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R-6258

(Unclassified Title)

ANNUAL SUMMARY REPORT,
INORGANIC HALOGEN OXIDIZERS
(29 May 1964 through 28 May 1965)

Prepared by D. Pilipovich
H. F. Bauer
C. B. Lindahl C. J. Schack
R. D. Wilson

Approved by J. Silverman
Section Chief Chemistry
Research Department

Contract Nonr 4428(00)
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First Assistant Commissioner
FOREWORD

The research reported herein was supported by the Advanced Research Projects Agency through 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 Nonr 4428(00) under ARPA Order No. 23, and covers the period 29 May 1964 through 28 May 1965. This work was carried out in the Synthetic Chemistry Group with Dr. D. Pilipovich, Principal Scientist of the Fluorine Chemistry Unit, as the Responsible Scientist. Full-time associates connected with the technical effort were Dr. H. F. Bauer, Dr. C. J. Schack, and Mr. R. D. Wilson. Dr. C. B. Lindahl joined the technical staff during the last two months.
ABSTRACT

The new oxidizer oxychlorine trifluoride, C1F_3O, has been prepared in high yields by the fluorination of Cl_2O. Preliminary results indicate this new oxidizer boils at 30 ±5°C.

Concomitant with the formation of C1F_3O, it was found that Cl_2O is acidic to CsF inasmuch as complexes of the type CsF·Cl_2O are formed. This material represents a new class of compounds.

The preparation of C1F_3O was attempted by a variety of routes. Metathetical reactions of C1F_5 did not yield C1F_3O nor did the careful hydrolysis of C1F_5 give rise to C1F_3O. The fluorination of commercial calcium hypochlorite gave inconclusive results. Discharge reactions of F_2 with Cl_2O and ClO gave no new species; nor did the discharge reaction of O_2 with C1F_3 and C1F_5 give rise to new compounds.

The preparation of Br_2O was accomplished for study with F_2 and CsF. The compound (IF_3O), was found to be best represented by the composition I0_2^+IF_6^-.

Using HNF_2 and C1F_3 in a variety of forms failed to yield CIF_2NF_2. The stoichiometry of the reaction was found to follow the equation

\[ \text{CIF}_3 + 3\text{HNF}_2 \rightarrow \text{CINF}_2 + \text{N}_2\text{F}_4 + 3\text{HF} \]

It was also found that the action of CIF on HNF_2 gave a quantitative yield of CINF_2 and represents a new preparation of CINF_2.

The reaction of NF_3O and BF_3Cl failed to give NF_2ClO.

The F^{19} n.m.r. examination of the systems FNO·CIF_5 and FNO_2·CIF_5 showed no interaction in the liquid state.

(Confidential Abstract)
CONTENTS

Foreword . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . ...
1. Infrared Spectra of ClF₃O

2. F¹⁹ NMR Data for ClF₃O

3. Nuclear Magnetic Resonance Spectra of FNO, FNO₂, ClF₅, FNO–ClF₅, and FNO₂–ClF₅
INTRODUCTION

This report presents the approaches taken during the past year in seeking new high-energy oxidizers. As will be seen, a variety of techniques were employed in attempts to achieve this goal. Because of the high potential of species such as $\text{ClF}_0$, much of the effort was directed toward the pursuit of either $\text{ClF}_3$ or $\text{ClF}_5$. Partial success was realized in that $\text{ClF}_3$ was synthesized; preliminary data are presented.

In addition to extensive work on both $\text{ClF}_x$ species and studies in the $\text{IF}_3$ system, this report also presents the rationale and results of the condensation reactions of $\text{HNF}_2$ and interhalogen fluorides. This reaction system has long awaited a more complete elucidation.
DISCUSSION

OXYCHLORINE TRIFLUORIDE (ClF₃O)

The studies of ClF₃O can be grouped into three categories: (1) direct fluorination of chlorine (I) oxides, (2) discharge reactions of chlorine fluorides, and (3) metathetical reactions of chlorine (V) fluoride.

Success was achieved using only the direct fluorination approach.

The preparation of ClF₃O was accomplished readily by the action of F₂ on Cl₂O (this will be discussed later). The characterization of ClF₃O is not yet complete but enough data have been obtained to infer the composition ClF₃O. Oxychlorine trifluoride is a water-white liquid and freezes to a white solid. Some preliminary physical characteristics are shown in Table 1.

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<tr>
<td>PROPERTIES OF ClF₃O</td>
</tr>
<tr>
<td>Melting Point, °C</td>
</tr>
<tr>
<td>Boiling Point, °C</td>
</tr>
<tr>
<td>Molecular Weight</td>
</tr>
<tr>
<td>Found (vapor density)</td>
</tr>
<tr>
<td>Calculated</td>
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Inconsistent elemental analyses were obtained, however, by the preliminary reduction of ClF₃O with anhydrous NH₃ and the subsequent analysis for Cl⁻ and F⁻. The average F/Cl ratio in three different samples was slightly
greater than 3 (3.2); however, material balances were not good. It is believed that the principal errors are introduced in the (1) volume measurement of ClF_3O, (2) partial reaction in transferring, and (3) possible presence of ClO_4^- and/or ClO_3^- in the final solutions. For example, it was found that it readily gives FCIO_2. Future reductions are contemplated with Hg as in the following equations:

\[ 4\text{Hg} + 2\text{ClF}_3\text{O} \rightarrow \text{HgCl}_2 + 3\text{HgF}_2 + \text{O}_2 \]

The infrared trace of ClF_3O is shown in Fig. 1. A spectrum using an IR-7 was measured, and bands were found at 1220 cm\(^{-1}\), 680 cm\(^{-1}\), 490 cm\(^{-1}\), 320 cm\(^{-1}\), and 286 cm\(^{-1}\). While it is not possible to assign the bands without also measuring the Raman effect, the spectrum permits us to say the compound ClF_3O does not have the \(\text{Cl}_3\text{F}\) structure, but probably possesses \(\text{C}_s\) symmetry. The \(\text{C}_s\) symmetry is best represented by a trigonal bipyramid with two apical fluorine atoms and the three equatorial positions being occupied by an electron pair, the oxygen atom and the unique fluorine:

\[ \text{O} \]

\[ \text{F} \]

\[ \text{F} \]

\[ \text{F} \]
Figure 1. Infrared Spectra of CIG$^9$.
The proposed structure of ClF$_3$O is somewhat analogous to the structures of both ClF$_3$ and SF$_4$ (Ref. 1 and 2). Such a structure should give rise to a $^{19}$F n.m.r. spectrum consisting of a doublet and a triplet in the ratio 2:1. The spectra obtained for the pure material as well as solutions in chlorine and Freon-11 show, however, only a single resonance for ClF$_3$O (Table 2).

