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A DIVISION OF NORTH AMERICAN AVIATION INC.
6633 CANOGA AVENUE CANOGA PARK CALIFORNIA

R-7149
(Unclassified Title)

FINAL REPORT,
INORGANIC HALOGEN OXIDIZERS
(30 May 1966 through 29 May 1967)

Group 4
Downgraded at 3-Year Intervals
Declassified After 12 Years

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Power Branch
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The research reported herein 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 30 May 1966 through 29 May 1967. The program manager was Dr. E. A. Lauton, Manager, Synthetic and Propellant Chemistry. The work was conducted in Oxidizer and Fluorine Chemistry with Dr. D. Pilipovich, Principal Scientist as principal investigator. Full-time staff members contributing to the technical effort were Dr. H. H. Rogers, Dr. C. J. Schack, and Dr. C. B. Lindahl.
New syntheses of ClF$_3$O were discovered utilizing ultraviolet-initiated reaction of FC1O$_2$ and FC1O$_3$. In the presence of F$_2$, ClF$_3$, or ClF$_5$, FC10$_2$ gave ClF$_3$O in high conversions and high yields. The most effective fluorinating agent was ClF$_5$. The same techniques were not successful in oxidizing ClF$_3$O to ClF$_5$O or BrF$_5$ to BrF$_7$. There is considerable evidence that FC10 is an intermediate in the synthesis of ClF$_3$O by ultraviolet activation. More complete ultraviolet data were obtained with the measurement of extinction coefficients of ClF$_5$, BrF$_5$, ClF$_3$O, FC10$_2$, and ClF.

Corona discharge activation in the systems FC1O$_2$-F$_2$ did not result in ClF$_3$O. Initial decomposition of FC1O$_2$ to ClF followed by fluorination to either ClF$_3$ or ClF$_5$ was observed.

A stable mass cracking pattern for ClF$_3$O was obtained with the most prominent peaks assignable to ClF0$^+$ (100 percent), ClF$_2$O$^+$ (80.60 percent), Cl$^-$ (29.35 percent), ClF$^-$ (21.23 percent), and ClO$^+$ (14.78 percent).

The $F^{19}$ n.m.r. spectrum of gaseous ClF$_3$O revealed two bands at -276 $\delta$ and -317 $\delta$ with respective ratios of 2 and 1. These bands could not be resolved further but support the proposed $C_3$ symmetry for ClF$_3$O rather than $C_{3v}$ symmetry already partially excluded by infrared studies.

A novel process for forming NF$_3$O has been discovered. It was determined that the action of ClF$_3$O on difluoramine, HF$_2$.
reproducibly formed NF$_3$O in 80-percent yields at temperatures below ambient. Perfluoroformamide, F$_2$NCFO, also reacted with ClF$_3$O to yield NF$_3$O.

Mass cracking patterns were obtained for both IF$_7$ and IF$_5$O. New, more precise physical properties were determined for IF$_5$O; the vapor pressure-temperature equation is $\log p_{\text{mm}} = 8.9874 - 1659.4/T$. The preparation of IF$_3$O$_2$ was attempted by reaction of IF$_5$O and SiO$_2$ at elevated temperatures. The pyrolysis of IF$_5$O yielded an unidentified volatile material which may be a new IF$_x$O compound. Reaction of IF$_5$O and HNF$_2$ yielded FNO and N$_2$F$_4$ as oxidation products.

A new, rapid method was developed for the synthesis of chlorine nitrate, ClNO$_3$. The process utilizes the reaction of ClF and HNO$_3$ at temperatures above -112 C. A similar interaction between BrF$_3$ and HNO$_3$ yielded limited amounts of BrNO$_3$. Fluorination of BrNO$_3$ led to a new solid complex of the type NO$_2$BrF$_x$. A characterization of the complex NO$_2$BrF$_x$ was carried out to distinguish it from the above solid.

The solid obtained by reaction of Cl$_2$O and AsF$_5$ has been shown to be principally ClO$_2$AsF$_6$. A physico-chemical characterization of the solid was conducted.

Preparation of ClNF$_2$O was attempted via a dissociative reorganization process involving NF$_3$O and PF$_4$Cl. Instead, a slow fluorination of the PF$_4$Cl to PF$_5$ resulted, accompanied by reduction of the NF$_3$O to FNO.
Oxychlorine trifluoride did not ionize in either BrF₃ or IF₅.

The specific conductivity of ClF₀ was measured at 25°C, the value obtained was 2 x 10⁻⁸ ohms⁻¹ cm⁻¹. The reaction of ClF₀ with AsF₅ was complex, producing products including O₂, AsF₃, FClO₂, and ClF₂OAsF₆. Attempts to prepare ClOAsF₆ were unsuccessful. All of the systems (ClF₂AsF₅, ClF₃AsF₃, and ClF₅AsF₃) involved redox reactions producing Cl₂ and ClF₂AsF₆.

Several possible synthetic routes to the uncharacterized chloroaryl fluoride (FCIC) were investigated. These encompassed reduction reactions of Florox using N₂F₄ and Cl₂, and the oxidation of ClF₀ with the mild fluorinating agent CF₂(OF)₂. Trace quantities of Compound C, suspected to be FCIO, were occasionally detected.

Various aspects of the chemistry of Cl-O species have been examined. Syntheses of Cl₂O₃ were conducted under static and flow conditions. Study of the new class of complexes of the MF·Cl₂O type has been expanded to include the systems RhF·Cl₂O, CsF·ClO₂, and CsF·ClO₃, and CsF·ClNO₃. The vigorous fluorination of ClO₂ proceeded explosively to ClF₃, Cl₂, and O₂.

Hydrolysis of KF·KClF₄ resulted in the formation of a new phase as shown by X-ray powder diffraction analysis which is thought to be a KF·KClF₄ hydrate. Preparation of ClF₃O via oxygen-fluorine exchange reactions was unsuccessful.

(Confidential Abstract)
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INTRODUCTION

The effort reported herein reflects considerable activity in the area of inorganic chemistry concerned with covalent fluorides. Particular emphasis has been placed on the reaction chemistry of interhalogen fluorides and oxyhalogen fluorides. The chemistry of CIF$_3$ and IF$_5$ appeared to be uniquely attractive with respect to reactions involving fluorination and/or oxygenation. This was verified in the case of CIF$_3$ and the following discussion section reflects to some extent the unusual chemistry of this material. Interest at Rocketdyne in IF$_5$ is focused on its potential utility as an intermediate for preparing IF$_3$O$_2$ and IF$_3$. These possibilities will be discussed with respect to both reduction reactions and thermal decomposition.

An intensive effort was conducted to utilize the compounds FClO$_2$ and FClO$_3$ as chemical intermediates for new oxidizers. The approach reflected in this area involved the use of ultraviolet radiation for excitation. The ultraviolet activation technique was successful to the extent that it revealed FClO$_2$ and FClO$_3$ to be intermediates for the preparation of CIF$_3$. The results in this area are presented in detail in the Discussion section of this report.

In attempting to reproduce reported results in synthesizing "ClOAsF$_3" , an unusual redox reaction was uncovered inasmuch as the reaction of Cl$_2$O and AsF$_5$ yielded ClO$_2$AsF$_6$. This led to a supposition that AsF$_5$ may catalyze redox reactions in other chlorine (I) compounds; this was subsequently demonstrated with CIF. The results will be discussed in connection with a variety of redox and complexing reactions involving ClO$_2$, AsF$_3$, CIF$_3$, and AsF$_3$. 

R-7149
Additional spectral data were generated for the novel compound ClF₃. Previous attempts to resolve the F¹⁹ n.m.r. spectrum had always resulted in a complete collapse of the bond structures due to exchange initiated by traces of HF. Vapor-phase measurements resolved the problem and the results will be discussed with particular emphasis on the techniques used to obtain these conclusive data.
ULTRAVIOLET ACTIVATED REACTIONS

The purpose of this study was twofold. First, new syntheses of ClF₂O were sought that utilized intermediates other than covalent hypochlorites. By using an initiator (in this case radiant energy) there exists a possibility of realizing more favorable reaction rates as well as obviating the use of either Cl₂O or ClONO₂. The second aspect of this study involved the possibility of synthesizing new halogen fluoride species such as ClF₃O₂, ClF₅O, and BrF₇. The use of suitable radiation at low temperatures appeared to offer a number of attractive features in achieving the objectives.

Absorption Spectra

Prior to conducting reactions by ultraviolet excitation, the spectra of proposed reactants and possible products which could not be found in the literature were determined. With a knowledge of the spectra, it was thought possible that selective activation of reactants might be achieved during irradiation.

Absorption spectra have been obtained for CIF, CIF₃, CIF₅O, FC1O₂, FC1O₃, and BrF₅ (Fig. 1) using a Cary Model 14 Recording Spectrophotometer. Extinction coefficients are presented in Table 1. The data for CIF₅ extend the results reported by Gatti (Ref. 1) to wavelengths shorter than 2640 angstroms. The wavelengths for the strongest absorptions for all compounds except CIF were below 2300 angstroms with indications that even stronger absorption occurred below 1900 angstroms.
Figure 1. Ultraviolet Absorption Spectra for ClF, ClF₃, ClF₅₀, FC1₀₂, FC1₀₅, and BrF₅.
# Table 1

## Extinction Coefficients

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavelength, angstroms</th>
<th>Absorbance Coefficient x 10^-2, mm Hg^-1 cm^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClF</td>
<td>2730</td>
<td>0.020 (Ref. 6)</td>
</tr>
<tr>
<td>ClF_5</td>
<td>2000 to 2100</td>
<td>1.1</td>
</tr>
<tr>
<td>ClF_3O</td>
<td>2205</td>
<td>2.8</td>
</tr>
<tr>
<td>FC10_2</td>
<td>2225</td>
<td>6.0</td>
</tr>
<tr>
<td>FC10_3</td>
<td>1860*</td>
<td>0.090</td>
</tr>
<tr>
<td>BrF_5</td>
<td>2080</td>
<td>2.0</td>
</tr>
<tr>
<td>F_2</td>
<td>2845</td>
<td>0.035 (Ref. 4)</td>
</tr>
<tr>
<td>ClF_3</td>
<td>2231*</td>
<td>1.34 (Ref. 7)</td>
</tr>
<tr>
<td>OF_2</td>
<td>2100*</td>
<td>0.075 (Ref. 5)</td>
</tr>
</tbody>
</table>

*Not a maximum; coefficient increasing toward shorter wavelengths
Reactions were investigated using CIF₃, FC₁₀₂, FC₁₀₃, and BrF₅ as the materials to be fluorinated. The materials employed as sources of active fluorine were F₂, CIF, ClF₂, ClF₅, OF₂, and BrF₅. Initial work was accomplished (Ref. 2) in irradiation cells with relatively small windows (17-millimeter-diameter openings). Because conversions in these cells were small, even with overnight irradiations, a new cell with 4-inch-diameter windows was built with which a large degree of conversion was nearly always obtained. Exposures were usually approximately 4 hours. Results for the actual reactant combinations and conditions are presented in Table 2. A Pyrex filter was sometimes used to restrict the applied radiation to wavelengths essentially longer than 3100 angstroms.

CIF₃O/F₂. Irradiation of CIF₃O/F₂ mixtures was conducted in an attempt to prepare CIF₅O. It was expected that the reaction might proceed by the activation of F₂ which would, in turn, react with CIF₃O forming CIF₅O. The small amounts of products obtained (Table 2), when the Pyrex filter was used in an attempt to minimize CIF₃O activation while maximizing F₂ activation, suggest that the reaction probably does not proceed by a mechanism involving activated fluorine. The large yield of CIF₅O obtained when the filter was not used indicates the probability that the CIF₃O was decomposed by the radiation and that the reaction may have proceeded by a route such as follows:

\[
\begin{align*}
\text{CIF}_3\text{O} & \xrightarrow{\text{UV}} \text{CIF}_3\text{O}^* \\
\text{CIF}_3\text{O}^* & \rightarrow \text{CIF}_3^* + \text{O}
\end{align*}
\]
TABLE 2
ULTRAVIOLET ACTIVATED REACTIONS

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Mole Ratio</th>
<th>Temperature, C</th>
<th>Time, hours</th>
<th>Pyrex Filter</th>
<th>Condensable Products, mole percent (co version)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}_2, \text{ClF}_3 )</td>
<td>8.2</td>
<td>30</td>
<td>4.4</td>
<td>Yes</td>
<td>( \text{ClF}_5, 1.8; \text{ClF}_3, 2.0; \text{FCIO}_2, 1.2 )</td>
</tr>
<tr>
<td>( \text{F}_2, \text{ClF}_3 )</td>
<td>7.0</td>
<td>-40</td>
<td>4.7</td>
<td>Yes</td>
<td>( \text{ClF}_5, 0.9; \text{FCIO}_2, 0.1 )</td>
</tr>
<tr>
<td>( \text{F}_2, \text{ClF}_3 )</td>
<td>6.5</td>
<td>-40</td>
<td>18.0</td>
<td>Yes</td>
<td>( \text{ClF}_5, 1.8; \text{FCIO}_2, 0.6 )</td>
</tr>
<tr>
<td>( \text{F}_2, \text{ClF}_3 )</td>
<td>7.1</td>
<td>-40</td>
<td>18.0</td>
<td>No</td>
<td>( \text{ClF}_5, 51; \text{ClF}_3, 4; \text{FCIO}_2, 2 )</td>
</tr>
<tr>
<td>( \text{FCIO}_2 )</td>
<td>—</td>
<td>-60</td>
<td>4.5</td>
<td>No</td>
<td>( \text{ClF}_3, 0, 1.5; \text{ClF}_3, 2.6; \text{ClF}, 78; \text{Cl}_2, 21; \text{FCIO}_3, 0.6 )</td>
</tr>
<tr>
<td>( \text{FCIO}_2 )</td>
<td>(b)</td>
<td>-60</td>
<td>4.5</td>
<td>No</td>
<td>( \text{ClF}_3, 1.5; \text{ClF}, 63, \text{FCIO}_3, 0.3 )</td>
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<tr>
<td>( \text{F}_2, \text{FCIO}_2 )</td>
<td>12.8</td>
<td>-60</td>
<td>5.4</td>
<td>No</td>
<td>( \text{ClF}_3, 0, 14; \text{ClF}_5, 59 )</td>
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<tr>
<td>( \text{F}_2, \text{FCIO}_2 )</td>
<td>5.6</td>
<td>-60</td>
<td>2.5</td>
<td>No</td>
<td>( \text{ClF}_3, 0, 5.0; \text{ClF}_5, 26 )</td>
</tr>
<tr>
<td>( \text{F}_2, \text{FCIO}_2 )</td>
<td>1.1</td>
<td>-60</td>
<td>4.2</td>
<td>No</td>
<td>( \text{ClF}_3, 0, 36; \text{ClF}_5, 8; \text{ClF}_3, 22; \text{FCIO}_3, 6 )</td>
</tr>
<tr>
<td>( \text{OF}_2, \text{FCIO}_2 )</td>
<td>1.0</td>
<td>-60</td>
<td>4.1</td>
<td>No</td>
<td>( \text{ClF}_3, 0, 20; \text{ClF}_3, 17; \text{ClF}, 57 )</td>
</tr>
<tr>
<td>( \text{ClF}, \text{FCIO}_2 )</td>
<td>2.0</td>
<td>-60</td>
<td>4.1</td>
<td>No</td>
<td>( \text{ClF}_3, 26; \text{ClF}_3, \text{Cl}_2, &quot;\text{FCIO}&quot; )</td>
</tr>
</tbody>
</table>

