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R-7239-2

(Unclassified Title)

QUARTERLY PROGRESS REPORT, INORGANIC HALOGEN OXIDIZERS

(1 September 1967 through 30 November 1967)

Group 4
Downgraded at 5-Year Intervals
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G.O. 8614

Sponsored by Office of Naval Research
Power Branch
Code 429

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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. Christie, 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 Cl₂ and O₂ in the Florox forming process was deduced and was verified experimentally by the preparation of Florox from Cl₂, F₂, and O₂. Additional reaction paths are proposed and have been partially substantiated.

The chlorofluoro chloronium (III) cation, Cl₂F⁺, a new oxidizing species, has been prepared in the form of its AsF₆⁻ and BF₄⁻ salts. The white crystalline Cl₂FAsF₆ 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:

\[ \text{Cl}_2\text{F}^+ \text{AsF}_6^-(s) = 2\text{ClF}(g) + \text{AsF}_5(g) \]

Low-temperature infrared measurements on both salts prove the ionic nature of the solids and indicate that Cl₂F⁺ has a bent structure (symmetry C₃v) with chlorine as the central atom. The Cl₂F⁺ cation is the first example of a catenated polyhalogen cation. Quantitative displacement of 2 ClF from the complex by 1 FNO₂ has been observed.

The synthesis of chlorine perchlorate from ClF and perchlorate species was unsuccessful. Only mixtures of chlorine oxyfluorides and chlorine oxides, including Cl₂O₆, were produced by these reactions. The utility of ClF as a chlorofluorinating agent was demonstrated in the preparation of some new covalent hypochlorites, R₄OC₁. 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 Br₂, Cl₂, and ClNO₃ at -50 to 0 °C. Solid BrNO₃ is pale yellow and melts to a golden colored liquid at -31 °C. The vapor pressure-temperature equation for -25 to 16 °C is log pₚₒₐₒ₈ = 9.6005 - 2254.5/T. Fluorination of BrNO₃ has shown that FNO₂ and BrF₅ are the principal products (95% yield). Limited amounts of a white solid NO₂⁺-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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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 (CIF₃₀) from FC₁₀₂ and FC₁₀₃. 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 CIF has been of continuing interest. One aspect of this is the nature of the CIF-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 7:1 CIF-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 CIF, other reactions have been discovered in which the use of CIF has led to synthetic routes to useful covalent materials. Thus, superior syntheses of CINF₂, CINO₃, and PF₄Cl were developed. Further application of CIF has now resulted in the preparation of some new perfluorohypochlorites.

The proven reaction of CINO₃ and F₂ as a route to Florox promoted consideration of a similar BrNO₃ fluorination as a method of forming the unknown BrFₓ₀ species. The availability of only impure BrNO₃ was an experimental difficulty encountered previously. However, fluorination of that material indicated that a new NO₂⁺ bromine fluoride complex was formed, possibly NO₂⁺BrFₓ₀⁻. The synthesis of pure BrNO₃ has now been carried out and its fluorination has been studied.
Discussion

Ultraviolet Activated Reactions

The preparation of ClF₃O from any vigorous fluorinating agent and an oxychlorine fluoride (FCIO₂ or FCIO₃) was demonstrated to be facile with uv radiation (Ref. 1). These routes were the first demonstrations of high-yield syntheses of ClF₃O 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 ClF₃O 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 F₂-FCIO₃ 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 FCIO₃ was suggested in Ref. 2:

\[
\begin{align*}
\text{FCIO}_3 & \xrightarrow{\text{uv}} \text{FCIO}_2 + \text{O} \\
\text{FCIO}_3 + \text{O} & \rightarrow \text{FCIO}_2 + \text{O}_2 \\
\text{FCIO}_2 & \xrightarrow{\text{uv}} \text{FCIO} + \text{O} \\
\text{FCIO}_2 + \text{O} & \rightarrow \text{FCIO} + \text{O}_2 \\
\text{FCIO} + \text{F}_2 & \rightarrow \text{ClF}_3\text{O} \\
\text{FCIO} + \text{O} & \rightarrow \text{FCI} + \text{O}_2
\end{align*}
\]