### TABLE 2

$^{19}$F NMR DATA FOR ClF$_3$O

<table>
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<tr>
<th>Sample</th>
<th>Chemical Shift Relative to F$_2^*$, ppm</th>
<th>Assignment</th>
<th>Temperature, °C</th>
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<tr>
<td>Cl$_2$ Solution</td>
<td>141 broad</td>
<td>ClF$_3$O</td>
<td>-60</td>
</tr>
<tr>
<td>(impure)</td>
<td>167 doublet</td>
<td>ClF$_5$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td></td>
<td>397</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Freon-11 Solution 12 m/o</td>
<td>141 singlet</td>
<td>ClF$_3$O</td>
<td>-88</td>
</tr>
<tr>
<td></td>
<td>414</td>
<td>CFC$_3$</td>
<td></td>
</tr>
<tr>
<td>Neat Liquid</td>
<td>161 singlet</td>
<td>ClF$_3$O</td>
<td>-65</td>
</tr>
<tr>
<td></td>
<td>165 singlet</td>
<td>ClF$_3$O</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>156 collapsed</td>
<td>ClF$_3$O(s)</td>
<td>-71</td>
</tr>
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The failure to observe two distinct types of fluorine, even at -88 °C, may be attributed either to exchange or to truly equivalent fluorines, as in a structure with $C_3v$ symmetry (Ref. 3). This latter possibility may be excluded on the basis of the infrared data for ClF$_3$O.
Low-temperature exchange on the other hand, also has been observed for a similar compound, SF₄, especially in the presence of trace impurities (Ref. 4). Splitting of the ClF₃O resonance was observed between -65 and -71°C when the pure material was examined. This appeared to be due to partial liquid entrapment in solid ClF₃O, since the relative peak intensities were very temperature-dependent, and complete collapse of the structure, indicating freezing, occurred at -68 ± 3°C. This premise was substantiated when no splitting or freezing occurred in a Freon-11 solution of ClF₃O at -88°C. The marked downfield solvent shift of 20 ppm suggested that ClF₃O was somewhat associated in the pure liquid, as was also indicated by its extrapolated normal boiling point of 30 ± 5°C.

A sample of ClF₃O in Cl₂ was run in a Kel-F n.m.r. tube with known impurities, FC1₀₂ and ClF₃, present. In addition, C₁F₅ used to passivate the tube, was also present. The absence of the expected FC1₀₂ or ClF₃ lines and the width of the observed ClF₃O resonance further attested to the likelihood of exchange involving ClF₃O. Unassigned singlet resonances at 373 and 397 ppm in the ratio 2:1 may have been due to ClF₃ or CF compounds arising from reaction with the Kel-F tube. Quartz n.m.r. tubes were used for the other ClF₃O samples without observing impurities such as SiF₄.

On the basis of the relative areas for the ClF₃O and CFC1₁F₁₉ resonances in a 12 m/o solution of ClF₃O, a ratio of 2.8 fluorines per molecule was calculated.
Fluorinations

The selection of starting materials for fluorination to C\(_2\)F\(_5\)O and subsequently C\(_2\)F\(_7\)O was restricted to chlorine (I) species; i.e., Ca(OCl)\(_2\) (commercial), Cl\(_2\)O and Cl\(_2\)AsF\(_3\). The first of these, Ca(OCl)\(_2\), was tested with F\(_2\) at 125°C and ambient temperature, and subsequently at -80°C with CsF. No new products were noted in all these experiments, with FC\(_1\)O\(_3\), FC\(_1\)O\(_2\), Cl\(_2\)O\(_6\) and Cl\(_2\)O\(_7\) being identified. Considering the extreme reactivity of C\(_2\)F\(_5\)O, it is not surprising that it was not observed in the fluorination of commercial calcium hypochlorite. Bunn (Ref. 5) has stated that X-ray examination of available material indicated a high Ca(OH)\(_2\) content. By analogy to C\(_1\)F\(_3\) and C\(_1\)F\(_5\), Ca(OH)\(_2\) and C\(_2\)F\(_5\)O are not expected to be compatible.

The use of C\(_1\)O\(_2\) offered more hope because good control could be exerted over reactant purity. Fluorine and C\(_1\)O\(_2\) were examined at 125°C, at ambient temperature, and at -80°C. As yet, C\(_2\)F\(_5\)O has been formed only at the lower temperatures. Very low yields are obtained using neat C\(_1\)O\(_2\) and F\(_2\). However, if the C\(_1\)O\(_2\) is complexed with an alkali metal fluoride, the subsequent fluorination gives C\(_1\)F\(_3\)O in yields consistently over 70 percent.

The only complex of C\(_1\)O\(_2\) fluorinated thus far is that formed with CsF. Marked vapor pressure lowering of C\(_1\)O\(_2\) on CsF has been observed up to 0°C. In fact, the complex formed is colorless (or white) with the blood red color of C\(_1\)O\(_2\) being completely discharged. Upon warming to ambient temperature, however, the addition compound slowly dissociates reversibly in the vacuum line to C\(_1\)O\(_2\).
In view of the above data, we are proposing that CsF adds to Cl₂O as in the equation:

\[ x\text{CsF} + \text{Cl}_2\text{O} \rightarrow x\text{CsCl}_{2}F_{x} \text{O} \quad x = 1 \text{ and/or } 2 \]

It is also proposed that the Cl₂O structure is intact in the suggested anions FC₁₀Cl⁻ and FC₁₀C₁F". Experimental verifications of these hypotheses are in progress.

Metathetical Reactions of ClF₅

Partial hydrolysis of ClF₅ to ClF₃O has been unsuccessful in the past. Instead, FC₁₀₂ was formed, indicating perhaps that ClF₃O is more reactive with water than is ClF₅ (Ref. 27). Less reactive conditions with a variety of oxygen sources were examined in a series of metathetical reactions. Arsenic pentafluoride was often used to promote the reaction of ClF₅ as cationic ClF₅⁺ with oxygen-containing materials. In no case was there evidence of ClF₃O formation or intermediates leading to it.

(1) ClF₅·AsF₅ + H₂O(s) \xrightarrow{0°C} ClF₅, HF, AsF₃O

(2) ClF₅·AsF₅ + (CF₃CO)₂O \xrightarrow{0°C} \text{vigorous reaction, apparatus rupture}

(3) ClF₅·AsF₅ + N₂O₃ \xrightarrow{-23°C} (NO₄AsF₆⁻), NO₂⁻AsF₆⁻, Cl₂

(4) ClF₅ (diluted with N₂) + HgO (yellow) \xrightarrow{0°C} FC₁₀₂

(5) ClF₅·AsF₅ + KNO₃ \xrightarrow{25°C} ClF₅, (K⁺AsF₅(NO₃⁻)*}
The reaction of C\(_1\)F\(_5\) with KNO\(_3\) and KC\(_1\)O\(_4\) was promoted by the addition of HF, probably through nitric and perchloric acid formation. Arsenic pentafluoride reacted with the bases \(\text{H}_2\text{O}\) and NO\(_3^-\) more readily than did C\(_1\)F\(_5\); consequently little promise is held for the formation of C\(_1\)F\(_3\)O by metathesis on the basis of the above reactions.

The synthesis of C\(_1\)F\(_3\)O was also attempted by the oxidation of C\(_1\)F\(_3\) by ozone.

\[
\text{C}\_1\text{F}_3 + \text{O}_3 \xrightarrow{?} \text{C}\_1\text{F}_3\text{O} + \text{O}_2
\]

The only reaction observed was the combined attack of C\(_1\)F\(_3\) and O\(_3\) on the Kel-F infrared cell in which the reaction was run. This was deduced from the observation that only CF materials were formed.
Discharge Reactions

However limited the use of the electric discharge may appear when used in a "conventional" manner, the fact remains that the ternary system \( \text{N}_2-\text{F}_2-\text{O}_2 \) does give products containing all three elements, i.e., \( \text{NF}_3 \). The question immediately arose as to whether \( \text{ClF}_3 \) and \( \text{ClF}_5 \) can result from the ternary mixture \( \text{Cl}_2-\text{F}_2-\text{O}_2 \). This obvious analogy was tested by subjecting this mixture to a discharge at -80 C. No new compounds were observed using a \( \text{F}_2-\text{Cl}_2-\text{O}_2 \) ratio of 6:1:1. Products found were \( \text{ClO}_2 \), \( \text{FCIO}_2 \), \( \text{ClIF}_3 \), and \( \text{ClIF}_5 \). Due to the accidental presence of air in the starting material, \( \text{NO}_2 \), \( \text{FNO} \), \( \text{FNO}_2 \), and \( \text{ClONO}_2 \) also were formed. Additional experiments were carried out at -196 C, and in addition to the above products, Compound B (Ref. 6) was found. This compound was identified as \( \text{WF}_6 \) which arose from the attack by \( \text{F}_2 \) on the tungsten used to achieve the glass-to-metal seals in the discharge apparatus. These results are consistent with those previously obtained in the Rocketdyne laboratories in discharge reactions of \( \text{Cl}_2 \) and \( \text{F}_2 \) where \( \text{O}_2 \) was known, at times, to be an impurity.

