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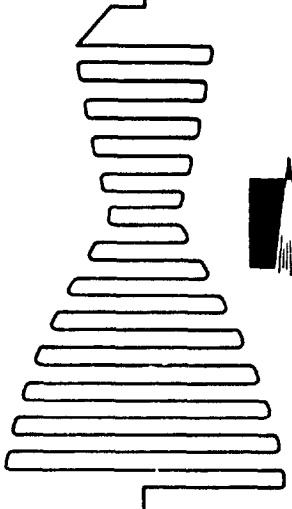

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QUARTERLY PROGRESS REPORT, INORGANIC HALOGEN OXIDIZERS

(29 August 1965 through 28 November 1965)

Group 4
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FOREWORD

The research reported herein was supported by the Advanced Research Projects Agency through the Office of Naval Research, Power Branch, Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Contract Nonr 4428(00) under ARPA Order No. 23, and covers the period 29 August 1963 through 28 November 1963. This work was carried out in the Synthetic Chemistry Group with Dr. D. Pilipovich, Principal Scientist. Full-time associates connected with the technical effort were Dr. H. F. Bauer, responsible for coordinating this report; Dr. C. J. Schack; and Dr. C. B. Lindahl.

ABSTRACT

The fluorination of KF and CsF complexes of Cl_2O has yielded ClF_3O. Thermal dissociation of $KClF_4O$ occurred below ambient temperature while heating was required to dissociate $CsClF_4O$.

Oxychlorine trifluoride has also been prepared from chlorine nitrate in a 95+ percent yield by fluorination of the complex $CsClFONO_2$. The reaction was independent of the presence of N_2O_4. Glow discharge experiments at -196 C with solid Cl_2O and activated fluorine gas have resulted in small quantities of ClF_3O, but ClF_5 and $FClO_2$ were the major products.

The hydrolysis of ClF_5 with potassium fluoride dihydrate and excess potassium fluoride was carried out in a flow system. No ClF_3O was obtained.

The ratio of CsF to ClF_3O in this complex has been determined to be 1.15 when using excess ClF_3O. Experiments with excess CsF also demonstrated an incomplete attainment of stoichiometry indicating unfavorable kinetics for the reaction. Reversible dissociation of the complex occurs below 150 C.

The basic behavior of ClF_3O was shown by its reaction with PF_5 and SiF_4 to form 1:1 and 2:1 complexes respectively The reaction of ClF_3O with FNO to form a reversible

complex demonstrated its acidic properties. Oxychlorine trifluoride was displaced from its CsF complex by ClF_3 and from its PF_5 complex with FNO. Vapor pressure/temperature equations for the $ClF_3O \cdot FNO$ and $(ClF_3O)_2SiF_4$ complexes were obtained.

The synthesis of ClF_5O was attempted by the fluorination of $CsClF_4O$ and by the reaction of KrF_2 with ClF_3O. Oxychlorine trifluoride was recovered in each case. Partial fluorination of $Cl_2O \cdot CsF$ was investigated as a route to chlorosyl fluoride and gave only traces of an unidentified substance thought to be FClO. The reduction of ClF_3O as a possible route to FClO was tried with the reducing agents Cl_2O, SO_2, Br_2, and BrF_3.

The complex of Br_2O and CsF has been fluorinated in hopes of forming BrF_3O or BrF_5O.

The fluorination of N_2O in the presence of CsF was attempted as a possible path to new F, N, O compounds. Neither complex formation nor reaction with fluorine was noted.

In an effort to demonstrate the existence of mercury hypochlorite as a possible intermediate, reaction products of Cl_2 and HgO, as well as Cl_2O and $HgCl_2$, were studied. No direct or reproducible evidence supporting mercury hypochlorite structures was obtained.

(Confidential Abstract)

CONTENTS

INTRODUCTION

During the present quarter, the studies revolving around oxychlorine trifluoride were expanded. In addition to studying the chemistry of its formation and intermediates involved, some attention was given to the chemistry of ClF_3O itself.

