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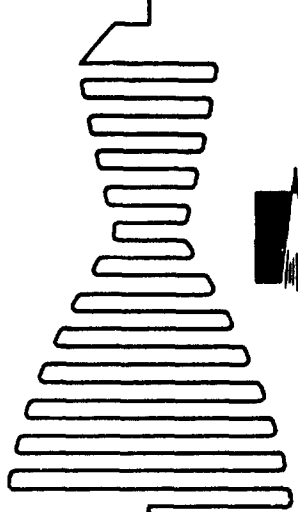

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QUARTERLY PROGRESS REPORT, INORGANIC HALOGEN OXIDIZERS

(29 November 1965 through 28 February 1966)

Group 4
Downgraded at 3-Year Intervals
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Contract Nonr 4428(00)

Sponsored by Advanced Research Projects Agency
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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 Nonr 4428(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 $Cl_2O + F_2$ in the presence of CsF, RbF, KF, and NaF as well as in their absence. Although the complexes of Cl_2O with CsF, RbF, and KF were probably involved, no substantial increase in conversion to Florox was obtained over the systems with uncomplexed Cl_2O. Oxychlorine trifluoride has also been synthesized from uncomplexed chlorine nitrate in 84-percent yield. Fluorination in situ of the $Cl_2 + HgO$ reaction products has also produced ClF_3O.

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 300 C and was complete below 586 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_3 as the remaining nonvolatile solid $CsClF_4$. The complex between ClF_3O and KF was less stable, dissociating slowly with pumping at ambient temperature. Investigation of the FNO complex of ClF_3O by F^{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_3O to FClO have been unsuccessfully attempted with AgF, Cl_2, and Cl_2O. Fluorination of Cl_2O by F_2, ClF_3, and ClF_5 has also failed to produce FClO. 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_3O.

As a new route to oxychlorine fluorides, the reported intermediate $ClO{\cdot}AsF_5$ 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_2O complexes failed, giving mainly BrF_5. Bromine nitrate has been prepared as a possible alternate precursor to BrF_3O or BrF_5O.

Although the nature of the bonding in the $Cl_2O{\cdot}CsF$ complex has not been clarified, a reproducible composition, $CsF{\cdot}1.5\ Cl_2O$ has been obtained near -80 C.

(Confidential Abstract)

CONTENTS

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 Cl_2O and $ClONO_2$ in Florox syntheses. These studies not only gave yield data of interest but also provided working quantities of ClF_3O for further chemical investigation.

The studies on ClF_3O are of a dual nature. One area is concerned with both the possible redox reaction of ClF_3O 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 Br_2O and $BrONO_2$. These studies are logical extensions in the area of interhalogen derivatives as dictated by the ease of formation of ClF_3O.

DISCUSSION

FLOROX STUDIES

Florox Synthesis from Cl_2O

The preparation of ClF_3O by fluorination of Cl_2O 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 ClF_3O 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

Alkali Metal Fluoride	Percent Yield	Side Products
CsF	0 to 82	$FClO_2$, ClF_5
RbF	> 25	$FClO_2$, ClF_3
KF	43, 29	$FClO_2$, ClF_5, ClF
NaF	73, 81	$FClO_2$, ClF
None	39, 63	$FClO_2$, ClF, ClF_5

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 Cl_2O in metal reaction systems were kept substantially the same.

Synthesis of Florox from $ClNO_3$

The synthesis of Florox by fluorination of the CsF complex of $ClNO_3$ was described in earlier reports (Ref. 1 and 2). It was of interest also to utilize $ClONO_2$ as an intermediate for the preparation of FClO. Accordingly, a reaction was attempted using uncomplexed $ClNO_3$ and F_2 at -80 C. After several days it was found that Florox was formed in 84-percent yield:

$$ClONO_2 + 2F_2 \longrightarrow ClF_3O + FNO_2 \qquad (1)$$

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 ClF_3O were eliminated.

Synthesis from $HgCl_2$-Cl_2O

The synthesis of ClF_3O from Cl_2O in the past has required the vacuum transfer of Cl_2O from an apparent $Cl_2O \cdot HgCl_2$ complex with warming to another reaction vessel. It has been found that if the solid products from the HgO + Cl_2 reaction are fluorinated in situ, ClF_3O and ClF_3 are produced. This is the first time Florox has been prepared in this manner:

$$HgCl_2 \cdot Cl_2O + F_2 \longrightarrow ClF_3O + ClF_3 \qquad (2)$$

Thermal Decomposition of Florox

Pyrolysis of the nonvolatile solid formed by low-temperature fluorination of the Cl_2O-CsF complex has, on at least three occasions, yielded traces of an unknown species thought to be FClO (Compound C). It was thought that Compound C might result from pyrolysis of ClF_3O as in Eq. 3.

