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R-5883-6

(Unclassified Title)

QUARTERLY PROGRESS REPORT, INORGANIC HALOGEN OXIDIZERS
(29 November 1965 through 28 February 1966)

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

Contract Nonr 4428(00)

Sponsored by Advanced Research Projects Agency
Washington 25, D.C.
ARPA Order No. 23

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REVISIONS
DATE 30 March 1966

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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 Contract N000428(00) under ARPA Order No. 23, and covers the period 29 November 1965 through 28 February 1966. This work was carried out in the Synthetic Chemistry Group with Dr. E. A. Lawton as Group Scientist. Dr. D. Pilipovich provided the technical direction as Project Scientist. Full-time associates connected with the technical effort were Dr. H. F. Bauer, responsible for coordinating this report; Dr. C. J. Schack; and Dr. C. B. Lindahl.
ABSTRACT

Oxychlorine trifluoride, Florox, has been synthesized from Cl₂O - F₂ in the presence of CsF, RbF, KF, and NaF as well as in their absence. Although the complexes of Cl₂O with CsF, RbF, and KF were probably involved, no substantial increase in conversion to Florox was obtained over the systems with uncomplexed Cl₂O. Oxychlorine trifluoride has also been synthesized from uncomplexed chlorine nitrate in 84-percent yield. Fluorination in situ of the Cl₂ - HgO reaction products has also produced ClF₃O.

Florox was stable in excess hydrogen fluoride or excess oxygen at ambient temperature and stable to 5-day storage at 71°C in Monel. In a flow system, thermal decomposition of Florox started near 500°C and was complete below 586°C. The predominant product recovered above 500°C was chlorine monofluoride.

The complex between Florox and CsF dissociated below 150°C and allowed complete removal of contaminant ClF₃ as the remaining nonvolatile solid CsClF₄. The complex between ClF₃O and KF was less stable, dissociating slowly with pumping at ambient temperature. Investigation of the FNO complex of ClF₃O by F₁⁹ n.m.r. showed exchange at -77°C; an infrared study at -196°C indicated the complex to be predominantly covalent.
Attempts to reduce ClF$_3$O to FCIO have been unsuccessfully attempted with AgF, Cl$_2$, and Cl$_2$O.

Fluorination of Cl$_2$O by F$_2$, ClF$_3$, and ClF$_5$ has also failed to produce FCIO. However, fluorination of the products of the chlorine-mercuric oxide reaction has produced some unknown, labeled Compound C, in small quantity. Some infrared evidence for traces of Compound C was also obtained in the thermal dissociation of ClF$_3$O.

As a new route to oxychlorine fluorides, the reported intermediate ClO'AsF$_3$ has been investigated. Characterization has been unsuccessful thus far, and the solid chlorine content from mass balance and analysis has been quite low.

The synthesis of new bromine oxyfluorides from Br$_2$O complexes failed, giving mainly BrF$_3$. Bromine nitrate has been prepared as a possible alternate precursor to BrF$_3$O or BrF$_3$O.

Although the nature of the bonding in the Cl$_2$O·CsF complex has not been clarified, a reproducible composition, CsF·1.5 Cl$_2$O has been obtained near -80 C.

(Confidential Abstract)
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INTRODUCTION

The work reported herein reflects effort during the past quarter in the general area of interhalogen fluorides and their derivatives. The laboratory studies encompassed roughly three areas of interest. One area involved the completion of previously initiated low-temperature fluorinations of Cl₂O and ClO₂NO₂ in Florox syntheses. These studies not only gave yield data of interest but also provided working quantities of ClF₆O for further chemical investigation.

The studies on ClF₆O are of a dual nature. One area is concerned with both the possible redox reaction of ClF₆O and the decomposition reactions which may lead to FClO. In addition, both infrared and n.m.r. examination of the complexes are of interest and are reported herein.

Finally, the preparation of Br, F, O species is being sought through the fluorination of Br₂O and BrO₂NO₂. These studies are logical extensions in the area of interhalogen derivatives as dictated by the ease of formation of ClF₆O.
DISCUSSION

FLOROX STUDIES

Florox Synthesis from Cl₂O

The preparation of ClF₅O by fluorination of Cl₂O in the presence of alkali metal fluoride has been extended to NaF and RbF in addition to the previously reported results with KF and CsF (Ref. 1). In addition, preparation of ClF₅O in good yield has been achieved in the absence of added alkali metal fluoride. The results of preparative runs are presented in Table 1.