The stepwise degradation of FCIO₂ or FCIO₃ 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 FCIO₂ should be a
### Table 1

#### Ultraviolet Activated Reactions

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reactants</th>
<th>Reactant Ratio, (\text{F}_2/\text{FC}10_3)</th>
<th>Temperature, °C</th>
<th>Time, hours</th>
<th>Condensable Product.a</th>
<th>Percent Conversion</th>
<th>Percent Yield (\text{ClF}_3)</th>
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<tr>
<td>1</td>
<td>FC10_3</td>
<td>---</td>
<td>-60</td>
<td>1/2</td>
<td>Unreacted FC10_3, ClF, small amount FC10_2</td>
<td>(74%) (25.5%) (2.5%)</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>FC10_3</td>
<td>---</td>
<td>-60</td>
<td>1/2</td>
<td>Unreacted FC10_3, ClF, small amount FC10_2</td>
<td>(68.5%) (28%) (3.5%)</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>F_2, FC10_3</td>
<td>1.1</td>
<td>-60</td>
<td>1</td>
<td>ClF_2O, ClF_3, unreacted FC10_3, small amount FC10_2</td>
<td></td>
<td>30 (60)</td>
</tr>
<tr>
<td>4</td>
<td>F_2, FC10_3</td>
<td>1.2</td>
<td>-60</td>
<td>1/2</td>
<td>ClF_2O, ClF_3, unreacted FC10_3, small amount FC10_2</td>
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<td>12 (33)</td>
</tr>
<tr>
<td>5</td>
<td>F_2, FC10_3</td>
<td>2.0</td>
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<td>1</td>
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<td></td>
<td>27 (41)</td>
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<td>40 (51)</td>
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<tr>
<td>8</td>
<td>ClF, O_2</td>
<td>1.0</td>
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<td>1</td>
<td>Unreacted ClF, small amounts ClF_3, FC10_2, Cl_2</td>
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<td>--</td>
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<tr>
<td>9</td>
<td>ClF_3O</td>
<td>---</td>
<td>-60</td>
<td>1</td>
<td>Unreacted ClF_3O (92%), small amounts ClF_3, FC10_2</td>
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<td>1/2</td>
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<td>12</td>
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<td>-60</td>
<td>1</td>
<td>Unreacted ClF and FC10_3, small amounts of ClF_3 and ClF_3O, Cl_2</td>
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<td>--</td>
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<td>13</td>
<td>O_2, FC10_3</td>
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<td>-60</td>
<td>1</td>
<td>Unreacted FC10_3, ClF, small amounts of FC10_2 and Cl_2</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

*aAll 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 \( \text{FCIO}_3 \) decomposition. This was verified experimentally both in the presence and absence of \( \text{F}_2 \).

However, other results expected as a consequence of the proposed scheme were not observed. The overall equation for the decomposition of \( \text{FCIO}_2 \) is:

\[
\text{FCIO}_2 \xrightarrow{\text{uv}} \text{ClIF} + \text{O}_2
\]

Thus, \( \text{FCIO}_3 \), when irradiated alone, should yield lower relative concentrations of \( \text{FCIO}_2 \) (i.e., lower \( \text{FCIO}_2/\text{ClIF} \) 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 \( \text{FCIO}_2 \), a stronger absorber in the uv than \( \text{FCIO}_3 \), would be expected to decompose at a more rapid rate than \( \text{FCIO}_3 \) itself.

Considering the postulated reaction sequence, it should be possible to rationalize yield data on \( \text{ClIF}_3 \) 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 \( \text{ClIF}_3 \) should be a function of \( \text{FCIO}_3 \) conversion only and certainly should be constant with respect of time. (Actually, since \( \text{ClIF}_3 \) 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 \( \text{ClIF}_3 \) and not the highest yields.

The concentration of \( \text{F}_2 \) also seems to strongly affect the yield of \( \text{ClIF}_3 \). If \( \text{FCIO} \) 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 \( \text{ClIF}_3 \). The results in Table 1 and in Ref. 2 are
both contrary to this postulate. The enhanced absorbancy of F₂ or ClF₃ coupled with the high partial pressure may affect the conversion of FCIO₃ but certainly should not lower the yield of ClF₃0.