Subjecting mixtures of \( \text{Cl}_2 \), \( \text{F}_2 \), and \( \text{O}_2 \) to the electric discharge does not appear to be promising using the technique described above. It appeared that variations in the discharge technique may offer more versatility in product control than the techniques now employed. One method decided upon was to utilize a gas-solid reaction where the gas is some excited species such as \( \text{F}_2^* \) or \( \text{O}_2^* \). The solid substrate is in essence a cold wall where excess energy can be readily dissipated. The essential difference from the previous experiments is that specific bond formation is sought by the interaction of an excited species with a readily oxidized material as opposed to an overall excitation followed by random and fortuitous...
recombinations. The following equations demonstrate the reactions considered:

\[
\begin{align*}
CIF_3 + O^* & \rightarrow CIF_3O^* \rightarrow CIF_3O + Q \\
CIF_3 + O^* & \rightarrow CIF_3O^* \rightarrow CIF_3O + Q \\
FCIO_2 + F* & \rightarrow CIF_3O_2^* \rightarrow CIF_3O_2 + Q \\
CIF_3 + F* & \rightarrow CIF_2OCIF_2^* \rightarrow CIF_2OCIF_2 + Q \\
CIF_3 + CIF_3O & \rightarrow CIF_3 + FCIO_2 \\
CIF_3 + CIF_3O & \rightarrow CIF_3 + CIF_3O
\end{align*}
\]

Thus, either \( O_2 \) or \( F_2 \) can be considered for the above oxidations, depending on the choice of the starting material.

The advantages of the solid-gas reaction at once became obvious for several reasons. First, it can be predicted that a higher degree of control can be exerted with regard to the structure of the products. This is dictated by the fact that one of the reactants, the solid, is the wall at which immediate dissipation of excess energy is anticipated. This is particularly important when it is realized that wall reactions enhance product formation in a discharge reaction. Concomitantly, another feature is suggested in that higher yields of complex moieties may be realized. It should be recalled (Ref. 7) that in the discharge preparation of \( NF_30 \) from various gas mixtures the same low yields were obtained for the starting material combinations \( NF_3O, NF_2O, NF_2F, \) and \( NF_2OF \). This is no doubt based upon the statistical nature of a favorable combination of the excited \( F, N, \) and \( O \) to give the desired product.
To test the above assumptions, a model reaction was selected for study at -196 C. The desired reaction was:

$$\text{FNO} + \text{F}^* \rightarrow \text{F}_2\text{NO}^* \rightarrow \text{F}_2\text{NO} + Q$$

The use of FNO was selected because it not only has an oxidizable "central" atom but it should give the known compound NF$_3$O. The apparatus used was a U-shaped Pyrex discharge tube connected to a glass U-trap. Both were maintained at -196 C, and a constriction was placed in the trap about 10 inches downstream from the discharge zone. Nitrosyl fluoride was then condensed at the constriction, and F$_2$ was introduced into the discharge tube at a pressure below 50 millimeters.

Examination of the products in the trap showed NF$_3$O to be present, representing a 5-percent conversion of the FNO. A separate experiment, a control without FNO, yielded no NF$_3$O in the trap. The control was carried out in view of the fact that the F$_2$ supply often is contaminated with small amounts of air. Subsequent experiments showed the FNO (a)-F* reaction to be reproducible. In view of the moderate success with the model selected, it appeared desirable to extend it to halogen oxides.

The selection of reactants in seeking routes to new F Cl, and O species is quite limited. Prime consideration should be given to the valence of the "central" atom. On this basis, then, all chlorine (VII) species do not appear to be desirable since neither oxidations can occur nor is the replacement of O on chlorine probable. Consequently, perchloryl fluoride does not appear to be a suitable precursor for discharge studies. The chlorine compounds which meet the imposed requirements are FC1O$_2$. 
(or ClO$_2$) and Cl$_2$O. Each can be envisioned as giving rise directly to the sought oxychlorofluorides:

\[
\begin{align*}
\text{Cl}_2\text{O} \rightarrow & \text{ClO}^- + \frac{1}{2} \text{Cl}_2 \\
\text{F}^- + \text{ClO}^- \rightarrow & \text{FCIO} \\
\text{FCIO} + \text{F}_2 \rightarrow & \text{ClF}_3\text{O}
\end{align*}
\]

The reaction of Cl$_2$O as written proceeds through the rupture of a ClO bond which requires little energy in Cl$_2$O. The photodecomposition of chlorine monoxide proceeds initially according to the first step of the equation Cl$_2$O $\rightarrow$ ClO$^-$ + 1/2 Cl$_2$ as does the chlorine-atom sensitized decomposition (Ref. 3).

To extend fluorination to halogen oxides, the selected precursors were subjected to conditions similar to those in the FN0(s)-F$^*$ experiments. For example, chlorine monoxide was frozen at -196 C on the reactor wall just downstream from the glow discharge electrodes. Fluorine passing between the electrodes is converted to fluorine atoms. These radicals are then able to bombard the solid reactant and effect fluorination.

By maintaining starting materials and products at -196 C, side reactions are minimized and hence the possibility of conversion to new energetic species is maximized.

In extending the solid-gas reaction to chlorine systems, two electrical discharge tubes have been employed. The first design maintained the Cl-0 compound to be attacked at -196 C but left the electrodes above the bath where they were cooled by an air blower.
Chlorine monoxide was reacted twice with essentially the same result. All of the Cl₂O was used up, but the only ClO species formed was ClO₂. Also formed were Cl₂ and much SiF₄. The chlorine dioxide and chlorine probably arose directly from the decomposition of Cl₂O.

\[
\begin{align*}
\text{Cl}_2\text{O} & \rightarrow \text{ClO}^- + \text{Cl}^+ \\
\text{ClO}^- + \text{Cl}_2\text{O} & \rightarrow \text{ClO}_2 + 2\text{Cl}^- 
\end{align*}
\]

Initiation of this sequence by F atoms comparable to the known Cl atom process is possible. A chain radical reaction promoted by the product Cl atoms makes fluorine necessary only for initiation and not propagation. Thus, small amounts of ClF could have been formed but not detected.

Air contamination in one run was noted by the production of a small quantity of chlorine nitrate. This again is a well-characterized product of ClO radical reactions (Ref. 8):

\[
\text{ClO}^- + \text{NO}_2^- \rightarrow \text{ClNO}_3 
\]

Due to difficulties with the method originally selected for the preparation of FC₁₀₂, ClO₂ was present as an impurity. Nevertheless, since ClO₂ is the precursor of FC₁₀₂ it was expected that it would not adversely affect the reaction. In fact, fluorination of ClO₂ would itself indicate that suitable fluorination conditions were being approached.