(a) All products were determined quantitatively but values are listed only if origin of product was only from compound being fluorinated

(b) Flow experiment

(c) Lamp defective, not full brightness

(d) Full brightness, 2 to 3 hours
### TABLE 2 (Concluded)

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Ratio (to 1)</th>
<th>Temperature, °C</th>
<th>Time, hours</th>
<th>Condensable Products, mole percent (conversion)</th>
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</thead>
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<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>-60</td>
<td>4.1</td>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, 28; CIF&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>-60</td>
<td>4.0</td>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, 70; CIF&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>-60</td>
<td>3.0</td>
<td>None</td>
</tr>
<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>-60</td>
<td>4.1</td>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, 53; CIF&lt;sub&gt;3&lt;/sub&gt;, 15</td>
</tr>
<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>-60</td>
<td>5.8</td>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, 14; CIF&lt;sub&gt;3&lt;/sub&gt;, 67; CIF&lt;sub&gt;3&lt;/sub&gt;, 7; BIF&lt;sub&gt;5&lt;/sub&gt;</td>
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<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>4.1</td>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, 7; 2; CIF&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>-60</td>
<td>22.0&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>None</td>
</tr>
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<td>1.0</td>
<td>-60</td>
<td>17.5&lt;sup&gt;(d)&lt;/sup&gt;</td>
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</tr>
<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>-60</td>
<td>6.0&lt;sup&gt;(d)&lt;/sup&gt;</td>
<td>No</td>
</tr>
<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>-60</td>
<td>4.5</td>
<td>No</td>
</tr>
<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>-60</td>
<td>5.1</td>
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<tr>
<td>CIF&lt;sub&gt;5&lt;/sub&gt;, FC10&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>-60</td>
<td>4.6</td>
<td>No</td>
</tr>
</tbody>
</table>

- All products were determined quantitatively, but values are listed only if origin.
- Flow experiment, not full brightness.

*Notes:
(a) Flow experiment, not full brightness.
(b) Lamp defective, not full brightness.
(c) Full brightness; 2 to 3 hours.
Low temperatures (-40°C) were used for this reaction to determine if the activation of CIF₃₀ might occur without its decomposition. It is possible that the use of even lower temperatures during ultraviolet radiation would cause the reaction to proceed in the following manner:

\[
\text{CIF}_3 + \text{F}_2 \rightarrow \text{CIF}_5
\]

(4)

Unfortunately, the rather low vapor pressure of CIF₃₀ (less than 10 millimeters at -60°C) would permit the formation at any one time of only small quantities of the proposed compound, CIF₃₀. Because CIF₃₀ could be more volatile than CIF₃ and would, therefore, remain in the vapor state, rapid decomposition by ultraviolet radiation to CIF₅ and O₂ would be expected. Therefore, the possibility of forming CIF₃₀ by reducing the temperature below -40°C appears unlikely.

Reactions of FCIO₂. Initial irradiations of FCIO₂ at 25°C both alone and with F₂ (Ref. 2) indicated that partial decomposition of FCIO₂ to CIF and O₂ occurred accompanied by fluorination to CIF₃ and/or CIF₅. Because the objective of this work was the preparation of CIF₃₀₂, the reactions were repeated at reduced temperatures where this compound should be more stable. No experimental evidence for the formation of CIF₃₀₂ was found. However, substantial yields (up to 86 mole percent) of CIF₃₀ were obtained from...
irradiations of ClO\textsubscript{2}F with most fluorinating agents used (Table 2). These experiments represent the first examples in which ClF\textsubscript{3} (Florox) has been prepared in good yield from an intermediate other than a covalent hypo-
chlorite.

Chloryl fluoride is a stronger absorber than any of the materials used to fluorinate it and its activation is considered to be the initial step in the reactions. The proposed mechanism for the overall reaction (Eq. 7 through 10) involves the generation and subsequent fluorination of FC10.

\[
\begin{align*}
\text{FC10}_2 & \xrightarrow{\text{UV}} \text{FC10}_2^* \\
\text{FC10}_2^* & \rightarrow [\text{FC10}] + 0 \\
\text{FC10}_2 + 0 & \rightarrow [\text{FC10}] + 0_2 \\
[\text{FC10}] + F_2 & \rightarrow \text{ClF}_30
\end{align*}
\]

The detection of a compound thought to be FC10 (Ref. 3) during the ClF/FC10\textsubscript{2} experiment tends to support the existence of FC10 as an intermediate. This compound may have also formed during the irradiation of FC10\textsubscript{2} (Table 2). The supposed FC10 is known to be very reactive and relatively unstable (Ref. 3) and the failure to observe it more frequently was not unexpected. A flow experiment was conducted in an attempt to prepare FC10; however, neither FC10 nor ClF\textsubscript{3}0 was found.

As at room temperature, the -60 C ultraviolet irradiation of FC10\textsubscript{2} alone produced principally ClF and 0\textsubscript{2}, but the efficiency of the lower temperature was demonstrated by the formation of some ClF\textsubscript{3}0. Either FC10\textsubscript{2} itself or the product ClF may have served as the active fluorinating agent.
The weaker group of ultraviolet absorbers (Table 1; F₂, OF₂, and ClF) resulted in 20 to 30 percent conversion of FC1O₂ to ClF₃O under approximately similar conditions. Of these, elemental fluorine yielded the best conversions to Florox and unlike any other fluorine source also formed ClF₅. Of the three fluorinating agents in the group, only F₂ was examined at F/F₃C₅O₂ ratios higher than two. These higher ratios were found to yield lesser amounts of ClF₅O and more ClF₅. No satisfactory explanation of this result can be made at this time because the presence of a large excess of F₂ would a priori lead to a predicted higher yield. Further, the limited number of experiments and the lack of replicate runs preclude sufficient evidence for advancing final conclusions. The low absorptivity of F₂ relative to FC1O₂ (Table 1 and Fig. 1) eliminates the possibility that the F₂ may be preferentially absorbing the available radiation.

The conversion of FC1O₂ to ClF₅O using the strong absorbers ClF₅, ClF₇, and BrF₄ appears to be limited by the amount of the fluorinating agent in the vapor phase and therefore capable of activation. Thus, ClF₅ is more effective than ClF₃ while BrF₄, which has only several millimeters vapor pressure at the test temperature, did not produce any ClF₅O despite the fact that it reacted. The significance of ultraviolet activation of the fluorine donor may be indicated by the fact that ClF₅ is a much better fluorine donor than F₂ itself. However, the greater efficacy of ClF₅ may be due to its lower activation requirements and chemical reactivity. This consideration, coupled with the vapor concentration of the agent, may be an important feature. In the latter interpretation, the role of the ultraviolet radiation would be primarily involved in decomposing FC1O₂.

Following the encouraging results with FC1O₂, an examination of similar reactions with FC1O₂ was initiated. Perchloryl fluoride was considered as a precursor to ClF₅O₂ because its decomposition to an activated FC1O₂ capable of fluorination seemed possible. Although FC1O₂
absorbs only weakly where other ClF compounds absorb strongly (Fig. 1), reasonable radiation times did effect its decomposition. Both CIF and some FCIO₂ were formed. The latter is important because it demonstrates that the desired Cl-O bond cleavage does occur. Large quantities could not be expected because the strong absorptivity of FCIO₂ results in its own decomposition.

Fluorination of the activated FCIO₃ was attempted with ClF₅ because of its proven effectiveness with FCIO₂. No unknown products were observed but it was determined that ClF₅O was the major product. This is almost certainly due to stepwise loss of oxygen from FCIO₃ to yield FCIO which is then fluorinated to ClF₅O.

Thus, both FCIO₂ and FCIO₃ appear to undergo the progressive loss of oxygen on ultraviolet irradiation. Once chlorosyl fluoride, FCIO, is formed, it is sufficiently stable at -40 to -60 °C to allow fluorination to ClF₅O. Florox is the most complex product obtained due to the fact that it is essentially frozen out and thus not subject to any extensive ultraviolet activated reaction or decomposition. If ClF₅O is to be synthesized, activation of F₂ without the activation of FCIO₂ must be accomplished. The use of filtered (more than 3100 angstroms) radiation appears to be the most probable means of preventing extensive FCIO₂ activation. While this approach was attempted for the synthesis of ClF₅O from ClF₅O and F₂, it has not yet been utilized for the attempted preparation of ClF₃O₂.

\[
\text{BrF}_5/F_2. \text{ It was thought possible that BrF}_7 \text{ might be formed by activation of BrF}_5 \text{ in the presence of } F_2 (\text{Eq. 11 and 12}).
\]

\[
\begin{align*}
\text{BrF}_5 & \rightarrow \text{BrF}_7^* \quad \text{(11)} \\
\text{BrF}_7^* + F_2 & \rightarrow \text{BrF}_7 \quad \text{(12)}
\end{align*}
\]
Operation below ambient temperatures was employed to maximize the probability of forming BrF₇ and to prevent the BrF₇⁺ from decomposing to BrF₆ and F₂. Further, a large excess of F₂ was also used to increase the chances of forming BrF₇ (Eq. 12) and to suppress the decomposition of BrF₇⁺.

Infrared analysis of the products from the irradiations conducted at -40 and -60 C indicated that no new products were formed. However, several unidentified absorptions, probably caused by traces of impurities, were found in the infrared spectra of the products obtained from most experiments. Observed absorptions were at 1028, 1220, 1280, 1315, and 1910 cm⁻¹.

CORONA DISCHARGE ACTIVATION

Previous experiments on the corona-activated reaction of FC₁₀₂ with a large excess of F₂ (Ref. 8) had suggested that the products of the reaction were primarily CIF and FC₁₀₂ rather than the desired ClF₃O₂. However, leaks in the reaction system have since been found which indicate the possibility that the FC₁₀₂ originated in a manner other than the disproportionation of FC₁₀₂. Therefore, the experiment was repeated.

During one experiment, the amount of FC₁₀₂ which passed through the discharge yielded the following product distribution: ClF₃ 37 m/o; ClF₅, 3 m/o; CIF, 10 m/o; FC₁₀₂, 0.5 m/o; and SiF₄ (unreacted), 37 m/o; and SiF₄, 2.6 m/o. The SiF₄ apparently resulted from reaction of the F₂ with a Pyrex flowmeter.

The rather good chlorine material balance (more than 85 percent) permits a course of decomposition of FC₁₀₂ to be postulated. First, the presence of only a trace amount of FC₁₀₂ precludes a substantial disproportionation.
of FC10₂. Therefore, the most probable route for the reaction involves the decomposition of FC10₂ as shown in the following mechanisms:

\[
\text{FC10}_2 \xrightarrow{\text{Corona Discharge}} \text{ClF} + O_2
\]

\[
\text{ClF} + F_2 \xrightarrow{\text{Corona Discharge}} \text{ClF}_3
\]

\[
\text{ClF}_3 + F_2 \xrightarrow{\text{Corona Discharge}} \text{ClF}_5
\]

Thus, it appears that corona activation of FC10₂ causes decomposition rather than providing a reactive excited species capable of being fluorinated to ClF₂0₂.

ClF₃₀ PROPERTIES

Mass Spectrum

Previous attempts to obtain a fragmentation pattern of ClF₃₀ were unsuccessful (Ref. 9). At that time, it was suspected that the extremely corrosive chemical was not reaching the isotron in the CEC 21-103C Mass Spectrometer. This problem was compounded because only small quantities of Florox were then available.

It is most desirable to obtain one measurement that in itself leads to an unambiguous identification. The availability of larger quantities of Florox coupled with a modification of the inlet system to the previously mentioned mass spectrometer enabled this to be achieved. The difference in corrosivity between ClF₃₀ and ClF₅ toward the micromanometer is demonstrated by the
The fact that stable patterns could be obtained for ClF₂ while ClF₃O completely decomposed in the inlet system. Elimination of both the micromanometer and a 3-liter expansion volume made it possible to obtain a stable mass cracking pattern reproducibly, using an ionizing current of 10.5 microamperes and an ionizing voltage of 70 electron volts. The composite spectrogram obtained is presented in Table 3.

The spectral pattern in Table 3 is normalized to the most intense peak obtained at high mass range using a magnet current of 0.60 ampere. The spectrum of ClF₃O was corrected for the following impurities: SiF₄, IC10₃, C₂, ClO₂, COF₂, CO₂, O₂, and HF. It was apparent, from several patterns, that little variation in relative intensity was observed for the key mass/charge pattern ratios corresponding to ClF₃O⁺ and ClF₂O⁺. Some variation was noted in the calculated intensity of the ClO⁺ peak after correcting for Cl-O containing impurities. Further refinement in the determination of this value is dependent on a more accurate accounting of impurity contributions to this peak.

