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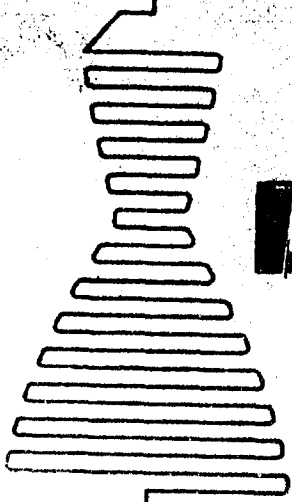
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6633 CANOGA AVENUE CANOGA PARK CALIFORNIA

R-7149

(Unclassified Title)

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

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

Contract Nonr 4428(00)
G.O. 8614

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Power Branch
Code 429

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FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Navy Contract Nonr 4428(00) and covers the period 30 May 1966 through 29 May 1967. The program manager was Dr. E. A. Lawton, Manager, Synthetic and Propellant Chemistry. The work was conducted in Oxidizer and Fluorine Chemistry with Dr. D. Pilipovich, Principal Scientist as principal investigator. Full-time staff members contributing to the technical effort were Dr. H. H. Rogers, Dr. C. J. Schack, and Dr. C. B. Lindahl.

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ABSTRACT

New syntheses of ClF_3O were discovered utilizing ultraviolet-initiated reaction of FClO_2 and FClO_3 . In the presence of F_2 , ClF_3 , or ClF_5 , FClO_2 gave ClF_3O in high conversions and high yields. The most effective fluorinating agent was ClF_5 . The same techniques were not successful in oxidizing ClF_3O to ClF_5O or BrF_5 to BrF_7 . There is considerable evidence that FClO is an intermediate in the synthesis of ClF_3O by ultraviolet activation. More complete ultraviolet data were obtained with the measurement of extinction coefficients of ClF_5 , BrF_5 , ClF_3O , FClO_2 , and ClF .

Corona discharge activation in the systems $\text{FClO}_2\text{-F}_2$ did not result in ClF_3O . Initial decomposition of FClO_2 to ClF followed by fluorination to either ClF_3 or ClF_5 was observed.

A stable mass cracking pattern for ClF_3O was obtained with the most prominent peaks assignable to ClFO^+ (100 percent), ClF_2O^+ (80.60 percent), Cl^- (29.35 percent), ClF^- (21.23 percent), and ClO^+ (14.78 percent).

The F^{19} n.m.r. spectrum of gaseous ClF_3O revealed two bands at -276ϕ and -317ϕ with respective ratios of 2 and 1. These bands could not be resolved further but support the proposed C_s symmetry for ClF_3O rather than C_{3v} symmetry already partially excluded by infrared studies.

A novel process for forming NF_3O has been discovered. It was determined that the action of ClF_3O on difluoramine, HNF_2 ,

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reproducibly formed NF_3O in 80-percent yields at temperatures below ambient. Perfluoroformamide, $\text{F}_2\text{NCF}_2\text{O}$, also reacted with ClF_3O to yield NF_3O .

Mass cracking patterns were obtained for both IF_7 and IF_5O . New, more precise physical properties were determined for IF_5O ; the vapor pressure-temperature equation is $\log p_{\text{mm}} = 8.9874 - 1659.4/T$. The preparation of IF_3O_2 was attempted by reaction of IF_5O and SiO_2 at elevated temperatures. The pyrolysis of IF_5O yielded an unidentified volatile material which may be a new IF_xO compound. Reaction of IF_5O and HNF_2 yielded FNO and N_2F_4 as oxidation products.

A new, rapid method was developed for the synthesis of chlorine nitrate, ClNO_3 . The process utilizes the reaction of ClF and HNO_3 at temperatures above -112°C . A similar interaction between BrF_5 and HNO_3 yielded limited amounts of BrNO_3 . Fluorination of BrNO_3 led to a new solid complex of the type $\text{NO}_2\text{BrF}_x\text{O}$. A characterization of the complex NO_2BrF_4 was carried out to distinguish it from the above solid.

The solid obtained by reaction of Cl_2O and AsF_5 has been shown to be principally ClO_2AsF_6 . A physico-chemical characterization of the solid was conducted.

Preparation of ClNF_2O was attempted via a dissociative reorganization process involving NF_3O and PF_4Cl . Instead, a slow fluorination of the PF_4Cl to PF_5 resulted, accompanied by reduction of the NF_3O to FNO .

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Oxychlorine trifluoride did not ionize in either BrF_3 or IF_5 . The specific conductivity of ClF_3O was measured at 25 C, the value obtained was 2×10^{-8} ohms⁻¹ cm⁻¹. The reaction of ClF_3O with AsF_3 was complex, producing products including O_2 , AsF_5 , FClO_2 , and $\text{ClF}_2\text{OAsF}_6$. Attempts to prepare ClOAsF_6 were unsuccessful. All of the systems (ClF-AsF_5 , ClF-AsF_3 , and $\text{ClF}_3\text{-AsF}_3$) involved redox reactions producing Cl_2 and ClF_2AsF_6 .

Several possible synthetic routes to the uncharacterized chlorooyl fluoride (FClO) were investigated. These encompassed reduction reactions of Florox using N_2F_4 and Cl_2 and the oxidation of Cl_2O with the mild fluorinating agent $\text{CF}_2(\text{OF})_2$. Trace quantities of Compound C, expected to be FClO , were occasionally detected.

Various aspects of the chemistry of Cl-O species have been examined. Syntheses of Cl_2O_3 were conducted under static and flow conditions. Study of the new class of complexes of the $\text{MF}\cdot\text{Cl}_2\text{O}$ type has been expanded to include the systems $\text{RbF}\cdot\text{Cl}_2\text{O}$, $\text{CsF}\cdot\text{ClO}_2$, and $\text{CsF}\cdot\text{ClO}_2$, and $\text{CsF}\cdot\text{ClNO}_3$. The vigorous fluorination of ClO_2 proceeded explosively to ClF_3 , Cl_2 , and O_2 .

Hydrolysis of $\text{KF}\cdot\text{KClF}_4$ resulted in the formation of a new phase as shown by X-ray powder diffraction analysis which is thought to be a $\text{KF}\cdot\text{KClF}_4$ hydrate. Preparation of ClF_3O via oxygen-fluorine exchange reactions was unsuccessful.

(Confidential Abstract)

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Appendix A

A New Synthesis of Chlorine Nitrate A-1

Appendix B

A Redox Reaction of Dichlorine Oxide with Arsenic Pentafluoride:
 An Unusual Synthesis of ClO₂AsF₆ B-1

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**CONFIDENTIAL****INTRODUCTION**

The effort reported herein reflects considerable activity in the area of inorganic chemistry concerned with covalent fluorides. Particular emphasis has been placed on the reaction chemistry of interhalogen fluorides and oxyhalogen fluorides. The chemistry of ClF_3O and IF_5O appeared to be uniquely attractive with respect to reactions involving fluorination and/or oxygenation. This was verified in the case of ClF_3O and the following discussion section reflects to some extent the unusual chemistry of this material. Interest at Rocketdyne in IF_5O is focused on its potential utility as an intermediate for preparing IF_3O_2 and IF_3O . These possibilities will be discussed with respect to both reduction reactions and thermal decomposition.

An intensive effort was conducted to utilize the compounds FClO_2 and FClO_3 as chemical intermediates for new oxidizers. The approach reflected in this area involved the use of ultraviolet radiation for excitation. The ultraviolet activation technique was successful to the extent that it revealed FClO_2 and FClO_3 to be intermediates for the preparation of ClF_3O . The results in this area are presented in detail in the Discussion section of this report.

In attempting to reproduce reported results in synthesizing " ClOAsF_5 ," an unusual redox reaction was uncovered inasmuch as the reaction of Cl_2O and AsF_5 yielded ClO_2AsF_6 . This led to a supposition that AsF_5 may catalyze redox reactions in other chlorine (I) compounds; this was subsequently demonstrated with ClF . The results will be discussed in connection with a variety of redox and complexing reactions involving ClO_2 , AsF_3 , ClF_3O , and AsF_5 .



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Additional spectral data were generated for the novel compound ClF_3O . Previous attempts to resolve the F^{19} n.m.r. spectrum had always resulted in a complete collapse of the bond structures due to exchange initiated by traces of HF. Vapor-phase measurements resolved the problem and the results will be discussed with particular emphasis on the techniques used to obtain these conclusive data.

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DISCUSSION

ULTRAVIOLET ACTIVATED REACTIONS

The purpose of this study was twofold. First, new syntheses of ClF_3O were sought that utilized intermediates other than covalent hypochlorites. By using an initiator (in this case radiant energy) there exists a possibility of realizing more favorable reaction rates as well as obviating the use of either Cl_2O or ClONO_2 . The second aspect of this study involved the possibility of synthesizing new halogen fluoride species such as ClF_3O_2 , ClF_5O , and BrF_7 . The use of suitable radiation at low temperatures appeared to offer a number of attractive features in achieving the objectives.

Absorption Spectra

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

Absorption spectra have been obtained for ClF , ClF_5 , ClF_3O , FClO_2 , FClO_3 , and BrF_5 (Fig. 1) using a Cary Model 14 Recording Spectrophotometer. Extinction coefficients are presented in Table 1. The data for ClF_5 extend the results reported by Gatti (Ref. 1) to wavelengths shorter than 2640 angstroms. The wavelengths for the strongest absorptions for all compounds except ClF were below 2300 angstroms with indications that even stronger absorption occurred below 1900 angstroms.

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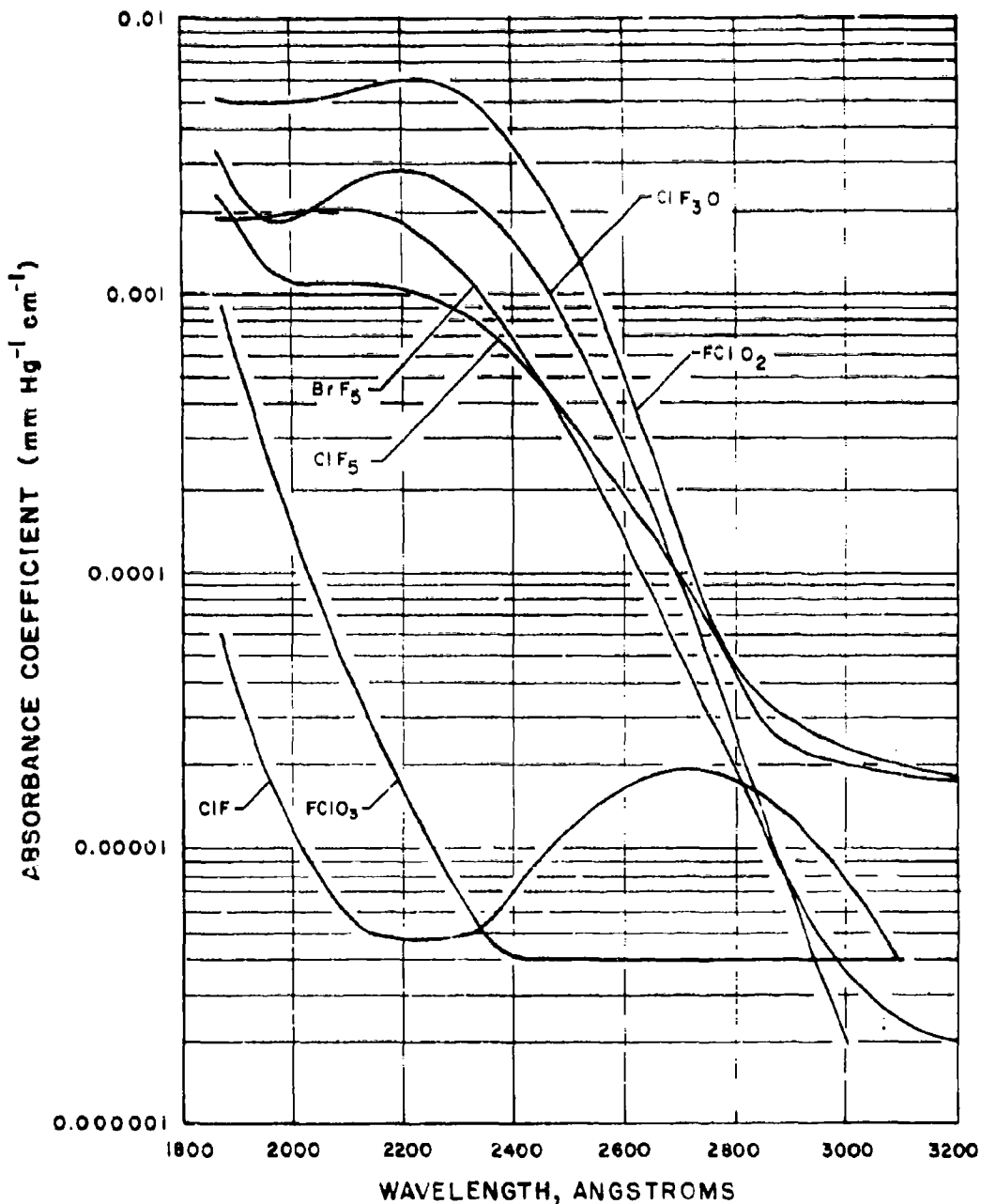


