INORGANIC HALOGEN OXIDIZER RESEARCH

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The use of PtF_6 for the synthesis of novel, high-oxidation state species was studied. Reaction of $XeOF_4$ and PtF_6 yields only $XeF_5^+PtF_6^-$. Several XeF_5^+ salts were characterized by ^{19}F nmr and vibrational spectroscopy, and force fields were computed for the isoelectronic series XeF_5^+, IF_5, TeF_5^-, and SbF_5^{--}.

A novel and interesting reaction between O_2^+ salts and various halogen fluorides was discovered. It produces several blue and purple, low-temperature

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stable free radicals, which were studied by esr spectroscopy. Several O_2^+ salts were studied by esr in the solid phase, and showed an interesting temperature dependence. The reaction of O_2^+ salts with $(CF_3)_2NO$ failed to give the $(CF_3)_2NO^+$ cation, but yielded the novel compound $[(CF_3)_2NO]_2CF_2$.

A novel halogen perchlorate, $Cs^+Br(ClO_4)_2^-$, was discovered and characterized. New and improved syntheses of the anhydrous metal perchlorates, $Ti(ClO_4)_4$ and $CrO_2(ClO_4)_2$, were found and the bidentate nature of the ClO_4 ligand established by spectroscopy.

Work on aliphatic fluorocarbon perchlorates was completed. The intermediate of empirical composition $(R_fI(ClO_4)_2$ was shown to have the ionic structure, $R_{f_2}I^+I(ClO_4)_4^-$. Its pyrolysis furnishes R_fClO_4 in high yield. In the aromatic series, either ring opening, addition across double bonds, or formation of $C_6F_5(IClO_4)_2$ were observed. A vibrational analysis of CF_3OClO_3 was carried out showing the covalent monodentate nature of the ligand.

Work on the low-temperature ozanization of positive halogen compounds was completed and summarized. Attempts to extend our improved $NO_2^+ClO_4^-$ synthesis to the unknown compound $NO_2^+BrO_4^-$ were unsuccessful. Similarly, attempts to synthesize the novel halogen heptoxides, Br_2O_7 and I_2O_7, have not as yet materialized.

CONTENTS

FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 473, with Lt. R. S. Miller as Scientific Officer. This report covers the period 1 April 1973 through 31 December 1973. The program has been directed by Drs. D. Pilipovich and K. O. Christe. The scientific effort was carried out by Drs. K. O. Christe, C. J. Schack, E. C. Curtis and Mr. R. D. Wilson. The program was administered by Drs. D. Pilipovich and L. Grant, Mangers, Exploratory Chemistry, and Dr. B. Tuffly, Program Manager.

ABSTRACT

We have continued to study the use of PtF_6 for the synthesis of novel, high-oxidation state species. The reaction between $XeOF_4$ and PtF_6 yields only $XeF_5^+PtF_6^-$, but not $XeOF_5^+$. The results indicate that the previously reported (Ref. 1) $XeOF_5$ may not exist. Several XeF_5^+ salts were characterized by ^{19}F nmr and vibrational spectroscopy, and force fields were computed for the isoelectronic series XeF_5^+, IF_5^-, and SbF_5^{--}.

A novel and interesting reaction between O_2^+ salts and various halogen fluorides was discovered. It produces several blue and purple, low-temperature stable free radicals, which were studied by esr spectroscopy. These species might be identical with the extremely explosive and ill-characterized products previously observed (Ref. 2) by Grosse and Streng. Several O_2^+ salts were studied by esr in the solid phase, and showed an interesting temperature dependence. The reaction of O_2^+ salts with $(CF_3)_2NO$ failed to give the $(CF_3)_2NO^+$ cation, but yielded the novel compound $[(CF_3)_2NO]_2CF_2$. Attempts to use O_2^+ as a cationic polymerization catalyst for C_3F_6 or COF_2 were unsuccessful. An improved synthesis for $O_2^+BF_4^-$ was found.

A novel halogen perchlorate, the $Cs^+Br(ClO_4)_2^-$ salt, was discovered and its structure was established by vibrational spectroscopy. A new and improved synthesis of anhydrous metal perchlorates was discovered and applied to the synthesis of $CrO_2(ClO_4)_2$ and $Ti(ClO_4)_2$. The bidentate covalent nature of the perchlorate ligand in the titanium compound was established by vibrational spectroscopy.

Our investigation of synthetic methods for the preparation of the Rocketdyne discovered fluorocarbon perchlorates was continued. Work on the aliphatic series was completed and the results were summarized in the form of several manuscripts. An interesting intermediate, having the empirical composition $R_fI(ClO_4)_2$, was isolated and shown to have the ionic structure, $[(R_f)_2I]^+[I(ClO_4)_4^-]$. Its pyrolysis yields R_fClO_4 in high yield. In the aromatic series, either ring opening, addition across the double bonds, or formation of $C_6F_5I(ClO_4)_2$ were observed. Efforts will be continued to prepare an aromatic fluorocarbon perchlorate by controlled pyrolysis of the latter. A vibrational analysis of the simplest fluorocarbon perchlorate, CF_3ClO_4,

was carried out demonstrating the covalent monodentate nature of the ligand. Attempts to synthesize the novel compound CF_3NO_3 were unsuccessful.

The possible extension of our recently discovered (Ref. 3,4) uv-synthesis of NF_4^+ salts was examined toward the preparation of other oxidizers involving species possessing higher ionization potentials than NF_3. Both species examined, N_2 and Kr, did not interact, thus placing the oxidation potential of the postulated (Ref. 4) SbF_6 radical at about 13-14ev.

Our work on the low-temperature ozonization of positive halogen compounds was completed and summarized in manuscript form. Attempts were unsuccessful to extend our improved $NO_2^+ClO_4^-$ synthesis (Ref. 3) to the novel compound $NO_2^+BrO_4^-$. Similarly, continued efforts to synthesize the novel halogen heptoxides, Br_2O_7 and I_2O_7, have as yet not materialized.

Attempts to duplicate previously reported syntheses of $FBrO_2$(Ref. 5) and IF_3O_2 (Ref. 6, 7) have so far been unsuccessful. Work in this area will be continued.

Numerous structural studies either have been completed or are under progress. The compounds studied include SF_5Br, SF_4, SF_4O, ClF_3O, CF_3O^-, NF_3O, and NF_4^+ salts. In these areas we are collaborating with other laboratories at the Universities of Ulm, Leicester, and University of California at Berkely, and the National Bureau of Standards, Washington.

During the past 9 months, 20 papers were either published, submitted for publication, or presented at meetings covering work done under this contract.

INTRODUCTION

This report covers a 9-month period and describes our efforts in the area of halogen chemistry. As in the past years, our research was kept diverse and covered areas ranging from the exploration of new synthetic methods and the syntheses of novel compounds to structural studies. As in the past, we have summarized completed pieces of work in manuscript form suitable for publication. Thus, time spent for report and manuscript writing is minimized, and widespread dissemination of our data achieved.

During the past 9 months, the following papers were published, submitted for publication, or presented at meetings. All of these arose from work sponsored under this program.

PUBLICATIONS DURING PAST CONTRACT YEAR

Papers Published

1. "The Preparation of Chlorine Monofluoride," by C. J. Schack and R. D. Wilson, Synthesis inorg. metal-org. Chem., 3, 393 (1973).
2. "Halogen Perchlorates: Additions to Perhaloolefins," by C. J. Schack, D. Pilipovich, and J. F. Hon, Inorg. Chem., 12, 897 (1973).
3. "The Hexafluorochlorine (VII) Cation, ClF_6^+, Synthesis and Vibrational Spectrum," by K. O. Christe, Inorg. Chem., 12, 1580 (1973).
4. "Chlorine Trifluoride Dioxide, ClF_3O_2, Synthesis and Properties," by K. O. Christe and R. D. Wilson, Inorg. Chem., 12, 1356 (1973).
5. "The Difluoroperchloryl Cation, $ClO_2F_2^+$," by K. O. Christe, R. D. Wilson and E. C. Curtis, Inorg. Chem., 12, 1358 (1973).
6. "On the Reaction of $Cl_2F^+AsF_6^-$ with Xenon," by K. O. Christe and R. D. Wilson, Inorg. Nucl. Chem. Letters, 9, 845 (1973).
7. "Vibrational Spectra of Trifluoroacetates," by K. O. Christe and D. Naumann, Spectrochim. Acta, 29A, 2017 (1973).

8. "Chlorine Trifluoride Dioxide. Vibrational Spectrum, Force Constants, and Thermodynamic Properties," by K. O. Christe and E. C. Curtis, Inorg. Chem., 12, 2245 (1973).

9. "A New Synthesis of NF_4^+ Salts and its Mechanistic Interpretation Involving a New and Exceptionally Powerful Oxidizing Species," by K. O. Christe, R. D. Wilson, and A. E. Axworthy, Inorg. Chem., 12, 2478 (1973).

10. "On Halogen Pentafluoride-Lewis Acid Adducts," by K. O. Christe and W. Sawodny, Inorg. Chem., 12, 2879 (1973).

Papers in Press

11. "Vibrational Assignment of SF_4," by K. O. Christe, W. Sawodny, and P. Pulay, J. Mol. Structure.

12. "On the Existence of ClF_5O," by K. O. Christe, R. D. Wilson, D. Pilipovich, R. Bougon, O. Glemser, and K. Züchner, Angew. Chem., intern. ed.

13. "Reactions of the $(CF_3)_2NO$ Radical with Strong Oxidizers," by K. O. Christe, C. J. Schack, R. D. Wilson, and D. Pilipovich, J. Fluor. Chem.

14. "Cesium Bis(perchlorato)bromate(I), $Cs^+[Br(OCO_3)_2]^-$," by K. O. Christe and C. J. Schack, Inorg. Chem.

15. "Halogen Fluorides," by K. O. Christe, Pure Appl. Chem.

Papers Presented at Meetings

16. "The Synthesis of Fluorocarbon Perchlorates from Fluorocarbon Halides," by C. J. Schack and D. Pilipovich, 7th Internat. Symp. Fluorine Chem., Santa Cruz, California, (July 1973).

17. "Chlorine Oxyfluorides," by K. O. Christe," E. C. Curtis, and R. D. Wilson, 7th Internat. Symp. Fluorine Chem., Santa Cruz, California, (July 1973).

18. "New Synthesis of NF_4^+ Salts," by K. O. Christe, R. D. Wilson, and A. E. Axworthy, 7th Internat. Symp. Fluorine Chem., Santa Cruz, California (July 1973).

19. "Halogen Fluorides," by K. O. Christe, main lecture at 24th Congress of the Internat. Union of Pure and Appl. Chem., Hamburg, Germany (September 1973).

20. "Inorganic Halogen Oxidizers," by K. O. Christe, Invited lectures at University of California at Berkeley (May 1973) and Ulm, Germany (September 1973).

DISCUSSION

PtF_6 CHEMISTRY

Since PtF_6 enabled us to synthesize the novel and interesting oxidizers ClF_6^+, $ClF_2O_2^+$, and ClF_3O_2 (Ref. 3), its potential for the preparation of high-oxidation state compounds was further investigated. The synthesis of $XeOF_5^+$ (a +VIII xenon compound) from $XeOF_4$ and $KrF^+SbF_6^-$ was reported by Bartlett (Ref. 1). Since $XeOF_4$ and halogen pentafluorides are pseudo-isoelectronic and PtF_6 can oxidize ClF_5 to ClF_6^+, PtF_6 might also be capable of oxidizing $XeOF_4$. A thorough examination of the $XeOF_4$ -PtF_6 system showed that the only Xe containing cation formed in this reaction is XeF_5^+. In addition, evidence for a weak $XeOF_4$ molecular adduct was obtained, which might be responsible for the Raman bands attributed by Bartlett to $XeOF_5^+$. As soon as KrF_2 is available, we will repeat Bartlett's experiment to unequivocally identify this species by ^{19}F nmr spectroscopy. Since $XeOF_5^+$ and XeF_5^+ have very similar structures and, hence, also similar spectra, we have investigated the vibrational and nmr spectra of $XeF_5^+AsF_6^-$ and $XeF_5^+BF_4^-$. All fundamentals of XeF_5^+ were observed and a normal coordinate analysis was carried out for the isoelectronic series XeF_5^+, IF_5, TeF_5^-, and SbF_5^{--}. The results were written up in manuscript form and are given in Appendix A. Attempts to synthesize pure PtF_5 by vacuum pyrolysis of $NO_2^+PtF_6^-$ or $ClO_2^+PtF_6^-$ were unsuccessful.

Since our previous reactions (Ref. 3) between the $(CF_3)_2NO$ radical had resulted in deflagrations, we have substituted PtF_6 by the milder oxidizers MoF_6, ReF_6, and O_2^+ salts. The aim of these reactions was to produce the $(CF_3)_2NO^+$ cation that through a subsequent FNO displacement reaction could be easily converted to $(CF_3)_2N(O)F$, a CF_3 derivative of the known energetic oxidizer NF_3O. The results from this study are given in manuscript form in Appendix B and resulted in the synthesis and characterization of the novel compound $(CF_3)_2NOCF_2ON(CF_3)_2$.

In our previous work on ClF_6^+ we had postulated (Ref. 3) the existence of a stable intermediate ClF_5^+ radical cation. In order to establish this hypothesis by esr spectroscopy, an inert solvent must be found for the ClF_5 -PtF_6 reaction. The use of BrF_5 as a solvent was examined, however, no ClF_6^+ salt was formed under these conditions.

O_2^+ CHEMISTRY

The O_2^+ salts are strong, one-electron oxidizers and therefore, very useful synthetic reagents. Its reactions with $(CF_3)_2NO$ were studied for the reasons mentioned in the preceding paragraph. The results from this study are given in manuscript from in Appendix B.

We have studied the usefulness of $O_2^+SbF_6^-$ as a catalyst for cationic polymerization of monomers that are extremely difficult to polymerize. In the temperature range studied (-50 to 180 C) no polymerization of C_3F_6 or COF_2 was observed. The successful polymerization of these monomers would have resulted in interesting new polymers, such as a simple perfluorinated polyether.

More than 10 years ago, Streng and Grosse reported (Ref. 2,8) the existence of purple and blue compounds for halogen fluoride -O_2F_2 systems. However, these colored compounds were only stable at low temperature and exploded on warmup. Compositions such as ClF_3O_2 were assigned to these products and in a subsequent British publication (Ref. 9) it was speculated on the nature of these species. In the course of our study of synthetic uses for O_2^+ salts, we have surprisingly discovered that ClF_3 reacts smoothly with $O_2^+SbF_6^-$ at low temperature producing purple and blue compounds which decompose upon warmup in a controllable fashion to yield ClF_5 and $FClO_2$. Obviously, the deeply colored intermediates must be some interesting free radicals. It was also found that $O_2^+AsF_6^-$ in HF produces at low temperature a blue solution, producing the same esr signal as that observed for the ClF_3-$O_2^+SbF_6^-$ system. A systematic esr study of these systems is underway in collaboration with Dr. Goldberg from the Science Center of our corporation.

We have also studied the esr spectra of the neat solids, $O_2^+BF_4^-$, $O_2^+AsF_6^-$, and $O_2^+Sb_2F_{11}^-$ over the temperature range 25 to -196 C. Very interesting effects of the temperature on the spectra were observed and will be discussed in detail in manuscript form in the next report.

The only synthetic methods reported (Ref. 10, 11) for $O_2^+BF_4^-$ involve O_2F_4 that must be made either by low-temperature glow-discharge or γ-irradiation. Furthermore, O_2F_4 is unstable and, therefore, difficult to handle. We have now discovered

a more convenient synthesis using uv photolysis of an O_2-F_2-BF_3 mixture and trapping the unstable product, $O_2^+BF_4^-$, in the lower section of the reactor at -78 C.

HALOGEN PERCHLORATES

The new salt $Cs^+Br(OClO_3)_2^-$ was prepared according to

$$CsBr + 2ClOClO_3 \rightarrow Cs^+ Br(OClO_3)_2^- + Cl_2$$

Its structure and the nature of its perchlorate ligands was established by vibrational spectroscopy. An interesting correlation between vibrational spectra and the nature of the ligands was established allowing distinction between covalent and ionic and between mono and bidentate perchlorato groups. The data were summarized in manuscript form and are given in Appendix C.

METAL PERCHLORATES

Since certain transition metal perchlorates have significant potential as burning-rate modifiers for solid propellants, a systematic study using $ClOClO_3$ for their synthesis was initiated. It was shown that anhydrous $CrO_2(ClO_4)_2$ and $Ti(ClO_4)_4$ can be prepared by this technique in high-yield and purity. $Ti(ClO_4)_4$ is stable, not shock sensitive, and based on our structural study, contains four bidentate perchlorato ligands. Attempts to prepare an anhydrous iron perchlorate from $FeCl_2$ and $ClOClO_3$ were unsuccessful. The results from our study are summarized in manuscript form in Appendix D.

ALIPHATIC FLUOROCARBON PERCHLORATES

Fluorocarbon perchlorates are energetic compounds and might find use as plasticizers, particularly in metalized solid propellants. We have therefore spent considerable effort to explore the scope of our technique. It was found that single perchlorato-groups can be introduced into aliphatic fluorocarbons in high yield. However, the introduction of one perchlorato group per carbon atom in longer aliphatic chains, dramatically decreases the yield and compounds containing two or more perchlorato

groups per carbon atom are very unstable. They rapidly decompose with Cl_2O_7 elimination and formation of a carbonyl group. Our research in the aliphatic area has been completed and our results, uncovering much interesting novel chemistry, are summarized in manuscript form in Appendices E, F, and G.

AROMATIC FLUOROCARBON PERCHLORATES

This area will be discussed here in detail, since it was not written in manuscript form. In the preceding report (Ref. 3), it was shown that chlorine perchlorate and pentafluorophenyl iodide reacted according to the equation:

$$C_6F_5I + 2Cl_2O_4 \longrightarrow C_6F_5I(ClO_4)_2 + Cl_2$$

This complex solid resembled derivatives sometimes obtained from Cl_2O_4 and perfluoroalkyl iodides, $R_fI(ClO_4)_2$ (Ref. 12). Unfortunately, the hoped for, novel perfluoroaryl perchlorate, $C_6F_5ClO_4$, was not obtained. The exact nature of this aromatic example of a complex iodo perchlorate has not yet been established. However, there is strong evidence that the corresponding alkyl moieties are the salt like materials, $[(R_f)_2I]^+[I(ClO_4)_4]^-$. This evidence is mainly spectroscopic and is discussed in detail in Appendix G of this report. Furthermore, we have found that these complexes are subject to controlled decomposition as shown:

$$[(R_f)_2I]^+[I(ClO_4)_4]^- \longrightarrow 2\ R_fClO_4 + 2\ "IClO_4"$$

Thus, the free covalent fluorocarbon perchlorate is generated from the solid (see Appendix G). If applicable to the pentafluorophenyl iodide case, the expected reaction is:

$$[(C_6F_5)_2I]^+[I(ClO_4)_4]^- \longrightarrow 2\ C_6F_5ClO_4 + 2\ "IClO_4"$$

Hence, there is still promise that this reaction of Cl_2O_4 will yield the first example of the, as yet unknown, class of compounds, the aromatic perchlorates.