TABLE 1

SYNTHESIS OF FLOROX

<table>
<thead>
<tr>
<th>Alkali Metal Fluoride</th>
<th>Percent Yield</th>
<th>Side Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsF</td>
<td>0 to 82</td>
<td>FC10₂, ClF₅</td>
</tr>
<tr>
<td>RbF</td>
<td>&gt; 25</td>
<td>FC10₂, ClF₅</td>
</tr>
<tr>
<td>KF</td>
<td>43, 80</td>
<td>FC10₂, ClF₅, ClF</td>
</tr>
<tr>
<td>NaF</td>
<td>73, 81</td>
<td>FC10₂, ClF</td>
</tr>
<tr>
<td>None</td>
<td>39, 63</td>
<td>FC10₂, ClF, ClF₅</td>
</tr>
</tbody>
</table>

The variation in yields caused by different added alkali metal fluorides is not necessarily significant because of the difference in yields in
apparently identical preparations (particularly during CsF experiments where the most data have been gained). Amounts of reactants and reaction times involved, and the partial decomposition of Cl₂O in metal reaction systems were kept substantially the same.

Synthesis of Florox from ClNO₃

The synthesis of Florox by fluorination of the CsF complex of ClNO₃ was described in earlier reports (Ref. 1 and 2). It was of interest also to utilize ClONO₂ as an intermediate for the preparation of FClO. Accordingly, a reaction was attempted using uncomplexed ClNO₃ and F₂ at -80 °C. After several days it was found that Florox was formed in 84-percent yield:

\[ \text{ClNO}_3 + 2\text{F}_2 \rightarrow \text{ClF}_3\text{O} + \text{FNO}_2 \]  

(1)

Thus, it has been demonstrated that the use of CsF was not essential and two steps of the previous reaction sequences, complexing and pyrolysis, to liberate ClF₃O were eliminated.

Synthesis from HgCl₂·Cl₂O

The synthesis of ClF₃O from Cl₂O in the past has required the vacuum transfer of Cl₂O from an apparent Cl₂O·HgCl₂ complex with warming to another reaction vessel. It has been found that if the solid products from the HgO + Cl₂ reaction are fluorinated in situ, ClF₃O and ClF₃ are produced. This is the first time Florox has been prepared in this manner:

\[ \text{HgCl}_2\cdot\text{Cl}_2\text{O} + \text{F}_2 \rightarrow \text{ClF}_3\text{O} + \text{ClF}_3 \]  

(2)
Thermal Decomposition of Florox

Pyrolysis of the nonvolatile solid formed by low-temperature fluorination of the \( \text{Cl}_2 \text{O-C}_6 \text{F} \) complex has, on at least three occasions, yielded traces of an unknown species thought to be FClO \( (\text{Compound C}) \). It was thought that Compound C might result from pyrolysis of CIF\(_3\) as in Eq. 3.

\[
\text{CIF}_3 \rightarrow \text{FClO} + \text{F}_2 \quad (3)
\]

Representative results of experiments where Florox at low pressure was passed through a Monel tube held at temperatures from 300 to 585°C are presented in Table 2. As is seen in Table 2, decomposition of CIF\(_3\) does not occur to a large extent under these flow conditions at temperatures less than 400°C. Products found at 300°C were CIF\(_3\) and possibly

<table>
<thead>
<tr>
<th>Temperature, C</th>
<th>Percent Florox Recovered</th>
<th>Condensable Product Formed at -196°C (as percent of Florox passed)</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>--</td>
<td>( \sim 1.5 )</td>
<td>CIF(_3), FCIO (_2)</td>
</tr>
<tr>
<td>400</td>
<td>99</td>
<td>2</td>
<td>CIF, trace Compound C</td>
</tr>
<tr>
<td>450</td>
<td>82</td>
<td>16</td>
<td>CIF</td>
</tr>
<tr>
<td>500</td>
<td>46</td>
<td>54</td>
<td>CIF</td>
</tr>
<tr>
<td>585</td>
<td>38</td>
<td>62</td>
<td>FCIO (_2), CIF</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>98</td>
<td>CIF, trace Compound C</td>
</tr>
</tbody>
</table>
FCIF. At 400 C. small amounts of CIF as well as ClF$_3$ were found, and at higher temperatures CIF was the only product. Two reactions yielded traces of unknown material, possibly Compound C. Material balances agree with the expected evolution of one molecule of CIF (or ClF$_3$) per molecule of decomposed ClF$_3$O according to the overall reaction:

$$\text{ClF}_3\text{O} \rightarrow \text{ClF} + \text{F}_2 + \frac{1}{2} \text{O}_2 \quad (4)$$

Possible decomposition routes involve either of the following pairs:

$$\text{ClF}_3\text{O} \rightarrow \text{ClF}_3 + \frac{1}{2} \text{O}_2 \quad (5)$$

$$\text{ClF}_3 \rightarrow \text{ClF} + \frac{1}{2} \text{F}_2 \quad (6)$$

or

$$\text{ClF}_3\text{O} \rightarrow \text{FCIO} + \text{F}_2 \quad (7)$$

$$\text{FCIO} \rightarrow \text{ClF} + \frac{1}{2} \text{O}_2 \quad (8)$$

These studies are being continued for a more complete elucidation of the decomposition.

