinetic constants, a value of 41 kcal mol^{-1} was obtained for the sum of the overall heat of sublimation and the activation energy for the decomposition of NF_5. In 1973, Christe and coworkers proposed[4] an alternate mechanism for the formation of NF_4^+ salts. This mechanism accounted for the fact that NF_4^+ salts can be synthesized by uv-photolysis. It involved the following steps.

$$F_2 \rightleftharpoons 2\dot{F}$$

$$\dot{F} + AsF_5 \rightleftharpoons \dot{A}sF_6$$

$$\dot{A}sF_6 + NF_3 \rightleftharpoons \dot{N}F_3^+AsF_6^-$$

$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftharpoons NF_4^+AsF_6^-$$

Part of this mechanism was later experimentally confirmed by ESR studies[5-7] which showed that the $\dot{N}F_3^+$ radical cation is indeed formed as intermediate in both the low-temperature uv-photosynthesis and the γ-irradiation induced decomposition of NF_4^+ salts.

Since the observation of $\dot{N}F_3^+$ as an intermediate[5-7] is incompatible with the mechanism proposed[3] by Solomon and since at elevated temperatures metal reactors rapidly absorb F_2-Lewis acid mixtures, a reinvestigation of the thermal decomposition of NF_4AsF_6 in an inert sapphire reactor was undertaken. In particular, a more detailed investigation of the suppression effects of NF_3, F_2, and AsF_5 was expected to yield valuable information. Furthermore, no quantitative data had previously been available on the decomposition rates of NF_4BF_4 and the formation rates of NF_4SbF_6.

Experimental Section

<u>Thermal Decomposition Studies</u>. The samples of NF_4BF_4[8] and NF_4AsF_6[8,9] were prepared as previously described and showed no dedectable impurities. All decomposition experiments were carried out in a sapphire reactor (Tyco Co.). The reactor was connected by a Swagelok compression fitting, containing a

Teflon front ferrule, to a stainless steel valve and a pressure transducer (Validyne, Model DP7, 0-1000 mm ± 0.5%), the output of which was recorded on a strip chart. The reactor had a volume of 38.7 ml and was heated by immersion into a constant temperature (± 0.05°C) circulating oil bath. The reactor was passivated at 250°C with F_2-BF_3 or F_2-AsF_5 mixtures until the pressure remained constant over a period of several days, and weighed amounts of NF_4^+ salts were added in the dry nitrogen atmosphere of a glove box. After immersion of the reactor into the hot oil bath, the reactor was evacuated, and the pressure change was monitored as a function of time. Control experiments were carried out at the beginning and end of each series of measurements to ascertain that the rates had not significantly changed during each series. The composition of the gaseous decomposition products was shown by chemical analysis, infrared spectroscopy, and gas chromatography to be 1:1:1 mixtures of NF_3, F_2, and the corresponding Lewis acid. For the curve fitting of the kinetic data the method of linear least squares was used with the listed uncertainties being 2σ of the calculated slope.

Formation of NF_4SbF_6. Because of the high corrosivity of high pressure NF_3-F_2-SbF_5 mixtures at elevated temperatures, the NF_3-F_2-SbF_5 reaction system could not be monitored directly with a pressure transducer or gage. Consequently, 9 identical passivated 95 ml Monel cylinders were each loaded with 50 mmol of SbF_5, and a twofold excess of NF_3 and F_2 was added. The cylinders were simultaneously placed into an oven preheated to 250°C and were removed separately from the oven after certain time intervals. After cooling the cylinders, all material volatile at 25°C was pumped off, and the amount of NF_4^+ salt formed was determined by the observed weight increase and spectroscopic analyses.

Results and Discussion

Thermal Decomposition of NF_4BF_4 and NF_4AsF_6. The thermal decomposition of NF_4BF_4 and NF_4ASF_6 in a constant volume reactor was studied by total pressure measurements over a temperature range of about 35°C for each compound. Since screening experiments had shown that even well passivated nickel or Monel reactors rapidly reacted with mixtures of hot F_2 and BF_3 or AsF_5, a sapphire reactor was used. This reactor was found to be completely inert toward these gas mixtures over extended time periods. Furthermore, it was found that the decomposition rates increased with increasing sample size. However, the rates did not increase linearly with the sample size because the increased pressure enhances the suppression of the rates (see below). In order to minimize the effect of changes in the sample size during a given series of experiments, the largest feasible samples and the smallest available reactor volume were used. In this manner, only a small percentage of the sample was decomposed in a given series of experiments. The first and the last experiment of each series were carried out under identical conditions and showed that the change in rate due to the small, but inevitable, sample size change was indeed negligible.

The results of our measurements on NF_4BF_4 and NF_4AsF_6 are summarized in Tables 1 and 2. In agreement with the previous report[3] on the thermal decomposition of NF_4AsF_6, smooth decomposition curves were obtained. The decomposition rates steadily decreased with increasing pressure in the reactor and the initial rates were restored upon evacuation of the reactor, indicating that the decomposition products suppress the decomposition rates. This was confirmed by studying the influence of different gases on the decomposition rates of NF_4BF_4 and of NF_4AsF_6. The addition of He did not noticeably influence the rates, whereas F_2 and NF_3 resulted in a weak suppression. However, the addition of BF_3 to NF_4BF_4 or of AsF_5 to NF_4AsF_6 resulted in strong rate suppressions (see Tables 1 and 2).

For all decomposition experiments, plots of $P^{3/2}$ versus time resulted in straight lines (see Figures 1 and 2) indicating a 3/2 reaction order. The resulting global kinetic constants are given in Table 3. Arrhenius plots of these constants resulted in straight lines (see Figure 3) and in the following global decomposition activation energies, $E_{NF_4BF_4} = 36.6 \pm 0.8$ kcal mol^{-1} and $E_{NF_4AsF_6} = 44.7 \pm 4.2$ kcal mol^{-1}, the latter value being in good agreement with that of 41 kcal mol^{-1} previously reported.[3]

The fact that the small mol fraction ranges of sample decomposition studied in these experiments were truly representative for the overall decomposition rates, was established by following the decomposition of small samples at somewhat higher temperatures over almost the entire mol fraction (α) range. A typical decomposition curve obtained for NF_4BF_4 at 253°C (see Figure 4) does not exhibit any sigmoid character and the $P^{3/2}$ versus time plot is linear for about the first 25% of α.

Although the results previously reported[3] for the decomposition of NF_4AsF_6 in Monel resulted in a linear $P^{3/2}$ versus time plot, the reported rates were by a factor of about seven higher than ours. Unfortunately the sample size and the exact reactor volume used in reference 3 were not given. However, the estimated reactor volume (100 cc Monel cylinder + Wallace-Tiernan FA 145-780 gage) and the reported method of the NF_4AsF_6 synthesis suggest that the previously used sample weight to reactor volume ratios were almost certainly significantly smaller than those of our experiments. This should have resulted in rates lower than ours. The only possible explanations for the previously reported[3] higher rates are absorption of the suppressing AsF_5 by Monel and/or inaccurate temperature control (heating of the cylinder in a tube furnace).

A large discrepancy of $\sim 10^6$ exists between the previously reported[3] and our kinetic constants (see Table 3). Most of this discrepancy ($\sim 10^5$) appears to be computational.

Furthermore, the previously reported[3] data for the suppression by AsF_5 are inconsistent. Whereas the experimental data in Tables 6 and 7 of reference 3 show strong rate suppression by AsF_5, the kinetic constants given in Table 8 of reference 3 imply only mild suppression by AsF_5. The previously reported[3] strong rate suppression by NF_3 could not be confirmed by the present study. Our data (see Table 3) show that NF_3 is only a weak suppressor, comparable to F_2, and that AsF_5 or BF_3 are the only strong suppressors. This is an important observation, because the alleged[3] strong suppression by NF_3 had caused us to propose in a previous publication[4] a mechanism for the formation of NF_4AsF_6 involving the incorrect (see below) steps $\dot{F} + AsF_5 \longrightarrow \dot{A}sF_6$ and $\dot{A}sF_6 + NF_3 \rightarrow \dot{N}F_3^+AsF_6^-$.

Thermal Synthesis of NF_4SbF_6. Whereas the thermal synthesis of NF_4AsF_6 proceeds at too slow a rate for practical kinetic measurements, the rate of formation of NF_4SbF_6 is sufficiently fast. However, SbF_6^- tends to form polyantimonates, such as $Sb_2F_{11}^-$ or $Sb_3F_{16}^-$,[5,9-11] with SbF_5 which makes a kinetic evaluation of any experimental data very difficult. In view of the importance of the thermal synthesis of NF_4SbF_6 (this compound serves as a starting material for the metathetical syntheses of most other NF_4^+ salts)[11-15] and because of the complete absence of data on its formation rate, nine reactions were carried at 250°C and at a pressure of about 110 atm to determine its formation rate. The results are summarized in Table 4 and Figure 5 and show that at this temperature the initial formation rate of NF_4^+ salts is surprisingly rapid. The subsequent slow-down of the reaction is probably caused by a lowering of the SbF_5 partial pressure in the system due to the formation of polyantimonate anions. Their thermal dissociation equilibria to SbF_6^- and SbF_5 will then control the SbF_5 pressure in the system and become the rate limiting steps.

<u>Reaction Mechanism.</u> As pointed out in the introduction, the formation and decomposition mechanism of NF_4^+ salts is of great interest because it appears to involve an unusual hypervalent species, such as $\dot{N}F_4$, $\dot{N}F_5$, $\dot{A}sF_6$ or $\dot{B}F_4$. The following experimental data are known, and the correct mechanism must be compatible with all of these conditions.

(1) Certain NF_4^+ salts, such as NF_4SbF_6 and NF_4AsF_6, can, depending upon the system pressure, either be formed or decomposed at the same temperature.[5,9-11] This implies pressure dependent equilibria and reversibility of the formation and decomposition reactions.

(2) ESR measurements have shown[5-7] that the $\dot{N}F_3^+$ radical cation is a crucial intermediate in both the low-temperature uv-photolytic synthesis and γ-irradiation induced decomposition of NF_4^+ salts. Furthermore, the fluroination of $\dot{N}F_3^+$ to NF_4^+ appears to require F atoms.[6]

(3) In the thermal decomposition of either NF_4BF_4 or NF_4AsF_6, BF_3 or AsF_5 act as strong rate suppressors, whereas both NF_3 and F_2 suppress the decomposition rates only mildly (see above results).

(4) Filtered uv-radiation[4,8] or heating[9] to 120°C supply sufficient activation energy for the formation of NF_4^+ salts. This is a strong indication that the first step in the synthesis must be the dissociation of F_2 into two fluorine atoms ($D°(F_2)$=36.8 kcal mol^{-1}).[16]

(5) The tendency to form NF_4^+ salts by thermal activation strongly decreases with decreasing Lewis acid strength, i.e. $SbF_5 > AsF_5 > PF_5 > BF_3$.[4,8,9] Since the corresponding NF_4^+ salts all possess sufficient thermal stability, a mechanism[3] involving the initial formation of NF_5, followed by its reaction with the corresponding Lewis acid, cannot explain the lack of thermal formation of salts, such as NF_4PF_6 or NF_4BF_4. It can be explained, however, by the formation of intermediates of lower thermal stability, such as $\dot{N}F_3^+$ salts. For SbF_6^- or AsF_6^-, these NF_3^+ salts were shown to still possess the lifetime required for their efficient conversion to NF_4^+ salts, whereas $NF_3^+BF_4^-$ was found to be of considerably lower thermal stability[7].

(6) ESR flow-tube experiments[17] gave no indication for interaction between $\dot{F}$ atoms and AsF_5, as expected for the reaction step $AsF_5 + \dot{F} \longrightarrow \dot{A}sF_6$.

(7) Infrared matrix isolation studies of the thermal decomposition products from either NF_4AsF_6[3] or $(NF_4)_2NiF_6$[18] gave no evidence for the formation of NF_5.

(8) Lewis acids, such as BF_3, PF_5, AsF_5 or SbF_5, do not form stable adducts with NF_3, even at low temperatures.[18,19]

Since NF_3, F_2 and F have ionization potentials of 13.00,[20] 15.69[21] and 17.44 eV,[22] respectively, any mechanism involving the initial formation of either NF_3^+, F_2^+ or F^+ can be ruled out, based on condition (4). This leaves us with the following 4 possible schemes.

Scheme 1:

$$NF_3 + AsF_5 \rightleftharpoons NF_2^+AsF_6^-$$

$$F_2 \rightleftharpoons 2\dot{F}$$

$$\dot{N}F_2^+AsF_6^- + \dot{F} \rightleftharpoons \dot{N}F_3^+AsF_6^-$$

$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftharpoons NF_4^+AsF_6^-$$

Scheme 2:

$F_2 \rightleftharpoons 2\dot{F}$

$\dot{F} + AsF_5 \rightleftharpoons \dot{A}sF_6$

$\dot{A}sF_6 + NF_3 \rightleftharpoons \dot{N}F_3^+AsF_6^-$

$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftharpoons NF_4^+AsF_6^-$

Scheme 3:

$F_2 \rightleftharpoons 2\dot{F}$

$\dot{F} + NF_3 \rightleftharpoons \dot{N}F_4$

$\dot{N}F_4 + \dot{F} \rightleftharpoons NF_5$

$NF_5 + AsF_5 \rightleftharpoons NF_4^+AsF_6^-$

Scheme 4:

$F_2 \rightleftharpoons 2\dot{F}$

$\dot{F} + NF_3 \rightleftharpoons \dot{N}F_4$

$\dot{N}F_4 + AsF_5 \rightleftharpoons \dot{N}F_3^+AsF_6^-$

$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftharpoons NF_4^+AsF_6^-$

Scheme 1 can be ruled out because it does not comply with conditions (8) and (3). In Scheme 1, NF_3 would be expected to suppress as strongly as AsF_5. Scheme 2 can be eliminated because it violates condition (3), i.e. NF_3 should be a stronger suppressor than AsF_5, and because of condition (6). Scheme 3 is unacceptable because it does not comply with (2) and (5). Scheme 4 is the only mechanism which agrees with all experimental data and therefore is our preferred mechanism. This mechanism differs from all the mechanisms previously proposed. It appears to be generally applicable to NF_4^+ salts, except for certain decomposition reactions in which NF_4^+ oxidatively fluorinates the anion.[18]

In view of the rather complex mechanism of scheme 4 and the observed fractional reaction order for the decomposition process, a mathematical analysis of the kinetic data was too complex and beyond the scope of the present study.

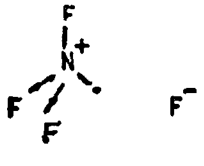
Born-Haber Cycle for NF_4BF_4. It was of interest to examine the thermodynamic soundness of scheme 4. NF_4BF_4 was chosen for this purpose because it is the only NF_4^+ salt for which the heat of formation has experimentally been determined.[23] The following Born-Haber cycle can be written where all heats of formation or reaction are given in kcal mol^{-1}.

$$\begin{tikzcd}
F_{2(g)} + NF_{3(g)} + BF_{3(g)} \arrow[r, shift left, "-34.6(5)"] & NF_4^+BF_4^-{}_{(s)} \arrow[l, shift left] \\
0 \quad -31.4 \quad -271.4 \arrow[d, shift left] & -337.4 \arrow[dd, shift left, "(4)"'] \\
\dot{F}_{(g)} + \dot{F}_{(g)} + NF_{3(g)} + BF_{3(g)} \arrow[u, shift left, "+36.8\ (1)"] \arrow[d, shift left] & \\
\dot{F}_{(g)} + \dot{N}F_{4(g)} + BF_{3(g)} \arrow[u, shift left, "(2)"] \arrow[r, shift left, "-18\ (3)"] & \dot{F}_{(g)} + \dot{N}F_3^+BF_4^-{}_{(s)} \arrow[l, shift left] \arrow[uu, shift left]
\end{tikzcd}$$

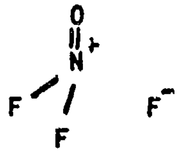
From the known heats of reaction of NF_3,[24] BF_3,[24] and NF_4BF_4,[23] the heat of reaction (5) is known to be -34.6 kcal mol^{-1}. Furthermore, the heat of dissociation of F_2, reaction (1), is known[16] to be 36.8 kcal mol^{-1}. A reasonably close estimate for step (3), the heat of formation of solid $NF_3^+BF_4^-$ from NF_4 and BF_3, can be made from the known heat of dissociation of $NF_2O^+BF_4^-$. Since NF_3O and $\dot{N}F_4$ are expected to be quite similar (see below), it is reasonable to assume that step (3) has a heat of reaction similar to that of $NF_3O + BF_3 \longrightarrow NF_2O^+BF_4^-$, i.e. -18 kcal mol^{-1}. Consequently, the sum of steps (2) and (4) should be about -53 kcal mol^{-1}. Whereas the heat of reaction of step (2) is difficult to estimate, the heat of reaction of (4) is easier to estimate because it represents the dissociation energy of the fourth N-F bond in NF_4^+. In NF_3, the heat of dissociation of the third N-F bond is 58 kcal mol^{-1},[26,27] and it seems reasonable to assume that the dissociation energy of the fourth N-F bond in NF_4^+ is similar to or slightly less than this value.

Consequently, step (2) should be approximately thermochemically neutral.

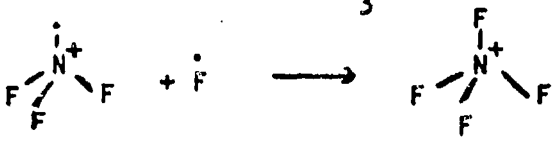
The proposition that step (2) and step (4) should so markedly differ in their heats of reaction, although both involve the formation of one additional N-F bond, is not unreasonable. In step (2) a hypervalent $\dot{N}F_4$ radical is formed which would possess nine valence electrons on the central nitrogen atom. By analogy with the known NF_3O molecule,[28] this energetically unfavorable structure can be circumvented by assuming strong contributions from resonance structures, such as



and



These resonance structures result in a strong polarization, i.e. weakening of all N-F bonds, when compared to those in NF_3. This is demonstrated by the bond lengths of 1.371 and 1.43 A observed for NF_3[29] and NF_3O[28], respectively. Thus the energy gained by the formation of a fourth N-F bond in the NF_4 radical is largely compensated by a significant weakening of the remaining N-F bonds. In contrast, the reaction of the $\dot{N}F_3^+$ radical cation with a fluorine atom, i.e.



does not significantly change the nature of the existing N-F bonds and, therefore, is expected to result in a heat of reaction close to the energy of this bond.

It should be pointed out that the global activation energy (36.6 ± 0.8 kcal mol^{-1}) of the decomposition of NF_4BF_4 to $NF_3 + F_2 + BF_3$ and the heat of formation of NF_4BF_4 from $NF_3 + F_2 + BF_3$ (-34.6 kcal mol^{-1}) are the same within experimental error. It is difficult to say whether this is coincidental or if it implies that the corresponding forward reactions, i.e. steps (2), (3) and (4) of the Born-Haber cycle occur without activation energy. Examples of the latter case are known for the endothermic dissociation of solids, such as carbonates.[30] If for NF_4^+ salts the global decomposition activation energies should indeed be identical to the heats of formation from NF_3, F_2 and the corresponding Lewis acid, a value of about -372 kcal mol^{-1} can be predicted for $\Delta H_{fNF_4AsF_6}$ based on $E_{NF_4AsF_6} = 45$ kcal mol^{-1} and $\Delta H_{fAsF_5} = 29.55$ kcal mol^{-1}.

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Table 1. Thermal Decomposition of NF_4BF_4[a] in a Sapphire Reactor[b]

T(°C)	182.2	188.9	190.8					197.4	204	213.3	215
				He(500)[c]	F_2(500)[c]	NF_3(500)[c]	BF_3(500)[c]				
Time (hrs)	pressure change (mm Hg)										
0	0	0	0	0	0	0	0	0	0	0	0
1	28	40	45	44	38	38	5	64	91	160	180
2	42	66	74	73	64	64	11	103	142	261	285
3	55	86	97	98	84	87	16	134	191	341	367
4	66.5	102	116	117	102	105	21	161	228	409	440
5	77	117	135	136	122	122	26	186	266	468	509
6	86.5	132	152	153	139	138	31	208	300	522	572
7	96	146	168	169	155	152	35	230	336	579	633
8	104	159	183		169	166	39	250		628	689
9	112	171	197		182	180	43	269		675	741
10	120.5	182	210		195	192	47	288		721	791
12	135	204	236		218	217	56	324		806	891
14	149	225	260		238	239	65	355		895	980
16	162	247	280		258	263	73	390			
18		267	300		277		82				
20					295		91				

---

a) sample size 2.65 g

b) reactor volume 38.7 ml

c) The values given in parantheses indicate the pressure (in mm Hg) of the added gas at the beginning of each experiment.

Table 2. Thermal Decomposition of NF_4AsF_6[a] in a Sapphire Reactor[b]

T(°C)	200	218	227	238					
					He(736)[c]	F_2 (197)[c]	NF_3(567)[c]	AsF_5(247)[c]	AsF_5(724)[c]
Time (hrs)	pressure change (mm Hg)								
0	0	0	0	0	0	0	0	0	0
1	2.6	9.9	16	27	28	25	21	5	4
2	4.0	16.0	25	44	45	42	34	8.5	7
3	5.2	20.8	33	58	59	55	44	12	9
4	6.2	25.3	40	71	73	68	54	16.5	11
5	7.2	29.4	46.5	83	85	79	63	20	12
6	8.3	32.2	52.5	93.5	95	90	72	24	13
7	9.2	36.6	57	103.5	105	101	81	28	14
8	10.0	40.0	62	113	115	110	90	32	15.5
9	10.8	43.0	67.5	123	124	120	98	35	17
10	11.6	46.0	72.5	132	133	129	106	38	18
12	13.2	51.4	82	149	151	145	122	45	21
14	14.7	56.6	91	165	166	161	140	52	23
16	16.1	61.4	99.5	181	181	176	160	59	25
18	17.4	66.2	107	197.5	196	190	176	65	
20			115.5	214	213	205	192	72	
25			134				226		
30							252		

---

a) sample size 1.86 g

b) reactor volume 38.7 ml

c) The values given in parantheses indicate the pressure (mm Hg) of the added gas at the beginning of each experiment

Table 3. Global Kinetic Constants[a] for the Thermal Decomposition of NF_4BF_4 and NF_4AsF_6

NF_4BF_4		NF_4AsF_6	
Temp. (°C)	k x 10^9	Temp. (°C)	k x 10^{10}
182.2	0.96 ± 0.01	200	0.284 ± 0.002
188.9	1.74 ± 0.02	218	1.99 ± 0.03
190.8	2.11 ± 0.04	227	4.00 ± 0.02
197.4	3.39 ± 0.05	238	9.69 ± 0.10
204	6.08 ± 0.08	238(He 736)	9.62 ± 0.08
213.3	12.79 ± 0.22	238(F_2 197)	9.22 ± 0.05
215	14.68 ± 0.18	238(NF_3 567)	8.60 ± 0.16
190.8(He 500)	2.29 ± 0.03	238(AsF_5 247)	1.94 ± 0.12
190.8(F_2 500)	1.86 ± 0.04	238(AsF_5 724)	0.48 ± 0.08
190.8(NF_3 500)	1.92 ± 0.02		
190.8(BF_3 500)	0.314 ± 0.02		

---

a) Mol $^{3/2}$ liter $^{-3/2}$ sec^{-1}, error limits 2σ

Table 4. Conversion of $NF_3 + F_2 + SbF_5$ to NF_4SbF_6 at 250°C[a]

Reaction Time (hr)	Product Composition $NF_4^+SbF_6^- \cdot xSbF_5$ X	Conversion of SbF_5 to NF_4SbF_6 (mol %)
1	1.08	48.1
2	0.89	52.9
3	0.78	56.2
6	0.59	62.9
12	0.34	74.6
24	0.17	85.5
50	0.13	88.5
85	0.106	90.4
120	0.064	94.0

(a) Mole ratios of starting materials, $NF_3:F_2:SbF_5 = 2:2:1$. Starting pressure: 110 atm, residual pressure calculated for 100% conversion to NF_4SbF_5: 44 atm. The Monel cylinders (95 ml volume) were placed horizontally in the oven, preheated to 250°C. One hour was required until the cylinders reached 250°C. This point was taken as zero reaction time.

Diagram Captions

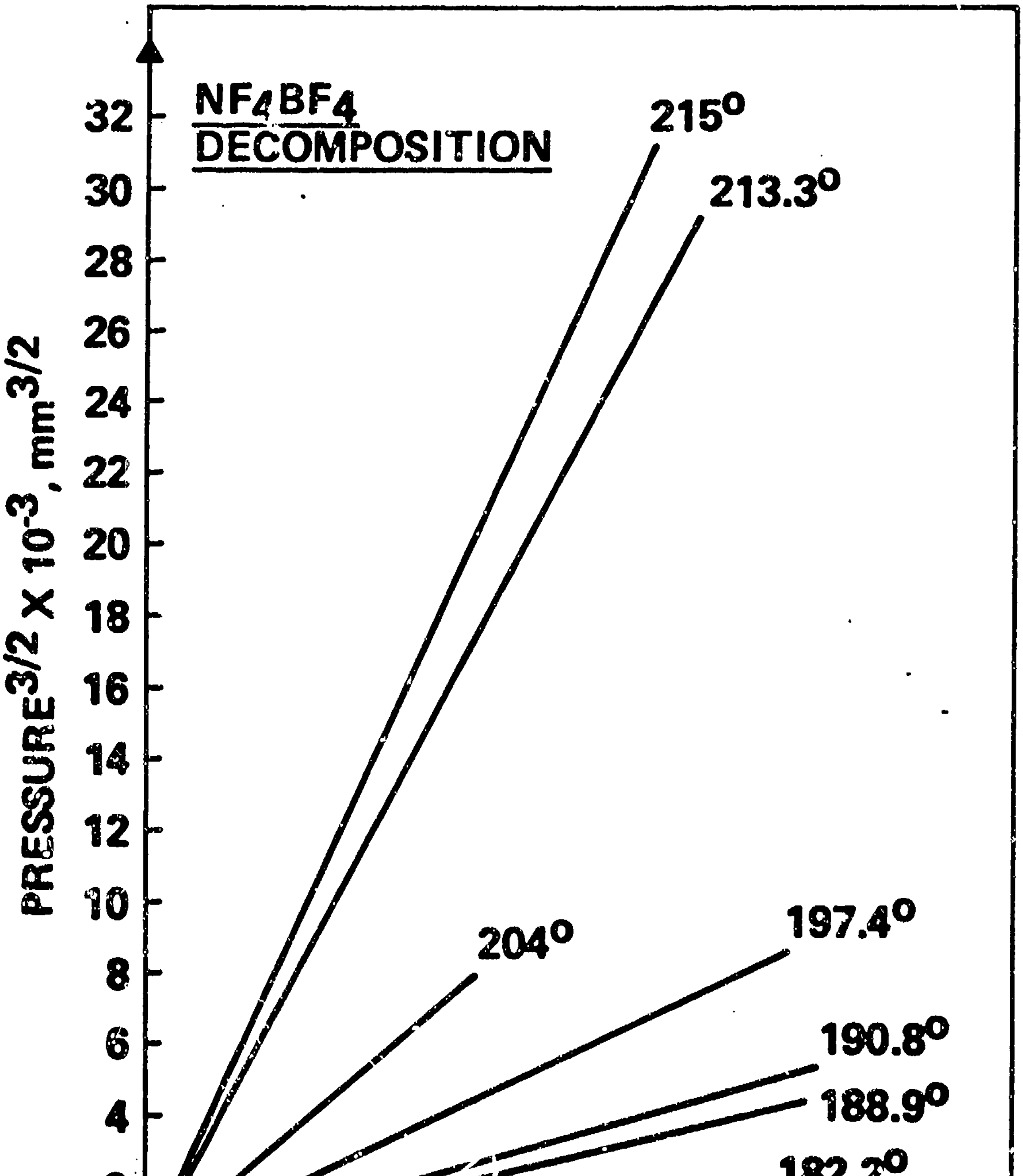
Figure 1. Total pressure ($P^{3/2}$) curves for the thermal decomposition of 2.65 g of NF_4BF_4 at different temperatures (°C).

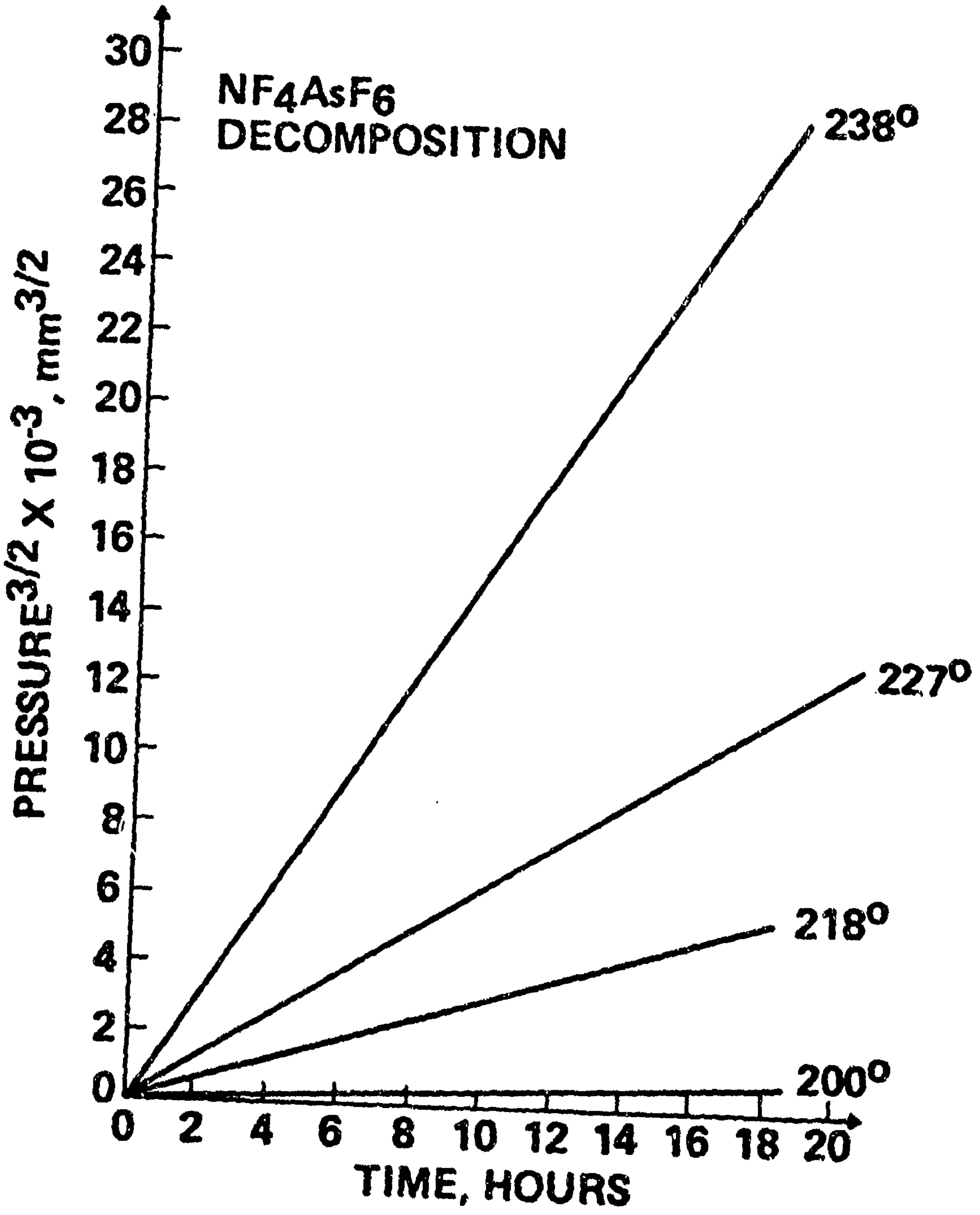
Figure 2. Total pressure ($P^{3/2}$) curves for the thermal decomposition of 1.86 g of NF_4AsF_6 at different temperatures (°C).

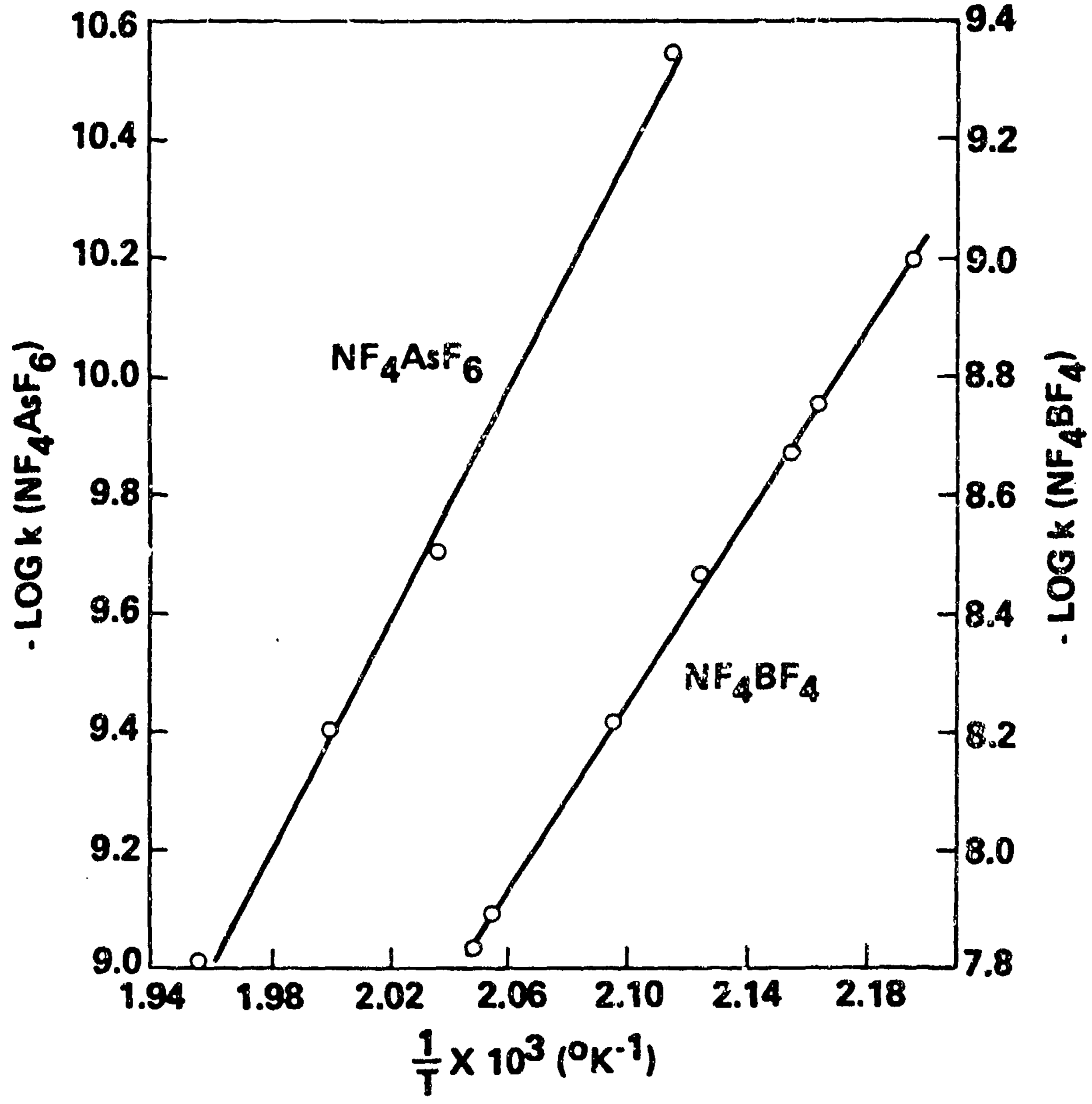
Figure 3. Arrhenius plots for NF_4BF_4 and NF_4AsF_6.