When Cl_2O_4 and C_6F_5Br were reacted, a completely different result was obtained (Ref. 3). Here it again appeared as though 1 mols of Cl_2O_4 reacted for each mol of C_6F_5Br. However, the product was a liquid and obviously nonaromatic, since it lacked the strong 1500 cm^{-1} infrared band characteristic of aromatic rings, and its mass cracking pattern also failed to show the "normal" ion peaks of an aromatic species (Ref. 13). Attack on the ring π bonding system, as well as displacement of bromine was evident. Moreover, this attack has now been proved to have caused cleavage of the ring itself. This result was previously considered (Ref. 3) based on an always present infrared bond in the product near 1870 cm^{-1}. This region is typical for C=O bonds in acylfluorides (Ref. 14) and strongly suggests ring opening.

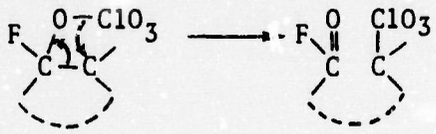
That this ring opening did occur has now been verified by ^{19}F nmr spectroscopy. Spectra of different vacuum distillation fractions of the liquid product all contained the characteristic acylfluoride resonance at approximately -25 ppm (Ref. 15). Unfortunately, the product was a mixture since there was more than one type of $-C\overset{O}{\underset{F}{<}}$ present. Some fractions showed three such resonances and all contained at least two, although the proportions of each varied. In addition, the spectra also showed several other resonances in the region from 97-142 ppm with most of these occurring between 117 and 125 ppm. Since fluorine nmr chemical shifts for alkylfluorine can vary widely in this region, depending on their environment, exact assignments cannot be made. Nevertheless, it should be noted that the principle resonances are all in the region characteristic for one fluorine attached to an inner carbon of an alkyl chain, which also has another electronegative substituent different from fluorine bound to it; eg. $F-\overset{|}{\underset{|}{C}}-Cl$, $F-\overset{|}{\underset{|}{C}}-Br$, or $F-\overset{|}{\underset{|}{C}}-ClO_4$ (see Appendix G).

Examination of the nmr spectra of the various fractions also revealed that the ratio of non-acylfluorines to acylfluorines was 4:1. Thus, the original five fluorines of C_6F_5Br are retained on treatment with Cl_2O_4; four in the alkyl chain and one in the acylfluoride end group. These observations pose still another interesting question with respect to the products of this reaction. Namely, if all the fluorines are retained and a C=O function is formed, it cannot have been

through decomposition of an R_fClO_4 group in the usual fashion shown:

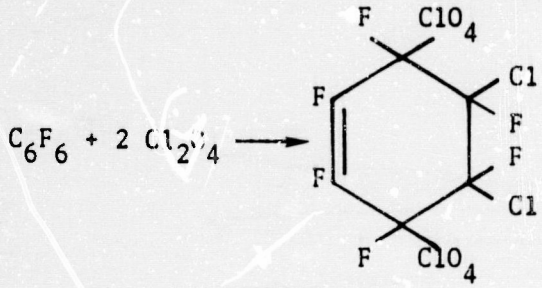
$$F\text{-}\overset{|}{\underset{|}{C}}\text{-}OClO_3 \xrightarrow{cat.} \rangle C{=}O + FClO_3$$

Furthermore, $FClO_3$ was not observed as a product of these reactives. An alternate decomposition path might involve the generation of Cl_2O_7 as part of the process leading to the carbonyl group formation. Such paths are more complex and have not been observed in other R_fClO_4 systems. Also, the small amounts of Cl_2O_7 found do not correspond to the apparent conversion of one carbon from each ring into a carbonyl group. Still another mechanism seems possible, perhaps most likely, and is shown schematically.



Thus, ring opening and carbonyl formation are accompanied by the transfer of ClO_3 to an adjacent carbon. Perchloryl (ClO_3) groups on carbon are known from reactions of $FClO_3$ (Ref. 16), although the main reactions usually entailed substitution of the F from $FClO_3$ onto carbon (Ref. 17). Fluorocarbon-ClO_3 moieties are unknown and even in hydrocarbon perchlorate systems, other investigators have not reported C-ClO_3 functions (Ref. 18). Additional effort is needed to separate and purify this mixture of perchlorato acylfluorides to better identify them, and thus, conclusively demonstrate whether they also contain perchloryl (ClO_3) substituents.

The widely different reactions of Cl_2O_4 experienced with C_6F_5I and C_6F_5Br prompted an examination of the "parent" member of this class of compounds, hexafluorobenzene. At -45 C a nearly quantitative uptake of 2 Cl_2O_4 for each C_6F_6 was observed. Chlorine was not liberated and no displacements occurred. Instead Cl_2O_4 addition occurred similar to that of fluoroolefins (Ref. 19) with single addition of Cl- and -$OClO_3$ elements across double bonds. Although the ClO_4 groups could be ortho, meta, or para to each other in $C_6F_6Cl_2(ClO_4)_2$, all the evidence indicates it is the symmetrical adduct shown:



Most informative in this respect was the ^{19}F nmr spectrum that exhibited only three types of fluorine in the ratio of 1:1:1. Hence, the six F's of the product must be present in equivalent pairs, 2:2:2. Figure 1 shows the three ^{19}F resonances under high-resolution conditions. It is apparent from the figure that each type of F is extensively split by spin-spin coupling to several different neighboring fluorines (there are five different couplings possible for each fluorine with the remaining five fluorines in the ring). However, the basic pattern shown by the three peaks, i.e., a multiplet for the one and doublets for the others, may be used for assigning these resonances when considered along with chemical shifts noted. In general, the highest chemical shifts found in fluorocyclohexenes are due to the olefinic fluorines (Ref. 15, 20). Thus, the highest shift here (142.4 ppm) is ascribed to the two olefinic fluorines. This peak is basically split into a doublet by two adjacent, equivalent fluorines, those of the para $>CFClO_4$ groups. By the same reasoning, the other doublet peak (125.3 ppm) must represent the other two fluorines also adjacent to the two para $>CFClO_4$ functions. Hence, the 125.3 ppm peak is assigned to the two $>CFCl$ groups. This leaves the multiplet at 113.5 ppm for assignment to the para $>CFClO_4$ fluorines. The complex multiplet arises from near equal coupling to the two different types of adjacent fluorine, olefinic, and $>CFCl$, and in a first approximation might be considered as a doublet of doublets.

It should be mentioned that in compounds of this kind, i.e., fluorocyclohexenes, there is the possibility for geometric nonequivalence of fluorines in the non-planar ring system. Thus, some $>CFCl$ or $>CFClO_4$ fluorines might be axial and some equatorial. However, it has been found that both types of fluorines are nmr equivalent and couple equally.

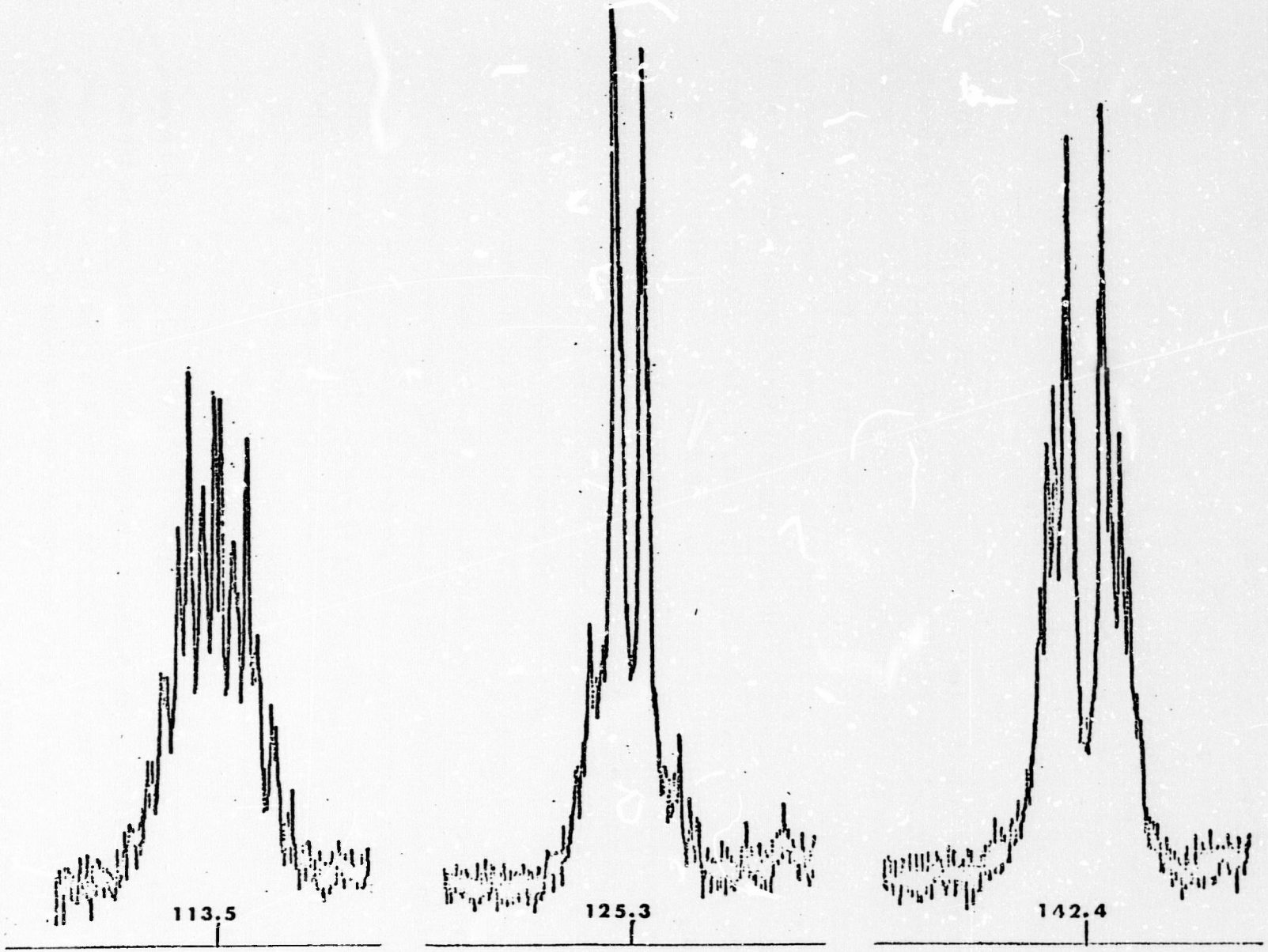


Figure 1. ^{19}F Resonances Under High-Resolution Conditions

In addition it might be deemed possible that the two perchlorato groups are not para but ortho to one another, which would lead to a structure also having only three types of fluorine. This is considered most unlikely owing to the strong mutual replusion of the bulky ClO_4 groups (see Appendix G).

The infrared and Raman spectra of $C_6F_6Cl_2(ClO_4)_2$ are shown in Fig. 2. The cyclohexene double-bond stretch is quite noticeable at 1740 cm^{-1} in the region typical for that group (Ref. 14). This helps to "prove" that the hexafluorobenzene has been converted to a cyclohexene by the addition of two Cl_2O_4 molecules. The usually very strong bands caused by covalent perchlorate substituents (1290, 1030, and 605 cm^{-1}) confirm the presence of that group in the compound. Mass spectra of the more complex fluorocarbon perchlorates are sometimes less informative for two reasons. First, parent peaks are usually not observed because of the ready loss of ClO_3^+ and rapid extensive fragmentation. Second, recombination ions can obscure the "true" fragmentation pattern. In the case of $C_6F_6Cl_2(ClO_4)_2$, it was found that these phenomena were suppressed sufficiently that an informative spectrum was obtained. Although a parent ion m/e was not observed, m/e values for the fragments, parent minus ClO_4, ClO_5, Cl_2O_6, Cl_2O_7, and Cl_3O_7 were observed. Other important ions corresponded to fragments such as $C_3F_3Cl_2O_7^+$, $C_6F_5Cl_2O^+$, $C_6F_4Cl_2O_2^+$, $C_6F_4ClO_2^+$, $C_6F_3O_2^+$, $C_4F_4ClO^+$, and $C_3F_3Cl_2^+$. Very intense peaks were present for the $C_3F_3^+$ and ClO_x^+(X=1-3) ions as expected. Relative intensities of groups of peaks assigned to various chlorine containing fragments (caused by distribution of chlorine isotopes) confirmed the number of Cl atoms in the fragments and hence, partially the assignments.

That a third molecule of Cl_2O_4 did not add across the last double bond is not surprising in view of the fact that Cl_2O_4 was shown not to react with isolated, alicyclic olefinic bonds, of either perfluorocychlohexene or perfluorocyclobutene.

REACTIONS OF CHLORINE NITRATE WITH TRIFLUOROMETHYL IODIDE

In view of the preparation of CF_3OClO_3 from CF_3I and Cl_2O_4 and the recent successful synthesis of CF_3OONO_2 (Ref. 21), an attempt to prepare the unknown CF_3ONO_2 was conducted using CF_3I and $ClNO_3$. The expected reaction was:

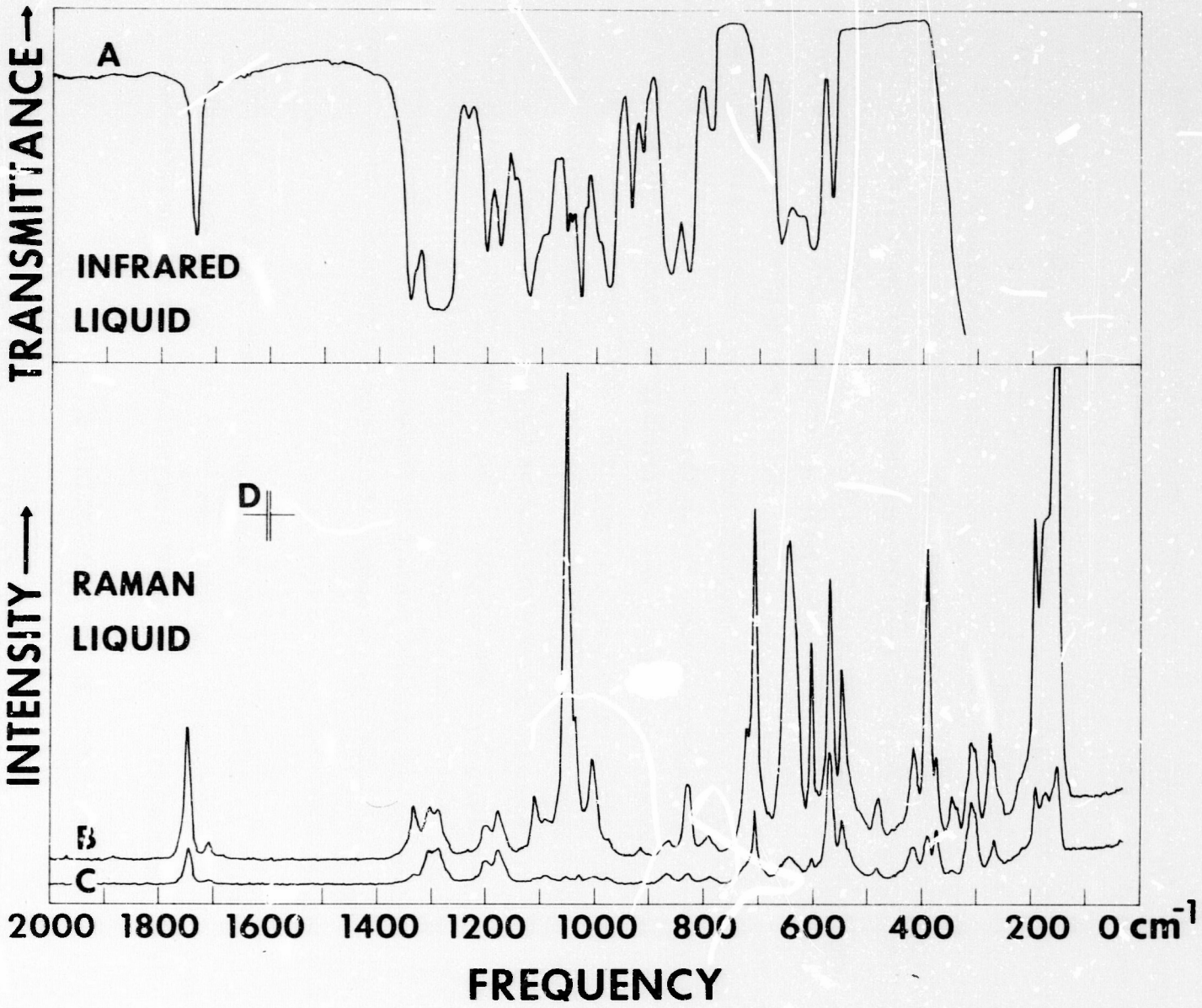


Figure 2. "$C_6F_6Cl_4O_8$" A, Liquid/AgCl Plates; B, Incident Polarization Perpendicular; C, Parallel; D, Spectral Slit Width

$$CF_3I + 2\ ClNO_3 \longrightarrow [CF_3I(NO_3)_2] + Cl_2$$
$$\downarrow$$
$$CF_3ONO_2 + INO_3$$

A smooth reaction occurred below -45 C giving the expected Cl_2 by-product. However, warming to ambient temperature produced a mixture of unreacted CF_3I along with COF_2, N_2O_5, and a varicolored orange solid of indeterminate composition. While COF_2 might be expected as one product of the decomposition of CF_3ONO_2, its co-product FNO_2 was not observed.

$$CF_3ONO_2 \not\longrightarrow COF_2 + FNO_2$$

An alternate decomposition involving the formation of N_2O_5 and COF_2, while more complex is more in keeping with the observations.

$$CF_3I(NO_3)_2 \longrightarrow [CF_3I{=}O] + N_2O_5$$

$$[CF_3I{=}O] \longrightarrow COF_2 + [FI{=}O]$$

$$[FI{=}O] + ClNO_3 \longrightarrow \text{solids}$$

Carbonylfluoride and N_2O_5 were obtained in nearly a 1:1 ratio and more $ClNO_3$ reacted than required just for the formation of $CF_3I(NO_3)_2$. This complex reaction, which did not furnish the desired CF_3ONO_2, was not examined farther.

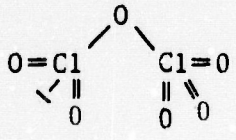
uv-PHOTOLYSIS REACTIONS OF F_2-SbF_5

We have previously shown (Ref. 3, 4) that the uv-photolysis of F_2 - Lewis acid mixtures produces a very powerful oxidizing species capable of fluorinating NF_3 to NF_4^+. We have now extended this reaction to the N_2 - F_2 - SbF_5 and the Kr - F_2 - SbF_5 systems in order to obtain an estimate of the oxidizing power of this species. Both Kr and N_2 have higher ionization potentials than NF_3. Small amounts of white solids formed in these systems. However, their spectroscopic examination revealed no evidence for the presence of N_2F^+ or NF_4^+ and KrF^+ salts, respectively.