Since the results are not consistent with the postulated reaction sequence, experiments were conducted to determine the effect of the decomposition products of FCIO₃ on the reactants and on the intermediates. Irradiating ClF and O₂ did not indicate the fixation of O₂ but did show the disproportionation of ClF:

\[ 3\text{ClF} \xrightarrow{\text{uv}} \text{Cl}_2 + \text{ClF}_3 \]

Chlorine was also a product of the ClF-O₂-FCIO₃ and O₂-FCIO₃ systems. The ClF₃ which was always formed along with ClF₃0 may have arisen from several reactions, namely:

\[ 3\text{ClF} \xrightarrow{\text{uv}} \text{Cl}_2 + \text{ClF}_3 \]
\[ \text{Cl}_2 + 3\text{F}_2 \xrightarrow{} 2\text{ClF}_3 \]
\[ \text{ClF}_30 \xrightarrow{\text{uv}} \text{ClF}_3 + \frac{1}{2} \text{O}_2 \]

Since Cl₂ is formed in these reactions and easily dissociated in the uv, the possibility existed that Cl₂ may participate in the actual formation of ClF₃0. The catalytic effect of Cl₂ in the recombination of atomic oxygen has been recognized (Ref. 3), and was thought to involve a ClO radical intermediate:

\[ \text{O} + \text{Cl}_2 \rightarrow \text{ClO} + \text{Cl} \]
\[ \text{O} + \text{ClO} \rightarrow \text{O}_2 + \text{Cl} \]

Recently, the postulate of the ClO radical being formed was proved in studying the reaction of atomic oxygen and Cl₂ (Ref. 4). Thus, the fixation of the intermediate ClO radical in the FCIOₓ - F₂ system may be promoted by the use of Cl₂.
The formation of ClO radicals in the flash photolysis of Cl₂ and O₂ led Benson and Buss (Ref. 5) to suggest that the rate-controlling step in the recombination catalysis is the termolecular reaction:

\[ \text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClO} + \text{M} \]

\[ M = \text{O}_2 \]

with a subsequent decomposition to ClO:

\[ \text{ClO}_2 + \text{Cl} + \text{O}_2 \]

This postulate suggested that the ClO moiety may be trapped with F₂ in an experiment with an activated mixture of F₂, Cl₂, and O₂. 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 ClF₃O was obtained (Table 2, Reaction 1). As is evident, the Cl₂ and F₂ were introduced into the cell in a stoichiometric amount with O₂ being in excess. A material balance exceeding 98 percent was realized with all of the Cl₂ being reacted.

The reproducible formation of ClF₃O from the elements offered additional latitude in exploring the possible intermediates responsible for ClF₃O 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 Cl₂ was the principal species being activated and that the termolecular reaction proposed by Benson and Buss may well be occurring in the Cl₂-F₂-O₂ system. Certainly some F₂ activation should occur but little or no O₂ activation is possible with the lamp used. For example:

\[ \text{Cl}_2 \xrightarrow{\text{uv}} 2\text{Cl} \]  \hspace{1cm} (7)

\[ \text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClO}_2 + \text{M} \]  \hspace{1cm} (8)

\[ \text{ClO}_2 + \text{Cl} + \text{Cl} \]  \hspace{1cm} (9)

\[ \text{ClO} + 3/2 \text{F}_2 \rightarrow \text{ClF}_3 \text{O} \]  \hspace{1cm} (10)

\[ \text{Cl} + 3/2 \text{F}_2 \rightarrow \text{ClF}_3 \]  \hspace{1cm} (11)
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<th>Reaction Number</th>
<th>Mole Ratio Cl₂:F₂:O₂</th>
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<th>Time, hours</th>
<th>Condensable Products</th>
<th>Percent Yield ClF₂O₂</th>
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<tr>
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<td>-60</td>
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<td>ClF₃O, ClF₅</td>
<td>16</td>
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<td>-60</td>
<td>1*</td>
<td>ClF₅, trace amounts ClF₃O, ClF₅</td>
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<td>1**</td>
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</tr>
<tr>
<td>14</td>
<td>1:3:3:10</td>
<td>-40</td>
<td>1**</td>
<td>ClF₃O, ClF₅, ClF, small amount FCO₂</td>
<td>5</td>
</tr>
</tbody>
</table>

*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 CIF₃).