Figure 1. Ultraviolet Absorption Spectra for ClF , ClF_3 , ClF_5 , FClO_2 , FClO_3 , and BrF_5

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TABLE 1

EXTINCTION COEFFICIENTS

Compound	Wavelength, angstroms	Absorbance Coefficient $\times 10^{-2}$, $\text{mm Hg}^{-1} \text{cm}^{-1}$
ClF	2730	0.020 (Ref. 6)
ClF ₅	2000 to 2100	1.1
ClF ₃ O	2205	2.8
FClO ₂	2225	6.0
FClO ₃	1860*	0.090
BrF ₅	2080	2.0
F ₂	2845	0.035 (Ref. 4)
ClF ₃	2231*	1.34 (Ref. 7)
OF ₂	2100*	0.075 (Ref. 5)

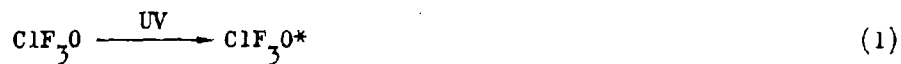
*Not a maximum; coefficient increasing toward shorter wavelengths

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**CONFIDENTIAL**Reactions

Reactions were investigated using ClF_3O , FClO_2 , FClO_3 , and BrF_5 as the materials to be fluorinated. The materials employed as sources of active fluorine were F_2 , ClF , ClF_3 , ClF_5 , OF_2 , and BrF_5 . Initial work was accomplished (Ref. 2) in irradiation cells with relatively small windows (17-millimeter-diameter openings). Because conversions in these cells were small, even with overnight irradiations, a new cell with 4-inch-diameter windows was built with which a large degree of conversion was nearly always obtained. Exposures were usually approximately 4 hours. Results for the actual reactant combinations and conditions are presented in Table 2. A Pyrex filter was sometimes used to restrict the applied radiation to wavelengths essentially longer than 3100 angstroms.

$\text{ClF}_3\text{O}/\text{F}_2$. Irradiation of $\text{ClF}_3\text{O}/\text{F}_2$ mixtures was conducted in an attempt to prepare ClF_5O . It was expected that the reaction might proceed by the activation of F_2 which would, in turn, react with ClF_3O forming ClF_5O . The small amounts of products obtained (Table 2), when the Pyrex filter was used in an attempt to minimize ClF_3O activation while maximizing F_2 activation, suggest that the reaction probably does not proceed by a mechanism involving activated fluorine. The large yield of ClF_5 obtained when the filter was not used indicates the probability that the ClF_3O was decomposed by the radiation and that the reaction may have proceeded by a route such as follows:

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TABLE 2

ULTRAVIOLET ACTIVATED REACTIONS

Reactants	Mole Ratio (to 1)	Temperature, C	Time, hours	Pyrex Filter	Condensable Products, (a) mole percent (co. version)
F ₂ , ClF ₃	8.2	30	4.4	Yes	ClF ₅ , 1.8; ClF ₃ , 2.0; FClO ₂ , 1.2
F ₂ , ClF ₃	7.0	-40	4.7	Yes	ClF ₅ , 0.9; FClO ₂ , 0.1
F ₂ , ClF ₃	6.5	-40	18.0	Yes	ClF ₅ , 1.8; FClO ₂ , 0.6
F ₂ , ClF ₃	7.1	-40	18.0	No	ClF ₅ , 51; ClF ₃ , 4; FClO ₂ , 2
FClO ₂	—	-60	4.5	No	ClF ₃ 0, 1.5; ClF ₃ , 2.6; ClF, 78; Cl ₂ , 21; FClO ₃ , 0.6
FClO ₂	(b)	-60	4.5	No	ClF ₃ , 1.5; ClF, 63; FClO ₃ , 0.3
F ₂ , FClO ₂	12.8	-60	5.4	No	ClF ₃ 0, 14; ClF ₅ , 59
F ₂ , FClO ₂	5.6	-60	2.5	No	ClF ₃ 0, 5.0; ClF ₅ , 26
F ₂ , FClO ₂	1.1	-60	4.2	No	ClF ₃ 0, 36; ClF ₅ , 8; ClF ₃ , 22; FClO ₃ , 6
OF ₂ , FClO ₂	1.0	-60	4.1	No	ClF ₃ 0, 20; ClF ₃ , 17; ClF, 57
ClF, FClO ₂	2.0	-60	4.1	No	ClF ₃ 0, 26; ClF ₃ , Cl ₂ , "FClO"

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

(b) Flow experiment

(c) Lamp defective, not full brightness

(d) Full brightness, 2 to 3 hours

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**CONFIDENTIAL**TABLE 2
(Concluded)

Reactants	Mole Ratio (to 1)	Temperature, C	Time, hours	Pyrex Filter	Condensable Products, (a) mole percent (conversion)
ClF_3 , FClO_2	1.0	-60	4.1	No	ClF_3 , 0, 28; ClF
ClF_5 , FClO_2	1.0	-60	4.0	No	ClF_3 , 0, 70; ClF
ClF_5 , FClO_2	1.0	-40	3	No	ClF_3 , 0, 53; ClF_3 ; ClF , 15
BrF_5 , FClO_2	1.0	-60	4.1	No	ClF_3 , 14; ClF , 67; FClO_3 , 7; BrF_3
FClO_3		-60	5.8	No	ClF , 18; FClO_2 , 0.6
ClF_5 , FClO_3	1.0	-60	4.1	No	ClF_3 , 0, 7.2; ClF_3
F_2 , BrF_5	12	-40	22.0 ^(c)	No	None
F_2 , BrF_5	20	-40	17.5	No	None
F_2 , BrF_5	12	-60	6.0 ^(d)	No	None
F_2 , BrF_5	13.5	-62	4.5	No	None
F_2 , BrF_5	12.9	-62	5.1	No	None
F_2 , BrF_5	1.3	-62	4.6	No	None

Small amounts of impurities or unidentified compounds from most BrF_5 experiments

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

(b) Flow experiment

(c) Lamp defective, not full brightness

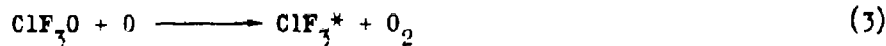
(d) Full brightness, 2 to 3 hours

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Low temperatures (-40°C) were used for this reaction to determine if the activation of ClF_3O might occur without its decomposition. It is possible that the use of even lower temperatures during ultraviolet radiation would cause the reaction to proceed in the following manner:



Unfortunately, the rather low vapor pressure of ClF_3O (less than 10 millimeters at -60°C) would permit the formation at any one time of only small quantities of the proposed compound, ClF_5O . Because ClF_5O could be more volatile than ClF_3O and would, therefore, remain in the vapor state, rapid decomposition by ultraviolet radiation to ClF_5 and O_2 would be expected. Therefore, the possibility of forming ClF_5O by reducing the temperature below -40°C appears unlikely.

Reactions of FClO_2 . Initial irradiations of FClO_2 at 25°C both alone and with F_2 (Ref. 2) indicated that partial decomposition of FClO_2 to ClF and O_2 occurred accompanied by fluorination to ClF_3 and/or ClF_5 . Because the objective of this work was the preparation of ClF_3O_2 , the reactions were repeated at reduced temperatures where this compound should be more stable. No experimental evidence for the formation of ClF_3O_2 was found. However, substantial yields (up to 86 mole percent) of ClF_3O were obtained from

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irradiations of ClO_2F with most fluorinating agents used (Table 2). These experiments represent the first examples in which ClF_3O (Florox) has been prepared in good yield from an intermediate other than a covalent hypochlorite.

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



The detection of a compound thought to be FClO (Ref. 3) during the ClF/FClO_2 experiment tends to support the existence of FClO as an intermediate. This compound may have also formed during the irradiation of FClO_2 (Table 2). The supposed FClO is known to be very reactive and relatively unstable (Ref. 3) and the failure to observe it more frequently was not unexpected. A flow experiment was conducted in an attempt to prepare FClO ; however, neither FClO nor ClF_3O was found.

As at room temperature, the -60°C ultraviolet irradiation of FClO_2 alone produced principally ClF and O_2 , but the efficiency of the lower temperature was demonstrated by the formation of some ClF_3O . Either FClO_2 itself or the product ClF may have served as the active fluorinating agent.

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The weaker group of ultraviolet absorbers (Table 1; F_2 , OF_2 , and ClF) resulted in 20 to 30 percent conversion of $FClO_2$ to ClF_3O under approximately similar conditions. Of these, elemental fluorine yielded the best conversions to Florox and unlike any other fluorine source also formed ClF_5 . Of the three fluorinating agents in the group, only F_2 was examined at $F_2/FClO_2$ ratios higher than two. These higher ratios were found to yield lesser amounts of ClF_3O and more ClF_5 . No satisfactory explanation of this result can be made at this time because the presence of a large excess of F_2 would a priori lead to a predicted higher yield. Further, the limited number of experiments and the lack of replicate runs preclude sufficient evidence for advancing final conclusions. The low absorbtivity of F_2 relative to $FClO_2$ (Table 1 and Fig. 1) eliminates the possibility that the F_2 may be preferentially absorbing the available radiation.

The conversion of $FClO_2$ to ClF_3O using the strong absorbers ClF_3 , ClF_5 , and BrF_5 appears to be limited by the amount of the fluorinating agent in the vapor phase and therefore capable of activation. Thus, ClF_5 is more effective than ClF_3 while BrF_5 , which has only several millimeters vapor pressure at the test temperature, did not produce any ClF_3O despite the fact that it reacted. The significance of ultraviolet activation of the fluorine donor may be indicated by the fact that ClF_5 is a much better fluorine donor than F_2 itself. However, the greater efficacy of ClF_5 may be due to its lower activation requirements and chemical reactivity. This consideration, coupled with the vapor concentration of the agent, may be an important feature. In the latter interpretation, the role of the ultraviolet radiation would be primarily involved in decomposing $FClO_2$.

$FClO_3/ClF_5$. Following the encouraging results with $FClO_2$, an examination of similar reactions with $FClO_3$ was initiated. Perchloryl fluoride was considered as a precursor to ClF_3O_2 because its decomposition to an activated $FClO_2$ capable of fluorination seemed possible. Although $FClO_3$

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absorbs only weakly where other ClF compounds absorb strongly (Fig. 1), reasonable radiation times did effect its decomposition. Both ClF and some FClO_2 were formed. The latter is important because it demonstrates that the desired Cl=O bond cleavage does occur. Large quantities could not be expected because the strong absorptivity of FClO_2 results in its own decomposition.

Fluorination of the activated FClO_3 was attempted with ClF_5 because of its proven effectiveness with FClO_2 . No unknown products were observed but it was determined that ClF_5O was the major product. This is almost certainly due to stepwise loss of oxygen from FClO_3 to yield FClO which is then fluorinated to ClF_5O .

Thus, both FClO_2 and FClO_3 appear to undergo the progressive loss of oxygen on ultraviolet irradiation. Once chlorosyl fluoride, FClO , is formed, it is sufficiently stable at -40 to -60 C to allow fluorination to ClF_5O . Florox is the most complex product obtained due to the fact that it is essentially frozen out and thus not subject to any extensive ultraviolet activated reaction or decomposition. If ClF_5O_2 is to be synthesized, activation of F_2 without the activation of FClO_2 must be accomplished. The use of filtered (more than 3100 angstroms) radiation appears to be the most probable means of preventing extensive FClO_2 activation. While this approach was attempted for the synthesis of ClF_5O from ClF_3O and F_2 , it has not yet been utilized for the attempted preparation of ClF_5O_2 .

