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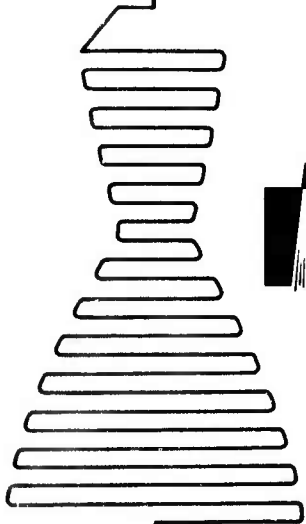
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6633 CANOGA AVENUE CANOGA PARK, CALIFORNIA

R-5883-3

(Unclassified Title)

QUARTERLY PROGRESS REPORT,  
INORGANIC HALOGEN OXIDIZERS

(1 December 1964 through 28 February 1965)

Group 4  
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Declassified After 12 Years

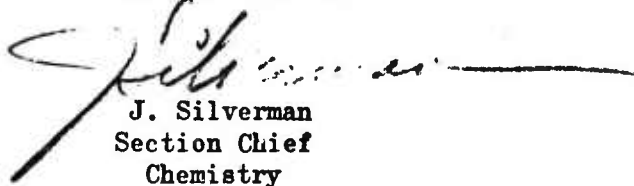
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**FOREWORD**

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.O. 8614 in compliance with Section H of Contract Nonr 4428(00) 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.

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## ABSTRACT

The synthesis of  $F_3ClO$  was attempted by reactions of  $ClF_5$  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  $FClO_2$ ,  $ClO_2$ , 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  $-80\text{ C}$  in the presence of  $CsF$ ,  $Cl_2O$  reacted with  $F_2$  to give an unidentified compound which may be a new Cl-F-O species.

The dissociation of the complex  $NF_2O^+BF_3Cl^-$  was examined in the hope of producing  $ClNF_2O$ . The only chlorine-containing product found was  $Cl_2$ .

Fluorine nitrate and the potassium fluoride-difluorine complex were reacted in the hope of forming  $NF_2ONO_2$ . The products were  $N_2F_4$ ,  $NO_2$ , and  $FNO_2$ , suggesting the initial formation of  $NO_3\cdot$  and  $NF_2\cdot$  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

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iodine pentafluoride were reacted with difluoramine. Various complexes of both  $\text{ClF}_3$  and  $\text{HNF}_2$  were explored as well. The major product was  $\text{ClNF}_2$  (as high as 95 percent), and the absence of  $\text{Cl}_2$  and  $\text{ClF}$  strongly suggested  $\text{NF}_2\text{ClF}_2$  as an intermediate. Inability to isolate  $\text{NF}_2\text{ClF}_2$  was attributed to an enhanced reactivity of the Cl-F bonds toward  $\text{HNF}_2$ . The relative reactivities for the systems examined were:  $\text{ClF}_3\text{-HNF}_2 > \text{ClF}_5\text{-HNF}_2 > \text{ClF}_3\text{-HNF}_2\text{:BF}_3 > \text{ClF}_2^+\text{BF}_4^-\text{-HNF}_2 > \text{RbClF}_4\text{-HNF}_2 \sim \text{KF-KClF}_4\text{-HNF}_2$ . Difluoramine reactions with  $\text{IF}_5$  resulted in degradation products which included  $\text{I}_2$ .

The synthesis of  $\text{NF}_2\text{ClO}_2$  was attempted by reacting  $\text{HNF}_2$  with  $\text{FClO}_2$  as well as its  $\text{BF}_3$  complexes. In the absence of  $\text{BF}_3$ , deflagrations occurred, probably due to  $\text{ClO}_2$  impurities. In the presence of  $\text{BF}_3$ , the principal nitrogen-containing product was  $\text{NOBF}_4$ .

(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  $\text{ClF}_5$  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.

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## DISCUSSION

Recent attention has been given to the synthesis of  $\text{FClO}$ ,  $\text{F}_3\text{ClO}$ , and  $\text{F}_2\text{N-ClF}_2$ . Efforts have also been made toward the fluorination of  $\text{BrF}_5$  and the formation of new  $\text{NF}_2\text{O}$  compounds.

