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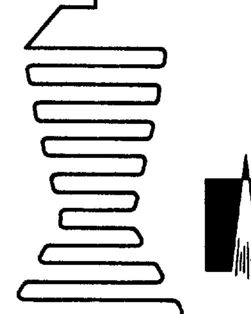

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INORGANIC HALOGEN OXIDIZERS

(1 September 1967 through 30 November 1967)

Group 4
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FOREWORD

The research reported herein was performed by members of the technical staff of the Rocketdyne Research Division and was supported by the Office of Naval Research, Power Branch Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Navy Contract Nonr 4428(00) and covers the period 1 September 1967 through 30 November 1967. The program manager was Dr. E. A. Lawton, Manager, Synthetic and Propellant Chemistry. The work was conducted in Oxidizer and Fluorine Chemistry with Dr. D. Pilipovich, Principal Scientist as project scientist. Full-time staff members contributing to the technical effort were Dr. C. J. Schack, Dr. K. O. Christe, and Mr. R. D. Wilson.

ABSTRACT

Ultraviolet activated fluorinations of chlorine oxyfluorides at low temperatures to produce Florox were continued. Experiments were designed to corroborate the previously proposed mechanism of the reaction. Results were obtained that were incompatible with those predicted from the postulate. The involvement of elemental Cl_2 and O_2 in the Florox forming process was deduced and was verified experimentally by the preparation of Florox from Cl_2, F_2, and O_2. Additional reaction paths are proposed and have been partially substantiated.

The chlorofluoro chloronium (III) cation, Cl_2F^+, a new oxidizing species, has been prepared in the form of its AsF_6^- and BF_4^- salts. The white crystalline Cl_2FAsF_6 complex is stable at -78 C and is completely dissociated in the gas phase at 25 C. A pressure-temperature curve gives a heat of reaction of 32.83 kcal $mole^{-1}$ for the dissociation process:

$$Cl_2F^+ AsF_6^-(s) = 2ClF(g) + AsF_5(g)$$

Low-temperature infrared measurements on both salts prove the ionic nature of the solids and indicate that Cl_2F^+ has a bent structure (symmetry C_s) with chlorine as the central atom. The Cl_2F^+ cation is the first example of a catenated polyhalogen cation. Quantitative displacement of 2 ClF from the complex by 1 FNO_2 has been observed.

The synthesis of chlorine perchlorate from ClF and perchlorate species was unsuccessful. Only mixtures of chlorine oxyfluorides and chlorine oxides, including Cl_2O_6, were produced by these reactions. The utility of ClF as a chlorofluorinating agent was demonstrated in the preparation of some new covalent hypochlorites, R_fOCl. These syntheses are catalyzed by alkali metal fluorides but may also be affected by reaction of preformed complexes. Preliminary characterization of hypochlorites has been carried out.

High-purity bromine nitrate has been prepared by the reaction of Br_2, Cl_2, and $ClNO_3$ at -30 to 0 C. Solid $BrNO_3$ is pale yellow and melts to a golden colored liquid at -31 C. The vapor pressure-temperature equation for -25 to 10 C is $\log p_{mm} = 9.6905 - 2254.5/T$. Fluorination of $BrNO_3$ has shown that FNO_2 and BrF_5 are the principal products (95+ percent yield). Limited amounts of a white solid NO_2^+-bromine fluoride complex are also formed. Partial analysis of this complex indicates no oxygen is present in the anion.

(Confidential Abstract)

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INTRODUCTION

This program is concerned with the synthesis of new halogen fluorides and oxyfluorides. To achieve this goal, a variety of techniques have been employed in the synthesis of intermediates and their conversion to new fluorides. Of particular recent interest is the use of ultraviolet irradiation as an activating agent on the interaction of chlorine-fluorine-oxygen containing materials. Previous efforts in this area have resulted in the preparation of Florox (ClF_3O) from $FClO_2$ and $FClO_3$. A more detailed analysis of the processes involved in these syntheses has been undertaken. This has been directed toward the verification of a proposed mechanism through correlation of predicted and experimental results. However, discrepancies have been found which indicate that a considerably more complex path is involved than that originally considered.

The chemistry and synthetic utility of ClF has been of continuing interest. One aspect of this is the nature of the ClF-Lewis acid complexes. A literature report has indicated such complexes to be of 1:1 stoichiometry and earlier work under this contract had indicated that a 3:1 ClF-Lewis acid reaction occurred. Definitive results were sought therefore, both as to the stoichiometry of the interaction and also the nature of the resultant complex ions. In addition to the ionic derivatives of ClF, other reactions have been discovered in which the use of ClF has led to synthetic routes to useful covalent materials. Thus, superior syntheses of $ClNF_2$, $ClNO_3$, and PF_4Cl were developed. Further application of ClF has now resulted in the preparation of some new perfluorohypochlorites.

The proven reaction of $ClNO_3$ and F_2 as a route to Florox promoted consideration of a similar $BrNO_3$ fluorination as a method of forming the unknown BrF_xO species. The availability of only impure $BrNO_3$ was an experimental difficulty encountered previously. However, fluorination of that material indicated that a new NO_2^+ bromine fluoride complex was formed, possibly $NO_2^+BrF_xO^-$. The synthesis of pure $BrNO_3$ has now been carried out and its fluorination has been studied.

DISCUSSION

ULTRAVIOLET ACTIVATED REACTIONS

The preparation of ClF_3O from any vigorous fluorinating agent and an oxychlorine fluoride ($FClO_2$ or $FClO_3$) was demonstrated to be facile with uv radiation (Ref. 1). These routes were the first demonstrations of high-yield syntheses of ClF_3O not involving inorganic hypochlorites as intermediates. In the previous quarter, it was demonstrated that a marked improvement could be realized in the uv synthesis of ClF_3O by utilizing a more powerful uv source. The early work was accomplished using a 100-watt high-pressure mercury source and the improvements resulted when a 450-watt source was used.

During the past quarter, more attention was directed toward determining possible intermediate reactions in order to unscramble the sequence of processes occurring. Initial reactions utilized the F_2-$FClO_3$ system and are summarized in Table 1. Several features of the uv reaction are noteworthy and inexplicable (at least within the constraints of the working model of the mechanism). A stepwise decomposition of $FClO_3$ was suggested in Ref. 2:

$$FClO_3 \xrightarrow{uv} FClO_2 + O \qquad (1)$$

$$FClO_3 + O \longrightarrow FClO_2 + O_2 \qquad (2)$$

$$FClO_2 \xrightarrow{uv} FClO + O \qquad (3)$$

$$FClO_2 + O \longrightarrow FClO + O_2 \qquad (4)$$

$$FClO + F_2 \longrightarrow ClF_3O \qquad (5)$$

$$FClO + O \longrightarrow FCl + O_2 \qquad (6)$$

The stepwise degradation of $FClO_2$ or $FClO_3$ seemed reasonable and offered a variety of choices in experimental confirmation.