BrF_5/F_2 . It was thought possible that BrF_7 might be formed by activation of BrF_5 in the presence of F_2 (Eq. 11 and 12).

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Operation below ambient temperatures was employed to maximize the probability of forming BrF_7 and to prevent the BrF_5^* from decomposing to BrF_3 and F_2 . Further, a large excess of F_2 was also used to increase the chances of forming BrF_7 (Eq. 12) and to suppress the decomposition of BrF_5^* .

Infrared analysis of the products from the irradiations conducted at -40 and -60 C indicated that no new products were formed. However, several unidentified absorptions, probably caused by traces of impurities, were found in the infrared spectra of the products obtained from most experiments. Observed absorptions were at 1028, 1220, 1250, 1280, 1315, and 1910 cm^{-1} .

CORONA DISCHARGE ACTIVATION

Previous experiments on the corona-activated reaction of FClO_2 with a large excess of F_2 (Ref. 8) had suggested that the products of the reaction were primarily ClF and FClO_3 rather than the desired ClF_3O_2 . However, leaks in the reaction system have since been found which indicate the possibility that the FClO_3 originated in a manner other than the disproportionation of FClO_2 . Therefore, the experiment was repeated.

During one experiment, the amount of FClO_2 which passed through the discharge yielded the following product distribution: ClF_3 , 37 m/o; ClF_5 , 3 m/o; ClF , 10 m/o; FClO_3 , 0.5 m/o; FClO_2 (unreacted), 37 m/o; and SiF_4 , 2.6 m/o. The SiF_4 apparently resulted from reaction of the F_2 with a Pyrex flowmeter.

The rather good chlorine material balance (more than 85 percent) permits a course of decomposition of FClO_2 to be postulated. First, the presence of only a trace amount of FClO_3 precludes a substantial disproportionation

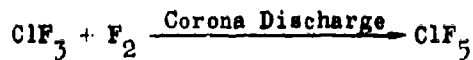
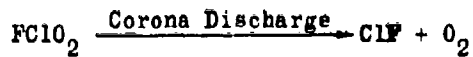
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of FClO_2 . Therefore, the most probable route for the reaction involves the decomposition of FClO_2 as shown in the following mechanisms:



Thus, it appears that corona activation of FClO_2 causes decomposition rather than providing a reactive excited species capable of being fluorinated to ClF_3O_2 .

ClF_3O PROPERTIES

Mass Spectrum

Previous attempts to obtain a fragmentation pattern of ClF_3O were unsuccessful (Ref. 9). At that time, it was suspected that the extremely corrosive chemical was not reaching the isotron in the CEC 21-103C Mass Spectrometer. This problem was compounded because only small quantities of Florox were then available.

It is most desirable to obtain one measurement that in itself leads to an unambiguous identification. The availability of larger quantities of Florox coupled with a modification of the inlet system to the previously mentioned mass spectrometer enabled this to be achieved. The difference in corrosivity between ClF_3O and ClF_5 toward the micromanometer is demonstrated by the

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fact that stable patterns could be obtained for ClF_5 while ClF_3O completely decomposed in the inlet system. Elimination of both the micromanometer and a 3-liter expansion volume made it possible to obtain a stable mass cracking pattern reproducibly, using an ionizing current of 10.5 microamperes and an ionizing voltage of 70 electron volts. The composite spectrogram obtained is presented in Table 3.

The spectral pattern in Table 3 is normalized to the most intense peak obtained at high mass range using a magnet current of 0.60 ampere. The spectrum of ClF_3O was corrected for the following impurities: SiF_4 , FClO_3 , Cl_2 , ClO_2 , COF_2 , CO_2 , O_2 , and HF . It was apparent, from several patterns, that little variation in relative intensity was observed for the key mass/charge pattern ratios corresponding to ClFO^+ and ClF_2O^+ . Some variation was noted in the calculated intensity of the ClO^+ peak after correcting for Cl-O containing impurities. Further refinement in the determination of this value is dependent on a more accurate accounting of impurity contributions to this peak.

F^{19} n.m.r. Study of Florox

The F^{19} n.m.r. spectrum of the gas phase of ClF_3O was obtained to substantiate the proposed C_s symmetry. A Varian DP60 spectrometer was used which was equipped with a high-resolution 56 MHz radio-frequency unit and high-resolution magnet. To detect the weak signals from the gaseous sample, a Princeton Applied Research lock-in-amplifier was used operating at 1.5 Hz to allow observation of any possible fine structure in the spectrum. The samples were the gas phases in equilibrium with the liquid phases of two purified ClF_3O samples containing different amounts of HF , and a gas-phase sample which had no liquid present. To observe the gas-phase resonances of the liquid samples, the n.m.r. probe was inverted and the sample maintained in place with a piece of tape. Calibration was effected with a

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TABLE 3

MASS CRACKING PATTERN OF ClF_5O

Mass/Charge	Relative Intensity, percent	Ion
16	13.19	O^+
19	27.29	F^+
35	29.35	Cl^+
37	7.58	Cl^+
51	14.78	ClO^+
53	4.32	ClO^+
54	21.23	ClF^+
56	7.10	ClF^+
70	100.00	ClFO^+
72	32.05	ClFO^+
89	80.60	ClF_2O^+
91	26.22	ClF_2O^+
108	--	--
110	--	--

NOTE: The sensitivity factor was not calculated because no accurate pressure measurement was made

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sample of CClF_3 contained in a capillary tube; surface tension held the liquid up in the top of the tube in the inverted probe. Sidebands at 9600 Hz generated from an auxiliary low-frequency oscillator, were used for magnetic field sweep calibration. The results are presented in Table 4.

Some of the features in the n.m.r. spectra of both gas and liquid are noteworthy. The sample containing only a gas phase revealed two different spectra. The initial spectrum showed F^{19} peaks at -223 , -262 , and -300ϕ . Upon aging for 2 days, the -223 ppm band disappeared. Subsequent gas-phase measurements on samples containing liquids revealed two peaks at -276 and -317ϕ . The first measurements were less precise than the latter because they involved the use of a much lower side-band frequency (1200 vs 9600 Hz for the others). Thus, the -262 and -300ϕ bands are the subsequently observed bands at -276 and -317ϕ .

No assignment is readily available for the -223ϕ (actually -247ϕ). It could possibly be assigned to the high field band of ClF_5 . However, its disappearance, as well as the absence of splitting, make this unlikely. (There is a remote possibility that ClF_5 may "disappear" through dissolution into the Kel-F tube walls). Another possibility, however remote, is the presence of an isomeric species.

The liquid spectra revealed only one line and are unremarkable except for the fact that the chemical shift is consistent with the measured HF concentration. The complete collapse of the doublet in the liquid phase, caused by the exchange initiated by the low HF content, may preclude the resolution of liquid spectra. Additional studies will be conducted with samples containing alkali fluoride salts in anticipation that their bifluorides are completely insoluble in the Florox sample.

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TABLE 4

 F^{19} N.M.R. DATA ON $ClF_3O^{(a)}$

Sample Description	Phase in Probe	HF ^(b) Concentration	F^{19} Chemical Shifts, ϕ	Peak Intensity
Gas	Gas	--	-223 ^(d)	2
			-262	2
			-300	1
Gas ^(c)	Gas	--	-262 ^(d)	2
			-300	1
Liquid + Gas	Gas	--	-276	2
			-317	1
Liquid + Gas	Liquid	0.015 Molar	-276	--
Liquid + Gas	Liquid	0.0004 Molar	-289	--

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

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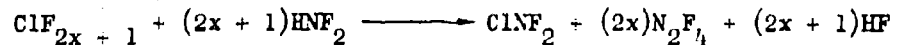
Specific Conductivity of ClF₃O

The specific conductivity of ClF₃O at 25 C has been measured at Rocketdyne and a preliminary value of 2×10^{-8} ohms⁻¹cm⁻¹ has been determined. The apparatus used was that described in Ref. 10.

FLOROX CHEMISTRY

Reaction of ClF₃O With NF₂ Compounds (A New Synthesis of NF₃O)

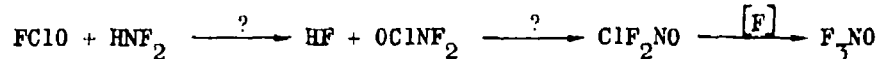
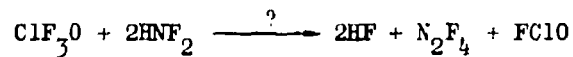
Studies of the reactions of chlorine fluorides and difluoramine have been shown to proceed as follows (Ref. 9):



where

$$x = 0, 1, \text{ or } 2$$

The course of these reactions appears to involve reduction of the ClF_x moiety to ClF followed by condensation to yield ClNF₂. Because Florox is similar to the chlorine fluorides chemically, it was proposed that a similar reaction sequence might occur. However, after the reduction of ClF₃O to FC10, a condensation with HNF₂ might yield OC1NF₂:

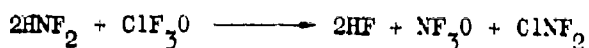




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Accordingly, a 1:1 reaction of ClF_3O and HNF_2 was conducted at low pressure and below 0 C. A smooth reaction followed, yielding no noncondensables. No unreacted HNF_2 was observed and 55 percent of the ClF_3O was recovered. The N-F containing products consisted of equal proportions of ClNF_2 and NF_3O and a small amount of N_2F_4 .

Thus, the course of the reaction appeared as follows:



Based on this equation, the yield of NF_3O and ClNF_2 was 80 percent. The concomitant oxygenation and fluorination of an NF_2 group is intriguing because of the possible reaction intermediates involved. It appears probable that the final fluorination step involves ClNF_2O , as in the preceding equation, or the ONF_2 radical. The mild reaction conditions coupled with the high yield of NF_3O are unprecedented during all previous syntheses of NF_3O .

Several repetitions of this experiment using higher HNF_2 to ClF_3O ratios (2 to 2.7:1) yielded similar results. The reaction temperature was varied between -78 and -112 C. One of the experiments at -112 C yielded only 75 percent of the anticipated total of N_2F_4 , ClNF_2 , and NF_3O when pumped on at that temperature. The remaining NF_2 materials were obtained only on warming above that temperature. This indicated that a $\text{ClF}_3\text{O-HNF}_2$ complex may exist at the low temperature. An attempt to confirm this on a scaled up reaction at -112 C was unsuccessful. This may have resulted from insufficient cooling through the relatively thick walled Kel-F reactor. The use of a thinner wall Teflon or alumina container as well as a lower temperature (-125 C) will constitute a final attempt at stabilizing any possible complex.

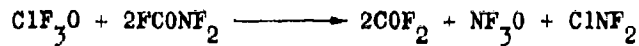
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The possible general reaction of ClF_3O with NF_2 compounds to yield NF_3O was also considered. To test this possibility, a reaction with perfluoroformamide, FCONF_2 , was performed. The products were NF_3O , ClNF_2 , N_2F_4 , and COF_2 . Assuming a stoichiometry as follows:



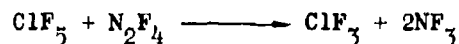
the NF_3O yield was 21 percent. Although this yield is somewhat low, it does confirm the utility of ClF_3O as a versatile oxygenating and fluorinating agent.

POSSIBLE SYNTHESIS OF CHLOROSYL FLUORIDE (FClO)

An unidentified compound, referred to as Compound C, has been observed on a number of occasions (Ref. 3). Infrared evidence is consistent with the proposed chlorosyl fluoride (FClO) as well as reaction environments from which it is obtained. However, this material is elusive in that all preparative methods have thus far been irreproducible. The pursuit of this material, while not an all encompassing end in itself, offered the possibility of exploring a wide variety of reactions of ClF_3C as well as other halogen fluorides.

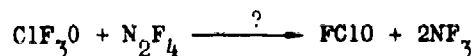
Reduction Reactions of ClF_3O

One reducing agent that appeared to be of interest in exploring the reduction of ClF_3O was N_2F_4 . It has already been shown that ClF_5 undergoes smooth reduction to ClF_3 as in the following equation (Ref. 11).