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 CIF₃O is formed at short reaction times with almost all of the Cl₂ being consumed to CIF₃. (These results could suggest a subsequent CIF₃-O₂ 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:

\[
\text{ClF} + \text{AsF}_5 \rightarrow \text{Cl}^+\text{AsF}_6^-
\]

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

\[
3\text{ClF} + \text{AsF}_5 \rightarrow \text{ClF}_2^+\text{AsF}_6^- + \text{Cl}_2
\]

Determination of the combining ratio between ClF and AsF₅ would allow a clearcut choice between Eq. 12 and 13. Quantitative synthesis of the
solid complex from either excess CIF or excess AsF$_5$ resulted in a 1.00:2.02 and 1.09:2.00 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 CIF (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:

$$\log P_{(mm)} = 11.7124 - \frac{2591.6}{T}$$

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 (ΔH) of 32.83 kcal/mole was calculated from the process:

$$\text{Cl}_2F^+\text{AsF}_6^- (s) \rightleftharpoons \text{AsF}_5(g) + 2 \text{ClF}(g)$$

From $\Delta F^o_T = -RT \ln K_p \text{ atm}$, a free energy change, $\Delta F^o_{298} = -2.16 \text{ kcal/mole}$, and from $\Delta S^o_T = (\Delta H^o - \Delta F^o_T)T^{-1}$, an entropy change, $\Delta S^o_{298} = 117.41 \text{ cal deg}^{-1} \text{ mole}^{-1}$ were found for the dissociation process at 25°C. A heat of formation of $\text{Cl}_2F^+\text{AsF}_6^- (s)$, $\Delta H^o_{f298} = -355.4 \text{ kcal mole}^{-1}$, was calculated based upon $\Delta H^o_{f298}$ of ClF(g) = 13.5 kcal mole$^{-1}$ (Ref. 7) and $\Delta H^o_{f298}$ 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 CIF 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$^+\text{AsF}_5^-$) occurs. Thus, it seems that the Cl$^+\text{AsF}_5^-$ complex reported by Schmeisser, does not even form as an intermediate and that Schmeisser most probably mistook the 2 ClF$^-\text{AsF}_5$ complex for Cl$^+\text{AsF}_5^-$. 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 2ClF₅AsF₅, displaced ClF in a mole ratio of NO₂F:ClF = 1.00:1.94. The infrared spectrum of the solid residue showed after removal of all the excess 2ClF₅AsF₅ (by pumping at ambient temperature) the following bands characteristic of NO₂⁺AsF₆⁻ (Ref. 9 and 10); 2360 m (υ₂₆_N₂O₆⁵), 695 vs (υ₂₆_ASF₆⁻), 601 m (δ₂₆_N₂O₆⁵⁵), and 402 m (δ₂₆_ASF₆⁻). Hence, the following reaction took place:

\[
\text{Cl}_2\text{F}^+\text{AsF}_6^- + \text{NO}_2\text{F} \rightarrow \text{NO}_2\text{O}^+\text{AsF}_6^- + 2 \text{ClF}
\]

The ionic nature of the 2ClF₅AsF₆ 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-BF₃ system shows that again the complex Cl⁺BF₄⁻, reported by Schmeisser (Ref. 6), does not form. Quantitative synthesis, using an excess of ClF, resulted in a BF₃ 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 BF₃ appeared to be extremely slow. The 2ClF₅BF₃ complex is considerably less stable than the corresponding AsF₅ adduct. This is not surprising because BF₃ when compared to AsF₅, is known to act as a weaker Lewis acid towards halogen fluorides (Ref. 11).

