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QUARTERLY PROGRESS REPORT,
INORGANIC HALOGEN OXIDIZERS
(1 December 1964 through 28 February 1965)

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The research reported herein was supported by the Advanced Research Projects Agency and was monitored by the Office of Naval Research, Power Branch, Code 429, Washington 25, D.C., with Mr. Richard L. Hanson as Scientific Officer. This report was prepared under Rocketdyne G.0. 8614 in compliance with Section H of Contract N000144201001 under ARPA Order No. 23, and covers the period 1 December 1964 through 28 February 1965.

The Responsible Scientist for this program is Dr. D. Pilipovich, Principal Scientist, Fluorine Chemistry Unit, with Dr. H. F. Bauer, Dr. C. J. Schack, and Mr. R. D. Wilson serving as full-time associates. The work was carried out in the Synthetic Chemistry Group under the direction of Dr. E. A. Lawton, Group Scientist.
ABSTRACT

The synthesis of $F_3ClO$ was attempted by reactions of $ClF_3$ with yellow mercuric oxide and systems involving potassium nitrate and perchlorate. No evidence of $F_3ClO$ was found, even as an intermediate. The reaction of $ClF_3$ and $O_3$ gave $FC1O_2$, $ClO_2$, and unidentified compounds with infrared bands at 5.1, 8.7, and 12.9 microns.

Calcium hypochlorite and chlorine monoxide were fluorinated under a variety of conditions. At $-80^\circ$ C in the presence of $CaF$, $Cl_2O$ reacted with $F_2$ to give an unidentified compound which may be a new $Cl-F-0$ species.

The dissociation of the complex $NF_2O^+BF_3Cl$ was examined in the hope of producing $CINF_2O$. The only chlorine-containing product found was $Cl_2$.

Fluorine nitrate and the potassium fluoride-difluorine complex were reacted in the hope of forming $NF_2O(NO_2)$. The products were $N_2F_4$, $NO_2$, and $FNO_2$, suggesting the initial formation of $NO_3^-$ and $NF_2^-$ radicals.

The fluorination of $BrF_5$ at low temperatures was attempted by electrical discharge techniques. No new $BrF$ species were indicated.

In an effort to synthesize $NF_2$-substituted interhalogen compounds, chlorine trifluoride, chlorine pentafluoride, and
iodine pentafluoride were reacted with difluoramine. Various complexes of both ClF₃ and HNF₂ were explored as well. The major product was CINF₂ (as high as 95 percent), and the absence of Cl₂ and ClF strongly suggested NF₂ClF₂ as an intermediate. Inability to isolate NF₂ClF₂ was attributed to an enhanced reactivity of the Cl-F bonds toward HNF₂. The relative reactivities for the systems examined were: ClF₃-HNF₂ > ClF₅-HNF₂ > CINF₂ > ClF₃-HNF₂BF₃ > ClF₂⁺BF₄⁻-HNF₂ > KBF₄-HNF₂ > HNF₂. Difluoramine reactions with IF₅ resulted in degradation products which included I₂.

The synthesis of NF₂ClO₂ was attempted by reacting HNF₂ with FCIO₂ as well as its BF₃ complexes. In the absence of BF₃, deflagrations occurred, probably due to ClO₂ impurities. In the presence of BF₃, the principal nitrogen-containing product was NOBF₄.

(Confidential Abstract)
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INTRODUCTION

This report is the third quarterly progress report on a program directed toward the preparation of new inorganic oxidizers. Of particular interest are new oxyhalogen fluorides, oxynitrogen fluorides, and difluoramino-substituted interhalogens and oxyhalogen fluorides. Metathetical reactions and routes involving the formation of radical intermediates are being explored to this end. Low-temperature catalytic fluorinations also are being employed. In the previous report periods, fluorination by discharge-excited fluorine was used, but no new stable compounds were formed. Metathetical reactions of ClF₅ with several oxygen sources had also proved unsuccessful. Difluoramine reactions with interhalogens began during the second quarter and constitute a major portion of the current effort.
DISCUSSION

Recent attention has been given to the synthesis of FC10, F2C10, and F2N-C1F2. Efforts have also been made toward the fluorination of BrF5 and the formation of new NF20 compounds.