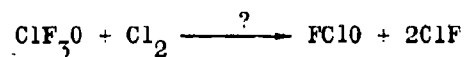
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The obvious analogy, then, is the oxidation of N_2F_4 with Florox:



Tetrafluorohydrazine and ClF_3O do not react at ambient temperature. To produce appreciable reaction, tests were conducted at 100 C. Even at 100 C over a 24-hour period, 85 percent of the ClF_3O was recovered unchanged. A trace of Compound C was found among the products which also included NF_3 , and unreacted N_2F_4 . At 130 C and after 65 hours, the $ClF_3O-N_2F_4$ reaction produced FNO , FNO_2 , NF_3O , NF_3 , and ClF . No Compound C was formed and 46 percent of the ClF_3O was recovered.

The reduction of ClF_3O with Cl_2 was re-examined in the hope that the following reaction could be observed:



During previous experiments (Ref. 3) no reaction of Cl_2 was observed at ambient temperature with either ClF_3O or its CsF complex. The results of a series of experiments at elevated temperatures are presented in Table 5.

TABLE 5
REACTIONS OF Cl_2 WITH ClF_3O

Temperature, C	Time, hours	Percent ClF_3O Reacted	Products
71	120	27	$FC10_2$, ClF_3
100	42	37	$FC10_2$, ClF_3
150	21	25	Trace C, $FC10_2$, ClF_3
200	16	100	ClF , O_2

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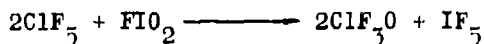
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During the one run at 150 C, a trace of Compound C was produced, but no other run produced evidence for this elusive species. At or below 150 C, FClO_2 and ClF_3 were produced from partial reaction of ClF_3O ; while at 200 C, the ClF_3O reacted completely with Cl_2 to produce ClF as in:

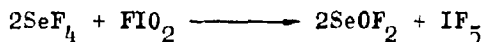


Attempted Synthesis of Florox

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



These exchanges were based on the known reaction of FIO_2 (Ref. 12):



No ClF_3O was observed as a product in either reaction. The reaction between ClF_5 and FIO_2 produced FClO_2 and lesser amounts of FClO_3 . With I_2O_5 and ClF_5 , primarily FClO_2 with smaller amounts of ClO_2 resulted.

Mixed Interhalogens

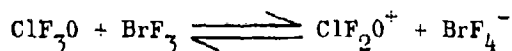
Complex interhalogen fluorides based on ClF_3O would form an interesting type of compound, therefore, the acid-base equilibria of ClF_3O (a moderately strong base) with the strong acids, BrF_3 and IF_5 , have been studied. Both

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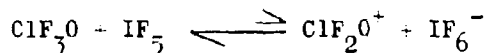
systems were miscible, yielding clear solutions with extended liquidus ranges. However, vapor pressure measurements revealed that the solutions were nonideal. Conductivity measurements were then used to assess the extent of any possible ionization.

In the $\text{BrF}_3\text{-ClF}_3\text{O}$ system, the addition of 4 mole percent ClF_3O to BrF_3 increased the resistance of the solvent slightly. On this basis, it was concluded that the self-ionization of BrF_3 is unaffected, and the resistance increase is caused by the addition of the less conductive ClF_3O . Thus, the following equation does not appear to be operative:



Elucidation of the $\text{IF}_5\text{-ClF}_3\text{O}$ system was complicated by difficulty in purifying and transferring the IF_5 . Several measurements were made and are shown in Table 6. The widely differing values for the initial resistance of IF_5 apparently indicate the material was impure. In each case, the addition of ClF_3O resulted in a lowering of the resistance of the IF_5 . However, it was not quantitatively reproducible and certainly does not suggest ionization of the ClF_3O . In addition, removal of the ClF_3O did not raise the resistance of the IF_5 .

It is therefore apparent that lowering of the resistance of the IF_5 was caused by impurity addition and that the following equilibrium exists slightly, if at all:

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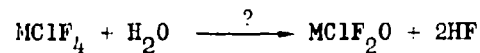
TABLE 6

CONDUCTIVITY IN THE IF_5-ClF_3O SYSTEM AT 25 C

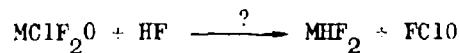
IF_5 Resistance, ohms	Resistance After Florox Addition, ohms
76	44
59	55
173	120
293	236

Hydrolysis of $MClF_4$

Another possible route examined for the preparation of $FClO$ involved controlled hydrolysis of anionic interhalogen fluoride species. The systems studied were $KClF_4-H_2O$ and $CsClF_4-H_2O$. The desired reactions were:



with possible displacements as in:



Static reactions have been run where H_2O was added both to $CsClF_4$ and $KClF_4$. In addition, a flow reaction was run where H_2O saturated N_2 was passed through $CsClF_4$ at ambient temperature. In the flow run, large amounts of ClO_2 and Cl_2 were generated.

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Results on the static systems were variable. Approximately three to five molar equivalents of water were added to three KClF_4 samples. Upon pumping, unreacted water and approximately 6, 18, and 45 percent of the original tetrafluorochlorate chlorine were evolved as volatile chlorine containing species. Similarly, with three CsClF_4 samples 2, 75, and 85 percent of the original tetrafluorochlorate was evolved. The volatiles were principally elemental chlorine with smaller amounts of ClO_2 in two cases, and FClO_2 in one. The variation in evolved chlorine may be caused by the technique of water addition. If the water reacts slowly and smoothly, hydrates are probably formed. However, if the reaction is rapid, hot spots might develop which could cause violent reaction and yield elemental chlorine as a product.

Subsequent reaction of three of the residual solids with excess HF yielded H_2O . Thus, it appears probable that stable hydrates were formed. Because the hydrolytic reactions of the ClF_4^- ion, in general, proved to be complex and vigorous, the study in this area has been limited to examining the postulate of the formation of stable hydrates. Reference samples for KF-KClF_4 and $\text{KF-H}_2\text{O}$ were prepared and their X-ray powder patterns were obtained. Although the patterns were complex, comparison of the $\text{KF-KClF}_4\text{-H}_2\text{O}$ data listed in Table 7 with KF-KClF_4 and $\text{KF-H}_2\text{O}$ reference patterns revealed that another phase was present. Comparison of ASTM reference patterns for $\text{KF}\cdot 2\text{H}_2\text{O}$, KHF_2 , KClO_2 , KClO_3 , KClO_4 , KO_2 , and KO_3 has also revealed that these compounds do not account for the unreferenced lines. This X-ray evidence for a new phase and the chemical observation that the KF-KClF_4 mixture hydrolyzed only slightly with water indicated the high probability of the formation of hydrate(s) of the type $\text{KClF}_4\cdot x\text{H}_2\text{O}$. Halocarbon mulls of the solid product on two occasions showed only the halocarbon peaks in the infrared and no OH stretching vibrations were observed.

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TABLE 7

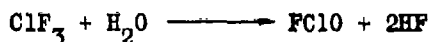
X-RAY POWDER DATA FOR $\text{KF-KClF}_4 \cdot \text{H}_2\text{O}$

Observed Diffraction, angstroms	Relative Intensity
5.1	3
4.9	3
4.6	3
4.45	3
4.2	3
3.16	40
3.06	100*
2.78	30
2.58	10
2.41	10*
2.33	30
2.24	8
2.08	60*
2.04	10
2.00	5
1.82	5
1.75	5
1.70	10*
1.65	10
1.61	3
1.58	3
1.45	20*
1.42	10
1.34	5
1.32	10*
1.20	5
1.13	3

*Peaks of intensity 10 or greater which cannot be referenced

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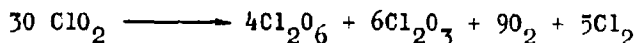
The reaction of uncomplexed ClF₃ was examined with H₂O to test the hypotheses that a condensation would evolve as follows:



The first reaction, using excess ClF₃ at ambient temperature, yielded trace amounts of Compound C and ClF. Four additional runs, however, conducted both at ambient temperature and at -18 C produced only Cl₂, ClO₂, ClF, and FClO₂.

Chlorine Sesquioxide

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



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

The reported synthetic technique was used and produced trace amounts of the new species formed as a brown solid ring at the neck of the -45 C cold bath. However, only extremely small amounts of the material were produced by this method. [McHale and Von Elbe (Ref. 13) produced approximately 0.2 mmole (0.024 gram) in their runs.] Attempts to increase the quantity of

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product involved raising the quantity of ClO_2 irradiated, lowering the reaction temperature, using a Kel-F reactor, and use of flow systems. An attempt to increase the quantity of product by irradiating approximately 1 milliliter of ClO_2 resulted in a violent explosion.*

*CAUTIONARY NOTE: In this attempted preparation, approximately 1 liquid milliliter of chlorine dioxide, contained in a 250-cc Pyrex reaction vessel, was slowly warmed from -196 to -45 C where it has a reported vapor pressure of 37 millimeters. The ultraviolet lamp was then turned on. After approximately 5 minutes, the ClO_2 exploded with sufficient force to shatter the 1/4-inch Plexiglas safety shield surrounding it at a distance of 1 foot. In later preparations, much smaller quantities of ClO_2 were used.

Employing a lower reaction temperature (-64 C) than that of McHale and von Elbe (-45 C) led to more reproducible results. However, the amounts of Cl_2O_3 formed remained small. In a typical experiment at -64 C, irradiation of 3.3 mmoles of ClO_2 produced 1.34 mmoles of Cl_2 . Thus, less than 20 percent of the starting ClO_2 was converted to solid chlorine-containing species, and the yield of Cl_2O_3 was less than 0.31 mmole. Attempts to sublime the brown solid even very short distances resulted in its decomposition.

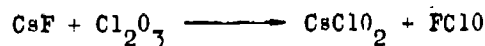
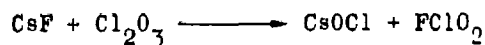
To raise product output and still maintain a low concentration of the treacherous ClO_2 , the preparation was converted from a static system to a recirculating flow system. Passage of Cl_2 through NaClO_2 produces ClO_2 . Thus, Cl_2 could be continually fed into the system and passed through NaClO_2 producing ClO_2 which is then irradiated. Unreacted ClO_2 and Cl_2 would be recirculated at low pressure through the NaClO_2 and irradiation areas. Oxygen produced could be removed by an occasional bleedoff. With only a low pressure of ClO_2 in the system, it should be possible to prepare moderate amounts of Cl_2O_3 . Several runs were made using the recirculating system, however, in only one case was any material produced, and continued

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reaction caused it to decompose. Keeping sufficient ClO_2 in the irradiated volume was the apparent problem. This was, in turn, dependent on the rate of formation of ClO_2 and the efficiency of pumping. Because of the lack of success, the recirculating system was abandoned.

Chemical reaction of Cl_2O_3 was attempted by allowing it to react with CsF . This would occur by either of the following routes:



Formation of Cl_2O_3 in a reaction vessel containing CsF was successful. While no reaction was observed with CsF , this may have been caused by failure to achieve a suitable contact between the solid reactants.

To provide a medium for reaction and to allow possible transfer from the glass system, an attempt was made to dissolve the material in CFCl_3 ; however, little, if any, solubility was observed in the CFCl_3 . Because of this solubility problem, difficulties in handling ClO_2 , and the difficulty in preparing even trace quantities of the new material, investigation on Cl_2O_3 was terminated.

Oxidation of Cl_2O With $\text{CF}_2(\text{OF})_2$

Mild fluorinations of Cl_2O or other appropriate ClO species offer an additional route to chlorosyl fluoride. Previous experiments in this mode utilized fluorine with excess Cl_2O (Ref. 3). Complexes and low temperatures were thought to be conducive to moderating the reaction such that a

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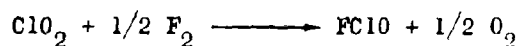
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chlorine (III) compound would result. Results with F_2 revealed, however, that once reaction was initiated, oxidation was complete to ClF_3O . This strongly implied that the molecule $FClO$ was much more susceptible to oxidation than Cl_2O .

Rather than using F_2 as the fluorinating agent, the use of $CF_2(OF)_2$ was considered. Over a period of 15 days at Dry Ice temperature, Cl_2O decomposed completely to Cl_2 and O_2 with a very small amount of $FClO_2$ formed. The $CF_2(OF)_2$ was recovered essentially unchanged.

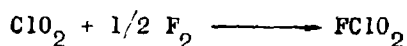
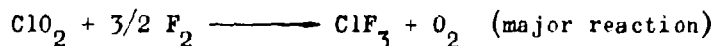
Fluorination of Chlorine Dioxide

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



Vigorous conditions would, however, be required because mild conditions produced $FClO_2$ (Ref. 14).