### ATTEMPTED SYNTHESIS OF $\text{F}_3\text{ClO}$

#### Metathetical Reactions

Various metathetical reactions of  $\text{ClF}_5$  with oxygen sources have been attempted in the hope of producing  $\text{F}_3\text{ClO}$  (Ref. 1). Although these routes to  $\text{F}_3\text{ClO}$  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  $\text{ClF}_5$ , diluted by  $\text{N}_2$ , was passed through a Kel-F U-tube packed with  $\text{HgO}$  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  $\text{F}_3\text{ClO}$  through decomposition of the hypothetical species  $\text{F}_4\text{ClONO}_2$  or  $\text{F}_4\text{ClOClO}_3$ . Should  $\text{F}_3\text{ClO}$  disproportionate to  $\text{ClF}_5$  and  $\text{FClO}_2$ , it was hoped that these reactions would at least provide some evidence of disproportionation.

The reaction of  $\text{ClF}_4^+\text{AsF}_6^-$  with  $\text{KNO}_3$  yielded only  $\text{ClF}_5$  and solids which did not contain chlorine. Hydrogen fluoride was added to increase low-temperature contact and favor  $\text{KF}$  formation. In the presence of stoichiometric amounts of  $\text{HF}$ , the products were  $\text{ClO}_2$ ,  $\text{FClO}_2$ ,  $\text{FClO}_3$ , and

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solids, presumably  $\text{KHF}_2$  and  $\text{NO}_2^+\text{AsF}_6^-$ . Elimination of  $\text{AsF}_5$  as a reactant gave similar results except that  $\text{FNO}_2$  was observed. The addition of HF probably changed the reactant  $\text{KNO}_3$  to  $\text{HONO}_2$ , thus promoting the observed reactions. The presence of large amounts of  $\text{ClO}_2$  and  $\text{FClO}_3$  indicated that  $\text{ClF}_5$  reacted with a hydroxy compound (Ref. 2). The decomposition of  $\text{F}_4\text{ClONO}_2$  to  $\text{F}_3\text{ClO}$  might have been followed by disproportionation to  $\text{ClF}_5$  and  $\text{FClO}_2$  but not to large amounts of  $\text{FClO}_3$ .

The reaction of  $\text{ClF}_5$  and  $\text{KClO}_4$  with HF added was not expected to involve a hydroxy compound exclusively, since  $\text{HOClO}_3$  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 H<sub>2</sub> caused  $\text{ClO}_2$ ,  $\text{FClO}_2$ , and  $\text{FClO}_3$  to be formed. Even the application of conditions sufficient for incipient reaction gave identical products, suggesting that the fluorination of  $\text{ClO}_4^-$  to give oxygen is the only reaction. Again, no evidence for  $\text{F}_3\text{ClO}$ , even as an intermediate, was obtained.

#### Oxidation Reactions

Another route to  $\text{F}_3\text{ClO}$  under consideration is the combination of  $\text{ClF}_3$  and atomic oxygen. The reaction of  $\text{SF}_4$  and a mixture of  $\text{NO}_2$  and  $\text{O}_2$  under ultraviolet light is known to give  $\text{F}_4\text{SO}$  (Ref. 3). The reaction of  $\text{ClF}_3$  and  $\text{O}_3$  was intended to produce  $\text{F}_3\text{ClO}$ . A 2:1  $\text{O}_3$ - $\text{ClF}_3$  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  $\text{O}_3$  through  $\text{ClF}_3$ , a short-lived product could have escaped detection in a flow reaction where products are examined later

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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  $\text{ClF}_3$  to  $\text{FClO}_2$  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  $\text{FClO}$  or  $\text{F}_3\text{ClO}$  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  $\text{FClO}_2$  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  $\text{FClO}$ ,  $\text{F}_3\text{ClO}$ , and  $\text{F}_5\text{ClO}$ , 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  $\text{FClO}_3$ . The same reaction at room temperature produced  $\text{FClO}_3$ ,  $\text{FClO}_2$ , and a trace of  $\text{Cl}_2\text{O}_6$  as volatiles. When the hypochlorite was mixed with dried, powdered  $\text{CsF}$  and reacted with fluorine at -80 C, the gas products were  $\text{FClO}_3$ ,  $\text{FClO}_2$ ,  $\text{ClO}_2$ , and a trace of  $\text{SO}_2\text{F}_2$ . Bunn (Ref. 6) has stated that the X-ray examination of calcium hypochlorite