F¹⁹ n.m.r. Study of Florox

The F¹⁹ n.m.r. spectrum of the gas phase of ClF₃O was obtained to substantiate the proposed C₃₅₄ symmetry. A Varian DP60 spectrometer was used which was equipped with a high-resolution 56 MHz radio-frequency unit and high-resolution magnet. To detect the weak signals from the gaseous sample, a Princeton Applied Research lock-in-amplifier was used operating at 1.5 Hz to allow observation of any possible fine structure in the spectrum. The samples were the gas phases in equilibrium with the liquid phases of two purified ClF₃O samples containing different amounts of HF, and a gas-phase sample which had no liquid present. To observe the gas-phase resonances of the liquid samples, the n.m.r. probe was inverted and the sample maintained in place with a piece of tape. Calibration was effected with a
# Table 3

**Mass Cracking Pattern of ClF₃₀**

<table>
<thead>
<tr>
<th>Mass/Charge</th>
<th>Relative Intensity, percent</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>13.19</td>
<td>F⁻</td>
</tr>
<tr>
<td>19</td>
<td>27.29</td>
<td>Cl⁺</td>
</tr>
<tr>
<td>35</td>
<td>29.33</td>
<td>Cl⁺</td>
</tr>
<tr>
<td>37</td>
<td>7.58</td>
<td>Cl₂⁺</td>
</tr>
<tr>
<td>51</td>
<td>14.78</td>
<td>ClO⁻</td>
</tr>
<tr>
<td>53</td>
<td>4.32</td>
<td>ClO⁻</td>
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<tr>
<td>54</td>
<td>21.23</td>
<td>ClF⁺</td>
</tr>
<tr>
<td>56</td>
<td>7.10</td>
<td>ClF⁻</td>
</tr>
<tr>
<td>70</td>
<td>100.00</td>
<td>ClF₀⁺</td>
</tr>
<tr>
<td>72</td>
<td>32.03</td>
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<td>89</td>
<td>80.60</td>
<td>ClF₂₀⁺</td>
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<td>91</td>
<td>26.22</td>
<td>ClF₂₀⁺</td>
</tr>
<tr>
<td>108</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>110</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

**Note:** The sensitivity factor was not calculated because no accurate pressure measurement was made.
A sample of CClF₃ contained in a capillary tube; surface tension held the liquid up in the top of the tube in the inverted probe. Sidebands at 9600 Hz generated from an auxiliary low-frequency oscillator, were used for magnetic field sweep calibration. The results are presented in Table 4.

Some of the features in the n.m.r. spectra of both gas and liquid are noteworthy. The sample containing only a gas phase revealed two different spectra. The initial spectrum showed F1⁹ peaks at -223, -262, and -300 ω. Upon aging for 2 days, the -223 ppm band disappeared. Subsequent gas-phase measurements on samples containing liquids revealed two peaks at -276 and -317 ω. The first measurements were less precise than the latter because they involved the use of a much lower side-band frequency (1200 vs 9600 Hz for the others). Thus, the -262 and -300 ω bands are the subsequently observed bands at -276 and -317 ω.

No assignment is readily available for the -223 ω (actually -247 ω). It could possibly be assigned to the high field band of ClF₅. However, its disappearance, as well as the absence of splitting, make this unlikely. (There is a remote possibility that ClF₅ may "disappear" through dissolution into the Kel-F tube walls). Another possibility, however remote, is the presence of an isomeric species.

The liquid spectra revealed only one line and are unremarkable except for the fact that the chemical shift is consistent with the measured HF concentration. The complete collapse of the doublet in the liquid phase, caused by the exchange initiated by the low HF content, may preclude the resolution of liquid spectra. Additional studies will be conducted with samples containing alkali fluoride salts in anticipation that their bifluorides are completely insoluble in the Florox sample.
<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Phase in Probe</th>
<th>HF (b) Concentration</th>
<th>$^{19}$F Chemical Shifts, $\delta$</th>
<th>Peak Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Gas</td>
<td>--</td>
<td>-225$^d$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-262</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-300</td>
<td>1</td>
</tr>
<tr>
<td>Gas (c)</td>
<td>Gas</td>
<td>--</td>
<td>-262$^d$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-300</td>
<td>1</td>
</tr>
<tr>
<td>Liquid + Gas</td>
<td>Gas</td>
<td>--</td>
<td>-276</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-317</td>
<td>1</td>
</tr>
<tr>
<td>Liquid + Gas</td>
<td>Liquid 0.015 Molar</td>
<td></td>
<td>-276</td>
<td>--</td>
</tr>
<tr>
<td>Liquid + Gas</td>
<td>Liquid 0.0004 Molar</td>
<td></td>
<td>-289</td>
<td>--</td>
</tr>
</tbody>
</table>

(a) All spectra taken at ambient temperature  
(b) Measured by proton n.m.r.  
(c) Same as preceding sample, only 2 days "older"  
(d) Side-band frequency of 1200 Hz used
Specific Conductivity of ClF₃₀

The specific conductivity of ClF₃₀ at 25°C has been measured at Rocketdyne and a preliminary value of 2 x 10⁻⁸ ohms⁻¹ cm⁻¹ has been determined. The apparatus used was that described in Ref. 10.

FLOROX CHEMISTRY

Reaction of ClF₃₀ With NF₂ Compounds (A New Synthesis of NF₃₆)

Studies of the reactions of chlorine fluorides and difluoramine have been shown to proceed as follows (Ref. 9):

\[
\text{CIF}_{2x+1} + (2x+1)\text{HNF}_2 \rightarrow \text{ClNF}_2 + (2x)\text{N}_2\text{F}_4 + (2x+1)\text{HF}
\]

where

\[x = 0, 1, \text{or } 2\]

The course of these reactions appears to involve reduction of the ClFₓ moiety to ClF followed by condensation to yield ClNF₂. Because Florox is similar to the chlorine fluorides chemically, it was proposed that a similar reaction sequence might occur. However, after the reduction of ClF₃₀ to FC₁₀, a condensation with HNF₂ might yield OCINF₂:

\[
\text{ClF}_4 + 2\text{HNF}_2 \rightarrow 2\text{HF} + \text{N}_2\text{F}_4 + \text{FC}10
\]

\[
\text{FC}10 + \text{HNF}_2 \rightarrow \text{HF} + \text{OCINF}_2 \rightarrow \text{ClF}_2 \text{NO} \rightarrow \text{F}_3 \text{NO}
\]
Accordingly, a 1:1 reaction of ClF₃₋O and HNF₂ was conducted at low pressure and below 0 °C. A smooth reaction followed, yielding no noncondensables. No unreacted HNF₂ was observed and 55 percent of the ClF₃₋O was recovered. The N-F containing products consisted of equal proportions of ClNF₂ and NF₃₋O and a small amount of N₂F₄.

Thus, the course of the reaction appeared as follows:

\[ 2\text{HNF}_2 + \text{ClF}_3O \rightarrow 2\text{HF} + \text{NF}_3O + \text{ClNF}_2 \]

Based on this equation, the yield of NF₃₋O and ClNF₂ was 80 percent. The concomitant oxygenation and fluorination of an NF₂ group is intriguing because of the possible reaction intermediates involved. It appears probable that the final fluorination step involves ClNF₂, as in the preceding equation, or the ONF₂ radical. The mild reaction conditions coupled with the high yield of NF₃₋O are unprecedented during all previous syntheses of NF₃₋O.

Several repetitions of this experiment using higher HNF₂ to ClF₃₋O ratios (2 to 2.7:1) yielded similar results. The reaction temperature was varied between -78 and -112 °C. One of the experiments at -112 °C yielded only 75 percent of the anticipated total of N₂F₄, ClNF₂, and NF₃₋O when pumped on at that temperature. The remaining NF₂ materials were obtained only on warming above that temperature. This indicated that a ClF₃₋O-HNF₂ complex may exist at the low temperature. An attempt to confirm this on a scaled up reaction at -112 °C was unsuccessful. This may have resulted from insufficient cooling through the relatively thick walled Kel-F reactor. The use of a thinner wall Teflon or alumina container as well as a lower temperature (-125 °C) will constitute a final attempt at stabilizing any possible complex.
The possible general reaction of CIF₃ with NF₂ compounds to yield NF₃O was also considered. To test this possibility, a reaction with perfluoroor- formamide, FCONF₂, was performed. The products were NF₃O, ClNF₂, N₂F₄, and COF₂. Assuming a stoichiometry as follows:

\[
\text{CIF}_3 + 2\text{FCONF}_2 \rightarrow 2\text{COF}_2 + \text{NF}_3\text{O} + \text{ClNF}_2
\]

the NF₃O yield was 21 percent. Although this yield is somewhat low, it does confirm the utility of CIF₃O as a versatile oxygenating and fluorinating agent.

POSSIBLE SYNTHESIS OF CHLOROSYL FLUORIDE (FC₁₀)

An unidentified compound, referred to as Compound C, has been observed on a number of occasions (Ref. 3). Infrared evidence is consistent with the proposed chlorosyl fluoride (FC₁₀) as well as reaction environments from which it is obtained. However, this material is elusive in that all preparative methods have thus far been irreproducible. The pursuit of this material, while not an all encompassing end in itself, offered the possibility of exploring a wide variety of reactions of ClF₃C as well as other halogen fluorides.

Reduction Reactions of CIF₃O

One reducing agent that appeared to be of interest in exploring the reduction of CIF₃O was N₂F₄. It has already been shown that CIF₅ undergoes smooth reduction to CIF₃ as in the following equation (Ref. 11).

\[
\text{CIF}_5 + \text{N}_2\text{F}_4 \rightarrow \text{CIF}_3 + 2\text{NF}_3
\]
The obvious analogy, then, is the oxidation of $N_2F_4$ with Florox:

$$CIF_3O + N_2F_4 \rightarrow FCIO + 2NF_3$$

Tetrafluorohydrazine and CIF$_3$O do not react at ambient temperature. To produce appreciable reaction, tests were conducted at 100°C. Even at 100°C over a 24-hour period, 85 percent of the CIF$_3$O was recovered unchanged. A trace of Compound C was found among the products which also included NF$_3$, and unreacted $N_2F_4$. At 130°C and after 65 hours, the CIF$_3$O-$N_2F_4$ reaction produced FNO, FNO$_2$, NF$_3$O, NF$_3$, and CIF. No Compound C was formed and 46 percent of the CIF$_3$O was recovered.

The reduction of CIF$_3$O with Cl$_2$ was re-examined in the hope that the following reaction could be observed:

$$CIF_3O + Cl_2 \rightarrow FCIO + 2ClF$$

During previous experiments (Ref. 3) no reaction of Cl$_2$ was observed at ambient temperature with either CIF$_3$O or its CsF complex. The results of a series of experiments at elevated temperatures are presented in Table 5.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Time, hours</th>
<th>Percent CIF$_3$O Reacted</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>71</td>
<td>120</td>
<td>27</td>
<td>FCIO$_2$, CIF$_3$</td>
</tr>
<tr>
<td>100</td>
<td>42</td>
<td>37</td>
<td>FCIO$_2$, CIF$_3$</td>
</tr>
<tr>
<td>150</td>
<td>21</td>
<td>25</td>
<td>Trace C, FCIO$_2$, CIF$_3$</td>
</tr>
<tr>
<td>200</td>
<td>16</td>
<td>100</td>
<td>CIF, O$_2$</td>
</tr>
</tbody>
</table>
During the one run at 150 C, a trace of Compound C was produced, but no other run produced evidence for this elusive species. At or below 150 C, \( \text{FCIO}_2 \) and \( \text{ClF}_3 \) were produced from partial reaction of \( \text{ClF}_3\text{O} \); while at 200 C, the \( \text{ClF}_3\text{O} \) reacted completely with \( \text{Cl}_2 \) to produce \( \text{ClF} \) as in:

\[
\text{Cl}_2 + \text{ClF}_3\text{O} \rightarrow 3\text{ClF} + \frac{1}{2} \text{O}_2
\]

**Attempted Synthesis of Florox**

Oxygen-fluorine exchange reactions as possible routes to oxychlorine fluorides were studied using the reaction systems \( \text{FIO}_2-\text{ClF}_3 \) and \( \text{I}_2\text{O}_5-\text{ClF}_3 \). The desired reactions were:

\[
\begin{align*}
2\text{ClF}_3 + \text{FIO}_2 & \rightarrow 2\text{ClF}_3\text{O} + 2\text{F}_2 \\
5\text{ClF}_3 + \text{I}_2\text{O}_5 & \rightarrow 5\text{ClF}_3\text{O} + 2\text{IF}_5
\end{align*}
\]

These exchanges were based on the known reaction of \( \text{FIO}_2 \) (Ref. 12):

\[
2\text{SeF}_4 + \text{FIO}_2 \rightarrow 2\text{SeOF}_2 + 2\text{F}_2
\]

No \( \text{ClF}_3\text{O} \) was observed as a product in either reaction. The reaction between \( \text{ClF}_3 \) and \( \text{FIO}_2 \) produced \( \text{FCIO}_2 \) and lesser amounts of \( \text{FCIO}_3 \). With \( \text{I}_2\text{O}_5 \) and \( \text{ClF}_3 \), primarily \( \text{FCIO}_2 \) with smaller amounts of \( \text{ClO}_2 \) resulted.

**Mixed Interhalogens**

Complex interhalogen fluorides based on \( \text{ClF}_3\text{O} \) would form an interesting type of compound, therefore, the acid-base equilibria of \( \text{ClF}_3\text{O} \) (a moderately strong base) with the strong acids, \( \text{BrF}_3 \) and \( \text{IF}_5 \), have been studied. Both
systems were miscible, yielding clear solutions with extended liquidus ranges. However, vapor pressure measurements revealed that the solutions were nonideal. Conductivity measurements were then used to assess the extent of any possible ionization.