An examination of the preceding sequence enables several valid predictions to be made concerning the outcome of an experiment. For example, at constant pressure and temperature, the decomposition of $FClO_2$ should be a

TABLE 1

ULTRAVIOLET ACTIVATED REACTIONS

Reaction Number	Reactants	Reactant Ratio, $F_2/FClO_3$	Temperature, C	Time,* hours	Condensable Products	Percent Conversion	Percent Yield ClF_3O
1	$FClO_3$	---	-60	1/2	Unreacted $FClO_3$, ClF, small amount $FClO_2$ [percent of product = (74%) (23.5%) (2.5%)]	32	
2	$FClO_3$	---	-60	1/2	Unreacted $FClO_3$, ClF, small amount $FClO_2$ [percent of product = (68.5%) (28%) (3.5%)]	26	
3	F_2, $FClO_3$	1.1	-60	1	ClF_3O, ClF_3, unreacted $FClO_3$. small amount $FClO_2$	30	60
4	F_2, $FClO_3$	1.2	-60	1/2	ClF_3O, ClF_3, unreacted $FClO_3$, small amount $FClO_2$	12	33
5	F_2, $FClO_3$	2.0	-60	1	ClF_3O, ClF_3, unreacted $FClO_3$, small amount $FClO_2$	27	41
6	F_2, $FClO_3$	1.0	-60	1/2	ClF_3O, ClF_3, reacted $FClO_3$, small amount $FClO_2$	17	46
7	F_2, $FClO_3$	1.0	-60	1 1/2	ClF_3O, ClF_3, unreacted $FClO_3$, small amount $FClO_2$	40	51
8	ClF, O_2	1.0	-60	1	Unreacted ClF, small amounts ClF_3, $FClO_2$, Cl_2	--	--
9	ClF_3O	---	-60	1	Unreacted ClF_3O (92%), small amounts ClF_3, $FClO_2$	--	--
10	ClF_3O	---	-60	1/2	Unreacted ClF_3O (90%), small amounts ClF_3, $FClO_2$, Cl_2	--	--
11	ClF_3O	---	-40	1	Unreacted ClF_3O (72%), small amount ClF_3	--	--
12	ClF, O_2, $FClO_3$	1:1:1	-60	1	Unreacted ClF and $FClO_3$, small amounts of ClF_3 and ClF_3O, Cl_2	--	--
13	O_2, $FClO_3$	1.0	-60	1	Unreacted $FClO_3$, ClF, small amounts of $FClO_2$ and Cl_2	--	--

*All reaction periods do not include a 10-minute lamp warm-up period.

function of time, i.e., longer radiation periods would result in a greater proportion of $FClO_3$ decomposition. This was verified experimentally both in the presence and absence of F_2.

However, other results expected as a consequence of the proposed scheme were not observed. The overall equation for the decomposition of $FClO_2$ is:

$$FClO_2 \xrightarrow{uv} ClF + O_2$$

Thus, $FClO_3$, when irradiated alone, should yield lower relative concentrations of $FClO_2$ (i.e., lower $FClO_2/ClF$ ratios) at longer reaction times. This was not the case, however, since ratios of 1:6 and 1:10 were found at 2- and 1/2-hour irradiation times, respectively. The result was unexpected because $FClO_2$, a stronger absorber in the uv than $FClO_3$, would be expected to decompose at a more rapid rate than $FClO_3$ itself.

Considering the postulated reaction sequence, it should be possible to rationalize yield data on ClF_3O formation as a function of time. The average yield of 1/2-hour irradiations was 40 percent compared to an average greater than 50 percent for runs of 1 hour and more. From the proposed scheme, the yield of ClF_3O should be a function of $FClO_3$ conversion only and certainly should be constant with respect of time. (Actually, since ClF_3O is decomposed by uv, the yield should decrease somewhat with longer reaction time). Although there is scatter in the results, there is no doubt that the experiments at 1/2 hour led to lower yields of ClF_3O and not the highest yields.

The concentration of F_2 also seems to strongly affect the yield of ClF_3O. If FClO is formed and fluorinated as in Eq. 5, it is not unreasonable to expect that a higher relative concentration of fluorinating agent should favor a higher yield of ClF_3O. The results in Table 1 and in Ref. 2 are both contrary to this postulate. The enhanced absorbancy of F_2 or ClF_5 coupled with the high partial pressure may affect the conversion of $FClO_3$ but certainly should not lower the yield of ClF_3O.

Since the results are not consistent with the postulated reaction sequence, experiments were conducted to determine the effect of the decomposition products of $FClO_3$ on the reactants and on the intermediates. Irradiating ClF and O_2 did not indicate the fixation of O_2 but did show the disproportionation of ClF:

$$3ClF \xrightarrow{uv} Cl_2 + ClF_3$$

Chlorine was also a product of the $ClF\text{-}O_2\text{-}FClO_3$ and $O_2\text{-}FClO_3$ systems. The ClF_3 which was always formed along with ClF_3O may have arisen from several reactions, namely:

$$3ClF \xrightarrow{uv} Cl_2 + ClF_3$$

$$Cl_2 + 3F_2 \longrightarrow 2ClF_3$$

$$ClF_3O \xrightarrow{uv} ClF_3 + 1/2\ O_2$$

Since Cl_2 is formed in these reactions and easily dissociated in the uv, the possibility existed that Cl_2 may participate in the actual formation of ClF_3O. The catalytic effect of Cl_2 in the recombination of atomic oxygen has been recognized (Ref. 3), and was thought to involve a ClO radical intermediate:

$$O + Cl_2 \longrightarrow ClO + Cl$$

$$O + ClO \longrightarrow O_2 + Cl$$

Recently, the postulate of the ClO radical being formed was proved in studying the reaction of atomic oxygen and Cl_2 (Ref. 4). Thus, the fixation of the intermediate ClO radical in the $FClO_x$ - F_2 system may be promoted by the use of Cl_2.

The formation of ClO radicals in the flash photolysis of Cl_2 and O_2 led Benson and Buss (Ref. 5) to suggest that the rate-controlling step in the recombination catalysis is the termolecular reaction:

$$Cl + O_2 + M \longrightarrow ClOO + M$$

$$M = O_2$$

with a subsequent decomposition to ClO:

$$ClOO + O \longrightarrow ClO + O_2$$

This postulate suggested that the ClO moiety may be trapped with F_2 in an experiment with an activated mixture of F_2, Cl_2, and O_2. The first attempt under this program to "fix" the ClO radical postulated to form as above was successful inasmuch as a 16 percent yield of ClF_3O was obtained (Table 2, Reaction 1). As is evident, the Cl_2 and F_2 were introduced into the cell in a stoichiometric amount with O_2 being in excess. A material balance exceeding 98 percent was realized with all of the Cl_2 being reacted.

The reproducible formation of ClF_3O from the elements offered additional latitude in exploring the possible intermediates responsible for ClF_3O formation in the uv reaction. The fact that more than 80 percent of the lamp output was at wavelengths longer than 3000 angstroms coupled with the facile reaction observed suggested that Cl_2 was the principal species being activated and that the termolecular reaction proposed by Benson and Buss may well be occurring in the Cl_2-F_2-O_2 system. Certainly some F_2 activation should occur but little or no O_2 activation is possible with the lamp used. For example:

$$Cl_2 \xrightarrow{uv} 2Cl \tag{7}$$

$$Cl + O_2 + M \longrightarrow ClOO + M \tag{8}$$

$$ClOO + Cl_2 \longrightarrow 2ClO + Cl \tag{9}$$

$$ClO + 3/2\ F_2 \longrightarrow ClF_3O \tag{10}$$

$$Cl + 3/2\ F_2 \longrightarrow ClF_3 \tag{11}$$

TABLE 2

ULTRAVIOLET ACTIVATED REACTIONS USING Cl_2, F_2, AND O_2

Reaction Number	Mole Ratio $Cl_2:F_2:O_2$	Temperature, C	Time, hours	Condensable Products	Percent Yield ClF_3O
1	1:3:10	-60	1*	ClF_3O, ClF_3	16
2	1:3:10	-60	1*	ClF_3O, ClF_3	16
3	1:3:1	-60	1*	ClF_3, trace amounts ClF_3O, ClF_5	Trace
4	1:3.3:18.7	-60	1**	ClF_3O, ClF_3, trace amount $FClO_2$	8
5	1:1.1:11.5	-60	1**	ClF_3O, ClF_3, ClF, trace amount $FClO_2$, possibly small amount of unreacted Cl_2	2 to 3
6	1:3.5:10.7	-60	1/4**	ClF_3, trace ClF_3O	Trace
7	1:3.4:9	-60	2**	ClF_3O, ClF_3, trace ClF_5	18
8	1:3.2:10	-60	1/4**	ClF_3, trace amounts of ClF_5, ClF_3O (Note: poor Cl_2 balance in experiment)	Trace
9	1:3.5:10	-60	1/4**	ClF_3, trace amount of ClF_3O	Trace
10	1:3.3:10	-60	1/2**	ClF_3, ClF_3O, small amounts of $FClO_2$, ClF_5	2
11	1:3:10	-60	1/6**	ClF, ClF_3, small amount $FClO_2$, possibly some unreacted Cl_2	0
12	1:3.2:10	-60	1/12**	ClF, ClF_3, small amount $FClO_2$, possibly some unreacted Cl_2	0
13	1:3.2:10	-40	1**	ClF, small amount $FClO_2$, possibly Cl_2	***
14	1:3.3:10	-40	1**	ClF_3O, ClF_3, ClF, small amount $FClO_2$	5

*Reaction periods do not include a 10-minute lamp warm-up period.