These data suggest that the oxidizing power of the $SbF_6^{\cdot}$ radical, which we postulated based on our previous successful NF_4^+ synthesis, is between 13 and 14 ev. A previous report by Streng (Ref. 22) that KrF_2 can be prepared by uv photolysis of Kr and F_2 was examined. No evidence for KrF_2 formation was obtained in either quartz or Pyrex vessels. A glow-discharge apparatus was built and will be used for synthesizing KrF_2.

LOW-TEMPERATURE OZONIZATION REACTIONS

Our low-temperature ozonization studies of positive halogen compounds were completed and summarized in manuscript form in Appendix H. They resulted in a new mixed halogen oxide $O_2BrOClO_3$ and in a new and improved synthesis of the useful oxidizer, $NO_2^+ClO_4^-$, eliminating the use of one (ClO_2) of the two shock sensitive materials required for the conventional synthesis (Ref. 23). Attempts to synthesize the novel oxidizer, $NO_2^+BrO_4^-$, by an extension of this method were unsuccessful. New insight into the structure of Cl_2O_6 was obtained suggesting for it the oxygen-bridged chloryl perchlorate structure:



SYNTHESIS OF NOVEL HALOGEN HEPTOXIDES

We have continued our efforts to synthesize the novel halogen heptoxides, Br_2O_7 and I_2O_7 according to:

$$2MeXO_4 + SO_3 \rightarrow Me_2SO_4 + X_2O_7$$

whereas Cl_2O_7 is formed in good yield from $CsClO_4$ (Ref. 3), free Br_2O_7 or I_2O_7 could not be isolated in this fashion, probably owing to complex formation between the product and SO_3. Consequently, the SO_3 starting material was substituted by FSO_2-O-SO_2F, which should not form any adducts with the halogen oxides and is more volatile than SO_3. Its reaction with $CsClO_4$ was studied as a model reaction for

Br_2O_7 and I_2O_7. Four reactions between $CsClO_4$ and $S_2O_5F_2$ were carried out at -45, -25, 0, and +25 C, respectively. However, in all cases, only unreacted starting materials were recovered. The new Br_2O_7 and I_2O_7 species would be excellent candidates for high-detonation pressure explosives.

ATTEMPTED SYNTHESES OF $HOIOF_4$, IO_2F_3, AND $FBrO_2$

These reported compounds are interesting starting materials for the synthesis of novel oxidizers and therefore, were of interest to us. Engelbrecht and Peterfy first reported the synthesis of $HOIOF_4$ and its derivative, IO_2F_3, in 1969 (Ref. 6) according to:

$$Ba_3H_4(IO_6)_2 + 14\ HSO_3F \longrightarrow 2HOIOF_4 + 8H_2SO_4 + 3\ Ba(SO_3F)_2$$

$$SO_3 + HOIOF_4 \longrightarrow IO_2F_3 + HSO_3F$$

Since that time, the discoverers amplified somewhat on the preparation and properties of these compounds (Ref. 7), but nothing regarding the chemistry of these interesting iodine (VII) materials has appeared.

In order to examine this chemistry, two attempts were made to prepare $HOIOF_4$ following the reported procedure as closely as possible. After addition of the barium salt to a large excess of fluorosulfonic acid, the impure $HOIOF_4$ and HSO_3F were vacuum distilled away from the $Ba(SO_3F)_2$. Upon addition of 65 percent oleum (the SO_3 source specified) to the distillate, yellow needles of IO_2F_3 were supposed to form. However, this occurred only fleetingly in that small amounts of yellow solid formed but they quickly redissolved. Efforts to concentrate the solution and sublime IO_2F_3 from it as reported were unsuccessful. Even on long term pumping at low pressure and various temperatures up to 70 C, no sublimate was obtained and there was left a pale yellow, pasty solid. This was an iodine species, but had much $-SO_3F$ also. Further attempts to prepare these compunds awaits the verification of the purity of the starting barium salt, a purchased material.

Similarly, attempts were unsuccessful to duplicate the $FBrO_2$ synthesis from $KBrO_3$ and BrF_5 previously reported by Schmeisser (Ref. 5). Reactions between these two starting materials were carried out over a fairly wide temperature range and did not produce isolable quantities of $FBrO_2$.

MISCELLANEOUS STRUCTURAL STUDIES

A number of structural studies are under progress, which have not yet been mentioned in the above discussion. Our continuing interest in the novel chlorine oxyfluoride, ClF_5O, and its cation, ClF_4O^+, prompted us to study the vibrational spectrum of SF_4O. The latter is isoelectronic with ClF_4O^+ and therefore, expected (Ref. 23) to exhibit a very similar vibrational spectrum. The exact knowledge and understanding of the SF_4O spectrum would be of great help in identifying a possible ClF_4O^+ salt. Inspection of previous literature on SF_4O (Ref. 24 through 26) strongly indicated the need for re-examination. Therefore, we have prepared a carefully purified SF_4O sample and recorded its infrared and Raman spectra in the solid, liquid, gaseous, and matrix-isolated state. We have also measured for most fundamentals the ^{32}S- ^{34}S isotopic shifts. It was found that 10 of 12 bands previously attributed (Ref. 26) to SF_4O are either due to impurities or were misassigned. A normal coordinate analysis of the compound is in progress. The results will be given in detail in the next report.

Inspection of our SF_4O data (see above) also revealed that the assignments for SF_4 are still unsatisfactory. We have therefore re-examined the complete vibrational spectrum of solid, liquid, gaseous, and matrix-isolated SF_4 and measured the sulfur isotopic shifts. The assignments indeed needed correction and the normal coordinate analysis is presently being redone.

The vibrational spectrum of NF_3O (Ref. 27, 28) is very unusual. Since we had a sample of $Cs^+CF_3O^-$ on hand from other studies, it appeared very interesting to examine its vibrational spectrum. It was found that CF_3O^- which is isoelectronic with NF_3O, exhibits a spectrum very similar to that observed for NF_3O, indicating that the latter is not unique. A detailed vibrational and force constant analysis is in progress, the results of which will be given in next year's report.

A structural study of ClF_3O by microwave spectroscopy was initiated at the National Bureau of Standards in collaboration with Dr. F. Iovas. Experimental measurements were started last September during a brief stay of K. Christe at NBS.

A vibrational analysis of SF_5Br was carried out in collaboration with Drs. N. Bartlett and A. Roland of the University of California at Berkeley and an input was written for a joint paper.

Samples of three different NF_4^+ salts were synthesized and sent to Dr. M. Symons of the University of Leicester, England, who will study their esr spectra after exposure to γ-irradiation.

EXPERIMENTAL

REACTION OF Cl_2O_4 WITH PERFLUOROBENZENE

Hexafluorobenzene (1.11 mmol) and Cl_2O_4 (2.64 mmol) were combined at -196 C in a 10-ml cylinder, and then allowed to react at -25 C for one week. On recooling to -196 C, only a trace of noncondensable gas was observed. While warming toward room temperature, the volatile materials present were separated by fractional condensation. These consisted solely of unreacted Cl_2O_4 (0.46 mmol). When opened in the dry box, the cylinder was found to contain a clear, colorless, somewhat viscous liquid, 0.501 g. The weight calculated for 1.11 mmol of the bis-adduct, $C_6F_6Cl_4O_8$ was 0.505 g. Thus, the yield of this adduct was 99.2 percent.

REACTIONS OF Cl_2O_4 WITH CYCLIC PERFLUOROOLEFINS

Perfluorocyclohexene (2.24 mmol) and Cl_2O_4 (2.30 mmol) were placed at -196 C into a 30-ml cylinder and warmed then to -45 C. After 4 weeks, the volatile products were examined by infrared and found to be unchanged c-C_6F_{10} and Cl_2O_4. Similarly, 1 week at -23 C produced no evidence for reaction of these materials. Therefore, they were allowed to warm slowly to ambient temperature and were left there for 6 days. This resulted in the decomposition of the Cl_2O_4 to Cl_2 and O_2, but no addition to the olefin occurred.

Perfluorocyclobutene (1.15 mmol) and Cl_2O_4 (1.26 mmol) were also kept for 4 weeks in a 10-ml cylinder at -45 C. Monitoring by infrared showed no new materials and the c-C_4F_6 and Cl_2O_4 were unchanged.

REACTION OF $ClNO_3$ AND TRIFLUOROMETHYL IODIDE

Chlorine nitrate (4.02 mmol) and CF_3I (1.75 mmol) were successively condensed into a 30-ml stainless-steel cylinder cooled to -196 C. After warming slowly, the reactor was kept at -45 C for 6 days. Recooling to -196 C showed that no noncondensables had formed. Vacuum fractionations of those materials, volatile at -45 C, showed them to be unreacted $ClNO_3$ (0.40 mmol) and by-product Cl_2 (1.79 mmol) with

traces only of COF_2 and CF_3I. Warming to room temperature yielded N_2O_5 (1.14 mmol), COF_2 (1.07 mmol), and unreacted CF_3I (0.65 mmol). There remained in the reactor a sticky, varicolored orange solid (0.219 g).

REACTION OF $CsClO_4$ WITH PYROSULFURYL FLUORIDE

A 30-ml cylinder was loaded with $CsClO_4$ (2.01 mmol) in the dry box and $S_2O_5F_2$ (0.81 mmol) was condensed over it at -196 C. The mixture was then kept at -45 C for a week. The only volatile material present at that time was $S_2O_5F_2$ (0.81 mmol) indicating that no reaction had occurred. Similarly, when contacted for 1 week at -25 C, 0 C, or 25 C the $S_2O_5F_2$ was fully recoverable and thus unreacted.

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Vibrational Spectrum and Force Constants of the XeF_5^+ Cation

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Received . . . . . .

Abstract

The infrared 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^{--}.

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] $XeOF_5^+$. 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 infrared 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^{--} 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 Section

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%). Solid products were handled in the dry nitrogen atmosphere of a glove box.

Infrared 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 4880Å 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 infrared spectroscopy.

Synthesis of $XeF_5^+BF_4^-$. Boron trifluoride (17.55 mmol) was added in increments at 25° to a Teflon FEP U-trap containing XeF_6 (17.15 mmol). The mixture was kept at 25° for 12 hours. Unreacted BF_3 (0.4 mmol) was pumped off at 0° leaving behind 5.384g (17.14 mmol) of $XeF_5^+BF_4^-$.

Synthesis of $XeF_5^+AsF_6^-$. Arsenic pentafluoride (3.95 mmol) was added at -196° to a Teflon FEP ampoule containing $XeF_5^+BF_4^-$ (1.88 mmol). The mixture was kept at -80° for 20 hours. The volatile material was removed in vacuo

and consisted of BF_3 (1.86 mmol) and unreacted AsF_5 (2.08 mmol). The white solid residue weighed 783 mg in good agreement with the weight (781 mg) calculated for 1.88 mmol of $XeF_5^+AsF_6^-$.

Results and Discussion

^{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 mol 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 I). 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 I).

Vibrational Spectra. Figures 1 and 2 show the infrared 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 II and are compared with those reported for isoelectronic IF_5.[12,22,23]

Table I

^{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

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 infrared 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^{--} [8] have also been recorded, but again no detailed vibrational analysis was given.

Inspection of Figures 1 and 2 and of Table II 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 $XeF_5^+BF_4^-$, the spectra are quite similar. The only deviations from the selection rules for BF_4^- of symmetry T_d are observed in the infrared

Table II. Infrared 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[a]							Assignment (point group)		
IF_5[b]		$XeF_5^+BF_4^-$			$XeF_5^+AsF_6^-$		XF_5	BF_4^-	AsF_6^-
IR	Ra	IR	R		IR	R	(C_{4v})	(T_d)	(O_h)
		solid	solid	HF soln	solid	solid HF soln			
		1289w 1268vw,sh			1300vw		$\nu_2+\nu_7(E)$	$\nu_1+\nu_4(F_2)$	
		1192m,sh				741(1.6) 725(0.6)			$\nu_3(F_{1u})$
		950 to 1150vs,br	1159(0+) 997(0.1) 969(0.1)	1040(0+)dp		715(0+)		$\nu_3(F_2)$	
		773m	775(0.5)	776(0.5)p	740 to 630vs	688(2)		$\nu_1(A_1)$	
			672sh						
710s	710s,p	672s,sh	667(6.5)	679(5.4)p		673(2.7) 679(6.3)p	$\nu_1(A_1)$		$\nu_1(A_{1g})$
640vs	631	652vs	655sh			663(2.6)	$\nu_7(E)$		
	616vs,p 604m	614w	615(10)	625(10)p 610sh		631(10) 625(10)p 600sh 610sh	$\nu_2(A_1)$ $\nu_4(B_1)$		
		526m 513w	525(0.3)	525(0.1)dp	595vw 570w 548m 537w	600sh 545(1) 557(0+)dp		$\nu_4(F_2)$	$\nu_2(E_g)$
372m	372w	416m 407m	416(0.4) 407(0.4)	410(0.3)dp	408sh	411(0.5) 408(0.7)dp	$\nu_8(E)$		
					387s	394(0.9) 380(0.1)			$\nu_4(F_{1u})$
					372w,sh	375(0.5) 375(0.7)dp 365(0.4)			$\nu_5(F_{2g})$
318m	318mp	353m	359(0.1) 349(0+)	358(0.1)p	345m	346(0.2) 352sh	$\nu_3(A_1)$	$\nu_2(E)$	
	276w		299(0.7) 267(0+)	302(0.4)dp		298(1.1) 299(1.0)dp 258(0+)	$\nu_6(B_2)$ $\nu_5(B_1)$		
	200vw		222(0.1)	218(0.1)dp		218(0.2) 217(0.2)dp	$\nu_9(E)$		
			154(0.1)	140br		130(0.1)	Bands due to lattice vibrations or weak F bridges		
			102(0+)			77(0+)			

(a) Uncorrected Raman intensities
(b) Data from ref 12, 22, and 23

spectrum of the solid, where ν_1 (A_1) and ν_2 (E) became infrared 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 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 $XeF_6 \cdot$ Lewis acid adducts has been established by single crystal X-ray diffraction studies,[3-5] 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 infrared 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 infrared 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 infrared 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 infrared 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 III 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^{--} (see Figure 3 and Table III) 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.

Table III. Comparison of the Fundamentals of the Isoelectronic Series XeF_5^+, IF_5, TeF_5^-, and SbF_5^{--}

Assignment in Point Group C_{4v}		Approx. Description of Vibration	Frequencies (cm^{-1})					
			XeF_5^+		IF_5[a]	TeF_5^-[b]		SbF_5^{--}[b]
			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

(a) Data from ref 12, 22, and 23
(b) Data from ref 12

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 infrared 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^{--}. The required potential and kinetic energy metrics were computed with a machine method [25] using the geometries shown in Table IV. The force constant definitions used are those of Begun et al.[23], except that the deformation

Table IV. Assumed Molecular Parameters for XeF_5^+, IF_5, TeF_5^-, and SbF_5^{--}

	XeF_5^+ [a]	IF_5 [b]	TeF_5^- [c]	SbF_5^{--} [d]
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

(a) K. Leary, D. H. Templeton, A. Zalkin, and N. Bartlett, Inorg. Chem., 12, 1726(1973).

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coordinates are weighted by unit (1Å) 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 V as sets A and B. The potential energy distribution showed that all vibrations were highly characteristic (88% 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 V) resulted in highly characteristic vibrations.

Inspection of Table V shows smooth force constant trends within the isoelectronic series XeF_5^+, IF_5, TeF_5^-, and SbF_5^{--}. Of the assignments previously reported [12] for IF_5, TeF_5^- and SbF_5^{--} 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 Figure 3. Assignment of either the 492 or 507 cm^{-1} single crystal Raman component [12] to ν_4 (B_1) might resolve this discrepancy and results in a better force field trend and is given as Set A in Table V. The 479 cm^{-1} single crystal Raman band might be

Table V. Comparison of the Symmetric and Internal Force Constants of the Isoelectronic Series XeF_5^+, IF_5, TeF_5^-, SbF_5^- Using the Assignments of Table III

		XeF_5^+				IF_5	TeF_5^-		SbF_5^-
		A	A'	B	B'		A	B	
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 [b]	0	-0.2 [b]	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
	$F_{33}=Mf_\beta+(1-M)f_\alpha+2Mf_{\beta\beta}+Mf_{\beta\beta'}+2(1-M)f_{\alpha\alpha}+(1-M)f_{\alpha\alpha'}+Nf_{\alpha\beta}+Nf_{\alpha\beta'}$ [c]			2.90		2.47	2.15		2.23
B_1	$F_{44}=f_r-2f_{rr}+f_{rr}$	4.17		5.03		4.08	2.66	3.75	1.68
	$F_{55}=f_\beta-2f_{\beta\beta}+f_{\beta\beta'}$			2.53		[2.25] [d]	[1.9] [d]		[1.9] [d]
B_2	$F_{66}=f_\alpha-2f_{\alpha\alpha}+f_{\alpha\alpha'}$			0.86		0.76	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_α [e]			0.77		0.67	0.39		0.42
	f_β			2.36		2.05	1.88		1.77
	$f_{\alpha\alpha}$			-0.05		-0.03	-0.13		-0.09
	$f_{\beta\beta}$			.15		0.09	0.14		0.15
	$f_{\beta\beta'}$			.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

(a) Stretching constants are in mdyn/Å and deformation constants in mdyn/Å radian^2; the preferred force constant sets are underlined.

(b) Interaction term required for the potential energy distribution of ν_1 and ν_2 to be most characteristic, i.e., 100S_1 and 98% S_2, respectively. For $F_{12}=0$, the following PED was obtained: $\nu_1=74S_1+26S_2$ and $\nu_2=74S_2+26S_1$.

(c) 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^-, 0.88, 1.28.

(d) Values estimated from the trends observed for F_{33} and F_{88}.

(e) The internal deformation constants were computed assuming $f_{\alpha\beta}=f_{\alpha\beta'}=f_{\alpha\alpha'}=0$

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 $\nu_6+\nu_8$=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 V, ν_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 V 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 oxidation state and the electronegativity of the central atom increase. This results in a decrease of the $\overset{\delta+}{X} - \overset{\delta-}{F}$ 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 V, 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^{--} 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 IV)

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 0.07Å.

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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Diagram Captions

Figure 1. Vibrational spectra of $XeF_5^+BF_4^-$: A, infrared 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.

Figure 2. Vibrational spectra of $XeF_5^+AsF_6^-$.

Figure 3. Plot of the stretching frequencies for the isoelectronic series SbF_5^{--}, TeF_5^-, IF_5, and XeF_5^+.