Using this mixture in the solid phase, it was found that the discharge reaction resulted in consumption of the FC₁₀₂ but not of the ClO₂. The products were FC₁0₃ and SiF₄, in addition to the ClO₂. The conversion of chloryl fluoride to perchloryl fluoride is certainly not the result of fluorination, and the failure of the ClO₂ to be fluorinated leads to the conclusion that fluorination conditions were lacking.
The formation of appreciable amounts of SiF$_4$ using this technique can account for the findings. The activated fluorine may react with the glass of the tube around the electrodes too fast to allow sufficient amounts to reach the intended reaction zone. In addition, oxygen that is liberated by the conversion of the silica to SiF$_4$ may be responsible for the oxidation of FC10$_2$ to FC10$_3$.

So severe was the etching of the apparatus near the electrodes and the thermal strain encountered during operation, that the discharge tube cracked after several experiments. A newly designed system was fabricated in which both electrodes and substrates could be immersed in a liquid nitrogen bath. This tube showed only limited etching after several experiments.

Again utilizing Cl$_2$O as the starting material, three experiments were conducted. Two distinct results were obtained, depending upon the purity of the fluorine. In the absence of air impurity, most of the chlorine monoxide was reacted after 20 minutes. The yield of FC10$_2$, ClO$_2$, and ClF$_5$, along with a trace of SiF$_4$, demonstrated that fluorination had been effected.

When air-contaminated fluorine passed through the discharge, the product composition was altered. As expected, ClO$_2$ and trace amounts of SiF$_4$ were formed. However, no FC10$_2$ was observed. Furthermore, appreciable yields of ClNO$_3$, ClF$_5$, and NF$_3$ were noted. These molecules are all known to result from the glow discharge reaction of the appropriate elements. The important point derived from the experiment is that fluorination of Cl in Cl=O bonds is much more difficult to achieve than the corresponding fluorination of the other atoms or groups.
Although purely hypothetical, the following reaction scheme indicates some of the possible intermediate hypofluorites and shows how they might give rise to ClF₂:

\[
\begin{align*}
\text{FCIO}_2 + F_2 \xrightarrow{\text{discharge}} & F_2\text{ClO}(0F) \\
[F_2\text{ClO}(0F)] + F_2 \xrightarrow{\text{discharge}} & [F_3\text{Cl}(0F)]_2 \\
[F_3\text{Cl}(0F)]_2 & \rightarrow \text{ClF}_5 + O_2 \\
2[F_3\text{Cl}(0F)]_2 & \rightarrow \text{ClF}_5 + \text{FCIO}_2 + O_2 + 2F_2
\end{align*}
\]

Since no ClF₃ was found, it is probably not involved in the conversion of FCIO₂ to ClF₂. The absence of ClF₃ also precludes Cl₂ as an intermediate. In discharge reactions of F₂ and Cl₂, the ratio of ClF₃ to ClF₂ was always found on the order of 10 to 1.

To determine the generality of displacing oxygen from XO₂ species by discharge fluorination, this reaction was carried out with sulfur dioxide. If any hypofluorites of sulfur are formed, they should be stable to warming (e.g., SF₆OF), and thus the intermediate character of Cl-OF species in the overall reaction could be demonstrated. Under the same conditions employed with FCIO₂, it was determined that SO₂F₂ and SF₆ were produced. Thus, fluorination and displacement did occur, but intermediate OF species were not isolated.

The reaction of ClF₅ in a discharge at -80 C was examined. It was hoped that ClF₂ or ClF₄ radicals might be generated. Such radicals might react with the glass reactor to form new F-Cl-O compounds or couple to yield compounds such as (F₄Cl)₂. The coupling reaction is analogous to the preparation of B₂Cl₄ in a mercury electrode discharge apparatus (Ref. 28).
The reaction of CIF₅ in a discharge at -80 C was examined. It was hoped that CIF₂ or CIF₄ radicals might be generated. Such radicals might react with the glass reactor to form new F-Cl-O compounds or couple to yield compounds such as (F₂Cl₄). The coupling reaction is analogous to the preparation of B₂Cl₄ in a mercury electrode discharge apparatus (Ref. 28).

In a series of experiments beginning at the lowest voltage at which a discharge could be maintained and then at higher voltages, it was determined that no new species were obtained. At the lower voltages, the CIF₅ was essentially unchanged. At higher voltages, the CIF₅ was completely destroyed, giving mainly F₂ and Cl₂. The other products were ClO₂, FCIO₃, and SiF₄.

The discharge reactions reported have indicated several areas in which new metastable compounds may have been produced. The formation of non-condensable gases during product workup may be indicative of the presence of O₂F₂. However, the characteristic color of O₂F₂ was never observed in any of the reaction mixtures.

OTHER OXYHALOGEN TRIFLUORIDES

It appears highly probable that CIF₅ is the first example of an interhalogen oxyfluoride of molecular composition XF₅. The existence of an iodine compound of that empirical composition has been known for some time (Ref. 9). However, examination of the chemical and physical properties of this material makes it most unlikely that the empirical composition is the same as the molecular composition. For example, IF₃ is a solid which does not melt to 110 C but decomposes according to the following equation:

\[ 2\text{IF}_5 \rightarrow \text{FIO}_2 + \text{IF}_3 \]
This non-melting characteristic and reasonably high decomposition temperature are, for the simple IF$_3$O molecule, extremely unlikely, especially in view of the fact that IF$_2$O (of proven molecular composition) has a melting point of +4.5°C (Ref. 10). It seems more probable that the material is actually I$_2$O$_2$IF$_6^-$, as has been speculated previously (Ref. 9). Attempts to prepare and isolate IF$_3$O for characterization have been only partially successful. The reactions tried were:

\[
\begin{align*}
I_2O_5 + 3IF_5 & \rightarrow 5IF_3O \\
IF_5 + H_2O & \rightarrow IF_3O + 2HF
\end{align*}
\]

The isolated samples have been of low fluorine content. Two problems are apparently being encountered in the first method. First of all, there has not been complete reaction of the I$_2$O$_5$, despite the use of IF$_5$ in excess of that originally reported; secondly, on work up of the solid products, the excess IF$_5$ has been pumped off while heating at 50 to 60°C. This temperature may be too high, and may result in the decomposition of IF$_3$O. The observed fluorine contents (5 to 6.5 percent) can only be explained on this basis.

The $^{19}$F n.m.r. spectra of I$_2$O$_5$ in IF$_5$ at ambient and elevated temperatures and also that of possible related species KIF$_6$ and KIF$_4$ in IF$_5$ (prepared according to Ref. 11 and 12) were run. Iodine pentafluoride alone showed no fluorine exchange from room temperature through +80°C. However, I$_2$O$_5$ in IF$_5$, when heated to form IF$_3$O, showed only a single slightly broadened band at +405 ppm, indicating complete exchange with the solvent. At room temperature, where the IF$_3$O is only slightly soluble in IF$_5$, the solvent exchange stopped, and there remained only one singlet peak at +405 ppm. This singlet is comparable to that of KIF$_6$ in IF$_5$ at +404 ppm, and lends
credence to the composition $^{19}\text{F}_2\text{IF}_6$ for $\text{IF}_3\text{O}$. No evidence for other $\text{F}^{19}$ absorptions was found. The spectrum of $\text{KIF}_4$ in $\text{IF}_5$ showed only collapse of the multiplet structure of the solvent, indicating slow fluorine exchange; this was different than either the supposed $\text{IF}_3\text{O}$ or $\text{KIF}_6$.