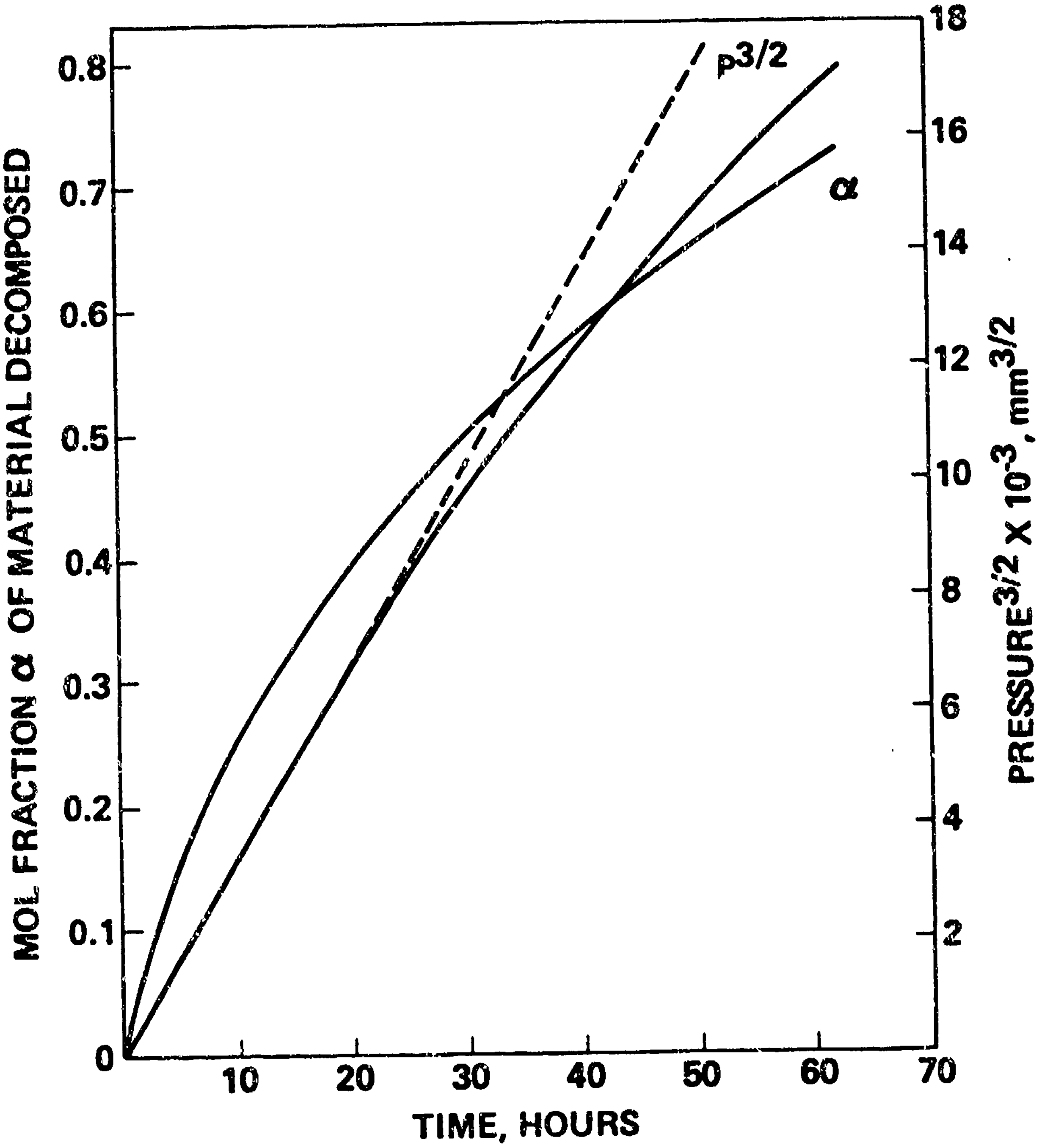
Figure 4. Decomposition curves for 75 mg of NF_4BF_4 at 253°C. The solid lines are the observed data and the broken line represents the ideal straight line for the $P^{3/2}$ versus t plot.

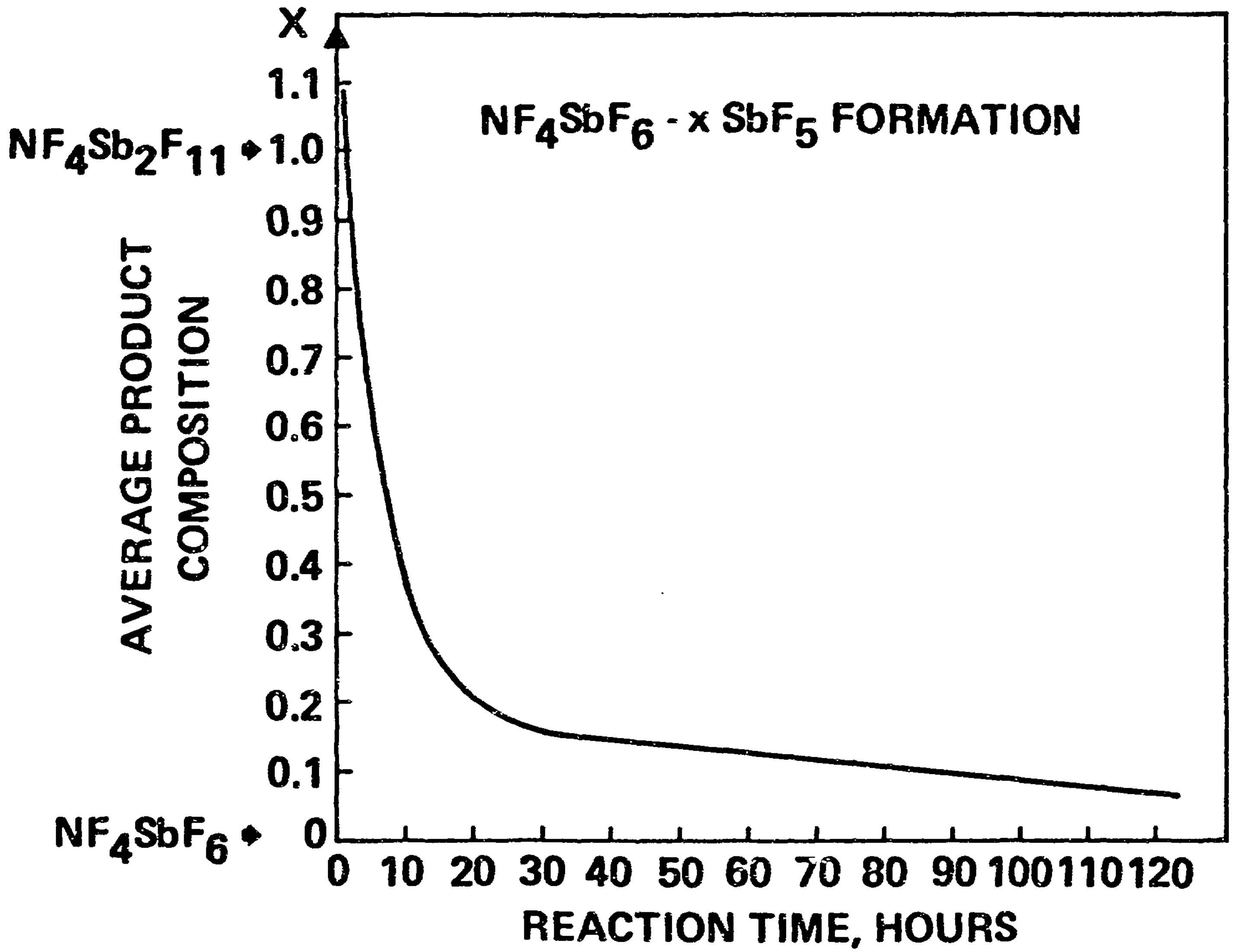
Figure 5. Formation rate of $NF_4SbF_6 \cdot xSbF_6$ from NF_3, F_2 and SbF_5 at 250°C.


NF4BF4
DECOMPOSITION
215°
213.3°
204°
197.4°
190.8°
188.9°
182.2°
PRESSURE3/2 X 10-3, mm3/2
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
2
4
6
8
10
12
14
16
18
20
TIME, HOURS


NF4AsF6
DECOMPOSITION
238°
227°
218°
200°
PRESSURE$^{3/2}$ X 10^{-3}, mm$^{3/2}$
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
14
16
18
20
TIME, HOURS


10.6
10.4
10.2
10.0
9.8
9.6
9.4
9.2
9.0
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
NF_4AsF_6
NF_4BF_4
- LOG k (NF_4AsF_6)
- LOG k (NF_4BF_4)
1.94
1.98
2.02
2.06
2.10
2.14
2.18
$\frac{1}{T} \times 10^3$ ($^oK^{-1}$)


MOL FRACTION α OF MATERIAL DECOMPOSED
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
TIME, HOURS
10
20
30
40
50
60
70
PRESSURE$^{3/2}$ X 10^{-3}, mm$^{3/2}$
2
4
6
8
10
12
14
16
18
P$^{3/2}$
α


$NF_4SbF_6 - x\ SbF_5$ FORMATION
X
1.1
$NF_4Sb_2F_{11}$ ◆ 1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
NF_4SbF_6 ◆ 0
AVERAGE PRODUCT COMPOSITION
0
10
20
30
40
50
60
70
80
90
100
110
120
REACTION TIME, HOURS

SULFUR TETRAFLUORIDE. ASSIGNMENT OF VIBRATIONAL SPECTRA AND FORCE FIELD

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(Received . . .)

ABSTRACT

The infrared spectra of SF_4 isolated in Ar and Ne matrices were studied. The observed ^{32}S - ^{34}S isotopic shifts were used to resolve the existing ambiguities concerning the assignments of the deformation modes and to obtain an improved valence force field.

INTRODUCTION

Although numerous papers have been published on the vibrational spectra and assignments of SF_4 [1-12], this molecule is still poorly understood and the assignment of most of the deformation modes is still open to question.

In this paper, we report new matrix isolation data and ^{32}S - ^{34}S isotopic shifts which allow unambiguous assignments for the deformation modes and the computation of an improved valence force field.

EXPERIMENTAL

The Ar or Ne matrix isolated samples of SF_4 were prepared by the reaction of S_2Cl_2 with AgF_2 using a previously described flow system [13] and He-cryostat [14]. The isotopically enriched samples were prepared from ^{34}S (>98% purity) and Cl_2. The infrared spectra were recorded on a Perkin-Elmer Model 325 spectrophotometer with an accuracy of ± 0.5 cm^{-1}. Most of the ^{32}S - ^{34}S isotopic shifts were determined with an accuracy of ± 0.05 cm^{-1}. The methods used for the normal coordinate analyses have previously been discribed [11].

RESULTS AND DISCUSSION

Infrared Spectra. Infrared spectra were recorded of SF_4 in both Ar and Ne matrices at 4 K for SF_4 of natural sulfur isotope abundance, 1:1 mixtures of $^{32}SF_4$ and $^{34}SF_4$, and pure $^{34}SF_4$ using sample to matrix ratios of 1:1000. The observed frequencies and ^{32}S - ^{34}S isotopic shifts are summarized in Table 1.

In agreement with previous experience [6, 13, 15, 16], neon matrices produced the best spectra and exhibited frequencies closest to those of the gas phase values. Because accurate anharmonicity corrections were not possible, all observed isotopic shifts were corrected by a factor of 1.01, a value close to those previously used for similar molecules [13, 16, 17]. The observed isotopic shifts are in fair agreement with the values previously reported [11] for some of these bands in an N_2 matrix.

For some of the bands, matrix splittings were observed. The usc of ^{34}S enriched samples facilitated distinction between isotopic and matrix splittings. For the 353 cm^{-1} fundamental, the splitting observed in a N_2 matrix had previously been interpreted [11] in terms of a coincidence of the two fundamentals ν_3 and ν_9. Although varying degrees of splitting were observed during the present study for the 353 cm^{-1} fundamental in Ar and Ne matrices (see Figure 1), these splittings are identical for both $^{32}SF_4$ and $^{34}SF_4$. Since it appears unlikely that ν_3 and ν_9 should exhibit identical sulfur isotopic shifts, these splittings are attributed to matrix splittings of a single fundamental. This conclusion is supported by the normal coordinate analysis, given below, which shows that the large isotopic shift observed for the 532 cm^{-1} deformation mode can be explained only by assigning this frequency to ν_3.

Normal Coordinate Analysis and Assignments. A listing of the 9 fundamentals of SF_4 and their assignment in point group C_{2v} is given in Table II, together with an approximate description of these modes. Based on the previous studies [1-12], the assignments for ν_1, ν_2, and ν_4 in the A_1 block, ν_6 in the B_1 block, and ν_8 in the B_2 block are well established. The remaining four modes are all deformation modes. Assuming no coincidences, three fundamentals at 532, 475, and 353 cm^{-1} are available for assignment to these four modes. Based on relative intensity considerations and the fact that all three fundamentals are infrared active, the missing fundamental should be the torsional mode ν_5 (A_2) which is infrared inactive. In similar molecules, this mode is generally of very low Raman intensity. Therefore, it would not be surprising that this mode has up to date not experimentally been observed for SF_4.

The assignment of the 532, 475, and 353 cm^{-1} fundamentals was established in the following manner. The 353 cm^{-1} band has previously been assigned [5, 6, 8, 10, 11] to ν_9 (B_2), and this assignment has recently been supported by microwave spectroscopy [1] . Since the ^{32}S - ^{34}S isotopic shifts of ν_8 and of the 353 cm^{-1} fundamental are now both known, a force field computation can be used to test the correctness of this assignment. If the assignment is correct, both observed isotopic shifts must result in an identical force field. As can be seen from Figure 2, the isotopic shifts observed for the 867 and the 353 cm^{-1} fundamental result in the same force field, thus establishing the 353 cm^{-1} fundamental as ν_9 (B_2).

A distinction between the two possible assignments (532 and 475 cm^{-1}) for ν_7 (B_1) can be made in a similar manner, since the sulfur isotopic shifts of ν_6 (B_1) and of the 532 cm^{-1} deformation mode (4.05 cm^{-1}) are known. From a computation of the B_1 force field (see Figure 3) it becomes obvious that the sulfur isotopic shift of ν_7 has to be less than 1 cm^{-1} in order to agree with the force field obtained from the isotopic frequencies of ν_6. Since the isotopic shift of 4.05 cm^{-1}, observed for the 532 cm^{-1} band, is much too large for ν_7, the 532 cm^{-1} fundamental must be ν_3 (A_1) and the 475 cm^{-1} one must be ν_7 (B_1). Additional support for this assignment was obtained from the computation of the A_1 block force field (See Table 3). No difficulty was encountered to duplicate the isotopic shifts observed for ν_1, ν_2, and ν_3.

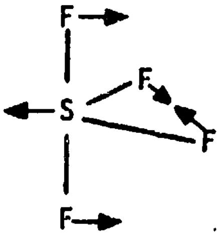
The missing frequency of ν_5 (A_2) was calculated to be 437 cm^{-1} assuming $F_{55} = F_{77}$. This assumption seemed most plausible because of the three possible $f_{\alpha\alpha}$ interaction constants, the one which involves two angles sharing a common equatorial fluorine ligand, i.e. $f_{\alpha\alpha}''$, should have the largest value and because in F_{55} and F_{77} $f_{\alpha\alpha}''$ has the same sign.

The assignments,thus obtained for SF_4,are summarized in Table 1 and can now be considered as being well established. They are in good agreement with the previously published [3] infrared gas-phase band contours and compare favorably with those [18] recently published for the closely related SF_4O molecule. Based on the results of this study on SF_4, it becomes necsssary, however, to exchange the assignments of ν_4 (A_1) and ν_9 (B_2) for SF_4O.

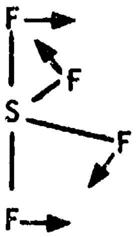
The force field of SF_4 is summarized in Table 3. The B_1 and B_2 block values represent a general valence force field. The A_1 block is still underdetermined (10 symmetry force constants and 7 frequency values), but is expected to be a good approximation to a general valence force field in view of the good agreement between the observed and calculated isotopic shifts. The off-diagonal symmetry force constants listed in Table 3 were required in order to be able to duplicate the observed sulfur isotopic shifts. The value of F_{23} is necessary to make $\Delta\nu_2$ close to zero. The relatively large isotopic shift of ν_3 can only be achieved by the use of an F_{34} value which concentrates the isotopic shifts of ν_3 and ν_4 almost exclusively in ν_3 and by the use of F_{13} and F_{14} which transfer some of the isotopic shift from ν_1 to ν_3. Since ν_3 is an almost equal mixture of F_{33} and F_{44} (see PED of Table 3), the isotopic shift balance between ν_1 and ν_3 can be equally well achieved by either F_{13} or F_{14}, as long as their sum equals to about 0.6 mdyn/radian. Therefore the chosen ratio between F_{13}

and F_{14} is somewhat arbitrary, and their values were made about equal for cosmetic reasons.

The potential energy distribution (PED) is given in Table 3 and shows that all fundamentals are highly characteristic, with the exception of ν_3 and ν_4. The latter are almost equal mixtures of F_{33} and F_{44}. As previously discussed in detail [10, 11] and shown by their eigenvectors (see Table 3), ν_3 is a symmetric and ν_4 is an antisymmetric combination of the symmetry coordinates S_3 and S_4, i.e.,



ν_3, symmetric combination of axial and equatorial bending



ν_4, antisymmetric combination of axial and equatorial bending

In view of these facts, a discussion is rather meaningless whether ν_3 or ν_4 is mainly axial or equatorial bending. Furthermore, it shows that ν_4 is the fundamental mainly involved in an intramolecular exchange process as suggested by Berry [19].

Additional experimental data which could be used as a constraint for the SF_4 assignment and force field, are centrifugal distortion constants [12] and mean amplitudes of vibration [20]. Since the observed centrifugal distortion constants "are not well determined" and have been shown [12] to be insensitive towards changes in the assignment of the deformation modes, they are not a useful constraint. Mean amplitudes of vibration have previously been reported [10] for SF_4 using five different assignments and force fields. These data showed that only $\langle q^2 \rangle^{\frac{1}{2}}\ F_3 \ldots F_4$ and $\langle q^2 \rangle^{\frac{1}{2}}\ F_1 \ldots F_3$ are sufficiently sensitive to variation of the assignment of the deformation modes in question and were approximately proportional to the values of F_{33} and $F_{44} + \sim\frac{1}{2} F_{33} + \sim\frac{1}{2} F_{55}$, respectively. Using these correlations and the above force field, $\langle q^2 \rangle^{\frac{1}{2}}\ F_3 \ldots F_4$ and $\langle q^2 \rangle^{\frac{1}{2}}\ F_1 \ldots F_3$

are estimated to be 0.071 and 0.067 Å, respectively, in excellent agreement with the observed values of 0.068 ± 0.01 and 0.067 ± 0.005 Å [20], thus lending additional support to our assignment. It should be pointed out that both the centrifugal distortion constants and the mean amplitudes of vibration , although useful for the detection of gross errors in the assignments, are not sensitive enough to be useful constraints for the force field of SF_4.

Acknowledgement. One of us (KOC) is indebted to Dr. E. C. Curtis for the use of his computer programs and helpful discussions and to the Office of Naval Research for financial support.

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TABLE 1. OBSERVED FREQUENCIES AND ^{32}S-^{34}S ISOTOPIC SHIFTS (cm^{-1}) OF SF_4 IN Ar AND Ne MATRICES

Ar		Ne			
Frequency	$\Delta\nu$	Frequency	$\Delta\nu$	$\Delta\omega$[a]	Gas-Phase Frequencies
883.5	11.2 ± 0.1	887.2	11.22 ± 0.05	11.33	892
858	10.4 ± 0.1	859.7	10.42 ± 0.05	10.52	867
705[b]	12.7 ± 0.1	721[b]	13.00 ± 0.05	13.13	730
550.5	0	557[b]	0	0	558
529[b]	3.9 ± 0.2	530.1	4.05 ± 0.05	4.09	532
354[b]	2.35 ± 0.1	352[b]	2.4 ± 0.1	2.42	353

(a) Corrected for anharmonicity

(b) These bands showed matrix splittings

TABLE 2. ASSIGNMENT OF NORMAL MODES OF SF_4

Species	Approximate Description of Mode	Frequency, cm^{-1}
A_1 ν_1	$\nu sym XF_2$ eq	892
ν_2	$\nu sym XF_2 ax$	558
ν_3	$\delta sciss XF_2 eq$ and ax, sym comb	532
ν_4	$\delta sciss XF_2 ax$ and eq, asym comb	228
A_2 ν_5	XF_2 twist	[437][a]
B_1 ν_6	$\nu asym XF_2 ax$	730
ν_7	$XF_2 eq$ wagging	475
B_2 ν_8	$\nu asym XF_2 eq$	867
ν_9	$\delta sciss XF_2 ax$ out of plane	353

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a) Value calculated from $F_{55} = F_{77}$

TABLE 3. FORCE FIELD,[a] COMPUTED AND OBSERVED HARMONIC SULFUR ISOTOPIC SHIFTS,[b] POTENTIAL ENERGY DISTRIBUTION[c] AND EIGENVECTORS OF SF_6

			$\Delta\omega$ comp	$\Delta\omega$ obsd	PED	Eigenvectors S_1	 S_2	 S_3	 S_4
A_1	$F_{11} = f_r + f_{rr}$	5.884	11.37	11.35±0.05	$95F_{11}$	-0.275	-0.014	0.123	0.194
	$F_{22} = f_R + f_{RR}$	3.476	0.07	0	$99F_{22}$	-0.010	0.229	-0.014	-0.028
	$F_{33} = 0.99 f_\beta + 0.01 f_\gamma - 0.15 f_{\beta\gamma}$	1.414	4.14	4.09±0.05	$30F_{33}+29F_{44}+26F_{34}$	0.045	0.018	0.187	0.238
	$F_{44} = 0.006 f_\beta + 0.71 f_\gamma + 0.29 (f_\alpha + f_{\alpha\alpha} + f_{\alpha\alpha}' + f_{\alpha\alpha}'') + 0.13 f_{\alpha\beta} + 1.80 f_{\alpha\gamma} + 0.11 f_{\beta\gamma}$	0.863	0.00		$91F_{33}+89F_{44}-80F_{34}$	0	-0.005	0.141	-0.178
	F_{13}	0.320							
	F_{14}	0.300							
	F_{23}	0.100							
	F_{34}	0.4913							
A_2	$F_{55} = f_\alpha - f_{\alpha\alpha} - f_{\alpha\alpha}' + f_{\alpha\alpha}''$	1.673	0						
						S_6	S_7		
B_1	$F_{66} = f_R - f_{RR}$	2.821	13.14	13.13±0.05	$101F_{66}+22F_{77}-23F_{67}$	0.335	-0.203		
	$F_{77} = f_\alpha + f_{\alpha\alpha} - f_{\alpha\alpha}' - f_{\alpha\alpha}''$	1.673	0.87		$84F_{77}+10F_{67}$	0.050	0.259		
	$F_{67} = \sqrt{2}(f_{R\alpha} - f_{R\alpha}')$	0.530				S_8	S_9		
B_2	$F_{88} = f_r - f_{rr}$	5.165	10.53	10.52±0.05	$105F_{88}-9F_{89}$	0.297	-0.096		
	$F_{99} = f_\alpha - f_{\alpha\alpha} + f_{\alpha\alpha}' - f_{\alpha\alpha}''$	1.914	2.48	2.42±0.1	$101F_{99}$	-0.003	0.196		
	$F_{89} = \sqrt{2}(f_{r\alpha} - f_{r\alpha}')$	0.700							
	f_r	5.525							
	f_R	3.149							
	f_{rr}	0.360							
	f_{RR}	0.328							

(a) Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch-bend interaction constants in mdyn/radian. For the force field computation, the frequency values of Table 2 were used and fitted to within 0.1 cm^{-1}.

(b) in cm^{-1}.

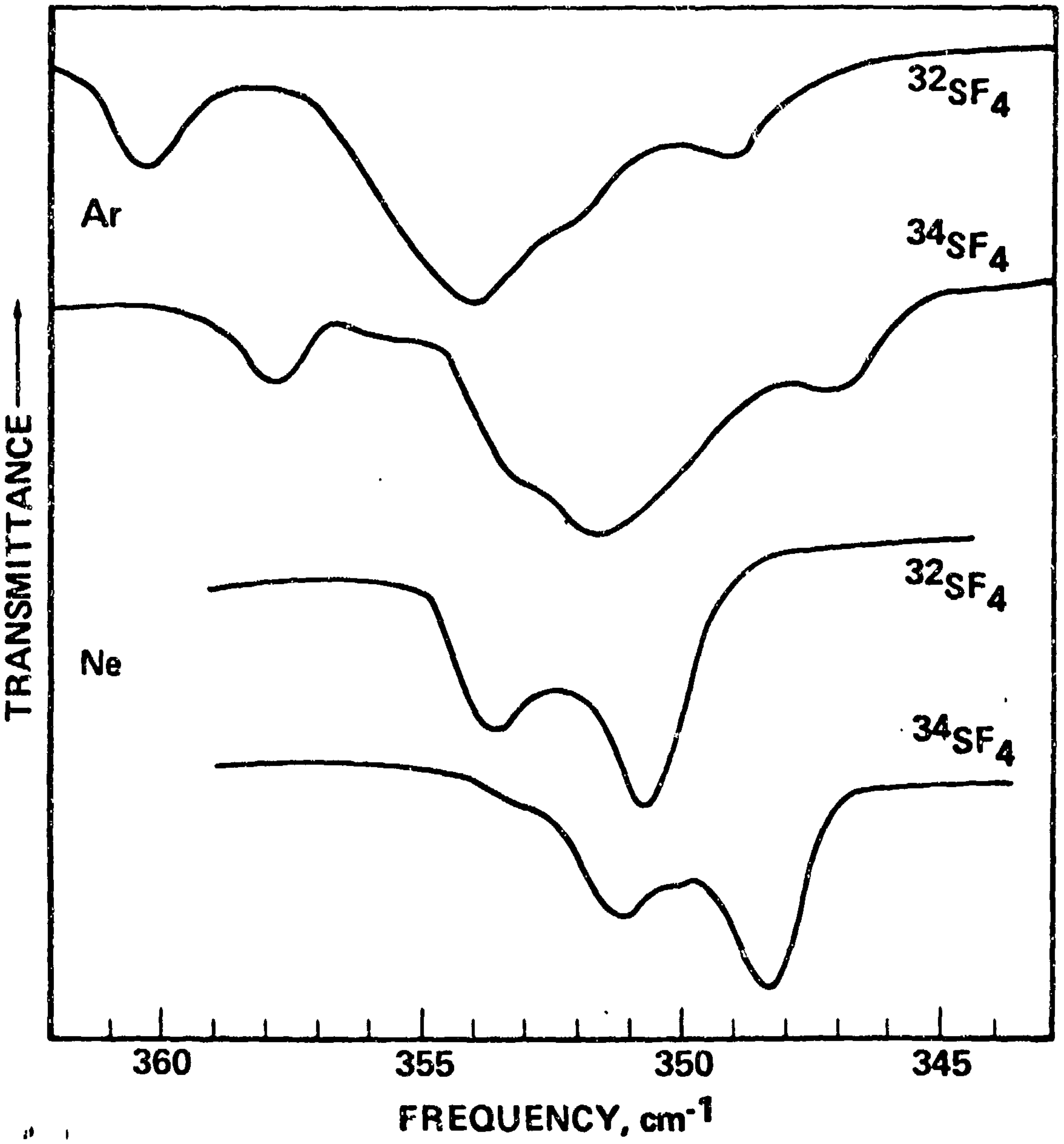
(c) Percent contributions. Contributions of less than 10% to the PED are not listed.

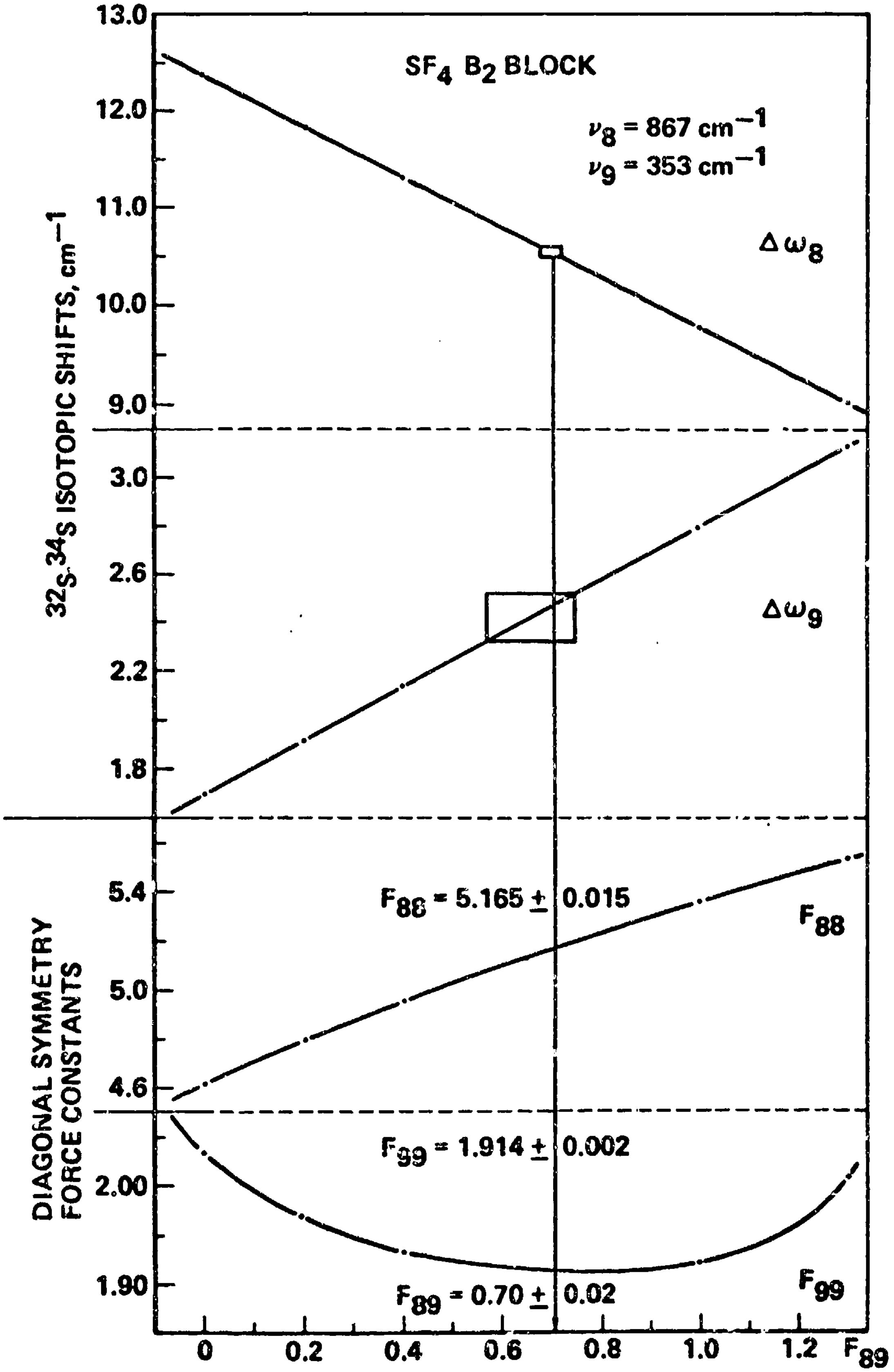
DIAGRAM CAPTIONS

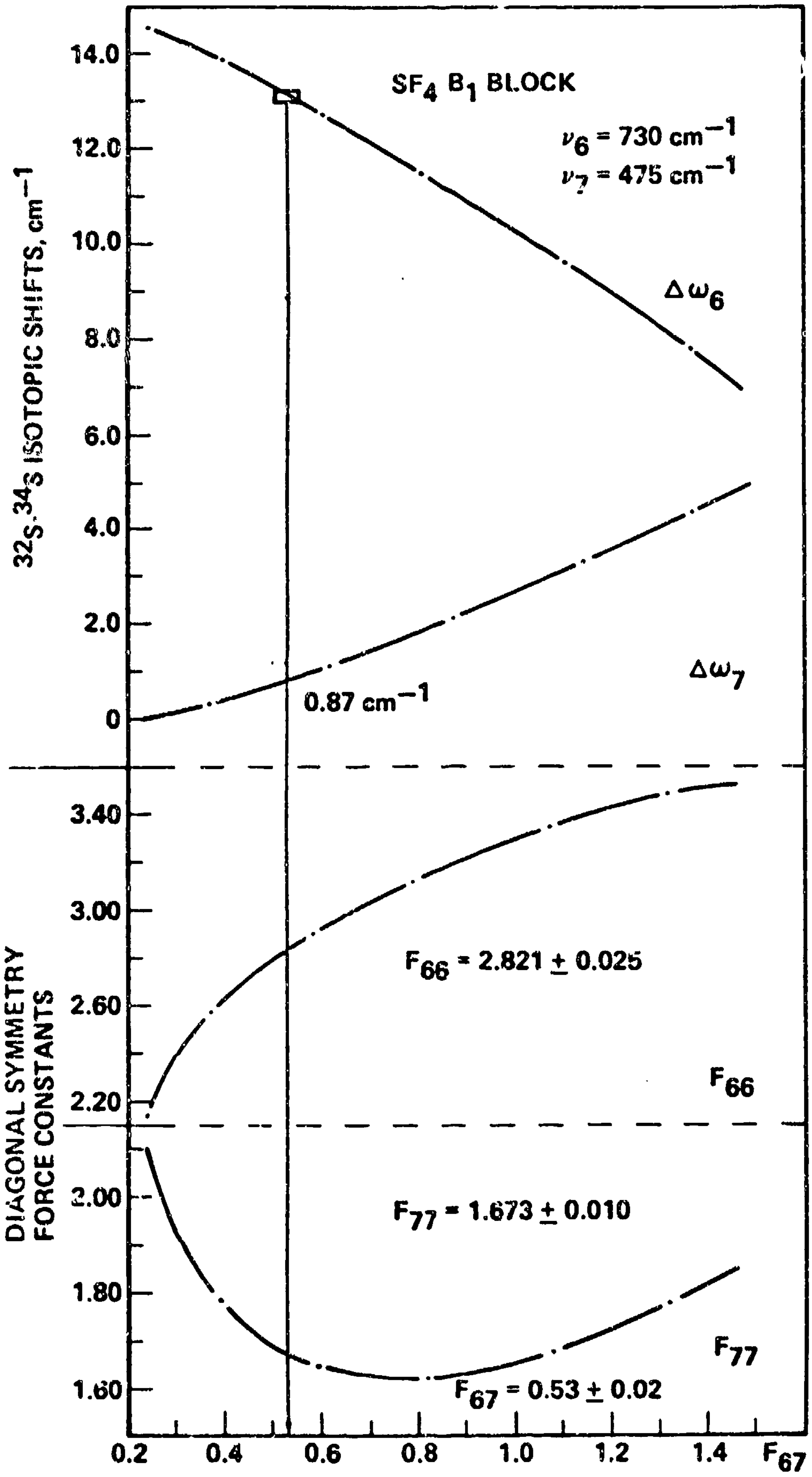
Figure 1. Infrared spectra of $^{32}SF_4$ and $^{34}SF_4$ in argon and neon matrices. The observed splittings are attributed to matrix effects.

Figure 2. Solution range of force constants and computed sulfur isotopic shifts for the B_2 block of SF_4. The rectangles indicate the uncertainties of the observed anharmonicity corrected isotopic shifts and the vertical line the resulting general valence force field. The units are cm^{-1} for the isotopic shifts and mdyn/Å, mdyn Å/radian^2, and mdyn/radian for F_{88}, F_{99}, and F_{89}, respectively.

Figure 3. Solution range of force constants and computed sulfur isotopic shifts for the B_1 block of SF_4. For further explanations, see caption of Figure 2.


$^{32}SF_4$
Ar
$^{34}SF_4$
TRANSMITTANCE
$^{32}SF_4$
Ne
$^{34}SF_4$
360
355
350
345
FREQUENCY, cm^{-1}


SF$_4$ B$_2$ BLOCK
ν_8 = 867 cm^{-1}
ν_9 = 353 cm^{-1}
$\Delta\omega_8$
$\Delta\omega_9$
^{32}S-^{34}S ISOTOPIC SHIFTS, cm^{-1}
13.0
12.0
11.0
10.0
9.0
3.0
2.6
2.2
1.8
DIAGONAL SYMMETRY FORCE CONSTANTS
5.4
5.0
4.6
2.00
1.90
F$_{88}$ = 5.165 ± 0.015
F$_{88}$
F$_{99}$ = 1.914 ± 0.002
F$_{99}$
F$_{89}$ = 0.70 ± 0.02
0
0.2
0.4
0.6
0.8
1.0
1.2
F$_{89}$



SF$_4$ B$_1$ BLOCK
ν_6 = 730 cm^{-1}
ν_7 = 475 cm^{-1}
$\Delta\omega_6$
$\Delta\omega_7$
0.87 cm^{-1}
^{32}S-^{34}S ISOTOPIC SHIFTS, cm^{-1}
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
3.40
3.00
2.60
2.20
2.00
1.80
1.60
DIAGONAL SYMMETRY FORCE CONSTANTS
F$_{66}$ = 2.821 ± 0.025
F$_{66}$
F$_{77}$ = 1.673 ± 0.010
F$_{77}$
F$_{67}$ = 0.53 ± 0.02
0.2
0.4
0.6
0.8
1.0
1.2
1.4
F$_{67}$

Contribution from the Rocketdyne Division of Rockwell International
Corporation, Canoga Park, California 91304

On Reactions of Fluorine Perchlorate with Fluorocarbons and the Polarity of the O-F Bond in Covalent Hypofluorites

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Received . . . .

Although $FOClO_3$ has been known for decades,[1,2] its reaction chemistry has remained virtually unexplored [illegible] is limited to references to unpublished work, cited in a review.[3] This lack of data is attributed to the previous report[2] that $FOClO_3$ consistently exploded during attempted freezing. During a study[4] of NF_4ClO_4, it was found that very pure $FOClO_3$ could be obtained in high yield by the thermal decomposition of NF_4ClO_4. The $FOClO_3$, prepared in this manner, could be manipulated and repeatedly frozen without explosions, thus allowing us to study some of its properties[5] and reaction chemistry.