ATTEMPTED SYNTHESIS OF F3C10

Metathetical Reactions

Various metathetical reactions of ClF5 with oxygen sources have been attempted in the hope of producing F3C10 (Ref. 1). Although these routes to F3C10 have not been successful, mercuric oxide appeared to be a promising oxygen source (Ref. 1) for a controlled Cl-O bond formation under mild conditions. A slow stream of ClF5, diluted by N2, was passed through a Kel-F U-tube packed with HgO on copper shot at 0 C. No new products were identified.

Since a straightforward substitution of an oxygen atom for two fluorine atoms has not been fruitful to date, it was hoped to form F3C10 through decomposition of the hypothetical species F4ClONO2 or F4ClOC103. Should F3C10 disproportionate to ClF5 and FC102, it was hoped that these reactions would at least provide some evidence of disproportionation.

The reaction of ClF4+AsF6− with KNO2 yielded only ClF5 and solids which did not contain chlorine. Hydrogen fluoride was added to increase low-temperature contact and favor KF formation. In the presence of stoichiometric amounts of HF, the products were ClO2, FC1O2, FC1O3, and
solids, presumably KHF₂ and NO₂⁻AsF₆⁻. Elimination of AsF₅⁻ as a reactant gave similar results except that FNO₂ was observed. The addition of HF probably changed the reactant KNO₃ to HONO₂, thus promoting the observed reactions. The presence of large amounts of ClO₂ and FCIO₃ indicated that ClF₅ reacted with a hydroxy compound (Ref. 2). The decomposition of F₄ClONO₂ to F₃ClO might have been followed by disproportionation to ClF₅ and FCIO₂ but not to large amounts of FCIO₃.

The reaction of ClF₅ and KCIO₄ with HF added was not expected to involve a hydroxy compound exclusively, since HOCIO₃ is a stronger acid than HF. Although no reaction was noted at 150 C for prolonged periods in the absence of HF, a stoichiometric amount of HCl caused ClO₂, FCIO₂, and FCIO₃ to be formed. Even the application of conditions sufficient for incipient reaction gave identical products, suggesting that the fluorination of ClO₄⁻ to give oxygen is the only reaction. Again, no evidence for F₃ClO, even as an intermediate, was obtained.

**Oxidation Reactions**

Another route to F₃ClO under consideration is the combination of ClF₃ and atomic oxygen. The reaction of SF₄ and a mixture of NO₂ and O₂ under ultraviolet light is known to give F₄SO (Ref. 3). The reaction of ClF₅ and O₂ was intended to produce F₃ClO. A 2:1 O₂:ClF₃ mixture was condensed into a Kel-F infrared gas cell at -196 C and allowed to warm to room temperature while scanning. Although Pennsalt (Ref. 4) has found no products from bubbling O₂ through ClF₃, a short-lived product could have escaped detection in a flow reaction where products are examined later.
By following infrared absorbances as a function of time, the rate of ozone decomposition was found to be apparently dependent on ozone concentration, in agreement with the results of Benson and Axworthy (Ref. 5), whereas the reaction of ClF₃ to FCIO₂ proceeded at a constant, slow rate. Ultraviolet irradiation of the mixture had no marked effect on these rates and may have been of insufficient power to penetrate the Kel-F cell body. Although no infrared bands definitely attributable to FCIO or FCIO₂ were found, unidentified bands at 5.1, 8.7, and 12.9 microns appeared and increased during the course of the reaction. Further study on this reaction is planned.

FLUORINATION OF Cl-O COMPOUNDS

The synthesis of new F-Cl-O compounds has been attempted previously by fluorination of compounds containing Cl-O bonds. Low-temperature reaction of FCIO₂ with excited fluorine yielded no new stable products (Ref. 1). Since compounds with only one Cl-O bond should provide a more facile route to compounds such as FCIO, F₃ClO, and F₅ClO, the fluorination of calcium hypochlorite and chlorine monoxide has been examined.