The chemistry of ClF_3O thus far is being pursued in two ways. The most important is the potential of ClF_3O as an intermediate in both fluorinations and reductions. Accordingly, the results of Rocketdyne studies in this connection will be presented in detail. Acid-base equilibria involving ClF_3O are also of interest. Some new species derived from ClF_3O in this context have been partially characterized.

Because preliminary characterization of ClF_3O is complete, more attention has been devoted to seeking other oxyhalogen fluorides. In this vein, fluorination studies of Br_2O were resumed.

TECHNICAL DISCUSSION

FLOROX STUDIES*

Synthesis of Oxychlorine Trifluoride From Cl_2O-Alkali Metal Fluoride Complexes

The fluorination of Cl_2O, complexed with alkali metal fluorides, has continued to provide the primary route to ClF_3O:

$$MF \cdot Cl_2O + F_2 \longrightarrow ClF_3O + MClF_4O + MClF_4$$

When CsF was used, part of the ClF_3O was evolved by warming to room temperature. Additional ClF_3O as well as ClF_3 was obtained by thermal dissociation of the residual solids.

In contrast, no additional ClF_3O was evolved when the products from the fluorination of $KF \cdot Cl_2O$ were heated above ambient temperature. The total yield was obtained by simply warming to ambient temperature. When the other product, ClF_3, was driven off by heating, the potassium fluoride could be reused with no loss of efficiency, similar to the satisfactory reuse of CsF in these fluorination reactions.

The ease of workup from KF-containing fluorinations suggests that $KClF_4O$ is appreciably dissociated at ambient temperature while $CsClF_4O$ requires considerable heating for complete dissociation. Moreover, a simple technique for the separation of ClF_3 from ClF_3O may be possible using KF. It was found that CsF was unsuitable in this regard.

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*Unclassified designation for ClF_3O

While a high conversion of Cl_2O to ClF_3O was not achieved using potassium fluoride, reasonably good yields have been obtained during initial experiments. At first, a yield of 9 percent based on Cl_2O was achieved. Subsequent runs in the same container gave yields of 44 percent based on Cl_2O and, following KF regeneration, 43 percent based on KF in a run with excess Cl_2O.

Electric Discharge Fluorination of Solid Cl_2O

Earlier in this program, the use of electric-discharge-activated fluorine was tried in reactions with solid Cl_2O to achieve the synthesis of ClF_3O. At that time (Ref. 1), it was observed that some ClF_5 was found but no ClF_3O. This reaction was re-examined using recirculated fluorine in a closed-loop system at low pressures rather than the simple flow-through method. As expected, a much more efficient fluorination was achieved. The yield of ClF_5 was approximately 45 percent (based on $2ClF_5$ for each Cl_2O). In addition, small quantities of ClF_3O were found along with some ClF_3 and much $FClO_2$.

Therefore, with the incorporation of this improved technique, the general utility of the electric discharge fluorination process has been improved and made more efficient. Also, it is expected that this activated gas solid reaction method might now be employed to demonstrate the synthesis of other highly fluorinated species, in particular ClF_5O.

$$ClF_3O + F_2^* \xrightarrow{-196\ C} ClF_5O \qquad (1)$$

Synthesis of Oxychlorine Trifluoride from $ClONO_2$

Two additional syntheses of ClF_3O via $ClNO_3$, CsF, and F_2 have been conducted in the same manner as reported previously (Ref. 2). The first, employing previously used CsF, gave no product. The second, utilizing fresh CsF, gave a 95+ percent yield of ClF_3O. In this reaction, it was noted that some of the ClF_3O was obtained as part of the volatile species, whereas in the past, it was observed only on pyrolysis of the solids left after completion of the fluorination. Nitryl fluoride was the only other major product obtained, thus confirming the postulated reaction sequence:

$$ClONO_2 + CsF \xrightarrow{-80 \text{ to } -18\ C} CsF \cdot ClONO_2 \qquad (2)$$

$$CsF \cdot ClONO_2 + 2F_2 \xrightarrow{-80\ C} CsF \cdot ClF_3O + FNO_2 \qquad (3)$$

$$CsF \cdot ClF_3O \xrightarrow{\Delta} ClF_3O + CsF \qquad (4)$$

It is also noteworthy that the $ClNO_3$ employed in this high-yield ClF_3O synthesis was contaminated with NO_2. The NO_2 impurity had no detrimental effect other than to consume fluorine in being converted to FNO_2.