The ionic nature, Cl₂F⁺BF₄⁻, 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 Cl₂F⁺ 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 C$_2$O$_{4}$As$_6$ at Two Different Concentrations.
Figure 2. Low-Temperature Infrared Spectrum of Solid Cl\textsubscript{2}F\textsuperscript{+} BrF\textsubscript{-} (The bands marked by an asterisk are due to solid ClO\textsubscript{2}F.)
## Table 3

**Infrared Spectra of Cl₂F⁺AsF₆⁻ and Cl₂F⁺BF₃⁻ as Solids at -196 °C and Their Assignment**

<table>
<thead>
<tr>
<th>Frequencies Observed, cm⁻¹</th>
<th>Intensity</th>
<th>Assignment (Pointgroup)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂F⁺BF₃⁻</td>
<td>Cl₂F⁺AsF₆⁻</td>
<td>Cl₂F⁺(Cs)</td>
</tr>
<tr>
<td>1305 m</td>
<td>1297</td>
<td>1312</td>
</tr>
<tr>
<td>1289 mw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1145 - 978 vs, b</td>
<td>828 v</td>
<td></td>
</tr>
<tr>
<td>766 mw</td>
<td>703 vs</td>
<td></td>
</tr>
<tr>
<td>528 mw, sh</td>
<td>520 m</td>
<td>ν₃(A'')Cl<strong>3⁵−F</strong></td>
</tr>
<tr>
<td>523 mw, sh</td>
<td>521 mw</td>
<td>ν₃(A',Cl<strong>3⁷−C1</strong>3⁵)</td>
</tr>
<tr>
<td>514 vw, sh</td>
<td>514 m</td>
<td>ν₃(A')Cl<strong>3⁷−C1</strong>3⁷</td>
</tr>
<tr>
<td>512 w, sh</td>
<td>402 m</td>
<td></td>
</tr>
<tr>
<td>519 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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$_2$F$^+$ 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:

\[
\text{Cl-F-Cl (I) Cl-F--Cl (II) or F-Cl (III) Cl-Cl-F (IV) and C1-Cl (V)}
\]

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 $D_{eh}$) 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$^+$ (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$_2$F$^+$ 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$_2$F$^+$. 

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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-Cl-\('\)]^-(\nu = 160\,\text{cm}^{-1}, \text{Ref. 13}) and bent [F-\text{Cl}_{\text{F}}]^{+}\, (\Delta \nu = 8\,\text{cm}^{-1}) \text{ions (Ref. 12). For a linear [ClClF]^+ cation} \, \Delta \nu \text{should be even larger than for ClF}_{2}^{-} because of the different mass of the two terminal atoms. The frequency difference of approximately 60\,\text{cm}^{-1}, \text{observed for ClF}_{2}^{+}, \text{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 ClF_{2}Cl\text{AsF}_{6}^{-}. For model III having only F-Cl bands, only two isotope bands (Cl_{35}^{35}_{-F} \text{and} Cl_{37}^{37}_{-F} \text{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}^{35}_{-F} \text{and} Cl_{37}^{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}^{35}_{-Cl}^{35}_{35}, Cl_{37}^{37}_{-Cl}^{37}_{35} + Cl_{35}^{35}_{-Cl}^{37}_{37}, \text{and} Cl_{37}^{37}_{-Cl}^{37}_{37}, \text{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 ClF_{2}^{+} 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 (ClF_{2}^{+}) results which yields a stable electron configuration for each atom. The ClF_{2}^{+} 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 $\text{Cl}_2\text{F}^+$ does not result in the parent molecule $\text{Cl}_2\text{F}_2$ (derived from $\text{ClF}$ by replacement of one F by one Cl atom) but in two molecules of $\text{ClF}$. This has been demonstrated by the replacement reactions with $\text{NO}_2\text{F}$ and the dissociation data obtained for the solid complex.

Since $\text{Cl}_2\text{F}^+$ 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:

$$\text{MCIO}_4 + \text{ClF} \rightarrow \text{MF} + \text{ClOCIO}_3$$

where

$M = \text{Na, Cs, NO}_2, \text{H}$

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

Numerous reactions were conducted with $\text{ClF}$ and $\text{NaClO}_4$ or $\text{CsClO}_4$, using reaction temperatures of $-78, -45$, and $0 \text{ C}$. 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 $\text{Cl}$-$\text{O}$ species was obtained. The identity of this compound as a perchlorate was based on its infrared spectrum and hydrolysis to $\text{HClO}_4$. Comparison of the infrared spectrum of this material and that of other covalent perchlorates revealed a dissimilarity but a spectrum of $\text{Cl}_2\text{O}_6$ was not available for comparison. A sample of...
Cl$_2$O$_6$ 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$_2$O$_6$. The volatility observed for the unknown Cl-O compound and that reported for Cl$_2$O$_6$ are quite different. However, it was found in preparing the "authentic" sample of Cl$_2$O$_6$ that its volatility and that of the ClF condensation reaction product were comparable and thus the reported vapor pressure data for Cl$_2$O$_6$ are in error.