**Apparatus was modified to include a window shade which is employed during lamp warm up; periods indicated are actual time reactants exposed to uv irradiation.

***Validity of experiment in question due to the small amount of fluorine-containing product recovered.

From the preceding sequence, it is apparent that Eq. 11 may function as both the termination step and competing step (formation of ClF_3).

The sequence (Eq. 7 through 11) is supported by several considerations of known reactant systems but also appears to fall short of predictions when the time variable is treated. From Table 2 it is seen that essentially no ClF_3O is formed at short reaction times with almost all of the Cl_2 being consumed to ClF_3. (These results could suggest a subsequent ClF_3-O_2 reaction). Despite the fact that much basic information has been acquired regarding the operative processes in these uv activated reactions, considerably more experimentation is necessary before a complete clarification of the reaction process is possible.

CHEMISTRY OF CHLORINE MONOFLUORIDE

Reactions of chlorine monofluoride have been the subject of continuing investigations under this program. This work has proved successful from both a synthetic viewpoint and also in elucidating basic modes of reaction of interhalogen fluorides. During this period, this work has been carried on in several areas.

Chlorine Monofluoride--Lewis Acid Systems

Previous work on the ClF-Lewis acid system is controversial. Schmeisser (Ref. 6) reported the formation of solid complexes containing the Cl^+ cation according to the following equation:

$$ClF + AsF_5 \longrightarrow Cl^+AsF_6^- \qquad (12)$$

Earlier results from this laboratory (Ref. 1) seemed to indicate a disproportionation of ClF according to the following equation:

$$3ClF + AsF_5 \longrightarrow ClF_2^+AsF_6^- + Cl_2 \qquad (13)$$

Determination of the combining ratio between ClF and AsF_5 would allow a clearcut choice between Eq. 12 and 13. Quantitative synthesis of the solid complex from either excess ClF or excess AsF_5 resulted in a 1.00:2.02 and 1.00:2.00 combining ratio, respectively, thus proving that neither Eq. 12 nor 13 occurs. The resulting white, crystalline solid is stable at -78 C and is completely dissociated (according to its infrared spectrum) into AsF_5 (g) + 2 ClF (g) at ambient temperature. These infrared data further support the observed 1:2 combining ratio. The vapor pressure-temperature relation was measured and a plot of log $p_{(mm)}$ vs 1/T resulted in a straight line, which can be expressed by the equation:

$$\log p_{(mm)} = 11.7124 - \frac{2391.6}{T}$$

By extrapolation, a dissociation pressure of 1 atmosphere was obtained at -2.4 C. At 25 C, the dissociation pressure amounts to 4864 millimeters. From the slope of the vapor pressure-temperature curve, a heat of reaction (Δ H) of 32.83 kcal/mole was calculated from the process:

$$Cl_2F^+AsF_6^-{}_{(s)} \rightleftharpoons AsF_{5(g)} + 2\ ClF_{(g)}$$

From $\Delta F^\circ_T = -RT \ln K_{p\ (atm)}$, a free energy change, $\Delta F^\circ_{298} = -2.16$ kcal/mole, and from $\Delta S^\circ_T = (\Delta H^\circ - \Delta F^\circ_T)T^{-1}$, an enthropy change, ΔS°_{298} - 117.41 cal deg^{-1} $mole^{-1}$ were found for the dissociation process at 25 C. A heat of formation of $Cl_2F^+AsF_6^-{}_{(s)}$, $\Delta H^\circ_{f298} = -355.4$ kcal $mole^{-1}$, was calculated based upon ΔH°_{f298} of $ClF_{(g)} = 13.5$ kcal $mole^{-1}$ (Ref. 7) and ΔH°_{f298} of $AsF_{5(g)} = 295.6$ kcal $mole^{-1}$ (Ref. 8).

The fact that the dissociation pressure-temperature curve is a straight line over the entire temperature range measured and that at all temperatures only ClF and AsF_5 gas in a 2:1 mole ratio (according to their infrared spectra) were given off, shows that no stepwise decomposition (including the formation of stable intermediates such as $Cl^+AsF_6^-$) occurs. Thus, it seems that the $Cl^+AsF_6^-$ complex reported by Schmeisser, does not even form as an intermediate and that Schmeisser most probably mistook the 2 $ClF \cdot AsF_5$ complex for $Cl^+AsF_6^-$. Elemental analysis of a sample of the complex (after hydrolysis in aqueous NaOH solution) showed an As to Cl mole ratio of 1.0:1.8, in agreement with a 1:2 and not a 1:3 or a 1:1 combining ratio.

Nitryl fluoride, when allowed to react with excess solid $2ClF \cdot AsF_5$, displaced ClF in a mole ratio of $NO_2F:ClF = 1.00:1.94$. The infrared spectrum of the solid residue showed after removal of all the excess $2ClF \cdot AsF_5$ (by pumping at ambient temperature) the following bands characteristic of $NO_2{}^+AsF_6{}^-$ (Ref. 9 and 10); 2360 m ($\nu_{as} NO_2{}^+$), 695 vs ($\nu_{as} AsF_6{}^-$) 601 m ($\delta\ NO_2{}^+$), and 402 m ($\delta_{as}\ AsF_6{}^-$). Hence, the following reaction took place:

$$Cl_2F^+AsF_6{}^- + NO_2F \longrightarrow NO_2{}^+AsF_6{}^- + 2\ ClF$$

The ionic nature of the $2ClF \cdot AsF_5$ adduct has been proven by its low-temperature infrared spectrum taken on an Infracord 337 (refer to Fig. 1). The observed frequencies are listed in Table 3 and their assignment will be subsequently discussed.

Investigation of the ClF-BF_3 system shows that again the complex $Cl^+BF_4{}^-$, reported by Schmeisser (Ref. 6), does not form. Quantitative synthesis, using an excess of ClF, resulted in a BF_3 to ClF combining ratio of 1.00: 2.03. The white crystalline solid obtained is stable at -127 C. At -112 C, it shows a measureable dissociation pressure. Attempts to obtain a dissociation pressure-temperature curve failed owing to difficulties in attaining equilibrium. Under the experimental conditions used, the recombining speed of ClF and BF_3 appeared to be extremely slow. The $2\ ClF \cdot BF_3$ complex is considerably less stable than the corresponding AsF_5 adduct. This is not surprising because BF_3 when compared to AsF_5, is known to act as a weaker Lewis acid towards halogen fluorides (Ref. 11).

The ionic nature, $Cl_2F^+BF_4{}^-$, of the adduct has also been proven by its low-temperature infrared spectrum (Fig. 2). The observed frequencies and their assignments are listed in Table 3.