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indicates that the composition is  $3 \text{Ca}(\text{OCl})_2$ ,  $2 \text{Ca}(\text{OH})_2$ ,  $2 \text{H}_2\text{O}$  and  $\text{Ca}(\text{OCl})_2$ ,  $2 \text{Ca}(\text{OH})_2$ . 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  $\text{Cl}_2\text{O}$  since oxygen is bonded only to chlorine. When  $\text{Cl}_2\text{O}$  and  $\text{F}_2$  were reacted in a stainless-steel cylinder at 125 C,  $\text{ClF}_3$ ,  $\text{FClO}_2$ , and  $\text{ClO}_2$  resulted. By condensing  $\text{Cl}_2\text{O}$  over dried CsF at -80 C and reacting with fluorine,  $\text{FClO}_2$  and  $\text{ClO}_2$  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 $\text{NF}_2\text{O}$ COMPOUNDS

### Attempted Synthesis of $\text{ClNF}_2\text{O}$

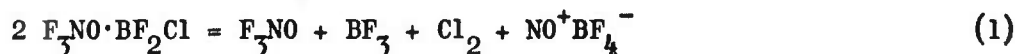
The existence of  $\text{ClNF}_2$  and  $\text{F}_3\text{NO}$  suggested the possibility that  $\text{ClNF}_2\text{O}$  may exist as well. The likely approach to the synthesis of this molecule was by the dissociation of the complex  $\text{NF}_2\text{O}^+\text{BF}_3\text{Cl}^-$ , where the dissociation products would be  $\text{F}_3\text{NO}$ ,  $\text{BF}_2\text{Cl}$ , and possibly some  $\text{ClNF}_2\text{O}$  and  $\text{BF}_3$ . Since  $\text{BF}_2\text{Cl}$  readily establishes an equilibrium with  $\text{BF}_3$ ,  $\text{BFCl}_2$ , and  $\text{BCl}_3$  at room temperature (Ref. 7), a 5:1  $\text{BF}_3$ - $\text{BCl}_3$  mixture was allowed to equilibrate; it was then frozen, and the excess  $\text{BF}_3$  was pumped off at -142 C. The residual mixture, rich in  $\text{BF}_2\text{Cl}$ , was reacted with  $\text{F}_3\text{NO}$  at -142 C and allowed to warm to -80 C. Further warming resulted in the formation of

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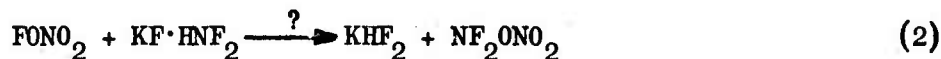
$\text{Cl}_2$ ,  $\text{F}_3\text{NO}$ ,  $\text{BF}_3$ , and a white solid, probably  $\text{NO}^+\text{BF}_4^-$ . The reaction written on the basis of the recovered products is:



Whether chlorine resulted from  $\text{BF}_2\text{Cl}$  oxidation or  $\text{ClNF}_2\text{O}$  instability is not known.

## Attempted Synthesis of $\text{NF}_2\text{ONO}_2$

In an effort to extend the synthesis of  $\text{ONF}_2$  compounds to inorganic chemistry, a method recently discovered at Rocketdyne with organic hypofluorites under Contract AF04(611)-9577 was applied to fluorine nitrate, an inorganic OF compound. Fluorine nitrate was reacted with the potassium fluoride-difluorammine complex in an attempt to produce  $\text{NF}_2\text{ONO}_2$ :