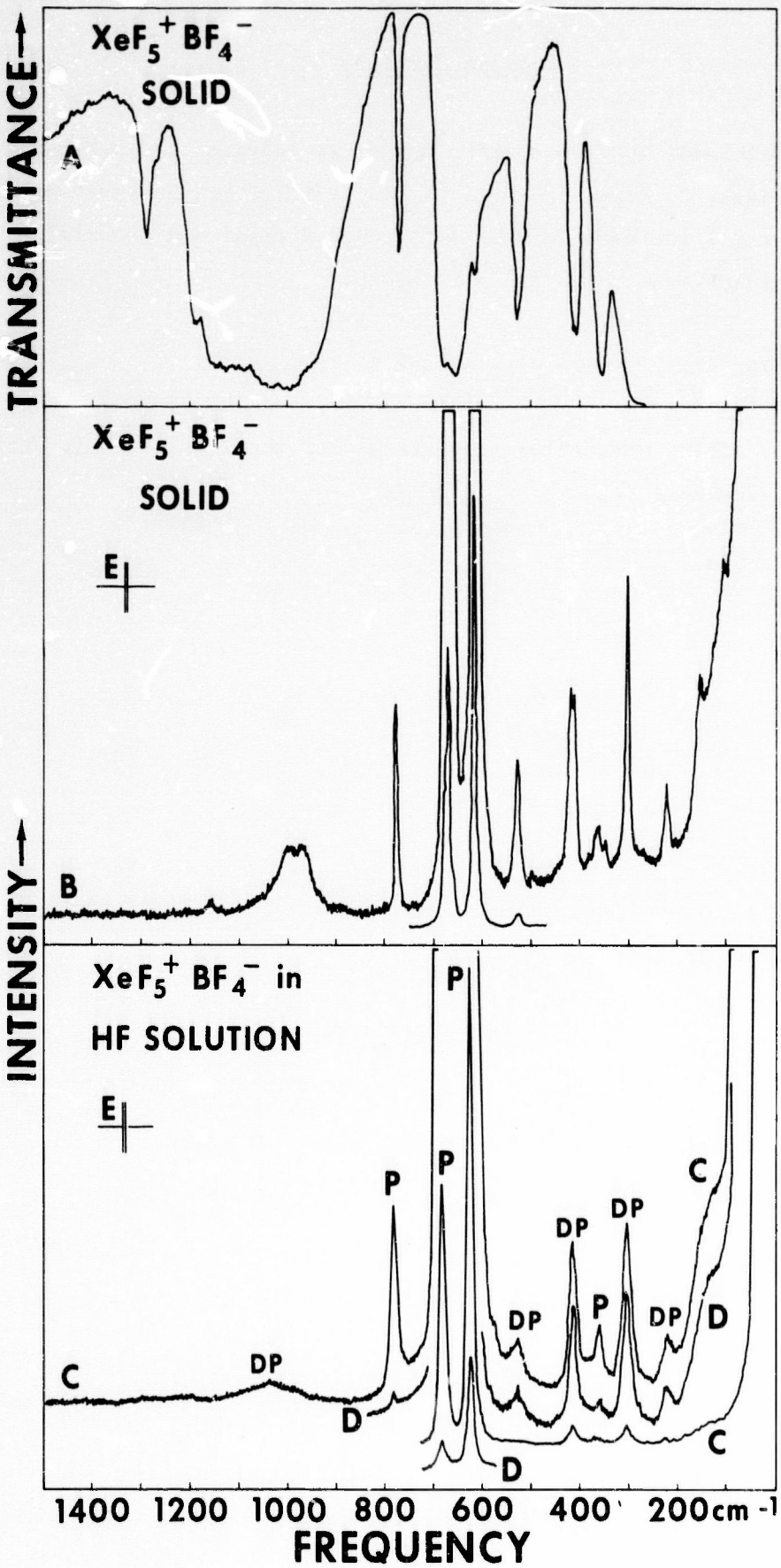

Figure 1.

R-9454/A-16

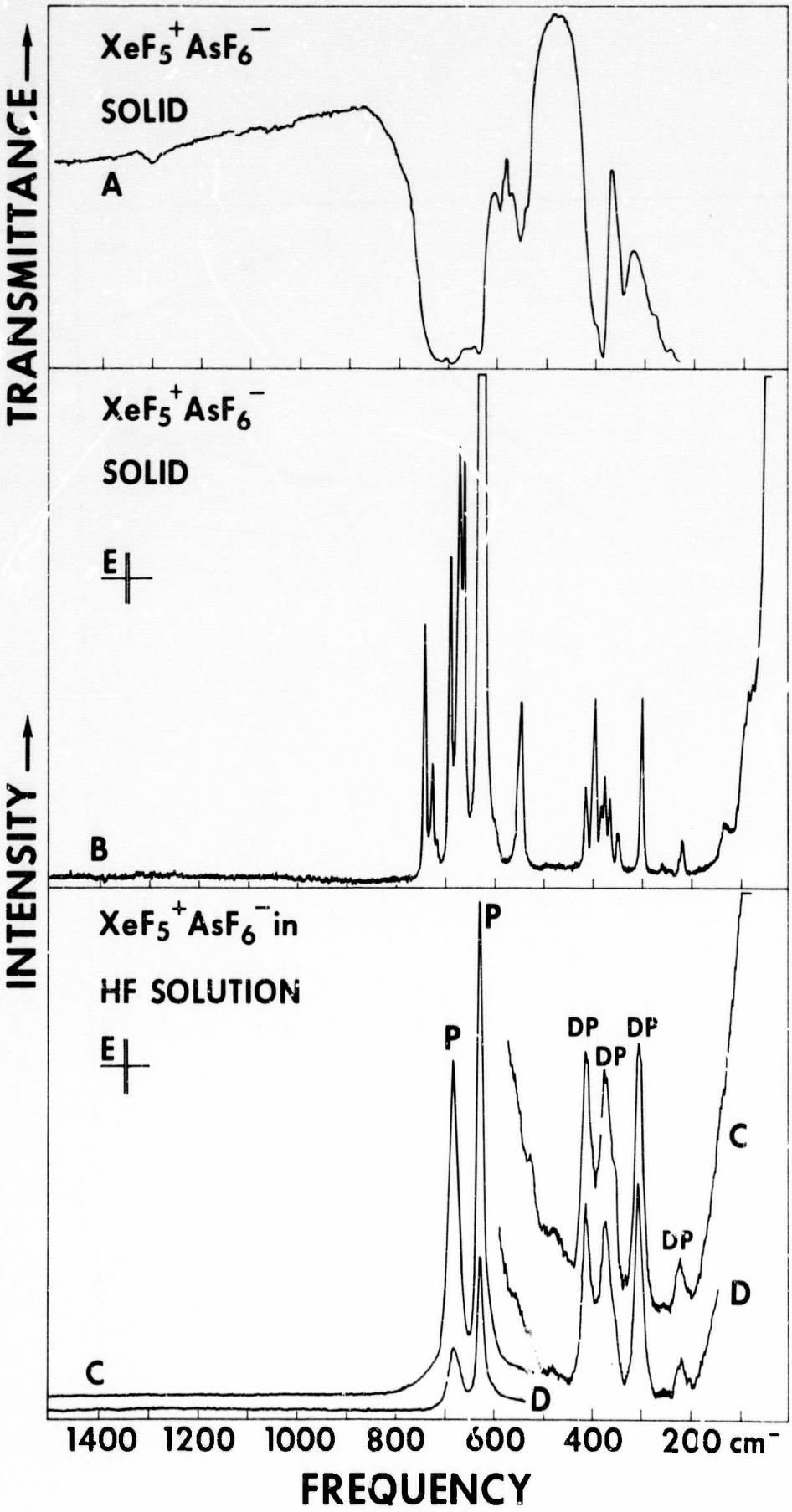

Figure 2.

R-9454/A-17

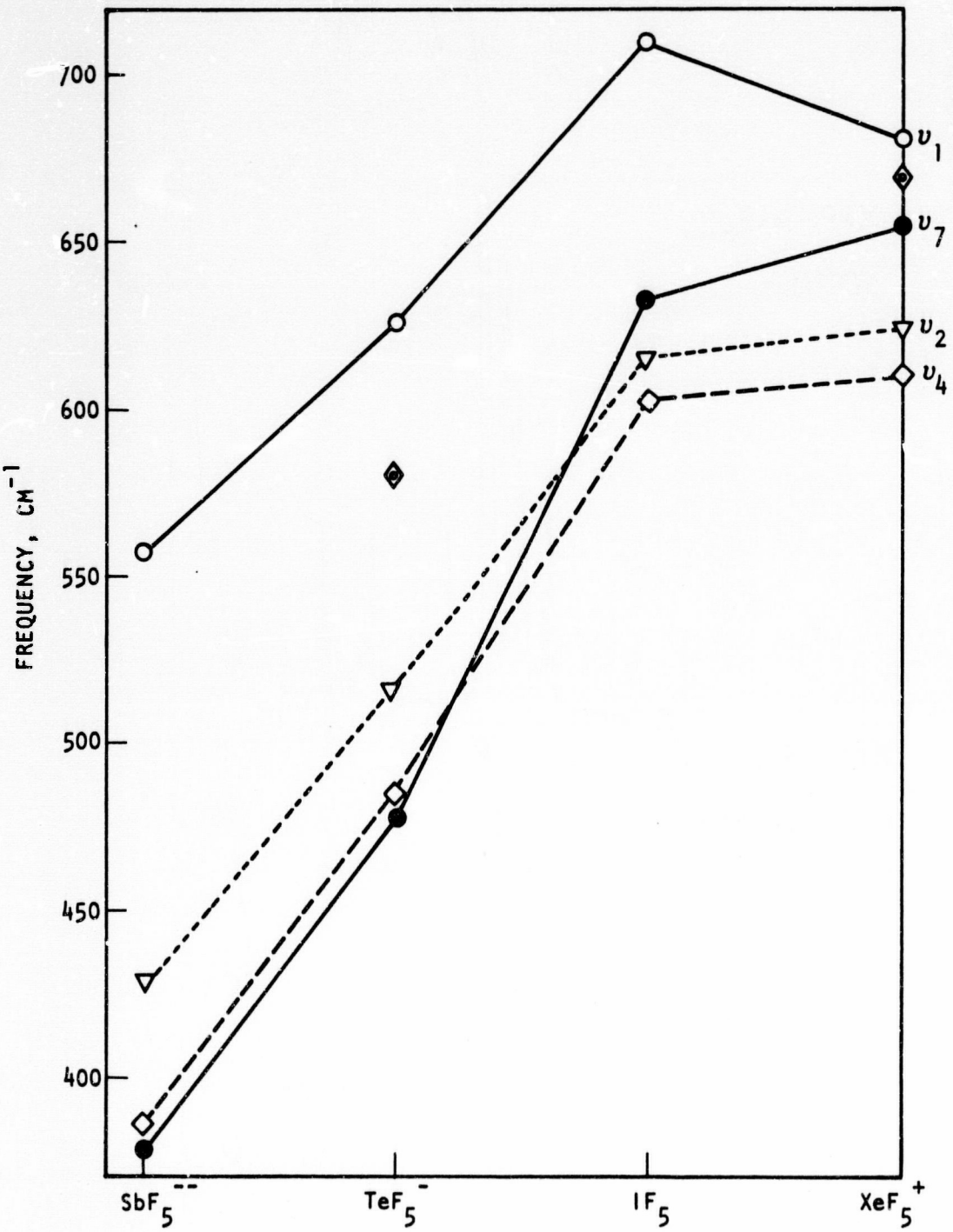

Figure 3.

R-9454/A-18

Reactions of the $(CF_3)_2NO$ Radical with Strong Oxidizers

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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 chemically producing CF_3 radicals at low temperature. This was demonstrated by a new and high yield synthesis of $(CF_3)_2NOCF_3$. In addition, the novel compound $[(CF_3)_2NO]_2CF_2$ was 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 pseudo-halogen with an oxidizing power similar to or higher than that of Cl_2.[3] Owing 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°.[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 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 or AgBr 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 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° in a passivated 25 ml sapphire-stainless steel reaction tube (Varian, Model CS-4250-3). After warming the mixture to 29° for one hour 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° for one hour in a sapphire reactor produced a small amount of a nonvolatile white solid. To increase the yield of this solid, the starting materials were recombined in the reactor and kept at 29° for 100 hours. 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 (8mg) 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° 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°. This procedure was repeated several times until the reaction was essentially completed and the reactor was kept at 25° for one 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°. The mixture was slowly warmed up to 25° 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 $O_2^+AsF_6^-$ irreversibly decomposed 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 ml 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°. The mixture was allowed to warm to -21° and was kept at this temperature for one 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° was required for $NO^+SbF_6^-$ formation and O_2 evolution. 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 3 and 16 mm at -31.2 and 0°, respectively. During fractional condensation, it slowly passes a -64° trap and is stopped at -78°. Its mass spectrum is given in Table I, its infrared and Raman spectrum in Table II. The ^{19}F nmr spectrum showed a 1:2:1 triplet at 67.96 (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, 68.39%.

Table I. Mass Spectrum (70ev) 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)

Table II. Vibrational Spectrum (cm^{-1}) of $[(CF_3)_2NO]_2CF_2$ and its Assignment Compared to Those of $[(CF_3)_2NO]_2CO$ and $[(CF_3)_2N]_2$

$(CF_3)_2N-N(CF_3)_2$ [a]		$(CF_3)_2NO-C(O)-ON(CF_3)_2$ [b]	$(CF_3)_2NOCF_2ON(CF_3)_2$		Tentative Assignment for $(CF_3)_2NOCF_2ON(CF_3)_2$
IR(gas)	RA(liquid)	IR(gas)	IR(gas)	RA(liquid)	
1333 s	1334 (4)	1317 vs	1322 vs	1325 (4)	
1310 s					
1292 s	1295 (3)	1269 vs	1291 vs	1285(10)p	CF_3str
	1278 (2)				
1232 s	1239 (9)p	1237 vs	1249 vs		
		1218 vs	1220 vs		CF_2str
				1230(6)br	
1205 s	1203(4)		1205 m		
1180 s	1176(3)		1189 m		
		1132 vs	1145 vs	1145(0+)br	νas CO_2
				1085(2)	
		1096 m	1070 w	1070(6)	νsymCO$_2$
		1038 s	1047 s	1046(18)p	νN-O
987vs	987(2)dp	975 s	976(2)	975(2)	νasNC$_2$
			960 w		
886 s	889(1)dp		893vw	895(14)p	
	864(1)p		852sh,vw	850(20)p	νsym NC$_2$
	832(2)p		835 w	835sh p	
			825sh	826(100)p	
785sh	764(2)p	777 w		775(13)p	
741 s	752(1)p	748 w	750 w	750(28)p	CF_3 def
722 s	724(2)p	713 s	719 s	718(1)	
			699 m	693(4)	
				681(5)	
652 w	652(3)p	668 w	640vw	635(0+)	
	592(6)p			590(5)dp	
	582(6)				
561 m	566(7)dp		555 w	562(12)dp	CF_3 def
536 m	538(2)dp		531 w	538(4)	
485sh	489(5)p		487 w	490(3)p	
			427vw	429(6)p	
	365sh,dp			368sh,dp	
	378(28)p			357(55)p	NC_2 def
	323(90)p				
	352(34)dp			338(34)dp	
250 m	252(4)dp			253sh,dp	
	237(7)dp			239(32)p	CF_3 rock
	202(2)dp			225(4)	
	153(6)dp			156(5)	
				130(12)p	
	108(3)dp			105(0+)dp	
	69 dp				

(a) values from ref. 15 (b) values from ref. 16

Results and Discussion

Of the strong oxidizers studied PtF_6 and O_2^+ salts are capable of oxidizing the $(CF_3)_2NO$ radical whereas MoF_6 is not under the given conditions. Rhenium hexafluoride with an electron affinity >-90 kcal/mol[12] appears to be able to slowly oxidize $(CF_3)_2$ NO 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 of significant amounts of CF_3 radicals. In the presence of unreacted $(CF_3)_2NO$ radicals, the CF_3 radical undergoes the following reaction

$$CF_3\cdot + (CF_3)_2NO\cdot \rightarrow (CF_3)_2NOCF_3$$

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 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 with unreacted $(CF_3)_2NO$ according to:

$$2(CF_3)_2NO + CF_2 \rightarrow [(CF_3)_2NO]_2CF_2$$

The formation of 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 can be considered as a derivative of the previously reported [14] $(F_2NO)_2$ CF_2 molecule in which the F on N atoms are replaced by CF_3 groups. The observed mass spectrum (Table I), vibrational spectrum (Table II), 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 II. These were made by comparison with the spectra previously reported for $(CF_3)_2$ N-N$(CF_3)_2$ [15] and $[(CF_3)_2NO]CO$ [16]. The general agreement between the vibrational spectra of the three compounds is excellent except for the difference in the relative Raman intensities of νsym NC_2 between $(CF_3)_2$-$NN(CF_3)_2$ and $[(CF_3)_2NO]_2CF_2$. As previously pointed out, [15] the Raman intensities observed for these modes in $(CF_3)_2$ $NN(CF_3)_2$ are much lower than those usually found for related $(CF_3)_2$ N-type molecules. A more detailed analysis is not warranted owing to the size of the molecule and to the possible existence of different rotational isomers as indicated by the nmr 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 related $(CF_3)_2NOCF_2$ X 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 (53.6) [21]. The fact that for $[(CF_3)_2NO]_2CF_2$ in addition to the 69.8 ppm CF_2 signal three other weak signals having similar chemical shifts were observed indicates the possible existence of rotational isomers which would not be surprising for this bulky molecule.

Acknowledgement

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Diagram Option

Figure 1. Vibrational Spectrum of $[(CF_3)_2NO]_2CF_2$. A and B infrared 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.