Hydrolysis of ClF_5 With Potassium Fluoride Hydrate

Previous attempts (Ref. 3) to produce ClF_3O by hydrolysis of ClF_5 have unsuccessfully utilized metal fluoride hydrates. Because HF is a product of such a reaction it may have been detrimental to the formation of ClF_3O:

$$HF + ClF_3O \rightleftharpoons [ClF_4OH] \xrightarrow{?} 1/2\ ClF_5 + 1/2\ FClO_2 + HF \qquad (5)$$

Therefore, the reaction was repeated using ClF_5, $KF \cdot 2H_2O$, and a large excess of KF so that the HF formed would be tied up as KHF_2. Chlorine pentafluoride at 60-mm pressure was passed through a 10:1 powdered mixture of KF and $KF \cdot 2H_2O$ in a Kel-F flow reactor. The first reaction yielded $FClO_3$, $FClO_2$, Cl_2, and noncondensibles. The second reaction gave mostly $FClO_2$ and small amounts of $FClO_3$.

The third reaction gave $FClO_2$ and unreacted ClF_5. The reactivity of ClF_3O, if formed, is apparently greater with metal fluoride hydrates than is ClF_5.

Studies of the Cesium Oxychlorine Tetrafluoride Complex

The reversible nature of the CsF-ClF_3O system has been reported (Ref. 2).

$$ClF_3O + CsF \underset{\Delta}{\overset{R.T.}{\rightleftharpoons}} Cs^+ClF_4O^- \qquad (6)$$

However, no information regarding the actual stoichiometry was obtained because all the earlier experiments were conducted with a large molar excess of CsF. When the complex formation was carried out using measured amounts of CsF and ClF_3O, and with an excess of the latter, an experimental composition $CsF_{1.15} \cdot ClF_3O$ was obtained. This composition is reasonably close to a 1:1 complex, especially considering the problem of solid/liquid contact.

The formation of cesium oxychlorine tetrafluoride was also examined using excess CsF rather than excess ClF_3O. After 3 days at ambient temperature, 83 percent of the ClF_3O was complexed and after 3 weeks at -16 C, 96 ±3 percent of the ClF_3O was complexed. The failure of all the ClF_3O to be

complexed is attributed to poor gas/solid contact after all the liquid ClF_3O has reacted because the $Cs^+ClF_4O^-$ complex has a negligible vapor pressure of ClF_3O even at room temperature.

Because cesium oxychlorine tetrafluoride has potential utility as an intermediate in the synthesis of chlorosyl fluoride or oxychlorine pentafluoride, its thermal stability is of interest. Available data indicate that ClF_3O can be completely liberated from the cesium fluoride complex by pumping for several hours at 150 C. However, the nature of the complex giving rise to ClF_3O in this reaction was not accurately known because it was the result of the fluorination of the $Cl_2O \cdot CsF$ complex. An attempt was made to thermally dissociate any $Cs^+ClF_4O^-$ present, leaving the byproduct ClF_3 in the complex form $Cs^+ClF_4^-$. The temperature required to liberate ClF_3O completely was well below that required to yield ClF_3 from $Cs^+ClF_4^-$ (Ref. 4). Yet, evolved ClF_3O was mixed with appreciable amounts of ClF_3. This observation might be indicative of the retention of a fluorinated ClOCl moiety such as Cs_2ClF_8O. It is planned to check this possibility by heating a mixture of the independently prepared salts, $Cs^+ClF_4O^-$ and $Cs^+ClF_4^-$, to see if the ClF_3O evolved in this case is also mixed with ClF_3. If warranted, additional studies with X-ray powder diffraction will be carried out.