$$ClF_3O \longrightarrow FClO + F_2 \qquad (3)$$

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 ClF_3O does not occur to a large extent under these flow conditions at temperatures less than 400 C. Products found at 300 C were ClF_3 and possibly

TABLE 2

PYROLYSIS OF ClF_3O

Temperature, C	Percent Florox Recovered	Condensable Product Formed at -196 C (as percent of Florox passed)	Products
300	--	~ 1.5	ClF_3, $FClO_2$
400	99	2	ClF, trace Compound C
450	82	16	ClF
500	46	54	ClF
500	38	62	$FClO_2$, ClF
585	0	98	ClF, trace Compound C

$FClO_2$. At 400 C, small amounts of ClF as well as ClF_3 were found, and at higher temperatures ClF 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 ClF (or ClF_3) per molecule of decomposed ClF_3O according to the overall reaction:

$$ClF_3O \longrightarrow ClF + F_2 + 1/2\ O_2 \qquad (4)$$

Possible decomposition routes involve either of the following pairs:

$$ClF_3O \longrightarrow ClF_3 + 1/2\ O_2 \qquad (5)$$

$$ClF_3 \longrightarrow ClF + 1/2\ F_2 \qquad (6)$$

or

$$ClF_3O \longrightarrow FClO + F_2 \qquad (7)$$

$$FClO \longrightarrow ClF + 1/2\ O_2 \qquad (8)$$

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_3O have occurred at Rocketdyne in loading stainless-steel lines which, except for possible HF contamination, were considered passive to ClF_3O. Therefore, the possibility of hydrogen fluoride catalyzed decomposition

or reaction with the metal was examined by adding substantially anhydrous HF to ClF_3O in stainless steel and in Kel-F. No loss of ClF_3O 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 ClF_3O in HF is noteworthy in that the protonation of the O atom in ClF_3O seemingly does not occur.

$$ClF_3O + HF \rightleftharpoons ClF_3OH^+ F^- \qquad (9)$$

This conclusion is based on previous studies in these laboratories in which it was demonstrated that hydroxyl groups were rapidly attacked by ClF_5. It is similarly reasoned that a protonated Florox would be highly reactive.

The Nature of the Florox–Nitrosyl Fluoride Complex

The possibility of utilizing ClF_3O in forming solid oxidizers with high-energy, basic reagents such as nitrosyl fluoride, suggested investigation of the ClF_3O complex with fluoride bases. The acidic nature of ClF_3O 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 FNO–ClF_3O mixture indicated a weak complex with a heat of reaction of about −5 kcal from the liquid reagents (Ref. 1). The F^{19} n.m.r. of the FNO–ClF_3O system has been

investigated at low temperatures in hopes of finding evidence for the ClF_4O^- ion. Addition of a fluoride to ClF_3O would be expected to shift the F^{19} 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 FNO (-61 ppm) and ClF_3O (150 ppm) in a 1:2 ratio. A weak resonance at 86 ppm was attributed to a $FClO_2$ impurity. Some exchange with FNO may be responsible for its downfield shift from its previously assigned position at 95 ppm. No resonances attributed to either FNO or ClF_3O were found. The results are summarized in Table 3.

TABLE 3

F^{19} N.M.R. SPECTRA OF OXYCHLORINE TRIFLUORIDE-NITROSYL FLUORIDE

Complex	Temperature, C	Chemical Shift* (F_2 = 0), ppm	Assignment
FNO-ClF_3O	-77	121	FNO-ClF_3O exchange
~ 1:1		86 (minor)	$FClO_2$
FNO-ClF_3O	26	124	FNO-ClF_3O exchange
~ 1:1		86 (minor)	$FClO_2$
ClF_3O (neat)	-60 to -70 (slow melting)	150	
FNO	-80	-61	
$FClO_2$	-60 to -80	95	

*Shifts were observed relative to an external $CFCl_3$ standard and recalculated for ϕ = 414 to obtain shifts relative to F_2.

A low-temperature infrared investigation of the FNO-ClF_3O system has been carried out as well. Although the solid complex may be of the form such as $ON\begin{smallmatrix}O\\F\end{smallmatrix}ClF_3$, the evidence obtained more clearly supports a molecular complex involving a fluorine bridge.