Separate experiments with an excess of either F_2 or ClO_2 resulted in rapid reactions. In these experiments, ClO_2 and F_2 were placed in separate 300-milliliter, stainless-steel bombs and allowed to mix rapidly by a simple turn of a valve. In each case, a clang similar to hitting the bombs together occurred upon mixing, indicating rapid explosive reaction. In the run at ambient temperature with excess fluorine, the products found were ClF_3 and $FClO_2$ in a ratio of approximately 5:1. Thus, the reactions observed were:



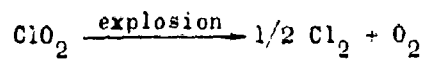
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With excess ClO_2 , an experiment at ambient temperature yielded only elemental Cl_2 (> 90-percent yield) as a product. Another experiment at 0 C produced Cl_2 (> 90-percent yield) and approximately 2-percent FClO_3 . Under the condition employed, the principal net reaction was explosive decomposition of ClO_2 :



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IODINE FLUORIDES AND OXYFLUORIDES

Iodine dioxide trifluoride, IF_3O_2 , represents an unknown composition for halogen oxyfluorides. A limited effort was conducted to synthesize this compound as a complement to the concurrent effort to prepare ClF_3O_2 . The known compound, IF_5O , offered a convenient starting material. Samples of IF_7 were first prepared from IF_5 and F_2 . The IF_7 was converted to IF_5O as follows (Ref. 15):



Significant discrepancies were noted between the reported vapor pressures of these compounds and the observed values. The measured values for IF_7 were approximately twice those reported, despite the fact that the only detectable impurity, IF_5O , was present only in trace quantities. An exact determination of the vapor pressure was not made but the material was converted to IF_5O . Following initial vacuum fractionation, final traces of SiF_4 and HF were removed from the IF_5O by treatment with KF . Analysis of this material by near infrared spectroscopy revealed less than 0.7% HF . The sample was tensiometrically homogeneous, the infrared spectrum was as reported (Ref. 16), and the vapor density yielded a molecular weight of 246 g/mole (238 calculated). The corrected vapor pressure-temperature equation for IF_5O is $\log p_{mm} = 8.9874 - 1659.4/T$. The heat of sublimation is 7.59 kcal/mole and a sublimation pressure of 760 mm is obtained at 1.4 C.

Additional information concerning both IF_7 and IF_5O was obtained. In particular, the previously unreported mass cracking patterns were determined. The inlet system of the mass spectrometer was altered as described earlier (Ref. 17) and the same operating conditions were employed. The mass spectrum of IF_5 was first determined as a comparative reference (Ref. 18). Reproducible spectra were obtained for both IF_7 and IF_5O and are shown in Tables 8 and 9.

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TABLE 8

MASS CRACKING PATTERN OF IF_7

Mass/Charge	Relative Intensity, percent	Ion
260	No parent	IF_7^+
241	75.68	IF_6^+
222	19.34	IF_5^+
203	100.00	IF_4^+
184	7.50	IF_3^+
165	6.45	IF_2^+
146	35.15	IF^+
127	50.26	I^+

TABLE 9

MASS CRACKING PATTERN OF IF_5O

Mass/Charge	Relative Intensity, percent	Ion
258	32.05	IF_5O^+
222	2.60	IF_5^+
219	17.40	IF_4O^+
203	100.00	IF_4^+
200	4.38	IF_3O^+
184	21.92	IF_3O^+
181	17.95	IF_2O^+
165	10.14	IF_2^+
162	28.77	IFO^+
143	12.19	IO^+
127	48.25	I^+

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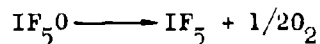
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In the case of IF_5 and IF_5O , parent ions were observed. Previous work with chlorine fluorides with this instrumentation never yielded parent ions. Recombination reactions were not observed and therefore no $IF_xO_2^+$ ions were observed. Only very minor quantities of impurities (SiF_4 and COF_2) were found and these could not be confused with mass/charge values of iodine-containing ions. The spectral patterns are normalized to the most intense peak.

The attempts to prepare IF_3O_2 utilized the reaction of IF_5O and SiO_2 (either Cab-0-Sil or 80 mesh silica) at elevated temperature. Because the formation of IF_5O from IF_7 and SiO_2 occurs readily at ambient temperature, it appeared that additional oxygenation of the central iodine atom might well occur under slightly more vigorous conditions:



Reactions were conducted at 130 C (Cab-0-Sil) and 145 C (silica). In each case, only a very small amount of SiF_4 formed and unreacted IF_5O was partially recovered. However, very extensive thermal decomposition of the IF_5O was noted and simply involved loss of oxygen.

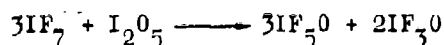


Thus no new covalent I-F-O material was obtained.

To ascertain the types of reactions that IF_5O might undergo and thereby gain insight into the methods most likely to be successful in converting it to IF_3O_2 , the potential acid/base characteristics were also examined. It was observed that IF_5O does not react with either the base, CaF , or the acid, AsF_5 . Thus, IF_5O is more "neutral" than any other known interhalogen fluoride.

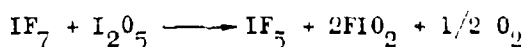
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Another reported method (Ref. 15) of preparing IF_5O is as follows:



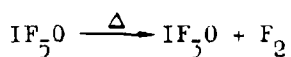
The supposed by-product of the reaction is iodine oxytrifluoride. Earlier efforts to form covalent IF_5O only resulted in the formation of the ionic $\text{IO}_2^+\text{IF}_6^-$ (Ref. 9). Therefore, this reaction was examined as a possible route to the expectedly covalent IF_5O . Lacking any experimental details, it was decided to use initially a reaction temperature of 130 C.

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

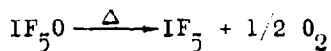


Thus, neither IF_5O or IF_3O were obtained. Any further attempt to secure IF_3O via these reactants will require milder conditions.

Among the unexplored properties of IF_5O is its thermal stability and susceptibility to pyrolytic breakdown. The latter was considered as a simple, straightforward route to IF_3O :



The alternative mode of thermal cleavage was also expected, especially in view of the results with SiO_2 , although this effect may have been catalytic.



The first test of the basic thermal stability revealed that IF_5O could be quantitatively recovered after 5 days at 75 C in a stainless-steel cylinder. Therefore the pyrolysis experiments were planned at considerably higher temperature (250 to 500 C) in a flow reactor. A supply of IF_5O

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was maintained at -78°C in a cylinder attached directly to the hot tube which was preheated to the desired temperature. The IF_3O was pumped through the heated zone, at a rate determined by the vapor pressure of IF_3O at -78°C , and quenched at -196°C shortly thereafter. Temperatures below 340°C were found to cause decomposition cleanly to IF_5 and O_2 . From 340 to 500°C , breakdown of the IF_5 to I_2 became noticeable and at the highest temperature was essentially complete. Many experiments produced traces of a volatile compound, which was identified as chromyl fluoride (CrO_2F_2) by infrared and mass spectral analysis (Ref. 19). Its formation is due to fluorination of chromium oxides obtained by reaction of chromium metal in the stainless-steel tube. The CrO_2F_2 was completely eliminated when the reactor tube was thoroughly passivated and therefore it appears that the decomposing IF_3O is not capable of producing both active fluorine and oxygen for converting the chromium to CrO_2F_2 .

To induce loss of fluorine alone from IF_3O and possibly also obtain oxygen transfer, flow pyrolyses were carried out using CuO -packed hot tubes. At temperatures of 250 to 350°C , it was found that small quantities of another volatile unknown were produced. This compound exhibited an infrared absorption at 945 cm^{-1} (PQR) which overlaps the $\text{I}=\text{O}$ absorption of IF_3O (925 cm^{-1} , PQR). It is possible that the proximity of infrared bands is indicative of the unknown being a new IF_xO species. Alternate synthetic conditions are being sought to increase the yield.

Reaction of IF_3O and HNF_2

The success attained with the $\text{ClF}_3\text{O}-\text{HNF}_2$ reactions prompted an examination of the corresponding $\text{IF}_3\text{O}-\text{HNF}_2$ system. Iodine oxyptafluoride represents the only other oxyhalogen fluoride of the type OXF_7 . The reaction proceeded

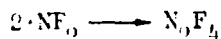
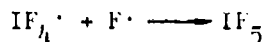
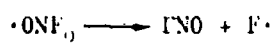
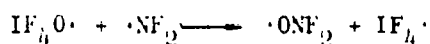
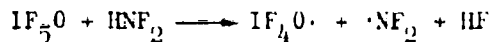
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smoothly at -78°C . The products were N_2F_4 , FNO , IF_5 , and HF and may involve many of the reactions shown below:



Thus, the primary difference between ClF_3O and IF_5O in their reaction with HNF_2 is that ClF_3O is a sufficiently reactive fluorinating agent to convert ONF_2 to NF_3O while IF_5O and IF_5 are not; therefore, the $\cdot\text{ONF}_2$ decomposes.

Preparation of ClNO_3

A new simplified preparation of chlorine nitrate from ClF and IClO_3 was demonstrated. The method and results are presented in the form of a manuscript in Appendix A.

PREPARATION OF BrNO_2

Some effort has been directed to effect the synthesis of pure BrNO_2 . Previous efforts yielded impure material in low yield (Ref. 5), but made it possible to obtain the previously unreported infrared spectrum. This

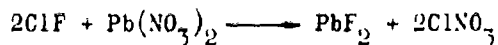
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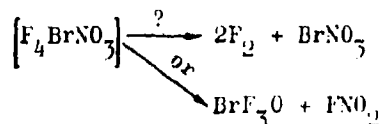
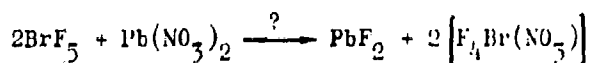


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has facilitated the identification of products in alternate syntheses. The best synthesis has utilized BrF_5 and HNO_3 , but product separation was difficult. The discovery of the following reaction (Ref. 20):



led to an attempt to utilize BrF_5 in an analogous system.



Bromine nitrate formed in this manner would be readily separated from unreacted starting materials and by-products. Agitation of the reactants at -45°C resulted in a dispersion but little or no reaction. On warming to ambient temperature, a mild reaction ensued, as evidenced by a gradual increase in the pressure of the system. After some time, the volatile products were fractionated, and some BrNO_3 was obtained. However, most of the gaseous products were -196°C noncondensables and decomposition products of BrNO_3 (NO_2 , N_2O_5 , Br_2). Therefore, it will be necessary to achieve reaction at lower temperatures and thereby preclude this secondary decomposition. This may be achieved by the reaction of BrF_5 as derived from the Br_2 , BrF_3 equilibrium. An examination of the NaNO_3 and BrF_5 system revealed that, when at room temperature, the reaction was too sluggish to yield any appreciable BrNO_3 .

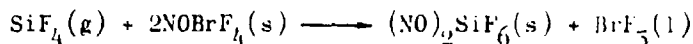
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FLUORINATION OF BROMINE NITRATE

Despite the failure to secure pure BrNO_3 , fluorination reactions were conducted using the impure material (contaminants being any or all of the following: BrF_5 , Br_2 , FNO_2 , HNO_3 , N_2O_5). Fluorine was used at a pressure of several atmospheres. At -80°C , no reaction was observed and some BrNO_3 was not recovered. Two reactions at ambient temperature yielded bromine pentafluoride and a solid. This solid was off-white to pale green (probably because of metal fluoride contamination). It has no vapor pressure at room temperature but heating to 50 to 60 C with pumping caused evolution of FNO_2 , Br_2 , and noncondensables. The infrared spectrum of the solid in the 2- to 15-micron region revealed the presence of the NO_2^+ cation ($2385 \pm 10 \text{ cm}^{-1}$). The assignment as NO_2^+ is based both on the evolution of FNO_2 and the infrared band position. Nitronium ion absorptions have been noted in this region for similar compounds, $\text{NO}_2^+\text{BF}_4^-$ 2380 cm^{-1} (Ref. 21) and $\text{NO}_2^+\text{ClO}_4^-$ 2360 cm^{-1} (Ref. 22); while nitrosonium ion absorptions are at somewhat lower frequencies, $\text{NO}^+\text{ClF}_2^-$ 2279 cm^{-1} (Ref. 23), and NO^+BF_4^- 2340 cm^{-1} (Ref. 21). This differentiation is important because only one ambient temperature, stable solid compound containing N, O, Br, and F functions has been reported, i.e., $\text{NO}^+\text{BrF}_4^-$ (Ref. 24). Therefore, this solid appears to be a new complex of the type $\text{NO}_2^+\text{BrF}_x^-$. A thorough characterization of $\text{NO}_2^+\text{BrF}_4^-$ was carried out (Ref. 25) and it was found to be quite different from this solid.