Several structural possibilities exist for 2:1 adducts of ClF with Lewis acids. The complexes could be either fluorine-bridged coordination complexes or ionic complexes containing the Cl_2F^+ cation. The first possibility can be definitely ruled out by comparison of the data of Table 3

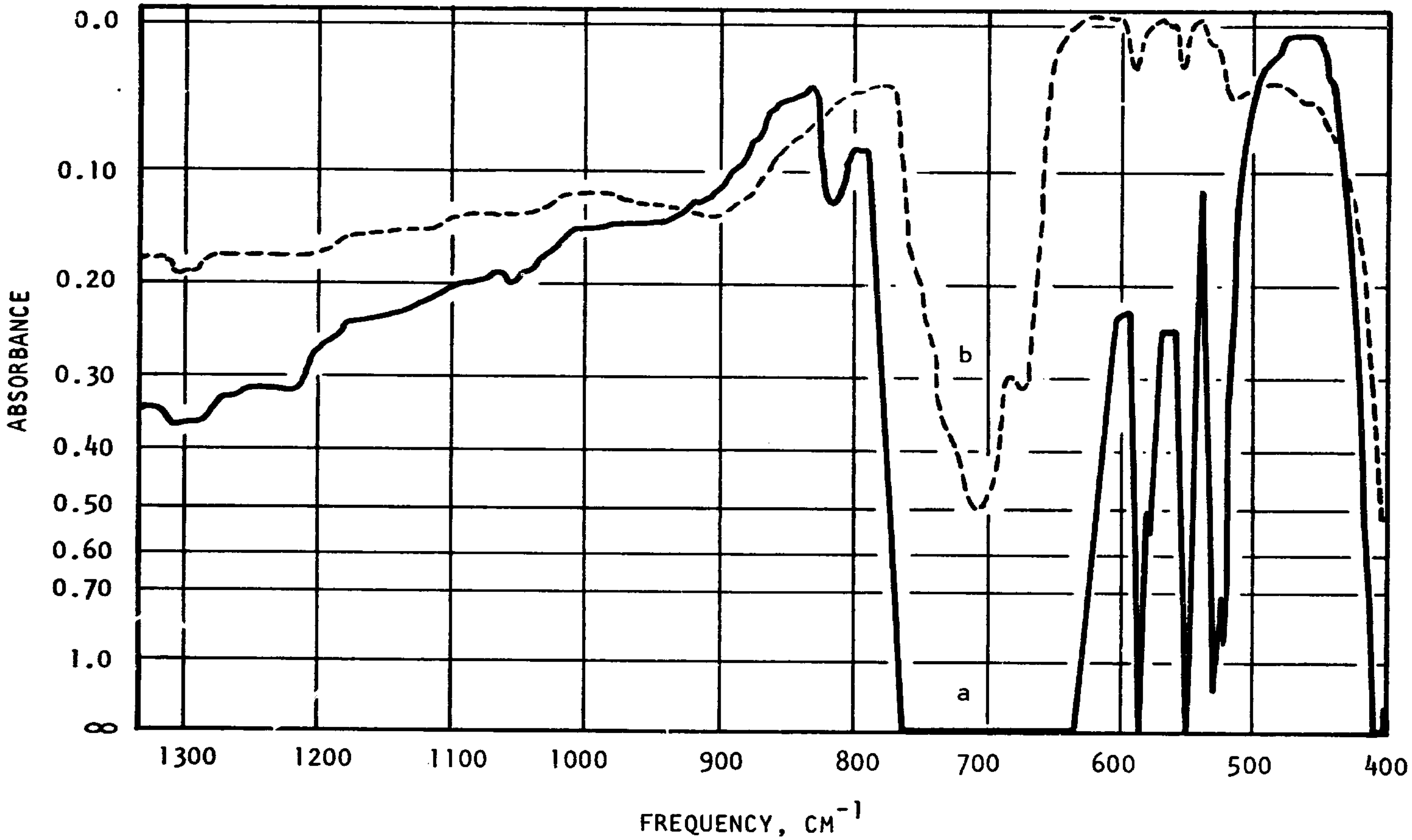


Figure 1. Low-Temperature Infrared Spectrum of Solid $Cl_2F^+AsF_6^-$ at Two Different Concentrations

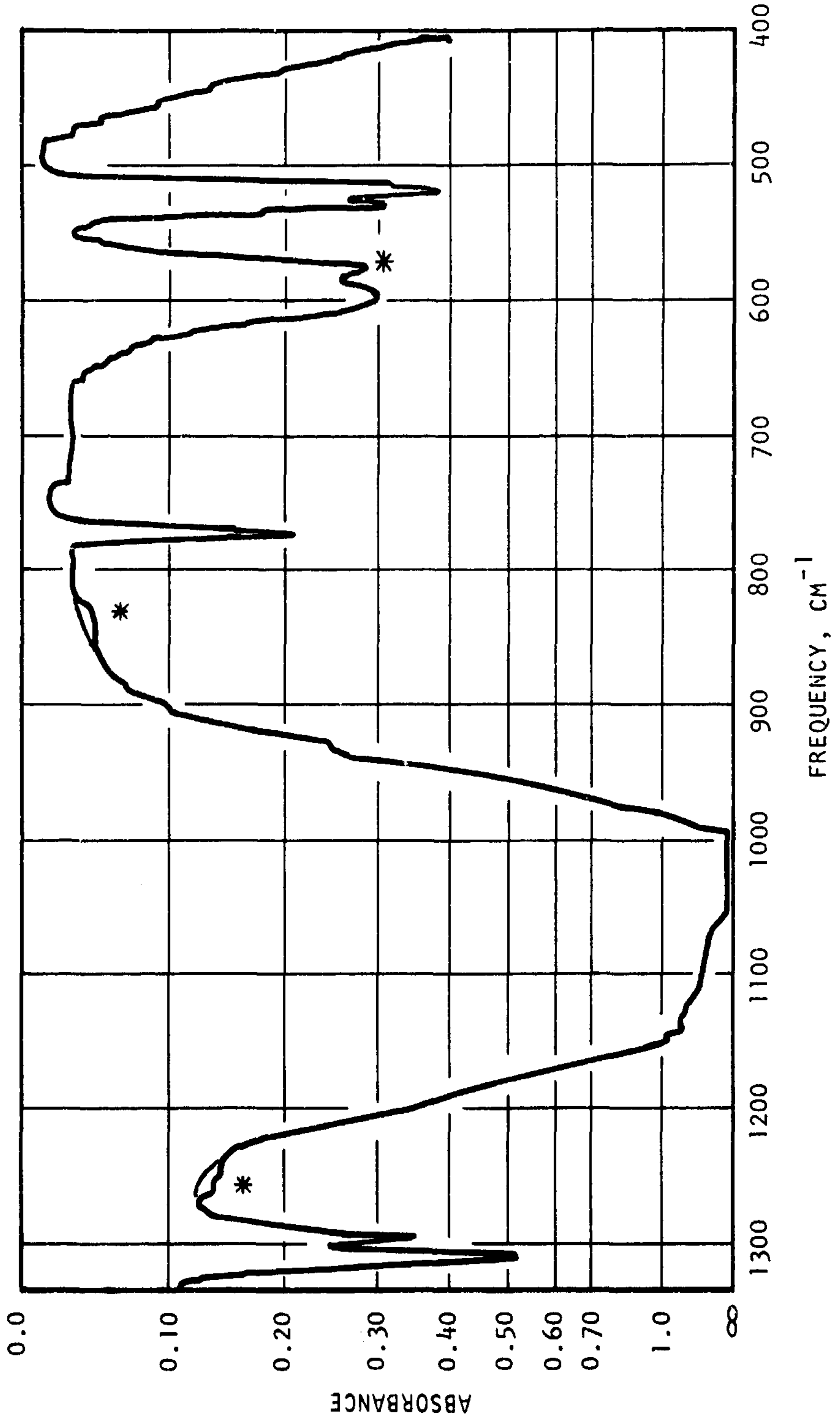


Figure 2. Low-Temperature Infrared Spectrum of Solid $Cl_2F^+BF_4^-$. (The bands marked by an asterisk are due to solid ClO_2F.)