Of particular interest to us were the reactions of $FOClO_3$ with fluorocarbons. Previous work[6] in our laboratory had demonstrated that $ClOClO_3$ and $BrOClO_3$ add readily to fluorocarbon double bonds resulting in covalent fluorocarbon perchlorates. Consequently, one would expect fluorine perchlorate to undergo a similar reaction. However, a literature citation[3] suggested that $FOClO_3$ does not add across the double bond in $Cl_2C{=}CF_2$. Furthermore, reactions of covalent hypofluorites, such as CF_3OF, are commonly interpreted in terms of a highly unusual $CF_3\overset{\delta^-}{O}-\overset{\delta^+}{F}$ type polarization of the O-F bond ("positive fluorine"). If the O-F bond in CF_3OF is indeed polarized in this direction, the fluorine in $FOClO_3$ should be even more positive because of the higher electronegativity of the perchlorato group. Since the direction of the addition of a hypohalite across an unsymmetrical olefinic double bond strongly depends on the direction and the degree of polarization of the O-Hal bond,[7] a study of the O_3ClOF-$CF_3CF{=}CF_2$ reaction system offered an ideal opportunity to experimentally test the validity of the "positive fluorine" concept.

Experimental Section

Caution! Although no explosions were encountered in the present study, $FOClO_3$ must be considered a highly sensitive material and should be manipulated only in small quantities with appropriate safety precautions.

Apparatus and Materials

Volatile materials were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and bellows-seal valves. Pressures were measured with a Heise Bordon Tube-type gauge (0-1500 mm ± 0.1%). Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. The ^{19}F NMR spectra was recorded on a Varian Model EM 390 spectrometer at 84.6 MHz using Teflon-FEP sample tubes (CS Laboratory Supplies) and $CFCl_3$ as an internal standard. Hexafluoropropylene and CF_3I were purchased while $CF_2{=}CF_2$ was prepared by pyrolyzing Teflon. Fluorine perchlorate was obtained from the decomposition of NF_4ClO_4.[4,5]

Reaction with Hexafluoropropylene

A 30 ml stainless steel cylinder was loaded at -196° with $FOClO_3$ (1.59 mmol) and C_3F_6 (2.05 mmol). The closed cylinder was warmed to -45° and kept at that temperature overnight. Separation of the products was achieved by vacuum fractionation in U traps cooled at -78, -95, and -196°. The coldest trap contained unreacted C_3F_6 together with $FClO_3$, C_2F_5CFO, and a small amount of $(CF_3)_2CO$. In the other traps only the colorless liquid, $C_3F_7OClO_3$ was found (1.18 mmol, 74% yield based on $FOClO_3$). The following temperature-vapor pressure data were measured (°C, mm): -46.6, 4; -22.7, 17; -9.3, 36; 0.0, 59; 10.6, 99; 22.0, 161. The vapor pressure-temperature relation is described by the equation $\log P_{mm} = 7.5257 - (1571.94/T°K)$ with a calculated normal boiling point of 65.2° and a heat of vaporization of 7.19 kcal/mol. A vapor density of 265 g/mol was measured compared to a calculated value of 268.5 g/mol for $C_3F_7ClO_4$. Strong mass spectral peaks were found for the ions $C_2F_4ClO_4^+$, $C_3F_7^+$, $CF_2ClO_4^+$, $C_3F_5O^+$, $C_3F_5^+$, $C_2F_5^+$, $C_2F_4O^+$, $C_2F_4^+$, $C_2F_3O^+$, ClO_3^+, $C_2F_2O^+$, CF_3^+ (base peak) ClO_2^+, COF_2^+, ClO^+, CF_2^+, and COF^+. Infrared bands were observed at (cm^{-1}, int.): 1340(sh), 1325(sh), 1290(vs), 1250(sh), 1235(vs), 1200(m), 1171(w), 1153(m), 1119(ms), 1088(m), 1026(s), 988(s), 968(m-s), 784(w), 746(m), 723(w), 676(m), 641(m-s), 614(s), and 530(w).

Reaction with Tetrafluoroethylene

Fluorine perchlorate (0.61 mmol) and C_2F_4 (0.62 mmol) were combined at -196° in a 10 ml stainless steel cylinder. By evaporation of the liquid nitrogen from a liquid nitrogen-dry ice slush used to cool the reaction cylinder, the temperature was allowed to slowly rise to -78° and finally over several days by loss of solid CO_2 to about -45°. Fractional condensation of the products at -112 and -196° permitted the isolation of $C_2F_5OClO_3$. (0.42 mmol. 68% yield) which was identified by its known vibrational, NMR and mass spectra.[8] Smaller amounts of CF_3CFO, C_2F_6, Cl_2, and O_2 were observed as by-products.

Reaction with Trifluoromethyl Iodide

Into a cold (-196°) 30 ml stainless steel cylinder CF_3I (0.66 mmol) and then $FOClO_3$ (1.40 mmol) were condensed. Warm-up to about -45° was accomplished slowly as noted in the preceding example. After several days at -45° the reactor was recooled to -196° and the presence of a considerable amount of non-condensable gas (oxygen) was noted. Fractionation of the condensible products showed a mixture of COF_2, CF_4, Cl_2, I_2, IF_5, and a solid iodine oxide to be the principal species present. However, a small amount CF_3OClO_3 (0.05 mmol, 8% yield) was also found and identified by comparison with reported data.[8]

Results and Discussion

Under carefully controlled reaction conditions, similar to those previously used for the polar additions of $ClOClO_3$ and $BrOClO_3$,[6] fluorine perchlorate was found to add across olefinic double bonds in high yield. With tetrafluoroethylene the following reaction occurred:

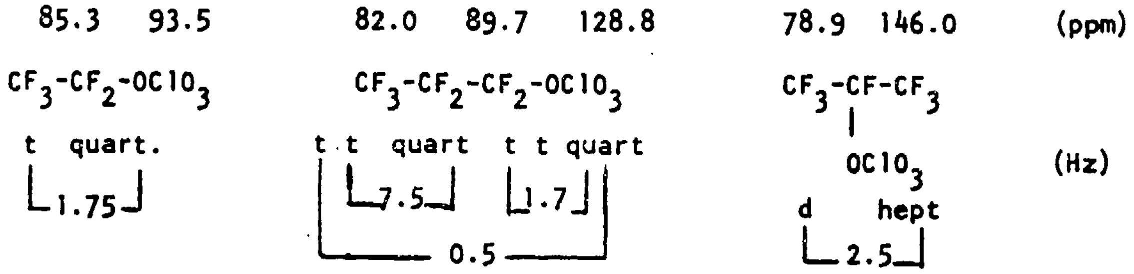
$$CF_2{=}CF_2 + FOClO_3 \xrightarrow{-45^\circ} CF_3CF_2OClO_3$$

With the unsymmetrical olefin perfluoropropylene a mixtures of two isomers was found:

$$CF_3CF{=}CF_2 + FOClO_3 \xrightarrow{-45^\circ} \underset{(68\%)}{CF_3CF_2CF_2OClO_3} + \underset{(32\%)}{CF_3CF(OClO_3)CF_3}$$

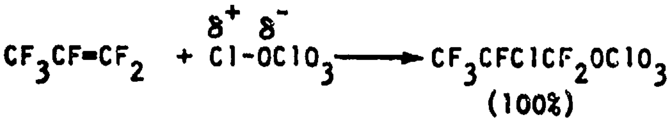
These two perfluoropropyl perchlorates are novel compounds which were identified by vapor density measurements and spectroscopic data. The presence of the covalent $-OClO_3$ group was demonstrated by infrared spectroscopy which showed the intense bands typical of this group[8] at 1290 ($\nu_{as}ClO_3$), 1026 ($\nu_s ClO_3$), and 614 cm^{-1} (ν Cl-O). Additional support for the covalent perchlorate structure was obtained from the mass spectrum which showed strong peaks for the ions, ClO_3^+, ClO_2^+, and ClO^+ but not for ClO_4^+, as is generally the case for fluorocarbon perchlorates. A parent ion was not observed and the highest m/e was $C_2F_4ClO_4^+$, *ie.* the parent minus a CF_3 group.

Gas chromatography of the product revealed a slight assymetry for the $C_3F_7ClO_4$ peak, thereby indicating the presence of isomers. This was confirmed by ^{19}F NMR spectroscopy showing that both possible adducts were formed. The observed chemical shifts and coupling constants, together with higher resolution data than previously reported[8] for $C_2F_5OClO_3$, are summarized below.



The resonances of fluorines geminal to a perchlorato group were broadened due to chlorine quadrupole relaxation. Based on their relative peak areas, the ratio of the two isomers was, n-68% and iso-32%.

The fact that in the reaction of $FOClO_3$ with $CF_3CF{=}CF_2$ both isomers are formed, significantly differs from the previously reported[6] $ClOClO_3$ and $BrOClO_3$ reactions where exclusive Markownikoff type additions occurred. The latter produced 100% of $CF_3CFXCF_2OClO_3$, as expected for a polar addition of the positively polarized terminal halogen to the carbon with the highest electron density.[7]



$$CF_3CF{=}CF_2 + \overset{\delta^+}{Cl}\text{-}\overset{\delta^-}{OClO_3} \longrightarrow \underset{(100\%)}{CF_3CFClCF_2OClO_3}$$

The formation of both isomers (n- and iso-) in the corresponding $FOClO_3$ reaction suggests that the F-O bond in $FOClO_3$ is not strongly polarized in either direction. This is not surprising in view of the known very small dipole moment (0.023D) of the closely related $FClO_3$ molecule[9] and the expected similar electronegativities of a $-ClO_3$ and an $-OClO_3$ group. The fact that the percentage of n-isomer was somewhat higher than that of the iso-isomer can be explained by steric effects (bulky CF_3 group) and is insufficient reason to postulate a strongly positive fluorine in $FOClO_3$. An alternate explanation for the formation of two isomers in the $FOClO_3$-$CF_3CF{=}CF_2$ reaction would be the assumption of a free radical mechanism. However, the high yield of the products (74%), the mild (-45°) and well controlled reaction conditions, and the absence of detectable amounts of C_3F_8 and $C_3F_6(OClO_3)_2$ in the reaction products render a free radical mechanism unlikely.

In contrast to the olefin addition reactions, the reaction of $FOClO_3$ with CF_3I was more difficult to control. The primary reaction path appears to have involved oxidation of the iodine followed by degradation to oxygenated and fluorinated species. Nevertheless, a modest yield (8%) of the desired perchlorate, CF_3OClO_3, was realized. By comparison, the $ClOClO_3$-CF_3I reaction is also vigorous, but can be controlled to give a nearly quantitative yield of CF_3OClO_3.[8]

In summary, it has been shown that $FOClO_3$ can add to carbon-carbon double bonds to produce alkyl perchlorates in good yield. The formation of two isomers in the reaction of $FOClO_3$ with the unsymmetrical olefin $CF_3CF{=}CF_2$ indicates that the O-F bond in $FOClO_3$ is of low polarity and does not justify the assumption of significant postive character for fluorine. Since a CF_3O- group is considerably less electronegative than a O_3ClO-group the above results imply that, contrary to general acceptance, covalent hypofluorites, such as CF_3OF, do not contain a positive fluorine. Indeed, it would be most difficult to rationalize how the addition of fluorine to a less electronegative element, such as carbon, would render the latter more electronegative than fluorine itself.

Acknowledgement

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Contribution from Rocketdyne, A Division of Rockwell International,
Canoga Park, California

Novel Onium Salts, Synthesis and Characterization of the Peroxonium Cation, H_2OOH^+

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E. C. Curtis

Received......

Abstract

The synthesis and properties of $H_3O_2^+Sb_2F_{11}^-$, $H_3O_2^+SbF_6^-$, and $H_3O_2^+AsF_6^-$, the first known examples of peroxonium salts, are reported. These salts were prepared by protonation of H_2O_2 in anhydrous HF solutions of the corresponding Lewis acids. They were isolated as meta-stable solids which underwent decomposition to the corresponding H_3O^+ salts and O_2 in the temperature range 20-50°C. The $H_3O_2^+$ salts were characterized by vibrational and NMR spectroscopy. Modified valence force fields were computed for the isoelectronic series H_2OOH^+, H_2NOH and H_2NNH^-. The similarity of their observed spectra and computed force fields suggests that the ions are isostructural with H_2NOH which possesses C_s symmetry with the unique hydrogen being *trans* to the other two hydrogens. The influence of protonation on the stretching frequency of the two central atoms is discussed for the series HOO^-, HOOH, H_2OOH^+, H_2NNH^-, H_2NNH_2, $H_3NNH_2^+$, $H_3NNH_3^{2+}$. Attempts to protonate both oxygen atoms in H_2O_2 to form $H_4O_2^{2+}(SbF_6^-)_2$ resulted in $H_3O_2^+Sb_2F_{11}^-$ as the only product. The strongly oxidizing Lewis acid BiF_5 underwent a redox reaction with H_2O_2 in HF, resulting in quantitative reduction of BiF_5 to BiF_3, accompanied by O_2 evolution. When a 2:1 excess of BiF_5 was used, an adduct formed having the approximate composition $BiF_3\cdot BiF_5$. Heating a mixture of solid $H_3O_2^+Sb_2F_{11}^-$ with a strongly fluorinating agent, such as BiF_5 or Cs_2NiF_6, resulted in a green chemiluminescence band centered at 5150 Å.

Introduction

Anhydrous HF-Lewis acid solutions are ideally suited to protonate less acidic substrates. This technique has successfully been applied to the isolation of novel salts containing the H_3O^+,[1-4] H_3S^+,[5,6] $NH_2F_2^+$,[7] and AsH_4^+ [6] cations. Since all these cations contain a single central atom, it appeared interesting to extend this method to a substrate containing two central atoms, such as H_2O_2. In such a case, both single and double protonation are possible, and the influence of protonation on the strength of the bond between the two central atoms can be studied. Such effects are well known[8] for the related hydrazine molecule. Although the HO_2^- anion is known,[9,10] to our knowledge the corresponding cations derived from H_2O_2 have only be postulated,[11] but not been characterized or isolated as salts.

Further interest was added to this study by the fact that H_2O_2 is a starting material for the generation of excited molecular oxygen which in turn is of great interest for a near resonant energy transfer iodine laser. Therefore, the combination of an $H_3O_2^+$ cation with a strongly oxidizing anion in the form of a stable salt could provide a suitable solid-propellant gas generator for excited oxygen.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in well passivated (with ClF_3 and HF) vacuum lines constructed either from Monel Teflon-FEP or entirely from Teflon PFA using injection molded fittings and valves (Fluoroware Inc.). Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Hydrogen fluoride was dried by treatment with F_2, followed by storage over BiF_5 to remove last traces of H_2O.[3] Antimony pentafluoride and AsF_5 (Ozark Mahoning Co.) were purified by distillation and fractional condensation, respectively. Bismuth pentafluoride (Ozark Mahoning Co.) was used as received. Hydrogen peroxide (90%, FMC Corporation) was purified by repeated fractional crystallization[12] and material of 99.95% purity, as analyzed by titration with $KMnO_4$ solution, was obtainable by this method. All equipment, used for handling H_2O_2, was washed with 12 n H_2SO_4, thoroughly rinsed with distilled H_2O and dried in an oven prior to use. The synthesis of Cs_2NiF_6 has previously been described.[13]

Infrared spectra were recorded in the range 4000-200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of dry powders at room temperature were obtained using pressed (Wilks minipellet press) disks between AgCl windows. Low-temperature spectra were obtained as dry powders between CsI plates using a technique similar to one previously reported.[14]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[15] for the elimination of plasma lines. Sealed quartz or Teflon-FEP tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded using a previously described[16] device. Polarization measurements were carried out according to method VIII listed by Claassen et al.[15]

Debye-Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries (~0.5-mm o.d.).

The ^{19}F and ^{1}H NMR spectra were recorded at 84.. and 90 MHz, respectively, on a Varian Model EM 390 spectrometer equipped with a variable-temperature probe.. Chemical shifts were determined relative to external $CFCl_3$ and TMS, respectively.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used for the determination of the thermal stability of the compounds. The samples were sealed in aluminum pans, and heating rates of 2.5 and 10°/min. were used.

For the chemiluminescence experiments, $H_3O_2Sb_2F_{11}$ was mixed with either solid BiF_5 or Cs_2NiF_6 and placed into the bottom of a Pyrex glass tube which was equipped with a stopcock. The tube was connected to a vacuum manifold and heated in a dynamic vacuum by a stream of hot air until gas evolution and chemiluminescence was observed. The emitted light was analyzed with a 0.5 m McKee-Pederson monochromator over the range 2000-10000 Å using a spectral slit width of 25 Å.

<u>Preparation of $H_3O_2^+AsF_6^-$.</u> In a typical experiment, AsF_5 (15.39 mmol) and anhydrous HF (50.76 mmol) were combined at -196° in a passivated Teflon FEP ampoule equipped with a valve. The mixture was allowed to melt and homogenize. The ampoule was then taken to the dry box and H_2O_2 of 99.95% purity (15.29 mmol) was syringed in at -196°. The ampoule was transferred back to the vacuum line and evacuated at -196°, it was then kept at -78° for 2 days to allow reaction.

After this period, no evidence was found for material noncondensible at -196°, i.e. no O_2 evolution. The mixture was warmed to -45° and a clear solution resulted. Material volatile at -45° was removed by pumping for 10 hr and was collected at -196°. A white solid residue resulted which was of marginal stability at ambient temperature. Based on the observed material balance (weight of 15.29 mmol $H_3O_2AsF_6$: calcd, 3.423g; found 3.47g), the conversion of H_2O_2 to $H_3O_2AsF_6$ was complete within experimental error. The compound was shown by infrared and Raman spectroscopy to contain the $H_3O_2^+$ cation and AsF_6^- anion.[1,7, 17-20]

Thermal Decomposition of $H_3O_2^+AsF_6^-$. A sample of $H_3O_2AsF_6$ (28.93 mmol) was allowed to decompose at ambient temperature. An exothermic reaction occurred generating 14.6 mmol of O_2 and a white solid residue which was identified by vibrational spectroscopy as $H_3O^+AsF_6^-$.[1]

Preparation of $H_3O_2^+SbF_6^-$. Antimony pentafluoride (27.96 mmol) was added in the dry box to a passivated Teflon FEP U-tube equipped with two valves and a Teflon coated magnetic stirring bar. Anhydrous HF (522.9 mmol) was added on the vacuum line at -196°, and the mixture was homogenized by stirring at 20°. In the dry box hydrogen peroxide (27.97 mmol) was syringed into the U-tube at -196°. The cold tube was transferred back to the vacuum line and was evacuated. The tube was warmed from -196° to -78° for one hour with agitation which resulted in the formation of a finely divided white solid, suspended in the liquid HF. When the mixture was warmed to 20°, the white solid completely dissolved. No gas evolution was observed during the entire warm-up operation, and no noncondensible material could be detected when the mixture was cooled again to -196°. The HF solvent was pumped off at -22° for three hours resulting in 7.566g of a white solid (weight calcd for 27.96 mmol of $H_3O_2SbF_6$ 7.570g), stable at 20°. The compound was shown by vibrational spectroscopy to be composed of $H_3O_2^+$ cations and SbF_6^- anions.[1,5,7,18,19] Additional support for the composition of the product was obtained by allowing a sample of $H_3O_2SbF_6$ to thermally decompose at about 45°. This decomposition produced O_2 and the known H_3OSbF_6 salt[1] in almost quantitative yield.

Preparation of $H_3O_2Sb_2F_{11}$. The synthesis of this compound was carried out in a manner identical to that described above for the preparation of $H_3O_2SbF_6$, except for using an excess of SbF_5. Thus, the combination of SbF_5 (14.83 mmol), HF (407 mmol), and H_2O_2 (6.83 mmol) produced 3.581g of a white solid (weight calcd for 6.83 mmol of $H_3O_2SbF_6 \cdot 1.17\ SbF_5$ 3.581g), stable up to about 50°. The compound was shown by vibrational and NMR spectroscopy to contain the $H_3O_2^+$ cation and $Sb_2F_{11}^-$ as the principal anion.

The H_2O_2-HF-BiF_5 System.. Bismuth pentafluoride (10.68 mmol), HF (394 mmol), and H_2O_2 (10.15 mmol) were combined in a passivated Teflon ampoule in a manner analogous to that described for the preparation of $H_3O_2SbF_6$. The mixture was warmed from -196° to ambient temperature. During the warm-up operation gas evolution was observed which was accompanied by the formation of a copious white precipitate which showed little solubility in HF at ambient temperature. Bands due to either BiF_6^- [3] or BiF_5 [21,22] (both are strong Raman scatterers) could not be detected in the Raman spectra of either the liquid or the solid phase. The evolved gas was removed from the ampoule at -196° and consisted of 10.1 mmol of O_2. The material volatile at 20° was pumped off, leaving behind 2.897g of a white solid which was identified by vibrational spectroscopy as BiF_3 [3,23] (weight calcd for 10.68 mmol BiF_3 2.841g).

When BiF_5 and H_2O_2 in a mole ratio of 2:1 were combined in a similar manner in anhydrous HF solution, the weight of the resulting white stable solid product closely corresponded to that expected for $BiF_3 \cdot BiF_5$. The product was characterized by vibrational spectroscopy which showed it to be an adduct and not a simple physical mixture of BiF_3 and BiF_5.

Results and Discussion

Synthesis. Based on the observed material balances, H_2O_2 is protonated in HF-MF_5 (M=As, Sb) solutions according to

$$H_2O_2 + HF + MF_5 \longrightarrow H_3O_2^+MF_6^-$$

No evidence was found for double protonation, i.e. $H_4O_2^{2+}$ formation, even when SbF_5 was used in a twofold excess. Instead, the polyanion $Sb_2F_{11}^-$ was formed according to

$$H_2O_2 + HF + 2SbF_5 \longrightarrow H_3O_2^+Sb_2F_{11}^-$$

It is interesting to compare these results with those previously reported[24] for the N_2H_4-HF-TaF_5 system for which double protonation, i.e. $N_2H_6^{2+} (TaF_6^-)_2$ and $N_2H_6^{2+} TaF_7^{2-}$ formation, has been observed. Although other effects, such as the relative solubilities of the possible products, are certainly important, the predominant reason for the exclusive single protonation of H_2C_2 appears to be its increased acidity. Whereas N_2H_4 is a weak base in aqueous solution (pK_b=5.77), H_2O_2 is a weak acid (pK_a=11.6). With increasing protonation, the acidity of the resulting cations further increases and $N_2H_5^+$ (pK_a=6.1) becomes a weak and $N_2H_6^{2+}$ (pK_a=-1) a strong acid.[24,25] Whereas $N_2H_5^+$ has an acidity comparable to that of H_2S(pK_a=7) which is known[5,6] to form stable H_3S^+ salts, $H_3O_2^+$ is too acidic to undergo further protonation to $H_4O_2^{2+}$.

Attempts were unsuccessful to prepare $H_3O_2^+$ salts derived from BiF_5. The latter is a relatively strong oxidizer and is readily reduced by H_2O_2 in HF solution according to

$$BiF_5 + H_2O_2 \longrightarrow BiF_3 + 2HF + O_2$$

When a twofold excess of BiF_5 was used, the following reaction was observed

$$2BiF_5 + H_2O_2 \longrightarrow BiF_3 \cdot BiF_5 + 2HF \pm O_2$$

The resulting $BiF_3 \cdot BiF_5$ product was shown by vibrational spectroscopy (Ra: 591(10), 583 (4.6), 538 (1.5), 521 (0.1), 496 (0.6), 475 sh, 232 (0.5)br, 120 (0.2) br; IR: 708w, 615 s, 606 sh, 575 s, 550 sh, 535 vs, 400-500 m vbr) not to be a physical mixture of BiF_3[3,23] and BiF_5.[21,22] By analogy with the known BiF_3-SbF_5 and SbF_3-SbF_5 systems,[26-28] a $BiF_3 \cdot BiF_5$ type adduct appears most plausible. However, in view of the complexity of the products formed in the SbF_3-SbF_5 system,[27,28] a detailed characterization of this $BiF_3 \cdot BiF_5$ adduct was beyond the scope of this study.

Properties. The $H_3O_2^+SbF_6^-$, $H_3O_2^+Sb_2F_{11}^-$, and $H_3O_2^+AsF_6^-$ salts are white crystalline solids. X-ray powder patterns were taken for $H_3O_2^+Sb_2F_{11}^-$, but contained too many lines to allow indexing. All these $H_3O_2^+$ salts are of marginal thermal stability and were shown to undergo exothermic decomposition to the well known[1] H_3O^+ salts according to

$$H_3O_2^+MF_6^- \longrightarrow H_3O^+MF_6^- + 1/2\ O_2$$

Of the above $H_3O_2^+$ salts, the AsF_6^- salt is the least stable and easily decomposes at room temperature. The $H_3O_2Sb_2F_{11}$ salt was found to be most stable. Based on DSC data, its decomposition starts with a small endotherm at 51°, followed by a large exotherm. In a sealed melting point capillary, decomposition accompanied by foaming was observed at about 65°. The thermal stability of $H_3O_2SbF_6$ is intermediate between those of $H_3O_2AsF_6$ and $H_3O_2Sb_2F_{11}$. It should be pointed out that the thermal stability of these $H_3O_2^+$ salts appears to decrease in the presence of free H_2O_2. Probably, the highly acidic $H_3O_2^+$ salt catalyses the exothermic decomposition of H_2O_2, with the evolved heat promoting the decomposition of the $H_3O_2^+$ salt itself.

The reaction of $H_3O_2^+$ salts with fluorinating agents appeared interesting as a potential method for the generation of excited molecular oxygen (O_2*). Antimony pentafluoride or SbF_6^- were not strong enough oxidizers to fluorinate $H_3O_2^+$, and BiF_6^- reacted at too low a temperature with H_2O_2 to permit isolation of the desired $H_3O_2BiF_6$ salt. Therefore, the concept could not be directly tested to produce O_2^* by the simple thermal decomposition of a salt composed of $H_3O_2^+$ and an oxidizing anion. However, when solid $H_3O_2Sb_2F_{11}$ was mixed at room temperature with a solid oxidizer, such as BiF_5 or Cs_2NiF_6, and when this mixture was heated to about 80°, a reaction occurred which was accompanied by green (5150 Å) chemiluminsescence. This 5150 Å band did not exhibit detectable fine structure, and no additional bands were observed over the range 2000-10000 Å. Consequently, the 5150 Å emission is not attributed to either vibrationally excited HF or O_2^*.

<u>Nuclear Magnetic Resonance Spectra</u>. The ^{19}F nmr spectrum of $H_3O_2SbF_6\cdot 1.17\ SbF_5$ was recorded for a SO_2 solution at -90°. It showed resonances (ϕ91, multiplet; 111, doublet of doublets; 133, quintet) characteristic[29] for $Sb_2F_{11}^-$. In addition, a weaker doublet at ϕ 102 was observed which is characteristic[29,30] for $SbF_5\cdot SO_2$. The quintet part of this species could not be directly observed since it exhibits a chemical shift similar to that of the quintet of $Sb_2F_{11}^-$. The observation of some $SbF_5\cdot SO_2$ is in excellent agreement with a previous report[29] that the highest polyanion observed for $SbF_6^-\cdot nSbF_5$ in SO_2 solution is $Sb_2F_{11}^-$.

with any remaining SbF_5 being converted to $SbF_5 \cdot SO_2$. In addition to the signals due to $Sb_2F_{11}^-$ and $SbF_5 \cdot SO_2$ a weak unresolved signal was observed at ϕ 106, in agreement with previous observations[29] on the t-BuF·3.8 SbF_5 system. This signal is tentatively assigned to some $SbF_5 \cdot H_2O$ or $SbF_5 \cdot H_2O \cdot SbF_5$ type species.[31]

Attempts were unsuccessful to observe the characteristic SbF_6^- signal in the ^{19}F NMR spectra of $H_3O_2SbF_6$ in different solvents. In SO_2ClF the compound was insoluble. In either HF or HF acidified with AsF_5 only a single peak was observed due to rapid exchange between all fluorine containing species. In SO_2 at -85°, only two unresolved signals were observed at ϕ 107 and 127 with an area ratio of 4:1 indicating the possible presence of some $(SbF_5)_n \cdot H_2O$ type species.[31] The failure to observe SbF_6^- for $H_3O_2SbF_6$ in SO_2 parallels the previous report [29] by Bacon and coworkers who found that, unlike $CsSb_2F_{11}$, the $CsSbF_6$ salt is rather insoluble in SO_2 and $Sb_2F_{11}^-$ is the only observable anion in this solvent.

The ^1H NMR spectrum of $H_3O_2Sb_2F_{11}$ in CH_3SOCH_3 solution showed a single broad asymmetric peak. Its line width and chemical shift were temperature dependent. At 20° its line width at half height was 81 Hz and δ was 11.80 relative to external TMS with a shoulder on the upfield side. At 0° the line narrowed to 36 Hz and broadened again at -60° to 72 Hz. With decreasing temperature the line became more symmetric and shifted downfield (δ 12.20 at -60°). The failure to observe two different types of protons and the variation of the observed line widths indicate rapid proton exchange for $H_3O_2^+$. The assignment of the observed signal to $H_3O_2^+$ is supported by its large downfield shift. For comparison, 99% pure H_2O_2 exhibits between 20 and -30° a chemical shift of δ 10.3 relative to external TMS. On protonation, this signal is expected to be shifted further downfield, as has previously been demonstrated[32] for numerous other species. The signal assigned to $H_3O_2^+$ also occurs significantly downfield from those previously reported for H_3O^+ [1,32,33] and $SbF_5 \cdot H_2O$ [31] and therefore cannot be due mainly to these species.

In $HF\text{-}AsF_5$ solution at -80°, only a single broad signal at δ 11.06 was observed for $H_3O_2Sb_2F_{11}$ indicating rapid proton exchange between $H_3O_2^+$ and the HF solvent. In SO_2 solutions of $H_3O_2Sb_2F_{11}$, two lines at δ 9.94 and 11.84, respectively, were observed at -80°. The relative intensity of the δ 9.94 signal varied from sample to sample and also as a function of temperature.

With decreasing temperature the peak area of the δ 9.94 signal decreased more rapidly than that of the δ 11.84 signal. These observations suggest that the two signals cannot belong to the same species. By comparison with previous reports,[1,32,33] the δ9.94 signal is assigned to H_3O^+ and the more intense δ11.84 signal is attributed to $H_3O_2^+$, in good agreement with our observations for the CH_3SOCH_3 solution. The line width of the δ11.84 signal was temperature dependent and showed a minimum (~7Hz) at about -60°, but no splittings could be observed. With increasing temperature, the δ 9.94 and 11.84 signals moved closer together indicating the onset of chemical exchange between the two species.

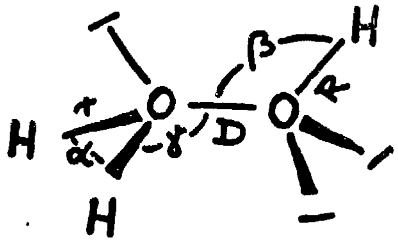
The observations of H_3O^+ in the proton spectrum and possibly of a small amount of an $(SbF_5)_n{\cdot}H_2O$ adduct in the fluorine spectrum suggest that $H_3O_2Sb_2F_{11}$ may undergo either a redox reaction or decomposition in SO_2 solution.

Vibrational Spectra. The infrared and Raman spectra of $H_3O_2AsF_6$, $H_3O_2SbF_6$, and $H_3O_2Sb_2F_{11}$ are shown in Figures 1, 2, and 3, respectively, and the observed frequencies are summarized in Table I. For the thermally more stable antimonate salts, spectra could be obtained at ambient temperature without the samples undergoing significant decomposition to the corresponding H_3O^+ salts. For $H_3O_2AsF_6$ only low-temperature spectra could be obtained.

The vibrational spectra of $H_3O_2SbF_6$ (see Figure 2) showed a pronounced temperature dependence. At room temperature, the Raman spectrum (traces C and E) exhibited three bands at 667, 555, and 282 cm^{-1}, respectively, characteristic for octahedral SbF_6^-.[1,5,7,18,19] When the sample temperature was lowered, the number of bands due to SbF_6^- significantly increased, indicating that the symmetry of SbF_6^- became lower than O_h. This transition was found to be reversible and to occur close to room temperature. Similar transitions have previously been observed for the corresponding H_3O^+[1], D_3O^+[34], and O_2^+[35] salts. They can be attributed to rapid motions of the ions in the crystal lattice at room temperature causing rotational averaging. With decreasing temperature, these motions are frozen out, causing the observed effects of symmetry lowering of the anions. Since the symmetry of the corresponding cations is low (no degeneracies), their vibrational spectra are much less affected.

Assignments for the $H_3O_2^+$ Cation. The assignments for $H_3O_2^+$ were made based on the following arguments. With the exception of the O-O torsional mode, which by comparison with the known frequency[36] of the corresponding N-O torsion in the isoelectronic H_2NOH molecule is expected to occur below 400 cm^{-1}, all of the fundamental vibrations of $H_3O_2^+$ should have frequencies higher than those of the anions. The bands due to the anions can be further identified by comparison with the ambient and low-temperature spectra previously reported for the corresponding H_3O^+[1] and $NH_2F_2^+$[7] salts. In view of the complexity of the low-temperature anion spectra, in Table I only the room temperature Raman spectrum of rotationally averaged SbF_6^- has been assigned. Keeping in mind that $Sb_2F_{11}^-$ spectra strongly depend on the nature of the counter cation, the room temperature spectrum of $Sb_2F_{11}^-$ in $H_3O_2Sb_2F_{11}$ is in fair agreement with those previously observed for this anion in numerous other salts.[37-41]

Thus, the intense bands occurring above 800 cm^{-1} should belong to $H_3O_2^+$. By comparison with the known trans structure of isoelectronic H_2NOH,[42] this cation should have the following structure of symmetry C_s



Consequently, 9 fundamentals (6 A' + 3 A") are expected for $H_3O_2^+$. These fundamentals should all be active in both the infrared and the Raman spectra. Of these, 8 should occur above 800 cm^{-1} (see above). As can be seen from Figures 1-3 and Table I, indeed 8 bands were observed in this frequency region. An approximate description of the $H_3O_2^+$ fundamental vibrations is given in Table II. There should be four stretching modes. Three of these should involve hydrogen ligands, while the fourth one is the oxygen-oxygen stretching mode.

The three hydrogen-oxygen stretching modes should occur above 2500 cm^{-1}. Their assignment, however, is somewhat complicated. By comparison with the known spectra of related molecules, such as CH_3NH_2,[43] H_2NOH,[36,44] H_2O, CH_3OH, and $\rangle CH_2$ group containing molecules,[45] we would expect the H_2O- group to exhibit 2 intense infrared bands in the OH stretching region. Of these two, the antisymmetric stretching mode should have a frequency 50-100 cm^{-1} higher than that of the symmetric stretching mode. In the Raman spectrum the symmetric stretching mode should be much more intense than the antisymmetric one. The unique -OH stretching mode should be of considerably lower infrared intensity than the two $-OH_2$ stretching modes.

Inspection of the Raman spectrum of $H_3O_2AsF_6$ shows a very narrow Raman line at 3440 cm^{-1} and a barely detectable broad line at 3230 cm^{-1}. Since the 3440 cm^{-1} Raman line shows only a rather weak infrared counterpart while the 3230 cm^{-1} one exhibits a very intense infrared counterpart and since no intense infrared band occurs above 3440 cm^{-1}, the 3440 cm^{-1} band is assigned to the unique -OH stretch and the 3230 cm^{-1} band to the symmetric $-OH_2$stretch of H_2OOH^+. The 3228 cm^{-1} infrared band exhibits a shoulder on both its high and its low frequency side. Instead of assigning these two shoulders to two separate bands, they might equally well be attributed to a single broad band onto which the sharper 3228 cm^{-1} band is superimposed. Such a broad band might be expected for the antisymmetric $-OH_2$ stretching mode, and its center (3275 cm^{-1}) results in a frequency value which agrees well with the above predicted frequency difference between the symmetric and the antisymmetric $-OH_2$ stretching mode. In the spectrum of $H_3O_2SbF_6$ the situation is almost identical. For $H_3O_2Sb_2F_{11}$, the infrared counterpart to the 3435 cm^{-1} Raman band is also rather narrow and occurs at the very edge of the intense and extremely broad infrared band. These observations seem to support our assignments, although it is not obvious why the Raman line for the unique -OH stretch should be so much sharper than that for the symmetric $-OH_2$ stretch. If the -OH stretch and the symmetric $-OH_2$ stretch would have comparable Raman line widths, the latter should have a greater peak height than the -OH stretch and should be easily observed.