Calcium Hypochlorite

Excess fluorine and calcium hypochlorite reacted at 125°C in a stainless-steel cylinder to form FCIO₅. The same reaction at room temperature produced FCIO₃, FCIO₂, and a trace of Cl₂O₆ as volatiles. When the hypochlorite was mixed with dried, powdered CsF and reacted with fluorine at -80°C, the gas products were FCIO₃, FCIO₂, ClO₂, and a trace of SO₂F₂. Bunn (Ref. 6) has stated that the X-ray examination of calcium hypochlorite
indicates that the composition is 3 Ca(OCl)$_2$, 2 Ca(OH)$_2$, 2 H$_2$O and Ca(OCl)$_2$, 2 Ca(OH)$_2$. Apparently, fluorination of the OH groups occurred in preference to the formation of new F-Cl-O species.

**Chlorine Monoxide**

A greater chance for success was anticipated in the fluorination of Cl$_2$O since oxygen is bonded only to chlorine. When Cl$_2$O and F$_2$ were reacted in a stainless-steel cylinder at 125 C, ClF$_3$, FCIO$_2$, and ClO$_2$ resulted. By condensing Cl$_2$O over dried CsF at -80 C and reacting with fluorine, FCIO$_2$ and ClO$_2$ were obtained in addition to an unidentified compound. Infrared absorptions in the Cl-O and Cl-F regions support a chlorine oxyfluoride candidate. This last experiment is being repeated in an attempt to produce sufficient quantities of the unknown for identification.

**REACTIONS LEADING TO NEW NF$_2$O COMPOUNDS**

**Attempted Synthesis of ClNF$_2$O**

The existence of ClNF$_2$ and F$_3$NO suggested the possibility that ClNF$_2$O may exist as well. The likely approach to the synthesis of this molecule was by the dissociation of the complex NF$_2$O$^+$BF Cl$^-$, where the dissociation products would be F$_3$NO, BF$_2$Cl, and possibly some ClNF$_2$O and BF$_5$. Since BF$_2$Cl readily establishes an equilibrium with BF$_3$, BFCl$_2$, and BCl$_3$ at room temperature (Ref. 7), a 5:1 BF$_3$-BCl$_3$ mixture was allowed to equilibrate; it was then frozen, and the excess BF$_3$ was pumped off at -142 C. The residual mixture, rich in BF$_2$Cl, was reacted with F$_3$NO at -142 C and allowed to warm to -80 C. Further warming resulted in the formation of
Cl<sub>2</sub>, F<sub>3</sub>N<sub>0</sub>, BF<sub>3</sub>, and a white solid, probably NO<sup>+</sup>BF<sub>4</sub><sup>-</sup>. The reaction written on the basis of the recovered products is:

\[
2 \text{F}_3\text{NO} \cdot \text{BF}_2\text{Cl} = \text{F}_3\text{NO} + \text{BF}_3 + \text{Cl}_2 + \text{NO}^+\text{BF}_4^- \quad (1)
\]

Whether chlorine resulted from BF<sub>2</sub>Cl oxidation or ClNF<sub>2</sub>O instability is not known.

**Attempted Synthesis of NF<sub>2</sub>ONO<sub>2</sub>**

In an effort to extend the synthesis of ONF<sub>2</sub> compounds to inorganic chemistry, a method recently discovered at Rocketdyne with organic hypo-fluorites under Contract AF04(611)-9577 was applied to fluorine nitrate, an inorganic OF compound. Fluorine nitrate was reacted with the potassium fluoride-difluoramine complex in an attempt to produce NF<sub>2</sub>ONO<sub>2</sub>:

\[
\text{FONO}_2 + \text{KF} \cdot \text{HNF}_2 \rightarrow \text{KHF}_2 + \text{NF}_2\text{ONO}_2 \quad (2)
\]