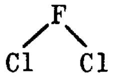
TABLE 3

INFRARED SPECTRA OF $Cl_2F^+AsF_6^-$ AND $Cl_2F^+BF_4^-$ AS SOLIDS AT -196 C AND THEIR ASSIGNMENT

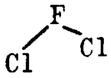
Frequencies Observed, cm^{-1}, Intensity		Assignment (Pointgroup)		
$Cl_2F^+BF_4^-$	$Cl_2F^+AsF_6^-$	$Cl_2F^+(Cs)$	$BF_4^-(T_d)$	$AsF_6^-(O_a)$
	1312 1297 vw			$(\nu_2 + \nu_3)$
1305 m 1289 mw			$(\nu_1 + \nu_4)$	
1145 - 978 vs, b			$\nu_3(F_2)$	
	828 w			$(\nu_2 + \nu_6)$
766 mw			$\nu_1(A_1)$	
	703 vs			$\nu_3(F_{1u})$
590 m	586 m	$\nu_1(A')Cl^{35}-F$		
582 w, sh	578 mw	$\nu_1(A')Cl^{37}-F$		
	(548 m)			
528 mw, sh	529 m	$\nu_3(A')Cl^{35}-Cl^{35}$		
523 mw, sh	521 mw	$\nu_3(A')Cl^{37}-Cl^{35}$		
	514 vw, sh	$\nu_3(A')Cl^{37}-Cl^{37}$		
519 m			$\nu_4(F_2)B^{10}$	-
512 w, sh			$\nu_4(F_2)B^{11}$	
	402 m			$\nu_4(F_{1u})$

with that reported for similar BF_4^- and AsF_6^- containing complexes such as $ClF_2^+BF_4^-$ and $ClF_2^+AsF_6^-$, respectively (Ref. 12). All vibrations characteristic of the BF_4^- and AsF_6^- anion have been observed with known frequencies and intensities. Therefore, the adducts of ClF with Lewis acids are ionic, containing the BF_4^- and AsF_6^- anion and consequently also the Cl_2F^+ cation. This cation could have either fluorine or chlorine as a central atom and could be either bent or linear, centrosymmetric or asymmetric. Thus, the following structures are possible:

Cl-FCl (I)   Cl-F—Cl (II)

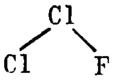


or



(III)

Cl-Cl-F (IV) and



(V)

All five models should exhibit three fundamental vibrations of which two are stretching and one is a deformation vibration. Model I (belonging to point group $D_{\infty h}$) is the only structure having a symmetry center. Therefore, only one of the stretching vibrations should be infrared active for Model I assuming that the selection rules apply strictly. For models II to V, all three fundamentals are expected to be infrared active. The data of Table 3 (observation of at least two stretching vibrations at approximately 585 and 525 cm^{-1}, respectively) thus rule out model I. The deformation vibration is expected to occur at a frequency below 400 cm^{-1}. This prediction is based on the calculation of the frequency of the deformation mode assuming that the force constants would be identical with those of ClF_2^+ (Ref. 12) and considering only the increase of mass resulting from the substitution of one fluorine atom by a chlorine atom. The frequency thus obtained is approximately 390 cm^{-1}. Because the force constants in Cl_2F^+ can be expected to be lower than those in ClF_2^+, the actual frequency of the deformation mode should be lower than 390 cm^{-1}. Hence, the two bands observed (in addition to the bands characteristic of the anions) most likely represent the two stretching modes of Cl_2F^+.

Distinction between the linear structures (II and IV) and the bent structures (III and V) can be made on the following basis. In a linear X-Y-Z model, very strong coupling should occur between the X-Y and Z-Y stretching vibration, thus resulting in a symmetric and antisymmetric stretching vibration. The latter are expected to be separated by a relatively large frequency difference. In a bent triatomic species however the frequency difference between the two stretching vibrations would be rather small. This prediction was demonstrated previously for linear $[F\text{-}Cl\text{-}F]^-$ (ν = 160 cm^{-1}, Ref. 13) and bent $[{}_{F}{\diagup}^{Cl}{\diagdown}_{F}]^{+}$ ($\Delta\nu$ = 8 cm^{-1}) ions (Ref. 12). For a linear $[Cl\text{-}Cl\text{-}F]^+$ cation $\Delta\nu$ should be even larger than for ClF_2^- because of the different mass of the two terminal atoms. The frequency difference of approximately 60 cm^{-1}, observed for Cl_2F^+, therefore eliminates the possibility of the linear models II and IV.

Distinction between the two remaining bent models (III and V) can be made on the basis of the isotope-splitting observed in the spectrum of $Cl_2F^+AsF_6^-$. For model III having only F-Cl bands, only two isotope bands (Cl^{35}-F and Cl^{37}-F in a 3:1 ratio) would be expected for both stretching vibrations. For model V, the higher frequency band (being the Cl-F stretching mode) should show two isotope bands in a 3:1 ratio (Cl^{35}-F and Cl^{37}-F, respectively), whereas the lower frequency band (being the Cl-Cl stretching mode) should show three isotope bands in a 2.2:1.5:0.2 ratio (Cl^{35}-Cl^{35}, Cl^{37}-Cl^{35} + Cl^{35}-Cl^{37}, and Cl^{37}-Cl^{37}, respectively). Comparison of these predictions with the data of Table 3 and Fig. 1 shows that only model V can be correct.

The fact that the Cl_2F^+ cation forms rather than a Cl^+ cation is not surprising since Cl^+, possessing only an electron sextet, should be relatively unstable. By the addition of 1 mole of ClF to Cl^+, a cation (Cl_2F^+) results which yields a stable electron configuration for each atom. The Cl_2F^+ cation could be considered either as a catenated cation derived from Cl^+ or as a derivative of ClF_2^+ in which one of the fluorine ligands has been replaced by a chlorine atom. In the latter case, addition of a fluoride anion to Cl_2F^+ does not result in the parent molecule Cl_2F_2 (derived from ClF_3 by replacement of one F by one Cl atom) but in two molecules of ClF. This has been demonstrated by the replacement reactions with NO_2F and the dissociation data obtained for the solid complex.

Since Cl_2F^+ can be considered as the first known example of a catenated interhalogen cation, its discovery may open a synthetic route to a large number of novel mixed interhalogen compounds.

Attempted Synthesis of Chlorine Perchlorate

The preparation of the unknown compound chlorine perchlorate was sought to explore its potential as a synthetic intermediate. The synthesis of chlorine perchlorate was attempted via condensation reactions of chlorine monofluoride and various perchlorate species as shown:

$$MClO_4 + ClF \longrightarrow MF + ClOClO_3$$

where

M = Na, Cs, NO_2, H

Condensation reactions of this type have proved useful in syntheses of chlorine nitrate (Ref. 14) and chlorodifluoramine (Ref. 15).

Numerous reactions were conducted with ClF and $NaClO_4$ or $CsClO_4$ using reaction temperatures of -78, -45, and 0 C. These reactions were of variable duration of up to 2 weeks. During nearly all experiments, a low yield (0 to 10 percent) of a volatile Cl-O species was obtained. The identity of this compound as a perchlorate was based on its infrared spectrum and hydrolysis to $HClO_4$. Comparison of the infrared spectrum of this material and that of other covalent perchlorates revealed a dissimilarity but a spectrum of Cl_2O_6 was not available for comparison. A sample of

Cl_2O_6 was prepared by uv irradiation of ClO_2 (Ref. 16). Its infrared spectrum over the 2.5- to 25-micron region proved that the unidentified Cl-O material from the ClF reactions was Cl_2O_6. The volatility observed for the unknown Cl-O compound and that reported for Cl_2O_6 are quite different. However, it was found in preparing the "authentic" sample of Cl_2O_6 that its volatility and that of the ClF condensation reaction product were comparable and thus the reported vapor pressure data for Cl_2O_6 are in error.

Reactions of NO_2ClO_4 and $HClO_4$ (72 percent) with ClF were also employed in the attempted preparation of $ClOClO_3$. The NO_2ClO_4 proved to be relatively unreactive but did give very small amounts of a mixture of known Cl-O and FCl-O compounds including Cl_2O_6 but no new material. The reaction of ClF and $HClO_4$ was readily accomplished but here also the only observed products were mixtures of known chlorine-oxygen compounds. Thus, none of the attempted reactions gave any evidence for the formation of the desired $ClOClO_3$ and efforts directed toward its synthesis were terminated.