**Stability of Florox in Hydrogen Fluoride**

At least two instances of nonexplosive decomposition of ClF$_3$O have occurred at Rocketdyne in loading stainless-steel lines which, except for possible HF contamination, were considered passive to ClF$_3$O. Therefore, the possibility of hydrogen fluoride catalyzed decomposition
or reaction with the metal was examined by adding substantially anhydrous HF to ClF₃O in stainless steel and in Kel-F. No loss of ClF₃O was observed by infrared analysis even with a ten-fold excess of HF at room temperature. Consequently, the observed decompositions have been attributed to nonpassive line connections.

The nonreaction of ClF₃O in HF is noteworthy in that the protonation of the O atom in ClF₃O seemingly does not occur.

\[
\text{ClF}_3\text{O} + \text{HF} \rightleftharpoons \text{ClF}_3\text{OH}^+ \text{F}^-
\]  

This conclusion is based on previous studies in these laboratories in which it was demonstrated that hydroxyl groups were rapidly attacked by ClF₃O. It is similarly reasoned that a protonated Florox would be highly reactive.

The Nature of the Florox-Nitrosyl Fluoride Complex

The possibility of utilizing ClF₃O in forming solid oxidizers with high-energy, basic reagents such as nitrosyl fluoride, suggested investigation of the ClF₃O complex with fluoride bases. The acidic nature of ClF₃O has already been investigated with some alkali metal fluorides and nitrogen oxyfluorides. The mode of complexing and the ionic nature of these complexes are of interest both from a fundamental point of view as well as having a possible utility in the synthesis of solid oxidizers.

The vapor pressure-temperature behavior of a 1:1 FN₅-CIF₃O mixture indicated a weak complex with a heat of reaction of about -5 kcal from the liquid reagents (Ref. 1). The F¹⁹ n.m.r. of the FN₅-CIF₃O system has been
investigated at low temperatures in hopes of finding evidence for the CIF₄⁻ ion. Addition of a fluoride to CIF₄ would be expected to shift the F¹⁹ resonance to higher fields because of increased shielding. Instead, a broad line was observed at 121 ppm relative to fluorine. This position is approximately that predicted because of exchange between FN0 (-61 ppm) and CIF₃₀ (150 ppm) in a 1:2 ratio. A weak resonance at 86 ppm was attributed to a FC10₂ impurity. Some exchange with FN0 may be responsible for its downfield shift from its previously assigned position at 95 ppm. No resonances attributed to either FN0 or CIF₃₀ were found. The results are summarized in Table 3.

### TABLE 3

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temperature, C</th>
<th>Chemical Shift* (F₂ = 0), ppm</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>FN0-CIF₃₀</td>
<td>-77</td>
<td>121</td>
<td>FN0-CIF₃₀ exchange</td>
</tr>
<tr>
<td>~ 1:1</td>
<td>26</td>
<td>124</td>
<td>FN0-CIF₃₀ exchange</td>
</tr>
<tr>
<td>FN0-CIF₃₀</td>
<td>-60 to -70</td>
<td>150</td>
<td>FC10₂</td>
</tr>
<tr>
<td>~ 1:1</td>
<td>(slow melting)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CIF₃₀</td>
<td>-80</td>
<td>-61</td>
<td></td>
</tr>
<tr>
<td>(neat)</td>
<td>-60 to -80</td>
<td>95</td>
<td></td>
</tr>
</tbody>
</table>

*Shifts were observed relative to an external CFCl₃ standard and recalculated for Φ = 41.4 to obtain shifts relative to F₂.*

R-5883-6
A low-temperature infrared investigation of the NO-CIF$_3$O system has been carried out as well. Although the solid complex may be of the form such as ON$_2$F$_2$ClF$_3$, the evidence obtained more clearly supports a molecular complex involving a fluorine bridge.

On becoming solid, the NO stretching frequency in FN0 and the C10 stretching frequency in CIF$_3$O each increased as seen in Table 4. This suggested that contributions such as NO$_3^-$F$^-$ and CIF$_2$O$^-$F$^-$ were increased slightly. On formation of the solid CIF$_3$O-FN0 complex, the C10 frequency was somewhat reduced while the NO frequency was increased and broadened. These observations suggested a partial transfer of the fluoride of nitrosyl fluoride to CIF$_3$O thus increasing the NO bond order while reducing that of the C10 bond. No meaningful interpretation of CIF or NF infrared data could be made. The N-F solid band was either past the range of the instrument (15.0 microns) or too weak to be observed.