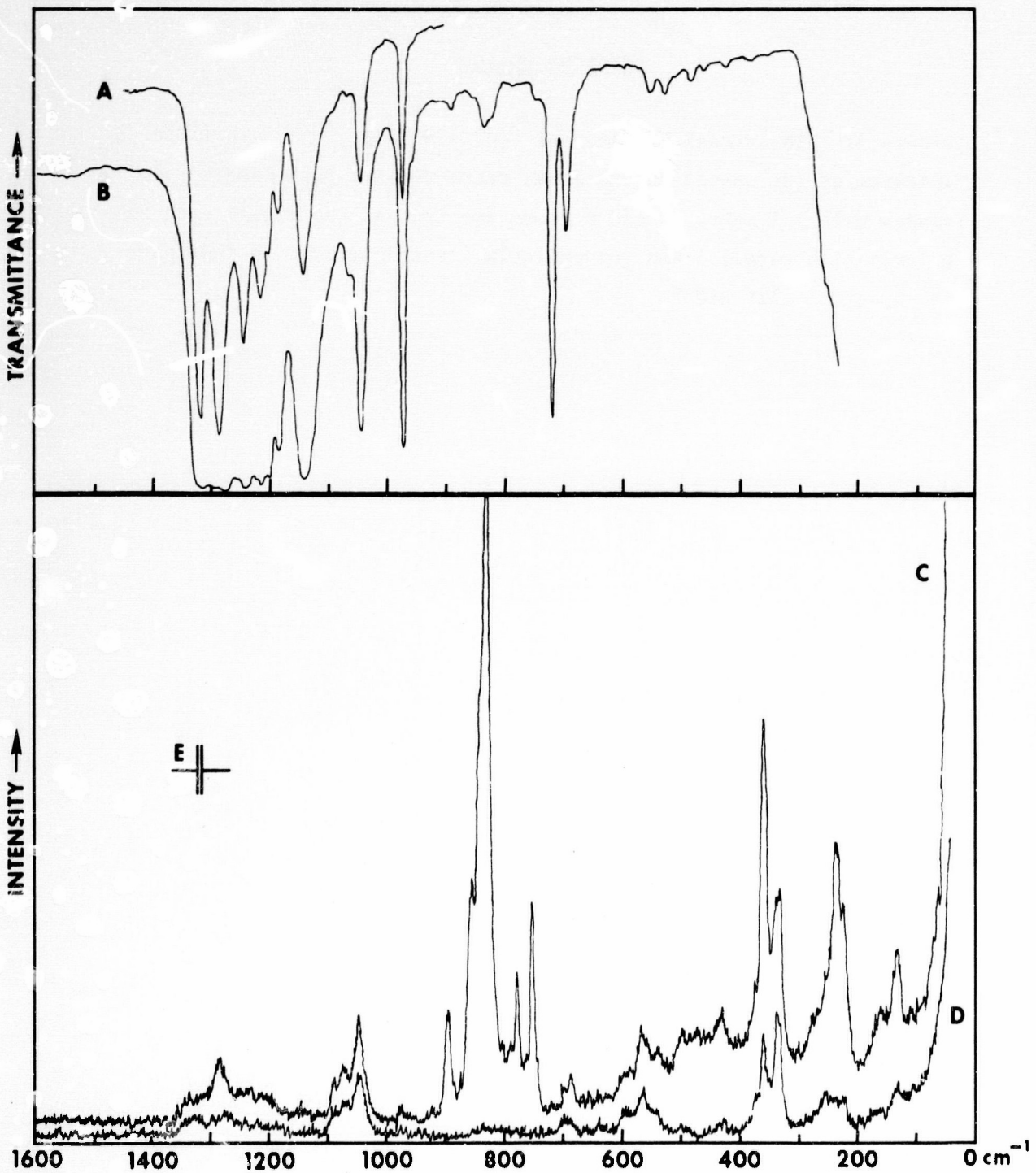
A
B
TRANSMITTANCE
C
D
E
INTENSITY
1600
1400
1200
1000
800
600
400
200
0 cm⁻¹

Figure 1.

Contribution from Rocketdyne, a Division of Rockwell International

Canoga Park, California 91304

Cesium Bis(perchlorato)bromate (I), $Cs^+[Br(OClO_3)_2]^-$

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Abstract

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 1F4Y). Pressures were measured with a Heise, Bourdon tube-type gage (0-1500 mm ± 0.1%). Anhydrous CsBr (ROC/RIC, 99.9% min.) 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 mini pellet press.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880Å 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 G.E. 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 G.E. 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 two

years. On recooling to -196° a few cc of non-condensable 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 was 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 six 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 two months at -45°, the solid product consisted of 32 mol% $CsBr(ClO_4)_2$ and 68% $CsClO_4$ 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:

$$CsBr + 2ClOClO_3 \longrightarrow CsClO_4 + BrOClO_3 + Cl_2$$

This reaction is followed by the much slower second step:

$$CsClO_4 + BrOClO_3 \longrightarrow CsBr(ClO_4)_2$$

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 towards $ClOClO_3$ 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 reducing 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 six 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 $CsBr(SO_3F)_2$.

Table I

X-Ray Powder Data for $CsBr(ClO_4)_2$

d,Å	Intensity	d,Å	Intensity
5.13	w	1.973	w
3.47	m	1.834	w
3.40	vs	1.709	ms
2.77	m	1.536	w
2.579	vw	1.512	vw
2.518	m	1.490	w
2.445	m	1.467	vw
2.188	s	1.411	m
2.018	ms	1.397	mw

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 seven. 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 band widths 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.

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)	ν as ClO_3 in phase (2A)
1115 vs, br	1105(0.3), br	ν as ClO_3 out of phase (2B)
1076 vw	1078 (10)	ν sym ClO_3 in phase (A)
947 vw	947 (6.2)	ν sym ClO_3 out of phase (B)
	933 (1.4)	
	904 (0.1)	
720 vs, br	719 (1.1)	ν as BrOCl out of phase (B)
633 m	633 (1.4)	ν sym BrOCl out of phase (B)
622 mw	625 (0.5)	
581 ms	584 (1.8)	δ sciss ClO_2 (A,B)
57? ms	578 (1.8)	δ as ClO_3 (A,B)
558 mw	558 (2.1)	δ umbrella ClO_3 (A,B)
	466 (1.2)	ν as BrOCl in phase (A)
	450 (1.5)	ν sym BrOCl in phase (A)
	407 (2.7)	δ rock ClO_3 (A)
	396 (2.5)	δ rock ClO_3 (B)

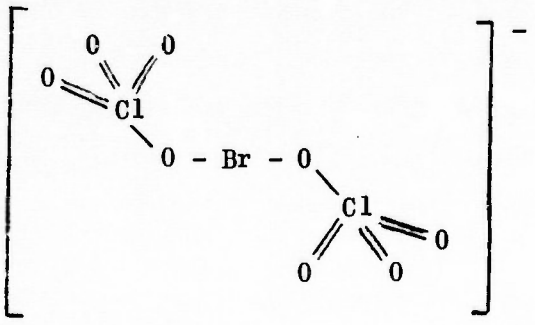
(a) uncorrected Raman intensities

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 $Cl\overset{O}{\underset{O}{<}}$ and the $Cl\overset{O}{\underset{O}{<}}$ group, 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 ν sym $Cl\overset{O}{\underset{O}{<}}$ 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 pseudo-isoelectronic 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 band widths 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 $X\text{-}OClO_3$ 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 pseudo-halide, the structure of $Br(OClO_3)_2^-$ should be analogous to those found for the pseudo-isoelectronic 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 five. 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 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.

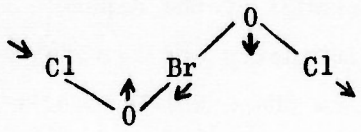
For an 11 atomic species of symmetry C_2 one would expect a total of 27 fundamentals. Of these, 13 belong to species A representing the in phase motions of the two ligands and 14 belong to species B representing the out of phase motions and the OBrO in plane deformation. These 27 modes may be broken 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 ~10cm^{-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 spectrum. The assignments are given in Table I and are supported by the observed band widths 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.

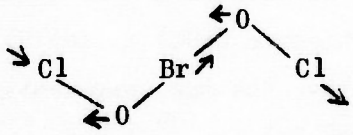
Table III

Summary of 27 Fundamentals Expected for $Br(OClO_3)_2^-$ in Point Group C_2

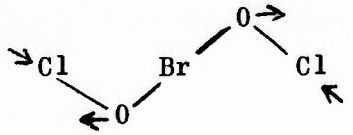
ClOBrOCl skeletal modes



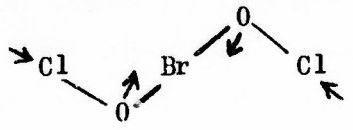
ν sym BrOCl out of phase (B)



ν asym BrOCl out of phase (B)



ν asym BrOCl in phase (A)



ν sym BrOCl in phase (A)

δ BrOCl in plane { in phase (A) / out of phase (B)

δ BrOCl out of plane = τ BrO { in phase (A) / out of phase (B)

δ OBrO in plane (B)

ClO_3 modes

ν asym ClO_3 { in phase (2A) / out of phase (2B)

ν sym ClO_3 { in phase (A) / out of phase (B)

δ asym ClO_3 { in phase (A) / out of phase (B)

δ sciss ClO_2 { in phase (A) / out of phase (B)

τ ClO_2 { in phase (A) / out of phase (B)

δ umbrella ClO_3 { in phase (A) / out of phase (B)

δ rock ClO_3 { in phase (A) / out of phase (B)

τ OCl { in phase (A) / out of phase (B)

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 of 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 band width. 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 indebed to Dr. L. Grant for helpful discussions and to the Office of Naval Research, Power Branch, for financial support.

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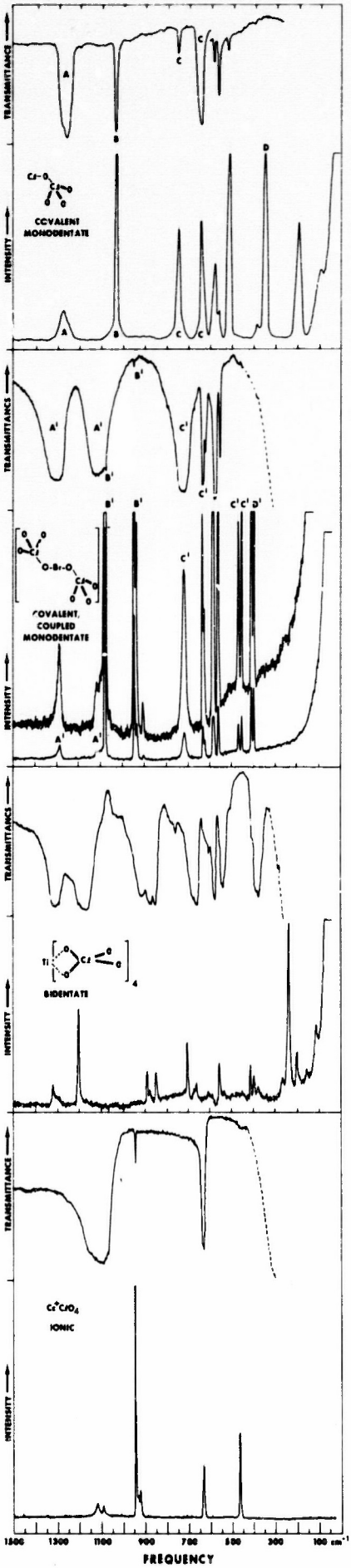
Diagram Caption

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^oK. 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 $ClOClO_3$.



R-9454

C-13/C-14

TITANIUM TETRAPERCHLORATE AND CHROMYL PERCHLORATE

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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 the perchlorate function. For example, they have been used to prepare the other halogen perchlorates,[6] $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$, and the novel fluorocarbon perchlorate[7], CF_3CClO_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:

$$TiCl_4 + 4ClOClO_3 \longrightarrow Ti(ClO_4)_4 + 4Cl_2$$

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 percent 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 infrared 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 eightfold 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 three months at ambient temperature. The ClO_4 content reported, 86.4 percent, significantly differs from the theoretical value of 89.25 percent. 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 infrared 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 infrared 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 $Cl\overset{O}{\underset{O}{\leqslant}}$ and the bridging $Cl\overset{O}{\underset{O}{\lessdot}}$ 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 four hours 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:

$$Ti(ClO_4)_4 \xrightarrow{\Delta} TiO_2 + 2Cl_2O_7 \xrightarrow{\Delta} 2Cl_2 + 7\ O_2$$

The observed O_2 to 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:

$$2Cl_2O_4 + CrO_2Cl_2 \longrightarrow CrO_2(ClO_4)_2 + 2Cl_2$$

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 infrared spectra of the liquid using rapid scanning. Bands were observed at 1305s, 1240vs, 1180s, 1030s, 980s, 875m, 850m, 735s, 685s, 660s, 580m, 545m, 510w, 435w, and 380m 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:

$$CrO_2(ClO_4)_2 \xrightarrow{\Delta} CrO_3 + Cl_2 + 3.5\ O_2$$

The observed O_2:Cl_2 ratio was 3.35:1.00 while the CrO_3 was identified by its infrared spectrum and m.p. Additional studies of metal halides with halogen perchlorates are in progress and will be reported later.

Acknowledgement

We are most grateful to the Office of Naval Research, Power Branch, for support of this work. Also, we thank Dr. L. R. Grant for helpful discussions.

Experimental Section

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 0.525g. The weight calculated for 1.22 mmol of $Ti(ClO_4)_4$ was 0.544g 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 four 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).

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°.

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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), 1180(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 catalyzed 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.

Acknowledgement

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The Infrared and Raman Spectra of Trifluoromethyl Perchlorate

Carl J. Schack* and Karl O. Christe

Received . . . . . .

Abstract

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] and $BrOClO_3$,[4] $Cs^+Br(OClO_3)_2^-$,[5] $I(OClO_3)_3$ and $Cs^+I(OClO_3)_4^-$[6] have been reported. Perchlorates bonded to hydrocarbons are also known but are very treacherous materials[1] and therefore havenot been investigated extensively. While spectroscopic studies of $O_3ClOClO_3$,[7,8] $HOClO_3$,[9] and the halogen perchlorates[5,6,10] have been completed, hydrocarbon 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 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 gage (0-1500 mm ± 0.1%). Trifluoromethyl perchlorate was prepared from CF_3I and $ClOClO_3$ as reported [3] 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 two years was not noticeably changed.

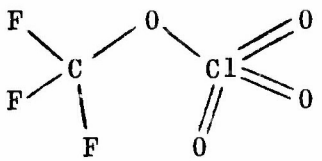
The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000-250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5 or 10 cm path length fitted with AgCl or AgBr windows. The instrument was calibrated by comparison with standard calibration 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 (~ 2mm ID) were used as sample containers for the liquid in the transverse-viewing-transverse-excitation techniques. 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, b.p. of 9.5°, Trouton Constant = 23.3, vapor phase molecular weight = 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 spectroscopically resemble a mixed ether, $B_3A\text{-}O\text{-}CD_3$. Therefore, CF_3OClO_3 should possess the following structure 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 spectrum. 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

Table I. Vibrational Spectra of CF_3OClO_3

Obsd. Freq, cm^{-1}, and intens [a]		
Infrared Gas	Raman Liquid	Assignment in Point Group C_s and Approximate Description of Mode
2635 vvw		$\nu_1 + \nu_{14} = 2638(A")$
2595 vw		$\nu_2 + \nu_{14} = 2595(A")$
2547 vw		$\nu_1 + \nu_{15} = 2549(A")$
2486 w		$2\nu_{15} = 2482(A')$
2455 vvw		?
2435 vw		$\nu_2 + \nu_3 = 2436(A')$
2345 w		$2\nu_3 = 2342(A')$
2290 vw-		$\nu_2 + \nu_4 = 2293(A')$
2220 vvw		$\nu_1 + \nu_5 = 2222(A')$
2195 vvw		$\nu_3 + \nu_4 = 2199(A')$
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 $\nu_4 + \nu_5 = 1942(A')$
1893 vvw		$\nu_9 + \nu_{14} = 1890(A")$ or $\nu_3 + \nu_6 = 1895(A')$
1877 vw		$\nu_3 + \nu_7 = 1877(A')$
1831 vw		$2\nu_5 = 1828(A')$ or $\nu_3 + \nu_{16} = 1831(A")$ or $\nu_2 + \nu_{17} = 1833(A")$
1780 vvw		$\nu_2 + \nu_{10} = 1777(A')$ or $\nu_3 + \nu_8 = 1786(A')$
1734 vvw		$\nu_4 + \nu_7 = 1734(A')$ or $\nu_3 + \nu_9 = 1731(A')$ or $\nu_3 + \nu_{17} = 1739(A")$
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 $\nu_2 + \nu_{11} = 1604(A')$
1533 vvw		$\nu_5 + \nu_8 = 1529(A')$ or $\nu_4 + \nu_{10} = 1540(A')$
1495 w		$\nu_4 + \nu_{18} = 1490(A")$
1476 vvw		$\nu_5 + \nu_9 = 1474(A')$
1438 vw		$\nu_2 + \nu_{13} = 1443(A')$ or $\nu_6 + \nu_7 = 1430(A')$

Table I. Vibrational Spectra of CF_3OClO_3 (cont'd)

Obsd. Freq, cm^{-1}, and intens[a]		
Infrared Gas	Raman Liquid	Assignment in Point Group C_s and Approximate Description of Mode
1308	1330(0.2)dp[b]	$\nu_{14}(A")$ ν antisym ClO_3 str
	1300(0.3)p	$\nu_1(A')$ ν antisym ClO_3 str
1265 s	1267(0.5)p	$\nu_2(A')$ ν antisym CF_3 str
1241 s	1240(0.1)	$\nu_{15}(A")$ ν antisym CF_3 str
1171 vs	1169(0.8)p	$\nu_3(A')$ ν sym CF_3 str
1074 vw		$\nu_9 + \nu_{10} = 1072(A')$
1028 vs	1031 (7.2)p	$\nu_4(A')$ ν sym ClO_3 str
914 m	917(1.1)p	$\nu_5(A')$ ν C-O str
852 vw		$\nu_{10} + \nu_{11} = 851(A')$
829 vvw		$\nu_{10} + \nu_{12} = 826(A')$
724 m	726(4.2)p	$\nu_6(A')$ δ umbrella CF_3
706 sh(PQR)	708(5.1)p	$\nu_7(A')$ δ scissor CF_2
660 sh	660(<0.1)	$\nu_{16}(A")$ δ antisym CF_3
615 s	616(0.5)p	$\nu_8(A')$ ν O-Cl str
568 mw	570(0.7)dp	$\nu_{17}(A")$ δ antisym ClO_3
560 sh	564(1.1)p	$\nu_9(A')$ δ scissor ClO_2
512 w	516(3.2)p	$\nu_{10}(A')$ δ umbrella ClO_3
	490(<0.1)	$\nu_{12} + \nu_{13} = 494(A')$
463 vvw	462(0.2)dp	$\nu_{18}(A")$ δ rock CF_3
339 sh	342(3.5)p	$\nu_{11}(A')$ δ wag CF_3
	320 dp?	$\nu_{19}(A")$ δ rock ClO_3
314 mw	316(10)p	$\nu_{12}(A')$ δ scissor C-O-Cl
	178(0.5)p	$\nu_{13}(A')$ δ wag ClO_3

a Uncorrected Raman intensities representing relative peak height.

b Qualitative polarization measurement

may be described as three stretching modes, three deformational modes, two rocking fundamentals, and one 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 not observed. No evidence for the two torsional fundamentals was found and they will not be considered further in our discussion.

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 group, respectively. The two antisymmetric ClO_3 stretches usually are almost degenerate and splitting into the individual modes is 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 modes 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 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} (averaged 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 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 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, 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 spectrum. 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 $\pm$ 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 [7,8] and the O-O-O bend in the trioxide CF_3OOOCF_3. The former has been assigned 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 Hammacker, [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; and (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. 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 group indicates hindered rotation for both groups. Except for the two torsional modes, all predicted fundamentals were observed and assigned and indicate the need for reassigning the two lowest frequency vibrations in Cl_2O_7.

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Diagram Caption

Figure 1. Vibrational spectra of CF_3OClO_3: Infrared of the gas: A, 5mm in a 5 cm path length cell with AgCl windows; B and C 18 mm and 125 mm respectively in a 10 cm path length cell with AgBr windows. Raman of the liquid at $\sim -100^{\circ}$: D, incident polarization perpendicular; E, incident polarization parallel; F, indicates the spectral slit width.