Reactivity of Oxychlorine Trifluorine With Monel

Previous experiments in Monel with F_2 showed 63- to 70-percent ClF_3O recovery at 200 to 236 C over 16-hour periods (Ref. 2). It was recently found that heating ClF_3O with CsF to 200 C in Monel for 3 days, converted all the ClF_3O to $FClO_2$, ClF, and ClF_3. These conflicting results may be the result of the formation of the F_2ClO radical which, in absence of fluorine, reacted with an incompletely passive Monel surface. It may be

recalled that 16-hour experiments in stainless steel at 200 C gave only Cl_2 and O_2 (Ref. 2) in the absence of fluorine. It is possible that while F_2ClO is a hypothetical precursor to $FClO_2$, ClF_3, and ClF in Monel, the same radical could give Cl_2 and O_2 with the more reactive stainless steel.

Oxychlorine Trifluoride Reactions With Acidic and Basic Fluorides

The ability of chlorine trifluoride to form complexes with both alkali metal fluorides and strong Lewis acids has been demonstrated with oxychlorine trifluoride as well. In addition to the previously reported reactions with boron trifluoride and arsenic pentafluoride (Ref. 2), ClF_3O reacted with both phosphorus pentafluoride and silicon tetrafluoride to form solid complexes. Phosphorus pentafluoride formed a colorless 1:1 complex with ClF_3O, which had less than 20 mm Hg pressure at ambient temperature. The solid could be moved by pumping but was presumably dissociated in the gas phase because no infrared spectral differences could be seen between the individual components and the vapor above the complex. A less stable complex was formed when ClF_3O and SiF_4 were mixed. When equimolar parts were brought to -80 C, one half of the SiF_4 reacted. Upon the addition of another equivalent portion of ClF_3O, the balance of the SiF_4 was complexed after temperature cycling. The vapor pressure of the 2:1 ClF_3O-SiF_4 mixture was measured at several temperatures between -80 and 14 C and the following vapor pressure/temperature equation was obtained:

$$\log_{10}p(\text{mm}) = 7.75 - 1545/T \qquad (7)$$

The enthalpy and entropy changes for the process $(ClF_3O)_2 \cdot SiF_4$ (solid) → $2ClF_3O$ (gas) + SiF_4 (gas) were calculated: $\Delta\tilde{H} \sim 22$ kcal, $\Delta\tilde{S} \sim 65$ e.u. An estimation of the enthalpy change in the process $2ClF_3O$ (l) + SiF_4 (g) → $(ClF_3O)_2SiF_4$ (s) was made from the heats of vaporization and sublimation of ClF_3O and SiF_4: $\Delta\tilde{H} \sim 2$ kcal. The complex may be written as either $(ClF_2O^+)_2SiF_6^=$ or $ClF_3O \longrightarrow SiF_4 \longleftarrow OClF_3$. Successive portions of the complex were removed at -23 C. Their infrared spectra showed a constant ratio of ClF_3O and SiF_4 absorbances indicating a 1.9 mole ratio.

The amphoteric behavior of ClF_3O was further demonstrated by its acidic reaction with nitrosyl fluoride. Apparently two complexes are formed, $FNO \cdot ClF_3O$ and $FNO \cdot 2ClF_3O$. The former complex was converted to the latter by pumping at -80 C. A vapor pressure/temperature curve was obtained for the $FNO \cdot ClF_3O$ complex from -80 to 0 C:

$$\log_{10} p(mm) = 8.47 - 1625/T \qquad (8)$$

The heat of reaction for the combination of the liquids FNO and ClF_3O to form the solid complex was calculated as about 5 kcal/mole of complex from the heats of vaporization of the liquids and the above equation.

The relatively high density, 1.9 g/cc, and heat of vaporization, 7.7 kcal/mole, of ClF_3O (Ref. 2) may be indicative of the existence of dimeric or bridged species in the liquid, e.g., $ClF_3\overset{\delta+}{O}-\overset{\delta-}{O}-ClF_3$. The addition of fluoride might then result in the formation of the observed 2:1 complex $NO^+ClF_4-\overset{\delta-}{O}-ClF_3$.

When an equimolar amount of nitrosyl fluoride was added to the $ClF_3O \cdot PF_5$ complex at -80 C, ClF_3O was liberated.

An infrared spectrum of the products volatile at room temperature showed only ClF_3O indicating the following reaction:

$$FNO\ (g) + ClF_3O \cdot PF_5\ (s) \longrightarrow NOPF_6\ (s) + ClF_3O\ (l) \qquad (9)$$

Thus, as expected, ClF_3O is a weaker base to PF_5 than is FNO.