A measure of the relative acidity of CIF$_3$O was estimated by the extent of FN0 fluoride transfer. An acidity range for materials relative to solid ENO was roughly defined by NO$_2$SbF$_6^-$ at one end, NO$_2$ = 2385 cm$^{-1}$, and FN0 solid at the other, NO$_2$ = 1980 cm$^{-1}$ (Ref. 3).

On the basis of the hypochromic shift of the NO frequency in the FN0-CIF$_3$O complex, CIF$_3$O was estimated to be about 15 percent as effective an acid as SbF$_6^-$ toward FN0. The low ionic character of the complex CIF$_3$O-FN0 does not make similar adducts such as CIF$_3$O-FNO$_2$ or CIF$_3$O-NF$_3$O promising as stable solid oxidizer formulations because the expected basic strengths of FNO$_2$ and NF$_3$O are less than that of FNO.

Fluorination of Calcium Hypochlorite

As a possibly more convenient route to CIF$_3$O, the low-temperature fluorination of 95-percent calcium hypochlorite, has been attempted. Also, the
TABLE 4

SELECTED INFRARED FEATURES IN THE FNO–CIF₃₀ SYSTEM

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature, °C</th>
<th>Temperature, cm⁻¹</th>
<th>CIF</th>
<th>ClO</th>
<th>NO</th>
<th>NF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIF₃₀</td>
<td>Ambient</td>
<td>674</td>
<td>1225</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>FNO</td>
<td>Ambient</td>
<td>--</td>
<td>--</td>
<td>1850</td>
<td>765</td>
<td></td>
</tr>
<tr>
<td>CIF₃₀–FNO</td>
<td>Ambient</td>
<td>670</td>
<td>1225</td>
<td>1850</td>
<td>765</td>
<td></td>
</tr>
<tr>
<td>CIF₃₀</td>
<td>-196</td>
<td>685</td>
<td>1250</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>FNO</td>
<td>-196</td>
<td>--</td>
<td>--</td>
<td>1600</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>FNO–CIF₃₀</td>
<td>-196</td>
<td>Broad</td>
<td>1230</td>
<td>2050</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>
search for chlorosyl fluoride was simultaneously pursued. Excess fluorine converted calcium hypochlorite to approximately equal amounts of \( \text{FCIO}_2 \) and \( \text{ClIF}_3 \) at -80°C with smaller amounts of \( \text{FCIO}_3 \). Similar results were obtained with lithium hypochlorite by workers at Picatinny Arsenal (Ref. 4).

In the presence of KF, only \( \text{FCIO}_2 \) and \( \text{ClIF}_3 \) were observed; the \( \text{ClIF}_3 \) was presumably tied up as the potassium fluoride complex. When limiting amounts of fluorine were used instead, the products were \( \text{FCIO}_2 \) and \( \text{ClIF}_3 \).

It is of interest that the covalent hypochlorites \( \text{ClOCl} \) and \( \text{CINO}_2 \), or \( \text{ClF}_2 \) upon fluorination while the ionic species, \( \text{Ca(OCI)}_2 \), fails to react to the same products. These contrasting results suggest not only different mechanisms of fluorination but also that the "neutralization" of charge on an anionic substrate is a primary process in a fluorination reaction.

If we consider the \( \text{OCl}^- \) ion in a fluorination reaction, the primary step in its reaction with \( \text{F}^- \) can be one of two reactions; i.e.

\[
\text{OCl}^- + \text{F}^- \rightarrow \text{OCl} + \text{F}^-
\]  

(10)

\[
\text{OCl}^- + 2\text{F}^- \rightarrow \text{ClOF}_2 - F_2 \rightarrow \text{ClIF}_4
\]

(11)

When the initial step is as in Eq. 10 or a "neutralization," the resulting short-lived \( \text{OCl}^- \) may rapidly decompose to \( \text{Cl}_2 \) and \( \text{O}_2 \). On the other hand, the initial oxidation of the chlorine atom (Eq. 11) always yields a stable anion. Perhaps the concept of charge neutralization can be further tested by examination of the fluorination of \( \text{KClF}_2 \) under flow conditions at temperatures below which neither of the following equilibria may be established:

\[
\text{KClF}_2 \leftrightarrow \text{KF} + \text{ClF}
\]

\[
\text{KClF}_4 \leftrightarrow \text{KF} + \text{ClF}_3
\]
Such reactions are:

\[ \text{ClF}_2^- + F^- \rightarrow \text{ClF}_2 + F^- \quad (12) \]

\[ \cdot \text{ClF}_2 + F^- \rightarrow \text{ClF}_3 \quad (13) \]

\[ \text{ClF}_3^- + \text{KF} \rightarrow \text{KClF}_4 \quad (14) \]