Whereas the modes involving mainly O-H bonds should be of low Raman and of high infrared intensity, the O-O stretching mode should be quite intense in the Raman spectrum and occur in the frequency range 800-1000 cm^{-1}. It is therefore assigned to the strong Raman line occurring in all samples between 868 and 880 cm^{-1}. As expected, this band shows a counterpart of medium intensity in the infrared spectra. In the spectra of $H_3O_2SbF_6 \cdot 1.17 SbF_5$ ("$H_3O_2Sb_2F_{11}$") this band shows a splitting into two components, separted by about 10 cm^{-1}. This splitting might be due to the sample not having an exact 1:2 stoichiometry and therefore containing a mixture of different polyantimonates. For the two well defined 1:1 adducts $H_3O_2AsF_6$ and $H_3O_2SbF_6$, no splittings of this band could be detected.

Of the five deformation modes expected for $H_3O_2^+$ of symmetry C_s, four involve the O-H bonds and should occur in the frequency range 1000-1700 cm^{-1}. Indeed, four infrared bands were observed in this frequency range for $H_3O_2Sb_2F_{11}$ with counterparts in the Raman spectrum. Their assignment to the individual modes (see Table II) was made by analogy to those known[45] for related molecules, such as H_2O, CH_3OH, CH_3NH_2, and CH_2X_2.

The $-OH_2$ scissoring mode should have the highest frequency and occur between 1500 and 1600 cm^{-1}. It is therefore assigned to the band observed in most spectra at about 1535 cm^{-1}. The $-XH_2$ in-plane deformation mode is usually very intense in the infrared spectrum and occurs for H_2NOCH_3 [36] and H_2NOH [36,44] at 1150 and 1115 cm^{-1}, respectively. For H_2OOH^+ it is therefore assigned to the strong infrared band at about 1130 cm^{-1}. The $-XH_2$ twisting mode is usually very weak and occurs in H_2NNH_2, H_2NOH [36], and H_2NNH^- [46] at 1260, 1297, and 1232 cm^{-1}, respectively. It is therefore assigned to the medium weak band observed for $H_3O_2Sb_2F_{11}$ at 1228 cm^{-1}. There is only one frequency (∿1420 cm^{-1}) left for assignment to the -OOH in-plane deformation mode. This assignment is in fair agreement with the value of 1345 cm^{-1} attributed to the corresponding -COH deformation in CH_3OH.[45]

The fifth deformation mode, the O-O torsion, is expected to occur in the 300-400 cm^{-1} frequency region. Since numerous bands due to either the anion or anion-cation interactions occur in this region, no assignments are proposed at this time for this mode.

In summary, with the exception of the O-O torsional mode, all fundamentals of H_2OOH^+ have been observed and assigned. The assignments are summarized in Table III and are compared to those of isoelectronic H_2NOH [36,44] and H_2NNH^- [46]. The similarity of the vibrational spectra of H_2OOH^+, H_2NOH, and H_2NNH^- suggests that the two ions are isostructural with NH_2OH for which a trans structure of symmetry C_s was established[42] by microwave spectroscopy and confirmed [47] by ab initio molecular orbital theory. As expected for salts containing cations with hydrogen ligands and anions with fluorine ligands, strong cation-anion interactions were observed. These result in a lowering of the oxygen-hydrogen stretching frequencies and cause splittings of the anion bands in the spectra at low-temperature at which rotational averaging processes are frozen out.

Normal Coordinate Analyses. Normal coordinate analyses were carried out for H_2OOH^+ and the isoelectronic H_2NOH molecule and H_2NNH^- anion to support the above assignments and the contention that the three isoelectronic species are isostructural. Furthermore, it was important to establish whether the fundamental vibration assigned to the stretching mode of the two central atoms is highly characteristic and therefore can be taken as a direct measure for their bond strength.

For the computation of the force fields the vibrational frequencies and assignments of Table II were used. The required potential and kinetic energy metrics were computed by a machine method[48] using the geometries given in Table III. Since the frequency of the x-y torsion mode, $\nu_9(A'')$ is unknown for both H_2OOH^+ and H_2NNH^- and since, based on its expected low frequency, coupling with other modes should be negligible, this fundamental was omitted from the normal coordinate analyses. For H_2OOH^+ and H_2NNH^-, the bond angles were assumed to be identical to those known [42] for H_2NOH, and the bond lengths were estimated by comparison with those known for the similar H_2O_2 and N_2H_4 molecules. The bending coordinates were weighted by unit (1Å) distance.

The force constants of these H_2XYH type species were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. Since in the A' block the X-Y stretching force constant

F_{66} was found to strongly depend on the values of the stretch-bend interaction constants F_{46} and F_{56}, the diagonal symmetry force constants were computed as a function of F_{46} and F_{56}. As can be seen from Figures 4 and 5, the values of YH (F_{11}) and XH_2 (F_{22}) stretching force constants are unaffected by the choice of F_{46} and F_{56}, but the X-Y stretch (F_{66}) depends strongly on the choice of F_{46} and F_{56}. In the absence of additional experimental data, such as oxygen isotopic shifts, the uncertainty in the value of F_{66} obtained by underdetermined force fields, must therefore be considered to be substantial. In the absence of such additional data, we have chosen for the isoelectronic H_2XYH series a force field which resulted in a highly characteristic potential energy distribution (PED) for all fundamentals (see Table IV). The XY stretching force constants obtained in such a manner represent minimal values, but could be higher by as much as 0.4 mdyn/Å if larger positive values are assumed for F_{46} and F_{56}. A moderate size value was found necessary for F_{35} to obtain a characteristic PED for ν_3 and ν_5.

In a recent paper, Botschwina and coworkers have reported[49] a partial ab initio harmonic force field for H_2NOH. Since this type of computation can yield valuable information about the off-diagonal force constants, a comparison with the results of Table IV appeared interesting. Botschwina et al. report a value of 0.629 mdyn/rad for F_{46} (using the force constant designation of Table IV of our work) and predict values of 8.1 ± 0.1 mdyn/Å and 0.9 ± 0.05 mdyn Å/rad^2 for F_{11} and F_{33}, respectively. The latter two values and the positive sign of F_{46} are in fair agreement with the anharmonic force field of Table IV, although the value computed[49] for F_{46} appears to be high. A calculation of a force field with $F_{46}=0.63$ and $F_{56}=0$ resulted in ν_5 and ν_6 in becoming almost equal mixtures of F_{55} and F_{66} and an unacceptably high value of about 5 mdyn/Å for F_{66}. Assuming a positive value for F_{56} resulted in even less acceptable force constants.

A comparison of the results of Table IV shows that the force fields of isoelectronic H_2OOH^+, H_2NOH, and H_2NNH^- are indeed very similar and suggests that all members of this series are isostructural. The small deviations observed within the series (higher values of F_{11}, F_{22} and F_{77} for H_2NOH) can be readily explained. For H_2NOH, gas phase frequencies of the isolated molecule were used, whereas in the H_2OOH^+ and H_2NNH^- salts the anion-cation interactions lower the stretching frequencies somewhat (see above).

The question whether ν_6, the fundamental vibration assigned to the stretching mode of the two central atoms, is highly characteristic or not, also needed to be answered. The fact that ν_6 is of very high Raman intensity, whereas ν_5 is barely observable, and the known high polarizabilities of the central atoms relative to those of the hydrogen ligands, argue strongly in favor of ν_6 being predominatly the O-O stretching mode. Furthermore, the value of the O-O stretching force constant F_{66} (3.93 mdyn/Å) and the highly characteristic nature of ν_6 (101% F_{66}) of H_2OOH^+ are in excellent agreement with the previously reported[50] findings for gaseous HOOH, (F_{O-O}= 3.776 mdyn/Å, ν_{O-O} = 105% F_{O-O}). For solid HOOH a value (F_{O-O} = 3.999 mdyn/Å) was found [51] which is slightly higher than that in H_2OOH^+. A further argument in favor of highly characteristic X-Y stretching frequencies in these and closely related molecules is based on the vibrational spectra observed for deuterated molecules, such as DOOD.[50,51] If the fundamental assigned to the O-O stretch in HOOH would contain strong contributions from X-H bending modes, its frequency should significantly decrease on deuteration.

In summary, it appears justified to assume that the fundamentals, assigned to the stretching modes of the two central atoms in these molecules and ions, are highly characteristic and that a highly characteristic PED might be a good criterion for selecting a plausible force field.

Influence of Progressive Protonation on the Bond Strength of the Two Central Atoms. It seemed interesting to examine how in an H_mXYH_n type species the replacement of a free valence electron pair of a central atom by a hydrogen ligand influences the strength of the X-Y bond. Further interest was added to this problem by the fact that these X-Y bonds are single bonds, thus resulting in hindered rotation and rotational conformers. In the literature,[8,52] the concept has been advanced that in a singly bonded X-Y system the replacement of a free valence electron pair on X or Y by a bonded ligand will diminish the overall ligand or electron pair repulsions, thereby strengthening the X-Y bond. The results of the present study combined with previous literature data offered an excellent opportunity to examine the validity of this simple repulsion concept for the progressively protonated series HOO^-, $HOOH$, H_2OOH^+, which is isoelectronic with H_2NNH^-, followed by H_2NNH_2, $H_2NNH_3^+$, $H_3NNH_3^{2+}$.

For this series the energetically most favored rotational isomers and the stretching frequencies of the two central atoms are summarized in Table V. Stretching frequencies are preferred over force constants because for $HOOH$,[51] H_2OOH^+ and H_2NNH^- these frequencies are highly characteristic and because of the lack of reliable fully determined force fields for most of these species. In Table V, frequency ranges are given for $HOOH$, $H_3NNH_2^+$ and N_2H_4. For the first two, these ranges are caused by the fact that the frequencies vary somewhat for different phases. For N_2H_4, the large given range is mainly due to the uncertainty in the assignment of the N-N stretching mode (see footnote k of Table V). In spite of these limitations, inspection of the listed frequencies reveals that there is a definite X-Y stretching frequency increase with progressive protonation, but also that the increase of the O-O stretching frequency from HOO^- to H_2OOH^+ (30 cm^{-1}) is much smaller than that (201 cm^{-1}) encountered for the H_2NNH^- to $H_3NNH_3^{2+}$ part of the series.

This marked difference is difficult to explain by the simple free valence electron pair repulsion concept[8,52] which should result in a more uniform trend and cannot account for the eclipsed structure of H_2NOH.[42] A better explanation for the observed trends can be given based on the following considerations. (i) The preferred rotational isomers (see Table V) indicate that in an H_mXYH_n type species, in which the X and Y central atoms possess free valence electron pairs, attractive forces exist between a free valence electron pair on one central atom and a hydrogen ligand bonded to the other central atom. In terms of molecular orbital theory, this effect can be considered to be the result of both dipolar attraction and back donation from lone pair orbitals of one central atom into antibonding orbitals of the other.[47] On the other hand, free valence electron pairs on X are repelled by free pairs on Y and the same holds for vicinal hydrogen ligands. These effects explain the eclipsed configuration of H_2NOH,[42] the staggered one of C_2H_6,[53] and the gauche ones of the remaining species. (ii) When going from HOO^- to $H_3NNH_3^{2+}$, the number of repulsions between vicinal ligands (including the free valence electron pairs) decreases from two for HOO^- to zero for H_2OOH^+ and H_2NNH^- and then increases again to three for $H_3NNH_3^{2+}$. (iii) It is known that for peroxides a weakening of the oxygen-ligand bonds results in a strengthening of the O-O bond (FOOF, ν_{OO} = 1257 cm^{-1}; HOOH, ν_{OO} = 864 cm^{-1})[57,12] and vice versa. Furthermore, it is known[8] that the $\overset{\delta-}{X}$—$\overset{\delta+}{H}$ polarity of an X-H bond increases by the addition of a second H^+ to X. This increase in bond polarity upon progressive protonation weakens the X-H bonds and therefore should strengthen the X-X bond. In our opinion, this polarity effect is the major reason for the observed increase of the X-X stretching frequency within this series.

The fact that the stepwise increases within the series of Table V are small to the right of H_2XXH and large to the left of it, suggests that the attractions between a free valence electron pair and a vicinal hydrogen ligand are at a maximum for H_2XXH and counteract the general polarity effect caused by the progressive protonation. This explanation seems plausible because both dipole interaction and back donation should decrease the $\overset{\delta-}{X}$-$\overset{\delta+}{H}$ polarity of the X-H bond by transferring electron density from the free valence electron pair orbital to the vicinal hydrogen ligand. Although this picture is oversimplified and neglects other effects, such as possible changes in hybridization, it can nevertheless qualitatively account for the observed trends within this series. Molecular orbital calculations would be desirable, but were beyond the scope of this study. In view of the great difficulties encountered with FOOF,[58] such calculations might not be trivial.

The above analysis indicates that the replacement of a free valence electron pair on one of the two central atoms by a hydrogen ligand could either decrease <u>or</u> increase the vicinal ligand (or electron pair) repulsion. The direction of the effect depends on whether the two central atoms possess less than three or three and more hydrogen ligands. With less than three hydrogen ligands, a free pair-free pair repulsion is replaced by a free pair-XH bond attraction, whereas with three or more hydrogen ligands an attraction is replaced by a vicinal hydrogen-hydrogen ligand repulsion. The importance of the attractive forces in this type of molecules is in agreement with the results from molecular orbital calculations.[47,59]

The above results suggest that the previously proposed[8,52] simple free valence electron pair repulsion concept applies only to H_mXYH_n species with $\sum m+n < 3$. In these limited cases, replacement of a free valence electron pair by a ligand will result in decreased ligand-ligand repulsion. However this decreased repulsion counteracts the polarity effect and therefore does not strengthen, but actually weakens the bond between the two central atoms. Consequently, the simple free valence electron pair repulsion concept cannot account, even in these limited cases, for the observed increase in the stretching frequency of the two central atoms.

The above results show that for a comparison, such as that given in Table V, a large enough number of molecules and ions must be available to have confidence in the observed trends. Furthermore, the assignments must be well established, the fundamental vibrations used must be highly characteristic, and interionic or intermolecular effects, such as hydrogen bridging in ionic solids or condensed phases, must be less pronounced than the trends to be observed. Finally, force constants should be compared only if their differences are significantly larger than their uncertainties.

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Diagram Captions

Figure 1. Vibrational spectra of $H_3O_2^+AsF_6^-$. Trace A: infrared spectrum of the solid as a dry powder between CsI disks, recorded at -196°. Trace B: Raman spectrum of the solid in a glass tube, recorded at -100° with a spectral slitwidth of 8 cm^{-1} and a sensitivity of 100,000. Inserts C and D were recorded with a spectral slitwidth of 10 cm^{-1} at sensitivities of 380,000 and 250,000, respectively.

Figure 2: Vibrational spectra of $H_3O_2^+SbF_6^-$. Traces A and B: infrared spectra of the solid recorded at -196° at two different sample concentrations. Traces C and E: Raman spectra of the solid, recorded at 25° with spectral slitwidths of 5 and 10^{-1} cm, respectively. Trace D: Raman spectrum of the solid, recorded at -110°.

Figure 3. Vibrational spectra of $H_3O_2^+Sb_2F_{11}^-$. Trace A: infrared spectrum of the solid as a dry powder between pressed AgCl disks. Traces B, C, and D: Raman spectra of the solid, recorded at 25° with spectral slit widths of 5, 10, and 2.5 cm^{-1}, respectively.

Figure 4. Diagonal symmetry force constants (stretching constants, F_{11}, F_{22} and F_{66} in mdyn/Å and deformation constants F_{33}, F_{44}, and F_{55} in mdyn Å/rad^2) of the A' block of H_2OOH^+ as a function of the stretch-bend interaction constant F_{46} (in mdyn/rad). All the remaining off-diagonal symmetry force constants were assumed to be zero.

Figure 5. Diagonal symmetry force constants of the A' block of H_2OOH^+ as a function of F_{56}.

Table I . Vibrational Spectra of $H_3O_2AsF_6$, $H_3O_2SbF_6$, and $H_3O_2Sb_2F_{11}$ and Their Assignments

Obsd freq (cm^{-1}) and rel Intens[a]							Assignment (point group)	
$H_3O_2AsF_6$		$H_3O_2SbF_6$			$H_3O_2Sb_2F_{11}$		$HOOH_2^+$ (C_s)	SbF_6^- (O_h)[b]
Ir (-196°)	Ra (-100°)	Ir (-196°)	Ra (-110°)	Ra (25°)	Ir (25°)	Ra (25°)		
				3440 (0+)	3447 s	3435 (0+)	ν_1 (A')	
3440 sh	3440 (6.8)	3440 sh			3000- } vs,		ν_7 (A'')	
3400-3150 vs		3400-3150 vs			2600 } vbr		ν_2 (A')	
3228 vs	3230 (0+)br	3230 vs						
					2178 w			
				1539 (0+)	1531 m	1530 (0+)	ν_3 (A')	
1535 w	1547 (0.4)							
				1426 (0+)	1420 ms	1419 (0+)	ν_4 (A')	
1425 mw	1417 (1)	1421 mw						
		1280 w						
					1228 mw	1227 (0+)	ν_8 (A'')	
				1130 (0+)br	1137 s	1135 (0+)	ν_5 (A')	
1115 m		1126 mw						
1100- } m,vbr		1065 sh						
900 }		965 sh						
		915 w						
						878 (1.5) }		
870 m	873 (10)	876 mw	879 (8.6)	880 (5.4)				
					869 m	868 (3) }	ν_6 (A')	
						771 (0.2)		
			689 (5)		730- }	688 (10)		
728 vs	734 (39)		677 (10)	667 (10)	vs,br	664 (0.5)		$\nu_1(A_{1g})$
	711 (1.5)		642 (7)			649 (5.4)		
665 vs	673 (9.5)	666 vs			640 }			
635 sh		615 s						
585 m		571 ms			594 mw			
	559 (24)		560 (2)					
550 ms		514 m		555 (0.7) br	565 m	576 (0.7)		$\nu_2(E_g)$
	528 (1.4)		530 (0.5)					
470 m		375 mw			508 m			
	400 (0+)		326 (1)			301 (2.5)		
388 vs		309 ms						
	370 (5.0)		283 (5)	282 (4)		280 (1)		$\nu_5(F_{2g})$
348 ms			263 (0.9)					
	316 (1.2)		226 (0.5)	226 (0+)		236 (2)		
	202 (2.5)		200 (1.5)					
	189 sh		174 (3.2)	167 (0+)		167 sh		
	149 sh		126 (2.4)	122 (0+)		144 (0.6)		
	129 (3.2)					112 sh		

---

a) Uncorrected Raman intensities.

b) The assignments given for SbF_6^- are for the room temperature Raman spectrum of $H_3O_2SbF_6$ in which SbF_6^- appears to be octahedral due to rotational averaging. In the low-temperature spectra the symmetry of the MF_6^- anion is much lower than O_h (see text).

Table II. Comparison of the Vibrational Spectrum of $H_3O_2^+$ with Those of Isoelectronic H_2NOH and $H_3N_2^-$

Assignment for H_2XYH in Point group C_s		Approximate Description of Mode	Obsd Frequencies (cm^{-1})		
			H_2OOH^+	H_2NOH[b]	H_2NNH^-[c]
A'	ν_1	$\nu(YH)$	3440	3656	3202
	ν_2	$\nu sym(XH_2)$	3229	3297	3100
	ν_3	$\delta sciss(XH_2)$	1536	1605	1599
	ν_4	$\delta(XYH)$ in plane	1421	1357	1330
	ν_5	$\delta wag(XH_2)$	1136	1115	1103
	ν_6	$\nu(XY)$	875	895	847
A''	ν_7	$\nu asym(XH_2)$	3275	3350	3155
	ν_8	$\tau(XH_2)$	1228	1297	1232
	ν_9	$\tau(XY)$	[386][a]	386	[386][a]

(a) Estimated frequency values.

(b) Data from Ref. 44, but revised according to Ref. 36.

(c) Data from Ref. 46, but with revised assignments for ν_4 and ν_5.

Table III. Geometries[a] Used for the Normal Coordinate Analyses of the Isoelectronic H_2XYH Molecules and Ions

	H_2OOH^+	H_2NOH	H_2NNH^-
r (XH)	0.98	1.016	1.03
R (YH)	0.99	0.962	1.03
D (XY)	1.475	1.453	1.47
α (∢ HXH)	107.06	107.06	107.06
β (∢ XYH)	101.22	101.22	101.22
γ (∢ HXY)	103.15	103.15	103.15

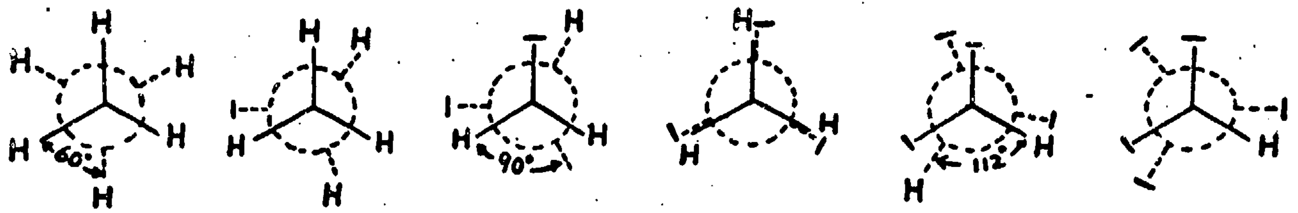
(a) Bond distances in Å and ∢ in °.

Table IV. Anharmonic Symmetry Force Constants[a] and Potential Energy Distribution[b] of H_2OOH^+, H_2NOH, and H_2NNH^-, Computed[c] with the Frequencies and Assignments of Table III

		Symmetry Force Constants			PED			
		H_2OOH^+	H_2NOH	H_2NNH^-		H_2OOH^+	H_2NOH	H_2NNH^-
A'	$F_{11}=f_R$	6.607	7.46	5.675	F_{11}	100	100	100
	$F_{22}=f_r+f_{rr}$	5.92	6.13	5.42	F_{22}	100	100	100
	$F_{33}=f_\alpha$	0.628	0.733	0.748	F_{33}	95	99	99
	$F_{44}=f_\beta$	1.054	0.902	0.977	F_{44}	94	98	98
	$F_{55}=f_\gamma+f_{\gamma\gamma}$	0.715	0.72	0.728	F_{55}	95	97	96
	$F_{66}=f_D$	3.93	3.87	3.15	F_{66}	101	99	103
	$F_{35}=\sqrt{2}\,f_{\alpha\gamma}$	0.1	0.1	0.1				
	$F_{46}=f_{D\beta}$	0.2	0.2	0.2				
	$F_{56}=\sqrt{2}\,f_{D\gamma}$	0.3	0.3	0.3				
A''	$F_{77}=f_r-f_{rr}$	5.884	6.089	5.401	F_{77}	100	100	100
	$F_{88}=f_\gamma-f_{\gamma\gamma}$	0.782	0.922	0.850	F_{88}	100	100	100

(a) Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad^2, and stretch-bend interaction constants in mdyn/rad; (b) Percent contributions. Contributions of less than 9% to the PED are not listed. (c) All interaction constants except for F_{35}, F_{46} and F_{56}, were assumed to be zero.

Table V. Preferred Rotational Number of Vicinal Ligand Repulsions (R) and Attractions (A) and Frequencies (cm^{-1}) of the Stretching Mode of the Two Central Atoms of $H_3NNH_3^{2+}$ [a], $H_3NNH_2^{+}$ [b], H_2NNH_2 [c], H_2NNH^{-} [d], H_2OOH^{+} [d], HOOH, [e] and HOO^{-} [f]



3R	2R-1A	1R-2A	3A	2A-1R	1A-2R
$H_3NNH_3^{2+}$	$H_3NNH_2^{+}$	H_2NNH_2	H_2NNH^{-}		
1048[g]	949[h]-968[i]	850-938[j]	847[k]		
			H_2OOH^{+}	HOOH	HOO^{-}
			875[l]	864-881[m]	836[n]

(a) Geometry of preferred rotational isomer is based on that of isoelectronic C_2H_6, ref. 53.

(b) Geometry assumed to be analogous to that of isoelectronic CH_3NH_2, ref. 54.

(c) Ref. 55.

(d) Geometry is based on that of isoelectronic H_2NOH, ref. 42.

(e) Ref. 56.

(f) For HOO^{-}, a preferred rotational isomer does not exist. The structure is given exclusively for didactic purposes.

(g) From Raman spectrum of $N_2H_6F_2$ in anhydrous HF solution (B. Frlec and H. H. Hyman, Inorg. Chem., 6, 2233 (1967).

(h) From infrared spectrum of solid $(N_2H_5)TaF_7$ (ref. 24).

(i) From Raman spectrum of N_2H_5Cl in aqueous HCl solution (J. T. Edsall, J. Chem., Phys. 5, 225 (1937); see also J. C. Decius and D. P. Pearson, J. Amer. Chem. Soc., 75, 2436 (1953).

(j) The assignments for the N-N stretching mode in N_2H_4 are not well established and significantly differ for the ga and condensed phases (see for example ref. 46 and J. R. Durig, S. F. Bush, and E. E. Mercer, J. Chem. Phys., 44, 4238 (1966). The latter authors assigned the N-N stretch in N_2H_4 to bands in the 1087-1126 cm^{-1} frequency region which does not fit the general trends listed in this table).

(k) From infrared spectrum of solid NaN_2H_3 (ref. 46).

(l) This work

(m) Ref. 12

(n) Ref. 10.

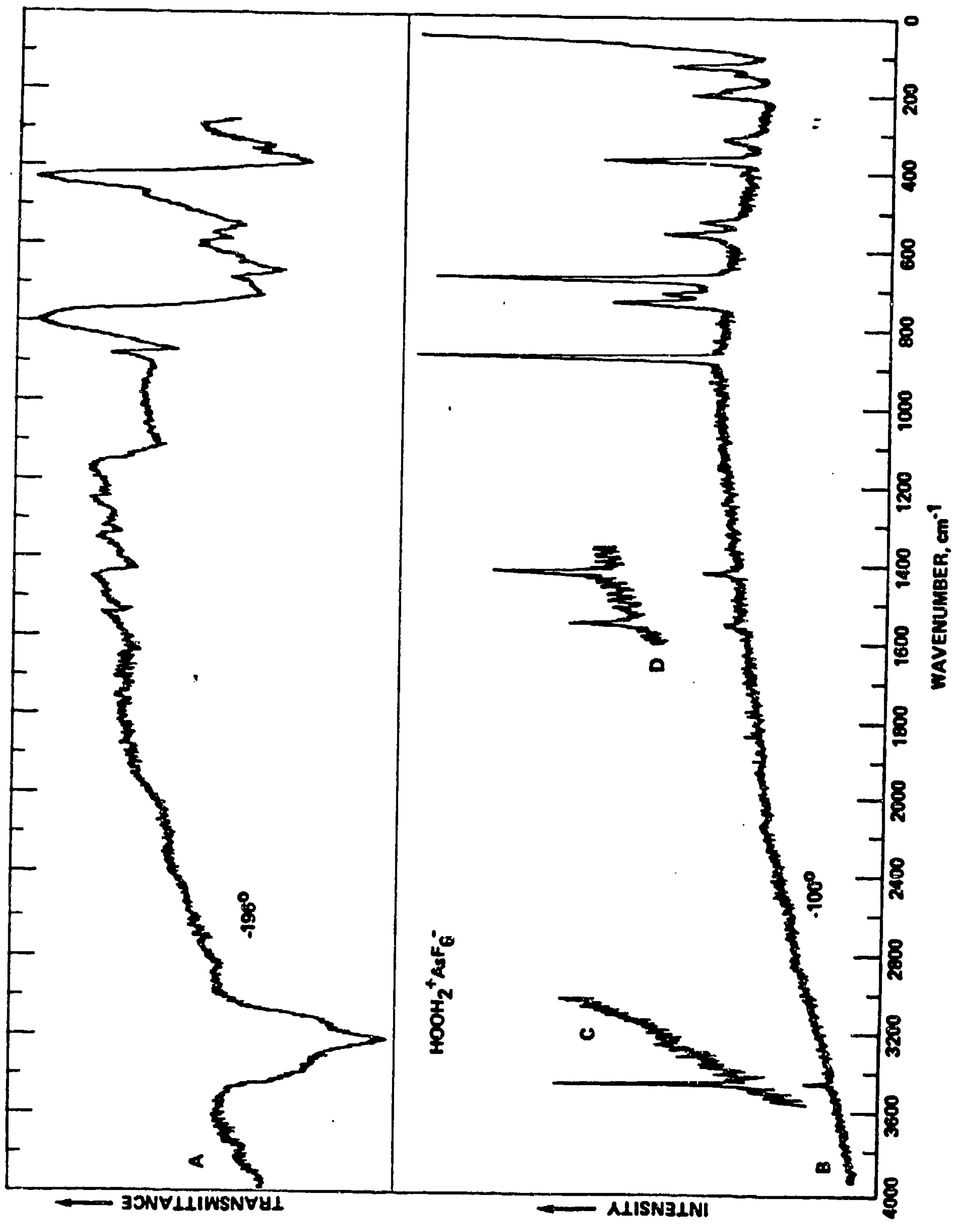
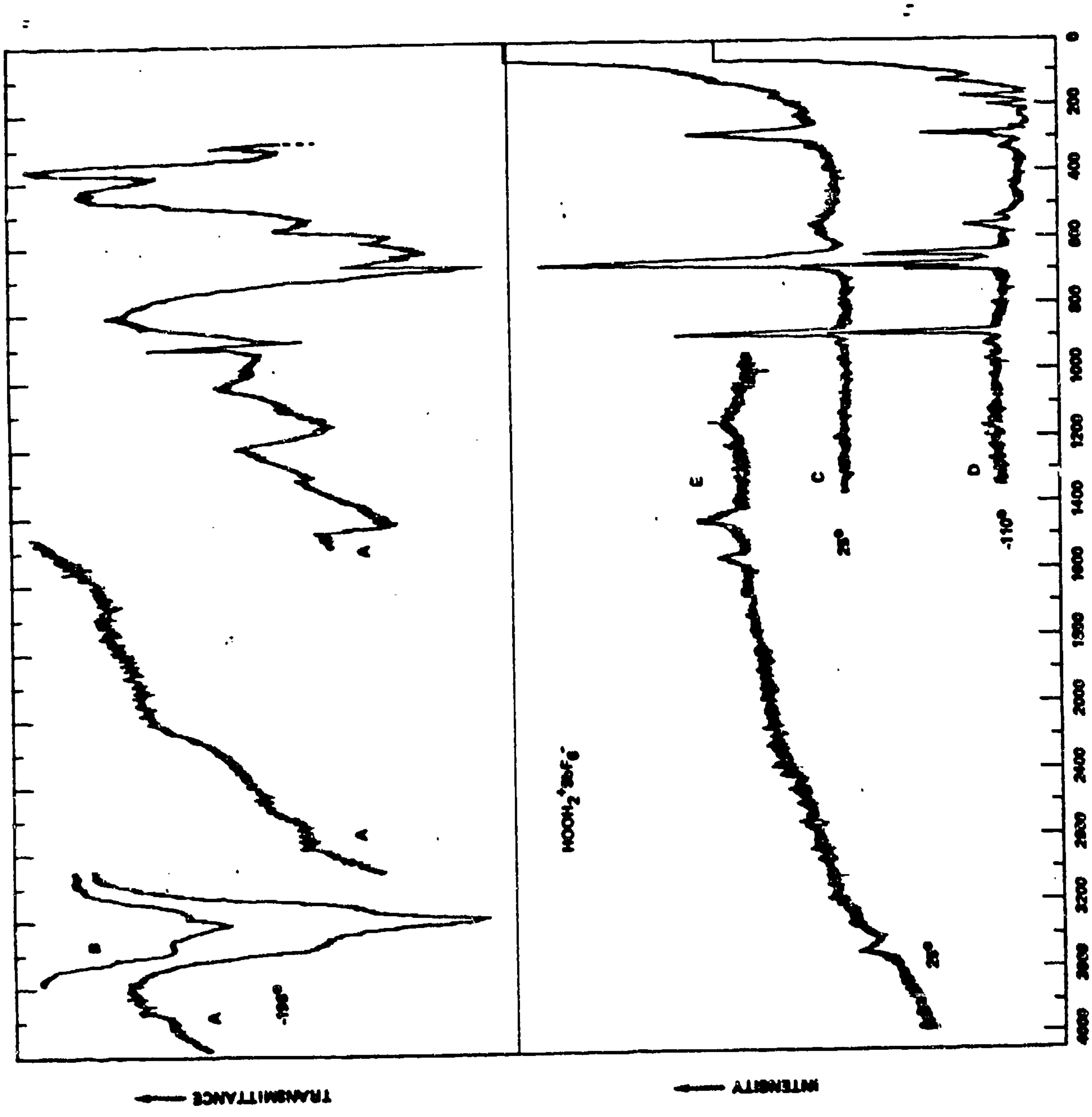

A
-196°
TRANSMITTANCE
HOOH$_2^+$AsF$_6^-$
C
D
B
-100°
INTENSITY
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200
0
WAVENUMBER, cm^{-1}

FIGURE 1



TRANSMITTANCE
INTENSITY
A
B
-196°
A
A
HOOH$_2^+$SbF$_6^-$
E
25°
C
25°
D
-110°
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2400
2800
3200
3600
4000
WAVENUMBER, cm^{-1}

FIGURE 2

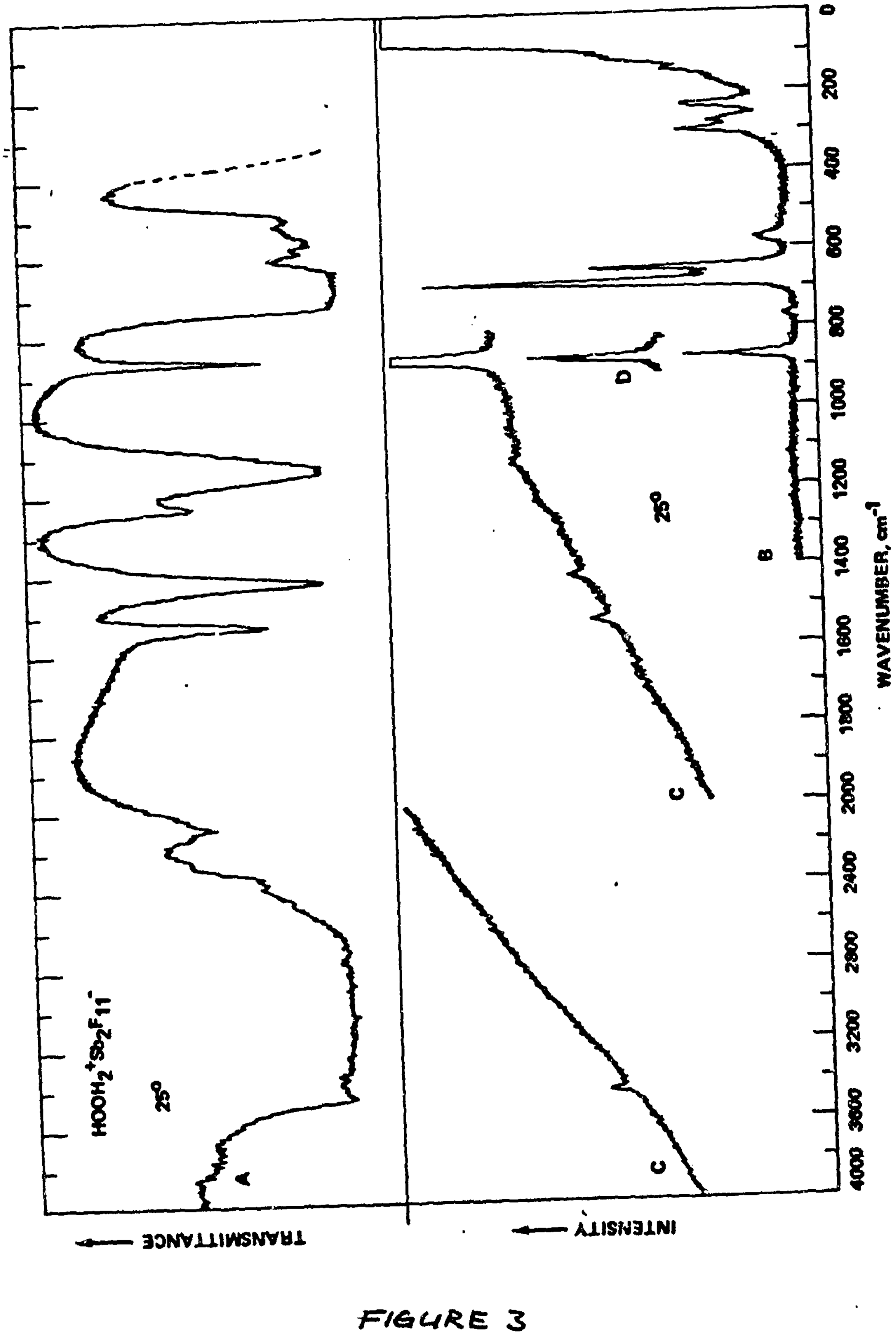

HOOH$_2^+$Sb$_2$F$_{11}^-$
25°
A
C
C
D
B
25°
TRANSMITTANCE
INTENSITY
WAVENUMBER, cm^{-1}
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
200
0