The isolation of $(\text{IF}_3\text{O})_2$ of good purity will enable us to conduct infra-red characterization experiments and perhaps give conclusive proof of the composition of the material.

The preparation of $\text{BrF}_3\text{O}$ has not been reported. However, the known existence of a suitable precursor, $\text{Br}_2\text{O}$, to that used in the formation of $\text{ClF}_3\text{O}$, namely $\text{Cl}_2\text{O}$, makes the synthesis of $\text{BrF}_3\text{O}$ and $\text{BrF}_5\text{O}$ appear feasible. The production of $\text{Br}_2\text{O}$ in the same manner as $\text{Cl}_2\text{O}$, using yellow $\text{HgO}$ and $\text{Br}_2$ with nitrogen carrier gas, was unsuccessful. The preparation of this material in $\text{CFC}_1\text{Cl}_3$ solution at low temperature ($-23^\circ\text{C}$) was carried out. While not yet completely freed of $\text{Br}_2$, a brown-black solid believed to be $\text{Br}_2\text{O}$ has been observed. Furthermore, vapor phase chromatography of a partially decomposed sample has shown that $\text{Br}_2$ and $\text{O}_2$ are the only products present. While a pure $\text{Br}_2\text{O}$ sample might be desirable, it is not necessary since it will be necessary to use the compound in solution to form the CsF complex prior to fluorination. Bromine contamination should not affect this complex formation. Also, this proposed synthesis of $\text{BrF}_3\text{O}$ may be simplified by the formation of the CsF complex in situ as the $\text{Br}_2\text{O}$ is being generated. Experiments utilizing both these routes are planned.
DIOXYHALOGEN TRIFLUORIDES

Several attempts have been made to prepare \( \text{FI}_2 \) and \( \text{FBrO}_2 \) for use as intermediates in catalytic fluorinations. It is expected that these materials would lead to the new compounds \( \text{IF}_3 \text{O}_2 \) and \( \text{BrF}_3 \text{O}_2 \). In this way it is hoped that information regarding the feasibility of similar fluorinations of \( \text{FClO}_2 \) will be acquired.

The preparation of \( \text{FI}_2 \text{O}_2 \) has been unsuccessful via the following reaction (Ref. 13):

\[
\text{I}_2\text{O}_5 + \text{F}_2 \rightarrow 2\text{FI}_2 \text{O}_2 + \frac{1}{2} \text{O}_2
\]

It has not been possible to completely remove the solvent from the product. Syntheses of this compound will be attempted by the thermal decomposition of \( \text{IF}_3 \text{O} \) (Ref. 9) as this becomes available.

The preparation of \( \text{FBrO}_2 \) from \( \text{KBrO}_3 \) and \( \text{BrF}_3 \) (Ref. 14) has been hampered by the low purity \( \text{BrF}_3 \) available. Substitution of \( \text{ClF}_3 \) as a reactant was unsuccessful. When pure \( \text{BrF}_3 \) is obtained, this procedure will be tried again.

DIIFLUORAMINO DERIVATIVES OF CHLORINE FLUORIDES

A series of studies was conducted employing difluoramine and other inorganic moieties to achieve the synthesis of new -NF\(_2\) containing inorganic oxidizers. A primary effort was directed to the preparation of \( \text{F}_2\text{ClNF}_2 \) compounds. It should be recalled that products of this type were sought some time ago (Ref. 24). In the cited work, \( \text{NF}_3 \text{O} \) was first produced due to \( \text{ClO}_2 \) impurities. For the present work, extremely high purity \( \text{ClF}_3 \) was used.
The Reaction of Difluoramine and Chlorine Trifluoride

The amphoteric character of both difluoramine (Ref. 15 and 16) and chlorine trifluoride (Ref. 17 and 18) has been well established. Utilization of this acid-base property was attempted in an effort to achieve a condensation reaction between these materials.

\[
\text{ClF}_3 + \text{HNF}_2 \rightarrow \text{F}_2\text{ClNF}_2 + \text{HF}
\]

It was determined that the reaction proceeds rapidly and smoothly to yield chlorodifluoramine and tetrafluorohydrazine as follows:

\[
\text{ClF}_3 + 3\text{HNF}_2 \rightarrow \text{ClNF}_2 + \text{N}_2\text{F}_4 + 3\text{HF}
\]

Despite attempts at limiting the amount of available difluoramine, it was not possible to isolate the simple condensation product, F\(_2\)ClNF\(_2\). When equimolar or excess amounts of chlorine trifluoride were employed, it was found that chlorodifluoramine was the principal product (yields up to 95 percent based on the limiting reagent). Thus the establishment of a Cl-N bond is a primary occurrence. However, the substitution of the NF\(_2\) group on chlorine apparently increases the reactivity of the remaining fluorine atoms in the molecule markedly. This results in their subsequent reaction with more difluoramine or the surfaces of the reaction vessel.

Since the reaction of chlorine and difluoramine to form chlorodifluoramine is known (Ref. 19) to be slow, the failure to find chlorine as a product regardless of the reactant stoichiometry shows that a straightforward reduction of the ClF\(_3\) to Cl\(_2\) does not occur.
It was also independently established that chlorine monofluoride and difluoramine react in equimolar quantities to form chlorodifluoramine.

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

This reaction is also not accompanied by any reduction to chlorine.

Two routes to the formation of ClNF₂ can be considered. They are visualized in the following sequences:

a. \[ \text{ClF}_2 + \text{HNF}_2 \rightarrow \text{ClF}_2\text{NF}_2 + \text{HF} \]

b. \[ \text{ClF}_2\text{NF}_2 + 2\text{HNF}_2 \rightarrow \text{ClNF}_2 + \text{N}_2\text{F}_4 + 2\text{HF} \]

a'. \[ \text{ClF}_2 + 2\text{HNF}_2 \rightarrow \text{ClF} + 2\text{HF} + \text{N}_2\text{F}_4 \]

b'. \[ \text{ClF} + \text{HNF}_2 \rightarrow \text{ClNF}_2 + \text{HF} \]

It was tempting to choose the condensation shown in (a) as being the initial step with the subsequent reduction of the condensation product, ClF₂NF₂. However, due to the experimentally confirmed reaction (b'), it appears that the primary process is probably the reduction of ClF₃ by HNF₂.

Additional Difluoramine-Chlorine Fluoride Systems

After repeated attempts with varying stiochiometries of chlorine trifluoride and difluoramine failed to yield F₂ClNF₂, several other variations in the form of the reactants were utilized. In particular, ClF₃BF₄⁻, KF·KClF₄, and RbClF₄, complexes of ClF₃, were used. In some instances a HNF₂·BF₃ complex was employed.
The reaction of neat ClF₃ and HNF₂ was found to be very rapid, even instantaneous. Therefore, B₃F₃ was used to complex either ClF₃ or HNF₂, both to slow down the reaction and also to prevent subsequent reaction of the remaining Cl-F bonds. The desired moderation in the reaction rate was achieved. For example, at -80 °C, when equimolar amounts of ClF₃ and HNF₂.B₃F₃ were mixed, the appearance of ClNF₂ and other N-F species was still noted after 4 days, although most of the total yield was obtained after 40 minutes. This pronounced decrease in the rate of the reaction is probably caused by the complexing of ClF₃ by the B₃F₃ made available by reaction of HNF₂, as well as the decrease in free HNF₂ concentration.