In an attempt to liberate the complexed bromine species, a displacement reaction similar to that reported (Ref. 24) for $\text{NO}^+\text{BrF}_4^-$ was attempted:



The solid obtained from the fluorination of BrNO_3 was exposed to SiF_4 at room temperature for several hours. No reaction occurred and the SiF_4 was recovered quantitatively.

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It has been demonstrated that ClF_3O is a weaker F^- acceptor than ClF_3 (Ref. 3) and a similar trend might be expected for $\text{BrF}_3\text{O}-\text{BrF}_3$. Therefore, because $\text{NO}_2^+\text{BrF}_4^-$ is unstable it is probable that $\text{NO}_2^+\text{BrF}_4\text{O}^-$ would be more unstable. This indicates that the solid may be an oxygenated bromine (III) species, which arises as follows:



Bromine nitrate of improved purity is needed to confirm this.

CHLORINE FLUORIDE-ARSENIC FLUORIDE SYSTEMS

In the course of examining potentially synthetically useful chlorine oxide species, an attempt was made to study the reported $\text{ClO}-\text{AsF}_3$ complex (Ref. 26). The results of this investigation are presented in Appendix B. As a corollary to this study, the interaction of chlorine fluorides, including Florox, and arsenic fluorides were considered as routes to valuable intermediates.

Reaction of Florox and Arsenic Trifluoride

The reaction of ClF_3O with AsF_3 was studied as a possible synthetic route to either FClO species (such as the unknown $\text{ClO}^+\text{AsF}_6^-$) or other solid species which might be fluorinated to produce ClF_3O_2 or ClF_3O . Several experiments were conducted at different reactant ratios and the formation of FClO_2 , AsF_3 , O_2 and white solids was noted. The presence of $\text{ClO}_2^+\text{AsF}_6^-$ in the solid was confirmed both physically by infrared spectra of mulls

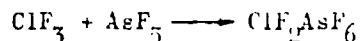
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and chemically by displacement of ClO_2 by N_2O_4 addition. An X-ray powder pattern of the solid has lines due to $\text{ClO}_2^+\text{AsF}_6^-$ as well as other lines which have not yet been identified. These lines could correspond to species such as $\text{ClF}_2\text{O}^+\text{AsF}_6^-$, $\text{ClF}_2^+\text{AsF}_6^-$, $\text{Cl}^+\text{AsF}_6^-$, and $\text{AsCl}_4^+\text{AsF}_6^-$ or to $\text{ClO}^+\text{AsF}_6^-$, a source of FClO .

A sample of the preceding solid was fluorinated at -78°C for 12 days producing no volatile species. Addition of ClF and later ClF_3 produced small quantities of FClO_2 but no other volatiles. Finally, the N_2O_4 addition to the solid was repeated to determine if any change had occurred as a result of the fluorinations. It was determined that now no ClO_2 was evolved but instead, ClF_3O was produced. Other volatile products were FNO_2 and FClO_2 which probably arose by reaction of ClF_3O with N_2O_4 and ClO_2 . The ClF_3O evolved by N_2O_4 addition either came from "oxygenation" of ClF species by N_2O_4 , from fluorination of the ClO_2^+ species, from simple displacement from species such as $\text{ClF}_2\text{O}^+\text{AsF}_6^-$, or from fluorination of a new reduced Cl-O species (such as ClO^+). In any case, prior to the F_2 , ClF , and ClF_3 treatment, N_2O_4 displaced only ClO_2 from the solid while after these reactions ClF_3O , FNO_2 , and FClO_2 were produced. As a result, various aspects of this reaction were studied both to elucidate the interesting chemistry involved and to determine if a new route to ClF_3O were present.

To help clarify the preceding reactions in the $\text{ClF}_3\text{O}-\text{AsF}_5$ system, reactions between chlorine fluorides (ClF and ClF_3) and arsenic fluorides (AsF_3 and AsF_5) were studied. The following reaction (Ref. 27) is the only one reported in the literature:

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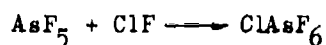
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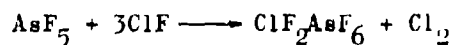
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Arsenic Pentafluoride-Chlorine Fluoride

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



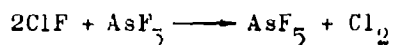
However, what was observed was a slow, rather unusual redox reaction which appeared to follow the equation:



For example, after a 13-day reaction period at ambient temperature using equimolar amounts of reagents, one third of the ClF and much of the AsF_5 was recovered along with Cl_2 and a nonvolatile solid. Treatment of the solid with FNO_2 displaced ClF_2 , confirming the presence of the ClF_2^+ salt. In a subsequent reaction, a ratio of 3.1 ClF/ AsF_5 was found, confirming the expected stoichiometry.

Arsenic Trifluoride-Chlorine Fluoride

The reaction of AsF_3 and ClF produced Cl_2 , AsF_5 and a nonvolatile solid. It is apparent that the reaction proceeds as:



This is then followed by the reaction between ClF and AsF_5 to yield ClF_2AsF_6 and Cl_2 .

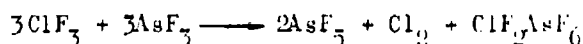
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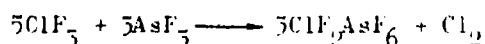
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Arsenic Trifluoride-Chlorine Trifluoride

Equimolar amounts of AsF_3 and ClF_3 were also allowed to react to determine if they formed a complex, ClF_2AsF_4 . Instead, an oxidation-reduction reaction was observed producing AsF_5 and Cl_2 . Although the solid product was not examined, the stoichiometry of the reaction is such that the following is proposed:



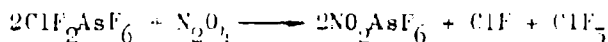
This suggests a possible overall reaction ratio of:



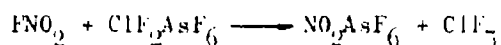
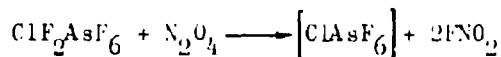
when sufficient ClF_3 is available.

Reaction of the ClF_2AsF_6 With N_2O_4

"Oxygenation" of complexed ClF_x species with N_2O_4 might be a possible source of ClF_3O . Accordingly, a sample of ClF_2AsF_6 was prepared from ClF_3 and AsF_3 . Reactions of the solid with N_2O_4 produced ClF_3 , ClF , a trace of FClO_2 , and possibly Cl_2 . The overall reaction thus appeared to be:



The production of ClF and ClF_3 may arise as in the following sequence:



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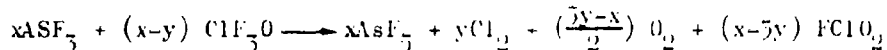
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Fluorination of ClO_2AsF_6

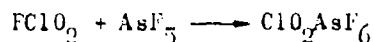
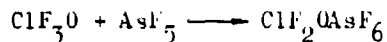
A sample of ClO_2AsF_6 was prepared by reaction of FClO_2 and AsF_5 . Three fluorination experiments were conducted on this salt to determine if this is a possible route to ClF_3O . The runs were conducted for 2-1/2 days at ambient temperature and for 2-1/2 and 27 days at -78 C. In all cases, only small amounts of ClO_2 and FClO_2 were produced as volatile products in the fluorination reactions. Subsequent displacement reactions using ClF_3 , N_2O_4 , and FNO_2 also failed to produce any evidence for fluorination of the ClO_2^+ species.

Displacement Reactions Using FNO_2

Excess FNO_2 was allowed to react with the $\text{ClF}_3\text{O} \cdot \text{AsF}_5$ solid product to displace the chlorine-containing species (perhaps including FClO) complexed by AsF_5 . Quantitative displacements were obtained on several different samples. The liberated products were ClF_3O and FClO_2 (e.g., utilizing 0.63 gram of solid; 1.76 mmoles of ClF_3O , and 0.56 mmole of FClO_2 were found; the calculated weight of solid for 1.76 mmoles $\text{ClF}_3\text{O} \cdot \text{AsF}_5$ and 0.56 mmole ClO_2AsF_6 is 0.63 gram). These data reveal that the solids prepared were mixtures of variable ratios of ClO_2AsF_6 and $\text{ClF}_3\text{O} \cdot \text{AsF}_5$ and contained no ClOAsF_6 . The oxidation-reduction reaction observed is expressed by the very general reaction:



Of course, complexes between AsF_5 and FClO_2 or ClF_3O are formed as in:



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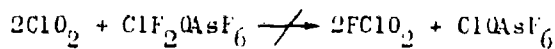
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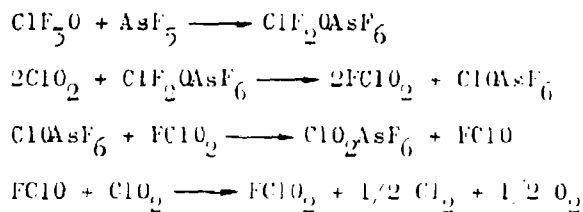
The relative amounts depend upon the ratio of the reactants and the course of the reaction. Therefore, the ClF_3O found in the initial series of reactions arose by displacement from the initially formed $\text{ClF}_2\text{OAsF}_6$.

Reaction of $\text{ClF}_2\text{OAsF}_6$ With ClO_2

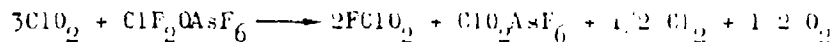
In an attempt to produce ClOAsF_6 , ClO_2 was allowed to react with $\text{ClF}_2\text{OAsF}_6$ in anticipation of the following:



However it was determined that when $\text{ClF}_2\text{OAsF}_6$ is treated with 2 equivalents of ClO_2 , FClO_2 is formed in slightly greater than a 1:1 stoichiometry. In addition, Cl_2 and O_2 are formed in the reaction. On the basis of the liberation of ClO_2 , when the resulting solid is treated with NO_2 the following reaction appears to offer the only logical sequence:



The overall reaction ($\text{ClO}_2 + \text{ClF}_2\text{OAsF}_6$) may be expressed as:



The last reaction predicts an $\text{FClO}_2/\text{ClO}_2$ ratio of 0.66. Observed were 0.61 and 0.54. It does not appear likely that the salt ClOAsF_6 will be readily made.

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ALKALI METAL FLUORIDE-ClO COMPLEXES

The previously reported (Ref. 3) cesium fluoride-chlorine monoxide complex represents a new type of compound. In an effort to extend this class of compounds, investigations of related systems ($\text{Cl}_2\text{O}-\text{RbF}$, ClO_2-CsF , and $\text{ClONO}_2-\text{CsF}$) have been conducted. The stoichiometry and structure of these compounds are of interest not only because of their unique nature but also because they may provide insight into the paths leading to the formation of oxychlorine fluorides upon fluorination.

Chlorine monoxide in contact with RbF at -78°C for 5 days could still be completely pumped off at that temperature. While this only indicates that a stable, undissociated complex is not formed, it contrasts sharply to the 1.5:1 complex ratio observed for $\text{Cl}_2\text{O}-\text{CsF}$ under these conditions. This RbF sample was commercial material that had been powdered in the dry box. Other measurements on this system using "activated" RbF (fused and then powdered in the dry box) yielded the results shown in Table 10.

TABLE 10

VAPOR PRESSURE OF Cl_2O OVER RbF

Temperature, C	Pressure, millimeters	
	Pure Cl_2O *	Cl_2O over RbF
-64	21	16
-45	71	65
-23	240	220

*Ref. 28

The reported pressures are approximate due to slow equilibrium and thus it can only be concluded that complexing is very weak.

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The interaction of ClO_2 and excess CsF was studied at -23°C with no vapor pressure reduction noted. An experiment at -45°C yielded inconclusive results. A problem encountered during this work was the apparent absorption of ClO_2 in the Teflon reactor; the absorbed ClO_2 cannot easily be removed by pumping, thus complicating measurements.