FIGURE 3

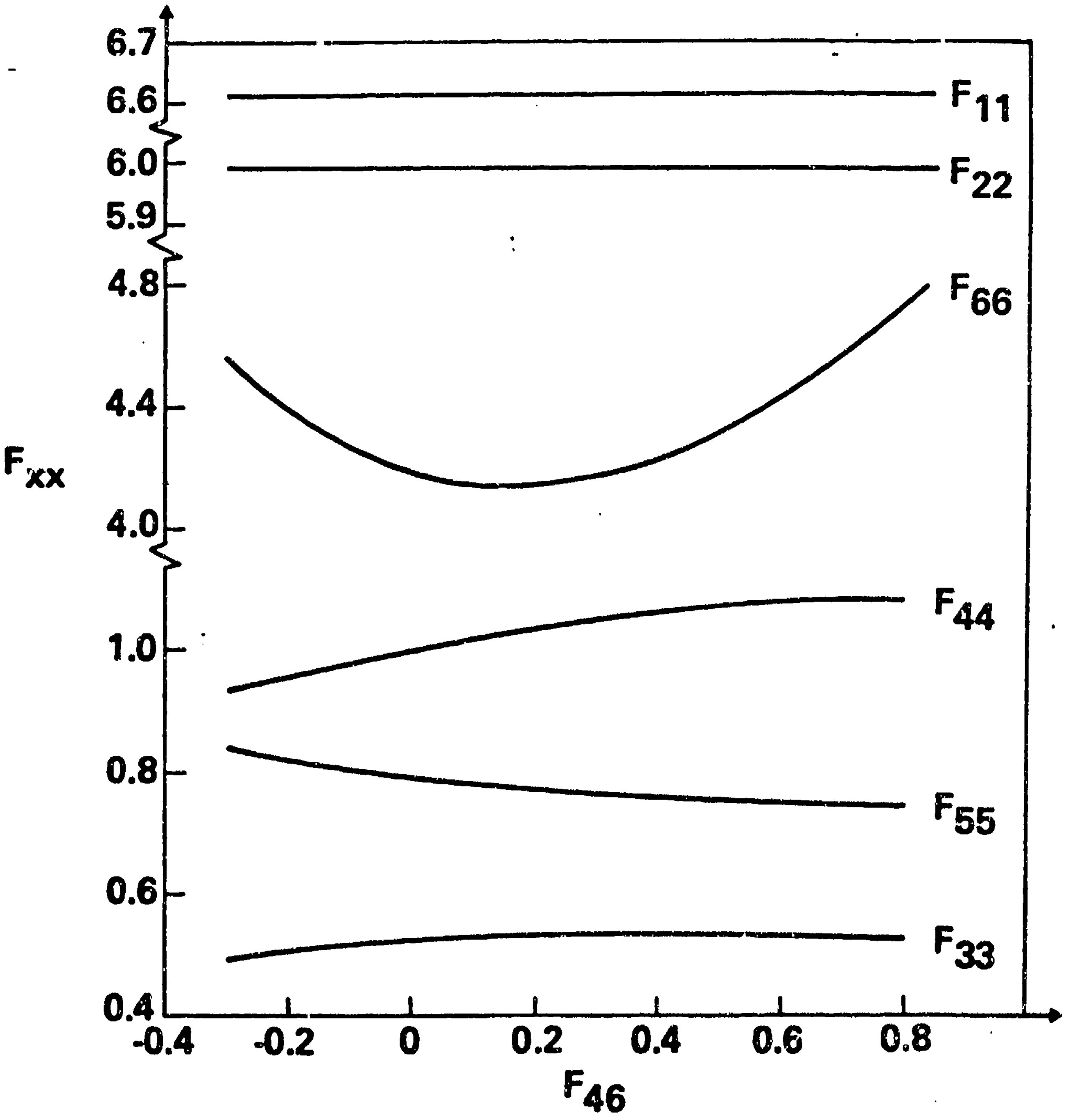

6.7
6.6
6.0
5.9
4.8
4.4
4.0
1.0
0.8
0.6
0.4
F_{xx}
F_{11}
F_{22}
F_{66}
F_{44}
F_{55}
F_{33}
-0.4
-0.2
0
0.2
0.4
0.6
0.8
F_{46}

FIGURE 4

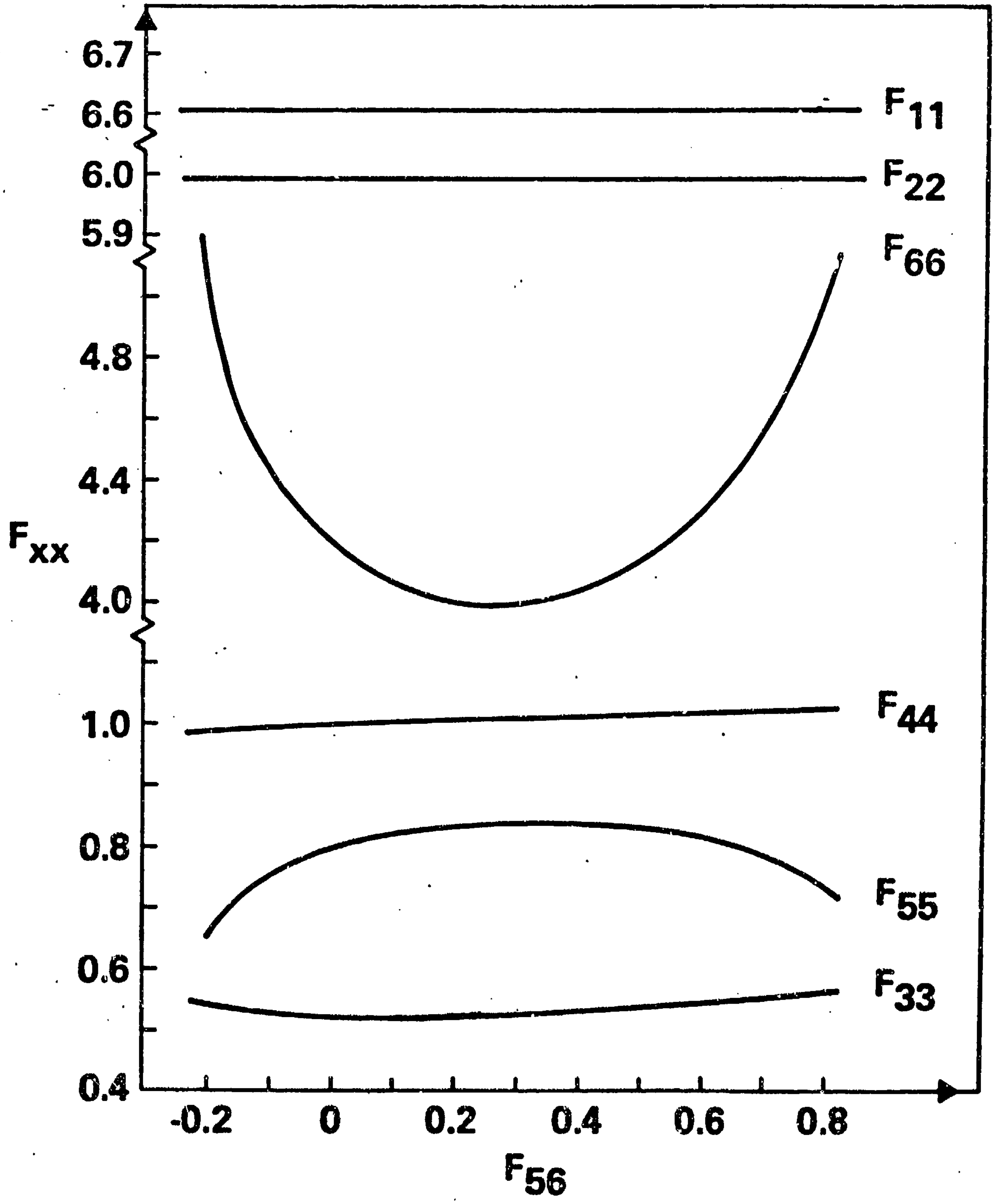

6.7
6.6
6.0
5.9
4.8
4.4
4.0
1.0
0.8
0.6
0.4
F_{xx}
F_{11}
F_{22}
F_{66}
F_{44}
F_{55}
F_{33}
-0.2
0
0.2
0.4
0.6
0.8
F_{56}

FIGURE 5

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SYNTHESIS OF CHLORINE AND BROMINE PERCHLORATE

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No Drawing. Filed May 25, 1970, Ser. No. 40,377
Int. Cl. C01b *11/02, 11/20*
U.S. Cl. 423—366 19 Claims

ABSTRACT OF THE DISCLOSURE

The new oxides chlorine perchlorate ($ClOClO_3$) and bromine perchlorate ($BrOClO_3$) are provided. Chlorine perchlorate is prepared by the reaction of cesium perchlorate or nitronium perchlorate with chlorine fluorosulfate or chlorine monofluoride. Bromine perchlorate is prepared by the reaction of cesium perchlorate or nitronium perchlorate with bromine fluorosulfate or by the reaction of chlorine perchlorate with elemental bromine.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention is in the field of inorganic chlorine and bromine oxides and to methods for their preparation.

(2) Description of the prior art

The four known stable oxides of chlorine are Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7. More recently, a fifth compound of limited stability has been reported with the empirical formula $ClO_{1.5}$ and the postulated composition of

$$OClClO_2$$

[J. Am. Chem. Soc., 89, 2795 (1967)]. The known stable oxides of bromine are Br_2O and BrO_3.

Fluorine perchlorate ($FOClO_3$) is a known compound. This compound can be prepared by the reaction of fluorine with concentrated perchloric acid. Fluorine perchlorate is highly reactive and tends to explode on freezing and during other simple operations. [J. Am. Chem. Soc., 69, 677 (1947).]

SUMMARY OF THE INVENTION

The new oxides chlorine perchlorate ($ClOClO_3$) and bromine perchlorate ($BrOClO_3$) are provided. Chlorine perchlorate is prepared by the reaction of cesium perchlorate or nitronium perchlorate with chlorine fluorosulfate or chlorine monofluoride. Bromine perchlorate is prepared by the reaction of cesium perchlorate or nitronium perchlorate with bromine fluorosulfate or by the reaction of chlorine perchlorate with elemental bromine.

Accordingly, an object of the present invention is the provision of new chlorine and bromine oxides and methods for their preparation.

Further objects will become apparent upon reading the undergoing specification and claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

New inorganic oxides of the formula $XOClO_3$ are provided wherein X is chlorine or bromine. The oxide of the formula $XOClO_3$ wherein X is chlorine is chlorine perchlorate. The oxide of the formula $XOClO_3$ wherein X is bromine is bromine perchlorate. These inorganic oxides are prepared by reacting a perchlorate of the formula $MClO_4$ wherein M is cesium or nitronium with a fluorosulfate of the formula XSO_3F wherein X is chlorine or bromine. This reaction is depicted as follows:

$$MClO_4+XSO_3F \rightarrow MSO_3F+XOClO_3$$

Chlorine perchlorate is produced at a temperature of about −20 to −80° C. when the fluorosulfate is chlorine fluorosulfate. This reaction is preferably conducted at a temperature of about −35 to −45° C. Bromine perchlorate is produced at a temperature of about −20 to −30° C. when the fluorosulfate is bromine fluorosulfate. This reaction is preferably conducted at a temperature of about −25° C.

The chlorine and bromine perchlorate preparative reaction is essentially complete in about 24 to 96 hours, however, longer reaction times are preferred in order to ensure complete consumption of the fluorosulfate since its vapor pressure and that of chlorine perchlorate and bromine perchlorate are too close to allow separation by a fractionation procedure. For the same reason, it is preferred that the perchlorate $MClO_4$ be employed in excess of the quantity theoretically required for complete reaction. At least 5% by weight excess perchlorate should be employed and preferably about 10 to 20%. The reaction occurs in high yield, for example, in the range of 75 to 95% of the theoretical yield.

Chlorine perchlorate can also be prepared by reacting cesium or nitronium perchlorate with chlorine monofluoride at a temperature of about −45 to −78° C. This reaction is depicted as follows:

$$MClO_4+ClF \rightarrow MF+ClOClO_3$$

wherein M is cesium or nitronium. It is preferred that a large excess of chlorine monofluoride be employed over the quantity of chlorine monofluoride theoretically required for complete reaction. It is preferred to employ a 3 to 5 fold excess. The reaction is preferably conducted at a temperature of about −78° C. The yields from this reaction are low (approximately 5%).

Bromine perchlorate can also be prepared by reacting elemental bromine with chlorine perchlorate at a temperature of about −35 to −78° C. The reaction is preferably conducted at a temperature of about −35 to −45° C. This reaction is depicted as follows:

$$Br_2+2ClOClO_3 \rightarrow Cl_2+2BrOClO_3$$

This reaction proceeds quantitatively and yields a purer product than the corresponding fluorosulfate reaction for the preparation of bromine perchlorate.

Chlorine perchlorate is a pale yellow liquid and nearly white when frozen. It is stable for limited periods of time at room temperature in clean, dry prepassivated stainless steel or perhalogenated plastic equipment. Storage at −45° C. in stainless steel cylinders has resulted in less than 1% decomposition per week over a 12 week period. Products of this low-temperature decomposition are Cl_2, O_2 and Cl_2O_6 which are readily separated from the chlorine perchlorate. The overall stability of chlorine perchlorate approaches that of the four known stable oxides of chlorine.

Bromine perchlorate is a red liquid which freezes below −78° C. It is unstable at ambient temperature and decomposes slowly at approximately −20° C.

Chlorine perchlorate and bromine perchlorate can be reacted with anhydrous metal chlorides (e.g., anhydrous potassium chloride) to form the respective anhydrous metal perchlorate (e.g., anhydrous potassium perchlorate) and the easily separated by-product chlorine. Because of their low melting points, the reaction of chlorine perchlorate and bromine perchlorate with anhydrous metal chlorides can be carried out at temperatures of about −78° C. thereby enabling close control of the reaction. The ability of chlorine perchlorate and bromine perchlorate to participate in these anhydrous metal chloride reactions without added solvent makes the compounds particularly useful. Chlorine perchlorate and bromine perchlorate can also be reacted with gaseous hydrogen chloride and hydrogen bromide at about −78° C. to form anhydrous perchloric acid and the easily separated by-products chlorine and bromine, respectively. Anhydrous perchloric acid can be prepared in this manner without the complications often encountered in the conventional preparation wherein the explosive by-product Cl_2O_7 is generated. In general, chlorine perchlorate and bromine perchlorate can be used in analogous manner to other oxides of chlorine, for example, in water treatment and purification.

EXAMPLE 1

A 30 ml. stainless steel cylinder was loaded with 2.45 g. (10.5 mmol) of cesium perchlorate ($CsClO_4$). After evacuation, chlorine fluorosulfate ($ClSO_3F$) (218 cm.^{3}, 9.73 mmol) was condensed into the cylinder at −196° C. The reaction was allowed to proceed by maintaining the cylinder at approximately −45° C. for 44 days. The products were separated by fractional condensation in U traps cooled to −78, −112 and −196° C. Little or no gases not condensable at −196° C. were found. The −196° C. fraction (8.0 cm.^{3}, 0.36 mmol) was primarily elemental chlorine with a small amount of sulfuryl fluoride (SO_2F_2), while the −78° C. fraction was negligibly small. Pure chlorine perchlorate ($ClOClO_3$) (207 cm.^{3}, 9.24 mmol) was retained at −112° C. The yield was 95%.

EXAMPLE 2

A similar reaction to Example 1 using nitronium perchlorate (NO_2ClO_4) (2.0 g., 13.7 mmol) and chlorine fluorosulfate (200 cm.^{3}, 8.93 mmol) produced chlorine perchlorate (170 cm.^{3}, 7.59 mmol) in 82% yield after 12 days.

The solid products from the reactions in Examples 1 and 2 were identified as cesium fluorosulfate-cesium perchlorate ($CsSO_3F$-$CsClO_4$) and nitronium fluorosulfate-nitronium perchlorate (NO_2SO_3F-NO_2ClO_4) mixtures by their infrared spectra.

Values for the molecular weight of chlorine perchlorate as determined by gas density, assuming ideal gas behavior, were 133, 135, 134 (calculated 135). The vapor pressure of chlorine perchlorate over the temperature range −47° C. to 21° C. is [T (° C.), P (mm.)]: −46.8, 8; −31.3, 21; −24.2, 32; 0.0, 119; 5.0, 150; 11.2, 202; 18.9, 283; 20.9, 305. The vapor pressure-temperature relationship is described by the equation $\log P_{mm} = 7.8156 - 1568.0/t.$ ° K. The normal boiling point calculated from the equation is 44.5° C., with a heat of vaporization of 7.17 kcal./mole and a Trouton constant of 22.6. Samples of chlorine perchlorate frozen as a ring in the upper part of a Teflon tube were observed to melt at −117±2° C. The densities measured in a Pyrex pycnometer at −78.8, 0.0 and 21.2° C. were 1.98, 1.82, and 1.75 g./ml. Over this temperature range the density ρ is given by the equation: $\rho = 1.806 - 2.30 \times 10^{-3}$ t. ° C. The infrared spectrum was recorded in stainless steel or trifluorochloroethylene cells fitted with silver chloride windows over the range 4000–400 cm.$^{-1}$ at a variety of pressures. The principal bands observed were: 1282 (v.s.), 1041 (s.), 752 (w.), 661 (sh.), 652 (s.), 585 (ch.), 574 (sh.), 561 (m.) and 511 (w.) cm.$^{-1}$.

EXAMPLE 3

A prepassivated 30 ml. stainless steel cylinder was loaded with nitronium perchlorate (2 g., 13.8 mmol) in the dry box. A less than equimolar amount of bromine fluorosulfate ($BrSO_3F$) (2.1 g., 11.8 mmol) was then condensed into the cylinder from the vacuum line and the reaction allowed to proceed at −20° for five days. The volatile products were separated by fractional condensation in U traps cooled to −45, −64 and −196° C. Unreacted bromine fluorosulfate was retained at −45° C. while the trap cooled to −196° C. contained only a small amount of the by-products chloryl fluoride ($FClO_2$) and perchloryl fluoride ($FClO_3$). Bromine perchlorate was trapped at −64° C.

EXAMPLE 4

A similar reaction to Example 3 using bromine fluorosulfate (1.5 g., 8.44 mmol) and cesium perchlorate (3 g. 12.9 mmol) instead of nitronium perchlorate yielded bromine perchlorate.

EXAMPLE 5

A prepassivated 30 ml. stainless steel cylinder was loaded at −196° C. with elemental bromine (Br_2) (1.36 mmol) that had been dried over phosphorus pentoxide (P_2O_5) and then chlorine perchlorate (2.76 mmol). The closed cylinder was left at −45° C. for five days. After recooling first to −78° C. and later at −64° C., the material which was volatile at those temperatures was pumped out and trapped at −78°, −112° and −196° C. The trapped material consisted of chlorine (1.38 mmol), chlorine perchlorate (0.04 mmol) and bromine perchlorate (~0.1 mmol), respectively, as indicated by vapor pressure and/or infrared spectra. The product bromine perchlorate (0.469 g., 2.61 mmol) was identified by elemental analysis and infrared spectrum.

We claim:

1. A compound of the formula $XOClO_3$ wherein X is chlorine or bromine.

2. The compound of claim 1 in which X is chlorine.

3. The compound of claim 1 in which X is bromine.

4. A method for preparing chlorine perchlorate of the formula $ClOClO_3$ comprising reacting a perchlorate of the formula $MClO_4$ wherein M is cesium or nitronium with chlorine fluorosulfate of the formula $ClSO_3F$ at a temperature of about −20 to −80° C.

5. The method of claim 4 in which the temperature is about −35 to −45° C.

6. The method of claim 4 in which the perchlorate of the formula $MClO_4$ is employed in excess of the quantity theoretically required for complete reaction with chlorine fluorosulfate.

7. The method of claim 6 in which at least 5% by weight excess perchlorate is employed.

8. The method of claim 6 in which about 10 to 20% by weight excess perchlorate is employed.

9. A method for preparing bromine perchlorate of the formula $BrOClO_3$ comprising reacting a perchlorate of the formula $MClO_4$ wherein M is cesium or nitronium with bromine fluorosulfate of the formula $BrSO_3F$ at a temperature of about −20 to −30° C.

10. The method of claim 9 in which the temperature is about −25° C.

11. The method of claim 9 in which the perchlorate of the formula $MClO_4$ is employed in excess of the quantity theoretically required for complete reaction with chlorine fluorosulfate.

12. The method of claim 11 in which at least 5% by weight excess perchlorate is employed.

13. The method of claim 11 in which about 10 to 20% by weight excess perchlorate is employed.

14. A method for preparing chlorine perchlorate of the formula $ClOClO_3$ comprising reacting a perchlorate of the formula $MClO_4$ wherein M is cesium or nitronium with chlorine monofluoride at a temperature of about −45 to −78° C.

15. The method of claim 14 in which the temperature is about −78°C.

16. The method of claim 14 in which chlorine monofluoride is employed in excess of the quantity theoretically required for complete reaction with the perchlorate of the formula $MClO_4$.

17. The method of claim 16 in which a 3 to 5 fold excess of chlorine monofluoride is employed.

18. A method for preparing bromine perchlorate of the formula $BrOClO_3$ comprising reacting bromine with chlorine perchlorate of the formula $ClOClO_3$ at a temperature of about −35 to −78° C.

19. The method of claim 18 in which the temperature is about −35 to −45° C.

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OSCAR R. VERTIZ, Primary Examiner

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3

United States Patent Office

3,780,165
Patented Dec. 18, 1973

3,780,165

SYNTHESIS OF CHLORINE FLUOROSULFATE AND BROMINE (I) FLUOROSULFATE

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Int. Cl. C01b 17/45
U.S. Cl. 423—466 4 Claims

ABSTRACT OF THE DISCLOSURE

This application discloses new processes for the preparation of chlorine fluorosulfate and bromine (I) fluorosulfate. Chlorine fluorosulfate is prepared by the reaction of chlorine monofluoride with sulfur trioxide. Bromine (I) fluorosulfate is prepared by the reaction of bromine with chlorine fluorosulfate.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention is in the field of inorganic chemistry and particularly in the field of halogen fluorosulfates.

(2) Description of the prior art

Chlorine fluorosulfate and bromine (I) fluorosulfate are known compounds. These halogen fluorosulfates have previously been prepared by the reaction of peroxydisulfuryl difluoride ($S_2O_6F_2$) with the appropriate halogen. More specifically, chlorine fluorosulfate has been produced by the combination of chlorine with peroxydisulfuryl difluoride at about 125° C. [Inorg. Chem., 2, 496 (1963)] and bromine (I) fluorosulfate has been prepared by treating peroxydisulfuryl difluoride with excess bromine at room temperature [J. Am. Chem. Soc., 82, 352 (1960)]. It has been reported, however, that the use of peroxydisulfuryl difluoride may be hazardous if the potentially explosive impurity, fluorine fluorosulfate, is not completely removed [Chem. Eng. News, 44 (8), 40 (1966)].

Bromine has been observed to react with excess fluorine fluorosulfate at room temperature to form a liquid product having the empirical formula $Br_2.3SO_3F_2$ [Inorg. Chem., 2, 496 (1963)].

Chlorine monofluoride has been shown to react in a variety of ways. For example, it can function as either a Lewis acid forming the ClF_2^- anion or a Lewis base forming the Cl_2F^+ cation. In addition, it can act as a chlorinating agent [Inorg. Chem., 6, 1938 (1967); ibid., 7, 586 (1968)], a fluorinating agent [Angew. Chem., 76, 385 (1964)] or a chlorofluorinating material. The latter form of reaction can be either catalyzed [J. Am. Chem. Soc., 91, 2902 (1969); ibid., 91, 2907 (1969)] or uncatalyzed [Advan. Fluorine Chem., 1, 18 (1960)].

SUMMARY OF THE INVENTION

An object of the present invention is the provision of improved processes for the preparation of chlorine fluorosulfate and bromine (I) fluorosulfate. Further objects will become apparent upon reading the undergoing specification and claims.

Chlorine fluorosulfate is prepared in accordance with the present invention by the reaction of chlorine monofluoride with sulfur trioxide. This reaction is preferably conducted at about room temperature using about 10 mol percent excess chlorine monofluoride. Bromine (I) fluorosulfate is prepared in accordance with the present invention by reacting bromine with chlorine fluorosulfate. This reaction is conveniently conducted at about room temperature using about a 1:1 to 2:1 mole ratio of chlorine fluorosulfate to bromine.

DESCRIPTION OF THE INVENTION

It has been found that the reaction of chlorine monofluoride and sulfur trioxide produces chlorine fluorosulfate in excellent yield. This reaction can be represented as follows: $SO_3+ClF\rightarrow ClOSO_2F$. The reaction sequence is an improvement over the previously reported preparation of chlorine fluorosulfate from chlorine and peroxydisulfuryl difluoride since the potentially explosive impurity fluorine fluorosulfate is never present and since the reaction can be conducted at about room temperature. In contrast to the reaction of chlorine monofluoride with thionyl fluoride (SOF_2) to prepare thionyl tetrafluoride (SOF_4) and the reaction of chlorine monofluoride with sulfur dioxide to prepare sulfuryl chloride fluoride ($ClSO_2F$) which only involve attack on the sulfur central atom, the reaction of chlorine monofluoride with sulfur trioxide results in addition across one of the S=O double bonds. Additionally, although the catalyzed conversion of thionyl tetrafluoride to chloroxysulfurpentafluoride (SF_5OCl) by chlorine monofluoride involves addition across one of the S=O double bonds of thionyl tetrafluoride, the present reaction is the first example of the uncatalyzed addition of chlorine monofluoride to an S=O group.

The reaction of chlorine monofluoride and sulfur trioxide can conveniently be conducted at a temperature of about −45 to 100° C.; however, this reaction is preferably conducted at a temperature of about 0 to 30° C. The chlorine fluorosulfate preparative reaction is usually essentially complete in an hour or less but longer reaction times can be employed if desired. While equimolar quantities of chlorine monofluoride and sulfur trioxide can readily be employed, it is preferred that chlorine monofluoride be employed in excess of the quantity theoretically required for complete reaction. It is generally preferred to employ about 10 mole percent excess chlorine monofluoride. However, the quantity of excess monofluoride employed is not critical and large excesses (e.g., 100 mole percent excess) can be used if desired. The chlorine fluorosulfate product is obtained in nearly quantitative yield and can be readily purified by vacuum fractionation or distillation.

It has been found that the reaction of bromine and chlorine fluorosulfate produces bromine (I) fluorosulfate in excellent yield. This reaction can be represented as follows: $Br_2+2ClOSO_2F\rightarrow Cl_2+BrOSO_2F$. As with respect to the preparation of chlorine fluorosulfate in accordance with the present invention, the present process represents an improvement over the previously reported preparation of bromine (I) fluorosulfate from bromine and peroxydisulfuryl difluoride since the potentially explosive impurity fluoride fluorosulfate is never present. In contrast to the previously reported reaction of bromine with excess fluorine fluorosulfate to form the adduct $Br_2.3SO_3F_2$, the present process results in the replacement of the chlorine atom of the chloroxy group of chlorine fluorosulfate with bromine.

The reaction of bromine with chlorine fluorosulfate is conveniently conducted at a temperature of about −45° to 80° C.; however, this reaction is preferably conducted at a temperature of about 0 to 30° C. The bromine (I) fluorosulfate preparative reaction is essentially complete in about 2 to 4 hours; however, it is preferred to allow the reaction to proceed for a longer period of time (e.g., about 8 hours). While equimolar quantities of bromine and chlorine fluorosulfate can readily be employed, it is preferred that bromine and chlorine fluorosulfate be employed in about a 1:2 mole ratio. When equimolar quantities of reactant are used, the resulting reaction will be represented as follows: $Br_2+ClOSO_2F\rightarrow BrCl+BrOSO_2F$. Although the reaction can be run employing more than a 2:1 mole ratio of chlorine fluorosulfate to bromine, this is generally not preferred since a large excess of chlorine fluorosulfate may result in the formation of bromine (III) fluorosulfate [$Br(OSO_2F)_3$] rather than $BrOSO_2F$. The bromine (I) fluorosulfate product is obtained in nearly quantitative yield and can be readily purified by vacuum fractionation or distillation.

The reactions of the present invention can conveniently be conducted by condensing the reactants into prepassivated cylinders (e.g., stainless steel cylinders) and allowing the cylinders to warm to room temperature or, if required, heating cylinders to the reaction temperature.

Chlorine and bromine (I) fluorosulfate are useful, among other things, as fluorosulfating agents. For example, they will react with addition across the double bonds of haloolefins in nearly quantitative yield. For example, chlorine fluorosulfate will combine with tetrafluoroethylene to form 2-chlorotetrafluoroethyl fluorosulfate [Inorg. Chem., 2, 496 (1963)]. Additionally, the defluorosulfurylation of the addition products of chlorine or bromine (I) fluorosulfate with haloolefins leads to fluorocarbon acyl fluorides or ketones. Another example of the fluorosulfating capability of these compounds is the reaction of bromine (I) fluorosulfate with sulfur dioxide to give trisulfuryl fluoride ($S_3O_8F_2$). The oxygenating capability of these compounds is further illustrated by the reaction of bromine (I) fluorosulfate with phosphorus trifluoride to yield phosphoryl fluoride [Inorg. Chem., 5, 2184 (1966)].

The following non-limitative examples illustrate the invention:

EXAMPLE 1

Sulfur trioxide (191 cm.^{3}, 8.53 mmol) and chlorine monofluoride (230 cm.^{3}, 10.2 mmol) were separately condensed into a prepassivated 30-ml. stainless steel cylinder cooled to −196° C. in a liquid nitrogen bath. The cylinder was slowly warmed to room temperature and allowed to remain at room temperature for 3 hours. The products were separated by fractional condensation in U-traps cooled to −78, −95, −142 and −196° C. The −142 and −196° C. fractions consisted of unreacted chlorine monofluoride with small amounts of chlorine and SO_2F_2. The other fractions contained the pale yellow product chlorine fluorosulfate in greater than 90% yield based on the amount of sulfur trioxide used.

EXAMPLE 2

Bromine (180 cm.^{3}, 8.04 mmol) and chlorine fluorosulfate (371.6 cm.^{3}, 16.6 mmol) were separately condensed into a prepassivated 30-ml. stainless steel cylinder cooled to −196° C. in a liquid nitrogen bath. The cylinder was slowly warmed to room temperature. The reaction was allowed to proceed by maintaining the cylinder at room temperature for 1 day. The products were separated by fractional condensation in U-traps cooled to −45, −78 and −196° C. The −196° C. fraction (192 cm.^{3}, 8.57 mmol) was identified as nearly pure chlorine contaminated only slightly with $S_2O_6F_2$. The trap cooled to −78° C. was completely empty while bromine (I) fluorosulfate (2.686 g., 15 mmol) was retained in the −45° C. trap. The yield was 93% of theoretical.

We claim:

1. A method for preparing chlorine fluorosulfate of the formula $ClOSO_2F$ consisting of reacting chlorine monofluoride with sulfur trioxide at a temperature of about −45 to +100° C. and then separating the reaction products and recovering chlorine fluorosulfate.

2. The method of claim 1 in which the reaction temperature is about 0 to 30° C.

3. The method of claim 1 in which the chlorine monofluoride is employed in excess of the quantity theoretically required for complete reaction with sulfur trioxide.

4. The method of claim 3 in which about 10 mole percent excess chlorine monofluoride is employed.

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MILTON WEISSMAN, Primary Examiner

U.S. Cl. X.R.

423—467

United States Patent [19]

Christe

[11] **3,873,676**

[45] **Mar. 25, 1975**

[54] **PROCESS FOR PREPARING STABLE CHLORINE TRIFLUORIDE DIOXIDE**

[75] Inventor: **Karl O. Christe**, Calabasas, Calif.

[73] Assignee: **North American Rockwell Corporation**, Canoga Park, Calif.

[22] Filed: **Sept. 18, 1972**

[21] Appl. No.: **290,031**

[52] **U.S. Cl.** **423/466,** 149/1
[51] **Int. Cl.** **C01b 7/24**
[58] **Field of Search** 149/1; 423/466

[56] **References Cited**

UNITED STATES PATENTS

3,320,031 5/1967 Grosse et al. 423/466

Primary Examiner—Leland A. Sebastian
Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

A stable form of chlorine trifluoride dioxide is disclosed for use as an oxidizer in formulating energetic compositions, such as propellants. The stable ClF_3O_2 is produced by reacting a $ClO_2F_2^+$ salt with a strong Lewis base at −78°C.

7 Claims, No Drawings

PROCESS FOR PREPARING STABLE CHLORINE TRIFLUORIDE DIOXIDE

BACKGROUND OF THE INVENTION

The invention herein described was made in the course of or under a contract with the Department of the Navy.

1. Field of Invention

This invention relates to compositions of matter and is particularly directed to a stable form of chlorine trifluoride dioxide and a method of producing the same.

2. Prior Art

Energetic compositions of matter are useful in providing energy sources for rocket engines, guided missiles, auxiliary power units for aircraft, ordnance, demolition and the like. Such compositions conventionally are produced by mixing a fuel with an oxidizer. Obviously, the energy of such compositions results primarily from the oxidation of the fuel. Hence, it is desirable to provide a highly energetic oxidizing agent. On the other hand, it is equally desirable that the oxidizing agent by a stable material, so as to prevent accidental or unintentional ignition or explosive decomposition of the composition. Numerous organic and inorganic compounds have been proposed heretofore for use as such oxidizing agents. However, it has been found that, as a general rule, stable compounds are low energy oxidizers and high energy oxidizers are unstable. Thus, although some useful oxidizing agents have been disclosed by the prior art, the search for a stable, high-energy, oxidizing material has continued. In recent years, studies have indicated that halogen oxyfluoride materials might provide a satisfactory oxidizing material. However, although empirical formulas may be stated for such materials and some of the properties of such materials may be predicted, the synthesis of these materials has proven to be extremely difficult and it is sometimes found that several materials, each having distinct structures and properties, are defined by a single empirical formula. Thus, U.S. Pat. No. 3,285,842 discloses a process for producing a material having the empirical formula chlorine trifluoride dioxide, ClF_3O_2, which the patent states to be violet liquid which is unstable at temperatures above −72°C. While it would be expected that this material would be a highly energetic oxidizing agent, the lack of stability renders it unsafe for use in the produciton of propellants and the like.

BRIEF SUMMARY AND OBJECTS OF INVENTION

These disadvantages of the prior art are overcome with the present invention and a compostion of matter is disclosed which is a form of chlorine trifluoride dioxide, yet which is stable at temperatures up to at least +25°C and, hence, can be safely employed for manufacturing propellants and the like. In addition, a method is disclosed for producing this stable form of chlorine trifluoride dioxide by reacting $ClF_2O_2{}^+PtF_6{}^-$ with a strong Lewis base at a temperature of about −78°C and separating the products of the reaction by distillation.

Accordingly, it is an object of the present invention to provide a new composition of matter.

Another object of the present invention is to provide a form of chlorine trifluoride dioxide which is stable at ambient temperatures.

A further object of the present invention is to provide a form of chlorine trifluoride dioxide which is safe for use in the production of propellants and the like.

An additional object of the present invention is to provide a method of producing a stable form of chlorine trifluoride dioxide. A specific object of the present invention is to provide a form of chlorine trifluoride dioxide which is stable at temperatures up to at least +25°C by reacting $ClF_2O_2{}^+$ salts with nitryl fluoride at a temperature of about −78°C and separating the products of the reaction by distillation.

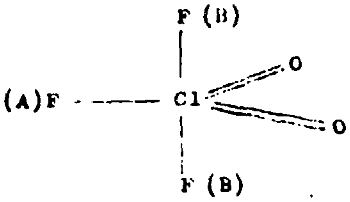
These and other objects and features of the present invention will be apparent from the following detailed description.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

In that form of the present invention chosen for purposes of illustration, stable chlorine trifluoride dioxide has been produced by reacting a $ClF_2O_2{}^+$salt, such as $ClF_2O_{115}PtF_6{}^-$, with a strong Lewis base at −78°C.

EXAMPLE I

A sample of $ClO_2{}^+PtF_6{}^-$ containing about 10% of $ClF_2O_2{}^+PtF_6{}^-$ was treated at −78°C in a sapphire reactor with a large excess of FNO for several days. No material noncondensible at −196°C (i.e., F_2) was observed. The products, volatile at 25°C were removed and separated by fractional condensation through a series of traps kept at −126°C, −142°C, and −196°C. The −142°C fraction contained a novel compound which was identified by its infrared spectrum as ClF_3O_2. The observed frequencies are listed in Table I and are in excellent agreement with those expected for a trigonal bypyramidal structure of symmetry C_{2v}.