Preparation of Hypochlorites

Examples of the formation of both inorganic and organic hypofluorites have been reported recently (Ref. 17 and 18). The best technique for the synthesis of these compounds involves fluorination of a central atom-oxygen double bond in the presence of CsF at low temperature. For example:

$$SOF_4 + F_2 \xrightarrow[-78\ C]{CsF} SF_5OF$$

$$COF_2 + F_2 \xrightarrow[-78\ C]{CsF} CF_3OF$$

This Lewis base catalysis of the oxidation of M=O groups has now been applied to chlorofluorination reactions and has resulted in the preparation of some perfluorohypochlorites, a class of compounds previously unknown. The preparations have been conducted at temperatures down to -78 C and have been found to rapidly produce hypochlorites in high yields. Some typical syntheses are summarized in the following reactions.

$$SOF_4 + ClF \xrightarrow[-78\ C]{KF\ CsF} SF_5OCl$$

$$KOCF_3/KF + ClF \xrightarrow{-45\ C} KF + CF_3OCl$$

$$COF_2 + ClF \xrightarrow[-78\ C]{CsF} CF_3OCl$$

$$CsOCF_2CF_3 + ClF \xrightarrow{0\ C} CsF + CF_3CF_2OCl$$

$$CF_3CFO + ClF \xrightarrow[-78\ C]{CsF} CF_3CF_2OCl$$

$$CF_3CFO + CsClF_2 \xrightarrow{0\ C} CF_3CF_2OCl + CsF$$

The identity of the product hypochlorites as such is based on the material balance observed in the syntheses and the vapor density of the products (SF_5OCl, calculated 178.5 gm/mole, found 177 gm/mole; CF_3OCl, calculated 120 gm/mole, found 110 gm/mole; C_2F_5OCl, calculated 170 gm/mole, found 164 gm/mole). In addition the infrared spectra of the products are similar to those of the corresponding known hypofluorites (Ref. 19) but lack any -OF absorptions. Finally, proof of the structure of the compounds was sought through derivative formation. Typical reactions obtained are:

$$SF_5OCl \xrightarrow[RT]{uv} SF_5OOSF_5\ 50\% + Cl_2\ SF_5OSF_5\ (t)$$

$$CF_3OCl \xrightarrow[RT]{uv} CF_3OOCF_3 + Cl_2$$

$$CF_3OCl + F_2 \xrightarrow{RT} CF_3OF$$

$$C_2F_5OCl \xrightarrow[RT]{uv} COF_2 + CF_3Cl$$

These reactions were nearly quantitative in the case of the perfluoroalkyl hypochlorites. The products observed in the photolysis of C_2F_5OCl probably arose in the following manner:

$$C_2F_5OCl \xrightarrow{uv} CF_3CF_2O\cdot + Cl\cdot$$

$$CF_3CF_2O\cdot \longrightarrow \cdot CF_3 + COF_2$$

$$\cdot CF_3 + Cl\cdot \longrightarrow CF_3Cl$$

The three hypochlorites prepared are of variable stability in metal-Teflon systems at ambient temperature. The observed relative thermal stabilities are $SF_5OCl < C_2F_5OCl < CF_3OCl$. Decomposition occurs through disproportionation to the precursors, ClF and M=O. Further characterizing data will be obtained for these compounds.

The mechanism by which these compounds are formed is probably the same as that postulated for the catalytic fluorination reactions. For example:

$$SOF_4 + MF \longrightarrow M^+\bar{O}SF_5^-$$

$$M^+\bar{O}SF_5 + ClF \longrightarrow MF + F_5SOCl$$

Only in the case of thionyl tetrafluoride has the necessity of MF in the reaction been shown as yet. Thus, no reaction was found for ClF and SOF_4 in the absence of an alkali metal fluoride.

PREPARATION AND FLUORINATION OF BROMINE NITRATE

The fluorination of chlorine nitrate to give ClF_3O (Ref. 14) suggests that the analogous reaction of bromine nitrate might lead to BrF_3O or BrF_5O. Previous efforts (Ref. 1) in this area were hampered by the poor purity of the available $BrNO_3$. An improved synthetic method has now been devised which produces good purity material although it does so slowly.

The synthesis of $BrNO_3$ has been accomplished through the in situ formation of BrCl from the elements, followed by reaction with $ClNO_3$.

$$Br_2 + Cl_2 \rightleftharpoons 2BrCl$$

$$BrCl + ClNO_3 \longrightarrow BrNO_3 + Cl_2$$

The second step of this preparative scheme has been reported (Ref. 20) but previous attempts (Ref. 14) to utilize it were unsuccessful. Reaction of Br_2 Cl_2, and $ClNO_3$ in approximately 1:5:5 molar ratio in glass ampoules at -30 to 0 C resulted in the formation of $BrNO_3$. The reaction has been carried out in the dark to minimize any possible photochemical decomposition. The product was obtained by fractional condensation at -64 C and the only impurity was a small amount of HNO_3. The principal problem encountered with this method was that the reaction is quite slow at -30 C while at 0 C some noncondensable gases are formed, probably due to decomposition of the desired product. Approximately 20 percent yield has been obtained in 1 week at -20 C.

Bromine nitrate is pale yellow as a solid and melts at -31 C to a golden liquid. The vapor pressure-temperature relationship for -25 to 10 C is described by the equation $\log p_{mm} = 9.6905 - 2254.5/T$. The derived heat of vaporization is 10.3 kcal/mole. The principal infrared absorptions for $BrNO_3$ are listed in Table 4.

TABLE 4

INFRARED SPECTRUM OF $BrNO_3$*

Frequency, cm^{-1}	Relative Intensity	Frequency, cm^{-1}	Relative Intensity
3390	vw		
2970	w	955	w
2550	vw	800	vs
1700	vs	735	w
1440	vw	722	w
1280	vs	645	vw
1205	vw	555	vw
1110	w	450 pqr	vw

*Spectrum taken on Perkin Elmer Models 137 and 337 spectrophotometers.

Fluorination of $BrNO_3$ at -30 C resulted in conversion to BrF_5 and FNO_2 only. Fluorination at ambient temperature or by slow warming from -78 C to ambient temperature also gave BrF_5 and FNO_2 but in addition resulted in the formation of small amounts of a white solid, stable at room temperature. Infrared spectra showed this solid to be the same as that obtained previously (Ref. 1) by fluorinating impure $BrNO_3$. However, now that good purity $BrNO_3$ has been successfully fluorinated, it has been found that the yields of free FNO_2 and BF_5 accounts for better than 95 percent of the starting Br and NO_2 leaving very little as the complexed solid. The freedom from metal fluoride and other contaminants facilitated the obtaining of an infrared spectrum of the neat solid. This spectrum contained only the previously observed NO_2^+ band (2385 cm^{-1}) and a broad band (centered at 575 cm^{-1}) due to Br-F absorptions. No indication was found of an absorption due to a Br=O group as would be expected if the solid is the desired $NO_2^+BrF_xO^-$ complex.

Chemical displacement of the Br-F function from this complex was attempted with Lewis acids.

$$NO_2^+BrF_xO^- + MF_n \longrightarrow NO_2\,MF_{n+1} + BrF_{x-1}O$$

$$MF_n = SiF_4,\ BF_3$$

No reaction was obtained between SiF_4 and the complex at ambient temperature. Similar conditions when utilizing BF_3 produced a slow reaction. After 2 days a small amount of BF_3 was consumed but the only volatile material observed other than unreacted BF_3 was Br_2. No noncondensable gases were formed. The solid left after this reaction was a mixture of NO_2BF_4 and the original complex.