Chlorodifluoramine was the principal nitrogen-containing product in these B₃F₃ systems whether 1:1, 1:2, or 2:1 molar proportions of ClF₃ and HNF₂ were used. The results of these experiments also showed that reaction temperatures above -80 °C led to an increased proportion of N₂F₄ among the products. The relative amount of N₂F₄ was also increased by an excess of ClF₃. Nitrogen trifluoride was found only in trace amounts at or below -80 °C, or when there was no excess of Cl-F reagent.

The solid compounds KF·KClF₄ and RbClF₄ were treated with pure HNF₂ and it was determined that reaction at -80 °C was very slow. The rubidium salt was the least reactive of the Cl-F species tested. Conclusions regarding the reactivity of the potassium salt are difficult to make, since in one experiment an explosion occurred upon warming the mixture directly to room temperature from -142 °C. However, when the intermediate temperature of -80 °C was maintained for some time before further warming, no explosion resulted.
The yields of CINF₂ obtained with these solid Cl–F compounds were approximately 50 percent or lower. The larger amounts of N₂F₄ found probably reflect the higher temperature needed to achieve reaction. The formation of N₂F₄ is increased, then, by increased temperature as well as by the absence of ClF₃ complexing moieties.

The RbF and KF formed or present initially in these reactions proved effective in scavenging the HF obtained during the reactions. To have the greater reactivity of the volatile ClF₃ and yet still eliminate the possible detrimental effects of free HF, some reactions were conducted using NaF to "neutralize" the HF. The results were not significantly different than those found in experiments run in the absence of NaF.

Recovery of Nitrogen-Containing Products. In those reactions conducted using Pyrex glass apparatus and BF₃ as a complexing agent, the complete recovery of difluoramine nitrogen as volatile compounds was not realized. The remaining 10 to 20 percent was probably present in a residual white solid. Upon hydrolysis, these solids gave off NO₂, indicating the presence of either NOBF₄ or NO₂BF₄. This solid did not contain Cl–N–F compounds since all of the reactant chlorine was obtained in the volatile materials.

Elimination of the glass side reactions was achieved by the use of an all Kel-F and Teflon reactor. However, both the neat and complexed reactants still gave essentially the same basic results with this apparatus. In this instance all the nitrogen of difluoramine was recovered in the form of volatile N–F compounds. Moreover, a better recovery of unreacted ClF₃ was possible.
Difluoramine-Chlorine Pentafluoride Systems. Chlorine pentafluoride and difluoramine were reacted in metal-Teflon, Pyrex, and Kel-F-Teflon reactors. As with chlorine trifluoride, the pentafluoride reacted with difluoramine to give mixtures of ClNF₂, N₂F₄ and NF₃. Unlike ClF₅, however, a smooth reaction at -80 C gave products which were more sensitive to the glass environment. Within minutes, the formation of NO₂ could be visibly detected. If not fractionated at once, practically no N-F or Cl-F materials were found. Instead, the degradation products NO₂, HNO₃, Cl₂, ClO₂ and FClO₃ were obtained. Rapid fractionation of an equimolar mixture yielded as much as 77 percent ClNF₂ with 23 percent recovery of ClF₅. The remaining HNF₂ was converted to N₂F₄ and NF₃. In the Kel-F-Teflon reactor, a good correspondence between the amount of ClNF₂ formed and the amount of ClF₅ reacted was also found. The presence of the side products N₂F₄ and NF₃ again indicated a high reactivity of the Cl-F bonds of the original intermediates.

Factors Affecting Reactivity of Cl-F Bonds. Several significant conclusions are possible regarding the reaction of these Cl-F compounds with HNF₂. The relative order of reactivity for the various systems is:

\[ \text{ClF}_5-\text{HNF}_2 > \text{ClF}_3-\text{HNF}_2 > \text{ClF}_2-\text{HNF}_2 > \text{ClF}-\text{HNF}_2 > \text{Cl}-\text{HNF}_2 \]

The place of ClF-HNF₂ in the series was not established owing to its high reactivity with glass, which precluded following the course of the reaction through increasing vapor pressure as in the other systems. Probably it is as rapid or more so than ClF₅-HNF₂. The place of KF-KClF₄ in this series is doubtful, but it is probably comparable to that of RbClF₄. It was determined that the predicted Cl-N bond is formed in all cases. The alternative
possible reactions:

\[
\begin{align*}
\text{CIF}_3 + \text{HNF}_2 & \rightarrow \text{NF}_3 + \text{HF} + \text{CIF} \\
\text{CIF}_5 + \text{HNF}_2 & \rightarrow \text{NF}_3 + \text{HF} + \text{CIF}_3 
\end{align*}
\]

cannot be occurring to any great extent, if at all, since no CIF or CIF$_3$ was observed in the reaction of CIF$_3$ or CIF$_5$, respectively. Very often there was a direct correspondence between the amounts of CINF$_2$ observed and the loss of CI-F species. This is consistent with the earlier noted result.

An interhalogen fluoride of reduced reactivity was also studied; the compound chosen was IF$_5$. The proposed reaction was examined in both the glass and plastic reactors.

\[
\begin{align*}
\text{IF}_5 + \text{HNF}_2 & \rightarrow \text{HF} + \text{IF}_4 \text{NF}_2 
\end{align*}
\]

Because of the relatively high temperature (0 C) necessary to melt the IF$_5$, the reaction was found to give unwanted degradation products, including I$_2$. In fact, only small amounts of N-F materials could be found.

REATIONS OF DIFLUORAMINE AND INORGANIC FLUOROX Compounds

The synthesis of inorganic ONF$_2$ compounds has been attempted by the reaction of difluoramine and the fluoroxy compounds, oxygen difluoride, fluorine nitrate, and fluorine perchlorate. These reactions may be represented by the general equation:

\[
\begin{align*}
\text{XOF} + \text{HNF}_2 & \rightarrow \text{XONF}_2 + \text{KHFO}_2 \\
\end{align*}
\]

where

\[
X = \text{NO}_2, \text{ or ClO}_3
\]

R-6258
The successful utilization of organic hypofluorite in the synthesis of new organic ONF2 compounds at Rocketdyne was the basis for this approach (Ref. 20). Since the yields of organic reactions appeared to be enhanced by adding N2F4, it is likely that the following types of reactions were involved:

\[ \text{XOF} + h\text{NF}_2 \xrightarrow{K^+} \text{KHF}_2 + \text{XO}^- + \text{NF}_2^- \]

The inorganic radical species from such reactions would be NO₃⁻ and ClO₄⁻. Although no reproducible evidence for ONF2 compounds was observed, the reaction products could be explained by the reaction of NF₂, or N₂F₄ with NO₃⁻ and ClO₄⁻ radicals or their decomposition products.

\[ \text{NF}_2^- + \text{NO}_3^- \rightarrow \text{NO}_2, \text{FNO}_2, \text{and N}_2\text{F}_4 \]
\[ \text{NF}_2^- + \text{ClO}_4^- \rightarrow \text{FNO} \text{and FCIO}_3, \text{with smaller quantities of N}_2\text{F}_4, \text{FNO}_2, \text{Cl}_2 \]