Oxychlorine trifluoride was also displaced from its complex with a fluoride base by using another acid. Addition of ClF_3 to $CsClF_4O$ at ambient temperature liberated ClF_3O according to the equation:

$$ClF_3\ (g) + Cs^+ClF_4O^-(s) \longrightarrow Cs^+ClF_4^-(s) + ClF_3O\ (l) \qquad (10)$$

This confirms ClF_3 to be a stronger Lewis acid than ClF_3O toward CsF.

STUDIES LEADING TO NEW OXIDIZERS

Attempted Synthesis of Oxychlorine Pentafluoride

Oxychlorine trifluoride provides a potential intermediate for making both chlorosyl fluoride and oxychlorine pentafluoride. By analogy with the fluorination of $Cs^+ClF_4^-$ to yield ClF_5, the fluorination of the complex $Cs^+ClF_4O^-$ would be expected to be a likely route to the new oxychlorine fluoride, ClF_5O.

$$Cs^+ClF_4O^- + F_2 \longrightarrow CsF + ClF_5O \qquad (11)$$

Experiments with increasingly vigorous conditions of temperature and pressure have not resulted in ClF_5O or any other new compounds.

Conditions imposed thus far have been 750 psi at 30 C, 850 psi at 100 C, and 1200 psi at 160 C. The ClF_3O was recovered essentially unchanged from the Monel reactor in each case.

Another possible route to ClF_5O is the direct fluorination of ClF_3O by KrF_2 (Ref. 5) at low temperatures. The possible utility of this reaction is indicated by the recent report of the preparation of ClF_3 and KrF_2 (Ref. 6).

$$ClF_3 + KrF_2 \longrightarrow ClF_5 + Kr \qquad (12)$$

$$ClF_3O + KrF_2 \xrightarrow{?} ClF_5O + Kr \qquad (13)$$

Good mixing of the reactants can only be achieved at temperatures above -65 C, the melting point of ClF_3O. In three reactions so far conducted, the materials were allowed to warm up together from that temperature to ambient temperature over several hours. No evidence was found, however, for the formation of any new materials. The KrF_2 underwent smooth thermal decomposition to Kr and F_2, and some ClF_3 contaminant was partially converted to ClF_5; the ClF_3O was recovered quantitatively. Additional experiments are planned using shorter warming periods.

Reduction of Florox

The nonvolatile solid formed by low-temperature fluorination of the Cl_2O-CsF complex has been heated to yield ClF_3O, ClF_3, and, on three occasions, ClF and traces of an unknown species. The unknown partially passed through a -156 C trap in a vacuum line. The two bands in the rock salt region were observed and are indicated in Fig. 1. Additional