Reactions of NO$_2$ClO$_4$ and HCIO$_4$ (72 percent) with ClF were also employed in the attempted preparation of ClOClO$_3$. The NO$_2$ClO$_4$ proved to be relatively unreactive but did give very small amounts of a mixture of known Cl-O and FC1-O compounds including Cl$_2$O$_6$ but no new material. The reaction of ClF and HCIO$_4$ 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:

\[
\text{SOF}_4 + F_2 \xrightarrow{\text{CsF}} -78^\circ \text{C} \rightarrow \text{SF}_2OF
\]

\[
\text{COF}_2 + F_2 \xrightarrow{\text{CsF}} -78^\circ \text{C} \rightarrow \text{CF}_3OF
\]

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 \degree C and have
been found to rapidly produce hypochlorites in high yields. Some typical
syntheses are summarized in the following reactions.

\[
\begin{align*}
\text{SOF}_4 + \text{ClF} & \xrightarrow{-78 \degree C} \text{SF}_5\text{OCl} \\
\text{KOCF}_3 / \text{KF} + \text{ClF} & \xrightarrow{-85 \degree C} \text{KF} + \text{CF}_3\text{OCl} \\
\text{COF}_2 + \text{ClF} & \xrightarrow{-78 \degree C} \text{CF}_3\text{OCl} \\
\text{CsOCF}_2\text{CF}_3 + \text{ClF} & \xrightarrow{0 \degree C} \text{CsF} + \text{CF}_3\text{CF}_2\text{OCl} \\
\text{CF}_3\text{CFO} + \text{ClF} & \xrightarrow{-78 \degree C} \text{CF}_3\text{CF}_2\text{OCl} \\
\text{CF}_3\text{CFO} + \text{CsClF}_2 & \xrightarrow{0 \degree C} \text{CF}_3\text{CF}_2\text{OCl} + \text{CsF}
\end{align*}
\]

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$_5$OCl, calculated 178.5 gm/mole, found 177 gm/mole; CF$_3$OCl, calculated
120 gm/mole, found 110 gm/mole; C$_2$F$_5$OCl, 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:

\[
\begin{align*}
\text{SF}_5\text{OCl} & \xrightarrow{\text{uv RT}} \text{SF}_5\text{OOSF}_5 50\% + \text{Cl}_2 \text{SF}_2\text{OSF}_5 (t) \\
\text{CF}_3\text{OC1} & \xrightarrow{\text{uv RT}} \text{CF}_3\text{OCFOCl} + \text{Cl}_2 \\
\text{CF}_3\text{OCl} + \text{F}_2 & \xrightarrow{\text{RT}} \text{CF}_3\text{OF} \\
\text{C}_2\text{F}_5\text{OCl} & \xrightarrow{\text{uv RT}} \text{COF}_2 + \text{CF}_3\text{Cl}
\end{align*}
\]

These reactions were nearly quantitative in the case of the perfluororalkyl
hypochlorites. The products observed in the photolysis of C$_2$F$_5$OCl probably
arose in the following manner:

\[
\text{C}_2\text{F}_5\text{OCl} \xrightarrow{\text{uv}} \text{CF}_3\text{CF}_2\text{O}^- + \text{Cl}^-
\]

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The three hypochlorites prepared are of variable stability in metal-Teflon systems at ambient temperature. The observed relative thermal stabilities are $\text{SF}_2\text{OCl} < \text{C}_2\text{F}_3\text{OCl} < \text{CF}_3\text{OCl}$. Decomposition occurs through disproportionation to the precursors, CIF 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:

$$\text{SOF}_4 + \text{MF} \rightarrow M^+ \text{OF}_5^-$$

$$M^+ \text{OF}_5^- + \text{ClF} \rightarrow \text{ClF} + F^+ \text{SOCl}$$

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 CIF and SOF$_4$ in the absence of an alkali metal fluoride.