In the BrF$_3$-ClF$_3$O system, the addition of 4 mole percent ClF$_3$O to BrF$_3$ increased the resistance of the solvent slightly. On this basis, it was concluded that the self-ionization of BrF$_3$ is unaffected, and the resistance increase is caused by the addition of the less conductive ClF$_3$O. Thus, the following equation does not appear to be operative:

$$\text{ClF}_3\text{O} + \text{BrF}_3 \rightleftharpoons \text{ClF}_2\text{O}^+ + \text{BrF}_4^-$$

Elucidation of the IF$_5$-ClF$_3$O system was complicated by difficulty in purifying and transferring the IF$_5$. Several measurements were made and are shown in Table 6. The widely differing values for the initial resistance of IF$_5$ apparently indicate the material was impure. In each case, the addition of ClF$_3$O resulted in a lowering of the resistance of the IF$_5$. However, it was not quantitatively reproducible and certainly does not suggest ionization of the ClF$_3$O. In addition, removal of the ClF$_3$O did not raise the resistance of the IF$_5$.

It is therefore apparent that lowering of the resistance of the IF$_5$ was caused by impurity addition and that the following equilibrium exists slightly, if at all:

$$\text{ClF}_3\text{O} + \text{IF}_5 \rightleftharpoons \text{ClF}_2\text{O}^+ + \text{IF}_6^-$$
TABLE 6

CONDUCTIVITY IN THE IF₅-CIF₃O SYSTEM AT 25°C

<table>
<thead>
<tr>
<th>IF₅ Resistance, ohms</th>
<th>Resistance After Florox Addition, ohms</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>44</td>
</tr>
<tr>
<td>59</td>
<td>55</td>
</tr>
<tr>
<td>173</td>
<td>120</td>
</tr>
<tr>
<td>293</td>
<td>236</td>
</tr>
</tbody>
</table>

Hydrolysis of MCIF₄

Another possible route examined for the preparation of FCIO involved controlled hydrolysis of anionic interhalogen fluoride species. The systems studied were KCIF₄-H₂O and CsCIF₄-H₂O. The desired reactions were:

\[ \text{MCIF}_4 + \text{H}_2\text{O} \rightarrow \text{MCIF}_2\text{O} + 2\text{HF} \]

with possible displacements as in:

\[ \text{MCIF}_2\text{O} + \text{HF} \rightarrow \text{MClF}_2 + \text{FCIO} \]

Static reactions have been run where H₂O was added both to CsCIF₄ and KClF₄. In addition, a flow reaction was run where H₂O saturated N₂ was passed through CsCIF₄ at ambient temperature. In the flow run, large amounts of ClO₂ and Cl₂ were generated.
Results on the static systems were variable. Approximately three to five molar equivalents of water were added to three KCIF₄ samples. Upon pumping, unreacted water and approximately 6, 18, and 45 percent of the original tetrafluorochlorate chlorine were evolved as volatile chlorine containing species. Similarly, with three CsClF₄ samples 2, 75, and 85 percent of the original tetrafluorochlorate was evolved. The volatiles were principally elemental chlorine with smaller amounts of ClO₂ in two cases, and FCIO₂ in one. The variation in evolved chlorine may be caused by the technique of water addition. If the water reacts slowly and smoothly, hydrates are probably formed. However, if the reaction is rapid, hot spots might develop which could cause violent reaction and yield elemental chlorine as a product.

Subsequent reaction of three of the residual solids with excess HF yielded H₂O. Thus, it appears probable that stable hydrates were formed. Because the hydrolytic reactions of the ClF₄⁻ ion, in general, proved to be complex and vigorous, the study in this area has been limited to examining the postulate of the formation of stable hydrates. Reference samples for KF-KClF₄ and KF-H₂O were prepared and their X-ray powder patterns were obtained. Although the patterns were complex, comparison of the KF-KClF₄-H₂O data listed in Table 7 with KF-KClF₄ and KF-H₂O reference patterns revealed that another phase was present. Comparison of ASTM reference patterns for KF-2H₂O, KHF₂, KCIO₂, KCIO₃, KClO₄, K₂O₂, and K₂O has also revealed that these compounds do not account for the unreferenced lines. This X-ray evidence for a new phase and the chemical observation that the KF-KClF₄ mixture hydrolyzed only slightly with water indicated the high probability of the formation of hydrate(s) of the type KClF₄·xH₂O. Halocarbon mulls of the solid product on two occasions showed only the halocarbon peaks in the infrared and no OH stretching vibrations were observed.
### TABLE 7

**X-RAY POWDER DATA FOR KF-KClF₄-H₂O**

<table>
<thead>
<tr>
<th>Observed Diffraction, Ångstroms</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>3</td>
</tr>
<tr>
<td>4.9</td>
<td>3</td>
</tr>
<tr>
<td>4.6</td>
<td>3</td>
</tr>
<tr>
<td>4.45</td>
<td>3</td>
</tr>
<tr>
<td>4.2</td>
<td>3</td>
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<td>3.16</td>
<td>40</td>
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<tr>
<td>3.06</td>
<td>100*</td>
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<tr>
<td>2.58</td>
<td>10</td>
</tr>
<tr>
<td>2.41</td>
<td>10*</td>
</tr>
<tr>
<td>2.33</td>
<td>30</td>
</tr>
<tr>
<td>2.24</td>
<td>8</td>
</tr>
<tr>
<td>2.08</td>
<td>60*</td>
</tr>
<tr>
<td>2.04</td>
<td>10</td>
</tr>
<tr>
<td>2.00</td>
<td>10</td>
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<tr>
<td>1.82</td>
<td>5</td>
</tr>
<tr>
<td>1.75</td>
<td>5</td>
</tr>
<tr>
<td>1.70</td>
<td>10*</td>
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<td>1.65</td>
<td>10</td>
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<tr>
<td>1.61</td>
<td>3</td>
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<tr>
<td>1.58</td>
<td>3</td>
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<tr>
<td>1.45</td>
<td>20*</td>
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<td>1.42</td>
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<td>1.34</td>
<td>5</td>
</tr>
<tr>
<td>1.32</td>
<td>10*</td>
</tr>
<tr>
<td>1.20</td>
<td>5</td>
</tr>
<tr>
<td>1.13</td>
<td>3</td>
</tr>
</tbody>
</table>

*Peaks of intensity 10 or greater which cannot be referenced*
Hydrolysis of ClF₃

The reaction of uncomplexed ClF₃ was examined with H₂O to test the hypotheses that a condensation would evolve as follows:

\[ \text{ClF}_3 + \text{H}_2\text{O} \rightarrow \text{FCIO} + 2\text{HF} \]

The first reaction, using excess ClF₃ at ambient temperature, yielded trace amounts of Compound C and ClF. Four additional runs, however, conducted both at ambient temperature and at -18 C produced only Cl₂, ClO₂, ClF, and FCIO₂.

Chlorine Sesquioxide

A paper (Ref. 13) entitled "Chlorine (III) Oxide, a New Chlorine Oxide" was recently published. The tentatively identified material, Cl₂O₃ was formed by the ultraviolet irradiation of ClO₂ in a Pyrex bulb with a cold finger held at -45 C. The stoichiometry reported was:

\[ 30 \text{ClO}_2 \rightarrow 4\text{Cl}_2\text{O}_6 + 6\text{Cl}_2\text{O}_3 + 9\text{O}_2 + 5\text{Cl}_2 \]

Because of the postulated structure, i.e., a catenated chlorine compound, the utility of Cl₂O₃ as an intermediate in several areas of research was of interest.

The reported synthetic technique was used and produced trace amounts of the new species formed as a brown solid ring at the neck of the -45 C cold bath. However, only extremely small amounts of the material were produced by this method. [McHale and Von Elbe (Ref. 13) produced approximately 0.2 mmole (0.024 gram) in their runs.] Attempts to increase the quantity of...
product involved raising the quantity of $\text{ClO}_2$ irradiated, lowering the reaction temperature, using a Kel-F reactor, and use of flow systems. An attempt to increase the quantity of product by irradiating approximately 1 milliliter of $\text{ClO}_2$ resulted in a violent explosion.*

*CAUTIONARY NOTE: In this attempted preparation, approximately 1 liquid milliliter of chlorine dioxide, contained in a 250-cc Pyrex reaction vessel, was slowly warmed from $-196$ to $-45 \degree C$ where it has a reported vapor pressure of 37 millimeters. The ultraviolet lamp was then turned on. After approximately 5 minutes, the $\text{ClO}_2$ exploded with sufficient force to shatter the 1/4-inch Plexiglas safety shield surrounding it at a distance of 1 foot. In later preparations, much smaller quantities of $\text{ClO}_2$ were used.

Employing a lower reaction temperature ($-64 \degree C$) than that of McHale and von Elbe ($-45 \degree C$) led to more reproducible results. However, the amounts of $\text{Cl}_2\text{O}_3$ formed remained small. In a typical experiment at $-64 \degree C$, irradiation of 3.3 mmoles of $\text{ClO}_2$ produced 1.34 mmoles of $\text{Cl}_2$. Thus, less than 20 percent of the starting $\text{ClO}_2$ was converted to solid chlorine-containing species, and the yield of $\text{Cl}_2\text{O}_3$ was less than 0.31 mmole. Attempts to sublime the brown solid even very short distances resulted in its decomposition.

To raise product output and still maintain a low concentration of the treacherous $\text{ClO}_2$, the preparation was converted from a static system to a recirculating flow system. Passage of $\text{Cl}_2$ through $\text{NaClO}_2$ produces $\text{ClO}_2$. Thus, $\text{Cl}_2$ could be continually fed into the system and passed through $\text{NaClO}_2$ producing $\text{ClO}_2$ which is then irradiated. Unreacted $\text{ClO}_2$ and $\text{Cl}_2$ would be recirculated at low pressure through the $\text{NaClO}_2$ and irradiation areas. Oxygen produced could be removed by an occasional bleedoff. With only a low pressure of $\text{ClO}_2$ in the system, it should be possible to prepare moderate amounts of $\text{Cl}_2\text{O}_3$. Several runs were made using the recirculating system, however, in only one case was any material produced, and continued
reaction caused it to decompose. Keeping sufficient ClO₂ in the irradiated volume was the apparent problem. This was, in turn, dependent on the rate of formation of ClO₂ and the efficiency of pumping. Because of the lack of success, the recirculating system was abandoned.

Chemical reaction of Cl₂O₃ was attempted by allowing it to react with CsF. This would occur by either of the following routes:

\[
\text{CsF} + \text{Cl}_2\text{O}_3 \rightarrow \text{CsOCl} + \text{FCIO}_2
\]

\[
\text{CsF} + \text{Cl}_2\text{O}_3 \rightarrow \text{CsClO}_2 + \text{FCIO}
\]

Formation of Cl₂O₃ in a reaction vessel containing CsF was successful. While no reaction was observed with CsF, this may have been caused by failure to achieve a suitable contact between the solid reactants. To provide a medium for reaction and to allow possible transfer from the glass system, an attempt was made to dissolve the material in CFC₁₅; however, little, if any, solubility was observed in the CFC₁₅. Because of this solubility problem, difficulties in handling ClO₂, and the difficulty in preparing even trace quantities of the new material, investigation on Cl₂O₃ was terminated.

Oxidation of Cl₂O With CF₂(OF)₂

Mild fluorinations of Cl₂O or other appropriate ClO species offer an additional route to chlorosyl fluoride. Previous experiments in this mode utilized fluorine with excess Cl₂O (Ref. 3). Complexes and low temperatures were thought to be conducive to moderating the reaction such that a
chlorine (III) compound would result. Results with \( F_2 \) revealed, however, that once reaction was initiated, oxidation was complete to \( ClF_3O \). This strongly implied that the molecule \( FCIO \) was much more susceptible to oxidation than \( Cl_2O \).

Rather than using \( F_2 \) as the fluorinating agent, the use of \( CF_2(OF)_2 \) was considered. Over a period of 15 days at Dry Ice temperature, \( Cl_2O \) decomposed completely to \( Cl_2 \) and \( O_2 \) with a very small amount of \( FCIO_2 \) formed. The \( CF_2(OF)_2 \) was recovered essentially unchanged.

Fluorination of Chlorine Dioxide

Because \( ClO_2 \) has been observed in some reactions which produced small amounts of Compound C (\( FCIO_2 \)), it was thought that fluorination of \( ClO_2 \) under certain reaction conditions might produce \( FCIO \) according to:

\[
ClO_2 + 1/2 F_2 \rightarrow FCIO + 1/2 O_2
\]

Vigorous conditions would, however, be required because mild conditions produced \( FCIO_2 \) (Ref. 14).

Separate experiments with an excess of either \( F_2 \) or \( ClO_2 \) resulted in rapid reactions. In these experiments, \( ClO_2 \) and \( F_2 \) were placed in separate 300-milliliter, stainless-steel bombs and allowed to mix rapidly by a simple turn of a valve. In each case, a clang similar to hitting the bombs together occurred upon mixing, indicating rapid explosive reaction. In the run at ambient temperature with excess fluorine, the products found were \( CIF_3 \) and \( FCIO_2 \) in a ratio of approximately 5:1. Thus, the reactions observed were:

\[
ClO_2 + 3/2 F_2 \rightarrow CIF_3 + O_2 \quad \text{(major reaction)}
\]
\[
ClO_2 + 1/2 F_2 \rightarrow FCIO_2
\]
With excess ClO₂, an experiment at ambient temperature yielded only elemental Cl₂ (> 90-percent yield) as a product. Another experiment at 0°C produced Cl₂ (> 90-percent yield) and approximately 2-percent FC10₃. Under the condition employed, the principal net reaction was explosive decomposition of ClO₂:

\[
\text{ClO}_2 \xrightarrow{\text{explosion}} \frac{1}{2} \text{Cl}_2 + \text{O}_2
\]
Iodine fluorides and oxyfluorides

Iodine dioxide trifluoride, IF$_3$O$_2$, represents an unknown composition for halogen oxyfluorides. A limited effort was conducted to synthesize this compound as a complement to the concurrent effort to prepare ClF$_3$O$_2$. The known compound, IF$_3$O, offered a convenient starting material. Samples of IF$_7$ were first prepared from IF$_5$ and F$_2$. The IF$_7$ was converted to IF$_3$O as follows (Ref. 15):

$$2\text{IF}_7 + \text{SiO}_2 \rightarrow 2\text{IF}_3\text{O} + \text{SiF}_4$$

Significant discrepancies were noted between the reported vapor pressures of these compounds and the observed values. The measured values for IF$_7$ were approximately twice those reported, despite the fact that the only detectable impurity, IF$_3$O, was present only in trace quantities. An exact determination of the vapor pressure was not made but the material was converted to IF$_3$O. Following initial vacuum fractionation, final traces of SiF$_4$ and IF$_7$ were removed from the IF$_3$O by treatment with KF. Analysis of this material by near infrared spectroscopy revealed less than 0.7% of IF$_7$. The sample was tensiometrically homogeneous, the infrared spectrum was as reported (Ref. 16), and the vapor density yielded a molecular weight of 246 g/mole (238 calculated). The corrected vapor pressure-temperature equation for IF$_3$O is

$$\log P = 8.9874 - 1699.4T$$

The heat of sublimation is 7.59 kcal/mole and a sublimation pressure of 760 mm is obtained at 74°C.