On becoming solid, the NO stretching frequency in FNO and the ClO stretching frequency in ClF_3O each increased as seen in Table 4. This suggested that contributions such as NO^+F^- and $ClF_2O^+F^-$ were increased slightly. On formation of the solid ClF_3O-FNO complex, the ClO 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 ClF_3O thus increasing the NO bond order while reducing that of the ClO bond. No meaningful interpretation of ClF 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 ClF_3O was estimated by the extent of FNO fluoride transfer. An acidity range for materials relative to solid FNO was roughly defined by $NO^+SbF_6^-$ at one end, NO = 2385 cm^{-1}, and FNO solid at the other, NO = 1980 cm^{-1} (Ref. 3).

On the basis of the hypochromic shift of the NO frequency in the FNO-ClF_3O complex, ClF_3O was estimated to be about 15 percent as effective an acid as SbF_5 toward FNO. The low ionic character of the complex ClF_3O-FNO does not make similar adducts such as ClF_3O-FNO_2 or ClF_3O-NF_3O promising as stable solid oxidizer formulations because the expected basic strengths of FNO_2 and NF_3O are less than that of FNO.

Fluorination of Calcium Hypochlorite

As a possibly more convenient route to ClF_3O, the low-temperature fluorination of 95-percent calcium hypochlorite, has been attempted. Also, the

TABLE 4

SELECTED INFRARED FEATURES IN THE FNO-ClF_3O SYSTEM

Sample	Temperature, C	Vibration, cm^{-1}			
		ClF	ClO	NO	NF
ClF_3O	Ambient	674	1225	--	--
FNO	Ambient	--	--	1850	765
ClF_3O-FNO	Ambient	670	1225	1850	765
ClF_3O	-196	685	1250	--	--
FNO	-196	--	--	1990	?
FNO-ClF_3O	-196	Broad	1230	2050	?

search for chlorosyl fluoride was simultaneously pursued. Excess fluorine converted calcium hypochlorite to approximately equal amounts of $FClO_2$ and ClF_3 at -80 C with smaller amounts of $FClO_3$. Similar results were obtained with lithium hypochlorite by workers at Picatinny Arsenal (Ref. 4). In the presence of KF, only $FClO_2$ and $FClO_3$ were observed; the ClF_3 was presumably tied up as the potassium fluoride complex. When limiting amounts of fluorine were used instead, the products were $FClO_2$ and [illegible]

It is of interest that the covalent hypochlorites ClOCl and $ClONO_2$ f ClF_3O upon fluorination while the ionic species, $Ca(OCl)_2$, fails to reac 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 ^-OCl ion in a fluorination reaction, the primary step in its reaction with F· can be one of two reactions; i.e.

$$^-OCl + F\cdot \longrightarrow OCl + F^- \qquad (10)$$

$$^-OCl + 2F\cdot \longrightarrow \bar{O}ClF_2 \xrightarrow{F_2} \bar{O}ClF_4 \qquad (11)$$

When the initial step is as in Eq. 10 or a "neutralization," the resulting short-lived OCl may rapidly decompose to Cl_2 and 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 $KClF_2$ under flow conditions at temperatures below which neither of the following equilibria may be established:

$$KClF_2 \rightleftharpoons KF + ClF$$

$$KClF_4 \rightleftharpoons KF + ClF_3$$

Such reactions are:

$$ClF_2^- + F\cdot \longrightarrow \cdot ClF_2 + F^- \quad (12)$$

$$\cdot ClF_2 + F\cdot \longrightarrow ClF_3 \quad (13)$$

$$ClF_3 + KF \longrightarrow KClF_4 \quad (14)$$

Thus, if the anion ClF_2^- is first "neutralized" (Eq. 12) there is a high probability of "liberating" 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:

$$ClF_2^- + F_2 \longrightarrow ClF_4^- \quad (15)$$

FLOROX COMPLEXES WITH ALL METAL FLUORIDES

The complex of ClF_3O and 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 ClF_3O in 19 hours. This complex was, as expected, weaker than the complexes KF-ClF_3 and CsF-ClF_3O.

One of the difficulties associated with the synthesis of Florox from Cl_2O, CsF, and F_2 is the problem of separating Florox from the by-product 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 ClF_3. During this period it has been determined that complexed Florox and ClF_3 can be separated effectively by careful thermal dissociation. Thus, at 150 C and with pumping, nearly all the Florox was evolved without any ClF_3. At 200 C a small additional amount of Florox was liberated, contaminated with trace amounts of ClF_3.