Thus, if the anion \( \text{ClF}_2^- \) is first "neutralized" (Eq. 12) there is a high probability of "liberating" \( \text{ClF}_3 \) from the system (the reaction in Eq. 14 would be slow under flow conditions). On the other hand, the oxidation of the central atom without the neutralization step results in the stable chlorotetrafluoride:

\[ \text{ClF}_2 + F_2 \rightarrow \text{ClF}_4^- \quad (15) \]

**FLOROX COMPLEXES WITH A. ALI METAL FLUORIDES**

The complex of \( \text{ClF}_3 \) and \( \text{KF} \) was prepared by reaction at ambient temperature. Although dissociation pressure was too small to be discernible by direct pressure measurement, continuous slow evolution upon pumping yielded 85 percent of the complexed \( \text{ClF}_3 \) in 19 hours. This complex was, as expected, weaker than the complexes \( \text{KF-ClF}_3 \) and \( \text{CsF-ClF}_3 \).

One of the difficulties associated with the synthesis of Florox from \( \text{Cl}_2\), CsF, and \( F_2 \) is the problem of separating Florox from the by-product \( \text{ClF}_3 \) (Ref. 1). While much of the Florox is obtained as a free gas on warming to room temperature, a considerable portion is retained in the solid phase as the CsF complex. Unprogrammed heating has previously shown that this additional product is liberated readily but is accompanied by
the evolution of CIF$_3$. During this period it has been determined that complexed Florox and CIF$_3$ can be separated effectively by careful thermal dissociation. Thus, at 150°C and with pumping, nearly all the Florox was evolved without any CIF$_3$. At 200°C a small additional amount of Florox was liberated, contaminated with trace amounts of CIF$_3$.

$$\text{CsClF}_4 \xrightarrow{130\degree C} \text{CsF} + \text{ClF}_2$$  \hspace{1cm} (16)

$$\text{CsClF}_4 \xrightarrow{150\degree C} \text{No ClF}_3$$  \hspace{1cm} (17)

**Reduction of Florox**

The reduction of CIF$_3$O with AgF was considered as in the following equation:

$$\text{ClF}_3O + 2\text{AgF} \rightarrow \text{FCIO} + 2\text{AgF}_2$$  \hspace{1cm} (18)

Accordingly, Florox was passed over hot silver fluoride at 135°C and the products were quenched immediately thereafter. Partial reaction gave chlorine and chloryl fluoride as the only products.

In other attempts to synthesize FCIO by chemical reduction of CIF$_3$O, Cl$_2$ and Cl$_2$O were utilized as potential reducing agents. With Cl$_2$, no reaction was observed at ambient temperature with either CIF$_3$O or its CsF complex. A series of reactions between Cl$_2$O and both CIF$_3$O and its CsF complex were run in varying reactant ratios at ambient temperature and at -18°C. In all cases the products were ClF and FCIO$_2$ in an overall reaction best described by:

$$\text{Cl}_2O + \text{CsClF}_4 \rightarrow \text{CsClF}_2 + \text{ClF} + \text{FCIO}_2$$  \hspace{1cm} (19)
It is possible that the sequence involves formation of the desired FC10 followed by its disproportionation:

\[
\text{Cl}_2\text{O} + \text{CsClF}_4 \rightarrow \text{CsClF}_2 + 2\text{FC10} \quad \text{(20)}
\]

\[
2\text{FC10} \rightarrow \text{FC10}_2 + \text{ClF} \quad \text{(21)}
\]

If the intermediate FC10 was generated, in no case was it stabilized through complex formation with CsF.

**Fluorination of Cl\textsubscript{2}O**

Because the observed unknown thought to be FC10 arises from the pyrolysis of the fluorination products of Cl\textsubscript{2}O, it is either formed by the pyrolysis or released from its complex, MCIF\textsubscript{2}O, by pyrolysis. Because the desired FC10 may be strongly complexed, even by KF, it was decided to explore the synthesis of FC10 from fluorination of Cl\textsubscript{2}O both in the presence of NaF and in the absence of any alkali metal fluoride. Instead of producing FC10, however, the low-temperature fluorination of Cl\textsubscript{2}O in both cases gave good yields (listed elsewhere in this report) of ClF\textsubscript{3}O. Therefore, it was decided to examine the action of the milder fluorinating agents, ClF\textsubscript{3} and ClF\textsubscript{5}, on alkali fluoride complexed Cl\textsubscript{2}O.