The experiment was conducted in a Kel-F ampoule and kept at -80°C for approximately 40 hours. Examination of the gaseous products after fractionation revealed the presence of only NO<sub>2</sub>, FNO<sub>2</sub>, and N<sub>2</sub>F<sub>4</sub>. None of the desired product was obtained. However, it is interesting to note that N<sub>2</sub>F<sub>2</sub>, NF<sub>3</sub>, FNO, and F<sub>3</sub>N<sub>0</sub> were absent as well. The results are consistent with the initial production of NO<sup>-</sup> and NF<sup>-</sup> radicals. Since N<sub>2</sub>F<sub>2</sub> was not a product, the formation of HF was probably due to the reaction of FONO<sub>2</sub> with HNF<sub>2</sub> rather than the decomposition of the KF-HNF<sub>2</sub> complex. The instability of the resultant NO<sup>-</sup> radical could then explain
the failure to achieve the desired NF₂ONO₂. A more stable radical such as Cl₃⁺ may allow the formation of the compound 0₂ClNF₂:

\[ \text{FCIO}_2 + \text{K}^+\text{HNF}_2 \rightarrow \text{KHF}_2 + 0_2\text{ClNF}_2 \]  

Studies on this reaction are in progress.

**FLUORINATION OF BrF₅**

The synthesis of BrF₅ had been attempted previously at Rocketdyne by the fluorination of CsBrF₆ as well as BrF₇ itself. Failure to obtain BrF₇ may have been due to its instability with respect to BrF₅ and F₂ except at low temperatures. Therefore, the reaction of BrF₅, frozen at -196°C, with a discharge-excited fluorine stream was attempted. When the frozen products were slowly warmed, no noncondensibles were observed, in contrast to similar fluorinations of N₂O₄ and FCIO₂ (Ref. 1). Similar negative results were obtained when a stream of premixed BrF₅ and excess F₂ was passed through a glow discharge and immediately frozen. The only Br-F compound found was the starting material.

**METATHETICAL REACTIONS OF HNF₂**

During this period a thorough investigation of the reactions between CI-F compounds and difluoramine was initiated and is continuing.

The reactions of CI-F compounds and difluoramine were undertaken as a possible method for producing new derivatives of interhalogen fluorides. Specifically, it was proposed (Ref. 8) that the low-temperature reaction of CIF₃ and HNF₂ might lead to the coordination of these two materials and the formation of a CI-N bond followed by the elimination of HF.
\[
\text{ClF}_3 + \text{HNF}_2 \rightarrow \left[ \text{Cl}^{-} : \text{NF}_2^+ \right] \rightarrow \text{F}_2\text{ClNF}_2 + \text{HF}
\]

This manner an \( \text{NF}_2 \)-substituted interhalogen might be synthesized.

**Apparatus Reactivity**

Initial efforts were conducted in a metal–Teflon vacuum system. However, it was soon determined that the decomposition of \( \text{HNF}_2 \) on the fluorine-treated metal surfaces occurred too rapidly to allow effective mixing of the reactants for reasonable time periods. This decomposition reaction resulted in the conversion of \( \text{HNF}_2 \) to tetrafluorohydrazine.

Later experiments utilized an all-Pyrex apparatus and mercury manometer to follow pressure changes in the system. A covering of halocarbon oil prevented contact of the difluoramine with the mercury. In thoroughly cleaned and dried Pyrex, known Cl–F compounds are stable for short periods.

**Difluoramine–Chlorine Trifluoride Systems**

In addition to the studies involving the action of pure and uncomplexed \( \text{ClF}_3 \) and \( \text{ClF}_5 \) on difluoramine, several other variations in the form of the reactants have been utilized. In particular, \( \text{ClF}_2^+\text{BF}_4^- \), \( \text{KF} \cdot \text{KClF}_4 \), and \( \text{RbClF}_4 \), complexes of \( \text{ClF}_3 \), have been used. In some instances an \( \text{HNF}_2 \cdot \text{BF}_3 \) complex has been employed.
Neat Reactions. When ClF$_3$ and HNF$_2$ were condensed together in a Pyrex reactor and then allowed to warm to melting, an instantaneous reaction was noted by a vapor pressure surge to a constant value. In one instance there was an accompanying audible pop but no flash or light emission. Subsequent fractionation of the volatile materials revealed that all the difluoramine was consumed when equimolar amounts of reagents were used. Some excess HNF$_2$ over a 1:1 stoichiometry also reacted. Based on the limiting reagent, the yields of ClNF$_2$ varied from 62 to 95 percent. Smaller amounts of N$_2$F$_4$ were produced accompanied by occasional traces of NF$_3$. In addition to these N-F moieties, slight but detectable concentrations of ClNO also were found. Although ClF$_3$ was not recovered, some FCIO$_2$ and ClO$_2$ were observed. These, together with the ClNO formation, indicated partial hydrolysces: ClF$_3$ + H$_2$O $\rightarrow$ FCIO$_2$, HF and ClNF$_2$ + H$_2$O $\rightarrow$ ClNO, HF. Though the system was initially dry, the action of HF on the Pyrex apparatus would result in O-H formation.