The observation of Br_2 as a displacement product is indicative of an unstable Br-F species. The absence of noncondensables and the infrared spectrum of the complex indicate the absence of oxygen in the compound. The most readily apparent unstable bromine fluoride is BrF which exists only in the following equilibrium (Ref. 21):

$$3\ BrF \rightleftharpoons BrF_3 + Br_2$$

If the observed Br_2 does arise from BrF, the coproduct BrF_3 would not have been observed due to the small quantities involved and its low vapor pressure.

Although no solid complexes of BrF have been reported, it is not unreasonable that the unknown complex, NO_2BrF_2, could be identical to the complex obtained in the $BrNO_3$ fluorination. To examine this possibility, a limited effort will be conducted to form NO_2BrF_2. This should be readily accomplished via FNO_2, Br_2, and F_2 if NO_2BrF_2 is a stable solid. Additional fluorinations of $BrNO_3$ with F_2 as a route to BrF_xO materials do not appear warranted due to the overwhelming cleavage at the Br-O bond rather than the O-NO_2 bond. Final attempts at effecting the desired bond breaking and fluorination will utilize ClF_5 as a fluorine source.

EXPERIMENTAL

ULTRAVIOLET IRRADIATION

Cell and Fractionation System

A specially designed ultraviolet reactor was connected to the system and consisted of a stainless-steel body and a 4-inch-diameter ultraviolet-grade sapphire window. The cell temperature was automatically controlled by a circulating methanol cooling system to within 3 C of the desired temperature and within a range of -60 C to ambient temperature. The cell apparatus was modified so that a new ultraviolet lamp could be used. This modification consisted of a metal housing above the cell window to hold the new lamp and a system to supply dry nitrogen which can be blown continuously across the cell window to prevent "frosting" during low-temperature reactions. The new lamp provided a greatly increased amount of irradiation; however, it also increased the amount of heat generated and it was necessary to cool the cell housing with a large fan.

Ultraviolet Source

Work was conducted with a Hanovia lamp No. 679-A-36 (power input 450 watts). The spectral energy distribution of radiated Hg lines include (wavelength in angstroms, and watts): 2967, 4.3; 2652, 4.0; 2537, 5.8; 2482, 2.3; 2380, 2.3; 2360, 2.3; 2224, 3.7.

Materials

The $FClO_2$ was prepared by the reaction of ClF_3 and $KClO_3$. Purification of $FClO_2$ was carried out by pumping off the Cl_2 impurity while holding the $FClO_2$ at -78 C. The chromatographic purity of the colorless liquid was better than 99.9 percent. The $FClO_3$ was purchased from Pennsalt. The ClF_5 prepared at Rocketdyne, had a purity of 99+ percent. Other materials were prepared by standard techniques.

CHLORINE MONOFLUORIDE REACTIONS

Synthesis of $Cl_2F^+AsF_6^-$

All reactions were carried out in a stainless-steel vacuum line equipped with Teflon FEP U-traps.

In a typical experiment, 96.7 mmoles of ClF (prepared in this laboratory and purified by fractional condensation) and 24.2 mmoles of AsF_5 (obtained from Ozark-Mahoning and purified by fractional condensation) were combined at -196 C in a U-trap. The mixture was allowed to warm slowly until melting and reaction occurred. When the pressure inside the trap reached 760 mm the mixture was cooled again to -196 C. This procedure was repeated several times until completion of the reaction. The content of the trap was maintained at -78 C and all volatiles were pumped off and condensed at -196 C. The content of the -196 C trap consisted of 48.8 mmoles of ClF. The observed vapor pressure-temperature data for the complex are presented in Table 5.

Synthesis of $Cl_2F^+BF_4^-$

The synthesis of $Cl_2F^+BF_4^-$ was similar to that of $Cl_2F^+AsF_6^-$ except that the U-trap containing the solid complex was maintained at -126 C when the excess ClF was removed in vacuo.

TABLE 5

VAPOR PRESSURE-TEMPERATURE DATA FOR $Cl_2F^+AsF_6^-$

Pressure, mm Hg	Temperature, C
1.7	-63.76
6.0	-54.30
16.5	-45.45
68.5	-30.11
120	-24.77
209	-11.15

Low-Temperature Infrared Spectra

The technique used to obtain the low-temperature infrared data is described in Ref. 22.

Displacement Reaction of $Cl_2F^+AsF_6^-$ With NO_2F

Nitryl fluoride (2.75 mmoles, prepared in this laboratory and purified by fractional condensation) was combined with a large excess of solid $Cl_2F^+AsF_6^-$ at -196 C. The temperature of the trap containing the mixture was cycled between -196 C and a temperature where the pressure inside the trap reached 1 atmosphere until the reaction was complete. The trap was maintained at -78 C and all volatiles were removed to a -196 C trap. The content of the -196 C trap was shown to consist of 5.33 mmoles of essentially pure ClF.

Reactions of ClF and Perchlorates

Samples of the substrate perchlorates were transferred to prepassivated 10- or 30-milliliter stainless-steel bombs in a nitrogen-filled dry box. The solid perchlorates were commercial dry, powdered, white solids ($NaClO_4$, $CsClO_4$, and NO_2ClO_4). Once the reactors were closed and re-evacuated, freshly fractionated ClF was condensed in at -196 C. The reactors were then changed to the desired reaction temperature (-78, -45, or 0 C) and left for up to 2 weeks. On completion of the reaction, the gaseous products were separated by fractional condensation at -78, -112, -142, and -196 C. Generally 80+ percent of the ClF was recovered (excesses of $MClO_4$ were used) and the remaining products were mixtures of $FClO_2$, $FClO_3$, Cl_2, and variable amounts of Cl_2O_6. No unidentified volatile species were found.

Synthesis of Hypochlorites

Method A. An alkali metal salt (MOR_f:M=K,Cs and $-OR_f$=OCF_3 or OC_2F_5) was placed in a prepassivated stainless-steel reactor. Chlorine monofluoride was condensed into the reactors at -196 C and the closed bomb was allowed to stand at temperatures between -78 and 0 C for time periods up to several weeks. Fractionation of the volatile products after even short time periods showed the reaction to be complete giving R_fOCl as the product and any excess ClF. Purification by fractional condensation was effected and both perfluoromethyl hypochlorite and perfluoroethyl hypochlorite were identified by vapor density measurements and infrared spectra.

Method B. A prepassivated, stainless-steel cylinder was loaded with MF(KF or CsF) in a dry box. After evacuation, measured amounts of an M=0 compound (M=0 is COF_2, CF_3CFO, or SOF_4) were condensed in at -196 C followed by a molar excess of freshly fractionated ClF. The reactor was then warmed to -78 C for 1 hour or more. Subsequent vacuum fractionation of the contents showed that conversion of M=O to the corresponding hypochlorite (CF_3OCl, C_2F_5OCl, SF_5OCl) had occurred in high yield. Proof of the composition of SF_5OCl was accomplished through vapor density measurement, synthetic material balance, and infrared spectroscopy just as had been accomplished earlier with the RFOCl compounds. The conversion of SOF_4 to SF_5OCl was shown to be slower with KF than with CsF and also it was shown that ClF and SOF_4 do not form SF_5OCl in the absence of KF or CsF under comparable conditions.

Method C. A sample of $CsClF_2$ solid contained in a 10-milliliter stainless-steel reactor was treated with CF_3CFO at approximately 0 C for 15 minutes. Fractionation of the gaseous materials at that time showed 25 percent of the CF_3CFO had been converted to C_2F_5OCl. Returning the gases over the $CsClF_2$ at -45 C for several hours resulted in nearly complete conversion to C_2F_5OCl.

Reactions of Hypochlorites

Chemical characterization of these hypochlorites was carried out to substantiate the formulations.