In the case of ClF\textsubscript{5}, reactions were conducted at -50 and 0 C with the preformed CsF·Cl\textsubscript{2}O complex and excess ClF\textsubscript{5}. At the lower temperature, incomplete reaction of the Cl\textsubscript{2}O was observed but at 0 C, all the Cl\textsubscript{2}O was consumed. No new products were found. The results of the reactions were in good agreement with the following stoichiometry:

\[
2\text{CsF}·\text{Cl}_2\text{O} + \text{ClF}_5 \xrightarrow{0 \degree C} 2\text{CsClF}_2 + 2\text{ClF} + \text{FC10}_2 \quad \text{(22)}
\]
The ClF₃ fluorinations utilized NaF to complex the Cl₂O because CsF was expected to complex ClF₃ faster than reaction with Cl₂O would occur. Again, no products of interest were formed. Correcting for the excess ClF₃, the complete reaction of Cl₂O agreed closely with the indicated equation:

\[
\text{Cl}_2\text{O} + \text{ClF}_3 \xrightarrow{-50 \degree C \text{ NaF}} 2\text{ClF} + \text{FCIO}_2
\]  

(23)

While both these reactions could be explained by the formation and subsequent disproportionation of FCIO:\n
\[
2\text{FCIO} \rightarrow \text{ClF} + \text{FCIO}_2
\]  

(24)

no direct evidence for this was obtained.

Earlier (Ref. 2) it was found that in situ fluorination of the products from the reaction of HgO and Cl₂ gave traces of an unknown which has been designated Compound C and may be FCIO. Also formed were ClF, ClF₃, and ClF₅. Because of the possible deleterious effect on concomitant HF formation to new F, Cl, O compounds, this reaction was repeated using vacuum dried HgO. Two reactions at -80 C were run and little, if any, HF was formed. The first reaction gave small quantities of Compound C but most of the initial Cl₂ was recovered. This latter result is attributed to decomposition of most of the Cl₂O prior to the fluorination step. Because only small amounts of the unknown were obtained and also because experience has shown that it is easily decomposed, no separation was attempted. Instead, an indirect proof of the nature of the unknown will be tried. The unknown is contaminated with ClF and small amounts
of FCIO₂ and ClF₅ which will not fluorinate to yield Florox. But Com-
pound C, if it is FC10, would be expected to fluorinate readily to ClF₃O.

\[
\text{CsF·FC10} + F₂ \rightarrow \text{CsF} + \text{ClF₃O} \quad (25)
\]

A test is now in progress.

ATTEMPTS AT NEW OXYHALOGEN FLUORIDE OXIDIZERS

Florox and Oxygen

The reaction between oxygen and ClF₃O has been studied both as a possible
route to the unknown oxidizer ClF₃O₂ and to determine if oxygen contami-
nation yields FC10₂.

\[
\text{ClF₃O} + 1/2 \text{O}_2 \rightarrow \text{ClF₃O}_2 \quad (26)
\]

\[
\text{ClF₃O} + 1/2 \text{O}_2 \rightarrow \text{FC10}_2 + F₂ \quad (27)
\]

When ClF₃O (both liquid and vapor) was exposed to O₂ at temperatures from
ambient to -196°C, no reaction occurred as demonstrated both by lack of
oxygen uptake and by an unchanged infrared spectrum.

Reaction of AsF₅ and Cl₁₀

As part of the effort to examine various single bonded Cl-O species as
possible precursors to oxychlorine fluoride or Florox, an investigation
of the reported compound, $\text{CIO} \cdot \text{AsF}_5$ (Ref. 5) was initiated. The reactions reported in the literature, together with the proposed fluorinations, are as follows:

$$\text{Cl}_2\text{O} + \text{AsF}_5 \xrightarrow{-80 \degree C} \text{Cl}_2\text{O} \cdot \text{AsF}_5 \quad (28)$$

$$\text{Cl}_2\text{O} \cdot \text{AsF}_5 \xrightarrow{-50 \degree C} 1/2 \text{Cl}_2 + \text{CIO} \cdot \text{AsF}_5 \quad (29)$$

$$\text{CIO} \cdot \text{AsF}_5 + \text{F}_2 \xrightarrow{\text{R.T.}} \text{FCIO} / \text{ClF}_3 \cdot \text{O} + \text{AsF}_5 \quad (30)$$