The experiment was conducted in a Kel-F ampoule and kept at  $-80^\circ\text{C}$  for approximately 40 hours. Examination of the gaseous products after fractionation revealed the presence of only  $\text{NO}_2$ ,  $\text{FNO}_2$ , and  $\text{N}_2\text{F}_4$ . None of the desired product was obtained. However, it is interesting to note that  $\text{N}_2\text{F}_2$ ,  $\text{NF}_3$ ,  $\text{FNO}$ , and  $\text{F}_3\text{NO}$  were absent as well. The results are consistent with the initial production of  $\text{NO}_3^\cdot$  and  $\text{NF}_2^\cdot$  radicals. Since  $\text{N}_2\text{F}_2$  was not a product, the formation of HF was probably due to the reaction of  $\text{FONO}_2$  with  $\text{HNF}_2$  rather than the decomposition of the  $\text{KF} \cdot \text{HNF}_2$  complex. The instability of the resultant  $\text{NO}_3^\cdot$  radical could then explain

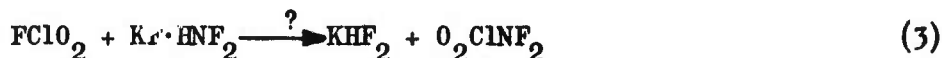
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the failure to achieve the desired  $\text{NF}_2\text{ONO}_2$ . A more stable radical such as  $\text{ClO}_2\cdot$  may allow the formation of the compound  $\text{O}_2\text{ClNF}_2$ :



Studies on this reaction are in progress.

## FLUORINATION OF $\text{BrF}_5$

The synthesis of  $\text{BrF}_7$  had been attempted previously at Rocketdyne by the fluorination of  $\text{CsBrF}_6$  as well as  $\text{BrF}_5$  itself. Failure to obtain  $\text{BrF}_7$  may have been due to its instability with respect to  $\text{BrF}_5$  and  $\text{F}_2$  except at low temperatures. Therefore, the reaction of  $\text{BrF}_5$ , frozen at  $-196^\circ\text{C}$ , 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  $\text{N}_2\text{O}_4$  and  $\text{FClO}_2$  (Ref. 1). Similar negative results were obtained when a stream of premixed  $\text{BrF}_5$  and excess  $\text{F}_2$  was passed through a glow discharge and immediately frozen. The only Br-F compound found was the starting material.

## METATHETICAL REACTIONS OF $\text{HNF}_2$

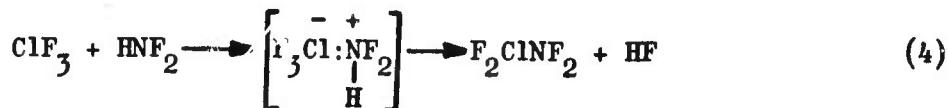
During this period a thorough investigation of the reactions between Cl-F compounds and difluoramine was initiated and is continuing.

The reactions of Cl-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  $\text{ClF}_3$  and  $\text{HNF}_2$  might lead to the coordination of these two materials and the formation of a Cl-N bond followed by the elimination of HF.

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in 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.

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Neat Reactions. When  $\text{ClF}_3$  and  $\text{HNF}_2$  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  $\text{HNF}_2$  over a 1:1 stoichiometry also reacted. Based on the limiting reagent, the yields of  $\text{ClNF}_2$  varied from 62 to 95 percent. Smaller amounts of  $\text{N}_2\text{F}_4$  were produced accompanied by occasional traces of  $\text{NF}_3$ . In addition to these N-F moieties, slight but detectable concentrations of  $\text{ClNO}$  also were found. Although  $\text{ClF}_3$  was not recovered, some  $\text{FClO}_2$  and  $\text{ClO}_2$  were observed. These, together with the  $\text{ClNO}$  formation, indicated partial hydrolyses:  $\text{ClF}_3 + \text{H}_2\text{O} \longrightarrow \text{FClO}_2, \text{HF}$  and  $\text{ClNF}_2 + \text{H}_2\text{O} \longrightarrow \text{ClNO}, \text{HF}$ . 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  $\text{HNF}_2\text{-ClF}_3$  reaction, experiments were carried out using  $\text{BF}_3$  as a complexing agent for  $\text{ClF}_3$  or  $\text{HNF}_2$ . This resulted in the desired moderation of the reaction rate. For example, at  $-80^\circ\text{C}$  when equimolar amounts of  $\text{ClF}_3$  and  $\text{HNF}_2\cdot\text{BF}_3$  were mixed, the appearance of  $\text{ClNF}_2$  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  $\text{ClF}_3$  by  $\text{BF}_3$  made available by reaction of  $\text{HNF}_2$ , as well as the decrease in free  $\text{HNF}_2$  concentration.