Reactions Involving Complexed Reagents. Because of the rapidity of the HNF$_2$-ClF$_3$ reaction, experiments were carried out using BF$_3$ as a complexing agent for ClF$_3$ or HNF$_2$. This resulted in the desired moderation of the reaction rate. For example, at -80°C when equimolar amounts of ClF$_3$ and HNF$_2$·BF$_3$ were mixed, the appearance of ClNF$_2$ and other N-F species was still noted after 4 days, although most of the total yield was obtained after 40 minutes. This pronounced decrease in the rate of reaction is probably due to the complexing of ClF$_3$ by BF$_3$ made available by reaction of HNF$_2$, as well as the decrease in free HNF$_2$ concentration.

Chlorodifluoramine was the principal nitrogen-containing product in these BF$_3$ systems whether 1:1, 1:2, or 2:1 molar proportions of ClF$_3$ and HNF$_2$ were used. The results of these experiments also showed that reaction
temperatures above -80 C led to an increased proportion of N$_2$F$_4$ among the products. The relative amount of N$_2$F$_4$ was also increased by an excess of HNF$_2$, while the NF$_3$ yield was increased by an excess of ClF$_3$. Nitrogen trifluoride was found only in trace amounts at or below -80 C or when there was no excess of Cl-F reagent.

The solid compounds KF·KClF$_4$ and RbClF$_4$ were treated with pure HNF$_2$ and it was determined that reaction at -80 C was very slow. The rubidium salt was the least reactive of the Cl-F moieties tested. Definite conclusions regarding the relative reactivity of the potassium salt can be made since in one experiment an explosion occurred upon warming the mixture to room temperature directly from -142 C. However, when the intermediate temperature of -80 C was maintained for some time before further warming, no explosion resulted.

The yields of ClNF$_2$ obtained with these solid Cl-F compounds were about 50 percent or lower. The larger amounts of N$_2$F$_4$ found probably reflect the higher temperatures needed to achieve reaction. The formation of N$_2$F$_4$ is increased, then, by increased temperature as well as by the absence of ClF$_3$ complexing moieties.

The RbF and KF formed or present initially in these reactions proved effective in scavenging the HF obtained during the reactions. To have the greater reactivity of the volatile ClF$_3$ and yet still eliminate the possible detrimental effects of free HF, some reactions were conducted using NaF to "neutralize" the HF. The results are not yet complete but do not appear to be significantly different than those found in experiments run in the absence of NaF.
Recovery of Nitrogen-Containing Products. The complete recovery of difluoramine nitrogen as volatile compounds was not realized. The remaining 10 to 20 percent was probably present in a residual white solid. Upon hydrolysis, these solids gave off \( \text{NO}_2 \), indicating the presence of \( \text{NOBF}_4 \).

This solid did not contain Cl-N-F compounds since all the reactant chlorine was obtained in the volatile materials.

To eliminate the side reactions caused by the glass apparatus, an all-Kel-F and Teflon reactor has been fabricated. Several reactions involving neat \( \text{ClF}_3 \) and \( \text{HNF}_2 \) have been conducted in this apparatus to date. For equimolar amounts of \( \text{ClF}_3 \) and \( \text{HNF}_2 \), the results were analogous to those obtained in the glass apparatus, i.e., \( \text{ClNF}_2 \) was the principal product (59 to 70 percent), with lesser amounts of \( \text{N}_2\text{F}_4 \) and \( \text{NF}_3 \) being formed. However, all the nitrogen of \( \text{HNF}_2 \) was recovered as these N-F compounds. Moreover, approximately one-third of the \( \text{ClF}_3 \) was recovered unreacted. These reactions were run at -80 \( ^\circ \) C. Future work will employ lower temperatures as well as variable mole ratios in the hope of forming and preserving the apparent intermediate \( \text{F}_2\text{F}_3 \).