At the outset of this work, it was noted that there is a literature discrepancy with regard to the infrared spectrum of $\text{AsF}_5$. Samples of $\text{AsF}_5$ (Ozark-Mahoning) gave an infrared spectrum nearly identical with that reported for $\text{AsOF}_3$ rather than $\text{AsF}_5$ (Ref. 6). But these vendor samples also gave the same infrared spectrum as that obtained for $\text{AsF}_5$ according to the unpublished thesis of L. K. Akers (Ref. 7). To establish the character of the supplied material, a vapor phase molecular weight determination was made. This gave a value of 169.7 grams/mol vs 169.9 for $\text{AsF}_5$ and 147.9 for $\text{AsOF}_3$. The mass spectrum of the material showed it to be 90-percent $\text{AsF}_5$ with approximately 10-percent As, O, F species. Because a vapor phase chromatogram showed only one component, it appears the sample was pure $\text{AsF}_5$. The As, O, and F impurities undoubtedly arose through reactions of the $\text{AsF}_5$ with an incompletely dry glass inlet system of the mass spectrometer, because HF and SiF$_4$ were also found in the mass spectrum.

Thus, the infrared spectrum reported by Akers (Ref. 7) is correct. Mitra’s spectrum for $\text{AsOF}_3$ (Ref. 6) consists of $\text{AsF}_5$ and the background produced on NaCl infrared cell windows after contact with $\text{AsF}_5$. Finally, Mitra’s
infrared spectrum for AsF₅ is identical in all respects with this window background band only (705 cm⁻¹). This was shown experimentally and it is probable that this band is attributable to an AsF₆⁻ species. For example, K + AsF₆⁻ salt (Ref. 8) has its strong band at 694 cm⁻¹ vs the 705 cm⁻¹ observed for this peak.

The reaction of Cl₂O and AsF₅ when examined at -80°C did not proceed as indicated in the literature. Mixing the two reactants at -196°C and warming to -80°C resulted in the formation of a dark red solid which, over a period of several hours, became almost black. Pumping on the sample at this point resulted in the evolution of Cl₂ (with little or no -196°C noncondensables). This Cl₂ represented most of the Cl in the original Cl₂O. Further warming to room temperature caused additional evolution of small amounts of Cl₂ and ClO₂. When excess Cl₂O was used, no AsF₅ was recovered in the volatile phase. Remaining at room temperature was a white solid which exhibited two infrared active bands at 7.9 and 14.6 microns. It fumed in moist air and exploded on contact with acid KI. Because the total amount of evolved Cl₂ was near that contained in the original Cl₂O, the composition of this solid approached AsF₅O. Fluorination of the reaction mixture from which only part of the Cl₂ was removed gave the same white solid product on work-up. Additional characterization work is presently in progress to elucidate the exact character of this new solid material.

The Fluorination of Br₂O

The synthesis of new oxybromine fluorides using Br₂O as a starting material was pursued. This work was based on the analogous, proven...
Cl₂O reactions which yielded oxychlorine trifluoride. Fluorination of 
MF complexed Br₂O at -50°C gave as volatile products, BrF₃, unreacted Br₂, 
and traces of unstable, unidentified material. While it was anticipated 
that the sought Br, F, O compounds might remain as complexed solids after 
the fluorination, pyrolysis up to ~400°C did not yield any new products. 
The failure of this reaction may be caused by the inherent instability 
of the starting material or thermal degradation of the desired products 
upon pyrolysis.

Because chlorine nitrate has also been shown to be a useful precursor to 
ClF₃O, it was decided to utilize bromine nitrate, BrONO₂, as an inter-
mediate in the preparation of new oxybromine fluorides. This compound 
offered two advantages over Br₂O. It is more stable than Br₂O, decompos-
ing around 0°C vs approximately -40°C for Br₂O. Also, based on the high 
yields of Florox obtained by fluorination of uncomplexed ClONO₂, the 
analogous application of BrONO₂ can be expected to give similar results 
while eliminating the necessity of complexing the desired products.