PREPARATION AND FLUORINATION OF BROMINE NITRATE

The fluorination of chlorine nitrate to give CIF$_5$O (Ref. 14) suggests that the analogous reaction of bromine nitrate might lead to BrF$_5$O or BrF$_5$O. 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$_3$:

$$\text{Br}_2 + \text{Cl}_2 \rightarrow 2\text{BrCl}$$

$$\text{BrCl} + \text{ClNO}_3 \rightarrow \text{BrNO}_3 + \text{Cl}_2$$
The second step of this preparative scheme has been reported (Ref. 20) but previous attempts (Ref. 14) to utilize it were unsuccessful. Reaction of Br₂, Cl₂, and Cl₃N0₃ in approximately 1:5:5 molar ratio in glass ampoules at -50 to 0 °C resulted in the formation of BrN0₃. 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 HN0₃. 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 BrN0₃ are listed in Table 4.

TABLE 4

INFRARED SPECTRUM OF BrN0₃*

<table>
<thead>
<tr>
<th>Frequency, cm⁻¹</th>
<th>Relative Intensity</th>
<th>Frequency, cm⁻¹</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3390</td>
<td>vw</td>
<td>955</td>
<td>w</td>
</tr>
<tr>
<td>2970</td>
<td>w</td>
<td>800</td>
<td>vs</td>
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<td>2550</td>
<td>vw</td>
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<td>w</td>
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<td>vw</td>
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<td>vw</td>
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<td>vs</td>
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<td>vw</td>
</tr>
<tr>
<td>1205</td>
<td>vw</td>
<td>450</td>
<td>pqr</td>
</tr>
</tbody>
</table>

* Spectrum taken on Perkin Elmer Models 137 and 337 spectrophotometers.
Fluorination of BrNO$_3$ at -30°C resulted in conversion to BrF$_3$ and FNO$_2$ only. Fluorination at ambient temperature or by slow warming from -78°C to ambient temperature also gave BrF$_3$ 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 BrF$_3$ 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$_x$O$^-$ complex.

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

\[
\text{NO}_2^+\text{BrF}_x\text{O}^- + \text{MF}_n \rightarrow \text{NO}_2^- \text{MF}_{n+1} + \text{BrF}_{x-1}^0
\]

\[
\text{MF}_n = \text{SiF}_4, \text{BF}_3
\]

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$_2$BF$_4$ 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):

\[ 3 \text{BrF} \rightleftharpoons \text{BrF}_3 + \text{Br}_2 \]

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$_2$BrF$_2$, could be identical to the complex obtained in the BrNO$_2$ fluorination. To examine this possibility, a limited effort will be conducted to form NO$_2$BrF$_2$. This should be readily accomplished via FNO$_2$, Br$_2$, and F$_2$ if NO$_2$BrF$_2$ is a stable solid. Additional fluorinations of BrNO$_2$ with F$_2$ as a route to BrF$_x$ 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$_3$ 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, 2.5; 2360, 2.3; 2224, 3.7.

Materials

The FC1O$_2$ was prepared by the reaction of ClF$_3$ and KClO$_3$. Purification of FC1O$_2$ was carried out by pumping off the Cl$_2$ impurity while holding
the FClO₂ at -78 C. The chromatographic purity of the colorless liquid was better than 99.9 percent. The FClO₃ was purchased from Pennsalt. The ClF₅ prepared at Rocketdyne, had a purity of 99+ percent. Other materials were prepared by standard techniques.

**CHLORINE MONOFLUORIDE REACTIONS**

**Synthesis of Cl₂F⁺AsF₆⁻**

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

In a typical experiment, 96.7 mmol of ClF (prepared in this laboratory and purified by fractional condensation) and 24.2 mmol of AsF₅ (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 mmol of ClF. The observed vapor pressure-temperature data for the complex are presented in Table 5.