Photochemical decomposition by uv irradiation (100-watt Hanovia utility lamp) was accomplished at ambient temperature. Irradiations were conducted using Pyrex containers and 1- to 2-hour reaction times. In the case of CF_3OCl, the reaction completely consumed the hypochlorite and formed CF_3OOCF_3 and Cl_2 in very high yield. In the case of C_2F_5OCl, the product volume again was almost precisely double that of the starting volume but infrared examination showed the products to be a 1:1 mixture of COF_2 and CF_3Cl. The photolysis of SF_5OCl resulted in approximately a 50 percent yield of SF_5OOSF_5 with a trace of SF_5OSF_5. No SF_5OCl was recovered as it had decomposed through thermal or uv excitation or both to give SOF_4 and ClF (observed as Cl_2, SiF_4).

Fluorination of CF_3OCl. The conversion of CF_3OCl to the known CF_3OF occurred in minutes at ambient temperature or below through reaction with excess F_2. Only a small amount of CF_3OCl was recovered and the only other C-F product in addition to CF_3OF was a trace of COF_2.

BROMINE NITRATE PREPARATION AND FLUORINATION

A typical preparation of $BrNO_3$ has employed Br_2 (100 cc), Cl_2 (400 to 500 cc), and $ClNO_3$ (400 to 500 cc) in a 30-milliliter glass ampoule. The closed ampoule was maintained at a constant temperature (-30, -21 or 0 C) for several days. To a degree, the course of the reaction could be followed by observing the color of the solution. Originally, this was very dark red but as Br_2 was converted to BrCl and $BrNO_3$ it gradually changed to cherry red. At -30 C, the reaction is very slow while at 0 C some noncondensable by-products are formed. The reactors were kept in the dark to limit any possible photochemical decomposition. Bromine nitrate was purified by removing most of the Cl_2, $ClNO_3$, and BrCl at -78 C. After this was accomplished, a final fractionation through -45 and -65 C traps yielded $BrNO_3$ whose infrared spectrum showed only negligible HNO_3 contamination. Vapor pressure-temperature readings for the -25 to 10 C range are presented in Table 6. A typical infrared spectrum of $BrNO_3$ is shown in Fig. 3.

TABLE 6

VAPOR PRESSURE-TEMPERATURE DATA FOR $BrNO_3$

Pressure, mm Hg	Temperature, C
4	-24.9
7	-18.5
10	-13.9
21	-3.5
29	+0.8
33	+2.7
44	+7.0

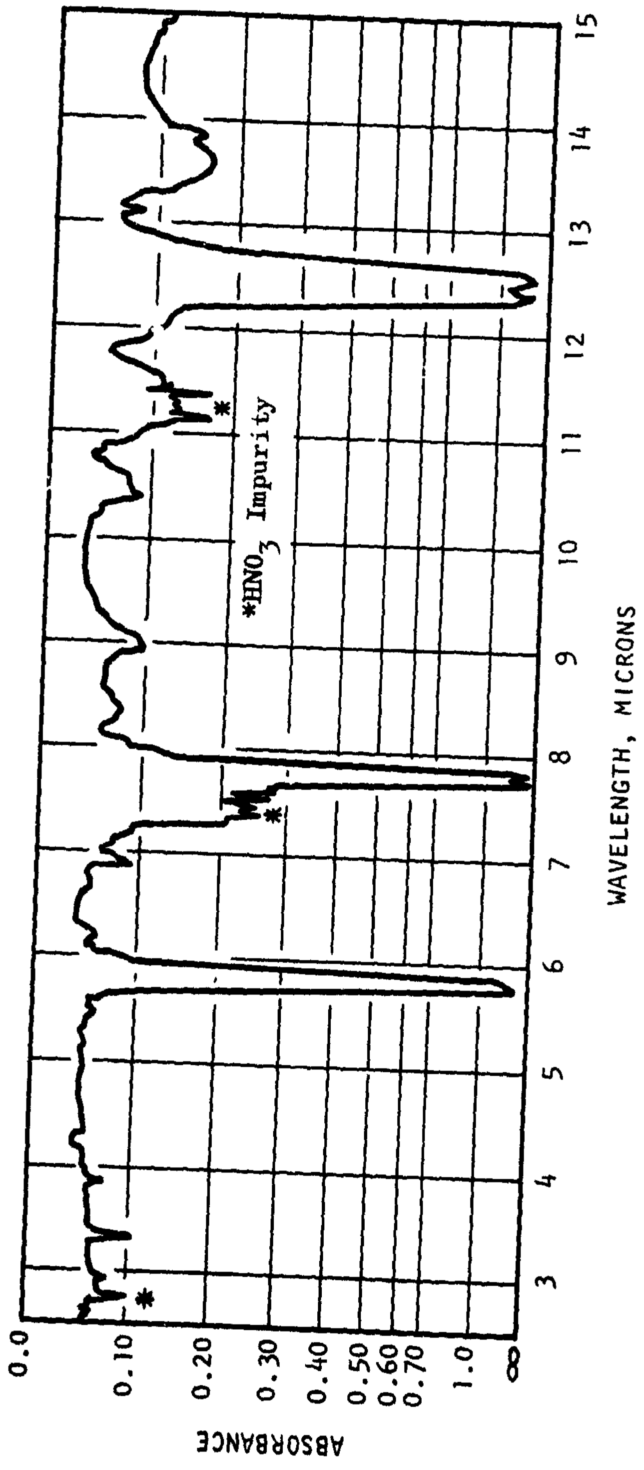


Figure 3. Bromine Nitrate Infrared Spectrum (5 cm path/20 mm Pressure)

Measured samples of $BrNO_3$ were condensed into 30-milliliter stainless-steel cylinders at -196 C followed by excess F_2. The reaction was allowed to proceed at a constant temperature (-30 C) or by slow warming to ambient temperature for overnight or longer. After removal of the excess F_2 at -196 C, the remaining volatile products were fractionated through traps cooled to -78, -142, and -196 C as the reactor warmed. These materials were found to be pure FNO_2 and BrF_5 and accounted for 95+ percent of the charged $BrNO_3$. Examination of the reaction cylinders in the dry box showed residual solids (tan or white in color) whose infrared spectrum, and hydrolytic and thermal decomposition during this and previous reporting periods (Ref. 1) have shown to be an NO_2^+ complex of an undetermined bromine fluoride. Chemical displacement of the anionic bromine fluoride species from this complex was attempted with SiF_4 and BF_3. The former did not react and the latter gave only slight reaction but liberated Br_2 only as an observed volatile product. The solid was shown by infrared spectroscopy to have been at least partially converted to NO_2BF_4.

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13. ABSTRACT

Ultraviolet activated fluorinations of chlorine oxyfluorides at low temperatures to produce Florox were continued. The involvement of elemental Cl_2 and O_2 in the Florox forming process was deduced and was verified experimentally by the preparation of Florox from Cl_2, F_2, and O_2. The chlorofluoro chloronium (III) cation, Cl_2F^+, a new oxidizing species, has been prepared in the form of its AsF_6^- and BF_4^- salts. The white crystalline $Cl_2F\ AsF_6$ complex is stable at -78 C and is completely dissociated in the gas phase at 25 C. Low-temperature infrared measurements on both salts prove the ionic nature of the solids and indicate that Cl_2F^+ has a bent structure (symmetry C_s) with chlorine as the central atom. The Cl_2F^+ cation is the first example of a catenated polyhalogen cation. The utility of ClF as a chlorofluorinating agent was demonstrated in the preparation of some new covalent hypochlorites, R_fOCl. These syntheses are catalyzed by alkali metal fluorides but may also be affected by reaction of preformed complexes. High-purity bromine nitrate has been prepared by the reaction of Br_2, Cl_2, and $ClNO_3$ at -30 to 0 C. Solid $BrNO_3$ is pale yellow and melts to a golden colored liquid at -31 C. The vapor pressure-temperature equation for -25 to 10 C is $\log p_{mm} = 9.6905 - 2254.5/T$. Fluorination of $BrNO_3$ has shown that FNO_2 and BrF_5 are the principal products (95+ percent yield). (C)

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