Although the observed products can be most easily explained by assuming the participation of ONF₂ radical species, the absence of NF₃O as a product is a possible deterrent to such a postulate. The absence of N₂F₂, as well, suggests that the NF diradical also is an unlikely participant in the reactions. Noncondensible gases, O₂ or F₂, were also absent in these reaction products.
THE REACTION OF DIFLUORAMINE-ALKALI METAL FLUORIDE COMPLEXES WITH DIFLUORODIAZIDE

The basic behavior of cis-N$_2$F$_2$ with AsF$_5$ suggested that a reaction between cis-N$_2$F$_2$ and HNF$_2$ to form HF and -NF=N-NF$_2$ or NF$_2$-N=N-NF$_2$ may be possible. Accordingly, this reaction was carried out with the HNF$_2$-KF complex and the HNF$_2$-CaF complex to provide a driving force by the formation of KHF$_2$ or CaHF$_2$ respectively. The reactants were slowly warmed from -142°C, and were recovered unchanged in the case of potassium fluoride complex. When the volatiles were removed from the N$_2$F$_2$-HNF$_2$-CaF mixture at -80°C and examined by their infrared spectrum, unknown material giving rise to absorptions at 5.35 μ, 6.2 μ, and 11.0 μ, were found. The peak at 11.0 μ may be due to NF$_3$, which in itself would indicate some reaction between N$_2$F$_2$ and HNF$_2$. Explosive decomposition of CaF·HNF$_2$ did not occur until near -20°C; therefore temperatures somewhat above -80°C may be investigated.

MISCELLANEOUS REACTIONS

Reaction of NF$_3$O With BF$_2$Cl

The reversible dissociation of NF$_3$OBF$_3$ complex suggested that some ClNF$_2$O might be synthesized by dissociation of the NF$_3$OBF$_2$Cl or NF$_3$OBF$_3$Cl$^-$ complex. An equilibrium mixture of boron fluoride chlorides, rich in BF$_3$ and BF$_2$Cl, was pumped on at -142°C to remove most of the BF$_3$. The residual mixture was reacted with NF$_3$O at -142°C and warmed to -80°C. The products recovered after further warming gave evidence of the following reaction:

$$2\text{NF}_3\text{O} \cdot \text{BF}_2\text{Cl} \rightarrow \text{NF}_3\text{O} + \text{BF}_3 + \text{Cl}_2 + \text{NOBF}_4$$

Whether chlorine resulted from BF$_2$Cl oxidation or ClNF$_2$O decomposition could not be determined.
Nuclear Magnetic Resonance Studies of FNO-CIF$_5$ and FNO$_2$-CIF$_5$ Mixtures

Slight interactions between FNO and CIF$_5$ or FNO$_2$ and CIF$_5$ were considered possible at low temperatures on the basis of previous evidence (Ref. 21 and 22). The appealing possibility of the low-temperature existence of the anions FNO$^-$ and FNO$_2^-$ warranted an examination of the FNO-CIF$_5$ systems by $^{19}$F NMR. Even slight interactions between these moieties should be detectable by this method. A comparison of the chemical shifts and splitting constants of the pure components and their mixtures was made, and no evidence for interaction was found. The data are summarized in Table 3. The assignment of the peak at 95 and 101 ppm to FC10$_2$ was subsequently checked against a pure FC10$_2$ spectrum which had a singlet resonance at 97 ppm at -80°C.

The disparity between the observations above and the reported complexes FNO-CIF$_5$ and FNO$_2$-CIF$_5$ is unexpected. One would expect some detectable intermolecular interactions; the fact that we detected no complex is attributed to our observing only the liquid phase in the n.m.r. tube.

Difluoramine-Chloryl Fluoride Reactions

Another approach designed to establish a Cl-N bond from an active Cl-F compound and HNF$_2$ involved FC10$_2$. This compound has been demonstrated to couple with an acidic hydrogen (Ref. 23):

$$\text{FC10}_2 + \overset{\text{HOSO}_2}\text{F} \rightarrow \overset{\text{0.61OSO}_2}\text{F} + \text{HF}$$
TABLE 3

NUCLEAR MAGNETIC RESONANCE SPECTRA OF

FNO, FNO₂, CIF₅, FNO-CIF₅, AND

FNO₂-CIF₅

<table>
<thead>
<tr>
<th>Components</th>
<th>Chemical Shift Relative to F₂⁺, ppm</th>
<th>J Value, cps</th>
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NOTE: External standard used to calibrate scale (CF₃CO)₂O
With HNF₂, the reaction might be expected to proceed as follows:

\[ \text{FCIO}_2 + \text{HNF}_2 \rightarrow \text{HF} + \text{O}_2\text{ClIF}_2 \]

Since ClO₂ and possibly FCIO₂ as contaminants have been credited with deflagrations in previous ClF₃-HNF₂ experiments (Ref. 24) the complex ClO₂⁺BF₄⁻ was employed as the reactant.

Chlorine dioxide was removed from the relatively nonvolatile complex at -80 C. The complex was then transferred to the Kel-F reactor, and HNF₂ was added at -142 C. Upon warming the mixture to -80 C, a deflagration occurred.

The gases, noncondensible at -196 C, came almost exclusively from the HNF₂. However, among the condensable products, there was a small amount of unidentified material with a sharp doublet infrared absorption at 7.6 and 7.7 microns. This does not correspond to FCIO₂, ClO₂, or FCIO₃ absorptions, and may indicate the desired compound. Unfortunately, the N-F region was obscured by the presence of NF₃, and the sample was too small to purify. Nearly all the FCIO₂⁺BF₄⁻ complex was recovered. It is likely that the deflagration was caused by ClO₂ which was formed during transfer of the complex into the reactor. Experiments in which both the FCIO₂ and HNF₂ are complexed with BF₃ have eliminated deflagrations, but the desired compound has not been prepared. The HNF₂ was converted to NOBF₄.
The Fluorination of BrF\textsubscript{5}

Since the high-pressure, high-temperature fluorination of CsBrF\textsubscript{6} and BrF\textsubscript{5} has been unsuccessful (Ref. 29), a low-temperature reaction with a discharge-excited fluorine stream was attempted. When the frozen products were warmed, no noncondensibles were observed. Similar negative results were obtained when a stream of premixed BrF\textsubscript{5} and excess F\textsubscript{2} was passed through a glow discharge and immediately frozen.

Fluorination of FNO

A room-temperature reaction of FNO and ClF\textsubscript{3} was conducted, and, in addition to the products FNO\textsubscript{2}, FC\textsubscript{10}, ClO\textsubscript{2}, and unreacted ClF\textsubscript{3}, an unknown was also observed in the infrared spectrum of the products. The unidentified material had infrared absorption peaks at 5.8 \( \mu \) (doublet), 7.2 \( \mu \) (broad), 8.4 \( \mu \) (singlet) and 9.7 \( \mu \) (PQR). This reaction will be re-examined.
EXPERIMENTAL DETAILS

PREPARATION OF Cl$_2$O

Chlorine monoxide was prepared in high purity from the reaction of chlorine gas diluted with nitrogen, and dry, freshly prepared yellow mercuric oxide (Ref. 25)

\[
2\text{Cl}_2 + (n+1)\text{HgO} \rightarrow \text{Cl}_2\text{O} + \text{HgCl}_2\cdot n\text{HgO}
\]

The Cl$_2$O was stored in Pyrex ampoules at -196 C.

ALKALI METAL FLUORIDES

To ensure dry potassium fluoride and cesium fluoride, both compounds are first fused, and then powdered and handled in a dry box.