Difluoramine-Chlorine Pentafluoride Systems

Chlorine pentafluoride and difluoramine have been reacted in the metal-Teflon, Pyrex, and Kel-F-Teflon reactors. At present this work has only encompassed the uncomplexed species, but it will be extended to complexed forms. As with chlorine trifluoride, the pentafluoride reacted with difluoramine to give mixtures of \( \text{ClNF}_2 \), \( \text{N}_2\text{F}_4 \), and \( \text{NF}_3 \). Unlike \( \text{ClF}_3 \), however, a smooth reaction at -80 \( ^\circ \) C gave products which were more sensitive to the
glass environment. Within minutes, the formation of NO₂ could be visibly detected. If not fractionated at once, practically no N-F or Cl-F materials were found. Instead, the degradation products N₂O₄, HNO₃, Cl₂, ClO₂, and FClO₃ were obtained. Rapid fractionation of an equimolar reaction mixture yielded as much as 77 percent ClNF₂ with 23-percent recovery of ClF₃. The remaining HNF₂ was converted to N₂F₄ and NF₃. In the Kel-F-Teflon reactor, a good correspondence between the amount of ClNF₂ formed and the amount of ClF₃ reacted also was found. The presence of the side products N₂F₄ and NF₃ again indicated a high reactivity of the Cl-F bonds of the original intermediates. Here also, the use of lower temperature was indicated as one means of decreasing this detrimental side reaction.

Factors Affecting Reactivity of Cl-F Bonds

Several significant conclusions are possible despite the failure to prove an exact stoichiometry for the reaction of these Cl-F compounds with HNF₂. The relative order of reactivity for the various systems was:

ClF₃-HNF₂ > ClF₅-HNF₂ > ClF₃-HNF₂-BF₃ > ClF₂⁺BF₄⁻-HNF₂ > RbClF₄-HNF₂

The place of KF·KClF₄ in this series is doubtful but it is probably comparable to that of RbClF₄. One very encouraging aspect is the fact that the predicted Cl-N bond is established through the interaction of these materials and is stable under these conditions. The alternative possible reactions

\[ \text{ClF}_3 + \text{HNF}_2 \rightarrow \text{NF}_3 + \text{HF} + \text{ClF} \]  \hspace{1cm} (5)

\[ \text{ClF}_5 + \text{HNF}_2 \rightarrow \text{NF}_3 + \text{HF} + \text{ClF}_3 \]  \hspace{1cm} (6)
cannot be occurring to any great extent if at all since no ClF or ClF$_3$, was observed in the reaction of ClF$_2$ or ClF$_5$, respectively. Very often there was a direct correspondence between the observed amounts of ClNF$_2$ and the loss of Cl-F species.

Therefore, it appears reasonably certain that the expected ClF-NF$_2$ moiety has at least a transient existence. However, the substitution of the NF$_2$ group into the Cl-F molecule seems to have caused a considerable enhancement in the reactivity of the remaining Cl-F bonds. This gives rise to the side reaction

$$\text{ClF}_x\text{NF}_2 + n\text{HNF}_2 \rightarrow n\text{HF} + \text{ClF}_{x-n}\text{NF}_2 + \frac{n}{2}\text{N}_2\text{F}_4$$

(7)

as well as reactions with the containing medium, in which case degradation may go even further as in the ClF$_2$ reactions. In fact, warming previously colorless fractions of reaction products in glass has upon occasion resulted in the formation of NO$_2$, SiF$_4$, and Cl$_2$.

Because of this apparent preferential reactivity of the Cl-F fluorines of ClF$_x\text{NF}_2$ with additional HNF$_2$, it was decided that an interhalogen fluoride of reduced reactivity should be examined. The compound chosen was IF$_5$.