$$CsClF_4O \xrightarrow{150\ C} CsF + ClF_3O \qquad (16)$$

$$CsClF_4 \xrightarrow{150\ C} \text{No } ClF_3 \qquad (17)$$

Reduction of Florox

The reduction of ClF_3O with AgF was considered as in the following equation:

$$ClF_3O + 2AgF \longrightarrow FClO + 2AgF_2 \qquad (18)$$

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 FClO by chemical reduction of ClF_3O, Cl_2 and Cl_2O were utilized as potential reducing agents. With Cl_2, no reaction was observed at ambient temperature with either ClF_3O or its CsF complex. A series of reactions between Cl_2O and both ClF_3O 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 $FClO_2$ in an overall reaction best described by:

$$Cl_2O + CsClF_4O \longrightarrow CsClF_2 + ClF + FClO_2 \qquad (19)$$

It is possible that the sequence involves formation of the desired FClO followed by its disproportionation:

$$Cl_2O + CsClF_4O \longrightarrow CsClF_2 + 2FClO \quad (20)$$

$$2FClO \longrightarrow FClO_2 + ClF \quad (21)$$

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

Fluorination of Cl_2O

Because the observed unknown thought to be FClO arises from the pyrolysis of the fluorination products of Cl_2O, it is either formed by the pyrolysis or released from its complex, $MClF_2O$, by pyrolysis. Because the desired FClO may be strongly complexed, even by KF, it was decided to explore the synthesis of FClO from fluorination of Cl_2O both in the presence of NaF and in the absence of any alkali metal fluoride. Instead of producing FClO, however, the low-temperature fluorination of Cl_2O in both cases gave good yields (listed elsewhere in this report) of ClF_3O. Therefore, it was decided to examine the action of the milder fluorinating agents, ClF_5 and ClF_3, on alkali fluoride complexed Cl_2O.

In the case of ClF_5, reactions were conducted at -50 and 0 C with the preformed $CsF \cdot Cl_2O$ complex and excess ClF_5. At the lower temperature, incomplete reaction of the Cl_2O was observed but at 0 C, all the Cl_2O was consumed. No new products were found. The results of the reactions were in good agreement with the following stoichiometry:

$$2CsF \cdot Cl_2O + ClF_5 \xrightarrow{0\ C} 2CsClF_2 + 2ClF + FClO_2 \quad (22)$$

The ClF_3 fluorinations utilized NaF to complex the Cl_2O because CsF was expected to complex ClF_3 faster than reaction with Cl_2O would occur. Again, no products of interest were formed. Correcting for the excess ClF_3, the complete reaction of Cl_2O agreed closely with the indicated equation:

$$Cl_2O + ClF_3 \xrightarrow[NaF]{-50\ C} 2ClF + FClO_2 \qquad (23)$$

While both these reactions could be explained by the formation and subsequent disproportionation of FClO;

$$2FClO \longrightarrow ClF + FClO_2 \qquad (24)$$

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 Cl_2 gave traces of an unknown which has been designated Compound C and may be FClO. Also formed were ClF, ClF_3, and ClF_5. 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 Cl_2 was recovered. This latter result is attributed to decomposition of most of the Cl_2O 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 $FClO_2$ and ClF_5 which will not fluorinate to yield Florox. But Compound C, if it is FClO, would be expected to fluorinate readily to ClF_3O.

$$CsF \cdot FClO + F_2 \longrightarrow CsF + ClF_3O \qquad (25)$$

A test is now in progress.

ATTEMPTS AT NEW OXYHALOGEN FLUORIDE OXIDIZERS

Florox and Oxygen

The reaction between oxygen and ClF_3O has been studied both as a possible route to the unknown oxidizer ClF_3O_2 and to determine if oxygen contamination yields $FClO_2$.

$$ClF_3O + 1/2\ O_2 \longrightarrow ClF_3O_2 \qquad (26)$$

$$ClF_3O + 1/2\ O_2 \longrightarrow FClO_2 + F_2 \qquad (27)$$

When ClF_3O (both liquid and vapor) was exposed to O_2 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 AsF_5 and Cl_2O

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, $ClO \cdot AsF_5$ (Ref. 5) was initiated. The reactions reported in the literature, together with the proposed fluorinations, are as follows:

$$Cl_2O + AsF_5 \xrightarrow{-80\ C} Cl_2O \cdot AsF_5 \quad (28)$$

$$Cl_2O \cdot AsF_5 \xrightarrow{-50\ C} 1/2\ Cl_2 + ClO \cdot AsF_5 \quad (29)$$