PREPARATION OF FLUORINE NITRATE

Fluorine nitrate was prepared by the reaction of F$_2$ on dried NaNO$_3$ (Ref. 26)

\[
\text{NaNO}_3(s) + F_2(g) \rightarrow \text{FNO}_3(g) + \text{NaF}(s)
\]

The FNO$_3$ was stored at ambient temperature in a stainless steel cylinder.

PREPARATION OF HNF$_2$

Difluoramine was prepared by the aqueous fluorination of urea followed by the treatment of the fluorinated urea solution with concentrated H$_2$SO$_4$. 

R-6258
The impure HNF\textsubscript{2} was purified by low-temperature fractionation, and was stored in glass ampoules at ambient temperature.

**FLUORINATION REACTIONS**

Over 20 reactions of the fluorination of Cl\textsubscript{2}O over CsF at -80 C have been carried out. Typical experiments utilize 5-millimole quantities of material. The fluorinations were carried out using a 300-milliliter, stainless steel, high-pressure, Hoke cylinder fitted with a high-pressure Hoke needle valve (Y 3002 H). The Cl\textsubscript{2}O was condensed into the cylinder from a metal high-vacuum system. The desired amount of fluorine was then condensed into the cylinder at -196 C. The cylinder was then warmed to the desired reaction temperature, usually -80 C. Solid starting material was handled in the dry box. Fractionation of the products was carried out in a metal vacuum system equipped with Teflon traps. The purification of oxychlorine trifluoride is readily accomplished in the vacuum line by trapping at -95 C. Identification of reaction products was by infrared analysis, using an infrared cell constructed of stainless steel and equipped with AgCl windows.

**PREPARATION OF FLUORINE PERCHLORATE**

Fluorine perchlorate was prepared by passing fluorine at 1 atm through 70 percent perchloric acid at 0 C in a Kel-F U-tube. Gas-liquid contact was increased by packing the U-tube with high-surface, inert, 12-mesh, aluminum oxide. The gas stream was passed through traps at -142 C and -196 C and then through a Fluorolube oil bubbler before venting over ammonia. The products in the -142 C trap were 60 percent fluorine.
perchlorate and 40 percent perchloryl fluoride. Three similar preparations proceeded without incident, including subsequent purification, warming, and transfer of the fluorine perchlorate. The fluorine perchlorate was identified by its infrared spectrum.

DIFLUORAMINE–FLUORINE PERCHLORATE REACTIONS

The reaction of difluoramine and fluorine perchlorate was carried out by warming the reactants in stainless steel from -152 C to room temperature. The reaction proceeded smoothly on the basis of observed gradual pressure changes. The reaction products were FC10_3, FNO, and smaller amounts of FN_2O, N_2F_4, and Cl_2. Some unreacted FC10_3 was recovered. The primary products, FNO and FC10_3, were presumed to arise from the reorganization of NF_2 and ClO_4 radicals. When KF was added to difluoramine before the introduction of fluorine perchlorate, an explosion occurred upon warming the reactants above -80 C.

REACTION OF CHLORINE TRIFLUORIDE AND DIFLUORAMINE

A reactor made of Kel-F and fitted with a Teflon valve was used for the reactions; into it was condensed chlorine trifluoride (8.1 cc, 0.362 mmoles) at -196 C. The valve was then closed and the reactor was connected to the glass vacuum line from which the difluoramine (24.2 cc, 1.07 mmoles) was condensed into the reactor at -142 C. The reactor was then closed again and the cooling bath changed to -78 C. After 30 minutes, the reactor was opened and fractionated on the metal high vacuum system. An infrared spectrum of the material in the -142 C fraction showed the absence of any Cl–F or N–F species, and indicated that HF
was the only absorbing compound present. Similar inspection of the -196 C fraction (16.2 cc) revealed that it consisted of 1 percent or less NF₃, the remainder being a 1:1 mixture of ClNF₂ and N₂F₄. Thus the reaction of ClF₃ and HNF₂ was complete and nearly quantitative.

REACTION OF CHLORINE MONOFLUORIDE AND DIFLUORAMINE

After carefully passivating the Kel-F reactor with ClF₃, it was evacuated and attached to the glass vacuum line. Difluoramine (32.1 cc, 1.43 mmole) was condensed in at -142 C. The closed reactor was then reattached to the metal vacuum line and ClF condensed in at -142 C, the quantity (32.0 cc, 1.44 mmole) being measured by pressure difference since ClF has a small vapor pressure at this temperature. After 30 minutes at -78 C, the product gases were separated by fractional condensation at -142 C and -196 C. The high-temperature fraction was found to be HF without any infrared-observable contaminants. The low-temperature sample (31.9 cc, 99.4 percent) did not contain any unreacted ClF, but was composed of a mixture of 97 percent ClNF₂ and 3 percent N₂F₄. The latter may have arisen through incomplete reaction of the difluoramine and its subsequent decomposition in the metal line during fractionation.

REACTION OF CHLORINE MONOFLUORIDE AND TETRAFLUOROHYDRAZINE

Equal volumes (22.4 cc, 1.0 mmole) of ClF and N₂F₄ were condensed into a Teflon U-trap incorporated into the metal vacuum system. After standing at -78 C for 30 minutes, the mixture was allowed to expand at ambient temperature (44.8 cc, 100 percent recovery) and an infrared sample was taken. It was observed that some slight decomposition of the N₂F₄ had
occurred, giving FNO and FNO₂. This may have been due to a minute air leak. However, the N₂F₄ recovery represented 92 to 94 percent of the starting material, and no indication of any NF₃ or ClNF₂ was present. The ClF which was also present could not be accurately measured due to overlap of its absorptions and those of FNO. Nevertheless, no reaction of ClF and N₂F₄ under these conditions was found.
REFERENCES


**ABSTRACT**

The new oxidizer oxychlorine trifluoride, ClF$_3$O, has been prepared in high yields by the fluorination of Cl$_2$O. Preliminary results indicate this new oxidizer boils at 30 ± 5 °C. Concomitant with the formation of ClF$_3$O, it was found that Cl$_2$O is acidic to CsF, inasmuch as complexes of the type CsF-Cl$_2$O are formed. This material represents a new class of compounds. The preparation of ClF$_3$O was attempted by a variety of routes. Metathetical reactions of ClF$_5$ did not yield ClF$_3$O nor did the careful hydrolysis of ClF$_5$ give rise to ClF$_3$O. The fluorination of commercial calcium hypochlorite gave inconclusive results. Discharge reactions of F$_2$ with CsF and ClO$_2$ gave no new species; nor did the discharge reaction of ClF with ClF$_3$ and ClF$_5$ give rise to new compounds. The preparation of Br$_2$O was accomplished for study with F$_2$ and CsF. The compound (IF$_3$O), was found to be best represented by the composition I$_2$•IF$_5$. Using HNF$_2$ and ClF$_3$ in a variety of forms failed to yield CIF$_2$HN$_2$. The r.t.o. chemistry of the reaction was found to follow the equation ClF$_3$ + HNF$_2$ -> ClNF$_2$ + N$_2$F$_4$ + 3HF. It was also found that the action of ClF on HNF$_2$ gave a quantitative yield of ClNF$_2$ and represents a new preparation of ClNF$_2$. The reaction of NF$_3$O and BF$_2$Cl failed to give N$_2$FCl. The F$^{19}$ n.m.r. examination of the systems FNO-CIF$_5$ and FNO$_2$-ClF$_3$ showed no interaction in the liquid state. (Confidential Abstract)
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