The proposed reaction

$$\text{IF}_5 + \text{HNF}_2 \rightarrow \text{HF} + \text{IF}_4\text{NF}_2$$

(8)

was examined in both the glass and plastic reactors. Because of the relatively high temperature (0°C) necessary to melt the IF$_5$, the reaction was found to give unwanted degradation products, including I$_2$. In fact, only small amounts of N-F materials could be found.
Difluoramine-Chloryl Fluoride Systems

Another approach designed to establish a Cl-N bond from an active Cl-F compound and HNF₂ involved FC₁₀₂. This compound has been demonstrated to couple with an acidic hydrogen (Ref. 9):

\[ \text{FC}_10_2 + \text{HOSO}_2\text{F} \rightarrow 0_2\text{ClOSO}_2\text{F} + \text{HF} \]  
(9)

With HNF₂, the reaction might be expected to proceed as follows:

\[ \text{FC}_10_2 + \text{HNF}_2 \rightarrow \text{HF} + 0_2\text{ClNF}_2 \]  
(10)

This product would not be subject to the degradation reactions of the ClFₙNF₂ molecule since there are no additional Cl-F bonds to react. However, ClO₂ and possibly FCIO₂ as contaminants have been credited with deflagrations in previous ClFₙ-1NF₂ experiments (Ref. 10). To facilitate removal of ClO₂ from FCIO₂ and at the same time to moderate the reactivity of the FCIO₂, the complex ClO₂⁺BF₄⁻ was employed.

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

The gases, noncondensible at -196 C, came almost exclusively from the HNF₂. However, among the condensible products, there was a small amount of unidentified material with a sharp doublet infrared absorption at 7.6 and 7.7 microns. This does not correspond to FCIO₂, ClO, or FCIO₃ absorptions, and may indicate the desired compound. Unfortunately, the N-F region was obscured by the presence of NF₃ and the sample was too small.
to purify. Nearly all the FClO₂\textsubscript{2}-BF\textsubscript{3} complex was recovered. It is likely that the deflagration was caused by ClO\textsubscript{2}, which was formed during transfer of the complex into the reactor. Experiments in which both the FClO\textsubscript{2} and HNF\textsubscript{2} are complexed with BF\textsubscript{3} have eliminated deflagrations, but the desired compound has not been prepared (the HNF\textsubscript{2} being converted to NOBF\textsubscript{4}). Other means of moderating the reaction are being sought. In conjunction with the continued use of HNF\textsubscript{2} as a means of introducing the NF\textsubscript{2} group into Cl-F moieties, efforts will be extended to include other reactions of NF\textsubscript{2}⁻ and :NF radicals.
EXPERIMENTAL DETAILS

PREPARATION OF MATERIALS

Halogen Fluorides

Chlorine trifluoride was prepared from KF·KC1F₄ as described previously (Ref. 1) and was also obtained from the Rocketdyne pilot plant production of ClF₅, contaminated in this case with 2 to 3 percent ClF₅ but no Cl-O compounds. ClF₅ from the Rocketdyne pilot plant (99+ percent purity) was used directly.

Iodine pentafluoride was transferred from a lecture bottle to a Teflon trap on the metal vacuum line. By pumping on the discolored solid as it warmed from -196 C, the colored impurities could be removed. The remaining IF₅ was found to be pure by infrared analysis.

Chloryl fluoride mixed with chlorine dioxide was formed from ClF₅ and KC1O₃. The ClF₃ was condensed into a stainless-steel bomb containing KC1O₃ and allowed to stand at room temperature overnight. Addition of BF₃ to this mixture at -80 C gave the white solid ClO₂⁺BF₄⁻ from which the uncomplexed ClO₂ was pumped off.

Preparation of Ozone

Oxygen was partially condensed at -196 C and then allowed to pass through an electrodeless discharge zone into another -196 C trap by removing the liquid nitrogen from the first dewar flask and quickly replacing the cold
flask. An intentionally inefficient voltage was used to give a 3-percent conversion to \( O_3 \) at 150 mm Hg. After pumping off the unconverted oxygen, conveniently small amounts of pure ozone remained. Several runs were shown to give reproducible quantities by measuring the \( O_3 \) pressure by means of a small manometer. Thereafter the ozone was condensed, without first expanding, into a Kel-F infrared gas cell fitted with AgCl windows, for further reaction.