This structure was confirmed by ^{19}F nuclear magnetic resonance spectroscopy. The observed signal consisted of a typical AB_2 pattern centered at −413 ppm relative to the external standard $CFCl_3$. The F-F coupling constant was measured to be 442 Hz. The B_2 part of the AB_2 pattern occurs downfield from the A part, proving that the B_2 fluorine atoms occupy the two axial positions. Additional structural proof was obtained from the Raman spectrum of the gas and the liquid showing strong absorptions at 1096, 684, 548, 527, 493, 290, and 229 cm^{-1}. The molecular weight of the compound was confirmed by vapor density measurements (measured, 122; calculated, 124).

Table I

Infrared Spectrum of ClF_3O_2 and its Tentative Assignment

Frequency (cm^{-1})	Intensity	Assignment for Point Group C_{2v}
1334	s	ν_{10} (B_2), $\nu_{as}ClO_2$
1096	s	ν_1 (A_1), $\nu_{sym}ClO_2$
699	vs	ν_7 (B_1), $\nu_{as}ClF_2Ax$
687	vs	ν_2 (A_1), νClF
598	ms	ν_{11} (B_2), δ_{sciss} ClO_2
543 } 532 }	mw	ν_3 (A_1) and ν_8 (B_1)

The solid residue obtained from the FNO displacement reaction showed the correct weight change expected for conversion into $NO^+PtF_6{}^-$. Its identity as $NO^+PtF_6{}^-$ was confirmed by infrared spectroscopy.

The stable chlorine trifluoride dioxide is white as a solid having a melting point of −81.2°C and colorless as a liquid having a boiling point of −21°C. It appears to be stable at 25°C. The observed stability and lack of color demonstrate that our product cannot be identical with the previously reported deeply violet and unstable $ClF \cdot O_2F_2$ and $ClF_3 \cdot O_2$ addition compounds supposedly having the empirical composition ClF_3O_2.

EXAMPLE II

A sample of $ClO_2{}^+{}_{PtF_6}{}^-$ containing about 10% of $ClO_2F_2{}^+{}_{PtF_6}{}^-$ was treated with a sufficient quantity of FNO_2 to maintain a liquid phase at −78°C in a stainless steel reactor for up to 12 hours. This reaction yielded solid $NO_2{}^+{}_{PtF_6}{}^-$ and gaseous ClF_3O_2 plus $FClO_2$. If desired, the chlorine trifluoride dioxide may then be separated by conventional distillation techniques, as in a multi-plate distillation tower.

Small amounts of material were purified by combining the ClF_3O_2 and $FClO_2$ at −196°C with a samll excess of BF_3. These materials were allowed to mix and warm to ambient temperature. This results in $ClF_2O_2{}^+{}_{BF_4}{}^-$, which is stable, plus $ClO_2{}^+{}_{BF_4}{}^-$, which has a dissociation pressure of 182 millimeters at 22°C and which can be rmoved by pumping. The $ClF_2O_2{}^+{}_{BF_4}$ is then reacted with sufficient FNO_2 to maintain a liquid phases at −78°C for up to 12 hours. This reaction produced solid $No_2{}^+{}_{BF_4}{}^-$ plus gaseous ClF_3O_2, the two gases may be pumped off and separated by passing the gases through a pair of traps maintained at −126°C and −196°C, respectively. The chlorine trifluoride dioxide will be caught in the −126°C trap.

Obviously, numerous variations and modifications may be made without dparting from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illlustrative only and are not intended to limit the scope of the present invention.

What is claimed is:

1. The method of producing stable chlorine trifluoride dioxide comprising the steps of:
reacting a $ClF_2O_2{}^+$ salt with a strong Lewis base compatible with ClF_3O_2.

2. The method of claim 1 wherein said salt is $ClF_2O_2{}^+{}_{PtF_6}{}^-$.

3. The method of claim 1 wherein said salt is $ClF_2O_2{}^+{}_{BF_4}$.

4.. The method of claim 1 wherein said reaction step is carried out at −78°C.

5. The method of claim 1 wherein the quantity of the Lewis base is sufficient to maintain the reaction in a liquid phase.

6. The method of claim 1 wherein the Lewis base is FNO_2.

7. The method of claim 1 wherein the Lewis base is FNO.

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United States Patent [19]
Christe et al.

[11] **3,873,677**
[45] **Mar. 25, 1975**

[54] IODINE PERCHLORATES

[75] Inventors: **Karl O. Christe**, Calabasas; **Carl J. Schack**, Chatsworth, both of Calif.

[73] Assignee: **The United States of America as represented by the Secretary of the Navy**, Washington, D.C.

[22] Filed: **May 24, 1973**

[21] Appl. No.: **363,708**

[52] U.S. Cl. **423/466**, 423/179, 423/462, 423/472, 423/504

[51] Int. Cl. **C01d 11/04**, C01b 7/00, C01b 7/24

[58] **Field of Search** 423/466, 462, 179, 475, 423/504

[56] **References Cited**

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Primary Examiner—Edward Stern
Attorney, Agent, or Firm—R. S. Sciascia; J. A. Cooke

[57] ABSTRACT

Iodine perchlorates of the formula $X(OClO_3)_n$ wherein X is selected from the group consisting of I^{+++} and CsI^{++}, wherein *n* equals 3 when X is I^{+++} and *n* equals 4 when X is CsI^{+4}, are prepared by reacting $ClOClO_3$ with either solid I or CsI at low temperatures. The iodine perchlorates are useful as energetic oxidizers

5 Claims, No Drawings

IODINE PERCHLORATES

BACKGROUND OF THE INVENTION

This invention generally relates to perchlorate compounds and more particularly to iodine perchlorates.

The alleged preparation of iodine trisperchlorate from iodine, ozone, and anhydrous $HClO_4$ is described by M. Schmeisser in "Handbook of Preparative Inorganic Chemistry," G. Brauer, Ed., Academic Press, New York, N. Y. 1963, Vol. 1, pg. 330. However, a crosscheck with the original publication, F. Fichter and H. Kappeler, Z. Anorg. Allgem. Chem., 91, 134 (1915), reveals that the original paper deals only with a compound having the empirical composition, $I(ClO_4)_3 \cdot 2H_2O$. Further, from the properties of $I(OClO_3)_3$, it appears unlikely that the Fichter, et al., compound was the bishydrate of $I(OClO_3)_3$

The bishydrate of iodine trisperchlorate, $I(OClO_3)_3 \cdot 2H_2O$, should be a less energetic oxidize. than the anhydrous form, and therefore would be less suitable for propellants. In view of this attempts have been made to obtain the bishydrate as well as the anhydrous material.

SUMMARY OF THE INVENTION

Accordingly, one object of this invention is to provide iodine perchlorates.

Another object of this invention is to isolate iodine perchlorates in this solid anhydrous form.

A further object of this invention is to provide iodine perchlorates which are highly energetic oxidizers.

A still further object of this invention is to provide a method of synthesizing iodine perchlorates.

Still another object of this invention is to achieve a high degree of purity in the iodine perchlorates synthesized.

Yet another is to provide a easy means for purifying the iodine perchlorates.

These and other objects of this invention are accomplished by providing compounds which are iodine perchlorates of the formula $X(OClO_3)_n$ wherein X is selected from the group consisting of I^{+++} and CsI^{++} wherein *n* equals 3 when X is I^{+++}, and *n* equals 4 when X is CsI^{++}. The iodine perchlorates are prepared by reacting chlorine perchlorate, $ClOClO_3$, with a substance selected from the group consisting of I_2 and CsI at low temperatures.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The iodine perchlorates of this invention are prepared by reacting chlorine perchlorate, $ClOClO_3$, with either iodine, I_2, or CsI. The reaction for preparing iodine trisperchlorate is as follows:

$$I_2 + 6ClOClO_3 \rightarrow 2I(OClO_3)_3 + b\ 3Cl_2$$

and the reaction for preparing the cesium tetrapechlorato iodate is as follows:

$$Cs^+I^- + 4ClOClO_3 \rightarrow Cs^+I(OClO_3^-)_4 + 2Cl_2.$$

The range of suitable reaction temperatures is limited by the slow reaction rates and the instability of the iodine perchlorate products. For examle, the iodine trisperchlorate reaction takes 70 hours at −50°C and the cesium tetrapherchlorato iodate reaction takes 5 weeks at 31 45°C to go to 99 percent completion and at lower temperatures the reaction takes still longer. On the other hand, while the $CsI(OClO_3)_4$ is stable at 23°C, iodine trisperchlorate rapidly decomposes, at this temperature.

Thus, the reaction temperature for producing $CsI(OClO_3)_4$ should be in the range −78° to 30°C, preferably −55° to −40°C; and the reaction temperature for producing iodine trisperschlorate should be in the range −78° to 0°C, preferably −55° to −40°C.

Purification of the product is simplified by reacting a stoichiometric excess of chlorine perchlorate with iodine or cesium iodide in an inert environment The excess of chlorine perchlorate is used to drive the reaction to 99 percent completion. The the solid $I(OClO_3)_3$ or $CsI(OClO_3)_4$ product can be separated from the byproduct chlorine and unreacted chlorine perchlorate at low temperatures under vacuum. Finally, since water is neither a reactant nor a product in either of the reactions, the anhydrous form of $I(OClO_3)_3$ or $CsI(OClO_3)_4$ is obtained when the reaction is run in an anhydrous environment. Additionally, because of the reactivity of the desired perchlorates it is most desirable to conduct the reactions in an inert environment which, within the context of this invention, is meant to include anhydrous conditions.

The general nature of the invention having been set forth, the following examples are presented as specific illustrations thereof. It will be understood that the invention is not limited to these specific examples but is susceptible to various modifications that will be recognized by one of ordinary skill in the art.

EXAMPLE 1

Iodine Trisperchlorate

$I(OClO_3)_3$

Iodine (0.915 mmol) was loaded into a 10 ml prepassivated Teflon FEP ampoule closed off by a stainless steel valve. Chlorine perchlorate (8.18 mmol) was added at −196°C. The ampoule was kept at −50°C for 70 hours. At this point, the dark iodine color had disappeared and a pale yellow (due to the presence of Cl_2) solid had formed. Upon cooling to −196°C, the ampoule did not contain any non-condensible reaction products. The ampoule was slowly warmed to −45°C. The volatile products were separated by fractional condensation and identified by infrared spectroscopy and their vapor pressure. They consisted of Cl_2 (2.70 mmol) and $ClOClO_3$ (2.74 mmol). The white, solid residue weighed 776 mg., in excellent agreement with the weight (777 mg) calculated for a complete conversion to $I(OClO_3)_3$.

EXAMPLE 2

Cesium Tetraperchlorato Iodate (III)

$CsI(OClO_3)_4$

A 10 ml prepassivated stainless steel cylinder was loaded with powdered anhydrous CsI (1.15 mmol), followed by $ClOClO_3$ (6.10 mmol) at b −196°C. The reaction was allowed to proceed by warming the cylinder to −45°C, where it was maintained for 5 weeks. On recooling to −196°C, no non-condensible gases were observed. Volatile products were pumped from the reactor for several hours while and after it had warmed to ambient temperature. Separation of these species was affected by fractional condensation and identification by infrared and vapor pressure measurements. They consisted of Cl_2 (2.34 mmol) and unreacted $ClOClO_3$ (1.45 mmol). The solid product was pale yellow in color and weighed 749 mg, indicating a 99 percent conversion of the CsI to $Cs^+I(OClO_3)_4^-$ had occurred.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described herein.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A method of preparing cesium tetraperchlorato iodate (III), $CsI(OClO_4)_4$, comprising:

contacting chlorine perchlorate and cesium iodide in an inert environment at a temperature in the range of −78°C to 30°C for 70 or more hours, provided that at least 4 moles of chlorine perchlorate are used per mole of cesium iodide.

2. The method of claim 1 wherein said contacting is performed at a temperature of −55°C to −40°C.

3. The method of claim 1, wherein more than 4 moles of said chlorine perchlorate is used per mole of cesium iodide.

4. Cesium tetraperchlorato iodate (III), $CsI(OCl_3)_4$, as produced by the process of claim 1.

5. The product of claim 4, wherein the said iodate compound is anhydrous.

* * * * *

United States Patent [19]
Christe

[11] **3,879,526**
[45] **Apr. 22, 1975**

[54] **HIGH ENERGY OXIDIZERS AND METHOD OF SYNTHESIZING SAME**

[75] Inventor: **Karl O. Christe**, Calabasas, Calif.

[73] Assignee: **Rockwell International Corporation**, El Segundo, Calif.

[22] Filed: **Dec. 4, 1972**

[21] Appl. No.: **312,014**

[52] **U.S. Cl.** **423/277**; 423/466; 423/592
[51] **Int. Cl.** ... **C01b 35/00**; C01b 7/24; C01g 55/00
[58] **Field of Search** 423/276, 466, 592, 277

[56] **References Cited**

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Primary Examiner—F. C. Edmundson
Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

The cation $ClO_2F_2^+$ is synthesized by reacting $FClO_2$ with PtF_6 to produce $ClO_2F_2^+PtF_6^-$ and several additional salts, containing this cation, are produced by displacement techniques.

15 Claims, No Drawings

HIGH ENERGY OXIDIZERS AND METHOD OF SYNTHESIZING SAME

BACKGROUND OF THE INVENTION

The invention herein described was made in the course of or under a contract with the Department of the Navy.

1. Field of the Invention

This invention relates to compositions of matter and is particularly directed to compounds containing the cation $ClO_2F_2^+$ and methods of synthesizing such compounds.

2. Prior Art

Compositions of matter which contain oxygen and fluorine have been found to be extremely useful in formulating energetic materials, such as solid propellants, explosives and the like. Many simple compounds containing these elements have been disclosed heretofore. However, it has been recognized that more energetic compositions could be formulated by synthesizing more complex compositions containing multiple atoms of these elements. Unfortunately, it has been found that these more complex compositions cannot be produced from elementary fluorine by conventional methods. Accordingly, considerable effort has been expended to discover and find methods for producing these complex compositions.

BRIEF SUMMARY AND OBJECTS OF INVENTION

These disadvantages of the prior art are overcome with the present invention and several compositions containing the cation $ClO_2F_2^+$ have been synthesized by reacting $FClO_2$ with PtF_6 to produce $ClO_2F_2^+PtF_6^-$ and employing displacement techniques to produce several additional salts containing this cation, such as $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$.

Accordingly, it is an object of the present invention to provide new, highly-energetic compositions of matter.

Another object of the present invention is to provide methods of synthesizing new, highly-energetic compositions of matter.

An additional object of the present invention is to provide complex compositions containing multiple atoms of oxygen and fluorine.

A specific object of the present invention is to provide several compositions containing the cation $ClO_2F_2^+$ by reacting $FClO_2$ with PtF_6 to produce $ClO_2F_2^+PtF_6^-$ and employing displacement techniques to produce additional salts containing this cation, such as $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$.

These and other objects and features of the present invention will be apparent from the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

In that form of the present invention chosen for purposes of illustration, it has been found that $FClO_2$ can be reacted with PtF_6 to produce $ClO_2F_2^+PtF_6^-$ and displacement techniques, using this reaction product, can be employed to produce additional salts containing the $ClO_2F_2^+$ cation. Among these additional salts are $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$.

EXAMPLE I

The $FClO_2$-PtF_6 System

Platinum hexafluoride (17.0 mmole) and $FClO_2$ (46.1 mmole) were combined at −196° (all temperatures in this and other examples are degrees centrigrade) in a passivated (with ClF_3) 75-ml stainless steel cylinder. The starting materials, platinum hexafluoride and $FClO_2$, are available commercially from Ozark Mahoning Co., Tulsa, Oklahoma. The temperature of −196° was selected as one at which the starting materials have no volatility. The cylinder was placed at room temperature to allow the mixture contained therein to slowly warm up to 25° without the addition of external heat. This required approximately 30 minutes to one hour, after which, the mixture was kept at this temperature for three days. The cylinder was cooled to −196° and 3.75 mmole of material volatile at this temperature was removed and identified as F_2 by its vapor pressure and mass spectrum. The products volatile at 25° were separated by fractional condensation through traps kept at −78°, −126° and −196°. The −126° fraction consisted of $FClO_2$ (28.7 mmole) and the −196° one of $FClO_2$ (0.3 mmole), ClF_5 (0.1 mmole), and a small amount of $FClO_3$. The cylinder contained a stable canary yellow solid (6.618 g), which was identified by infrared spectroscopy as a mixture of $ClO_2^+PtF_6^-$ and $ClO_2F_2^+PtF_6^-$. Hence, PtF_6 (17.0 mmole) had reacted with $FClO_2$ (17.1 mmole) in a 1:1 mole ratio yielding F_2 (3.75 mmole), $ClO_2^+PtF_6^-$ (12.2 mmole), and $ClO_2F_2^+PtF_6^-$ (4.8 mmole) as the main products. It was found that PtF_6 and $FClO_2$, when combined at −196° and allowed to slowly warm up to 25° by placing the container at room temperature for 30 minutes to one hour interacted according to:

$$2FClO_2 + 2PtF_6 \rightarrow ClO_2F_2^+PtF_6^- + ClO_2^+PtF_6^- \quad (1)$$

This mixture may then be employed as a starting material for producing a plurality of pure salts containing the $ClO_2F_2^+$ cation, as described in the following examples. The yield of $ClO_2F_2^+$ was not 50 percent as expected from the above equation, but generally about 25 percent owing to the following competing reaction:

$$2FClO_2 + 2PtF_6 \rightarrow 2ClO_2^+PtF_6^- + F_2 \quad (2)$$

In some of the experiments, small amounts of $ClF_6^+PtF_6^+$ or ClF_5 and $FClO_3$ were observed, depending on the exact reaction conditions. The formation of some $FClO_3$ is not surprising since it is known that $FClO_2$ readily interacts with nascent oxygen to yield $FClO_3$.

Further modification of the reaction conditions (rapid warm up of the $FClO_2$-PtF_6 mixture from −196° to either −78° or 25° and completion of the reaction at 25°) did not produce detectable amounts of either $ClO_2F_2^+$ or $ClF_6^+PtF_6^-$, but only $ClO_2^+PtF_6^-$ and ClF_5, F_2, and O_2. This indicates that the nature of the reaction products are more influenced by the warm-up rate of the starting materials from −196° to about −78° than by the final reaction temperature. Slow warm up favors the formation of $ClO_2F_2^+$, whereas rapid warm up yields ClF_6^+ or ClF_5 and F_2.

EXAMPLE II

Synthesis of $ClO_2F_2^+$ Salts

The synthesis of $ClO_2F_2^+PtF_6^-$ has been described in Example I. For the synthesis of $ClO_2F_2^+BF_4^-$, a mixture of $ClO_2F_2^+PtF_6^-$ (4.8 mmole) and $ClO_2^+PtF_6^-$ (12.2 mmole) was treated in a passivated (with ClF_3 and BrF_5) 75 ml stainless steel cylinder with FNO_2 (25.3 mmole) at −78° for 48 hours. The reaction products volatile at 25° consisted of $FClO_2$, ClF_3O_2, and unreacted FNO_2 and were separated by fractional condensation through a series of traps kept at −112°, −126°, −142° and −196°. The −126° fraction contained most of the ClF_3O_2 and some $FClO_2$. Attempts to further separate the ClF_3O_2 and $FClO_2$ mixture by fractional condensation were unsuccessful. Consequently, 2.76 mmole of this mixture was combined with BF_3 (3.00 mmole) at −196° in a passivated ampoule formed of perfluoroethylenepropylene copolymer and the temperature was cycled several times between −196 and 25°. The product was kept at −78° for several hours and unreacted BF_3 (0.22 mmole) was removed at this temperature in vacuo. Removal of volatile material in vacuo was continued at 20°. The volatile material (2.70 mmole) consisted according to its infrared spectrum of a 1:1 mixture of $FClO_2$ and BF_3. The white solid, nonvolatile residue (280 mg = 1.46 mmole) was identified by infrared, Raman, and ^{19}F nmr spectroscopy as $ClO_2F_2^+BF_4^-$.

For the preparation of the AsF_6^- salt, $ClO_2F_2^+BF_4^-$ (0.62 mmole) and AsF_5 (1.43 mmole) were combined at −196° in a passivated ampoule formed of perfluoroethylenepropylene copolymer. The contents of the ampoule was kept at −78° for 30 minutes and at 25° for 1 hour. Volatile products were removed at 25°C and consisted of unreacted AsF_5 (0.79 mmole) and BF_3 (0.59 mmole). The white, stable solid weighted 185 mg (weight calculated for 0.62 mmole of $ClF_2O_2^+AsF_6^-$ = 183 mg) and was identified as $ClF_2O_2^+AsF_6^-$ by infrared, Raman, and ^{19}F nmr spectroscopy.

Syntheses and Properties of $ClO_2F_2^+$ Salts

The synthesis of $ClO_2F_2^+PtF_6^-$ from $FClO_2$ and PtF_6 and its temperature dependence has been discussed above. The BF_4^- and AsF_6^- salts were prepared according to the following scheme:

$$ClO_2^+PtF_6^- + ClO_2F_2^+PtF_6^- + 2FNO_2 \rightarrow FClO_2 + ClF_3O_2 + 2NO_2^+PtF_6^- \qquad (3)$$

Unreacted FNO_2 and some of the $FClO_2$ could be separated from ClF_3O_2 by fractional condensation. The remaining $FClO_2$ was separated from ClF_3O_2 by complexing with BF_3. Since the resulting $ClO_2^+BF_4^-$ has a dissociation pressure of 182 mm at 22.1°, while $ClO_2F_2^+BF_4^-$ is stable, the former salt could be readily removed by pumping at 20°. Conversion of $ClO_2F_2^+BF_4^-$ to the corresponding AsF_6^- salt was accomplished through displacement of BF_4^- by the stronger Lewis acid AsF_5.

All three salts, synthesized with the $ClO_2F_2^+$ cation and fluorine-containing anions, $ClO_2F_2^+PtF_6^-$, $ClO_2F_2^+AsF_6^-$, and $ClO_2F_2^+BF_4^-$, are solids, stable at 24°, and react violently with water or organic materials. The PtF_6^- compound is canary yellow, while those of AsF_6^- and BF_4^- are white. The salts dissolve in anhydrous HF without decomposing. They are crystallinic in the solid state and the x-ray powder diffraction patterns of $ClF_2O_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$ are listed in Table I.

TABLE I

X-Ray Powder Patterns for $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$

$ClO_2F_2^+BF_4^-$		$ClO_2F_2^+AsF_6^-$		Continued	
d,A	Intensity	d,A	Intensity	d,A	Intensity
5.47	s	7.49	w	2.12	w
5.06	m	5.50	ms	2.01	w
4.37	ms	4.98	w	1.94	mw
4.15	w	4.35	ms	1.90	mw
3.70	vs	4.02	w	1.86	w
3.56	s	3.86	s	1.80	w
3.00	m	3.70	w	1.76	mw
2.77	m	3.57	m	1.72	w
2.57	vs	3.40	m	1.70	mw
2.41	m	3.02	mw	1.65	w
2.18	s	2.77	m	1.62	w
2.08	s	2.69	m	1.59	w
1.86	ms	2.60	w	1.54	w
1.80	w	2.41	w	1.50	w
		2.30	w	1.41	w
		2.20	w	1.37	w
				1.34	w

The powder pattern of $ClO_2F_2^+BF_4^-$ is much simpler than that of $ClO_2F_2^+AsF_6^-$. This is not surprising since the anion and cation in the former salt are both approximately tetrahedral and of similar size. The powder pattern of $ClO_2F_2^+BF_4^-$ can be indexed on the basic of an orthorhombic unit cell with a = 5.45, b = 7.23, and c = 13.00A. Assuming four molecules per unit cell and neglecting contributions from the highly charged central atoms to the volume, a plausible average volume of 16 A per F or O atom is obtained. However, the agreement between the observed and calculated reflections is somewhat poor for several lines and, hence, the above unit cell dimensions are tentative.

The thermal stability of $ClO_2F_2^+BF_4^-$ is higher than those of $ClO_2^+BF_4^-$, $ClF_2^+BF_4^-$, or other similar salts. This is in good agreement with the previously made correlations between the stability of an adduct and the structure of the parent molecule and its ions. Thus, tetrahedral $ClO_2F_2^+$ (see below) should be energetically much more favorable than trigonal bypyramidal ClF_3O_2.

F-nmr Spectra

A broad singlet at −310 ppm relative to external $CFCl_3$ has been observed for $ClO_2F_2^+PtF_6^-$ in anhydrous HF. The spectrum of $ClF_2O_2^+BF_4^-$ in HF shows a strong temperature dependence. At 30° it consists of a single peak at 185 ppm relative to external $CFCl_3$. With decreasing temperature the peak at first becomes broader, then separates at about 0° into signals at −301 ($ClO_2F_2^+$), 146 (BF_4^-), and 194 ppm (HF) which become narrower with further decrease in temperature. The observed peak area ratio of approximately 2:1 for the 146 and −301 ppm signals confirms their assignment of BF_4^- and ClO_2F_2—, respectively, and proves the ionic nature of the $ClF_3O_2 \cdot BF_3$ adduct in HF solution.

The spectrum of $ClF_2O_2^+AsF_6^-$ in HF (which was acidified with AsF_5) consists of two resonances at −307 ($ClO_2F_2^+$) and 105 ppm (HF, AsF_5, AsF_6^-), respectively. Rapid exchange between HF, AsF_5 and AsF_6^- preempted the measurement of the $ClO_2F_2^+$ to AsF_6^- peak area ratio.

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illustrative only and are not intended to limit the scope of the present invention.

What is claimed is:

1. The composition of matter consisting of a salt having the cation $ClO_2F_2^+$, and an anion selected from the group consisting of AsF_6^-, BF_4^- and PtF_6^-.

2. The composition of claim 1 wherein the anion of said salt is PtF_6^-.

3. The composition of claim 1 wherein the anion of said salt is BF_4^-.

4. The composition of claim 1 wherein the anion of said salt is AsF_6^-.

5. The method of synthesizing a salt having a difluoroperchloryl cation, said method comprising the steps of:

combining PtF_6 and $FClO_2$ in a container at a starting temperature at which these materials have no volatility,

gradually increasing the temperature of said materials without the addition of external heat until the reaction is complete,

separating the volatile products, and

removing the resulting $ClO_2F_2^+PtF_6^-$ salt from said container.

6. The method of claim 5 wherein said starting temperature is −196°C.

7. The method of claim 5 wherein said gradually increasing step comprises exposing said container to room temperature.

8. The method of claim 7 wherein said container is exposed to room temperature for a period of approximately 30 minutes to 1 hour.

9. The method of claim 7 wherein said room temperature is 25°C.

10. The method of claim 5 comprising the further steps of:

combining said $ClO_2F_2^+PtF_6^-$ salt with FNO_2 at a reaction temperature such that said FNO_2 is in a liquid state,

maintaining said reaction temperature until the reaction is complete,

separating the volatile products by fractional condensation in a series of traps kept at −112°C and −126°C, respectively,

combining the condensate of the −126°C trap with BF_3 at a temperature at which the materials have no volatility,

raising the temperature of said condensate to 20°C and removing all volatile materials, and

recovering the resulting $ClO_2F_2^+BF_4^-$ salt as a nonvolatile solid.

11. The method of claim 10 wherein said reaction temperature is −78°C.

12. The method of claim 10 wherein said maintaining step is continued for approximately 48 hours.

13. The method of claim 10 comprising the further steps of:

combining said $ClO_2F_2^+BF_4^-$ salt and AsF_5 in a container at a temperature at which these materials have no volatility,

raising the temperature of said container to a temperature at which said AsF_5 is liquid,

maintaining said container at said temperature at which AsF_5 is liquid until the reaction is complete,

raising the temperature of said container to ambient temperature,

removing the volatile materials, and

recovering the resulting $ClO_2F_2^+AsF_6^-$ salt as a nonvolatile solid.

14. The method of claim 13 wherein said temperature at which AsF_5 is liquid is −78°C.

15. The method of claim 13 wherein said maintaining step is continued for approximately 30 minutes.

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United States Patent [19]

Christe et al.

[11] **3,922,336**

[45] **Nov. 25, 1975**

[54] **IODINE PERCHLORATES**

[75] Inventors: **Karl O. Christe, Calabasas; Carl J. Schack, Chatsworth, both of Calif.**

[73] Assignee: **The United states of America as represented by the Secretary of the Navy, Washington, D.C.**

[22] Filed: **Mar. 18, 1975**

[21] Appl. No.: **559,601**

Related U.S. Application Data

[62] Division of Ser. No. 363,708, May 24, 1973, Pat. No. 3,873,677.

[52] U.S. Cl. **423/466**; 423/462; 423/472; 423/500

[51] **Int. Cl.²**... **C01B 7/24**; C01B 7/02; C01B 11/18

[58] **Field of Search** 423/466, 462, 500, 472

[56] **References Cited**

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Primary Examiner—Edward Stern
Attorney, Agent, or Firm—R. S. Sciascia; J. A. Cooke

[57] **ABSTRACT**

Iodine perchlorates of the formula $X(OClO_3)_n$ wherein X is selected from the group consisting of I^{++}115 and CsI^{+4}, wherein n equals 3 when X is I^{+++} and n equals 4 when X is CsI^{+4}; are prepared by reacting $ClOClO_3$ with either solid I or CsI at low temperatures. The iodine perchlorates are useful as energetic oxidizers.

3 Claims, No Drawings

IODINE PERCHLORATES

This is a division of application Ser. No. 363,708, filed May 24, 1973, now U.S. Pat. No. 3,873,677, issued Mar. 25, 1975.

BACKGROUND OF THE INVENTION

This invention generally relates to perchlorate compounds and more particularly to iodine perchlorates.

The alleged preparation of iodine trisperchlorate from iodine, ozone, and anhydrous $HClO_4$ is described by M. Schmeisser in "Handbook of Preparative Inorganic Chemistry", G. Brauer, Ed., Academic Press, New York, N.Y., 1963, Vol. 1, pg. 330. However, a crosscheck with the original publication, F. Fichter and H. Kappeler, Z. Anorg. Allgem. Chem., 91, 134 (1915), reveals that the original paper deals only with a compound having the empirical composition, $I(ClO_4)_3 \cdot 2H_2O$. Further, from the properties of $I(OClO_3)_3$, it appears unlikely that the Fichter et al compound was the bishydrate of $I(OClO_3)_3$.

The bishydrate of iodine trisperchlorate, $I(OClO_3)_3 \cdot 2H_2O$, should be a less energetic oxidizer than the anhydrous form, and therefore would be less suitable for propellants. In view of this attempts have been made to obtain the bishydrate as well as the anhydrous material.

SUMMARY OF THE INVENTION

Accordingly, one object of this invention is to provide iodine perchlorates.

Another object of this invention is to isolate iodine perchlorates in their solid anhydrous form.

A further object of this invention is to provide iodine perchlorates which are highly energetic oxidizers.

A still further object of this invention is to provide a method of synthesizing iodine perchlorates.

Still another object of this invention is to achieve a high degree of purity in the iodine perchlorates synthesized.

Yet another object is to provide a easy means of purifying the iodine perchlorates.

These and other objects of this invention are accomplished by providing compounds which are iodine perchlorates of the formula $X(OClO_3)_n$ wherein X is selected from the group consisting of I^{++} and CsI^{++} wherein n equals 3 when X is I^{+++}, and n equals 4 when X is CsI^{++}. The iodine perchlorates are prepared by reacting chlorine perchlorate, $ClOClO_3$, with a substance selected from the group consisting of I_2 and CsI at low temperatures.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The iodine perchlorates of this invention are prepared by reacting chlorine perchlorate, $ClOClO_3$, with either iodine, I_2, or CsI. The reaction for preparing iodine trisperchlorate is as follows:

$$I_2 + 6ClOClO_3 \qquad 2I(OClO_3)_3 + 3Cl_2$$

and the reaction for preparing the cesium tetraperchlorato iodate is as follows: $Cs^+I^- + 4ClOClO_3$ $Cs^+I(OClO_3)^-_4 + 2Cl_2$.

The range of suitable reaction temperatures is limited by the slow reaction rates and the instability of the iodine perchlorate products. For example, the iodine trisperchlorate reaction takes 70 hours at −50°C and the cesium tetraperchlorato iodate reaction takes 5 weeks at −45°C to go to 99% completion and at lower temperatures the reaction takes still longer. On the other hand, while the $CsI(OClO_3)_4$ is stable at 23°C, iodine trisperchlorate rapidly decomposes, at this temperature.

Thus, the reaction temperature for producing $CsI(OClO_3)_4$ should be in the range −78°C to 30°C, preferably −55°C to −40°C; and the reaction temperature for producing iodine trisperchlorate should be in the range −78°C to 0°, preferably −55°C to −40°C.

Purification of the product is simplified by reacting a stoichiometric excess of chlorine perchlorate with iodine or cesium iodide in an inert environment. The excess of chlorine perchlorate is used to drive the reaction to 99% completion. Then the solid $I(OClO_3)_3$ or $CsI(OClO_3)_4$ product can be separated from the byproduct chlorine and unreacted chlorine perchlorate at low temperatures under vacuum. Finally, since water is neither a reactant nor a product in either of the reactions, the anhydrous form of $I(OClO_3)_3$ or $CsI(OClO_3)_4$ is obtained when the reaction is run in an anhydrous environment. Additionally, because of the reactivity of the desired perchlorates it is most desirable to conduct the reactions in an inert environment which, within the context of this invention, is meant to include anhydrous conditions.

The general nature of the invention having been set forth, the following examples are presented as specific illustrations thereof. It will be understood that the invention is not limited to these specific examples but is susceptible to various modifications that will be recognized by one of ordinary skill in the art.

EXAMPLE 1

Iodine Trisperchlorate

$I(OClO_3)_3$

Iodine (0.915 mmol) was loaded into a 10 ml prepassivated Teflon FEP ampoule closed off by a stainless steel valve. Chlorine perchlorate (8.18 mmol) was added at −196°C. The ampoule was kept at −50°C for 70 hours. At this point, the dark iodine color had disappeared and a pale yellow (due to the presence of Cl_2) solid had formed. Upon cooling to −196°C, the ampoule did not contain any non-condensible reaction products. The ampoule was slowly warmed to −45°C. The volatile products were separated by fractional condensation and identified by infrared spectroscopy and their vapor pressure. They consisted of Cl_2 (2.70 mmol) and $ClOClO_3$ (2.74 mmol). The white, solid residue weighed 776 mg., in excellent agreement with the weight (777 mg) calculated for a complete conversion to $I(OClO_3)_3$.

EXAMPLE 2

Cesium Tetraperchlorato Iodate (III)

$CsI(OClO_3)_4$

A 10 ml prepassivated stainless steel cylinder was loaded with powdered anhydrous CsI (1.15 mmol), followed by $ClOClO_3$ (6.10 mmol) at −196°C. The reaction was allowed to proceed by warming the cylinder to −45°C, where it was maintained for five weeks. On recooling to −196°C, no non-condensible gases were observed. Volatile products were pumped from the reactor for several hours while and after it had warmed to ambient temperature. Separation of these species was affected by fractional condensation and identification by infrared and vapor pressure measurements. They consisted of Cl_2 (2.34 mmol) and unreacted $ClOClO_3$ (1.45mmol). The solid product was pale yellow in color and weighed 749 mg, indicating a 99% conversion of the CsI to $Cs^+I(OClO_3)_4^-$ had occurred.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described herein.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A method of preparing anhydrous iodine trisperchlorate, $I(OClO_3)_3$, comprising:

contacting in an inert environment chlorine perchlorate and iodine at a temperature in the range of −78°C to 0°C for 70 or more hours, provided that at least 6 moles of chlorine perchlorate are used per mole of iodine, I_2, to form said iodine trisperchlorate and subsequently recovering the iodine trisperchlorate.

2. The method of claim 1, wherein said contacting is performed at a temperature of −55°C to −40°C.

3. The method of claim 1, wherein more than 6 moles of said chlorine perchlorate is used per mole of iodine, I_2.

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United States Patent [19]
Christe

[11] **3,987,152**
[45] **Oct. 19, 1976**

[54] STABLE UNSUBSTITUTED SULFONIUM SALTS

[75] Inventor: **Karl O. Christe**, Calabasas, Calif.

[73] Assignee: **Rockwell International Corporation**, El Segundo, Calif.

[22] Filed: **Aug. 28, 1975**

[21] Appl. No.: **608,601**

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[51] **Int. Cl.^{2}** **C01B 17/45**
[58] **Field of Search** 423/467, 511, 563, 644

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Primary Examiner—Jack Cooper
Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

A stable unsubstituted sulfonium salt and method of isolating same.

2 Claims, No Drawings

STABLE UNSUBSTITUTED SULFONIUM SALTS

The invention herein described was made in the course of or under a contract of subcontract thereunder, (or grant) with the Department of the Navy.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to compositions of matter and is particularly directed to stable unsubstituted sulfonium salts and methods of isolating same.