The synthesis of BrONO₂ was conducted according to the reported litera-
ture procedure (Ref. 9).

\[ \text{Br}_2 + \text{Cl}_2 \xrightarrow{\text{UV}} 2\text{BrCl} \]  
(31)

\[ \text{BrCl} + \text{ClNO}_3 \rightarrow \text{BrNO}_3 + \text{Cl}_2 \]  
(32)

Fluorination of the product from which Cl₂ and excess ClNO₃ were removed 
is in progress at -50°C.
CESIUM FLUORIDE-CHLORINE MONOXIDE COMPLEX STUDIES

Further investigation of the stoichiometry of CsF-Cl₂O complexes has given reproducible ratios in contrast to previously reported experiments (Ref. 1). To determine the maximum ratio Cl₂O/CsF in the complex, formed at -80 C, large excesses of Cl₂O were stored over CsF for several days and then pumped on overnight at -80 C to remove the uncomplexed Cl₂O. Experimental Cl₂O/CsF ratios of 1.5, 1.42, 1.48, and 1.54 were obtained. In another run, pumping at -80 C for 3-1/2 days resulted in a 1.49 Cl₂O/CsF stoichiometry. Only 0.17 Cl₂O per CsF was removed after overnight pumping. It is apparent that a slow forming complex with a Cl₂O/CsF ratio at or near 1.5 is formed at -80 C. A sample of the complex was exposed to the air, hit with a hammer, and heated with a torch with no explosive results.
LOW-TEMPERATURE INFRARED CELL

The low-temperature infrared experiments were determined in a simple, infrared cell which was constructed as described elsewhere (Ref. 10). The completed assembled cell fits conveniently into a Perkin-Elmer 137 Infracord spectrometer and has a cooling capacity of 2 liters. It can be used at temperatures as low as 77 K and is relatively easy to use with slush baths because the cooling flask is insulated with 3-inch solid foam. The inner window of AgCl fits into a copper optical blank holder. The body is glass and is fitted with two outside AgCl windows.

Florox complexes were preformed in a metal vacuum line and condensed onto the inner AgCl window at -196 °C by means of a copper entrance tube directed at the window.

SYNTHESIS OF FLOROX

Oxychlorine trifluoride, ClF$_3$O, was synthesized by fluorination of Cl$_2$O at -80 °C in the presence and absence of added alkali metal fluoride. In most cases the reaction was conducted in a 300-milliliter stainless-steel cylinder previously passivated by exposure to at least one atmosphere of fluorine for a period of at least 16 hours. Chlorine monoxide and fluorine were introduced into the reactor by distillation in vacuo. Separation of the ClF$_3$O product from side products was achieved in all cases by fractional condensation.
Excess fluorine and any produced oxygen passed -196 C. The next most volatile side products were FClO₂, ClF, and Cl₂ and were removed by passage through a cold trap at -95 C with the ClF₃0 being retained. Chlorine trifluoride was partially retained at -95 C; therefore, removal of ClF₃ was achieved by repeated passage through a trap held at -80 C, with some loss of ClF₃0.
REFERENCES


4. TR 3285, *Oxidizer Chemistry*, AMCMS 5221.11.145.02, Liquid Rocket Propulsion Laboratory, U. S. Army Munitions Command, Picatinny Arsenal, Dover, New Jersey, November 1965, CONFIDENTIAL.


Oxychlorine trifluoride has been synthesized from ClO\textsubscript{2} + F\textsubscript{2} in the presence of CsF, KBF\textsubscript{4}, KF, and NaF as well as in their absence. Oxychlorine trifluoride has also been synthesized from uncomplexed chlorine nitrate in 84-percent yield. Fluorination in situ of the ClO\textsubscript{2} + AgO reaction products has also produced ClF\textsubscript{3}. Florox was stable in excess hydrogen fluoride or excess oxygen at ambient temperature and stable to 5-day storage at 71 C in Monel. In a flow system, thermal decomposition of Florox started near 700 C and was complete below 786 C. The predominant product recovered above 300 C was chlorine monofluoride. The complex between Florox and CsF dissociated below 150 C and allowed complete removal of contaminant ClF\textsubscript{3} as the remaining nonvolatile solid CsClF\textsubscript{4}. Investigation of the FNO complex of ClF\textsubscript{3} by F\textsuperscript{19} n.m.r. showed exchange at -77 C; an infrared study at -196 C indicated the complex to be predominantly covalent. Attempts to reduce ClF\textsubscript{3} to FCIO have been unsuccessfully attempted with AgF, Cl\textsubscript{2}, and ClO\textsubscript{2}. Fluorination of ClO\textsubscript{2} by F\textsubscript{2}, ClF\textsubscript{3}, and ClF\textsubscript{2} has also failed to produce FCIO. As a new route to oxychlorine fluorides, the reported intermediate ClO-AsF\textsubscript{5} has been investigated. The synthesis of new bromine oxyfluorides from Br\textsubscript{2}0 complexes failed, giving mainly BrF\textsubscript{5}. Bromine nitrate has been prepared as a possible alternate precursor to BrF\textsubscript{3} or BrF\textsubscript{5}. Although the nature of the bonding in the ClO- CsF complex has not been clarified, a reproducible composition, CsF-1.5 Cl\textsubscript{2}0 has been obtained near -80 C. (C)
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