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**CRITICAL REVIEW OF THE CHEMISTRY OF ADVANCED  
OXIDIZERS AND FUELS: SUPPLEMENTARY REVIEW  
OF OXIDIZERS, 1965-1967**

Edward W. Lawless  
Thomas Lapp  
Hope M. Howard  
Midwest Research Institute

March 1968

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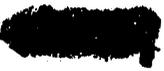
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## FOREWORD

This program has been conducted at Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri, 64110, under Contract No. FO4611-67-C-0079 (Midwest Research Institute Project No. 3044-C) and covers the period 1 February 1967 - 31 January 1968. Project personnel have consisted of Dr. Edward W. Lawless, who served as project leader, Dr. Thomas Lapp and Miss Hope M. Howard, all under the general supervision of Dr. Albert D. McElroy, Head of MRI's Physical and Inorganic Chemistry Section. Drs. Lapp and Lawless contributed the chapters on organic and inorganic derivatives, respectively, and Miss Howard prepared the physical properties tables and provided general assistance in document acquisition, control and publication. Dr. Harold Orel reviewed the manuscript editorially. Lt. C. S. Stone, Lt. Thomas E. McCann and Dr. L. Quinn have served as Project Engineers for the Air Force Rocket Propulsion Laboratory.

Under a previous contract, Midwest Research Institute completed and distributed two reviews related to the advanced propellant ingredients: "A Critical Review of the Chemistry of Advanced Oxidizers, Volumes I and II" (31 December 1965) and "A Critical Review of the Chemistry of Advanced Fuels" (1 March 1966). Because of the continuing research on such materials and the Air Force's interest in advanced propellant chemistry, the present review program was initiated with the objective of preparing three annual supplements to the previous MRI reviews. Because of funding cutbacks, this program was terminated during the first year. This review therefore covers only a portion of the propellant chemistry included in the previous review.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

This technical report has been reviewed and is approved.

W. H. EBELKE, Colonel, USAF  
Chief, Propellant Division

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ABSTRACT

This review summarizes much of the chemistry of advanced oxidizers which have been reported since the completion of the previous MRI report, "A Critical Review of the Chemistry of Advanced Oxidizers," Volumes I and II, 31 December 1965, which was prepared for the Advanced Research Projects Agency under Contract DA-31-ARO(D)-18, Mod. No. 2 & 3. The present review covers the areas of inorganic N-F, Cl-F and O-F oxidizers and organic NF oxidizers with N-containing functional groups, or N-N bonds. Other advanced oxidizers and advanced fuels which were described in the previous review could not be covered in detail in the present review because of contract termination, but properties data and literature references are tabulated for all types of advanced oxidizers. These tabulations include physical properties data on 170 compounds, thermodynamic data on 93 compounds and spectral information on 239 compounds. The review contains 29 tables, 535 references to technical reports or papers presented at symposia, 210 references to open literature publications, and 236 pages.

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## I. INTRODUCTION

The intense research effort on advanced oxidizers and fuels during the period 1955 - 1965 has recently been critically reviewed (284a). Although Government support of advanced propellant chemistry has since been much reduced, a substantial number of sponsored programs have continued and new research results are regularly appearing in the literature from industrial, academic and foreign laboratories. Hence, the objective of this program was to provide three annual supplementary critical reviews of the chemistry of advanced oxidizers and fuels. Because of the abrupt contract termination during the first year, the scope of this supplement was necessarily reduced to those chapters most nearly completed. This supplement is not, therefore, to be considered a complete review, even for the chapters included. Also, the recent flood of published papers resulting from declassification of much of the oxidizer chemistry could not be fully integrated. In order to make this document as useful as possible to the reader, extensive bibliographies have been made of technical reports received for review and of published papers noted in literature searches.

In general, the text is limited to coverage of one area of organic CNF oxidizers and the inorganic NF, ClF and OF, oxidizers. The properties tabulations include all data accumulated on oxidizers and fuels. The organic oxidizer area describes NF compounds with N-containing functional groups or NN bonds. These chapters summarize reactions of compounds which have, in addition to their  $\text{NF}_2$  content, one or more of the following N-containing groups or structural elements: amide ( $-\text{C}(=\text{O})\text{N}<$ ), amidine ( $-\text{C}(=\text{N})\text{N}<$ ), amine ( $-\text{NH}_2$ ), biguanide ( $>\text{N}-\text{C}(=\text{N})\text{NC}(=\text{N})\text{N}<$ ), biguanidine ( $>\text{NC}(=\text{N})\text{N}-\text{NC}(=\text{N})\text{N}<$ ), biurea ( $>\text{NC}(=\text{O})\text{N}-\text{NC}(=\text{O})\text{N}<$ ), cyanamide ( $>\text{N}-\text{CN}$ ), cyanide ( $-\text{CN}$ ), dicyanamide ( $-\text{N}(\text{CN})_2$ ), fluoramine ( $\text{NFH}$ ), fluorimine ( $=\text{NF}$ ), guanidine ( $>\text{NC}(=\text{N})\text{N}<$ ), imine ( $>\text{C}=\text{N}$ ), isocyanate ( $\text{NCO}$ ), or urea ( $>\text{NC}(=\text{O})\text{N}<$ ); N-containing rings such as piperidine, pyrrolidine or triazine, N-N, N=N and N- $\text{NO}_2$ . This portion is arranged into chapters divided according to the following general classes: (1) amines, (2) cyanides (nitriles), (3) amides, (4) imines, and (5) NN bonded compounds.