Preparation of \( Cl_2O \)

Chlorine monoxide was prepared fresh and in high purity from the reaction of chlorine gas diluted with nitrogen and dry yellow mercuric oxide (Ref. 11).

\[
2 \text{Cl}_2 + (n + 1) \text{HgO} \rightarrow \text{Cl}_2O + \text{HgCl}_2 \cdot n \text{HgO}
\]  

(11)

The \( Cl_2O \) was stored in Pyrex ampoules at -196°C.

Tetrafluorochlorine (III) Salts

The salts, \( \text{RbClF}_4 \) and \( \text{KF-KClF}_4 \), were made from \( \text{ClF}_3 \) and the appropriate alkali fluoride (Ref. 12). The \( \text{RbClF}_4 \) was a slightly crystalline white solid, while the \( \text{KF-KClF}_4 \) was in off-white powder.

Alkali Metal Fluorides

To ensure dry potassium fluoride and cesium fluoride, both compounds were first fused and then powdered and handled in a dry box.
Preparation of Fluorine Nitrate

Fluorine nitrate was prepared by the reaction of \( F_2 \) on dried \( \text{NaNO}_3 \) (Ref. 13).

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

(12)

The \( \text{FNO}_3 \) was stored at ambient temperature in a stainless-steel cylinder.

Preparation of \( \text{HNF}_2 \)

Difluoramine was prepared by the aqueous fluorination of urea followed by the treatment of the fluorinated urea solution with concentrated \( \text{H}_2\text{SO}_4 \). The impure \( \text{HNF}_2 \) was purified by low-temperature fractionation and was stored in glass ampoules at ambient temperature.

During the purification of one batch of impure \( \text{HNF}_2 \), the extreme sensitivity of difluoramine was again demonstrated by a violent explosion destroying a portion of the glass vacuum system.

REACTIONS

Reaction of \( \text{FNO}_3 \) and \( \text{HNF}_2 \)

Approximately 10 grams of dried KF were placed in the bottom of a Kel-F ampoule using a dry box. The ampoule was transferred to a glass vacuum system where 27.4 cc of \( \text{HNF}_2 \) were condensed over the KF. The ampoule
was warmed from -142 to -80 C to ensure contact of the HNF$_2$ with the KF. The ampoule was recooled to -142 C, and the FNO$_3$ (20.7 cc) was condensed over the KF-HNF$_2$. The ampoule was slowly warmed to -80 C and kept at this temperature for 42 hours. The reaction products were fractionated using the metal vacuum system and examined by infrared analysis.

Fluorination Reactions

Fluorinations were carried out using a 300-milliliter stainless-steel, high-pressure Hoke cylinder fitted with a high-pressure Hoke needle valve (Y3002H). The Cl$_2$O was condensed into the cylinder from a metal high-vacuum system. The desired amount of fluorine was then condensed into the cylinder at -196 C. The cylinder was then warmed to the desired reaction temperature. Solid starting material was handled in the dry box. Fractionation of the products was carried out in a metal vacuum system equipped with Teflon traps. Identification of reaction products was by infrared analysis using an infrared cell constructed of stainless steel and equipped with AgCl windows.

Reactions With HNF$_2$

The reactions of difluoramine and the halogen fluorides were performed by the following procedure. The least volatile compound of the pair was first condensed in the bottom part of the apparatus; the more volatile or lower-melting compound, usually HNF$_2$, was condensed above the other material. Changing the cooling baths after closing the system allowed the upper compound to melt and run down as a liquid into the second reactant.
In this manner, mixing was generally attained in the liquid state as well as in the vapor state. After selected reaction times at a particular temperature, fractionation under vacuum began. This was usually done without pumping so that the product NF₃ would not be lost, and was facilitated by the absence of any -196 C noncondensible gases in nearly all reactions.
REFERENCES