Additional information concerning both IF$_7$ and IF$_3$O was obtained. In particular, the previously unreported mass cracking patterns were determined. The inlet system of the mass spectrometer was altered as described earlier (Ref. 17) and the same operating conditions were employed. The mass spectrum of IF$_7$ was first determined as a comparative reference (Ref. 18). Reproducible spectra were obtained for both IF$_7$ and IF$_3$O and are shown in Tables 8 and 9.
### Table 8

**Mass Cracking Pattern of IF$_5$**

<table>
<thead>
<tr>
<th>Mass/Charge</th>
<th>Relative Intensity, percent</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>No parent</td>
<td>IF$_6^+$</td>
</tr>
<tr>
<td>241</td>
<td>73.68</td>
<td>IF$_5^-$</td>
</tr>
<tr>
<td>222</td>
<td>19.34</td>
<td>IF$_4^+$</td>
</tr>
<tr>
<td>203</td>
<td>100.00</td>
<td>IF$_3^+$</td>
</tr>
<tr>
<td>184</td>
<td>7.50</td>
<td>IF$_2^+$</td>
</tr>
<tr>
<td>165</td>
<td>6.45</td>
<td>IF$_+$</td>
</tr>
<tr>
<td>146</td>
<td>55.13</td>
<td>I$^+$</td>
</tr>
</tbody>
</table>

### Table 9

**Mass Cracking Pattern of IF$_5$O**

<table>
<thead>
<tr>
<th>Mass/Charge</th>
<th>Relative Intensity, percent</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>238</td>
<td>32.05</td>
<td>IF$_5$O$^+$</td>
</tr>
<tr>
<td>222</td>
<td>2.60</td>
<td>IF$_5^+$</td>
</tr>
<tr>
<td>219</td>
<td>17.40</td>
<td>IF$_7$O$^+$</td>
</tr>
<tr>
<td>203</td>
<td>100.00</td>
<td>IF$_7^+$</td>
</tr>
<tr>
<td>200</td>
<td>4.38</td>
<td>IF$_5$O$^+$</td>
</tr>
<tr>
<td>184</td>
<td>21.92</td>
<td>IF$_5$O$^+$</td>
</tr>
<tr>
<td>181</td>
<td>17.95</td>
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<tr>
<td>165</td>
<td>10.14</td>
<td>IF$_7^+$</td>
</tr>
<tr>
<td>162</td>
<td>28.77</td>
<td>IO$^+$</td>
</tr>
<tr>
<td>143</td>
<td>12.19</td>
<td>IO$^+$</td>
</tr>
<tr>
<td>127</td>
<td>48.25</td>
<td>I$^+$</td>
</tr>
</tbody>
</table>
In the case of IF\textsubscript{5} and IF\textsubscript{5}O, parent ions were observed. Previous work with chlorine fluorides with this instrumentation never yielded parent ions. Recombination reactions were not observed and therefore no IF\textsubscript{0}\textsuperscript{+} ions were observed. Only very minor quantities of impurities (SiF\textsubscript{4} and COF\textsubscript{2}) were found and these could not be confused with mass/charge values of iodine-containing ions. The spectral patterns are normalized to the most intense peak.

The attempts to prepare IF\textsubscript{5}O\textsubscript{2} utilized the reaction of IF\textsubscript{5}O and SiO\textsubscript{2} (either Cab-O-Sil or 80 mesh silica) at elevated temperature. Because the formation of IF\textsubscript{5}O from IF\textsubscript{5} and SiO\textsubscript{2} occurs readily at ambient temperature, it appeared that additional oxygenation of the central iodine atom might well occur under slightly more vigorous conditions:

\[ 2\text{IF}_5O + \text{SiO}_2 \rightarrow 2\text{IF}_5O_2 + \text{SiF}_4 \]

Reactions were conducted at 130 °C (Cab-O-Sil) and 145 °C (silica). In each case, only a very small amount of SiF\textsubscript{4} formed and unreacted IF\textsubscript{5}O was partially recovered. However, very extensive thermal decomposition of the IF\textsubscript{5}O was noted and simply involved loss of oxygen.

\[ \text{IF}_5O \rightarrow \text{IF}_5 + \frac{1}{2}O_2 \]

Thus no new covalent I-F-O material was obtained.

To ascertain the types of reactions that IF\textsubscript{5}O might undergo and thereby gain insight into the methods most likely to be successful in converting it to IF\textsubscript{5}O\textsubscript{2}, the potential acid/base characteristics were also examined. It was observed that IF\textsubscript{5}O does not react with either the base, CsF, or the acid, AsF\textsubscript{5}. Thus, IF\textsubscript{5}O is more "neutral" than any other known interhalogen fluoride.
Another reported method (Ref. 15) of preparing IF₅O is as follows:

\[ 3\text{IF}_7 + I_2O_5 \rightarrow 3\text{IF}_5O + 2\text{IF}_3O \]

The supposed by-product of the reaction is iodine oxytrifluoride. Earlier efforts to form covalent IF₅O only resulted in the formation of the ionic I⁰₂⁺IF₆ (Ref. 9). Therefore, this reaction was examined as a possible route to the expectedly covalent IF₅O. Lacking any experimental details, it was decided to use initially a reaction temperature of 150 °C.

At this temperature, vigorous reaction occurred but proceeded as follows:

\[ \text{IF}_7 + I_2O_5 \rightarrow \text{IF}_5 + 2\text{FI}O_2 + 1/2 O_2 \]

Thus, neither IF₅O or IF₃O were obtained. Any further attempt to secure IF₅O via these reactants will require milder conditions.

Among the unexplored properties of IF₅O is its thermal stability and susceptibility to pyrolytic breakdown. The latter was considered as a simple, straightforward route to IF₅O:

\[ \text{IF}_5O \xrightarrow{\Delta} \text{IF}_3O + F_2 \]

The alternative mode of thermal cleavage was also expected, especially in view of the results with SiO₂, although this effect may have been catalytic:

\[ \text{IF}_5O \xrightarrow{\Delta} \text{IF}_3 + 1/2 O_2 \]

The first test of the basic thermal stability revealed that IF₅O could be quantitatively recovered after 5 days at 75 °C in a stainless-steel cylinder. Therefore, the pyrolysis experiments were planned at considerably higher temperature (250 to 500 °C) in a flow reactor. A supply of IF₅O...
was maintained at -78 °C in a cylinder attached directly to the hot tube which was preheated to the desired temperature. The IF$_2$O was pumped through the heated zone at a rate determined by the vapor pressure of IF$_2$O at -78 °C, and quenched at -196 °C shortly thereafter. Temperatures below 340 °C were found to cause decomposition cleanly to IF$_3$ and O$_2$. From 340 to 500 °C, breakdown of the IF$_5$ to I$_2$ became noticeable and at the highest temperature was essentially complete. Many experiments produced traces of a volatile compound, which was identified as chromyl fluoride (CrO$_2$F$_2$) by infrared and mass spectral analysis (Ref. 10). Its formation is due to fluorination of chromium oxides obtained by reaction of chromium metal in the stainless-steel tube. The CrO$_2$F$_2$ was completely eliminated when the reactor tube was thoroughly passivated and therefore it appears that the decomposing IF$_2$O is not capable of producing both active fluorine and oxygen for converting the chromium to CrO$_2$F$_2$.

To induce loss of fluorine alone from IF$_2$O and possibly also obtain oxygen transfer, flow pyrolyses were carried out using CuO-packed hot tubes. At temperatures of 250 to 350 °C, it was found that small quantities of another volatile unknown were produced. This compound exhibited an infrared absorption at 945 cm$^{-1}$ (PQR) which overlaps the I=O absorption of IF$_2$O (925 cm$^{-1}$, PQR). It is possible that the proximity of infrared bands is indicative of the unknown being a new IF$_2$O species. Alternate synthetic conditions are being sought to increase the yield.

Reaction of IF$_2$O and INF$_2$

The success attained with the CIF$_2$O-INF$_2$$_2$ reactions prompted an examination of the corresponding IF$_2$O-INF$_2$$_2$ system. Iodine oxyptentafluoride represents the only other oxyhalogen fluoride of the type OXF$_x$. The reaction proceeded
smoothly at -78 C. The products were N₂F₄, FNO, NF₅, and HF and may involve many of the reactions shown below:

\[
\begin{align*}
1F_2O + HNF_2 & \longrightarrow 1F_4O^- + \cdotNF_2 + HF \\
1F_5O + \cdotNF_2 & \longrightarrow \cdotONF_2 + IF_5 \\
IF_4O^- + \cdotNF_2 & \longrightarrow \cdotONF_2 + IF_4^- \\
\cdotONF_2 & \longrightarrow FNO + F^- \\
IF_4^- + F^- & \longrightarrow IF_7 \\
2\cdotNF_2 & \longrightarrow N_2F_4
\end{align*}
\]

Thus, the primary difference between ClF₃O and IF₅O in their reaction with HNF₂ is that ClF₃O is a sufficiently reactive fluorinating agent to convert ONF₂ to NF₅O while IF₅O and IF₇ are not; therefore, the ONF₂ decomposes.

Preparation of CINO₃

A new simplified preparation of chlorine nitrate from ClF and FNO₃ was demonstrated. The method and results are presented in the form of a manuscript in Appendix A.

PREPARATION OF BrNO₃

Some effort has been directed to effect the synthesis of pure BrNO₃. Previous efforts yielded impure material in low yield (Ref. 5), but made it possible to obtain the previously unreported infrared spectrum. This
has facilitated the identification of products in alternate syntheses. The best synthesis has utilized BrF₅ and HNO₃, but product separation was difficult. The discovery of the following reaction (Ref. 20):

\[ 2ClF + Pb(NO₃)₂ \rightarrow PbF₂ + 2ClNO₃ \]

led to an attempt to utilize BrF₅ in an analogous system.

\[ 2BrF₅ + Pb(NO₃)₂ \rightarrow PbF₂ + 2\left[\text{F}_₄\text{Br(NO₅)}\right] \]

\[ \text{F}_₄\text{BrNO₅} \xrightarrow{\alpha_r} 2\text{F}_₂ + \text{BrNO₅} \]

\[ \text{BrF}_₅ + \text{NO}_₂ \]

Bromine nitrate formed in this manner would be readily separated from unreacted starting materials and by-products. Agitation of the reactants at -45 C resulted in a dispersion but little or no reaction. On warming to ambient temperature, a mild reaction ensued, as evidenced by a gradual increase in the pressure of the system. After some time, the volatile products were fractionated, and some BrNO₃ was obtained. However, most of the gaseous products were -196 C noncondensables and decomposition products of BrNO₃ (NO₂, N₂O₅, Br₂). Therefore, it will be necessary to achieve reaction at lower temperatures and thereby preclude this secondary decomposition. This may be achieved by the reaction of BrF as derived from the Br₂, BrF₃ equilibrium. An examination of the NaNO₃ and BrF₃ system revealed that, when at room temperature, the reaction was too sluggish to yield any appreciable BrNO₃.
FLUORINATION OF BROMINE NITRATE

Despite the failure to secure pure BrNO₃, fluorination reactions were conducted using the impure material (contaminants being any or all of the following: BrF₅, Br₂, FNO₂, HNO₃, N₂O₅). Fluorine was used at a pressure of several atmospheres. At -80 °C, no reaction was observed and some BrNO₃ was not recovered. Two reactions at ambient temperature yielded bromine pentafluoride and a solid. This solid was off-white to pale green (probably because of metal fluoride contamination). It has no vapor pressure at room temperature but heating to 50 to 60 °C with pumping caused evolution of FNO₂, Br₂, and noncondensables. The infrared spectrum of the solid in the 2- to 15-micron region revealed the presence of the NO₂⁺ cation (2385 ±10 cm⁻¹). The assignment as NO₂⁺ is based both on the evolution of FNO₂ and the infrared band position. Nitronium ion absorptions have been noted in this region for similar compounds. NO₂⁺BF₅⁻ 2380 cm⁻¹ (Ref. 21) and NO₂⁺ClO₂ 2360 cm⁻¹ (Ref. 22); while nitronium ion absorptions are at somewhat lower frequencies, NO₂⁺BrF₅⁻ 2379 cm⁻¹ (Ref. 23), and NO₂⁺BF₅⁻ 2340 cm⁻¹ (Ref. 21). This differentiation is important because only one ambient temperature, stable solid compound containing N, O, Br, and F functions has been reported, i.e., NO⁺BrF₅⁻ (Ref. 24). Therefore, this solid appears to be a new complex of the type NO₂⁺BrFₓ⁻. A thorough characterization of NO₂⁺BrF₅⁻ was carried out (Ref. 25) and it was found to be quite different from this solid.