$$ClO \cdot AsF_5 + F_2 \xrightarrow{R.T.} FClO/ClF_3O + AsF_5 \quad (30)$$

At the outset of this work, it was noted that there is a literature discrepancy with regard to the infrared spectrum of AsF_5. Samples of AsF_5 (Ozark-Mahoning) gave an infrared spectrum nearly identical with that reported for "$AsOF_3$" rather than AsF_5 (Ref. 6). But these vendor samples also gave the same infrared spectrum as that obtained for 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/mole vs 169.9 for AsF_5 and 147.9 for $AsOF_3$. The mass spectrum of the material showed it to be 90-percent 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 AsF_5. The As, O, and F impurities undoubtedly arose through reactions of the 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 "$AsOF_3$" (Ref. 6) consists of AsF_5 and the background produced on NaCl infrared cell windows after contact with AsF_5. Finally, Mitra's

infrared spectrum for AsF_5 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 AsF_6^- species. For example, K + AsF_6^- salt (Ref. 8) has its strong band at 694 cm^{-1} vs the 705 cm^{-1} observed for this peak.

The reaction of Cl_2O and AsF_5 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 Cl_2 (with little or no -196 C noncondensables). This Cl_2 represented most of the Cl in the original Cl_2O. Further warming to room temperature caused additional evolution of small amounts of Cl_2 and ClO_2. When excess Cl_2O was used, no AsF_5 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 Cl_2 was near that contained in the original Cl_2O, the composition of this solid approached $AsF_5 \cdot O$. Fluorination of the reaction mixture from which only part of the Cl_2 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 Br_2O

The synthesis of new oxybromine fluorides using Br_2O as a starting material was pursued. This work was based on the analogous, proven

Cl_2O reactions which yielded oxychlorine trifluoride. Fluorination of MF complexed Br_2O at -50 C gave as volatile products, BrF_5, unreacted Br_2, 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 ClF_3O, it was decided to utilize bromine nitrate, $BrONO_2$, as an intermediate in the preparation of new oxybromine fluorides. This compound offered two advantages over Br_2O. It is more stable than Br_2O, decomposing around 0 C vs approximately -40 C for Br_2O. Also, based on the high yields of Florox obtained by fluorination of uncomplexed $ClONO_3$, the analogous application of $BrONO_2$ can be expected to give similar results while eliminating the necessity of complexing the desired products.

The synthesis of $BrONO_2$ was conducted according to the reported literature procedure (Ref. 9).

$$Br_2 + Cl_2 \xrightarrow{UV} 2BrCl \qquad (31)$$

$$BrCl + ClNO_3 \longrightarrow BrNO_3 + Cl_2 \qquad (32)$$

Fluorination of the product from which Cl_2 and excess $ClNO_3$ were removed is in progress at -50 C.

CESIUM FLUORIDE-CHLORINE MONOXIDE COMPLEX STUDIES

Further investigation of the stoichiometry of CsF-Cl_2O complexes has given reproducible ratios in contrast to previously reported experiments (Ref. 1). To determine the maximum ratio Cl_2O/CsF in the complex, formed at -80 C, large excesses of Cl_2O were stored over CsF for several days and then pumped on overnight at -80 C to remove the uncomplexed Cl_2O. Experimental Cl_2O/CsF ratios of 1.3, 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 Cl_2O/CsF stoichiometry. Only 0.17 Cl_2O per CsF was removed after overnight pumping. It is apparent that a slow forming complex with a Cl_2O/CsF ratio at or near 1.3 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.

EXPERIMENTAL EFFORT

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_3O, was synthesized by fluorination of Cl_2O 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_3O 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 $FClO_2$, ClF, and Cl_2 and were removed by passage through a cold trap at -95 C with the ClF_3O being retained. Chlorine trifluoride was partially retained at -95 C; therefore, removal of ClF_3 was achieved by repeated passage through a trap held at -80 C, with some loss of ClF_3O.

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13 ABSTRACT Oxychlorine trifluoride has been synthesized from $Cl_2O + F_2$ in the presence of CsF, RbF, 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 Cl_2 + HgO reaction products has also produced ClF_3O. 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 300 C and was complete below 586 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_3 as the remaining nonvolatile solid $CsClF_4$. Investigation of the FNO complex of ClF_3O by F^{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_3O to FClO have been unsuccessfully attempted with AgF, Cl_2, and Cl_2O. Fluorination of Cl_2O by F_2, ClF_3, and ClF_5 has also failed to produce FClO. As a new route to oxychlorine fluorides, the reported intermediate $ClO{\cdot}AsF_5$ has been investigated. The synthesis of new bromine oxyfluorides from Br_2O complexes failed, giving mainly BrF_5. Bromine nitrate has been prepared as a possible alternate precursor to BrF_3O or BrF_5O. Although the nature of the bonding in the $Cl_2O{\cdot}CsF$ complex has not been clarified, a reproducible composition, $CsF{\cdot}1.5\ Cl_2O$ has been obtained near -80 C. (C)

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