2. Description of the Prior Art

Hydrogen sulfide has been found to be extremely useful as a reagent in forming numerous chemical compounds. However, the storage of hydrogen sulfide is hazardous due to its extreme toxicity and high volatility. Numerous attempts have been made to overcome these problems or to avoid such problems by providing a source of hydrogen sulfide which would not be subject to these problems, but which could be actuated, as desired, to supply the needed hydrogen sulfide. However, none of the prior art techniques have been entirely satisfactory. Thus, it has been known that the foregoing problems could be somewhat alleviated by using iron sulfide and, when desired, reacting this with hydrochloric acid to generate hydrogen sulfide. While this technique is effective, it still involves handling and storage of a highly corrosive acid.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

These disadvantages of the prior art are overcome with the present invention and a novel technique is provided for producing hydrogen sulfide while avoiding the problems of the prior art as set forth above. The advantages of the present invention are obtained by producing stable, solid, unsubstituted sulfonium salts which, when mixed with water, react to release hydrogen sulfide.

Stable alkyl sulfonium salts have been known heretofore and are very important, in industry, as detergents, etc. However, unsubstituted sulfonium salts have only been previously known to exist at low temperatures, of the order of −30° C, and in super-acid solutions, such as fluorosulfonic acid. Many papers have referred to sulfonium salts in solution. However, none of the prior art has suggested how these salts could be isolated. In contrast, Applicant has discovered a simple method for isolating stable solid unsubstituted sulfonium salts by protonation of H_2S in $HF + SbF_5$.

Accordingly, it is an object of the present invention to provide an improved technique for generating hydrogen sulfide.

Another object of the present invention is to provide a method of generating hydrogen sulfide which does not involve storage or handling of hazardous materials.

An additional object of the present invention is to provide stable solid unsubstituted sulfonium salts.

A further object of the present invention is to provide a method for producing stable solid unsubstituted sulfonium salts.

A specific object of the present invention is to provide a method of producing stable solid unsubstituted sulfonium salts by protonation of H_2S in $HF + SbF_5$.

These and other objects and features of the present invention will be apparent from the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

In that form of the present invention chosen for purposes of illustration, protonation of hydrogen sulfide in HF-SbF_5 will produce a stable solid unsubstituted sulfonium salt.

EXAMPLE

5.38 mmol of SbF_5 and 10 ml of liquid anhydrous HF were combined at −196° C in a Teflon ampule. The mixture was warmed to 25° C to given a homogenous solution. Thereafter, the solution was cooled to −196° C and 7.10 mmol of hydrogen sulfide was added. The mixture was warmed to −78° C, then slowly to 25° C. During the warm-up, a white solid formed, which was only partially soluble in the excess of HF. The volatile products were removed at 25° C in vacuo, leaving 1.452g of a white stable solid. The calculated weight for 5.38 mmol of $SH_3^+SbF_6^-$ is 1.457g. Moreover, the calculated microanalytical values for SH_3SbF_6 are Sb 44.95 and S 11.85 while the values obtained by measurement of the white solid are Sb 44.8 and S 11.9. Accordingly, it is concluded that the white solid is $SH_3^+SbF_6^-$. It was found that this material can be stored indefinitely at 25° C in Teflon containers.

To use the sulfonium salts to generate hydrogen sulfide, it has been found that the sulfonium salts react with water according to the formula:

$$SH_3^+SbF_6^- + H_2O \rightarrow H_3O^+SbF_6^- + H_2S\uparrow$$

Thus, the sulfonium salt can be stored safely as a stable solid and, when desired, can be combined with water to release H_2S.

Obviously, numerous variations and modifications can be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illustrative only and are not intended to limit the scope of the present invention.

What is claimed is:

1. An unsubstituted sulfonium salt having the formula $SH_3^+SbF_6^-$ which is a solid that is stable at 25° C.

2. The method of producing $SH_3^+SbF_6^-$ consisting of the steps of:

forming a homogenous mixture of SbF_5 and liquid anhydrous HF,

cooling said mixture to −196° C,

adding hydrogen sulfide, and

gradually warming the resulting mixture until a white solid is formed.

* * * * *

United States Patent [19]

Schack et al.

[11] **4,012,492**

[45] **Mar. 15, 1977**

[54] **SYNTHESIS OF ANHYDROUS METAL PERCHLORATES**

[75] Inventors: **Carl J. Schack**, Chatsworth; **Donald Pilipovich**, Agoura, both of Calif.

[73] Assignee: **The United States of America as represented by the Secretary of the** Navy, Washington, D.C.

[22] Filed: **June 10, 1975**

[21] Appl. No.: **585,549**

[52] **U.S. Cl.** **423/472;** 423/476; 423/500

[51] **Int. Cl.^{2}** **C01B 7/02;** C01B 11/00; C01G 23/00; C01G 37/00; C01G 31/00

[58] **Field of Search** 423/476, 472, 500

[56] **References Cited**

UNITED STATES PATENTS

3,075,827	1/1963	Cretzmeyer	423/476
3,102,784	9/1963	Gale	423/476
3,151,935	10/1964	Hoekje et al.	423/476 X
3,157,464	11/1964	Laran	423/476
3,615,179	10/1971	Rosenberg	423/476
3,694,172	9/1972	Schack et al.	423/472 X
3,873,677	3/1975	Christe et al.	423/472 X
3,922,336	11/1975	Christe et al.	423/500 X

Primary Examiner—Edward Stern
Attorney, Agent, or Firm—R. S. Sciascia; Philip Schneider; Thomas McDonnell

[57] **ABSTRACT**

Preparation of titanium tetraperchlorate, vanadium perchlorate, and chromyl perchlorate by the reactions of chlorine perchlorate with the respective anhydrous metal chlorides at a temperature from about −45° C to about 20° C. These perchlorates are useful in compounding gas generating compositions.

5 Claims, No Drawings

SYNTHESIS OF ANHYDROUS METAL PERCHLORATES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention pertains to the preparation of inorganic oxidizing salts and in particular to the preparation of anhydrous metal perchlorates.

2. Prior Art

Syntheses of anhydrous metal perchlorates have been restricted mainly to metals from Groups I and II. A few preparations have been reported for transition metal perchlorates as well as NO_2^+ and NH_4^+ complex perchlorates.

One method is known for the preparation of anhydrous titanium tetraperchlorate. This method proceeds by the reaction of anhydrous perchloric acid with anhydrous titanium tetrachloride. However the product is not pure as is evidenced by the data presented pertaining to the melting point, analysis, stability, yield, and polycrystalline form. A major disadvantage of the impurities in the product is the necessity of refrigeration. Other disadvantages of this synthesis are the scarcity, expense, and danger of anhydrous perchloric acid.

The known method for the preparation of chromyl perchlorate is through the reaction of chromyl chloride and dichlorine hexoxide. Although the reaction product is pure, the synthesis has the disadvantages which result from the scarcity, expense, and danger of anhydrous dichlorine hexoxide.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to form anhydrous metal perchlorates safely, quickly, and inexpensively.

Another object of this invention is to form anhydrous metal perchlorates in a high degree of purity.

These and other objects are achieved by a method which proceeds by the following reactions:

$$CrO_2Cl_2 + 2Cl_2O_4 \rightarrow 2Cl_2 + CrO_2(ClO_4)_2$$

$$TiCl_4 + 4Cl_2O_4 \rightarrow 4Cl_2 + Ti(ClO_4)_4$$

$$VOCl_3 + 3Cl_2O_4 \rightarrow VO(ClO_4)_3 + 3Cl_2$$

and which occur at a temperature from −45° C to 20° C.

DETAILED DESCRIPTION OF THE INVENTION

Due to the strong oxidizing strength of the perchlorate group the method of the invention must proceed in vessels constructed from stainless steel, platinum, teflon, monel or similar non-oxidizable materials or coated therewith. The reaction is carried out at ambient pressure and at a temperature from about −45° C to about 20° C but preferably from −25° C to 0° C. Stirring is optional because the bubbling of the by-product chlorine through the reaction solution provides sufficient agitation. Completion of the reaction is determined preferably by monitoring the chlorine gas by-product. Generally the reaction is complete within 4 to 6 hours and the perchlorate product may then be collected.

Preferably, chlorine perchlorate is prepared by the method disclosed in U.S. Pat. No. 3,694,172 by Schack et al.

The reactants are added in stoichiometric amounts. Thus for the synthesis of chromyl perchlorate the reactants are added in a CrO_2Cl_2-to-Cl_2O_4 mole ratio of 1:2. For the synthesis of vanadium perchlorate, the reactants are added in a $VOCl_3$-to-Cl_2O_4 mole ratio of 1:3. It is preferred that an extra 5 to 10 mole percent of Cl_2O_4 is added in order to decrease the reaction time. Since water produces impurities in the perchlorate product, the reactants and the system should be anhydrous.

The reactants may be added in any order or in any rate. However the reactions are exothermic; so, measures must be taken to ensure that reaction temperature does not exceed about 20° C. According to a preferred embodiment of this invention the reactants are added to the reaction vessel in the solid state, thereby minimizing the vapors of the reactants.

This embodiment is utilized in Example I given hereinafter. It is understood that the examples are given by way of illustration and are not intended to limit the disclosure or the claims to follow in any way.

EXAMPLE I

Titanium tetrachloride (1.22 mmol) and $ClOClO_3$ (6.01 mmol) were combined at −196° in a 75 ml stainless steel cylinder and then gradually warmed to −25°. After several days, recooling to −196° showed no noncondensable gases were present. The contents of the reactor were separated by fractional condensation in a series of U-traps cooled to −78°, −112°, and −196°. Nothing was trapped at −78° while the −112° fraction consisted solely of unreacted Cl_2O_4 (1.17 mmol), and the −196° fraction was Cl_2 (4.88 mmol). The pale yellow solid residue left in the reactor weighed 0.525 g. The weight calculated for 1.22 mmol of $Ti(ClO_4)_4$ was 0.544 g and therefore the yield of $Ti(ClO_4)$ was 97 percent. Vacuum sublimation of the $Ti(ClO_4)_4$ was carried out in a Pyrex apparatus at 50°-60° using a −78° cold finger. The sublimed material was nearly colorless and had a m.p. with dec. of 101°-2°. Almost no residue remained unsublimed. Anal. Calcd. for $Ti(ClO_4)_4$: Ti, 10.75; ClO_4, 89.25. Found: Ti, 10.8; ClO_4, 87.9. A sample of $Ti(ClO_4)_4$ (0.242 mmol) was heated in a stainless steel cylinder for 4 hours at 115° followed by 1.5 hr. at 190°. This produced O_2 (1.705 mmol), Cl_2 (0.481 mmol), and a white solid residue of TiO_2 (0.241 mmol). All temperatures are in degrees Centigrade.

EXAMPLE II

Chromyl chloride (1.41 mmol) and $ClOClO_3$ (3.16 mmol) were reacted at −45° for several days in a stainless steel cylinder. After separation and identification, the volatile products found were CrO_2F_2 (0.18 mmol), Cl_2 (2.59 mmol), and Cl_2O_4 (0.66 mmol). The $CrO_2(ClO_4)_2$ (1.23 mmol) remained in the cylinder. The CrO_2F_2 probably arose through reaction of CrO_2Cl_2 with the ClF_3 passivated metal surfaces in the reactor and/or vacuum line during transfers. Anal., Calcd. for $CrO_2(ClO_4)_2$: ClO_4, 70.3. Found: ClO_4, 69.6. A sample of $CrO_2(ClO_4)_2$ (0.65 mmol) was pyrolyzed for 15 hrs at 110° producing Cl_2 (0.66 mmol), O_2 (2.21 mmol) and CrO_3 (0.65 mmol), m.p. 195°-7°, lit. 196°. All temperatures are in degrees Centigrade.

As can be seen from the examples, the method of this invention produces a highly pure anhydrous metal perchlorate without the use of the scarce and dangerous anhydrous perchloric acid or dichlorine hexoxide. The anhydrous titanium perchlorate has been stored at room temperature for over three months without degradation.

Obviously many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed and desired to be secured by Letters Patent of the United States is:

1. A method of preparing an anhydrous metal perchlorate which comprises admixing for at least 4 hours at a temperature from −45° C to 20° C an anhydrous metal chloride selected from the class consisting of titanium tetrachloride, chromyl chloride, and vanadium oxytrichloride with chlorine perchlorate in a metal chloride-to-chlorine perchlorate mole ratio which is 1:4 if titanium tetrachloride is selected, or is 1:2 if chromyl chloride is selected, or is 1:3 if vanadium oxytrichloride is selected, and recovering said anhydrous metal perchlorate.

2. A method of preparing an anhydrous metal perchlorate which comprises admixing for at least 4 hours at a temperature from −45° C to 20° C an anhydrous metal chloride selected from the class consisting of titanium tetrachloride, chromyl chloride, and vanadium oxytrichloride with chlorine perchlorate in a metal chloride-to-chlorine perchlorate mole ratio which is from 1:4.2 to 1:4.4 if titanium tetrachloride is selected, or is from 1:2.1 to 1:2.2 if chromyl chloride is selected, or is from 1:3.15 to 1:3.3 if vanadium oxytrichloride is selected, and recovering said anhydrous metal perchlorate.

3. The method of claim 2 wherein said anhydrous metal chloride is titanium chloride.

4. The method of claim 2 wherein said anhydrous metal chloride is chromyl chloride.

5. The method of claim 2 wherein said anhydrous metal chloride is vanadium oxytrichloride.

* * * * *

United States Patent [19]

Schack

[11] **4,026,996**

[45] **May 31, 1977**

[54] **SYNTHESIS OF NITRYL PERCHLORATE**

[75] Inventor: **Carl J. Schack, Chatsworth, Calif.**

[73] Assignee: **Rockwell International Corporation,**
El Segundo, Calif.

[22] Filed: **May 28, 1974**

[21] Appl. No.: **474,130**

[52] U.S. Cl. **423/386**
[51] **Int. Cl.^{2}** **C01B 21/52**
[58] **Field of Search** 423/386, 476; 149/74,
149/75

[56] **References Cited**

UNITED STATES PATENTS

3,186,790	6/1965	Brown et al.	423/386
3,558,456	1/1971	Lakritz	423/386 X

Primary Examiner—Earl C. Thomas
Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

An improved method of synthesizing nitryl perchlorate by oxidizing chlorine nitrate with ozone.

2 Claims, No Drawings

SYNTHESIS OF NITRYL PERCHLORATE

The invention herein described was made in the course of or under a contact or subcontract thereunder, (or grant) with the Department of the U.S. Navy.

BACKGROUND

1. Field of the Invention

This invention relates to solid oxidizers and is particularly directed to methods of producing nitryl perchlorate.

2. Prior Art

Nitryl perchlorate, $No_2^+ClO_4^-$, has been known for many years as a powerful oxidizer. Heretofore, the conventional method of producing nitryl perchlorate has required the reaction of chlorine dioxide, ClO_2, with nitrogen dioxide, NO_2, and ozone, O_3. Unfortunately, chlorine dioxide, in either the gaseous or liquid state, tends to explode for no apparent reason. Consequently, any operation which involves chlorine dioxide is hazardous to people, buildings and equipment.

SUMMARY OF THE INVENTION

These disadvantages of the prior art are overcome with the present invention and an improved method of producing nitryl perchlorate is provided which eliminates the use of chlorine dioxide, with its attendant hazards, yet provides good yields and easy purification.

The advantages of the present invention are preferably attained by providing a method of producing nitryl perchlorate by reacting chlorine nitrate, $ClNO_3$, with ozone.

Accordingly, it is an object of the present invention to provide improved methods of producing oxidizers.

Another object of the present invention is to provide an improved method of producing nitryl perchlorate.

An additional object of the present invention is to provide a safer method of producing nitryl perchlorate.

A further object of the present invention is to provide a method of producing nitryl perchlorate without the use of chlorine dioxide.

A specific object of the present invention is to provide a method of producing nitryl perchlorate by reacting chlorine nitrate with ozone.

These and other objects and features of the present invention will be apparent from the following detailed description.

DETAILED DESCRIPTION OF INVENTION

In that form of the present invention chosen for illustration, a method of producing nitryl perchlorate is proposed which calls for reacting chlorine nitrate with ozone. It should be understood that, as used herein, the terms "nitryl perchlorate" and "nitronium perchlorate" are synonymous.

Chlorine nitrate is a liquid which boils at 22° C and is easily prepared, following the teachings of U.S. Pat. No. 3,472,635, assigned to the present assignee. Chlorine nitrate is not hazardous and is relatively insensitive to physical shock.

Although chlorine nitrate is well-known, the reaction of the present invention is unexpected. Conventionally, ClO—X compounds react with ozone to give chloryl species; such as

$$ClOClO_3 + 2O_3 \rightarrow O_3ClOClO_3 + 2O_2 \quad (1)$$

$$ClSO_3F + 2O_3 \rightarrow O_3ClOSO_2F + 2O_2 \quad (2)$$

or it does not react at all, as in

$$CF_3OCl + O_3 \rightarrow \text{No reaction} \quad (3)$$

The reaction of the present invention is

$$ClONO_2 +_3 \rightarrow NO_2^+CLO_4^- + 3O_2$$

This reaction has been observed to occur readily at temperatures as low as -78° C, in the presence of an inert fluorocarbon solvent, CF_3Cl, and at temperatures ranging from -45° C to ambient without a solvent. Conversions, using this method, have been as high as 89% and yields have been 100%. Moreover, the reactants, chlorine nitrate and ozone, and the by-product, oxygen, are gases; whereas the nitryl perchlorate is a solid. Consequently, purification is simple and the gases may be recovered and recycled.

EXAMPLE I

Chlorine nitrate (24.2 cm³, 1.08 mmol) and CF_3Cl solvent (approximately 250 cm³), were condensed into a 30 ml. stainless steel cylinder cooled to -196° C in a liquid nitrogen bath. Following that, ozone (72.6 cm³, 3.24 mmol) was also condensed in at -196° C and the closed cylinder was warmed to and maintained at -45° C. After 42 hrs. the reaction cylinder was recooled to -196° C and the oxygen that had formed was measured (53.4 cm³, 2.38 mmol) and pumped away. On warming the reaction to room temperature, the remaining products were separated by fractional condensation in U-traps cooled to -78°, -112°, and -196° C. Unreacted chlorine nitrate (7.6 cm³, 0.34 mmol) was retained at -112° C. Unreacted ozone and the CF_3Cl solvent were trapped at -196° C. There remained in the cylinder, the white solid, nitryl perchlorate (107 mg, 0.74 mmol) which was readily dentified by its infrared spectrum and comparison to an authentic sample. The conversion of $ClNO_3$ to $NO_2^+ClO_4^-$ was 68.6% and the yield of $NO_2^+ClO_4^-$ based on the material reacted was essentially quantitative.

EXAMPLE II

A 30-ml. stainless steel cylinder was loaded successively with $ClNO_3$(23.2 cm³, 1.03 mmol), CF_3Cl (approximately 480 cm³), and O_3 (90.5 cm³, 4.04 mmol) by condensing them in at -196° C. The reaction was allowed to proceed at -45° C for 72 hrs. At that time the oxygen now present was measured (106 cm³, 4.73 mmol) and pumped away followed by all the other volatile materials. There remained in the cylinder the white solid $No_2^+ClO_4^-$ (133 mg, 0.92 mmol). The yield of nitryl perchlorate was 89%.

EXAMPLE III

Chlorine nitrate (16.4 cm³, 0.73 mmol) and ozone (61.6 cm³, 2.75 mmol) were separately condensed into a 30 ml. stainless steel cylinder cooled to -196° C in a liquid nitrogen bath. The cylinder was then kept at -45° C for 66 hrs. The products were separated by fractional condensation in a series of U-traps cooled to -78° C, -112°, and -196° C after removal of the by-product O_2 (49.2 cm³, 2.20 mmol). Unreacted chlorine nitrate (7.8 cm³, 0.35 mmol) and ozone (20.2 cm³, 0.90 mmol) were the only other volatile species found. The solid product nitryl perchlorate (57 mg, 0.39 mmol) remained in the cylinder and was identified by its infrared spectrum. The conversion of $ClNO_3$ to $NO_2^+ClO_4^-$ was

53% and the yield based on the converted material was nearly quantitative.

EXAMPLE IV

Chlorine nitrate (20.4 cm^3, 0.91 mmol), CF$_3$Cl (approximately 300 cm^3) and ozone (72.0 cm^3, 3.21 mmol) were condensed successively into a 30 ml. stainless steel cylinder cooled to -196° C. The closed cylinder was allowed to warm to ambient temperature, approximately 20° C, for 4 hours. The volatile materials were then pumped out of the cylinder leaving behind the white solid, nitryl perchlorate (111 mg, 0.76 mmol). The yield of $NO_2^+ClO_4^-$ was 84%.

EXAMPLE V

A 30 ml stainless steel cylinder was charged with $ClNO_3$ (24.6 cm^3, 1.10 mmol), CF$_3$Cl (approximately 250 cm^3), and O_3 (85.2 cm^3, 3.80 mmol) by condensing them in at -196° C. The reaction was allowed to proceed at -78° C for 45 hours. By-product $_2$ (23.8 cm^3, 1.06 mmol) was then measured and removed. Other volatile species were separated by fractional condensation. Unreacted $ClNO_3$ (17.5 cm^3, 0.78 mmol) was recovered and the solid nitryl perchlorate formed was 45 mg, 0.31 mmol. The conversion of $ClNO_3$ to $NO_2^+ClO_4^-$ was 28% and the yield based on the converted material was nearly quantitative.

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illustrative only and are not intended to limit the scope of the present invention.

What is claimed is:

1. The method of synthesizing nitryl perchlorate comprising the step of:

combining chlorine nitrate and ozone in the presence of an inert fluorocarbon solvent at a temperature in the range from about −78° C to about ambient.

2. The method of claim 1 wherein:

said conbining step is performed in the presence of CF$_3$Cl.

* * * * *

United States Patent [19]

Christe

[11] **4,038,374**

[45] **July 26, 1977**

[54] STABLE CHLORINE TRIFLUORIDE DIOXIDE

[75] Inventor: **Karl O. Christe**, Calabasas, Calif.

[73] Assignee: **Rockwell International Corporation**,
El Segundo, Calif.

[21] Appl. No.: **714,458**

[22] Filed: **Aug. 16, 1976**

Related U.S. Application Data

[60] Continuation-in-part of Ser. No. 329,773, Dec. 5, 1974, abandoned, which is a division of Ser. No. 290,031, Sept. 18, 1972, Pat. No. 3,873,676.

[51] **Int. Cl.**^{2} **C01B 7/24**
[52] **U.S. Cl.** **423/466**; 423/462; 149/1
[58] **Field of Search** 423/462, 466

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,285,842	11/1966	Grosse et al.	423/466 UX
3,320,031	5/1967	Grosse et al.	423/466
3,873,676	3/1975	Christe	423/466

OTHER PUBLICATIONS

Inorg. Nucl. Chem. Letters, vol. 8 (May 1972), No. 5, pp. 453, 454, 455, Pergamon Press, Printed in Gt. Britain.

Primary Examiner—Edward Stern
Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

Chlorine trifluoride dioxide is disclosed for use as an oxidizer in formulating energetic compositions, such as propellants. The stable ClF_3O_2 is produced by reacting a $ClO_2F_2^+$ salt with a strong Lewis base at −78° C.

1 Claim, No Drawings

UNITED STATES PATENT AND TRADEMARK OFFICE

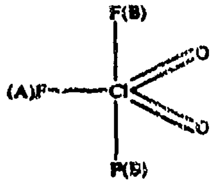
CERTIFICATE OF CORRECTION

Page 1 of 3

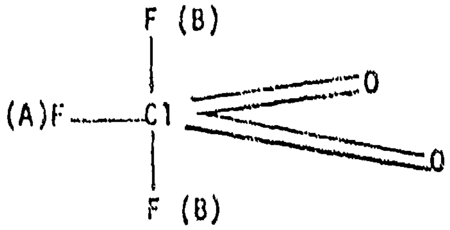
PATENT NO. : 4,038,374
DATED : July 26, 1977
INVENTOR(S) : Karl O. Christe

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 28, delete "agnet" and insert --agent--.
Column 1, line 52, delete "-71°C" and insert -- -72°C--.
Column 2, line 6, delete "$ClF_2O_2+PtF_6-$" and insert --$ClF_2O_2^+PtF_6^-$ --;
line 6, delete "lewis" and insert --Lewis--.
line 28, delete "ClF_2O_2+" and insert --$ClF_2O_2^+$--.
line 29, delete "$ClF_2O_2+PtF_6-$" and insert --$ClF_2O_2^+PtF_6^-$--.
line 33, delete "ClO_2+PtF_6-" and insert --$ClO_2^+PtF_6^-$--.
line 34, delete "$ClF_2O_2+PtF_6-$" and insert --$ClF_2O_2^+PtF_6^-$--.
line 41, delete "ClF" and insert --ClF--.
lines 46 to 54, the right-hand side of the formula should appear as:



double bond lines
should read



line 54, after "nuclear" insert --magnetic--.
Column 3, line 3, delete "ClF_3O_2" and insert --ClF_3O_2--.
lines 17 and 18, delete "$NO+PtF_6-$" and insert --$NO^+PtF_6^-$--.
line 25, delete "$ClF\cdot O_2F_2$" and insert --$ClF\cdot O_2F_2$--;
line 25, delete "$ClF_3\cdot\ O_2$" and insert --$ClF_3\cdot O_2$--.
line 27, delete "ClF_3O_2" and insert --ClF_3O_2--.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 4,038,374 (continued) Page 2 of 3

DATED July 26, 1977

INVENTOR(S) Karl O. Christe

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 29, delete "CIO_2+PtF_6-" and insert --$ClO_2^+PtF_6^-$ --;
line 29, after "of" delete "CI" and insert --Cl--.
line 30, delete "$O_2F_2+PtF_6-$" and insert --$O_2F_2^+PtF_6^-$ --.
line 33, delete "NO_2+PtF_3-" and insert --$NO_2^+PtF_6^-$ --;
line 33, delete "CIF_3O_2" and insert --ClF_3O_2--.
line 33, delete "$FCIO_2$" and insert --$FClO_2$--.
line 38, delete "CIF_3O_2" and insert --ClF_3O_2--;
line 38, delete "$FCIO_2$" and insert --$FClO_2$--.
line 40, delete "CIF-" and insert --ClF- --.
line 41, delete "${}_2O_2+BF_4-$" and insert --${}_2O_2^+BF_4^-$ --;
line 41, delete "CIO_2+BF_4-" and insert --$ClO_2^+BF_4^-$ --.
Column 4, line 1, delete "180" and insert --182--.
line 2, delete "$CIF_2O_2+BF_4-$" and insert --$ClF_2O_2^+BF_4^-$ --.
line 5, delete "NO_2+BF_4-" and insert --$NO_2^+BF_4^-$ --;
line 5, delete "CIF_3O_2" and insert --ClF_3O_2--.
line 17, delete "comprising" and insert --consisting--.
line 18, delete "CIF_3O_2" and insert --ClF_3O_2--.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 4,038,374 (continued) Page 3 of 3

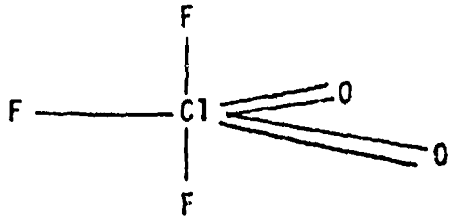
DATED : July 26, 1977

INVENTOR(S) : Karl O. Christe

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, lines 21 to 25,

should read



line 38, delete "-21 C" and insert -- -21°C--.

Signed and Sealed this

Twenty-second **Day of** *November 1977*

Attest:

Ruth C. Mason

RUTH C. MASON
Attesting Officer

Lutrelle F. Parker

LUTRELLE F. PARKER
Acting Commissioner of Patents and Trademarks

STABLE CHLORINE TRIFLUORIDE DIOXIDE

The invention herein described was made in the course of or under a contract with the Department of Navy.

CROSS-REFERENCE TO RELATED APPLICATIONS

The application is a continuation-in-part of Ser. No. 529,773 filed, Dec. 5, 1974, now abandoned, and which was a division of Ser. No. 290,031, filed Sept. 18, 1972, and issued Mar. 25, 1975, as U.S. Pat. No. 3,873,676.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to compositions of matter and is particularly directed to chlorine trifluoride dioxide and a method of producing the same.

2. Prior Art

Energetic compositions of matter are useful in providing energy sources for rocket engines, guided missiles, auxiliary power units for aircraft, ordnance, demolition and the like. Such compositions conventionally are produced by mixing a fuel with an oxidizer. Obviously, the energy of such compositions results primarily from the oxidation of the fuel. Hence, it is desirable to provide a highly energetic oxidizing agnet. On the other hand, it is equally desirable that the oxidizing agent be a stable material, so as to prevent accidental or unintentional ignition or explosive decomposition of the composition. Numerous organic and inorganic compounds have been proposed heretofore for use as such oxidizing agents. However, it has been found that, as a general rule, stable compounds are low energy oxidizers and high energy oxidizers are unstable. Thus, although some useful oxidizing agents have been disclosed by the prior art, the search for a stable, high-energy, oxidizing material has continued. In recent years, studies have indicated that halogen oxyfluoride materials might provide a satisfactory oxidizing material. However, although empirical formulas may be stated for such materials and some of the properties of such materials may be predicted, the synthesis of these materials has proven to be extremely difficult and it is sometimes found that several materials, each having distinct structures and properties, are defined by a single empirical formula. Thus, U.S. Pat. No. 3,285,842 discloses a process for producing a material which was believed to have the empirical formula chlorine trifluride dioxide, ClF_3O_2, which the patent states to be a violet liquid which is unstable at tempertures above −71° C. It was subsequently shown, however, that this composition does not contain the chemical compound ClF_3O_2, but consists of a mixture of chlorine fluorides and oxygen fluorides (K. O. Christe, R. D. Wilson, and I. B. Goldberg, J. Fluor-Chem., 7,543 (1976). This fact readily explains the great difference in physical and chemical properties between the composition and the novel composition disclosed in this invention. While it would be expected that the previously claimed composition would also be a highly energetic oxidizing agent, the lack of stability renders it unsafe for use in the production of propellants and the like.

Brief Summary and Objects of Invention

These disadvantages of the prior art are overcome with the present invention and a composition of matter is disclosed which based on its chemical structure truly is chlorine trifluride dioxide. It is sufficiently stable at +25° C and, hence, can be safely employed for manufacturing propellants and the like. In addition, a method is disclosed for producing chlorine trifluoride dioxide by reacting $ClF_2O_2^+ PtF_6^-$ with a strong lewis base at a temprature of about −78° C and separating the products of the reaction by distillation.

Accordingly, it is an object of the present invention to provide a new composition of matter having the chemical composition ClF_3O_2.

An additional object of the present invention is to provide a method of producing chlorine trifluoride dioxide.

A specific object of the present invention is to provide chlorine trifluoride dioxide by reacting $ClF_2O_2^+$ salts with nitryl fluoride at a temperature of about −78° C and separating the products of the reaction by distillation.

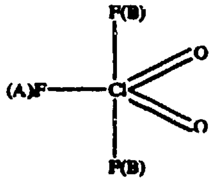
These and other objects and features of the present invention will be apparent from the following detailed description.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In that form of the present invention chosen for purposes of illustration, chlorine trifluoride dioxide has been produced by reacting a $ClF_2O_2^+$ salt, such as $ClF_2O_2^+PtF_6^-$, with a strong Lewis base at −78° C.

EXAMPLE 1

A sample of $ClO_2^+PtF_6^-$ containing about 10% of $ClF_2O_2^+PtF_6^-$ was treated at −78° C in a sapphire reactor with a large excess of FNO for several days. No material noncondensible at −196° C (i.e., F_2) was observed. The products, volatile at 25° C were removed and separated by fractional condensation through a series of traps kept at −126° C, −142° C, and −196° C. The −142° C fraction contained a novel compound which was identified by its infrared spectrum as ClF_3O_2. The observed frequencies are listed in Table 1 and are in excellent agreement with those expected for a trigonal bypyramidal structure of symmetry C_{2v}.



This structure was confirmed by ^{19}F nuclear resonance spectroscopy. The observed signal consisted of a typical AB_2 pattern centered at −413 ppm relative to the external standard $CFCl_3$. The F-F coupling constant was measured to be 443 Hz. The B_2 part of the AB_2 pattern occurs downfield from the A part, proving that the B_2 fluorine atoms occupy the two axial positions. Additional structural proof was obtained from the Raman spectrum of the gas and the liquid showing strong absorptions at 1096, 684, 548, 527, 493, 290, and 229 cm^{-1}. The molecular weight of the compound was confirmed by vapor density measurements (measured, 122; calculated, 124). These data establish beyond doubt (see K.O. Christe and R.D. Wilson, Inorg. Chem., 12, 1356 (1973) and K.O. Christe and E.C. Curtis, Inorg. Chem. 12, 2245 (1973) that contrary to the previous claim (U.S.P. 3,285,842) our novel composition has indeed the chemical composition ClF_3O_2.

Table I

Infrared Spectrum of ClF_3O_2 and its Tentative Assignment		
Frequency (cm^{-1})	Intensity	Assignment for Point Group C_{2v}
1334	s	$\nu_{10}(B_2)$, νasClO_2
1096	s	$\nu_1(A_1)$, νsymClO_2
699	vs	$\nu_7(B_1)$, νasClF_2Ax
687	vs	$\nu_2(A_1)$, νClF
598	ms	$\nu_{11}(B_2)$, δrock ClO_2
543)		
532)	mw	$\nu_3(A_1)$ and $\nu_8(B_1)$

The solid residue obtained from the FNO displacement reaction showed the correct weight change expected for conversion into $NO^+PtF_6^-$. Its identity as $NO^+PtF_6^-$ was confirmed by infrared spectroscopy.

The chlorine trifluoride dioxide is white as a solid having a melting point of about −81.2° C and colorless as a liquid having a boiling point of about −21° C. It is marginally stable at 25° C. The observed stability and lack of color furthermore demonstrate that our product cannot be identical with the previously reported deeply violet and unstable $ClF.O_2F_2$ and ClF_3. O_2 addition compounds supposedly having the empirical composition ClF_3O_2.

EXAMPLE II

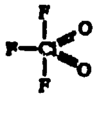
A sample $ClO_2^+PtF_6^-$ containing about 10% of $ClO_2F_2^+PtF_6^-$ was treated with a sufficient quantity of FNO_2 to maintain a liquid phase at −78° C in a stainless steel reactor up to 12 hours. This reaction yielded solid $NO_2^+PtF_3^-$ and gaseous ClF_3O_2 plus $FClO_2$. If desired, the chlorine trifluoride dioxide may then be separated by conventional distillation techniques, as in a multiplate distillation tower.

Small amounts of material were purified by combining the ClF_3O_2 and $FClO_2$ at −196° C with a small excess of BF_3. These materials were allowed to mix and warm to ambient temperature. This results in $ClF_2O_2^+BF_4^-$, which is stable, plus $ClO_2^+BF_4^-$, which has a dissociation pressure of 180 millimeters at 22° C and which can be removed by pumping. The $ClF_2O_2^+BF_4^-$ is then reacted with sufficient FNO_2 to maintain a liquid phase at −78° C for up to 12 hours. This reaction produced solid $NO_2^+BF_4^-$ plus gaseous ClF_3O_2 and FNO_2. The two gases may be pumped off and separated by passing the gases through a pair of traps maintained at −126° C and −196° C, respectively. The chlorine trifluoride dioxide will be caught in the −126° C trap.

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illustrative only and are not intended to limit the scope of the present invention.

What is claimed is:

1. A new composition of matter comprising of chlorine trifuloride dioxide, ClF_3O_2, having structure



having the infrared spectrum set forth in the following Table,

Table I

Infrared Spectrum of ClF_3O_2 and its Tentative Assignment		
Frequency (cm^{-1})	Intensity	Assignment for Point Group C_{2v}
1334	s	$\nu_{10}(B_2)$, νasClO_2
1096	s	$\nu_1(A_1)$, νsymClO_2
699	vs	$\nu_7(B_1)$, νasClF_2Ax
687	vs	$\nu_2(A_1)$, νClF
598	ms	$\nu_{11}(B_2)$, δrock ClO_2
543)		
532)	mw	$\nu_3(A_1)$ and $\nu_8(B_1)$

and being a white solid which melts at about −81° C to a colorless liquid and boils at about −21 C and is stable up to about +25° C.

* * * * *

United States Patent [19]
Christe

[11] **4,101,640**
[45] **Jul. 18, 1978**

[54] PRODUCTION OF OH_3^+ SALTS

[75] Inventor: **Karl O. Christe, Calabasas, Calif.**

[73] Assignee: **Rockwell International Corporation, El Segundo, Calif.**

[21] Appl. No.: **859,786**

[22] Filed: **Dec. 12, 1977**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 767,010, Feb. 9, 1977, abandoned, which is a continuation-in-part of Ser. No. 625,398, Oct. 24, 1975, abandoned.

[51] **Int. Cl.**^{2} **C01B 7/00**
[52] **U.S. Cl.** **423/462; 423/483**
[58] **Field of Search** **423/462, 489**

Primary Examiner—O. R. Vertiz
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Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] ABSTRACT

Strong Lewis acids added to wet HF protonate the water to form stable OH_3^+salts.