In an attempt to liberate the complexed bromine species, a displacement reaction similar to that reported (Ref. 24) for NO⁺BrF₅⁻ was attempted:

\[ \text{SiF}_4(g) + 2\text{NOBrF}_4(s) \rightarrow (\text{NO})_2\text{SiF}_6(s) + \text{BrF}_3(l) \]

The solid obtained from the fluorination of BrNO₃ was exposed to SiF₄ at room temperature for several hours. No reaction occurred and the SiF₄ was recovered quantitatively.
It has been demonstrated that ClF₃O is a weaker F⁻ acceptor than ClF₅ (Ref. 3) and a similar trend might be expected for BrF₃O-BrF₅. Therefore, because NO₂⁻BrF₄⁻ is unstable it is probable that NO₂⁻BrF₄O⁻ would be more unstable. This indicates that the solid may be an oxygenated bromine (III) species, which arises as follows:

\[ \text{BrONO}_2 + F_2 \rightarrow \text{FNO}_2 + \text{FBrO} \]

\[ \text{FNO}_2 + \text{FBrO} \rightarrow \text{NO}_2^{-} \text{BrF}_4 \text{O}^- \]

Bromine nitrate of improved purity is needed to confirm this.

**CHLORINE FLUORIDE-ARSENIC FLUORIDE SYSTEMS**

In the course of examining potentially synthetically useful chlorine oxide species, an attempt was made to study the reported ClO-AsF₅ complex (Ref. 26). The results of this investigation are presented in Appendix B. As a corollary to this study, the interaction of chlorine fluorides, including Florox, and arsenic fluorides were considered as routes to valuable intermediates.

**Reaction of Florox and Arsenic Trifluoride**

The reaction of ClF₃O with AsF₅ was studied as a possible synthetic route to either FCIO species (such as the unknown ClO⁻AsF₆⁻) or other solid species which might be fluorinated to produce ClF₃O₂ or ClF₇O. Several experiments were conducted at different reactant ratios and the formation of FCIO₂, AsF₅, O₂, and white solids was noted. The presence of ClO₂⁻AsF₆⁻ in the solid was confirmed both physically by infrared spectra of melts...
and chemically by displacement of ClO₂ by N₂O₄ addition. An X-ray powder pattern of the solid has lines due to ClO₂⁺AsF₆⁻ as well as other lines which have not yet been identified. These lines could correspond to species such as ClF₆⁺AsF₆⁻, ClF₆⁺AsF₆⁻, Cl⁺AsF₆⁻, and As⁺Cl⁻AsF₆⁻ or to ClO₂⁺AsF₆⁻, a source of FCIO.

A sample of the preceding solid was fluorinated at -78°C for 12 days producing no volatile species. Addition of ClF and later ClF₃ produced small quantities of FCIO₂ but no other volatiles. Finally, the N₂O₄ addition to the solid was repeated to determine if any change had occurred as a result of the fluorinations. It was determined that now no ClO₂ was evolved but instead, ClF₂O was produced. Other volatile products were FNO₂ and FCIO₂, which probably arose by reaction of ClF₃O with N₂O₄ and ClO₂. The ClF₃O evolved by N₂O₄ addition either came from "oxygenation" of ClF species by N₂O₄, from fluorination of the ClO₂⁺ species, from simple displacement from species such as ClF₆⁺AsF₆⁻, or from fluorination of a new reduced CI-O species (such as ClO⁺). In any case, prior to the F₂, ClF, and ClF₃ treatment, N₂O₄ displaced only ClO₂ from the solid while after these reactions ClF₃O, FNO₂, and FCIO₂ were produced. As a result, various aspects of this reaction were studied both to elucidate the interesting chemistry involved and to determine if a new route to ClF₃O were present.

To help clarify the preceding reactions in the ClF₃O-AsF₅ system, reactions between chlorine fluorides (ClF and ClF₃) and arsenic fluorides (AsF₅ and AsF₃) were studied. The following reaction (Ref. 27) is the only one reported in the literature:

\[ \text{ClF}_3 + \text{AsF}_7 \rightarrow \text{ClF}_2\text{AsF}_6 \]
Arsenic Pentfluoride-Chlorine Fluoride

Arsenic pentafluoride was reacted with ClF with the expectation that the reaction would proceed as:

\[ \text{AsF}_5 + \text{ClF} \rightarrow \text{ClAsF}_6 \]

However, what was observed was a slow, rather unusual redox reaction which appeared to follow the equation:

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

For example, after a 13-day reaction period at ambient temperature using equimolar amounts of reagents, one third of the ClF and much of the AsF$_5$ was recovered along with Cl$_2$ and a nonvolatile solid. Treatment of the solid with FNO displaced ClF$_3$, confirming the presence of the ClF$_2^+$ salt. In a subsequent reaction, a ratio of 3:1 ClF:AsF$_5$ was found, confirming the expected stoichiometry.

Arsenic Trifluoride-Chlorine Fluoride

The reaction of AsF$_3$ and ClF produced Cl$_2$, AsF$_3$, and a nonvolatile solid. It is apparent that the reaction proceeds as:

\[ 2\text{ClF} + \text{AsF}_3 \rightarrow \text{AsF}_5 + \text{Cl}_2 \]

This is then followed by the reaction between ClF and AsF$_3$ to yield ClF$_2$AsF$_6$ and Cl$_2$. 
Arsenic Trifluoride-Chlorine Trifluoride

Equimolar amounts of AsF$_3$ and ClF$_3$ were also allowed to react to determine if they formed a complex, ClF$_2$AsF$_4$. Instead, an oxidation-reduction reaction was observed producing AsF$_5$ and Cl$_2$. Although the solid product was not examined, the stoichiometry of the reaction is such that the following is proposed:

$$3\text{ClF}_3 + 3\text{AsF}_3 \rightarrow 2\text{AsF}_5 + \text{Cl}_2 + \text{ClF}_2\text{AsF}_6$$

This suggests a possible overall reaction ratio of:

$$5\text{ClF}_3 + 3\text{AsF}_3 \rightarrow 3\text{ClF}_2\text{AsF}_6 + \text{Cl}_2$$

when sufficient ClF$_3$ is available.

Reaction of the ClF$_2$AsF$_6$ With N$_2$O$_4$

"Oxygenation" of complexed ClF$_x$ species with N$_2$O$_4$ might be a possible source of ClF$_3$O. Accordingly, a sample of ClF$_2$AsF$_6$ was prepared from ClF$_3$ and AsF$_3$. Reactions of the solid with N$_2$O$_4$ produced ClF$_3$, ClF, a trace of FCIO$_2$, and possibly Cl$_2$. The overall reaction thus appeared to be:

$$2\text{ClF}_2\text{AsF}_6 + N_2O_4 \rightarrow 2\text{NO}_2\text{AsF}_6 + \text{ClF} + \text{ClF}_3$$

The production of ClF and ClF$_3$ may arise as in the following sequence:

$$\text{ClF}_2\text{AsF}_6 + N_2O_4 \rightarrow [\text{ClAsF}_6] + 2\text{NO}_2$$

$$\text{NO}_2 + [\text{ClAsF}_6] \rightarrow \text{N}_2\text{O}_2\text{AsF}_6 + \text{ClF}$$

$$\text{NO}_2 + \text{ClF}_2\text{AsF}_6 \rightarrow \text{N}_2\text{O}_2\text{AsF}_6 + \text{ClF}_3$$
Fluorination of ClO₂AsF₆

A sample of ClO₂AsF₆ was prepared by reaction of FCIO₂ and AsF₅. Three fluorination experiments were conducted on this salt to determine if this is a possible route to ClF₂O. The runs were conducted for 2-1/2 days at ambient temperature and for 2-1/2 and 27 days at -78 C. In all cases, only small amounts of ClO₂ and FCIO₂ were produced as volatile products in the fluorination reactions. Subsequent displacement reactions using ClF₂, N₂O₄, and FNO₂ also failed to produce any evidence for fluorination of the ClO₂⁺ species.

Displacement Reactions Using FNO₂

Excess FNO₂ was allowed to react with the ClF₂₀·AsF₃ solid product to displace the chlorine-containing species (perhaps including FCIO₂) complexed by AsF₅. Quantitative displacements were obtained on several different samples. The liberated products were ClF₂₀ and FCIO₂ (e.g., utilizing 0.63 gram of solid: 1.76 moles of ClF₂₀ and 0.56 mole of FCIO₂ were found; the calculated weight of solid for 1.76 moles ClF₂₀AsF₆ and 0.56 mole ClO₂AsF₆ is 0.63 gram). These data reveal that the solids prepared were mixtures of variable ratios of ClO₂AsF₆ and ClF₂₀AsF₆ and contained no ClO₃AsF₆. The oxidation-reduction reaction observed is expressed by the very general reaction:

\[ xAsF_3 + (x-y) ClF_2O \rightarrow xAsF_3 + yClO_2 + \left( \frac{x-y}{2} \right) O_2 + (x-3y) FCIO_2 \]

Of course, complexes between AsF₅ and FCIO₂ or ClF₂O are formed as in:

\[ ClF_2O + AsF_5 \rightarrow ClF_2OAaF_6 \]
\[ FCIO_2 + AsF_5 \rightarrow ClO_2AsF_6 \]
The relative amounts depend upon the ratio of the reactants and the course of the reaction. Therefore, the ClF.DO found in the initial series of reactions arose by displacement from the initially formed ClF₂AsF₆.

Reaction of ClF₂AsF₆ with ClO₂

In an attempt to produce ClO₂AsF₆, ClO₂ was allowed to react with ClF₂AsF₆ in anticipation of the following:

\[ 2\text{ClO}_2 + \text{ClF}_2\text{AsF}_6 \rightarrow 2\text{FCIO}_2 + \text{ClO}_2\text{AsF}_6 \]

However, it was determined that when ClF₂AsF₆ is treated with 2 equivalents of ClO₂, FCIO₂ is formed in slightly greater than a 1:1 stoichiometry. In addition, Cl₂ and O₂ are formed in the reaction. On the basis of the liberation of ClO₂, when the resulting solid is treated with FN₂O₃, the following reaction appears to offer the only logical sequence:

\[
\begin{align*}
\text{ClF}_2\text{O} + \text{AsF}_5 & \rightarrow \text{ClF}_2\text{OAsF}_6 \\
2\text{ClO}_2 + \text{ClF}_2\text{OAsF}_6 & \rightarrow 2\text{FCIO}_2 + \text{ClO}_2\text{AsF}_6 \\
\text{ClO}_2\text{AsF}_6 + \text{FCIO}_2 & \rightarrow \text{ClO}_2\text{AsF}_6 + \text{FCIO}_2 \\
\text{FCIO}_2 + \text{ClO}_2 & \rightarrow \text{FCIO}_2 + 1/2 \text{Cl}_2 + 1/2 \text{O}_2
\end{align*}
\]

The overall reaction (ClO₂ + ClO₂(AsF₆)) may be expressed as:

\[ 5\text{ClO}_2 + \text{ClF}_2\text{OAsF}_6 \rightarrow 2\text{FCIO}_2 + \text{ClO}_2\text{AsF}_6 + 1/2 \text{Cl}_2 + 1/2 \text{O}_2 \]

The last reaction predicts an FCIO₂/ClO₂ ratio of 0.66. Observed were 0.61 and 0.54. It does not appear likely that the salt ClO₂AsF₆ will be readily made.
ALKALI METAL FLUORIDE-CI\textsubscript{2}O COMPLEXES

The previously reported (Ref. 3) cesium fluoride-chlorine monoxide complex represents a new type of compound. In an effort to extend this class of compounds, investigations of related systems (Cl\textsubscript{2}O-RbF, ClO\textsubscript{2}-CaF, and ClO\textsubscript{2}O-CaF) have been conducted. The stoichiometry and structure of these compounds are of interest not only because of their unique nature but also because they may provide insight into the paths leading to the formation of oxychlorine fluorides upon fluorination.

Chlorine monoxide in contact with RbF at -78°C for 3 days could still be completely pumped off at that temperature. While this only indicates that a stable, undissociated complex is not formed, it contrasts sharply to the 1.5:1 complex ratio observed for Cl\textsubscript{2}O-CaF under these conditions. This RbF sample was commercial material that had been powdered in the dry box. Other measurements on this system using "activated" RbF (fused and then powdered in the dry box) yielded the results shown in Table 10.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Pressure, millimeters</th>
<th>Pure Cl\textsubscript{2}O</th>
<th>Cl\textsubscript{2}O over RbF</th>
</tr>
</thead>
<tbody>
<tr>
<td>-64</td>
<td>21</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>-45</td>
<td>71</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>-23</td>
<td>240</td>
<td>240</td>
<td></td>
</tr>
</tbody>
</table>

*Ref. 28

The reported pressures are approximate due to slow equilibrium and thus it can only be concluded that complexing is very weak.
The interaction of ClO₂ and excess CsF was studied at -23 C with no vapor pressure reduction noted. An experiment at -45 C yielded inconclusive results. A problem encountered during this work was the apparent absorption of ClO₂ in the Teflon reactor; the absorbed ClO₂ cannot easily be removed by pumping, thus complicating measurements.

A previously reported CINO₃-CsF complex (Ref. 3) formation was re-examined. After 6 days contact at -78 C, it was still possible to recover all the CINO₃ by pumping. In addition, no reduction in the vapor pressure of CINO₃ over excess CsF was observed at -78, -54, and -45 C. Again, a deficiency of CsF surface area may be responsible for this nonreproducible behavior.

An additional experiment was conducted to elucidate the CsF·1.5Cl₂O complex. In these experiments, F¹⁹ n.m.r. was used to analyze this complex in both CH₂CN and CH₃NO₂ at approximately -30 C. No F¹⁹ resonance was observed, apparently due to the slight solubility of CsF in these solvents. No more experiments are planned in the Cl₂O-CsF system. It has been concluded that ClO₂ and ClO₂NO₂ do not form complexes with CsF and that additional structural data for CsF·1.5Cl₂O complex will be difficult to obtain.