Chlorodifluoramine was the principal nitrogen-containing product in these  $\text{BF}_3$  systems whether 1:1, 1:2, or 2:1 molar proportions of  $\text{ClF}_3$  and  $\text{HNF}_2$  were used. The results of these experiments also showed that reaction

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temperatures above  $-80\text{ C}$  led to an increased proportion of  $\text{N}_2\text{F}_4$  among the products. The relative amount of  $\text{N}_2\text{F}_4$  was also increased by an excess of  $\text{HNF}_2$ , while the  $\text{NF}_3$  yield was increased by an excess of  $\text{ClF}_3$ . Nitrogen trifluoride was found only in trace amounts at or below  $-80\text{ C}$  or when there was no excess of Cl-F reagent.

The solid compounds  $\text{KF}\cdot\text{KClF}_4$  and  $\text{RbClF}_4$  were treated with pure  $\text{HNF}_2$  and it was determined that reaction at  $-80\text{ C}$  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  $-142\text{ C}$ . However, when the intermediate temperature of  $-80\text{ C}$  was maintained for some time before further warming, no explosion resulted.

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

The  $\text{RbF}$  and  $\text{KF}$  formed or present initially in these reactions proved effective in scavenging the  $\text{HF}$  obtained during the reactions. To have the greater reactivity of the volatile  $\text{ClF}_3$  and yet still eliminate the possible detrimental effects of free  $\text{HF}$ , some reactions were conducted using  $\text{NaF}$  to "neutralize" the  $\text{HF}$ . The results are not yet complete but do not appear to be significantly different than those found in experiments run in the absence of  $\text{NaF}$ .

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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  $-80^\circ\text{C}$ . Future work will employ lower temperatures as well as variable mole ratios in the hope of forming and preserving the apparent intermediate  $\text{F}_2\text{NF}_2$ .

## Difluoramine-Chlorine Pentafluoride Systems

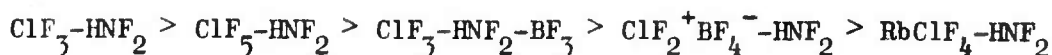
Chlorine pentafluoride and difluoramine have been reacted in the metal-Teflon, Pyrex, and Kel-F-Teflon reactors. At present this work has only encompassed the uncomplexed species, but it will be extended to complexed forms. As with chlorine trifluoride, the pentafluoride reacted with difluoramine to 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  $-80^\circ\text{C}$  gave products which were more sensitive to the



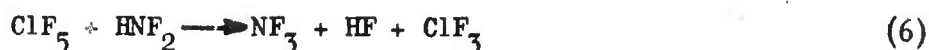
glass environment. Within minutes, the formation of  $\text{NO}_2$  could be visibly detected. If not fractionated at once, practically no N-F or Cl-F materials were found. Instead, the degradation products  $\text{N}_2\text{O}_4$ ,  $\text{HNO}_3$ ,  $\text{Cl}_2$ ,  $\text{ClO}_2$ , and  $\text{FCIO}_3$  were obtained. Rapid fractionation of an equimolar reaction mixture yielded as much as 77 percent  $\text{ClNF}_2$  with 23-percent recovery of  $\text{ClF}_5$ . The remaining  $\text{HNF}_2$  was converted to  $\text{N}_2\text{F}_4$  and  $\text{NF}_3$ . In the Kel-F-Teflon reactor, a good correspondence between the amount of  $\text{ClNF}_2$  formed and the amount of  $\text{ClF}_5$  reacted also was found. The presence of the side products  $\text{N}_2\text{F}_4$  and  $\text{NF}_3$  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  $\text{HNF}_2$ . The relative order of reactivity for the various systems was:



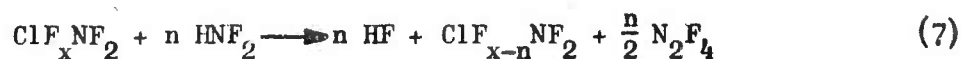
The place of  $\text{KF}\cdot\text{KClF}_4$  in this series is doubtful but it is probably comparable to that of  $\text{RbClF}_4$ . One very encouraging aspect is the fact that the predicted Cl-N bond is established through the interaction of these materials and is stable under these conditions. The alternative possible reactions





cannot be occurring to any great extent if at all since no ClF or ClF<sub>3</sub> was observed in the reaction of ClF<sub>3</sub> or ClF<sub>5</sub>, respectively. Very often there was a direct correspondence between the observed amounts of ClNF<sub>2</sub> and the loss of Cl-F species.

Therefore, it appears reasonably certain that the expected ClF<sub>x</sub>NF<sub>2</sub> moiety has at least a transient existence. However, the substitution of the NF<sub>2</sub> 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



as well as reactions with the containing medium, in which case degradation may go even further as in the ClF<sub>5</sub> reactions. In fact, warming previously colorless fractions of reaction products in glass has upon occasion resulted in the formation of NO<sub>2</sub>, SiF<sub>4</sub>, and Cl<sub>2</sub>.

Because of this apparent preferential reactivity of the Cl-F fluorines of ClF<sub>x</sub>NF<sub>2</sub> with additional HNF<sub>2</sub>, it was decided that an interhalogen fluoride of reduced reactivity should be examined. The compound chosen was IF<sub>5</sub>. The proposed reaction



was examined in both the glass and plastic reactors. Because of the relatively high temperature (0 C) necessary to melt the IF<sub>5</sub>, the reaction was found to give unwanted degradation products, including I<sub>2</sub>. In fact, only small amounts of N-F materials could be found.

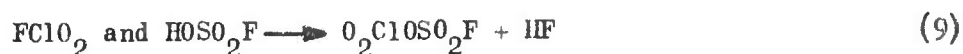
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## Difluoramino-Chloryl Fluoride Systems

Another approach designed to establish a Cl-N bond from an active Cl-F compound and  $\text{HNF}_2$  involved  $\text{FClO}_2$ . This compound has been demonstrated to couple with an acidic hydrogen (Ref. 9):



With  $\text{HNF}_2$ , the reaction might be expected to proceed as follows:



This product would not be subject to the degradation reactions of the  $\text{ClF}_x\text{NF}_2$  molecule since there are no additional Cl-F bonds to react. However,  $\text{ClO}_2$  and possibly  $\text{FClO}_2$  as contaminants have been credited with deflagrations in previous  $\text{ClF}_3\text{-HNF}_2$  experiments (Ref. 10). To facilitate removal of  $\text{ClO}_2$  from  $\text{FClO}_2$  and at the same time to moderate the reactivity of the  $\text{FClO}_2$ , the complex  $\text{ClO}_2^+\text{BF}_4^-$  was employed.

Chlorine dioxide was removed from the relatively nonvolatile complex at  $-80^\circ\text{C}$ . The complex was then transferred to the Kel-F reactor, and  $\text{HNF}_2$  was added at  $-142^\circ\text{C}$ . Upon warming the mixture to  $-80^\circ\text{C}$ , a deflagration occurred.

The gases, noncondensable at  $-196^\circ\text{C}$ , came almost exclusively from the  $\text{HNF}_2$ . However, among the condensable 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  $\text{FClO}_2$ ,  $\text{ClO}$ , or  $\text{FClO}_3$  absorptions, and may indicate the desired compound. Unfortunately, the N-F region was obscured by the presence of  $\text{NF}_3$  and the sample was too small

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to purify. Nearly all the  $\text{FClO}_2\text{-BF}_3$  complex was recovered. It is likely that the deflagration was caused by  $\text{ClO}_2$  which was formed during transfer of the complex into the reactor. Experiments in which both the  $\text{FClO}_2$  and  $\text{HNF}_2$  are complexed with  $\text{BF}_3$  have eliminated deflagrations, but the desired compound has not been prepared (the  $\text{HNF}_2$  being converted to  $\text{NOBF}_4$ ). Other means of moderating the reaction are being sought. In conjunction with the continued use of  $\text{HNF}_2$  as a means of introducing the  $\text{NF}_2$  group into Cl-F moieties, efforts will be extended to include other reactions of  $\text{NF}_2\cdot$  and  $:\text{NF}$  radicals.