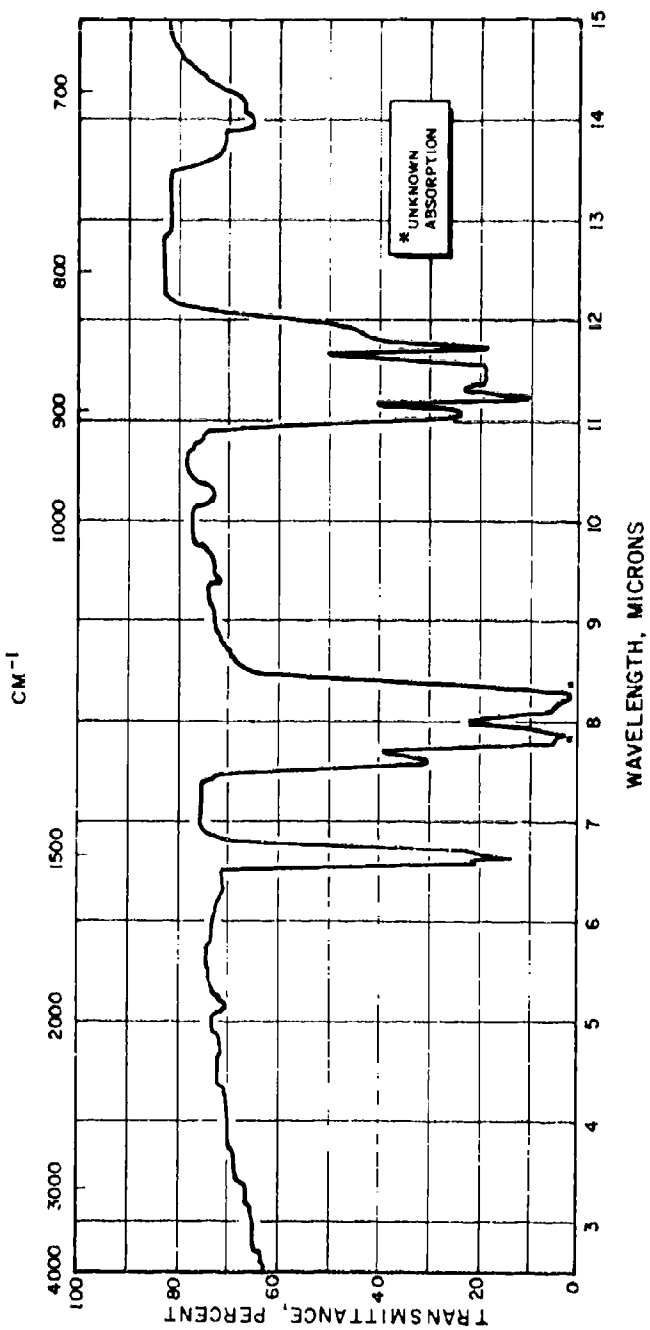

Figure 1. Pyrolysis of Cl_2O–CsF Fluorination Products

bands were noted at 645, 630, 610 (a possible pqr), and possibly at 467 cm^{-1}. This unknown may be a new F, Cl, O compound and specifically may be FClO. Mass spectrometric examination of a sample containing the unknown yielded no information. Three attempts to obtain the unknown by methathetical displacement by ClF_3 were unsuccessful:

$$Cs\ F_2ClO + ClF_3 \xrightarrow{?} Cs\ ClF_4 + FClO \qquad (14)$$

Because only traces of the new material were found thus far, several new approaches have been utilized in the search for this elusive material. The concomitant presence (or absence) of ClF suggests synthesis of the unknown and ClF by a simultaneous degradation of $Cs^+ClF_4O^-$ and $Cs^+ClF_4^-$ complexes by incomplete fluorination of the Cl_2O-CsF complex. Routine fluorinations of the Cl_2O·CsF complex to ClF_3O and ClF_3 have utilized 3:1 F_2:Cl_2O ratios. Intentional underfluorination to FClO and ClF would require a F_2:Cl_2O ratio of 1:1 according to the equation:

$$Cl_2O\cdot CsF + F_2 \longrightarrow FClO + ClF \qquad (15)$$

The incomplete fluorination at -80 C yielded ClF_3O and much unreacted Cl_2O but only traces of the unknown. Apparently once the Cl_2O-CsF complex was initially attacked by F_2 it was oxidized all the way to ClF_3O and ClF_3.

Another approach to the synthesis of FClO involves reaction of ClF_3O with appropriate reducing agents. With the reducing agent Cl_2O, FClO could arise as an oxidation product as well as a reduction product:

$$ClF_3O + Cl_2O \longrightarrow 2FClO + ClF \qquad (16)$$

Thus, local excesses would present less of a problem. The experiment was run with equimolar amounts of reactants held at ambient temperature in Monel for 3 days. While all of the Cl_2O reacted, only half of the ClF_3O was used. The products were $FClO_2$, smaller amounts of ClF, some chlorine, but no noncondensibles. Either FClO did not form or disproportionated according to the equation:

$$2FClO \longrightarrow FClO_2 + ClF \qquad (17)$$

Milder reaction conditions, such as shorter reaction time, lower temperatures, and complexed reactants are indicated for future experiments. Further reaction or disproportionation of any FClO formed may be reduced by complex formation as well.