MISCELLANEOUS REACTIONS

Reaction of NF₂O and PF₅Cl

The preparation of CINF₂O was sought because of its potential utility as a reactive source of the ONF₂ group. This was attempted by reaction with PF₅Cl through a dissociative reorganization process.

\[ \text{NF}_2O + \text{PF}_5\text{Cl} \rightarrow \text{NF}_2\text{OPF}_5\text{Cl} \rightarrow \text{CINF}_2\text{O} + \text{PF}_3 \]
The preparation of PF₄Cl itself was only recently reported (Ref. 29) using PF₅Cl₂ and SbF₃. It was thought that a simpler route would be:

$$\text{PF}_3 + \text{ClF} \rightleftharpoons \text{PF}_4\text{Cl}$$

Experiments verified this concept, and 40- to 50-percent yields were obtained in minutes by reaction at -142°C in Kel-F. The by-products were PF₅Cl₂ and PF₅. It is almost certain that increased yields could be attained at lower reaction temperatures but sufficient material for the present purposes was prepared in the indicated manner.

The conversion of NF₃O to ClNF₂O was attempted under a variety of conditions. Experiments were conducted at -80°C, -126 to -70°C, and also by repetitive cycling from -126 to -196°C, with the duration varying from several hours to several days. To completely consume either reactant generally required 2 days. No appreciable complexing of the reactants was detected. Trifluoramine oxide was completely stripped of its fluorine and the PF₄Cl converted to PF₅. Thus, the reaction did not take the desired course and only resulted in the slow fluorination of PF₄Cl:

$$\text{NF}_3\text{O} + 2\text{PF}_4\text{Cl} \rightleftharpoons \text{Cl}_2 + \text{PF}_5 + \text{NOF}_4$$

At higher temperatures, the observed course of this fluorination differed only slightly as indicated below:

$$2\text{NF}_3\text{O} + 3\text{PF}_4\text{Cl} \rightleftharpoons 2\text{Cl}_2 + \text{CINO} + 4\text{PF}_5 + \text{NOF}_4$$
Reactions of Cl-F and N-O Species

Several vigorous reactions of Cl-F (ClF$_3$/FCIO$_2$ mixtures) and N-O (N$_2$O$_4$, N$_2$O$_5$ mixtures) species were found to give rise to an unknown volatile compound as indicated by unidentifiable infrared absorbances at 5.8 microns (N=O?) and 9.7 microns PQR (Cl=O?). It appeared the compound might be O$_2$ClONO$_2$. Purification of the material was not achieved because of its continual decomposition. Several synthetic approaches were then examined as possible means of preparing this compound.

\[
\begin{align*}
\text{FCIO}_2 + \text{HNO}_3 & \rightarrow \text{HF} + \text{O}_2\text{ClONO}_2 \\
\text{FCIO}_2 + \text{N}_2\text{O}_5 & \rightarrow \text{FNO}_2 + \text{O}_2\text{ClONO}_2 \\
2\text{FCIO}_2 + \text{Pb(NO}_3)_2 & \rightarrow \text{PbF}_2 + 2\text{O}_2\text{ClONO}_2
\end{align*}
\]

All these reactions failed to produce the unknown or any other new material. Only mixtures of known Cl-O and N-O degradation products were observed. Because no simple, reproducible method was found for the synthesis of this unknown material, and because it has only been observed in trace quantities, a concentrated effort to determine its character was not considered feasible. Further synthetic efforts were suspended.
EXPERIMENTAL

ULTRAVIOLET IRRADIATION

Cells

Initial irradiations and spectrophotometric data were obtained with cells having a path length of 10 centimeters fabricated from 1-inch-ID nickel tubing. The windows were 0.02-inch-thick, 1-inch-diameter, ultraviolet-grade Linde sapphire, and appeared completely unaffected by the reactants used. The windows were held in place with flanges and Teflon O-rings. Hoke NW2M Monel bellows valves were found satisfactory as cell closures.

An additional cell with a sapphire window at one end only was also fabricated. It could be cooled during irradiation by immersion in a suitable cooling bath and provision was made for blowing dry nitrogen past the window to prevent fogging by atmospheric moisture. Because the window opening was 0.66 inch in diameter and the length of the cell 7.5 inches, only a small percentage of the available radiation reached the reactants. Therefore, a new stainless-steel cell was built with a 5-inch-diameter ultraviolet-grade sapphire window (thickness: 0.125 inch). The cell had a window opening of 3.5 inches and a depth of 2.9 inches. The amount of radiation reaching the reactants was greatly increased as a result of the much larger window area and shorter length. Copper coils were soldered to the cell walls and bottom so that the cell could be cooled. An automatically controlled circulating methanol system has been used to maintain cell temperature within 3°C of the set temperature which was continuously variable from room temperature to at least -60°C. Fogging of the window was prevented by circulating dry nitrogen between the sapphire window and an additional window placed above it.
Ultraviolet Source

Work was conducted with a Hanovia utility lamp No. 30620 (power input = 100 watts) with the protective housing removed to move the lamp as close as possible to the cell.

Materials

The materials used are described in Ref. 2 and 8. Purification of $\text{FCI}_2$ was carried out by pumping off the $\text{Cl}_2$ impurity while holding the $\text{FCI}_2$ at -78°C. The chromatographic purity of the colorless liquid was better than 99.9 percent. The $\text{ClO}_3^-$ was purchased from Pennsalt. The $\text{CIF}$ was prepared by corona discharge from $\text{Cl}_2$ and $\text{I}_2$ and purified by fractionation.

CORONA DISCHARGE ACTIVATION

The apparatus previously used for corona discharge experiments (Ref. 1) was also employed for this work. The "Large Gas Reactor" (Fig. 4, Ref. 3), which was immersed in a -78°C bath during the experiments, was supplied with energy from the Audio-Frequency Pulse Generator (Ref. 1, Fig. 8). The generator was modified for higher pulse repetition rates as a means of increasing energy output by decreasing the inductance of the 0.17 H choke to 25 mh or 67 mh, selectable by means of an added switch. The trigger generator was modified to cover a range of 55 to 4000 Hz by changing the 0.01-microfarad capacitor to 0.005 microfarad. A Cenco 79000 induction coil was used to generate the high-voltage pulses.
REACTION OF CIF$_3$ and HNF$_2$

A prepassivated Kel-F container fitted with a Teflon valve was used to avoid the incompatibility of CIF$_3$ (and generated HF) with glass and HNF$_2$ with metal. Florox (30 cc) was first condensed in at -196°C from the metal vacuum line and then HNF$_2$ (29 cc) was condensed in from the glass line at -142°C. The reaction was then allowed to proceed at a higher temperature for several minutes prior to fractionation on the metal line. All the HNF$_2$ was converted to an approximately 2:2:1 mixture of NF$_3$, CINO, and N$_2$F$_4$. When the CIF$_3$ to HNF$_2$ ratio was greater than approximately 1:2.5, unreacted CIF$_3$ was recovered. Some FClO$_2$ was found and probably arose from decomposition of CIF$_3$ in incompletely passivated parts of the line. Very minor quantities of CIF$_3$ were observed and may indicate a secondary reaction path through oxygen abstraction from CIF$_3$.

When the reaction was conducted at -112°C with CIF$_3$ (27.5 cc) and HNF$_2$ (36.5 cc), only 75 percent of the total NF product mixture was removed after 15 minutes pumping at that temperature. The remaining 25 percent was obtained on warming the reactor. An attempt was made to confirm this indication of a low-temperature complex but was unsuccessful. Use of an even lower temperature will be attempted but the very low vapor pressure of HNF$_2$ at lower temperature may cause contact problems because both reactants would be solid.

REACTION OF CIF$_3$, FCONF$_2$ and HNF$_2$

Florox (35.5 cc) and perfluoroformamide (36 cc) were reacted in the Kel-F container for 15 minutes while warming to ~0°C. A small amount of noncondensables was observed. Based on 2 moles of FCONF$_2$ reacting with 1 mole of CIF$_3$, the yield of NF$_3$ was 21 percent. The major NF products were CINO and N$_2$F$_4$. No FCONF$_2$ was recovered. Conversion to COF$_2$ being complete.
PREPARATION OF IF₇

Iodine pentafluoride and excess F₂ were heated at 130 °C in Monel or stainless-steel cylinders for several hours. Conversion to IF₇ was nearly quantitative. Rough purification was achieved by vacuum fractionation. Small samples containing barely detectable amounts of 10F₂ and no HF after KF treatment exhibited a vapor pressure of 560 mm at 0 °C compared to the literature value of 345 mm (Ref. 15). Mass spectral measurements and vapor density indicated no additional impurities.

PREPARATION OF IF₇₀

Iodine heptafluoride and excess SiO₂ (Ch₂-O-SiI) were react in stainless-steel cylinders overnight at ambient temperature. Most of the by-product SiF₄ was removed by vacuum fractionation; the final traces along with any HF were removed by complexing with KF. This material was pure by all measurements. Because of the wide discrepancy between the observed and the reported (Ref. 15) vapor pressure, the vapor pressure-temperature relationship was redetermined. The observed data and derived equation are presented in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Observed Pressure, mm</th>
<th>Calculated Pressure, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>-78.1</td>
<td>7</td>
<td>2.90</td>
</tr>
<tr>
<td>-46.9</td>
<td>46</td>
<td>47.0</td>
</tr>
<tr>
<td>-22.7</td>
<td>228</td>
<td>279</td>
</tr>
<tr>
<td>-10.4</td>
<td>464</td>
<td>470</td>
</tr>
<tr>
<td>0.0</td>
<td>824</td>
<td>818</td>
</tr>
</tbody>
</table>

\[ \log p_{\text{mm}} = 8.9874 - 1670.4/T \]
PYROLYSIS OF IF$_5$O

A cylinder containing IF$_5$O was attached to a straight stainless-steel (30 inches long, 12-inch heated zone) tube passing through a furnace and then connected to a Teflon U-trap and the vacuum line. The tube was heated to test temperature and passivated with CIF$_3$. When chlorine oxides were no longer generated, the system was completely pumped down. The IF$_5$O cylinder was cooled to -78 C and the U-trap was cooled to -196 C. Continuous pumping was maintained and a flow of IF$_5$O was begun (calibrated rate = 5.5 cc/min). Separate flow experiments were of 20 to 30 minutes duration.
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Previous methods for the preparation of chlorine nitrate involved the reaction of either Cl$_2$O or ClO$_2$ with NO$_2$ or N$_2$O$_5$.\(^1\) to circumvent the use of these hazardous chlorine oxides. A new route to this compound was sought as indicated by the following equation:

$$\text{ClF} + \text{HNO}_3 \rightarrow \text{CINO}_3 + \text{HF}$$

It has been found that this reaction constitutes a rapid and convenient synthesis of chlorine nitrate. The reaction occurs on contact of the ClF with solid HNO$_3$ in 85 to 95 percent yield. The product CINO$_3$ was purified by vacuum fractionation. The vapor pressure was measured over a considerably broader range (−80° to 26°) than that in the literature (−70° to −25°). The temperatures and vapor pressures are: −79.8°, 1 mm; −63.9°, 6 mm; −46.2°, 22 mm; −25.9°, 75 mm; 0.0°, 302 mm; 17.0°, 326 mm; and 26.1°, 866 mm. The vapor pressure-temperature relationship is described by $\log_{10} p = 7.9892 - 1509.4/T$.

Chlorine nitrate has a b.p. of 22.3° (vs. literature extrapolation of 18°) with a heat of vaporization of 6.9 kcal. mole and a Trouton Constant of 23.4. The compound is stable in metal systems after pretreatment with some CINO$_3$. Long-term storage in metal or glass at approximately −50°
has not resulted in any significant decomposition. Unlike \( \text{FNO}_2 \) and the 

(2) W. Kwasnik, "Handbook of Preparative Inorganic Chemistry," G. Brauer, 

chlorine oxides, no explosive incidents have been experienced with \( \text{ClNO}_3 \).

However, it should be handled with care in the absence of sensitivity test rep.

Experimental

Chlorine monofluoride and nominally anhydrous \( \text{INO}_3 \) (approximately 98 percent) were separately condensed at -190\(^{\circ}\) into a stainless-steel or 
Kel-F cylinder attached to a metal-Teflon vacuum line. The cylinder was 
closed and the temperature was changed to some higher constant temperature 
in the range -112\(^{\circ}\) to 0\(^{\circ}\). The reactor was then held at -78\(^{\circ}\) and the 
product was pumped out rapidly and trapped at -63\(^{\circ}\). Little or no HF was 
removed from the reactor in this manner as evidenced by the failure to 
generate SiF\(_4\) when the product was subsequently handled in glass. Sometimes HF was removed by allowing the products to stand over NaF for a 
period. The identity of the product was established by its infrared 
spectrum\(^3\) and molecular weight from vapor density measurements. Vapor 


phase chromatography, using a column packed with 50\% w of Hycar carbon 
Oil 4-11V and Kel-F low density molding powder according to Dayan and 
Neale\(^4\) gave an analysis of \( \text{ClNO}_3 \): 98.4\% Cl\(_2\), 1.6\%. For the purpose of 

(4) V. H. Dayan and D. C. Neale, Advances in Chemistry Series, No. 71, 

determining the stoichiometry, the more accurately measurable Cl\(_2\) was used 
as the limiting reagent. Typically, 11.9 mmoles of Cl\(_2\) was reacted with

A-2

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approximately 14 mmoles of HNO₃ and yielded 10.6 mmoles of ClNO₃ (89 per-
cent). In an alternative procedure, the HNO₃ was maintained at -78°C while
ClF gas was gradually admitted to the reactor. When the pressure ceased
to drop, the reaction was complete. Workup was as above. The synthesis
has been successfully conducted on a scale of several liters.

Acknowledgement. This work was supported by the Office of Naval
Research, Power Branch.
APPENDIX B

A REDOX REACTION OF DICHLORINE OXIDE WITH ARSENIC PENTAFLUORIDE:
AN UNUSUAL SYNTHESIS OF ClO₂AsF₆

By
C. J. Schack and D. Pilipovich

Dichlorine oxide (or chlorine monoxide) has been reported to form a complex with AsF₅ at -70° and at about -50° formed an odd molecule, ClO₂AsF₅, through elimination of Cl₂.¹ Inference of the structure as being

ClO₂AsF₅ has been drawn from the observed reaction stoichiometry and the fact that the postulated odd molecule reacted with NO₂ to give ClNO₂.