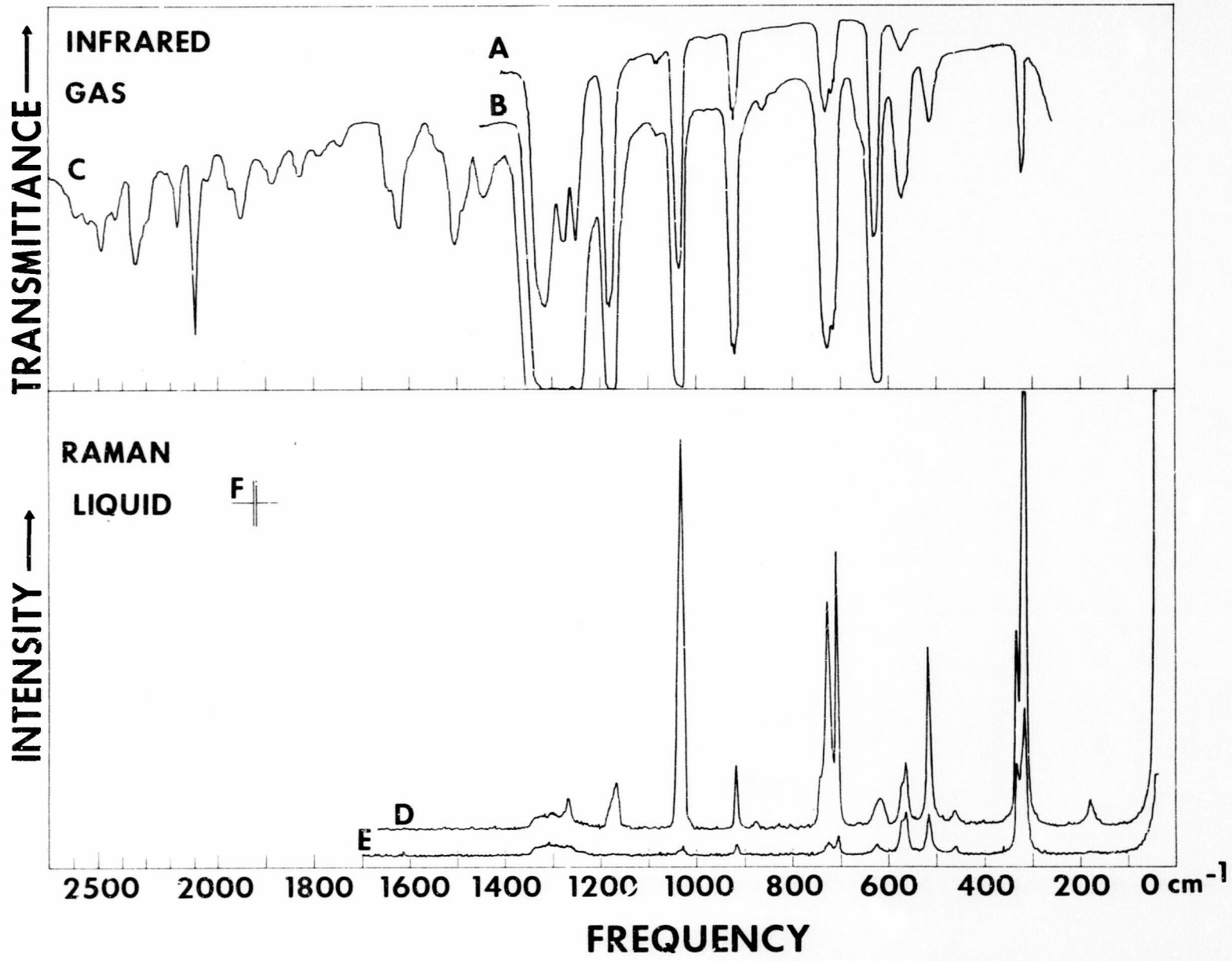

Figure 1.

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Halogen Perchlorates. Reactions with Fluorocarbon Halides

by Carl J. Schack*, Don Pilipovich and Karl O. Christe

Received . . . . . .

Abstract

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, $CF_3CF_2ClO_4$, $n\text{-}C_7F_{15}ClO_4$, $O_4ClCF_2CF_2ClO_4$, 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 $n\text{-}C_7F_{15}I(ClO_4)_2$. Based on their vibrational spectra, these intermediates have the ionic structure $[R_{f2}I]^+[I(ClO_4)_4]^-$. 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 or di, primary or 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] $CsI(ClO_4)$,[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:

$$XClO_4 + \diagdown C{=}C \diagup \longrightarrow X\text{-}\overset{|}{C}\text{-}\overset{|}{C}\text{-}ClO_4 \qquad (X = Cl,Br)$$

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 further investigate this new class of compounds and, in particular, to search for additional preparative routes which result exclusively in the introduction of a perchlorato group without simultaneous addition of bromine or chlorine atoms.

Experimental Section

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 4880Å 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 ID) 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.

CF_3I-Cl_2O_4 Reactions. Trifluoromethyl iodide (2.02 mmol) and Cl_2O_4 (4.24 mmol) were combined at -196° in a 30ml 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 percent based on CF_3I. The molecular weight observed by vapor density measurements was 167 versus a value of 168.4 g/mole calculated for CF_3ClO_4. Anal., Calc: F, 33.84; Cl, 21.04. Found; F, 33.3; Cl, 21.5. The ^{19}F nmr spectrum exhibited only one line at 60.4 ppm above internal $CFCl_3$ and measured quantities of CF_3ClO_4 and $CFCl_3$ reference were used to confirm by 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 homogeniety. The vapor pressure of the liquid was determined at various temperatures over the range -78 to 0°: (°C, mm) -77.7, 7; -62.3, 20; -45.8, 56; -32.0, 121; -24.3, 180; -16.2, 268; 0.0, 535. The vapor pressure-temperature relation is described by the equation $\log P_{mm} = 7.4828 - (1301.0/T°K)$. The extrapolated normal boiling point is 9.5°, with a heat of vaporization of 5.95 kcal. mol^{-1} and a Trouton constant of 23.3. 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 non-volatile 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 Cl_2O_4), CO_2, COF_2, 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 reacted 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 percent and the vapor density was 216g/mol; calculated for $CF_3CF_2ClO_4$ 218.4 g/mol. Anal.; Calc. F,43.48; Cl, 16.23. Found: F, 42.9; Cl, 16.0. Vapor-pressure-temperature measurements were made over the temperature range of -78 to 0°: (°C, mm) -77.9, 2; -45.5, 23; -31.1, 54; -23.7, 81; -14.3, 127; 0.0, 244. The vapor pressure-temperature relation is described by the equation log Pmm = 7.6356 -(1430.8/T°K) giving an extrapolated normal boiling point of 27.7°; a heat of vaporization of 6.54 kcal mol^{-1}; and a Trouton constant of 21.8. 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 Cl_2 and a little $FClO_3$ but no R_f species. After 2 hr. at room temperature, the reactor was reopened and was now found to contain "free" $CF_3CF_2ClO_4$ in approximately 95 percent yield, together with small 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 1.6g CsF for one 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 $(CF_3)_2$ CFI (1.53 mmol) were reacted 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 $(CF_3)_2$ CFI (0.09 mmol). The non-volatile residue weighed 0.703g, and it did not decompose on standing. The weight calculated for 1.44 mmol of $(CF_3)_2$ $CFI(ClO_4)_2$ was 0.711g. Examination of the residue in the dry box showed a loose, finely powdered, white solid, m.p. with decomposition 71-3°. Anal., Calc. for $C_3F_7I(ClO_4)_2$: ClO_4, 40.2. Found, 40.6. The solid fumes in air and liberates some I_2 on treatment with water together with oily droplets. When heated at 105° for 16 hr in a 10ml 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 reacted with four - six fold molar equivalents of Cl_2O_4 at and below -45°. Generally the chlorine by-product obtained indicated that even after one 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 with about 15mm vapor pressure at 20° and in a dynamic vacuum it slowly passes through traps cooled to -45°. Besides its ^{19}F nmr and infrared spectra, 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 non-volatile 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 (~2mm at 20°) were recovered. Based on its ^{19}F nmr spectrum (one peak at 92.2 ppm assignable to $-CF_2ClO_4$) and infrared spectrum, this material has been identified as the bis-perchlorate, $O_4ClCF_2CF_2ClO_4$.

$ICF_2CF_2CF_2I$ - 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 reacted 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 non-volatile product, $(O_4Cl)_2ICF_2CF_2CF_2I(ClO_4)_2$ according to the observed stoichiometry, deflagrated. The deflagration products were: O_2(~7mmol); Cl_2, CO_2, COF_2, CF_4, and some C_2F_6 (~6mmol total), together with I_2 and IF_5. No nonvolatile species was observed.

$n\text{-}C_7F_{15}I$ - Cl_2O_4 Reactions. n-Perfluoroheptyl iodide (1.42 mmol) and Cl_2O_4 (3.60 mmol) were reacted 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 pumping at room temperature, the white solid product left in the reactor weighed 0.985g. The weight calculated for 1.42 mmol $C_7F_{15}I(ClO_4)_2$ was 0.987g. The solid had an mpd of 56-8° 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 which exhibited ~2mm vapor pressure at 20°. The mass spectrum of this liquid resembled those reported [12] for $n\text{-}C_7F_{15}$- compounds. Some of the more important characteristic peaks were attributable to the ions: $C_7F_{14}ClO_4^+$, $C_7F_{15}O^+$, $C_7F_{15}^+$, $C_nF_{2n-1}O^+$, $C_nF_{2n-1}^+$ (n=3-6), and ClO_x^+(x=1-3). Thus this liquid was identified as $C_7F_{15}ClO_4$. The ^{19}F nmr spectrum agreed with this conclusion (see discussion).

A sample of $C_7F_{15}ClO_4$ (0.22 mmol) was heated with 1.1g 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 reacted 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 $C_4F_6Br_2(ClO_4)_2$. This material was further 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).

$CF_2=CFCF=CF_2+BrClO_4$ and Cl_2O_4 Reactions. Perfluorobutadiene (2.58 mmol) and $BrClO_4$ (5.80 mmol) 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 reacted at -78 to 0° furnishing $C_4F_6Cl_2(ClO_4)_2$ (2.15 mmol, 96% yeild). 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 reacted 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 percent 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 percent yield of the $CF_3CFBrCF_2ClO_4$. Bromine perchlorate and $CF_3CFBrCF_2Br$ were reacted using these same conditions and produced a 23 percent 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 six 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[8] $BrCF_2CFO$ and $FClO_3$ were formed in qualitative experiments by CsF catalyzed decomposition.

Discussion

Caution! The halogen perchlorates and the alkyl perchlorates are potential explosives. Safety precautions should be taken in handling and using these materials.

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:

$$R_fI + 2Cl_2O_4 \longrightarrow R_fI(ClO_4)_2 + Cl_2$$

$$R_fI(ClO_4)_2 \longrightarrow R_fClO_4 + [IClO_4]$$

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 formed 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 perfluroalkyl groups. Thus, an interhalogen compound has been formed from a C-F compound.

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:

$$5IF \rightleftharpoons 2I_2 + IF_5$$

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 I and Figures 1 and 2; ^{19}F nmr, Table II; and mass spectra) together with elemental analysis, 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. 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

Table I. Infared and Raman Spectra of Fluorocarbon Perchlorates (4000-500 cm^{-1} range)

CF_3ClO_4 IR[a]	CF_3ClO_4 Ra[b]	$CF_3CF_2ClO_4$ IR[a]	$BrCF_2CF_2ClO_4$ IR[a]	$ICF_2CF_2ClO_4$ IR[a]	$n\text{-}C_7F_{15}ClO_4$ IR[b]	$n\text{-}C_7F_{15}ClO_4$ Ra[c]	$(O_4ClCF_2CFCl)_2$ IR[b]	$(O_4ClCF_2CFBr)_2$ IR[b]	Tentative Assignment
					1368sb	1375w			
	1330vw		1320vs	1320vs	1350sh	1332w	1310vs	1310vs	
1308vs	1300vs	1308vs	1305vs	1303vs	1295vs	1300w	1295vs	1290vs	antisym ClO_3 str
1265s	1267vw	1250vs	1250s	1288s	1245vs		1245m	1225ms	C-F str region
1241s	1240vw	1204s	1204s	1197s	1210vs	1215vw	1227m	1190s	
1171vs	1169vw	1180s	1187m		1153vs	1160w	1180vs	1150s	
			1168s			1140vw	1135s	1115sh	
		1093vs	1112s	1105s	1108m	1112w	1100m	1098w	
			1068w	1076w	1052m	1051m	1058w		
1028vs	1031s	1035vs	1037vs	1038vs	1028vs	1035vs	1032vs	1028vs	sym ClO_3 str
							960s		
914m	917w	930w	940s	922s	947w	948vw	943s	933m	C-O str
				906s	900mw	908w	892m	900m	C-C str + certain C-Hal str
		848mw	850w		852w		861s	860m	
					840w		848m	843mw	
			810w	805m	825w	823w	809w	804w	
					785w		784m	780m	
					770w	767s	770m	762m	
					750m	750w		750m	
					743m	742w	732w		
724m	726m	752m			728m	728s			δ umbrella CF_3
706sh	708m				713ms	714m			δ scissor FCF_2
660sh	660vw	675s	665m	670s	669s	660s			δ CF_2
			643m	640s	643s	645s	650vs	645vs	
615s	616vw	612s	615m	614s	612s	617m	610vs	608vs	Cl-O str
568mw	570vw	582m			565sh	578w	572w	570sh	δ antisym ClO_3
560sh	564w								δ scissor $OClO_2$
512w	516m[c]	530w				515m[d]			δ umbrella ClO_3

[a] gas: [b] liquid: [c] Raman peaks below 500 cm^{-1}. For CF_3ClO_4 were at 462vw, 342m, 320vw, 316vs, and 178vw cm^{-1}.
[d] Raman peaks below 500 cm^{-1} For $n\text{-}C_7F_{15}ClO_4$ were at 470vw, 388m, 322m, 300m, 285w, 223mw cm^{-1}.

Table II. ^{19}F nmr Data[a,b]

Compound	CF_3-	-CF_2-	>CFX (X=Cl, Br)	-CFXClO$_4$ (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 $CFCl_3$; peak area ratio measurements agreed with the assignments.

[b]Data not from this work is taken from Ref. 8.

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 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 I). The C-O stretch for these compounds is also characteristic and is emphasized in Table I 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.

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 two years was unchanged. Even at elevated temperature (100° for 18 hr) in the presence of a known decomposition catalyst, [8] CsF, only 30 percent 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 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 21 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 mono perchlorate, 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 giving the same unambiguous result 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, $(CF_3)_2$ CFI and $nC_7F_{15}I$, it was found that this intermediate was an ambient temperature stable, isolable solid. The empirical compositions were analogous to those of the ethyl case, i.e., $(CF_3)_2CFI(ClO_4)_2$ mpd. 71-3° and $n\text{-}C_7F_{15}I(ClO_4)_2$ mpd. 56-8°. These solids fumed in air and formed ClO_4^- and some I_2 on hydrolysis. From their infrared and Raman spectra (Table III 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 III 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 $R_fI(ClO_4)_2$ possess the ionic structure $(R_f)_2I^+I(ClO_4)_4^-$. The related ionic structure $(R_f)_2I^+IF_4^-$ has been postulated [21]

Table III. Infrared and Raman Spectra of Solid Iodine Perchlorates (cm^{-1}, intensity)

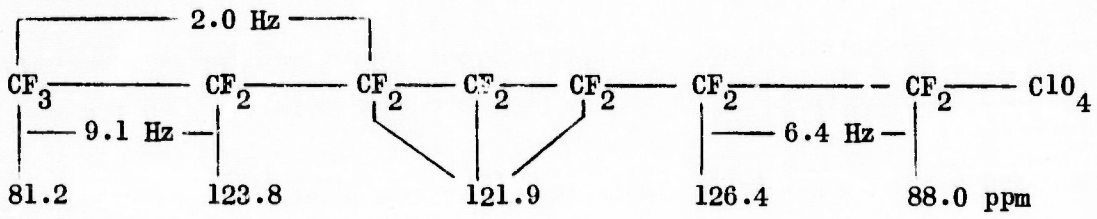
$i\text{-}C_3F_7I(ClO_4)_2$		$n\text{-}C_7F_{15}I(ClO_4)_2$		$Cs^+I(ClO_4)_4^-$
IR	Ra	IR	Ra	Ra
		1371 ms	1376 mw	
		1337 mw	1332 w	
	1308 w		1295 vw	
1295 vs,	1281 w	1278 sh	1278 w	
1250 vs, br	1257 mw	1230 vs,br	1259 w	
	1235 vw		1250 vw	1243 w, sh
	1220 vw		1236 vw	
	1205 vw		1218 vw	1207 mw
1190 sh	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	13[illegible] ms
	106 w			106 ms

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 $n\text{-}C_7F_{15}ClO_4$ 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 in a dynamic vacuum, the $n\text{-}C_7F_{15}I(ClO_4)_2$ 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. It implies that the positive charge in the cation resides largely on the two carbon atoms directly attached to iodine and that these carbon atoms are attacked by the anion resulting in R_fClO_4 formation. It also implies that 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 I). 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 $n\text{-}C_7F_{15}ClO_4$ nmr spectrum exhibited 5 peaks showing relative area ratios of 3:2:6:2:2. A schematic of the analyzed spectrum is shown:



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_f-CF_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 $n-C_6F_{13}CFO$. These products were identified by their infrared and mass spectra. The latter exhibited the parent ion peak, $C_7F_{14}O^+$, for the acyl fluoride.

The synthesis of 1,2 bis perchlorato tetrafluoroethane was attempted from ICF_2CF_2I and Cl_2O_4 based on the foregoing results. In each instance, 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^o. One of these reactions which had gone smoothly but incompletely at -45^o, deflagrated while being maintained at -25^o. 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 percent) was generally nowhere near as good as that obtained with other R_fI compounds. The $ICF_2CF_2ClO_4$ was difficult to separate from Cl_2O_7. It was observed to be a clear, colorless liquid of low volatility (~15 mm at 20^o) and stable at ambient temperature. The spectral properties of $ICF_2CF_2ClO_4$ (Tables I and II) allowed its unambiguous identification. Particularly noteworthy was the presence of a reasonably strong parent peak in the mass cracking pattern.

When a solvent was used to promote the substitution of the second I in ICF_2CF_2I, partial success was achieved although $ICF_2CF_2ClO_4$ was still the main product. A viscous liquid of low volatility was isolated in very small amounts which had an infrared spectrum (Table I) and ^{19}F nmr spectrum (one peak, Table II) which established it as $O_4ClCF_2CF_2ClO_4$. The infrared spectrum agreed very well with

that of $FSO_3CF_2CF_2SO_3F$ [24] when vibrations caused by the different end groups are discounted and only $-OCF_2CF_2O-$ bands are considered. An improved synthetic technique is required to more fully study this perchlorate.