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## EXPERIMENTAL DETAILS

## PREPARATION OF MATERIALS

Halogen Fluorides

Chlorine trifluoride was prepared from  $\text{KF} \cdot \text{KClF}_4$  as described previously (Ref. 1) and was also obtained from the Rocketdyne pilot plant production of  $\text{ClF}_5$ , contaminated in this case with 2 to 3 percent  $\text{ClF}_5$  but no Cl-O compounds.  $\text{ClF}_5$  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  $-196^\circ\text{C}$ , the colored impurities could be removed. The remaining  $\text{IF}_5$  was found to be pure by infrared analysis.

Chloryl fluoride mixed with chlorine dioxide was formed from  $\text{ClF}_3$  and  $\text{KClO}_3$ . The  $\text{ClF}_3$  was condensed into a stainless-steel bomb containing  $\text{KClO}_3$  and allowed to stand at room temperature overnight. Addition of  $\text{BF}_3$  to this mixture at  $-80^\circ\text{C}$  gave the white solid  $\text{ClO}_2^+ \text{BF}_4^-$  from which the uncomplexed  $\text{ClO}_2$  was pumped off.

Preparation of Ozone

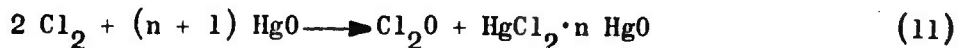
Oxygen was partially condensed at  $-196^\circ\text{C}$  and then allowed to pass through an electrodeless discharge zone into another  $-196^\circ\text{C}$  trap by removing the liquid nitrogen from the first dewar flask and quickly replacing the cold



flask. An intentionally inefficient voltage was used to give a 3-percent conversion to  $O_3$  at 160 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).



The  $Cl_2O$  was stored in Pyrex ampoules at  $-196$  C.

#### Tetrafluorochlorine (III) Salts

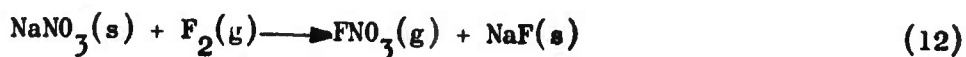
The salts,  $RbClF_4$  and  $KF \cdot KClF_4$ , were made from  $ClF_3$  and the appropriate alkali fluoride (Ref. 12). The  $RbClF_4$  was a slightly crystalline white solid, while the  $KF \cdot KClF_4$  was an off-white powder.

#### 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  $NaNO_3$  (Ref. 13).



The  $FNO_3$  was stored at ambient temperature in a stainless-steel cylinder.

Preparation of  $HNF_2$ 

Difluoramine was prepared by the aqueous fluorination of urea followed by the treatment of the fluorinated urea solution with concentrated  $H_2SO_4$ . The impure  $HNF_2$  was purified by low-temperature fractionation and was stored in glass ampoules at ambient temperature.

During the purification of one batch of impure  $HNF_2$ , the extreme sensitivity of difluoramine was again demonstrated by a violent explosion destroying a portion of the glass vacuum system.

## REACTIONS

Reaction of  $FNO_3$  and  $HNF_2$ 

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  $HNF_2$  were condensed over the KF. The ampoule

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was warmed from  $-142$  to  $-80$  C to ensure contact of the  $\text{HNF}_2$  with the KF. The ampoule was recooled to  $-142$  C, and the  $\text{FNO}_3$  (20.7 cc) was condensed over the KF- $\text{HNF}_2$ . 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  $\text{Cl}_2\text{O}$  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 $\text{HNF}_2$

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  $\text{HNF}_2$ , 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.

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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  $\text{NF}_3$  would not be lost, and was facilitated by the absence of any  $-196^\circ\text{C}$  noncondensable gases in nearly all reactions.

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