3 Claims, No Drawings

PRODUCTION OF OH_3^+ SALTS

The invention herein described was made in the course of or under a contract or subcontract thereunder, (or grant) with the United States Navy.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 767,010 filed Feb. 9, 1977 now abandoned, which is a continuation-in-part of Ser. No. 625,398 filed Oct. 24, 1975, and since abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to compositions of matter and methods of producing the same. More particularly, the present invention relates to stable OH_3^+ salts and methods of producing such salts by protonation of water from wet HF.

2. Description of the Prior Art

Hydrogen fluoride (FH) is widely used as a very good, inert, solvent. However, if the HF becomes wet, the water contained therein often tends to hydrolize the intended compounds. This destroys the compounds, sometimes with explosive results.

Numberous methods have been proposed heretofore for removing water from HF. Thus, it is known to react on alkali metal fluoride with HF to form the corresponding bifluoride, dry the bifluoride and pyrolize the biflouride to recover dry FH. Similarly, it has been known to remove water from HF electrolytically, using alternating current. Moreover, it has been known to treat HF with high pressure fluorine to remove water from the HF. Unfortunately, all of these prior art methods of removing water from HF are complicated, time-consuming and expensive. Furthermore, the latter method requires handling of gaseous fluorine under pressure which is quite hazardous to undertake.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

These disadvantages of the prior art are overcome with the present invention and a novel method of removing water from HF is proposed which is simple, fast, inexpensive and safe. Moreover, the method of the present invention yields a by-product which is useful and valuable.

The advantages of the present invention are preferably attained by adding a strong Lewis acid to wet HF to protonate the water into a solid, non-volatile residue. This residue is found to be an OH_3^+ salt, which is a strong solid acid and which is highly useful as a polymerization catalyst. The OH_3^+ salts are easily transported, are non-corrosive and are much safer to store and use than the liquid acids for which they may be substituted.

Accordingly, it is an object of the present invention to provide an improved method of removing water from HF.

Another object of the present invention is to provide a method of removing water from HF which method is simple, fast, economical and safe.

An additional object of the present invention is to provide a composition of matter which is a strong solid acid.

A further object of the present invention is to provide a composition of matter which is a strong solid acid which is highly useful as a polymerization catalyst.

Another object of the present invention is to provide a composition of matter which is a strong solid acid that is easily transported, non-corrosive, non-volatile, and safe to store and use.

A further object of the present invention is to provide stable OH_3^+ salts as a new composition of matter.

An additional object of the present invention is to provide a method of producing stable OH_3^+ salts.

A specific object of the present invention is the method of adding a strong Lewis acid to wet HF to protonate the water into a stable OH_3^+ salt.

These and other objects and features of the present invention will be apparent from the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

In that form of the present invention chosen for purposes of illustration, a strong Lewis acid is added to wet HF to protonate the water into a stable OH_3^+ salt. Suitable Lewis acids are SbF_5 or AsF_5.

EXAMPLE I

Preparation of $OH_3^+SbF_6^-$

In a typical experiment, SbF_5 (8.305 mmol) was placed in an ampoule and 8 ml of liquid anhydrous HF was added at −196° C. The mixture was warmed to 25° C to give a homogenous solution. Next, the ampoule was rechilled to −196° C and distilled water (8.30 mmol) was added. The mixture was then warmed to 25° C. Removal of all volatile material in vacuo at 25° C resulted in 2.116g of a white solid residue. The calculated weight for 8.30 mmol of $OH_3^+SbF_6^-$ is 2.115g. Moreover, a calculated analysis for $OH_3^+SbF_6^-$ yields H_2O 7.07; Sb 47.8 spectral analysis of the aforementioned residue yielded H_2O 6.93; Sb 48.0. The white solid was found to be stable up to 357° C, at which temperature it decomposed. The x-ray diffraction pattern for this material is shown in Table I.

TABLE I

X-Ray Powder Data for $OH_3^+SbF_6^{-*}$

d_{obsd} A	d_{calcd} A	Intens	h	k	l
8.75	8.77	m	0	0	1
4.78	4.80	m	2	0	1
4.38	4.39	s	0	0	2
3.47	3.49	m	2	0	2
3.32	3.34	vs	2	1	2
2.868	2.869	mw	4	0	0
2.785	2.784	m	4	1	0
2.241	2.251	m	5	1	0
2.190	2.194	s	0	0	4
2.053	2.049	mw	4 2	0 0	3 4
2.021	2.017	m	2	1	4
1.901	1.903	mw	3	0	4
1.877	1.877	m	3	1	4
1.779	1.777	mw	6	2	1
1.760	1.756	m	5	4	1
1.680	1.679	mw	6	3	1
1.663		m			
1.595		mw			
1.578		m			
1.515		vw			
1.505		w			
1.401		mw			
1.392		m			
1.347		mw			
1.341		m			
1.258		mw			
1.230		m			
1.187		mw			
1.155		mw			

TABLE I-continued

X-Ray Powder Data for $OH_3^+SbF_6^{-a}$					
d_{obsd} A	d_{calcd} A	Intens	h	k	l
1.100		mw			
1.075		mw			
1.052		mw			
1.030		mw			
1.010		m			
0.990		m			
0.972		w			
0.963		vw			
0.937		m			
0.922		m			
0.9072		mw			
0.8925		m			
0.8793		m			
0.8663		m			
0.8538		m			
0.8365		vw			
0.8306		m			
0.8251		w			
0.8195		m			
0.8144		w			
0.8091		w			
0.8037		w			
0.7988		m			
0.7890		m			
0.7880		w			
0.7794		m			
0.7786		w			

[a] Tetragonal, a = 11.48 A, c = 8.78 A, V = 1157.1 A, Z = 8, ρ_{calcd} = 2.93 g cm^{-3}, Cu Kα radiation, and Ni filter

EXAMPLE II

Preparation of $OH_3^+AsF_6^-$

In a typical experiment, H_2O (5.421 mmol) and anhydrous HF (8 ml of liquid) were combined at −196° C in an ampoule, followed by warm-up to 25° C. Arsenic pentafluoride (5.427 mmol) was added to this mixture at −196° C and the contents of the ampoule were allowed to warm slowly to room temperature. Removal of volatile material at 25° C in vacuo resulted in 1.128g of a white solid residue. The calculated weight for 5.421 mmol of $OH_3^{30}AsF_6^-$ is 1.127g. Furthermore, spectral analysis of the residue yielded H_2O 8.26; As 35.7, while the calculated analysis for $OH_3^+AsF_6^-$ yields H_2O 8.66; As 36.0. The white solid was found to be stable up to 193° C, at which temperature it decomposed. The x-ray diffraction pattern for the resulting material is shown in Table II.

TABLE II

X-Ray Powder Data for $OH_3^+AsF_6^{-a}$					
d_{obsd} A	d_{calcd} A	Intens	h	k	l
4.64	4.62	vs	1	1	1
4.01	4.00	vs	2	0	0
2.82	2.83	s	2	2	0
2.420	2.414	w	3	1	1
2.315	2.312	w	2	2	2
1.999	2.002	w	4	0	0
1.833	1.837	w	3	3	1
1.785	1.791	mw	4	2	0
1.636	1.634	m	4	2	2
1.542	1.541	mw	5 3	1 3	1 3
1.414	1.416	vw	4	4	0
1.355	1.353	w	5	3	1
1.335	1.335	w	6 4	0 4	0 2
1.267	1.266	vw	6	2	0

[a] Cubic, a = 8.015 A, V = 514.9 A^3, Z = 4, ρ_{calcd} = 2.890g cm^{-3}, Cu Kα radiation, and Ni filter

Further characterization of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$ may be found in an article entitled, "Novel Onium Salts. Synthesis and Characterization of $OH_3^+SbF_6^-$ and $OH_3^+AsF_6^-$", published in Inorganic Chemistry, Vol. 14, No. 9, p.2224, September 1975 and written by K. O. Christe, C. J. Schack and R. D. Wilson.

EXAMPLE III

Preparation of Dry HF

Using the methods of either Example I or II, it is easy to separate dry HF from the OH_3^+ salt by distillation, since HF boils at 20° C.

Thus, the methods of Examples I or II, coupled with the step of Example III, have dual utility, serving to remove water from HF and, also, serving to produce stable solid OH_3^+ salts.

Obviously, numerous variations and modifications can be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illustrative only and are not intended to limit the scope of the present invention.

I claim:

1. A composition of matter consisting of an OH_3^+ cation, and an anion consisting of the hexafluoride of a material selected from the group consisting of antimony and arsenic.

2. A composition of matter consisting of $OH_3^+SbF_6^-$ as a white solid which is stable up to 357° C, at which temperature it decomposes.

3. A composition of matter consisting of $OH_3^+AsF_6^-$ as a white solid which is stable up to 193° C, at which temperature it decomposes.

* * * * *

United States Patent [19]

Christe et al.

[11] **4,102,984**

[45] **Jul. 25, 1978**

[54] **PHOTOLYSIS METHOD FOR PRODUCING NF_4PF_6**

[75] Inventors: **Karl O. Christe**, Calabasas; **Carl J. Schack**, Chatsworth, both of Calif.

[73] Assignee: **Rockwell International Corporation**, El Segundo, Calif.

[21] Appl. No.: **732,244**

[22] Filed: **Oct. 14, 1976**

[51] **Int. Cl.**^{2} **C01B 25/10**
[52] **U.S. Cl.** **423/301**; 423/351
[58] **Field of Search** 423/301, 302, 351

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,503,719	3/1970	Christe et al.	423/351
3,708,570	1/1973	Tolberg	423/302

OTHER PUBLICATIONS

Christe et al., Inorganic Chemistry, vol. 12, No. 10, pp. 2478–2481, 1973.

Goetschel et al., Inorganic Chemistry, vol. 11, No. 7, pp. 1696–1701, 1972.

Primary Examiner—Earl C. Thomas
Assistant Examiner—Gregory A. Heller
Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

A method of producing NF_4PF_6 by ultraviolet photolysis at −196° C of a mixture of NF_3, F_2 and PF_5.

1 Claim, No Drawings

PHOTOLYSIS METHOD FOR PRODUCING NF_4PF_6

The invention herein described was made in the course of or under a contract or subcontract thereunder, (or grant) with the United States Navy.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to methods for producing materials and is particularly directed to an improved method for producing NF_4PF_6.

2. Description of the Prior Art

NF_4^+ salts are the key ingredients for solid propellant NF_3—F_2 gas generators, such as that taught by D. Pilipovich in U.S. Pat. No. 3,963,542 for chemical HF—DF lasers. Whereas NF_4SbF_6 and NF_4AsF_6 can be prepared with relative ease, using the methods of W. E. Tolberg et al, U.S. Pat. No. 3,708,570, and K. O. Christe et al, U.S. Pat. No. 3,503,719, these compounds suffer from the disadvantage of containing a relatively heavy anion, thus decreasing their performance in an NF_3—F_2 gas generator. This disadvantage can be overcome by replacing the SbF_6^- or AsF_6^- anion by the lighter PF_6^- anion. The existence of this salt has previously been claimed by Tolberg et al. (U.S. Pat. No. 3,708,570), but their production process was so inefficient that they could not isolate an amount of material sufficient for its isolation, identification, and characterization.

BRIEF SUMMARY AND OBJECTS OF INVENTION

This problem of synthesizing NF_4PF_6 is overcome by the present invention and an efficient method was found for producing NF_4PF_6. The method of the present invention involves low-temperature uv-photolysis of a mixture of NF_3, F_2, and PF_5 according to:

$$NF_3 + F_2 + PF_5 \xrightarrow[-196^\circ C]{h\nu} NF_4PF_6$$

This method provides NF_4PF_6 of high purity.

Accordingly, it is an object of the present invention to provide an improved process for the production of NF_4PF_6.

This and other objects and features of the present invention will be apparent from the following examples.

DETAILED DESCRIPTION OF THE INVENTION

In a typical experiment, NF_3 and PF_5 (27 mmol of each) were condensed into the cold (−196° C) bottom of a pan-shaped quartz reactor. This reactor had a flat top consisting of a 3-in. diameter optical grade quartz window. The vessel had a side arm connected by a Teflon O ring to a Fischer-Porter Teflon valve to facilitate removal of solid reaction products. The depth of the reactor was about 1.5 in. and its volume was 135 ml. The uv source consisted of a 900-W air-cooled high-pressure mercury arc (General Electric Model B-H6) and was positioned 1.5 in. above the flat reactor suface. The bottom of the reactor was kept cold by immersion in liquid N_2. Dry, gaseous N_2 was used as a purge gas to prevent condensation of atmospheric moisture on the flat top of the reactor. As a heat shield a 0.25 in. thick quartz plate was positioned between the uv source and the top of the reactor. Fluorine (9 mmol) was added and the mixture was photolyzed at −196° C for 1 h with a 900-W high-pressure Hg arc in the manner described above. After termintion of the photolysis, volatile material was pumped out of the reactor during its warm-up to room temperature. The non-volatile white solid product consisted of 10 mg of NF_4PF_6.

The salt NF_4PF_6 is a white, crystalline, hygroscopic solid, stable at room temperature, but rapidly decomposing at 245° C. Its characteristic x-ray diffraction powder pattern is listed in Table I. Its vibrational spectrum is listed in Table II and establishes the ionic nature of the salt, i.e. the presence of discrete NF_4^+ cations and PF_6^- anions. This was further confirmed by ^{19}F nmr spectroscopy in HF solution which showed the triplet (J_{NF} = 230 H_z at ϕ = −217) characteristic for NF_4^+.

TABLE I

X-RAY POWDER DATA FOR NF_4PF_6[a]

d obsd	d calcd	Int	h k l
5.40	5.36	ms	1 1 0
4.55	4.53	s	1 0 1
3.91	3.89	vs	1 1 1
3.79	3.79	s	2 0 0
2.91	2.91	ms	2 1 1
2.65	2.65	m	1 0 2
2.40	2.40	vw	3 1 0
2.307	2.305	m	3 0 1
2.204	2.205	vw	3 1 1
2.171	2.171	mw	2 1 2
1.882	1.883	ms	3 0 2, 0 0 3
1.825	1.827	vw	3 1 2, 1 0 3
1.784	1.785	w	3 3 0
1.747	1.747	mw	4 1 1
1.685	1.685	w	3 2 2, 2 0 3
1.646	1.646	w	2 1 3
1.622	1.622	w	4 2 1
1.536	1.540	vw	4 1 2
1.485	1.486	vw	5 1 0
1.464	1.463	vw	5 0 1
1.437	1.437	w	5 1 1
1.408	1.407	vw	5 2 0
1.365	1.365	vw	3 2 1, 1 1 4
1.333	1.335	w	5 0 2
1.318	1.319	vw	4 4 0
1.302	1.304	vw	2 1 4
1.259	1.259	w	4 3 3
1.214	1.216	w	6 1 1

[a] tetragonal, a = 7.577, C = 5.653A, Cu K_α radiation Ni filter

TABLE II

VIBRATIONAL SPECTRUM OF NF_4PF_6

Observed Frequency (cm⁻¹) Ir	Raman	Assignments for NF_4^+ (T_d)
2330 vw		$2\nu_3(A_1 + E + F_2) = 2320$
2320 w		
2005 w		$\nu_1 + \nu_3(F_2) = 2008$
1765 w		$\nu_3 + \nu_4(A_1 + E + F_2) = 1768$
1457 w		$\nu_1 + \nu_4(F_2) = 1457$
1221 mw		$2\nu_4(A_1 + E + F_2) = 1218$
1166 vs	1168 (1.5) 1150 (0.8)	$\nu_3(F_2)$
1135 vw		
1056 vw		$\nu_2 + \nu_4(F_1 + F_2) = 1069$
	880 (0.2)	$2\nu_2(A_1 + A_2 + E) = 880$

TABLE II-continued

VIBRATIONAL SPECTRUM OF NF_4PF_6

	849 (8.2)	$\nu_1(A_1)$
611 m		
	609 (7.4)	$\nu_4(F_2)$
608 m		
	441 (2.9)	$\nu_2(E)$
		Assignments for $PF_6^-(O_h)$
1590 w		$\nu_1 + \nu_3(F_{1u}) = 1590$
1414 w		$\nu_2 + \nu_3(F_{1u} + F_{2u}) = 1413$
1308 vw		$\nu_1 + \nu_4(F_{1u}) = 1307$
842 vs		
	838 (1.5)	$\nu_3(F_{1u})$
789 w		
749 w	748 (10)	$\nu_1(A_{1g})$
	571 (0.8)	$\nu_2(E_g)$
559 s		$\nu_4(F_{1u})$
474 vw	469 (1.2)	$\nu_5(F_{2g})$

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the form of the present invention described above is illustrative only and is not intended to limit the scope of the present invention.

We claim:

1. A process for the production of NF_4PF_6 characterized by photolyzing a mixture of NF_3, F_2 and PF_5 having an approximate mol ratio of 3:1:3 at −196° C and removing unreacted volatile starting materials from the non-volatile NF_4PF_6 product by pumping at ambient temperature.

* * * * *

United States Patent [19]

Christe et al.

[11] **4,107,275**

[45] **Aug. 15, 1978**

[54] METHOD FOR PRODUCING NF_4BF_4

[75] Inventors: **Karl O. Christe**, Calabasas; **Carl J. Schack**, Chatsworth; **Richard D. Wilson**, Canoga Park, all of Calif.

[73] Assignee: **Rockwell International Corporation**, El Segundo, Calif.

[21] Appl. No.: **731,198**

[22] Filed: **Oct. 12, 1976**

[51] **Int. Cl.**^{2} **C01B 35/14**

[52] **U.S. Cl.** **423/276**; 149/119; 423/351

[58] **Field of Search** 149/19.3, 109.4, 119; 423/276, 351, 472

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Primary Examiner—Edward A. Miller

Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] ABSTRACT

SbF_5 is heated in the presence of an excess of NF_3 and F_2 to 250° C until conversion of the SbF_5 to NF_4SbF_6 is complete. The NF_4SbF_6 may be used itself or may be combined, in 0–15 mol % excess, with $CsBF_4$ in anhydrous HF to produce NF_4BF_4.

5 Claims, No Drawings

METHOD FOR PRODUCING NF_4BF_4

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to methods of producing NF_4BF_4 and its precursor NF_4SbF_6.

2. Description of the Prior Art

Solid propellant gas generators, such as that described by D. Pilipovich in U.S. Pat. No. 3,963,542, are of great importance for chemical HF-DF lasers. These gas generators are based on NF_4^+ salts. Due to its high NF_3 and F_2 content, NF_4BF_4 is one of the materials most preferred in making these gas generators. However, there has not previously been an economically feasible method for producing NF_4BF_4 in a state of sufficient purity to permit its practical application.

Several methods have previously been reported for the synthesis of NF_4BF_4. This salt has been prepared either directly from NF_3, F_2, and BF_3 using glow discharge, bremsstrahlung or ultraviolet radiation, or indirectly from NF_4SbF_6 using a metathetical process. Of these, only the metathetical process is amenable to the larger scale production of NF_4BF_4 utilizing existing technology. The original metathetical NF_4BF_4 process involved the following steps:

$$CsF + HF \xrightarrow{HF} CsHF_2$$

$$NF_4SbF_6 + CsHF_2 \xrightarrow{HF} CsSbF_6\downarrow + NF_4HF_2$$

$$NF_4HF_2 + BF_3 \xrightarrow{HF} NF_4BF_4 + HF$$

Since the crude product, thus obtained, contained much $CsSbF_6$, its NF_4BF_4 content had to be increased by extraction with BrF_5. The use of BrF_5 resulted in the following side reaction:

$$NF_4BF_4 + CsSbF_6 \xrightarrow{BrF_5} CsBF_4\downarrow + NF_4SbF_6$$

The composition of the final product was reported to be: 91.5% NF_4BF_4 and 8.5% NF_4SbF_6. In addition to the low purity of the product and the requirement of BrF_5 as a recrystallization solvent, this process suffers from the following disadvantage. Highly concentrated solutions of NF_4HF_2 in HF are unstable decomposing to NF_3, F_2, and HF. This can cause a pressure build up in the metathesis apparatus which in turn can render filtration steps more difficult.

This process was somewhat improved upon by substituting CsF by AgF. This modification eliminated the BrF_5 extraction step and resulted in a product of the composition (mol %): NF_4BF_4 (89), $NF_4Sb_2F_{11}$ (7.9), $AgBF_4$ (3.1). However, the process still involved the handling of concentrated NF_4HF_2 solutions and consisted of a rather large number of steps. Furthermore, the cost of silver salts is rather high and, therefore, requires their recycling. This process can be described by the following steps:

$$AgF + HF \xrightarrow{\text{in } HF} AgHF_2 \text{ (filtration required to remove impurities)}$$

$$2\,AgHF_2 + NF_4SbF_6 \cdot SbF_5 \xrightarrow{\text{in } HF} 2\,AgSbF_6\downarrow + NF_4HF_2$$

$$NF_4HF_2 + BF_3 \xrightarrow{\text{in } HF} NF_4BF_4 + HF$$

$$AgHF_2 + BF_3 \xrightarrow{\text{in } HF} AgBF_4\downarrow + HF$$

$$AgSbF_6 \xrightarrow{\Delta T} AgF + SbF_5$$

Since these metathetical processes use NF_4SbF_6 as a precursor, a simple production method for this compound is also desirable. Two methods have previously been reported for the synthesis of $NF_4SbF_6 \cdot xSbF_5$ involving the use of either high pressure and temperature or uv-irradiation. Of these, the thermal method is more convenient for larger scale production. According to Tolberg et al. the most favorable reaction conditions are:

$$NF_3 + F_2 + SbF_5 \xrightarrow[\substack{100\text{–}125^\circ \\ 2 \text{ days}}]{3000 \text{ psi}} NF_4Sb_3F_{16}$$

$$NF_4Sb_3F_{16} \xrightarrow[\substack{200^\circ \\ 2\text{–}3 \text{ days}}]{\text{vacuum}} NF_4SbF_6 + 2SbF_5$$

The resulting product contained an appreciable amount of Monel salts and was removed from the reactor by cutting it open with a hacksaw and scraping out the hard clinkered product. Based on recent work done in our laboratory, temperatures (250°-260°), higher than those reported by Tolberg, are required for the vacuum pyrolysis of $NF_4SbF_6 \cdot xSbF_5$ to NF_4SbF_6 within a reasonable time period.

BRIEF SUMMARY AND OBJECTS OF INVENTION

These disadvantages of the prior art are overcome with the present invention. We have found that NF_4BF_4 of at least 97 mol % purity can be prepared by a simpler process using anhydrous HF at different temperatures as the only solvent. Furthermore, we have shown that the purity of the NF_4BF_4 can be raised to above 99 mol % by a single recrystallization from BrF_5. The cesium content in both products was shown to be less than 0.1 mol %, the principal impurity being NF_4SbF_6.

Our improved process consists of the following steps:

$$CsBF_4 + 1.1\,NF_4SbF_6 \xrightarrow[-78^\circ \text{ filtr}]{HF} CsSbF_6\downarrow + NF_4BF_4 0.1\,NF_4SbF_6$$

$$NF_4BF_4 + 0.1\,NF_4SbF_6 \xrightarrow[25^\circ]{\text{recryst. from } HF} \underset{(97\ m\ \%)}{NF_4BF_4\downarrow} + \text{mother liquor}$$

$$\underset{(97 m\ \%)}{NF_4BF_4} \xrightarrow[25^\circ]{\text{recryst. from } BrF_5} \underset{(99+\ m\ \%)}{NF_4BF_4\downarrow} + \text{mother liquor}$$

The important features of our process are:

1. The use of $CsBF_4$ instead of $CsHF_2$ eliminates one step and avoids the complications caused by NF_4HF_2.
2. The use of a 10 mol % excess of NF_4SbF_6 decreases the solubility of $CsSbF_6$ by the common ion effect.
3. Carrying out the $CsSbF_6$ filtration step at −78° decreases the SbF_6^- concentration since the solubilities of SbF_6^- salts in anhydrous HF decrease with decreasing temperature much more rapidly than those of BF_4^- salts. Furthermore, the amount of NF_4BF_4, retained in the $CsSbF_6$ filter cake by absorption of a certain volume of mother liquor, is minimized owing to the decreased solubilities.

4. Since NF_4BF_4 and NF_4SbF_6 have comparable solubilities in HF at room temperature, the 10% excess of NF_4SbF_6 used in the $CsSbF_6$ precipitation step can be removed as mother liquor by recrystallization from HF at room temperature. Unfortunately, the solubilities in HF at room temperature are so high that a significant percentage of the mother liquor is retained by the NF_4BF_4 precipitate. This problem can be minimized by using for this recrystallization a solvent in which these NF_4^+ salts are less soluble. Thus, a single recrystallization from BrF_5 raised the product purity above the 99 mol % level. Other suitable solvents could be used to replace BrF_5 in this step. The mother liquors of the recrystallization steps can be easily recycled into the $CsSbF_6$ precipitation step, thus avoiding the loss of any NF_4^+ values.

The sythesis of the NF_4SbF_6 precursor was also simplified. It was found that most of the drawbacks of the prior art can be avoided by drectly synthesizing NF_4SbF_6. For this purpose, NF_3, F_2, and SbF_5 in a 2:2:1 mol ratio are heated in a Monel cylinder to 250° for 72 hours. The size of the cylinder is chosen in such manner that at the completion of the reaction the autogenous pressure is about 70 atm. The excess of NF_3 and F_2 is removed under vacuum at room temperature and the desired NF_4SbF_6 product is extracted from the Monel cylinder with anhydrous HF using about 50 ml of liquid HF per 100 g of NF_4SbF_6. Since, contrary to a previous report, the formed Monel salt impurities (about 5%) are quite insoluble in anhydrous HF, they can be easily removed from the product by incorporating a porous Teflon filter into the HF solution transfer line. Based on elemental and spectroscopic analyses and the observed material balances, the resulting product was shown to be essentially pure NF_4SbF_6.

In summary, the combination of the two improved processes for the syntheses of NF_4SbF_6 and NF_4BF_4, respectively, results in a relatively simple and economical process for the production of NF_4BF_4 in a purity of about 97 mol %. The purity of the product can be increased to better than 99 mol % by a single recrystallization from BrF_5.

Accordingly, it is an object of the present invention to provide an improved, economically feasible process for the production of NF_4BF_4.

Another object of the present invention is to provide an economically feasible metathetical process for the production of high purity NF_4BF_4.

Another object of the present invention is to provide an improved process for the production of the NF_4SbF_6 precursor.

DETAILED DESCRIPTION OF INVENTION

These and other objects and features of the present invention will be apparent from the following examples. It is understood, however, that these examples are merely illustrative of the invention and should not be considered as limiting the invention in any sense.

EXAMPLE I

Antimony pentafluoride (1.8 mol) was placed into a passivated 2l Monel cylinder and NF_3 (3.6 mol) and F_2 (3.6 mol) were added at −196° C. The cylinder was heated to 250° C for 72 hours. The unreacted NF_3 (1.8 mol) and F_2 (1.8 mol) were pumped off at room temperature leaving behind NF_4SbF_6 (1.8 mol). The NF_4SbF_6 product was characterized by elemental analysis, infrared, Raman and ^{19}F nmr spectroscopy, and its x-ray powder diffraction pattern, and did not contain any significant amounts of polyantimonate anions.

EXAMPLE II

Cesium tetrafluoroborate (2.15 mol) and NF_4SbF_6 (2.27 mol) were placed in a 2l Teflon reactor equipped with a filter top. Anhydrous HF (27.5 mol) was added and the mixture was agitated at 25° C for 1 hour. The reactor was cooled to −78° C, inverted and the $CsSbF_6$ precipitate was separated from the NF_4BF_4 solution by filtration. The filtrate was pumped to dryness, resulting in 310g of product which based on its elemental and spectroscopic analyses had the composition (in mol %): NF_4BF_4 95.0; NF_4SbF_6 4.6; $CsSbF_6$ 0.4. The purity of this crude product was increased to 97 or 99 + mol % by recrystallization at 25° C from anhydrous HF or BrF_5, respectively.

It should be understood that, in addition to its use as a precursor for NF_4BF_4, the NF_4SbF_6 may itself be used as a solid propellant gas generator or may be used as a fluorinating agent in other chemical processes.

Obviously, numerous variations and modifications may be made without departing from the processes of the present invention. Therefore, it should be clearly understood that the form of the present invention described above is illustrative only and is not intended to limit the scope of the present invention.

We claim:

1. Improved metathetical process for the production of NF_4BF_4, comprising the steps of combining $CsBF_4$ with a 0–15 mol % excess of NF_4SbF_6 in anhydrous HF at room temperature, cooling the mixture to −78° C and removing the $CsSbF_6$ precipitate by filtration at −78° C.

2. Process according to claim 1, wherein the excess of NF_4SbF_6 used is from 5 to 10 mol %.

3. Process according to claim 1, wherein the crude product is recrystallized at room temperature from anhydrous HF.

4. Process according to claim 1, wherein the crude product is recrystallized at room temperature from BrF_5.

5. The process of producing NF_4BF_4 comprising the steps of:

heating SbF_5 in the presence of an excess of NF_3 and F_2 to 250° C until conversion of SbF_5 to NF_4SbF_6 is complete,

combining $CsBF_4$ with a 0-15 mol % excess of NF_4SbF_6 in anhydrous HF, and

removing the $CsSbF_6$ precipitate by filtration at −78° C.

* * * * *

United States Patent [19]
Christe

[11] **4,108,965**
[45] **Aug. 22, 1978**

[54] $(NF_4)_2NiF_6$ HIGH ENERGY SOLID PROPELLANT OXIDIZER AND METHOD OF PRODUCING THE SAME

[75] Inventor: **Karl O. Christe, Calabasas, Calif.**

[73] Assignee: **Rockwell International Corporation, El Segundo, Calif.**

[21] Appl. No.: **732,623**

[22] Filed: **Oct. 15, 1976**

[51] **Int. Cl.**² **C01G 53/00**
[52] **U.S. Cl.** **423/351**; 149/119; 423/472
[58] **Field of Search** 149/19.3, 119; 423/138, 423/140, 143, 351, 472

[56] **References Cited**

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Primary Examiner—Edward A. Miller
Attorney, Agent, or Firm— L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

The combination of the strongly oxidizing NF_4^+ cation with the strongly oxidizing NiF_6^{--} anion in the form of the stable salt $(NF_4)_2NiF_6$ produces a powerful oxidizer, useful for solid propellant formulations and NF_3-F_2 gas generators. A process for its production is described.

4 Claims, No Drawings

$(NF_4)_2NiF_6$ HIGH ENERGY SOLID PROPELLANT OXIDIZER AND METHOD OF PRODUCING THE SAME

The invention herein described was made in the course of or under a contract or subcontract thereunder, (or grant) with the United States Navy.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a high energy oxidizer and a method of producing the same. The composition of the present invention is particularly useful for applications, such as solid propellants and NF_3-F_2 gas generators.

2. Description of the Prior Art

For oxygen-containing oxidizers, the combination of an oxidizing cation with an oxidizing anion in the form of a stable solid has previously been achieved, as demonstrated by the well known existence of nitronium perchlorate $NO_2^+ClO_4^-$. Whereas fluorine compounds are generally stronger oxidizers than the corresponding oxygen compounds, the synthesis of very powerful, solid, ionic, fluorine containing oxidizers had previously not been possible owing to the incompatibility between energetic anions and the cations. Attempts to combine oxidizing highly fluorinated cations and anions had always resulted in decomposition, accompanied by elimination of elemental fluorine. Consequently, all the previously known solid highly fluorinated oxidizers consisted of the combination of an energetic ion with an non-energetic counter ion. The only progress made in this area consisted of minimizing the relative weight of the non-energetic counter ion. Obviously, the performance of such oxidizers could be significantly improved if the combination of an energetic anion with an energetic cation in the form of a stable solid were possible.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

The above-described problem of preparing fluorine containing high energy solid oxidizers is overcome by the present invention. We have found two highly energetic ions which can be combined to form a stable ionic solid. These ions are the NF_4^+ cation and the NiF_6^{2-} anion, and the resulting stable solid is the powerful oxidizer $(NF_4)_2NiF_6$. The oxidizing power of the NF_4^+ cation is well established. The oxidizing power of the NiF_6^{2-} anion is due to the fact that the parent compound NiF_4 is unstable and decomposes to NiF_2 and F_2. Thus, the thermal decomposition of $(NF_4)_2NiF_6$ proceeds according to:

$$(NF_4)_2NiF_6 \xrightarrow{\Delta T} 2NF_3 + 3F_2 + NiF_2$$

This high oxidizing power of $(NF_4)_2NiF_6$ renders it extremely useful for high energy solid propellant formulations. Of particular interest is its application to solid propellant NF_3-F_2 gas generators for chemical HF-DF lasers. For the latter application, $(NF_4)_2NiF_6$ possesses, in addition to an energetic counter ion, the desirable properties of being self-clinkering, and of containing a multiply charged counter ion, as disclosed in our copending application Ser. No. 731,197, filed Oct. 12, 1976. Consequently, it is not surprising that its theoretical performance in an NF_3-F_2 gas generator is superior to those of the best previously known systems, as becomes obvious from an inspection of Table I.

TABLE I

A Comparison of the Theoretical Performance of Various NF_4^+ Based NF_3—F_2 Gas Generator Ingredients

System	Performance (weight % usable F)
$NF_4SbF_6 \cdot 1.2KF$	24.0
$NF_4BF_4 \cdot 1.2KF$	38.5
$(NF_4)_2SnF_6$	46.0
$(NF_4)_2TiF_6$	55.6
$(NF_4)_2NiF_6$	64.6

Since NiF_4 is only stable in the form of its NiF_6^{2-} anion, the $(NF_4)_2NiF_6$ salt cannot be prepared directly from NF_3, F_2, and NiF_4, but was prepared by the following indirect synthesis in anhydrous HF solution:

$$2\,NF_4SbF_6 + Cs_2NiF_6 \xrightarrow{\text{HF solution}} 2\,CsSbF_6\downarrow + (NF_4)_2NiF_6$$

It resulted in the precipitation of the rather insoluble salt $CsSbF_6$, while the soluble $(NF_4)_2NiF_6$ remained in solution. The two products were separated by a simple filtration step. The composition of the crude product was: (mol %) $(NF_4)_2NiF_6$, 81.7; NF_4SbF_6, 14.4; $CsSbF_6$, 3.9. The purity of this product can be easily increased by following the procedures outlined for NF_4BF_4 in our copending application Ser. No. 731,198, filed Oct. 12, 1976.

Accordingly, it is an object of the present invention to provide an improved fluorine containing high energy oxidizer derived from the combination of an energetic cation with an energetic anion in the form of a stable solid.

Another object of the present invention is to provide an improved high energy oxidizer for solid propellants.

Another object of the present invention is to provide an improved solid propellant NF_3-F_2 gas generator for chemical HF-DF lasers.

Another object of the present invention is to provide a novel composition of a matter consisting of $(NF_4)_2NiF_6$.

Another object of the present invention is to provide a process for the production of $(NF_4)_2NiF_6$.

These and other objects and features of the present invention will be apparent from the following example. It is understood, however, that this example is merely illustrative of the invention and should not be considered as limiting the invention in any sense. For example, the oxidizing anion is not limited to NiF_6^{2-}, but could be replaced by other suitable energetic transition metal fluoride anions.

EXAMPLE

In a typical example, Cs_2NiF_6 (13.45 mmol) and NF_4SbF_6 (27.9 mmol) were combined in a Teflon FEP U-trap containing a magnetic stirrer. The U-trap was closed off on one side by a valve and was connected on the other side through a Teflon filter containing union to a second U-trap. Anhydrous HF (10 ml liquid) was added to the first U-trap and the resulting mixture was stirred for 30 minutes at 25° C. The trap was cooled to −78° C and its contents were passed through the filter. The solid retained by the filter consisted of 10.0 g of $CsSbF_6$ (weight calcd for 27 mmol of $CsSbF_6$ = 9.95 g), whereas the solid (4.4 g) obtained after evaporation of the HF from the filtrate consisted of a mixture (mol %) of $(NF_4)_2NiF_6$ (81.7), NF_4SbF_6 (14.4), and $CsSbF_6$ (3.9). The composition of the product was established by chemical analyses for NF_3, Ni, Cs, and Sb. The ionic nature of the adduct was established by infrared spectroscopy which showed the strong bands at 1157 and 607 cm^{-1}, characteristic for NF_4^+, and a strong band at 640 cm^{-1}, characteristic for NiF_6^{--}. The $(NF_4)_2NiF_6$ salt is a dark red, crystalline, hygroscopic solid which is stable at room temperature.

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illustrative only and are not intended to limit the scope of the present invention.

I claim:

1. An improved, high energy, fluorine containing oxidizer consisting of a compound having NiF_6^{--} as an anion, and an energetic cation.

2. The compound $(NF_4)_2NiF_6$.

3. An improved solid propellant $NF_3 - F_2$ gas generator compound consisting of $(NF_4)_2NiF_6$.

4. A process for the production of $(NF_4)_2NiF_6$, comprising the steps of combining Cs_2NiF_6 and NF_4SbF_6 in a mol ratio of 1:2.0-2.30 in anhydrous HF and removing the $CsSbF_6$ precipitate by filtration at −78° C.

* * * * *

APPENDIX B

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