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 one 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 four week reaction of $BrCF_2CFBrCFBrCF_2Br$ and excess Cl_2O_4 produced the following reaction stoichiometry:

$$C_4F_6Br_4 + 4Cl_2O_4 \longrightarrow C_4F_6Br_2(ClO_4)_2 + 2BrClO_4 + 2Cl_2$$

This new fluorocarbon perchlorate was a stable, clear, colorless liquid with <1mm vapor pressure at room temperature. The presence of ClO_4 groups in the molecule was established by its infrared spectrum (Table I).

The ^{19}F nmr spectrum of the liquid showed that the product from the $C_4F_6Br_4$ reaction contained exclusively the bisperchlorato derivative in the form of 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 not a single line but was instead two lines (124.6 and 126.1 ppm) with the low field line having about one-quarter the intensity of the other. The proximity of these peaks indicates strongly that they are due to very similar fluorine substituents. It is probable that they represent two different rotational conformations, isomers caused by hindered rotation due to the many bulky groups on the carbon backbone. With Br atoms on adjacent carbons, it would be expected that these would preferentially acquire positions trans to one another. However, another configuration could be "frozen in" and give rise to the second type of >CFBr resonance.

An example of this type has been reported [26] for $BrCF_2CFBr_2$ which at -110° did not rotate freely and was found to adopt multiple conformations with the most populated one being that with two bromine atoms being trans. Variable-temperature studies of the nmr spectrum could resolve this point, but such work was beyond the scope of the present effort.

A final point of evidence aiding the identification of the perchlorate derived from this reaction was obtained by examining the product of the reaction:

$$CF_2{=}CFCF{=}CF_2 + 2BrClO_4 \longrightarrow C_4F_2Br_2(ClO_4)_2$$

This interaction proceeded smoothly and efficiently below room temperature to give the bis adduct in 87 percent yield. In all respects--appearance, physical properties, and spectral properties--this product was indistinguishable from that derived from $C_4F_6Br_4$ and Cl_2O_4. Thus, the first reaction step must have been the following exclusive and 1,2 addition to the diolefin.

$$CF_2{=}CFCF{=}CF_2 + BrClO_4 \longrightarrow O_4ClCF_2CFBrCF{=}CF_2$$

Additions to perfluorovinyl groups have previously been shown to occur in the same direction [8] and can be readily rationalized in terms of a polar mechanism, i.e., the relatively negative ClO_4 group of $BrClO_4$ always becomes bonded to the positively polarized terminal carbon. Once this mono adduct has formed, the remaining olefinic bond would be expected to add another $BrClO_4$ in the same fashion.

$$O_4ClCF_2CFBrCF{=}CF_2 + BrClO_4 \longrightarrow O_4ClCF_2CFBrCFBrCF_2ClO_4$$

Thus, the symmetrical bis perchlorate is formed with all perchlorate groups in the 1,4 positions.

The corresponding bis Cl_2O_4 adduct of perfluorobutadiene was also prepared to provide a sample for possible further ClO_4 substitution (see below). For the Cl_2O_4 addition, a 96 percent yield of the bis perchlorate was obtained. 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 spectra 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 shows that 1,4 addition occurred as a first step. The subsequent addition probably then occurs randomly. Equations illustrating this process are:

$$CF_2{=}CFCF{=}CF_2 + Cl_2O_4 \longrightarrow O_4ClCF_2CF{=}CFCF_2Cl$$

$$O_4ClCF_2CF{=}CFCF_2Cl + Cl_2O_4 \begin{cases} \nearrow O_4ClCF_2CF(ClO_4)CFClCF_2Cl \\ \searrow O_4ClCF_2CFClCF(ClO_4)CF_2Cl \end{cases}$$

In addition to the species resulting from 1,4 addition, the spectra also showed significant amounts of product resulting from the 1,2 process. Based on peak area estimates 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 products than 1,2 product.

Further substitution of bromine in $(O_4ClCF_2CFBr\rightarrow_2$ by a perchlorato ligand was sought using Cl_2O_4. The attempted reaction was:

$$(O_4ClCF_2CFBr\rightarrow_2 + 4Cl_2O_4 \longrightarrow (O_4ClCF_2CFClO_4\rightarrow_2 + 2Cl_2 + 2BrClO_4$$

From the evolved Cl_2, it appeared that ~40 percent 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 difference 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 bis ClO_4 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 percent of the $>CFX$ fluorines were of the X = ClO_4 type. It should be noted too that the changes in chemical shifts for the C-F's are in keeping with the substitution of a more electronegative group for Br. Furthermore, each of the three types of C-F found consisted of two or more unequal area peaks of similar shifts ($\pm$ 1 ppm), indicating the presence of different rotational isomers. The increased probability for rotational isomers in the tris perchlorato compound, when compared to the

corresponding bis substituted compound, is not surprising since ClO_4 is larger than Br and therefore it causes even more rotational hindrance.

Another R_fBr compound tested was $CF_3CFBrCF_2Br$. Except for $C_4F_6Br_4$, the best results for ClO_4 substitution of Br were derived from studies with this compound. As before, the objective was to replace both bromines with ClO_4 groups. When the reaction was conducted by letting the reactants warm slowly from 0° to ambient temperature, there was obtained a 45 percent yield of the 1-perchlorato derivative according to:

$$CF_3CFBrCF_2Br + 2Cl_2O_4 \longrightarrow CF_3CFBrCF_2ClO_4 + 2O_2 + BrCl + Cl_2$$

The identification of this perchlorate was straightforward since it was identical in its physical and spectral properties to the material previously synthesized [8] by $BrClO_4$ addition to the corresponding olefin. Other Cl_2O_4 reactions of $CF_3CFBrCF_2Br$ were conducted at -25° for up to 4 weeks. This produced a 35-percent yield of the same R_fClO_4. Also, experiments of this type were run at -25° or from 0° to room temperature in the presence of added $Cs^+ClO_4^-$ or $NO_2^+ClO_4^-$ to discover any possible catalytic effect. The ionic perchlorates were unaffected by the reagents and did not change the yield of $CF_3CFBrCF_2ClO_4$ which still ran about 35 percent. Bromine perchlorate was substituted for Cl_2O_4 and the reaction conducted by slow warming from 0° to room temperature. This gave a 23 percent yield of the same R_fClO_4.

Further studies with R_fBr species involved the discovery that $BrCF_2CF_2Br$ reacted very slowly and incompletely with Cl_2O_4. After 6 weeks reaction at -25°, these reactants had given $BrCF_2CF_2ClO_4$ but only in 11 percent yield after purification.

$$BrCF_2CF_2Br + 2Cl_2O_4 \longrightarrow BrCF_2CF_2ClO_4 + Cl_2 + BrClO_4$$

The product was characterized principally by its infrared and ^{19}F nmr spectra. The former correlates well with those of the known $ClCF_2CF_2ClO_4$ [8] and that 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 were found not to react with either Cl_2O_4 or $BrClO_4$ despite long contact times. These included 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.

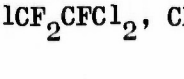
$$C_4F_6Br_4 > CF_3CFBrCF_2Br > BrCF_2CF_2Br >>> C_2F_5Br$$

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 reacted at -45° for 3 weeks producing the anticipated Cl_2 and $BrClO_4$ by-products. Unfortunately, the only carbon-containing materials accompanying those compounds were COF_2 and COFCl, accounting for 95 and 5 percent, respectively, of the CF_2Br_2. Chlorine heptoxide constituted the other significant product. These moieties most certainly arose from the sequence:

$$CF_2Br_2 + 4Cl_2O_4 \longrightarrow 2Cl_2 + 2BrClO_4 + [CF_2(ClO_4)_2] \longrightarrow COF_2 + Cl_2O_7$$

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. Inspite of the large amount of experimtal information, it remains difficult to rationalize all the observed reactions. For the alkyl iodides, a simple halogen elimination reaction according to

$$\underset{\delta+\ \ \delta-}{\text{C}\text{—Hal}} + \underset{\delta+\ \ \delta-}{\text{Hal—OClO}_3} \longrightarrow \text{C-OClO}_3 + \text{Hal—Hal}$$

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 reliably determine the mechanisms involved and to avoid undue speculation.

Acknowledgement

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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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Diagram Captions

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 perpendicular; D, incident polarization perpendicular.

Figure 2. Infrared spectrum of $C_7F_{15}ClO_4$: A, 2 mm 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, indicates spectral slit width.

Figure 3. Raman spectra of solids at -100°.

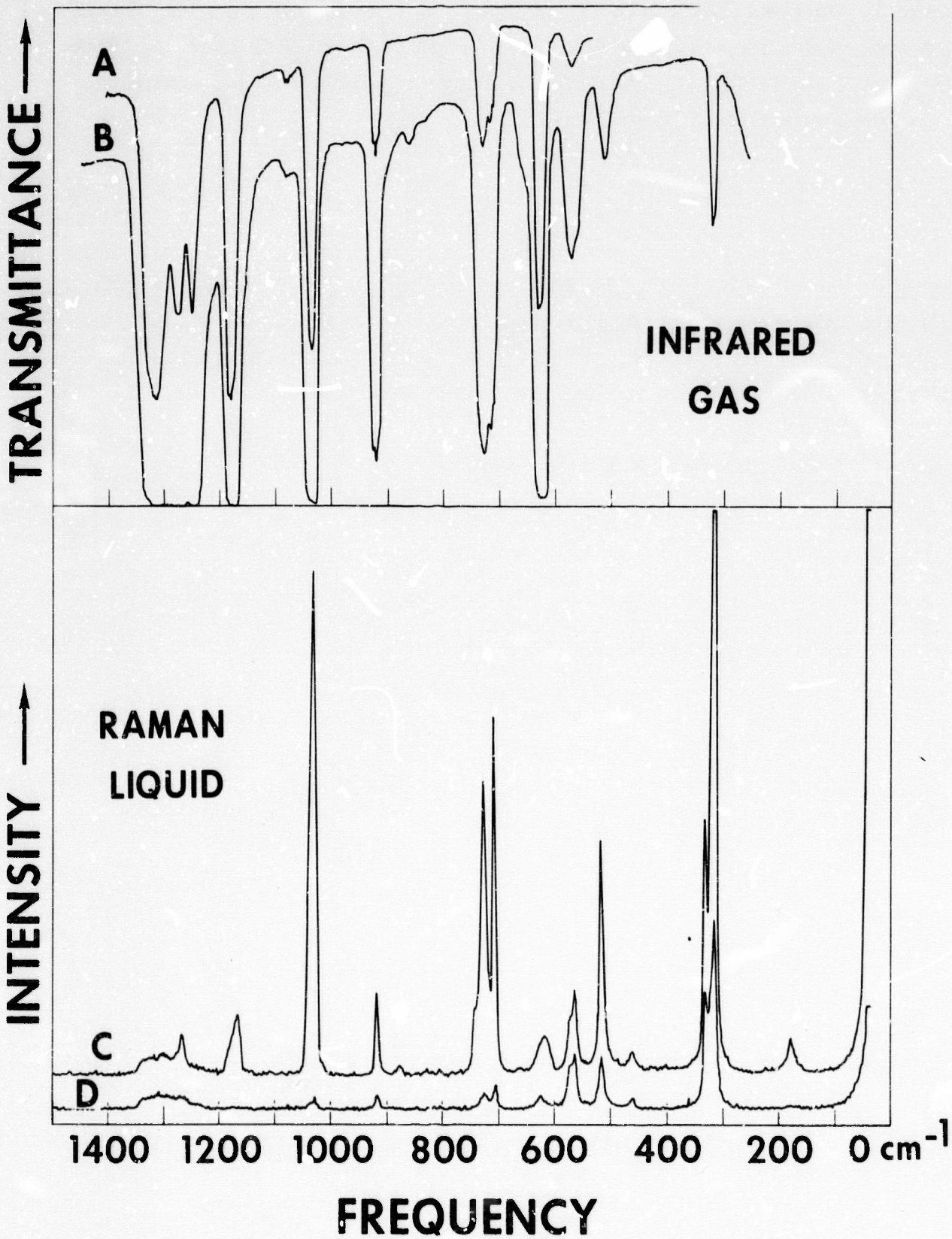

Figure 1.

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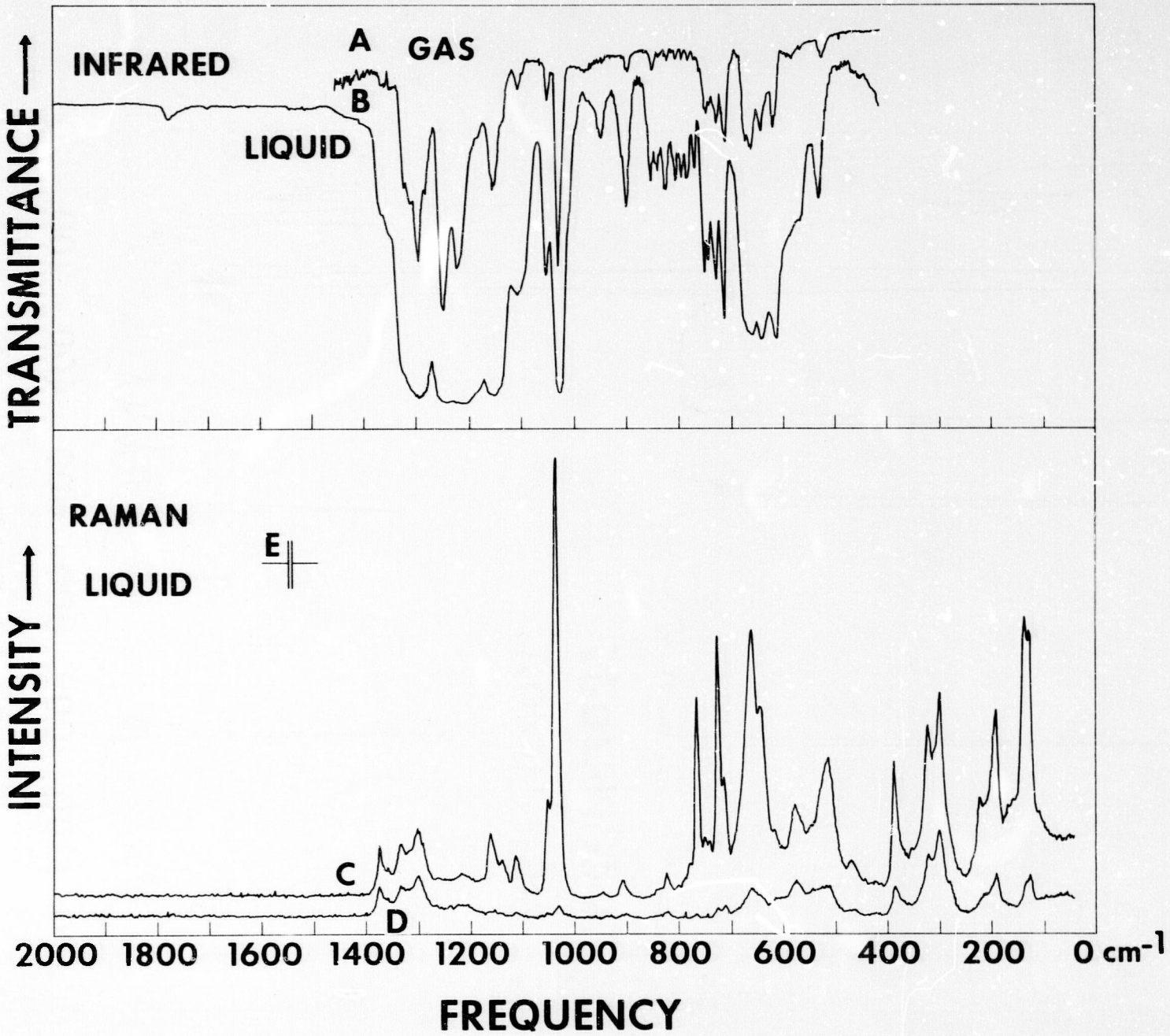

Figure 2.
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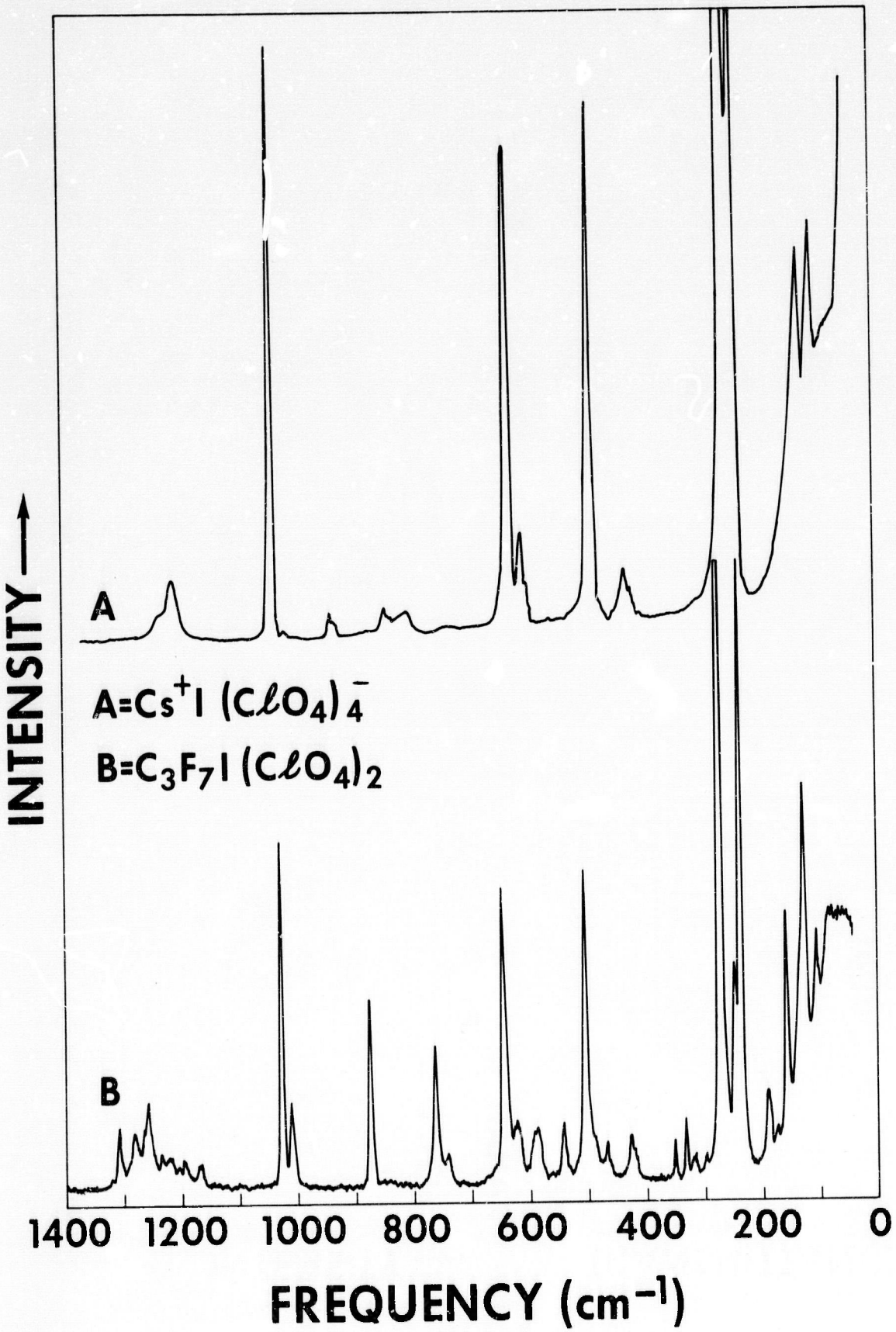

Figure 3.