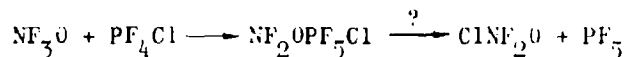
A previously reported ClNO_3 - CsF complex (Ref. 5) formation was re-examined. After 6 days contact at -78°C , it was still possible to recover all the ClNO_3 by pumping. In addition, no reduction in the vapor pressure of ClNO_3 over excess CsF was observed at -78 , -64 , and -45°C . Again, a deficiency of CsF surface area may be responsible for this nonreproducible behavior.

An additional experiment was conducted to elucidate the $\text{CsF}\cdot 1.5\text{Cl}_2\text{O}$ complex. In these experiments, F^{19} n.m.r. was used to analyze this complex in both CH_3CN and CH_2NO_2 at approximately -30°C . No F^{19} resonance was observed, apparently due to the slight solubility of CsF in these solvents. No more experiments are planned in the Cl_2O - CsF system. It has been concluded that ClO_2 and ClONO_2 do not form complexes with CsF and that additional structural data for $\text{CsF}\cdot 1.5\text{Cl}_2\text{O}$ complex will be difficult to obtain.

MISCELLANEOUS REACTIONS

Reaction of NF_3O and PF_4Cl

The preparation of ClNF_2O was sought because of its potential utility as a reactive source of the ONF_2 group. This was attempted by reaction with PF_4Cl through a dissociative reorganization process.

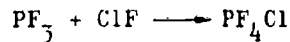
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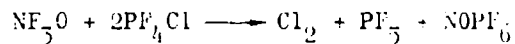
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The preparation of PF_4Cl itself was only recently reported (Ref. 29) using PF_3Cl_2 and SbF_3 . It was thought that a simpler route would be:

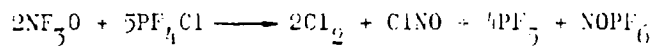


Experiments verified this concept, and 40- to 50-percent yields were obtained in minutes by reaction at -142 C in Kel-F. The by-products were PF_3Cl_2 and PF_5 . It is almost certain that increased yields could be attained at lower reaction temperatures but sufficient material for the present purposes was prepared in the indicated manner.

The conversion of NF_3O to $ClNF_2O$ was attempted under a variety of conditions. Experiments were conducted at -80 C , -126 to -70 C and also by repetitive cycling from -126 to -196 C , with the duration varying from several hours to several days. To completely consume either reactant generally required 2 days. No appreciable complexing of the reactants was detected. Trifluoramine oxide was completely stripped of its fluorine and the PF_4Cl converted to PF_5 . Thus, the reaction did not take the desired course and only resulted in the slow fluorination of PF_4Cl :



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



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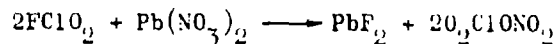
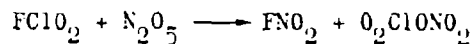
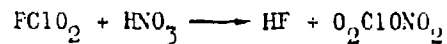
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Reactions of Cl-F and N-O Species

Several vigorous reactions of Cl-F ($\text{ClF}_3/\text{FClO}_2$ mixtures) and N-O (N_2O_4 , N_2O_5 mixtures) species were found to give rise to an unknown volatile compound as indicated by unidentifiable infrared absorbances at 5.8 microns ($\text{N}=\text{O}?$) and 9.7 microns PQR ($\text{Cl}=\text{O}?$). It appeared the compound might be O_2ClONO_2 . Purification of the material was not achieved because of its continual decomposition. Several synthetic approaches were then examined as possible means of preparing this compound.



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

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EXPERIMENTAL

ULTRAVIOLET IRRADIATION

Cells

Initial irradiations and spectrophotometric data were obtained with cells having a path length of 10 centimeters fabricated from 1-inch-OD nickel tubing. The windows were 0.02-inch-thick, 1-inch-diameter, ultraviolet-grade Linde sapphire, and appeared completely unaffected by the reactants used. The windows were held in place with flanges and Teflon O-rings. Hoke M482M Monel bellows valves were found satisfactory as cell closures.

An additional cell with a sapphire window at one end only was also fabricated. It could be cooled during irradiation by immersion in a suitable cooling bath and provision was made for blowing dry nitrogen past the window to prevent fogging by atmospheric moisture. Because the window opening was 0.66 inch in diameter and the length of the cell 7.5 inches, only a small percentage of the available radiation reached the reactants. Therefore, a new stainless-steel cell was built with a 4-inch-diameter ultraviolet-grade sapphire window (thickness: 0.125 inch). The cell had a window opening of 3.5 inches and a depth of 2.9 inches. The amount of radiation reaching the reactants was greatly increased as a result of the much larger window area and shorter length. Copper coils were soldered to the cell walls and bottom so that the cell could be cooled. An automatically controlled circulating methanol system has been used to maintain cell temperature within 3 C of the set temperature which was continuously variable from room temperature to at least -60 C. Fogging of the window was prevented by circulating dry nitrogen between the sapphire window and an additional window placed above it.

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Ultraviolet Source

Work was conducted with a Hanovia utility lamp No. 50620 (power input = 100 watts) with the protective housing removed to move the lamp as close as possible to the cell.

Materials

The materials used are described in Ref. 2 and 8. Purification of FClO_2 was carried out by pumping off the Cl_2 impurity while holding the FClO_2 at -78°C . The chromatographic purity of the colorless liquid was better than 99.9 percent. The ClO_3F was purchased from Pennsalt. The ClF was prepared by corona discharge from Cl_2 and F_2 and purified by fractionation.

CORONA DISCHARGE ACTIVATION

The apparatus previously used for corona discharge experiments (Ref. 1) was also employed for this work. The "Large Gas Reactor" (Fig. 4, Ref. 3), which was immersed in a -78°C bath during the experiments, was supplied with energy from the Audio-Frequency Pulse Generator (Ref. 1, Fig. 8). The generator was modified for higher pulse repetition rates as a means of increasing energy output by decreasing the inductance of the 0.17 H choke to 25 mh or 67 mh, selectable by means of an added switch. The trigger generator was modified to cover a range of 55 to 4000 Hz by changing the 0.01-microfarad capacitor to 0.005 microfarad. A Cenco 79800 induction coil was used to generate the high-voltage pulses.

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**CONFIDENTIAL****REACTION OF ClF_3O and HNF_2**

A prepassivated Kel-F container fitted with a Teflon valve was used to avoid the incompatibility of ClF_3O (and generated HF) with glass and HNF_2 with metal. Florox (30 cc) was first condensed in at -196°C from the metal vacuum line and then HNF_2 (29 cc) was condensed in from the glass line at -142°C . The reaction was then allowed to proceed at a higher temperature for several minutes prior to fractionation on the metal line. All the HNF_2 was converted to an approximately 2:2:1 mixture of NF_3O , ClNF_2 , and N_2F_4 . When the ClF_3O to HNF_2 ratio was greater than approximately 1:2.5, unreacted ClF_3O was recovered. Some FClO_2 was found and probably arose from decomposition of ClF_3O in incompletely passivated parts of the line. Very minor quantities of ClF_3 were observed and may indicate a secondary reaction path through oxygen abstraction from ClF_3O .

When the reaction was conducted at -112°C with ClF_3O (27.5 cc) and HNF_2 (36.5 cc), only 75 percent of the total NF product mixture was removed after 15 minutes pumping at that temperature. The remaining 25 percent was obtained on warming the reactor. An attempt was made to confirm this indication of a low-temperature complex but was unsuccessful. Use of an even lower temperature will be attempted but the very low vapor pressure of HNF_2 at lower temperature may cause contact problems because both reactants would be solid.

REACTION OF ClF_3O AND FCONF_2

Florox (35.5 cc) and perfluoroformamide (46 cc) were reacted in the Kel-F container for 15 minutes while warming to $\sim 0^\circ\text{C}$. A small amount of noncondensables was observed. Based on 2 moles of FCONF_2 reacting with 1 mole of ClF_3O , the yield of NF_3O was 21 percent. The major NF products were ClNF_2 and N_2F_4 . No FCONF_2 was recovered, conversion to COF_2 being complete.

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**CONFIDENTIAL**PREPARATION OF IF_7

Iodine pentafluoride and excess F_2 were heated at 150 C in Monel or stainless-steel cylinders for several hours. Conversion to IF_7 was nearly quantitative. Rough purification was achieved by vacuum fractionation. Small samples, containing barely detectable amounts of IOF_5 and no HF after KF treatment, exhibited a vapor pressure of 360 mm at 0 C compared to the literature value of 345 mm (Ref. 15). Mass spectral measurements and vapor density indicated no additional impurities.

PREPARATION OF IF_5O

Iodine heptafluoride and excess SiO_2 (Cab-0-Sil) were reacted in stainless-steel cylinders overnight at ambient temperature. Most of the by-product SiF_4 was removed by vacuum fractionation; the final traces along with any HF were removed by complexing with KF. This material was pure by all measurements. Because of the wide discrepancy between the observed and the reported (Ref. 15) vapor pressure, the vapor pressure-temperature relationship was redetermined. The observed data and derived equation are presented in Table 11.

TABLE 11

VAPOR PRESSURE-TEMPERATURE DATA FOR IF_5O

Temperature, C	Observed Pressure, mm	Calculated Pressure, mm
-78.1	3	2.90
-46.9	46	45.0
-22.7	228	250
-10.4	464	470
0.0	824	818

$$\log p_{\text{mm}} = 8.9874 - 1659.4/T$$

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PYROLYSIS OF IF_5O

A cylinder containing IF_5O was attached to a straight stainless-steel (30 inches long, 12-inch heated zone) tube passing through a furnace and then connected to a Teflon U-trap and the vacuum line. The tube was heated to test temperature and passivated with ClF_3 . When chlorine oxides were no longer generated, the system was completely pumped down. The IF_5O cylinder was cooled to -78 C and the U-trap was cooled to -196 C . Continuous pumping was maintained and a flow of IF_5O was begun (calibrated rate = 5.5 cc/min). Separate flow experiments were of 20 to 30 minutes duration.

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APPENDIX A

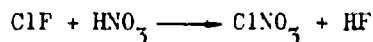
A NEW SYNTHESIS OF CHLORINE NITRATE

By
Carl J. Schack

Previous methods for the preparation of chlorine nitrate involved the reaction of either Cl_2O or ClO_2 with NO_2 or N_2O_5 .¹ To circumvent the

(1) (a) H. Martin, Angew. Chem., 70, 97 (1958). (b) M. Schmeisser, Inorg. Syn., 9, 127 (1967).

the use of these hazardous chlorine oxides, a new route to this compound was sought as indicated by the following equation.



It has been found that this reaction constitutes a rapid and convenient synthesis of chlorine nitrate. The reaction occurs on contact of the ClF with solid HNO_3 in 85 to 95 percent yield. The product ClNO_2 was purified by vacuum fractionation. The vapor pressure was measured over a considerably broader range (-80° to 26°) than that in the literature (-70° to -25°). The temperatures and vapor pressures are: -79.8° , 1 mm; -63.9° , 6 mm; -46.2° , 22 mm; -25.9° , 75 mm; 0.0° , 302 mm; 15.0° , 526 mm; and 26.1° , 866 mm. The vapor pressure-temperature relationship is described by $\log_{10} P_{\text{mm}} = 7.9892 - 1509.4/T$.

Chlorine nitrate has a b.p. of 22.3° (vs. literature extrapolation of 18°) with a heat of vaporization of 6.9 kcal/mole and a Trouton Constant of 23.4. The compound is stable in metal systems after pretreatment with some ClNO_2 . Long-term storage in metal or glass at approximately -40°



has not resulted in any significant decomposition. Unlike FNO_3^2 and the

(2) W. Kwasnik, "Handbook of Preparative Inorganic Chemistry," G. Brauer, Ed., Vol. I, Academic Press, New York, N.Y., 1963, p. 189.

chlorine oxides, no explosive incidents have been experienced with ClNO_3 . However, the material should be handled with care in the absence of sensitivity test reports.