The reaction of sulfur dioxide with ClF_3O was carried out between -80 and 45 C in hopes of fluorinating SO_2 to SO_2F_2 and forming FClO. The major reaction products were SOF_2 and $FClO_2$ with minor amounts of SO_2F_2. However, an overall decrease in the pressure of the system of 20 percent suggested some coupling or formation of a less volatile species. Infrared absorptions at 1485, 1240, 880, and 835 cm^{-1} indicated the presence of $SF_4(SO_3F)_2$ (Ref. 7). Fluorination of this material by F_2 resulted in $S_2O_6F_2$ and SF_6. No Cl-F absorptions above 660 cm^{-1} were seen.

The reaction of bromine trifluoride and oxychlorine trifluoride gave no new products. Bromine and oxychlorine trifluoride in a 1:3 mole ratio were reacted by slow warming from -80 C in anticipation of the following result:

$$Br_2 + 3ClF_3 \xrightarrow{?} 2BrF_3 + 3FClO \qquad (18)$$

Chlorine, chloryl fluoride, and some unreacted oxychlorine trifluoride were recovered. No evidence for BrF_5 or FClO was obtained. The failure to obtain FClO may have been caused by its reaction with bromine. Therefore, BrF_3 was tried as a reducing reagent:

$$ClF_3O + BrF_3 \xrightarrow{?} FClO + BrF_5 \qquad (19)$$

Bromine trifluoride and oxychlorine trifluoride did not react at room temperature. Higher temperatures may produce the desired reaction.

Attempted Synthesis of Oxybromine Fluorides by Fluorination of Br_2O

On the basis of analogy with the Cl_2O system, it was expected that Br_2O represents a likely starting material for the preparation of the unknown BrF_3O and BrF_5O compounds. Because of the high melting point of Br_2O and thermal instability above the melting point, the required CsF complex was formed using Freon 11 as a solvent for Br_2O. The complex was obtained after removal of the solvent and has been utilized for several fluorination reactions now in progress at -50 C. One partially completed experiment has shown that nearly all the added fluorine was consumed. The only volatile products observed, however, were Br_2 and BrF_5. No BrF_3 would be expected because it forms a stable complex with CsF. No new species were noted but this was not particularly discouraging because BrF_3O and possibly BrF_5O could be present as solid CsF complexes. Thermal dissociation of these solids is scheduled. The formation of BrF_5 in good yield was promising and may indicate the following reaction:

$$Br_2O \cdot CsF + 4F_2 = BrF_5 + BrF_3O \cdot CsF \qquad (20)$$

Fluorination of N_2O

Success in the CsF-catalyzed low-temperature fluorination of carbon dioxide suggested that the isoelectronic molecule N_2O might also be fluorinated under similar conditions. The fluorination of N_2O over dry powdered CsF was carried out in hopes of synthesizing new N, F, O compounds. The vapor pressure of N_2O over CsF showed no deviation from N_2O itself over the temperature range over which N_2O exists as a liquid. The acidity of N_2O is apparently insufficient to form a CsF complex. Fluorination of the N_2O-CsF mixture at -80 C for 5 days resulted in no reaction.

Cesium Fluoride-Chlorine Monoxide Complex Studies

The alkali metal complexes of Cl_2O and Br_2O represent a new class of compounds. The stoichiometry and structure of these compounds are of interest not only because of their unique nature but also because they may provide an insight into the paths leading to the formation of oxyhalogen fluorides upon fluorination. An investigation of the cesium fluoride-chlorine monoxide system was undertaken to determine the stoichiometry and stability of complexes. The ratio of Cl_2O to CsF was found to be variable, decreasing with increased temperature, pumping, and duration of the experiments. Moreover, the ratios were not reproducible. Large excesses of Cl_2O were held over CsF at -80 C for 17 days and longer and then pumped overnight to remove uncomplexed Cl_2O. The resultant ratios were 1.52, 0.82, and 0.25 during three separate experiments under these conditions and point out the nonreproducible surface conditions and degree of contact during formation of $Cl_2O \cdot CsF$ complexes. The pressure of Cl_2O above such complexes was less than 4 mm at -23 C.