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Contribution from Rocketdyne, a Division of Rockwell International

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Reactions of Ozone with Covalent Hypohalites

By Carl J. Schack and Karl O. Christe

Received:

Abstract

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 $Cl\text{-}\overset{|}{C}\text{-}\overset{|}{C}OSO_2F$ and $Cl\text{-}\overset{|}{C}\text{-}\overset{|}{C}\text{-}OClO_3$ 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:

$$BrONO_2 + 2\ O_3 \rightarrow O_2BrONO_2 + 2\ O_2$$

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 one 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 to a mmol 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:

$$ClOClO_3 + 2\ O_3 \rightarrow O_2ClOClO_3 + 2\ O_2$$

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 likely structures are the symmetric Cl-Cl bridged Model I and the asymmetric oxygen bridged Model II. Another structure suggested[15]

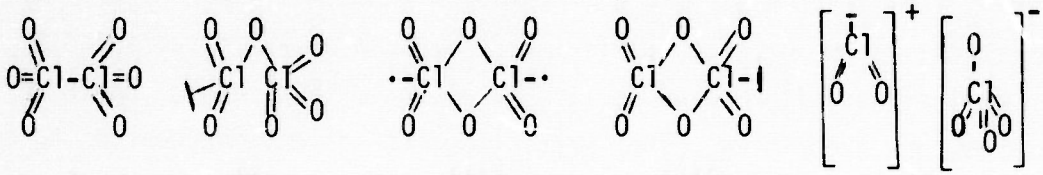
Table I

Ozone Reactions

Hypohalite mmol	O_3 mmol	Solvent	Temp. °C	Time hr.	Products[a] mmol
1.30 $ClOClO_3$	2.86	none	-78	24	0.47 Cl_2O_6, 0.83 $ClOClO_3$
1.35 $ClOClO_3$	3.24	(CF_3Cl) or none	-45	40	1.35 Cl_2O_6
1.23 ClO_2	3.16	none	-45	18	1.23 Cl_2O_6
1.06 $ClOSO_2F$	2.30	none	-45	70	1.03 ClO_2SO_3F
0.73 $ClONO_2$	2.55	none	-45	66	0.39 NO_2ClO_4, 0.33 $ClONO_2$
1.08 $ClONO_2$	3.24	CF_3Cl	-45	42	0.74 NO_2ClO_4, 0.34 $ClONO_2$
1.03 $ClONO_2$	4.04	CF_3Cl	-45	72	0.92 NO_2ClO_4, Cl_2
1.02 $ClOCF_3$	2.60	none	-45	300	0.98 $ClOCF_3$, COF_2
1.59 $BrOClO_3$	2.98	none	-45	72	1.58 (Br_2, Cl_2, BrCl), 7.41 O_2
1.29 $BrOClO_3$	3.06	CF_3Cl	-45	72	1.28 BrO_2ClO_4
1.06 $BrONO_2$	2.80	$CFCl_3$	-45	72	1.01 BrO_2NO_2
1.00 $BrONO_2$	3.15	$CFCl_3$	-23	100	5.42 O_2, Br_2, NO_2
1.25 $BrOSO_2F$	3.37	none	-45	130	5.14 O_2, 1.20 $BrOSO_2F$, Br_2, $S_2O_5F_2$

[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.

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].



I II IIIA IIIB IV

In addition, IIIA would be diradical which disagrees with the diamagnetism observed[17] for pure Cl_2O_6.

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

$$Cl_2O_6 \rightleftarrows 2ClO_3$$

The surprisingly low value of 1.5 kcal/mol for the "dissociation energy" of this supposed equilibrium 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^+ 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 $(ClO_2)_n$, 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 the following three different synthetic methods:

(i) $2ClO_2 + 2\ O_3 \rightarrow Cl_2O_6 + 2\ O_2$ (Ref. 7)

(ii) $ClOClO_3 + 2\ O_3 \rightarrow Cl_2O_6 + 2\ O_2$ (this work)

(iii) $ClOClO_3 \rightarrow Cl_2O_6$ (Ref. 3)

The identical nature of these 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 mm 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 percent 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.

Table II. ^{35}Cl-^{37}Cl Isotopic Shifts (cm^{-1}) of ClO_2

	^{35}Cl Frequency This Study	Isotopic Shifts				
		This Study	Ref. 22	Ref. 23	Ref. 24 IR	Ref. 24 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_3 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 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.* However, unambiguous identification and assignment of the bands

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*The set of bands ascribed to species B somewhat resembles that of $FClO_2$[27] shifted to a lower frequency. This indicates a $XClO_2$ 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:

$$O_2ClOClO_3 + H_2O \rightarrow HOClO_3 + HOClO_2$$

is 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 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]

<u>The $BrOClO_3$-O_3 System</u>. 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 unsuccessful and the reaction observed at -45° was:

$$BrOClO_3 + 2\ O_3 \rightarrow O_2BrOClO_3 + 2\ O_2$$

This stoichiometry was confirmed by an excellent oxygen material balance and by elemental analysis of the product which showed 6 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 NO_2ClO_4 from 1.35 $O_2BrOClO_3$) 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:

$$ClOSO_2F + 2\ O_3 \rightarrow O_2ClOSO_2F + 2\ O_2$$

Yields above 90 percent 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. Attempts to react ozone and chlorine nitrate at -78° in the absence of a solvent were unsuccessful. However, when a solvent was used or the temperature was raised to -45°, surprisingly chlorine was oxidized to the + VII oxidation state as shown:

$$ClONO_2 + 3\ O_3 \rightarrow NO_2^+ClO_4^- + 3\ O_2$$

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 towards 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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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 Sheft in (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, RuF_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),

$$LiF - NaF - KF + Cl_2 \xrightarrow{Melt} MeCl + ClF$$

$$MeCl + HF \longrightarrow MeF + HCl$$

$$\overline{HF + Cl_2 \longrightarrow ClF + HCl}$$

or pseudohalides, such as $ClOSO_2F$ (14),

$$CsF + ClOSO_2F \xrightarrow{-80^\circ} CsSO_3F + ClF$$

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 IF. 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).

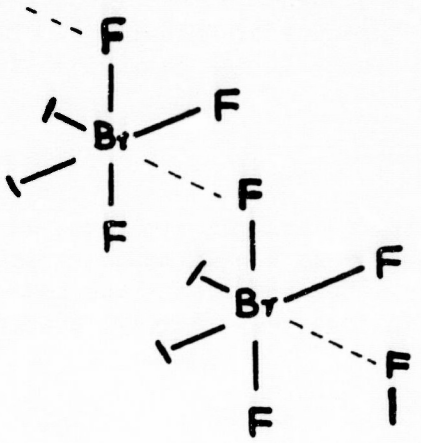


Figure 1. Association of BrF_3 through fluorine bridges

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:

$$|\underline{\bar{C}l} - \underline{\bar{F}}| \longleftrightarrow |\underline{\bar{C}l} = \underset{\sim}{\bar{F}}|$$

$$\delta+ \quad \delta- \qquad\qquad (-) \quad (+)$$

$$\mu_{exp.} = -0.88D$$

$$Cl - F$$

$$\delta- \quad \delta+$$

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 polarizability 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 oxidizing 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:

$$Me^+ X F_{n+1}^- \xleftarrow[+MeF]{+\text{Lewis base}} XF_n \xrightarrow[+YF_m]{+\text{Lewis acid}} XF_{n-1}^+ \; YF_{m+1}^-$$

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:

$$\diagdown C = C \diagup \; + \; XF \longrightarrow X - \underset{\diagup \quad \diagdown}{C} - \underset{\diagdown \quad \diagup}{C} - F$$

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≡S (41), S=O (42, 43) and C=O (44, 45) as demonstrated by the following equations:

$$N{\equiv}SF_3 + 2ClF \longrightarrow Cl_2NSF_5$$

$$SO_3 + ClF \longrightarrow ClOSO_2F$$

$$SF_4O + ClF \xrightarrow{CsF} SF_5OCl$$

$$OCF_2 + ClF \xrightarrow{CsF} CF_3OCl$$

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):

$$SF_4 + ClF \xrightarrow{CsF} SF_5Cl$$

$$CF_3PCl_2 + ClF \longrightarrow CF_3PCl_3F$$

$$CO + ClF \longrightarrow COFCl$$

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.

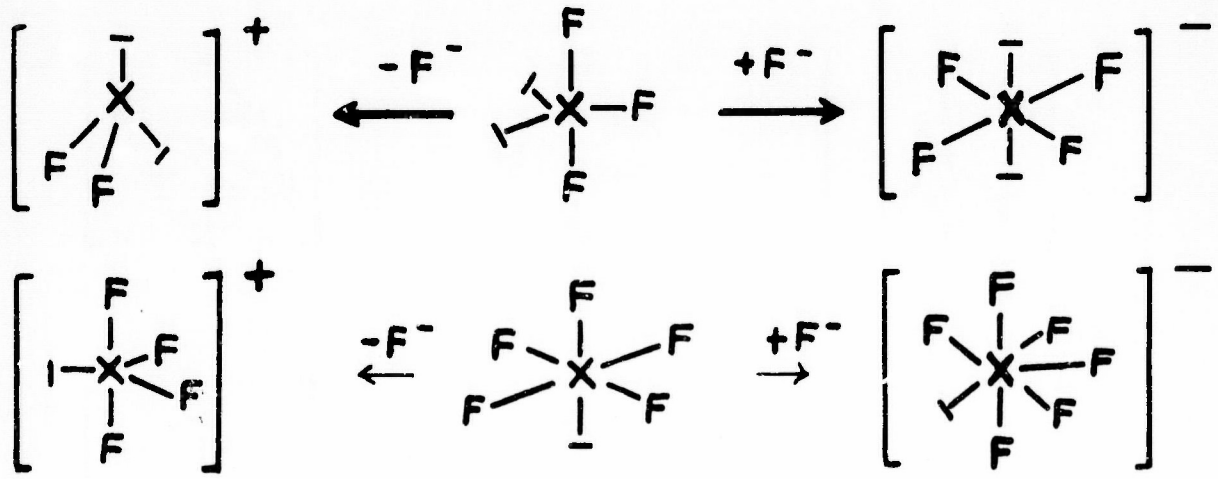
Cl_2F^+ Christe, Sawodny (1969)	ClF	ClF_2^- Christe, Guertin (1965)
ClF_2^+ Dale (1950)	ClF_3	ClF_4^- Asprey et al (1961)
ClF_4^+ Christe, Pilipovich (1967)	ClF_5	$[ClF_6^-]$
ClF_6^+ Roberto, Christe (1972)	$[ClF_7]$	$[ClF_8^-]$
(Br_2F^+)	BrF	BrF_2^- Surles et al (1973)
BrF_2^+ Woolf, Emeleus (1949)	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^-.

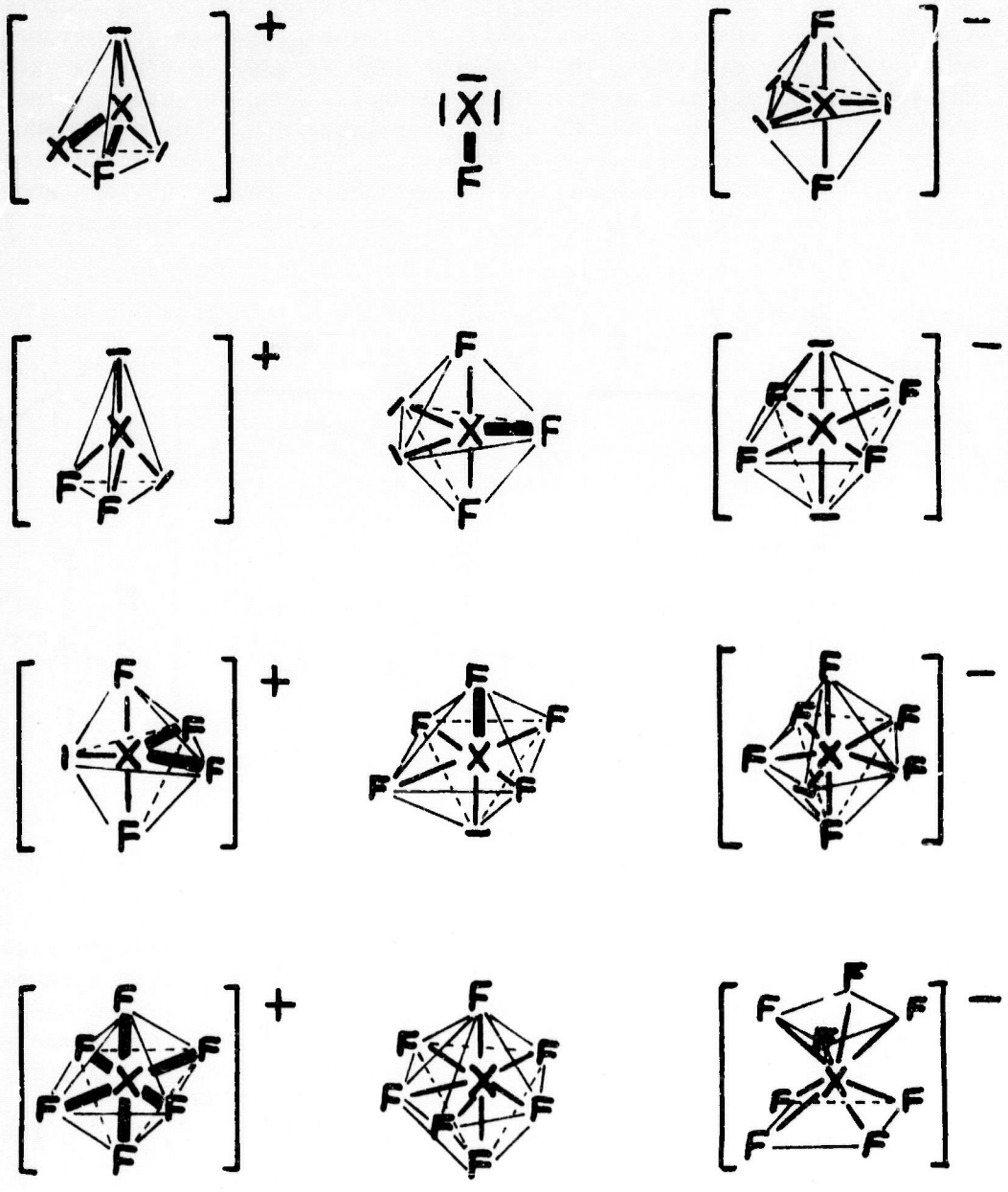


STRUCTURAL RELATIONS AND BONDING

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

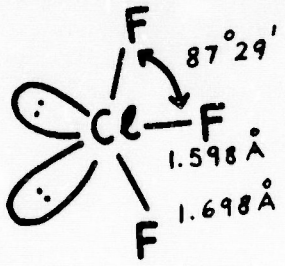


Figure 3. Distortion of ClF_3 from an ideal pseudo-trigonal bipyramidal configuration by increased repulsion from the free valence electron pairs.

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.

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 $[p\text{-}p]\sigma^2$ bonds with one p electron pair of the chlorine central atom, while the free Cl valence electron pairs form an sp^2 hybrid.

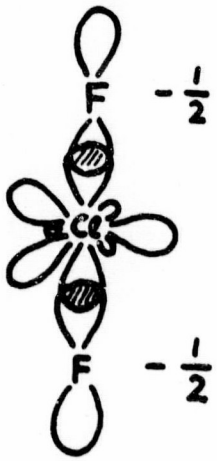


Figure 4. The schematic bonding in ClF_2^- as explained by a semi-ionic 3c–4e bond model

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).

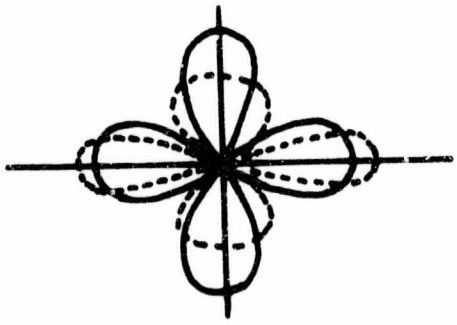
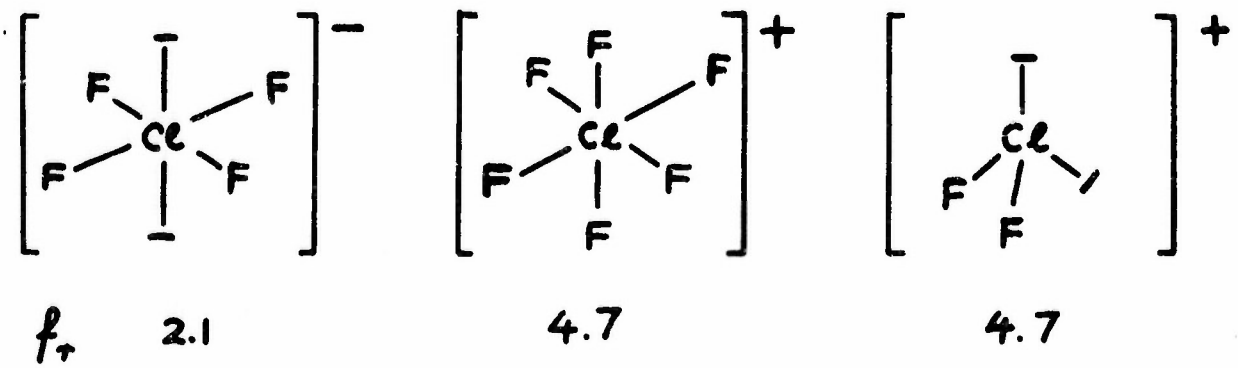


Figure 5. Influence of increasing (broken lines) bond lengths on the spatial distribution of free valence electron pairs assuming a hard sphere model.

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^+



f_r 2.1 4.7 4.7

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 stretch-

ing 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 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 $ClF_2^{\bullet}$ 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, $ClF_4^{\bullet}$, 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 $ClF_4^{\cdot}$.

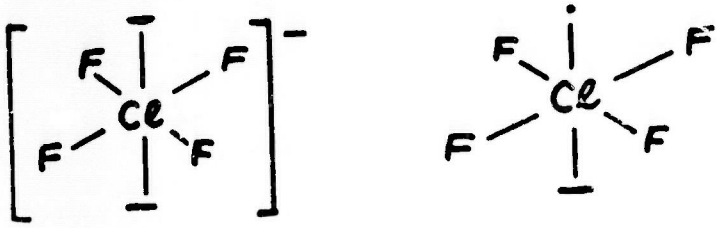


Figure 7. Structural relation between the $ClF_4^{\cdot}$ radical and the ClF_4^- anion.

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 characterized. 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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