Experimental

Chlorine monofluoride and nominally anhydrous HNO_3 (approximately 98 percent) were separately condensed at -196° into a stainless-steel or Kel-F cylinder attached to a metal-Teflon vacuum line. The cylinder was closed and the temperature was changed to some higher constant temperature in the range -112° to 0° . The reactor was then held at -78° and the product was pumped out rapidly and trapped at -95° . Little or no HF was removed from the reactor in this manner as evidenced by the failure to generate SiF_4 when the product was subsequently handled in glass. Sometimes HF was removed by allowing the products to stand over NaF for a period. The identity of the product was established by its infrared spectrum³ and molecular weight from vapor density measurements. Vapor

(3) K. Brandle, M. Schmeisser and W. Lutke, Chem. Ber., 95, 2500 (1960).

phase chromatography, using a column packed with 50% w/w of Halocarbon Oil 4-11V and Kel-F low density molding powder according to Dayan and Neale⁴ gave an analysis of ClNO_3 , 98.4%; Cl_2 , 1.6%. For the purpose of

(4) V. H. Dayan and B. C. Neale, Advances in Chemistry Series, No. 54, American Chemical Society, Washington, D. C., 1966, p. 225.

determining the stoichiometry, the more accurately measurable ClF was used as the limiting reagent. Typically, 11.9 mmoles of ClF was reacted with



approximately 14 μ moles of HNO_3 and yielded 10.6 μ moles of ClNO_2 (89 percent). In an alternative procedure, the HNO_3 was maintained at -78° while ClF gas was gradually admitted to the reactor. When the pressure ceased to drop, the reaction was complete. Workup was as above. The synthesis has been successfully conducted on a scale of several liters.

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

APPENDIX BA REDOX REACTION OF DICHLORINE OXIDE WITH ARSENIC PENTAFLUORIDE:
AN UNUSUAL SYNTHESIS OF ClO_2AsF_6 By
C. J. Schack and D. Pilipovich

Dichlorine oxide (or chlorine monoxide) has been reported to form a complex with AsF_5 at -78° and at about -50° formed an odd molecule, ClOAsF_5 , through elimination of Cl_2 .¹ Inference of the structure as being

(1) M. Schmeisser, W. Fink and K. Brandle, Angew. Chem. 69, 780 (1957).

the postulated odd molecule was drawn from the observed reaction stoichiometry and the fact that the postulated odd molecule reacted with NO_2 to give ClNO_3 .

We were interested in studying various aspects of the proposed odd molecule particularly as a ready source of the ClO radical. However, we felt that, prior to utilizing ClOAsF_5 as an intermediate, a more complete characterization was in order.

Experimental

Materials. Chlorine monoxide was prepared from Cl_2 and yellow HgO using a modified procedure.² Arsenic pentafluoride was purchased from

(2) C. J. Schack and C. B. Lindahl, Inorg. and Nucl. Chem. Letters, in press.

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



from KClO_3 and F_2 ³ and purified by fractional condensation. Nitrogen

(3) A. Engelbrecht, Angew. Chem., 66, 442 (1954).

tetroxide was purchased from the Matheson Co. and purified by fractional condensation. Phosphorus dichloride trifluoride was formed⁴ from PF_3 and Cl_2 .

(4) R. R. Holmes and W. P. Gallagher, Inorg. Chem., 2, 455 (1963).

Apparatus. Experiments were conducted in two vacuum systems, one constructed of glass, the other of stainless steel-Teflon. Solids were handled in an inert atmosphere glove box. Infrared spectra were taken on a Perkin-Elmer 157 Infracord using 5-cm gas cells fitted with AgCl windows or Halocarbon oil mulls between AgCl plates. Debye-Scherrer powder X-ray diffraction patterns were obtained with a G. E. ND5 instrument using $\text{CuK}\alpha$ radiation.

apor phase chromatography of reactants and products was carried out on a column packed with 50% w/w of Halocarbon Oil 4-11V and Kel-F low density molding powder according to Dayan and Neale.⁵

(5) V. H. Dayan and B. C. Neale, Advances in Chemistry Series, No. 54, American Chemical Society, Washington, D. C., 1966, p. 225.

Reactions of Cl_2O and AsF_3 . Measured quantities of Cl_2O (117 cc, 5.22 mmoles) and AsF_3 (85.0 cc, 3.79 mmoles) were separately condensed into the reactor (glass or Teflon tubes) at -196° . The temperature was changed to -78° and it was observed that the mixed reactants gradually developed a dark red color. Pumping on the mixture after a few hours at -78° resulted in the recovery of some of the starting materials and much Cl_2 . Subsequent warming of the reaction to ambient temperature gave additional small amounts of gaseous materials and a white solid. Little or no



-196° non-condensable gases were observed throughout the reaction. In all, 111 cc of volatile products were obtained. Infrared and gas chromatographic analysis indicated these products to be a mixture of AsF_5 (17.5 cc, 0.78 mmole) and Cl_2 (93.5 cc, 4.17 mmoles) with a trace of ClO_2 and no Cl_2O . The observed reactant-product ratio of $\text{Cl}_2\text{O}:\text{AsF}_5:\text{Cl}_2$ was 5.00:2.89:4.01. Similar reaction ratios were obtained when Cl_2O was used as the excess reagent. The solid product showed two infrared bands 1280 cm^{-1} (m, doublet) and $690\text{ to }700\text{ cm}^{-1}$ (s, broad). Based on the observed stoichiometry of the reaction and the known infrared frequencies of Cl-O^6 and AsF^7 compounds, it appeared the solid might be principally

(6) E. A. Robinson. Can. J. Chem., 41, 3021 (1963).

(7) R. Peacock and D. Sharp. J. Chem. Soc., 2766 (1959).

ClO_2AsF_6 . Accordingly, an authentic sample was prepared.

Preparation of ClO_2AsF_6 . Chloryl fluoride (111 cc, 4.96 mmoles) and AsF_5 (63.7 cc, 2.84 mmoles) were separately condensed into a Teflon ampoule at -196° . After 1 hour at room temperature, the unreacted gases were removed and measured (48.0 cc, 2.14 mmoles). An infrared spectrum showed only FClO_2 . The white solid product had an infrared spectrum identical to that of the solid from the $\text{Cl}_2\text{O-AsF}_5$ reaction. In addition, both solids fumed in air and exploded on contact with water. Powder X-ray patterns of both solids were obtained and were identical. The observed spacings and relative intensities are given in Table 1.

Reaction of ClO_2AsF_6 and NO_2 . Weighed amounts of ClO_2AsF_6 and excess NO_2 gas were reacted for 1 hour at 0° . The expected displacement⁸ of ClO_2

(8) M. Schmeisser and W. Fink. Angew. Chem., 69, 780 (1957).

was achieved but in poor yield; 20% for the solid from the Cl_2O reaction and 35% for the solid from the FClO_2 reaction.



TABLE 1

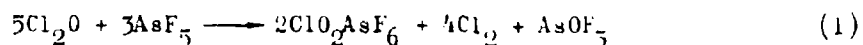
X-RAY POWDER DIFFRACTION DATA FOR ClO_2AsF_6

$d, \text{\AA}$	Relative Intensity	$d, \text{\AA}$	Relative Intensity
7.50	30	2.30	≤ 10
5.55	30	2.08	60
5.10	30	2.05	60
4.40	70	1.95	40
4.02	40	1.87	10
3.65	100	1.84	10
3.57	90	1.80	10
3.49	10	1.76	10
3.03	50	1.70	20
2.87	≤ 10	1.59	15
2.76	≤ 10	1.55	10
2.69	≤ 10	1.55	10
2.54	≤ 10		

Reaction of PF_3Cl_2 and Cl_2O . A 1:1 mixture of PF_3Cl_2 and Cl_2O was allowed to warm to room temperature at which point an infrared spectrum was taken. The only infrared absorbing material present was POF_3 . None of the PF_3Cl_2 , a strong infrared absorber, remained. The by-product Cl_2 was revealed by its color when frozen. No non-volatile solids were observed.

Results and Discussion

The reaction of Cl_2O with AsF_5 does not give the odd molecule ClOAsF_5 but gives instead the salt ClO_2AsF_6 . Further, the reaction appears to follow the stoichiometry shown in equation 1:

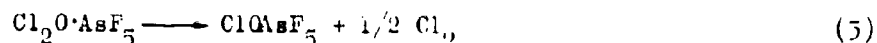




The reaction stoichiometry does not appear to be dependent on the experimental reactant ratios. The formation of ClO_2AsF_6 was confirmed by preparing an authentic sample and comparing their X-ray patterns



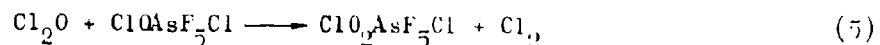
In the reaction of Cl_2O with AsF_5 , the evolution of Cl_2 apparently involves a much more complex process than a simple Cl-O bond rupture. The equation reported¹ for this process at -50° is shown in equation 3:



We would prefer to propose an initial step that infers an ionization of Cl_2O , i.e., an ionic complex is obtained, perhaps $\text{ClO}^+\text{AsF}_5\text{Cl}^-$:



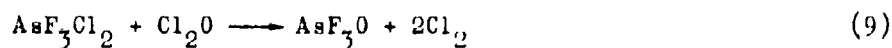
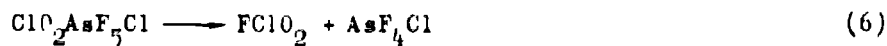
The oxidation of the ClO^+ species could then proceed with additional Cl_2O :



This step (equation 4) should not be considered unusual inasmuch as other chlorine oxides are capable of redox (e.g., ClO_2 gives some Cl_2O_6 on photolysis⁹).

(9) H. J. Schumacher, and G. Stiezer, Z. Physik. Chem., 57, 365 (1950).

The most difficult rationale is the formation of the AsF_6^- in the reaction. Admittedly a multiplicity of diverse reaction sequences could be proposed most of which would be difficult to experimentally verify. One possible path offered involves the dissociation of $\text{ClO}_2\text{AsF}_5\text{Cl}$ into its components with the subsequent reactions noted:



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

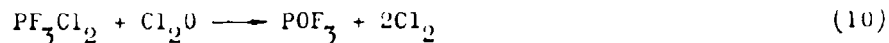
The identity of AsOF_3 was not established as a product since it is a non-volatile¹⁰ X-ray amorphous solid. In addition, we did not wish to further

 (10) K. Dehnicke and J. Wiedlein, Z. Anorg. allg. chem., 542, 225 (1966).

complicate matters by studying the reaction of AsF_3Cl_2 with Cl_2O as a test of equation 8 inasmuch as AsF_3Cl_2 "goes ionic" and is formulated as $\text{AsCl}_4^+\text{AsF}_6^-$ ¹¹. We did feel, however, that a suitable test of equation 8

 (11) H. M. Dess, R. W. Parry, and G. L. Vidall, J. Am. Chem. Soc., 78, 5730 (1956).

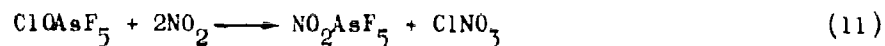
would be the reaction of PF_3Cl_2 and Cl_2O . Indeed, the rapid conversion of PF_3Cl_2 to POF_3 and Cl_2 as in equation 10:



strongly suggests that "covalent" AsF_3Cl_2 would react similarly. The reaction conditions are such that the reorganization of AsF_4Cl , postulated as an intermediate in equation 6, would give initially the covalent structure.



The initial report on the preparations of "ClOAsF₅" did offer the reaction of NO₂ as a proof of the radical present¹¹:



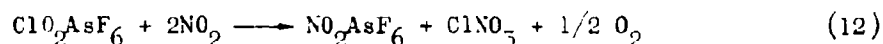
The existence of NO₂AsF₅ has already been questioned seriously and apparently disproved¹². Further, the formation of some ClNO₃ should be expected

(12) S. I. Morrow and A. R. Young, Inorg. and Nucl. Chem. Letters, 2, 349 (1966).

from ClO₂AsF₆ and NO₂ inasmuch as the reaction of ClO₂ and NO₂ gives ClNO₃¹³. It is quite likely that the reaction observed by Schweisser *et al.*

(13) H. Martin and Th. Jacobsen, Angew. Chem., 67, 524 (1955).

was the initial displacement of ClO₂ from ClO₂AsF₆ by NO₂ followed by a reaction of ClO₂ with NO₂, the overall reaction being:



Except for the formation of the oxygen, the reaction in equation 12 has the same stoichiometry of NO₂ to "solid" as that reported in equation 11. Thus, the proof of "ClOAsF₅" through its reactions or its synthesis is not conclusive.

Summary

The action of Cl₂O or AsF₅ does not give the odd molecule ClOAsF₅ as has been reported in the literature. Instead, the salt ClO₂AsF₆ is obtained. A rationale for the formation of the AsF₆⁻ ion was offered and involves reorganization reactions of arsenic chlorofluorides.

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