Investigation of Possible Mercury Hypochlorite Formation

In the course of preparing Cl_2O from yellow HgO and Cl_2, it was observed that at -80 C there was some complexing between the generated Cl_2O and the residual mercury salts. To determine if this complexing is caused by $HgCl_2$ or hypochlorite formation, several experiments were conducted on the possible reaction of $HgCl_2$ and Cl_2O at -80 C. The initial experiment indicated that there was some complexing and furthermore that the Cl_2O was converted partially to Cl_2. Additional effort and experiments failed to duplicate this first result and showed no complexing or reaction between these materials. Therefore, the observed complexing of Cl_2O in its synthesis from HgO remains unexplained.

X-ray powder analysis of the solid product formed by reaction of HgO with excess Cl_2 showed only lines corresponding to $HgCl_2$. Although the possibility of amorphous or isomorphous mercury hypochlorite exists, apparently the only important reaction with excess chlorine is:

$$HgO + 2Cl_2 \longrightarrow HgCl_2 + Cl_2O \qquad (21)$$

The unusual behavior of the solid product (i.e., turning brown and evolution of chlorine) may be attributed to complexes with Cl_2 or Cl_2O, or amounts of products other than $HgCl_2$ too small to be observed by simple X-ray powder analysis.

EXPERIMENTAL EFFORT

PREPARATION OF Cl_2O

The details of the new static method for preparing Cl_2O have been presented previously (Ref. 2). With the earlier dynamic method it was necessary to use freshly prepared yellow HgO. During this period, however, it was determined that the static method is efficient enough to permit the use of commercial yellow HgO. While the yields of Cl_2O are not quite as high as those achieved with the fresh HgO, they are nevertheless quite good; i.e., 90- to 97-percent Cl_2O using either 1:1 or 2:1 HgO to Cl_2 mole ratios. This compares to 95+ percent with fresh HgO. Using the flow technique, the commercial material produces only a 20- to 25-percent conversion of the Cl_2 to Cl_2O. Therefore, if desired, the preparation of fresh HgO may be avoided with only minimal loss of efficiency in the conversion using the static technique.

PREPARATION OF KrF_2

Krypton difluoride was prepared by circulating an approximately 1:1 molar mixture of Kr and F_2 through an electric discharge reactor cooled to -196 C. The apparatus and technique are nearly the same as that reported in the literature (Ref. 5). Changing the temperature of the discharge tube to -80 C resulted in no reaction.

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13 ABSTRACT The fluorination of KF and CsF complexes of Cl_2O has yielded ClF_3O. Thermal dissociation of $KClF_4O$ occurred below ambient temperature while heating was required to dissociate $CsClF_4O$. Oxychlorine trifluoride has also been prepared from chlorine nitrate in a 95+ percent yield by fluorination of the complex $CsClFONO_2$. The reaction was independent of the presence of N_2O_4. Glow discharge experiments at -196 C with solid Cl_2O and activated fluorine gas have resulted in small quantities of ClF_3O, but ClF_5 and $FClO_2$ were the major products. The hydrolysis of ClF_5 with potassium fluoride dihydrate and excess potassium fluoride was carried out in a flow system. No ClF_3O was obtained. The ratio of CsF to ClF_3O in this complex has been determined to be 1.15 when using excess ClF_3O. Experiments with excess CsF also demonstrated an incomplete attainment of stoichiometry, indicating unfavorable kinetics for the reaction. Reversible dissociation of the complex occurs below 150 C. Oxychlorine trifluoride was displaced from its CsF complex by ClF_3 and from its PF_5 complex with FNO. Vapor pressure/temperature equations for the $ClF_3O \cdot FNO$ and $(ClF_3O)_2SiF_4$ complexes were obtained. The synthesis of ClF_5O was attempted by the fluorination of $CsClF_4O$ and by the reaction of KrF_2 with ClF_3O. Partial fluorination of $Cl_2O \cdot CsF$ was investigated as a route to chlorosyl fluoride and gave only traces of an unidentified substance thought to be FClO. The reduction of ClF_3O as a possible route to FClO was tried with the reducing agents Cl_2O, SO_2, Br_2, and BrF_3. The complex of Br_2O and CsF has been fluorinated in hopes of forming BrF_3O or BrF_5O. (C)

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