We were interested in studying various aspects of the proposed odd molecule particularly as a ready source of the ClO radical. However, we felt that, prior to utilizing ClO₂AsF₅ as an intermediate, a more complete characterization was in order.

Experimental

Materials. Chlorine monoxide was prepared from Cl₂ and yellow ligroin using a modified procedure.² Arsenic pentfluoride was purchased from

(1) M. Schneisser, W. Fink and K. Brandle, Angew. Chem. 69, 760 (1957).


Ozark-Mahoning and used without purification after gas chromatography indicated a purity of better than 99.5%. Chloryl fluoride was prepared

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from KC1O₃ and F₂ and purified by fractional condensation. Nitrogen
tetroxide was purchased from the Matheson Co. and purified by fractional
condensation. Phosphorus dichloride trifluoride was formed from PF₅ and Cl₂.


**Apparatus.** Experiments were conducted in two vacuum systems, one
constructed of glass, the other of stainless steel-Teflon. Solids were
handled in an inert atmosphere glove box. Infrared spectra were taken on
a Perkin-Elmer 137 Infracord using 5-cm gas cells fitted with AgCl windows
or Halocarbon oil mulls between AgCl plates. Debye-Scherrer powder X-ray
diffraction patterns were obtained with a G. E. XRD instrument using
CuKa radiation.

A vapor phase chromatography of reactants and products was carried out
on a column packed with 50% w/w of Halocarbon Oil 411V and Kel-F low
density molding powder according to Dayan and Neale.

(5) V. H. Dayan and B. C. Neale, Advances in Chemistry Series, No. 54,

Reactions of Cl₂O and AsF₅. Measured quantities of Cl₂O (117 cc,
5.22 mmoles) and AsF₅ (85.0 cc, 3.79 mmoles) were separately condensed
into the reactor (glass or Teflon tubes) at -190°C. The temperature was
changed to -78°C and it was observed that the mixed reactants gradually
developed a dark red color. Pumping on the mixture after a few hours at
-78°C resulted in the recovery of some of the starting materials and much
Cl₂O. Subsequent warming of the reaction to ambient temperature gave additional small amounts of gaseous materials and a white solid. Little or no
-196°C non-condensable gases were observed throughout the reaction. In all, 111 cc of volatile products were obtained. Infrared and gas chromatographic analysis indicated these products to be a mixture of AsF$_3$ (17.5 cc, 0.78 mmole) and Cl$_2$ (93.5 cc, 4.17 mmoles) with a trace of ClO$_2$ and no Cl$_2$O. The observed reactant-product ratio of ClO$_2$:AsF$_3$:Cl$_2$ was 5.00:2.89:4.01. Similar reaction ratios were obtained when Cl$_2$O was used as the excess reagent. The solid product showed two infrared bands 1280 cm$^{-1}$ (m, doublet) and 690 to 700 cm$^{-1}$ (s, broad). Based on the observed stoichiometry of the reaction and the known infrared frequencies of Cl-O and AsF$_3$ compounds, it appeared the solid might be principally CIO$_2$As$_6$. Accordingly, an authentic sample was prepared.

Preparation of CIO$_2$As$_6$. Chloryl fluoride (111 cc, 4.96 mmoles) and AsF$_3$ (63.7 cc, 2.84 mmoles) were separately condensed into a Teflon ampoule at -196°C. After 1 hour at room temperature, the unreacted gases were removed and measured (48.0 cc, 2.14 mmoles). An infrared spectrum showed only FCIO$_2$. The white solid product had an infrared spectrum identical to that of the solid from the Cl$_2$O-AsF$_3$ reaction. In addition, both solids fumed in air and exploded on contact with water. Powder X-ray patterns of both solids were obtained and were identical. The observed spacings and relative intensities are given in Table 1.

Reaction of CIO$_2$AsF$_3$ and NO$_2$. Weighed amounts of CIO$_2$AsF$_3$ and excess NO$_2$ gas were reacted for 1 hour at 0°C. The expected displacement of ClO$_2$ was achieved but in poor yield: 20% for the solid from the Cl$_2$O reaction and 35% for the solid from the FCIO$_2$ reaction.


CIO$_2$As$_6$. Accordingly, an authentic sample was prepared.

Preparation of CIO$_2$As$_6$. Chloryl fluoride (111 cc, 4.96 mmoles) and AsF$_3$ (63.7 cc, 2.84 mmoles) were separately condensed into a Teflon ampoule at -196°C. After 1 hour at room temperature, the unreacted gases were removed and measured (48.0 cc, 2.14 mmoles). An infrared spectrum showed only FCIO$_2$. The white solid product had an infrared spectrum identical to that of the solid from the Cl$_2$O-AsF$_3$ reaction. In addition, both solids fumed in air and exploded on contact with water. Powder X-ray patterns of both solids were obtained and were identical. The observed spacings and relative intensities are given in Table 1.

R-7149 B-3
TABLE 1

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Reaction of PF₃Cl₂ and Cl₂O. A 1:1 mixture of PF₃Cl₂ and Cl₂O was allowed to warm to room temperature at which point an infrared spectrum was taken. The only infrared absorbing material present was POF₃. None of the PF₃Cl₂, a strong infrared absorber, remained. The by-product Cl₂O was revealed by its color when frozen. No non-volatile solids were observed.

Results and Discussion

The reaction of Cl₂O with AsF₅ does not give the odd molecule Cl₀AsF₅ but gives instead the salt Cl₁₀AsF₆. Further, the reaction appears to follow the stoichiometry shown in equation 1:

\[ 5\text{Cl}_2O + 3\text{AsF}_5 \rightarrow 2\text{Cl}_{10}\text{AsF}_6 + 4\text{Cl}_2 + \text{AsOF}_2 \]  

(1)
The reaction stoichiometry does not appear to be dependent on the experimental reactant ratios. The formation of $\text{ClO}_2\text{AsF}_6$ was confirmed by preparing an authentic sample and comparing their X-ray patterns.

$$\text{PClO}_2 + \text{AsF}_5 \rightarrow \text{ClO}_2\text{AsF}_6$$  \hspace{1cm} (2)

In the reaction of $\text{Cl}_2\text{O}$ with $\text{AsF}_5$, the evolution of $\text{Cl}_2$ apparently involves a much more complex process than a simple Cl-O bond rupture. The equation reported\(^1\) for this process at $-30^\circ$ is shown in equation 3:

$$\text{Cl}_2\text{O} \cdot \text{AsF}_5 \rightarrow \text{ClOAsF}_5 + \frac{1}{2} \text{Cl}_2$$  \hspace{1cm} (3)

We would prefer to propose an initial step that involves an ionization of $\text{Cl}_2\text{O}$, i.e., an ionic complex is obtained, perhaps $\text{ClO}^+\text{AsF}_5\text{Cl}^-$:

$$\text{Cl}_2\text{O} + \text{AsF}_5 \rightarrow \text{ClOAsF}_5\text{Cl}$$  \hspace{1cm} (4)

The oxidation of the $\text{ClO}^+$ species could then proceed with additional $\text{Cl}_2\text{O}$:

$$\text{Cl}_2\text{O} + \text{ClOAsF}_5\text{Cl} \rightarrow \text{ClO}_2\text{AsF}_6\text{Cl} + \text{Cl}_2$$  \hspace{1cm} (5)

This step (equation 4) should not be considered unusual inasmuch as other chlorine oxides are capable of redox (e.g., $\text{ClO}_2$ gives some $\text{Cl}_2\text{O}$ on photolysis\(^9\)).

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The most difficult rationale is the formation of the $\text{AsF}_6^-$ in the reaction. Admittedly a multiplicity of diverse reaction sequences could be proposed most of which would be difficult to experimentally verify. One possible path offered involves the dissociation of $\text{ClO}_2\text{AsF}_5\text{Cl}$ into its components with the subsequent reactions noted:

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\hspace{1cm} 11-5
\[
\begin{align*}
\text{ClO}_2\text{AsF}_3\text{Cl} & \rightarrow \text{FCIO}_2 + \text{AsF}_4\text{Cl} \quad (6) \\
2\text{AsF}_4\text{Cl} & \rightarrow \text{AsF}_3\text{Cl}_2 + \text{AsF}_3 \quad (7) \\
\text{AsF}_5 + \text{FCIO}_2 & \rightarrow \text{ClO}_2\text{AsF}_6 \quad (8) \\
\text{AsF}_3\text{Cl}_2 + \text{Cl}_2\text{O} & \rightarrow \text{AsF}_3\text{O} + 2\text{Cl}_2 \quad (9)
\end{align*}
\]

It is readily seen that the sum of equations 4 through 9, suitably weighted, gives equation 1.

The identity of AsOF\textsubscript{3} was not established as a product since it is a non-volatile X-ray amorphous solid. In addition, we did not wish to further complicate matters by studying the reaction of AsF\textsubscript{3}Cl\textsubscript{2} with Cl\textsubscript{2}O as a test of equation 8 inasmuch as AsF\textsubscript{3}Cl\textsubscript{2} "goes ionic" and is formulated as AsCl\textsubscript{4}AsF\textsubscript{6} \textsuperscript{11}. We did feel, however, that a suitable test of equation 8 would be the reaction of PF\textsubscript{3}Cl\textsubscript{2} and Cl\textsubscript{2}O. Indeed, the rapid conversion of PF\textsubscript{3}Cl\textsubscript{2} to POF\textsubscript{3} and Cl\textsubscript{2} as in equation 10:

\[
\text{PF}_3\text{Cl}_2 + \text{Cl}_2\text{O} \rightarrow \text{POF}_3 + 2\text{Cl}_2 \quad (10)
\]

strongly suggests that "covalent" AF\textsubscript{3}Cl\textsubscript{2} would react similarly. The reaction conditions are such that the reorganization of AsF\textsubscript{3}Cl, postulated as an intermediate in equation 6, would give initially the covalent structure.
The initial report on the preparations of "ClOAsF_5" did offer the reaction of NO_2 as a proof of the radical present:\[11]\:

\[
\text{ClOAsF}_5 + 2\text{NO}_2 \rightarrow \text{NO}_2\text{AsF}_5 + \text{ClN}_3
\] (11)

The existence of NO_2AsF_5 has already been questioned seriously and apparently disproved\(^{12}\). Further, the formation of some ClN_3 should be expected from ClO_2AsF_6 and NO_2 inasmuch as the reaction of ClO_2 and NO_2 gives ClN_3\(^{13}\). It is quite likely that the reaction observed by Schmeisser et al.\(^{13}\) was the initial displacement of ClO_2 from ClO_2AsF_6 by NO_2 followed by a reaction of ClO_2 with NO_2, the overall reaction being:

\[
\text{ClO}_2\text{AsF}_6 + 2\text{NO}_2 \rightarrow \text{NO}_2\text{AsF}_5 + \text{ClN}_3 + \frac{1}{2} \text{O}_2
\] (12)

Except for the formation of the oxygen, the reaction in equation 12 has the same stoichiometry of NO_2 to "solid" as that reported in equation 11. Thus, the proof of "ClOAsF_5" through its reactions or its synthesis is not conclusive.

**Summary**

The action of ClO_2 or AsF_6 does not give the odd molecule ClOAsF_5 as has been reported in the literature. Instead, the salt ClO_2AsF_6 is obtained. A rationale for the formation of the AsF_6\(^{-}\) ion was offered and involves reorganization reactions of arsenic chlorofluorides.

**Acknowledgement.** This work was supported by the Office of Naval Research, Power Branch.

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B-7/B-8
**INORGANIC HALOGEN OXIDIZERS**

Final Report (30 May 1966 through 29 May 1967)

Pilipovich, D.; Rogers, H. H.; Schack, C. J.; Lindahl, C. B.

**ABSTRACT**

New syntheses of ClF$_3$O were discovered utilizing ultraviolet-initiated reaction of FCIO$_3$ and FCIO$_5$. In the presence of F$_2$, ClF$_3$, or ClF$_3$, FCIO$_3$ gave ClF$_3$O in high conversions and high yields. The same techniques were not successful in oxidizing ClF$_3$O to ClF$_5$O or BrF$_3$ to BrF$_5$. There is considerable evidence that FCIO$_3$ is an intermediate in the synthesis of ClF$_3$O by ultraviolet activation. Corona discharge activation of FCIO$_3$-F$_2$ did not result in C$_2$F$_2$. A stable mass cracking pattern for ClF$_3$O was obtained with the most prominent peaks assignable to ClF$_2$O and ClF$_2$O$^+$. The $^{19}$F n.m.r. spectrum of gaseous ClF$_3$O revealed two bands at -2760 and -3170 with respective ratios of 2 and 1. These bands support the proposed C$_2$ symmetry for ClF$_3$O. Novel processes were discovered for forming NF$_3$ at low temperature from ClF$_3$O and HNF$_2$ or PCONF$_3$. Mass cracking patterns of IF$_3$ and IF$_5$ were determined. The vapor pressure-temperature equation for IF$_3$$_O$ was determined as log $P_{\text{mm}}$ = 8.9874 - $1659.4/T$. Pyrolysis of IF$_3$$_O$ yielded an unidentified volatile material which may be a new IF$_4$$_O$ compound. Reaction of IF$_3$$_O$ and HNF$_2$ yielded FNO and N$_2$F$_4$ as oxidation products. A new method for the synthesis of ClNO$_3$ was developed using ClIF and HNO$_2$. A similar reaction of BrF$_5$ and HNO$_2$ gave limited amounts of BrNO$_2$. Fluorination of BrNO$_2$ produced limited solid of type NO$_2$BrF$_3$. The solid, NO$_2$BrF$_3$, was characterized. Reaction of ClF$_3$O and AsF$_5$ gives principally ClO$_2$AsF$_5$, which was characterized. Oxochlorine trifluoride did not ionize in BrF$_5$ or IF$_5$. The reaction of ClF$_3$O and AsF$_5$ produced ClOF$_3$, AsF$_5$ and other products involving redox reactions. Similar redox reactions were encountered in other ClFx-AsF$_5$ systems. Hydrolysis of K$_2$ClIF$_3$ resulted in the formation of a new phase thought to be a KF-KClIF$_3$ hydrate.
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