**Synthesis of Cl₂F⁺BF₄⁻**

The synthesis of Cl₂F⁺BF₄⁻ was similar to that of Cl₂F⁺AsF₆⁻ 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 Cl₂F⁺AsF₆⁻

<table>
<thead>
<tr>
<th>Pressure, mm Hg</th>
<th>Temperature, °C</th>
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<tr>
<td>209</td>
<td>-11.15</td>
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Low-Temperature Infrared Spectra

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

Displacement Reaction of Cl₂F⁺AsF₆⁻ With NO₂F

Nitryl fluoride (2.75 mmole, prepared in this laboratory and purified by fractional condensation) was combined with a large excess of solid Cl₂F⁺AsF₆⁻ 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 mmole 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 (NaClO₄, CsClO₄, and NO₂ClO₄). 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 NaClO₄ were used) and the remaining products were mixtures of FC10₂, FC10₃, Cl₂, and variable amounts of Cl₂O₆. No unidentified volatile species were found.

Synthesis of Hypochlorites

Method A. An alkali metal salt (MOR₄: M=K, Cs and -OR₄=OCF₃ or OCF₂F) 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 RfOCl 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=O compound (M=O is COF₂, CF₂CFO, or SOF₄) 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 hypo-
chlorite (CF₃OCl, C₂F₅OCl, SF₅OCl) had occurred in high yield. Proof of
the composition of SF₅OCl was accomplished through vapor density measurement,
synthetic material balance, and infrared spectroscopy just as had been accom-
plished earlier with the RFOCl compounds. The conversion of SOF₄ to SF₅OCl
was shown to be slower with KF than with CsF and also it was shown that ClF
and SOF₄ do not form SF₅OCl in the absence of KF or CsF under comparable
conditions.

Method C. A sample of CsClF₂ solid contained in a 10-milliliter stainless-
steel reactor was treated with CF₃CFO at approximately 0°C for 15 minutes.
Fractionation of the gaseous materials at that time showed 75 percent of
the CF₃CFO had been converted to C₂F₅OCl. Returning the reactants over the
CsClF₂ at -45°C for several hours resulted in nearly complete conversion
to C₂F₅OCl.

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
CF₃OCl, the reaction completely consumed the hypochlorite and formed
CF₃OCF₃ and Cl₂ in very high yield. In the case of C₂F₅OCl, 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 COF₂ and
CF₃Cl. The photolysis of SF₅OCl resulted in approximately a 50 percent
yield of SF₅OSF₅ with a trace of SF₅OSF₆. No SF₅OCl was recovered as
it had decomposed through thermal or uv excitation or both to give SOF₄
and ClF (observed as Cl₂, SiF₄). 

R-7239-2
Fluorination of CF$_3$OCl. The conversion of CF$_3$OCl to the known CF$_3$OF occurred in minutes at ambient temperature or below through reaction with excess F$_2$. Only a small amount of CF$_3$OCl was recovered and the only other C-F product in addition to CF$_3$OF 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 (-50, -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$_3$

<table>
<thead>
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<th>Pressure, mm Hg</th>
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</tbody>
</table>

CONFIDENTIAL
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$_2$BF$_4$. 
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INORGANIC HALOGEN OXIDIZERS

Abstract: Ultraviolet activated fluorinations of chlorine oxyfluorides at low temperatures to produce Florox were continued. The involvement of elemental Cl₂ and O₂ in the Florox forming process was deduced and was verified experimentally by the preparation of Florox from Cl₂, F₂, and O₂. The chlorofluoro chloronium (III) cation, Cl₂F⁺, a new oxidizing species, has been prepared in the form of its AsF₆⁻ and BF₄⁻ salts. The white crystalline Cl₂F⁺AsF₆ 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 Cl₂F⁺ has a bent structure (symmetry C₁) with chlorine as the central atom. The Cl₂F⁺ cation is the first example of a catenated polyhalogen cation. The utility of CIF as a chlorofluorinating agent was demonstrated in the preparation of some new covalent hypochlorites, R-ClOCl. 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 Br₂, Cl₂, and Cl(NO₃) at -30 to 0°C. Solid Br(NO₃)₂ 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 in mm = 9.6905 - 2254.377. Fluorination of Br(NO₃)₂ has shown that FNO₂ and BrF₅ are the principal products (95% percent yield). (C)
<table>
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**Halogen Oxidizers**

**Chlorine Oxyfluorides**