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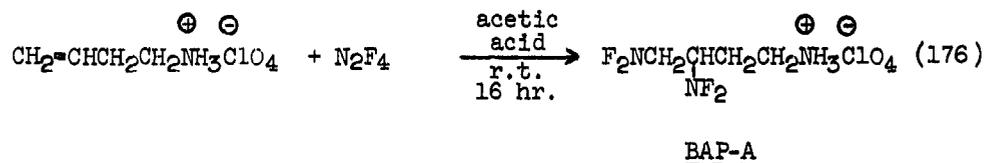
## CHAPTER I

### ORGANIC NF COMPOUNDS: AMINES, FLUORAMINES, AND AMINE FLUORINATIONS

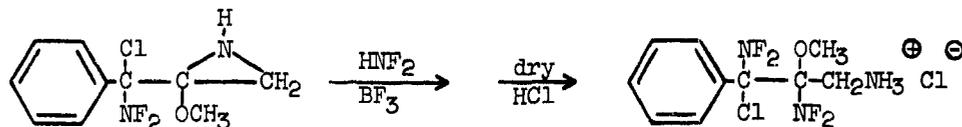
#### I-A. Amines and Fluoramines

Relatively few investigations have been conducted using fluorine-containing amines because of their strong tendencies to eliminate hydrogen fluoride or difluoramine.

The formation of 1:1 complexes and amine salts has been reported for a limited number of amines. Tris(difluoramino)methylamine (code name: Tris-A) was found to form a 1:1 complex with triphenylphosphine oxide (85b). Addition of a solution of perchloric acid in ethanol to 2,2',2''-tris(difluoramino)triethylamine resulted in the formation of a white hygroscopic solid, which probably is the normal amine perchlorate salt:  $(\text{NF}_2\text{CH}_2\text{CH}_2)_3\text{NH}^+\text{ClO}_4^-$  (268). The reaction of existing amine salts in acetic acid with tetrafluorohydrazine has been utilized for the production of 2,3-bis(difluoramino)propylmethylammonium perchlorate (code name: AMAP-A) from the corresponding 2-propenylmethylammonium perchlorate (176). In an analogous reaction, the same investigators also produced 3,4-bis(difluoramino)-butylammonium perchlorate (code name: BAP-A):



In addition to tetrafluorohydrazine, difluoramine ( $\text{HNF}_2$ ) has also been utilized in the preparation of fluorine-containing amine salts, as well as the free amines. The reaction of  $\alpha,\alpha,\alpha$ -chloro-(difluoramino-(2-methoxy-2-aziridyl))-toluene with difluoramine in  $\text{BF}_3$ , followed by treatment with dry  $\text{HCl}$ , produces the substituted propylamine hydrochloride (451a, 453).



In a similar manner the reaction shown below resulted in hydrolysis instead of the anticipated product (449).

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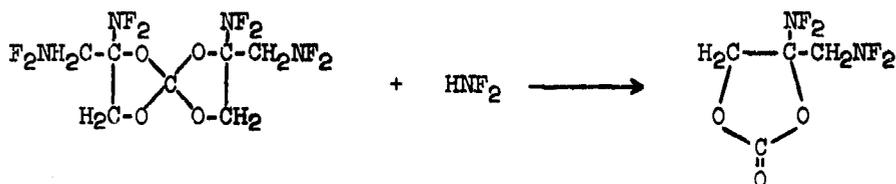


X = -H or -Cl

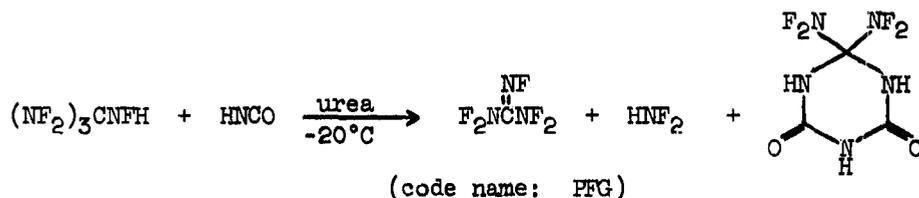
Using HNF<sub>2</sub> in fuming sulfuric acid, N,N-dimethyl-4-piperidinium methylsulfate can be converted to the corresponding N,N-dimethyl-4,4-bis(difluoramino)piperidinium methylsulfate. The product was identified in the reaction mixture but all attempts to isolate the pure material were unsuccessful (449). In a similar manner, HNF<sub>2</sub> in 96% H<sub>2</sub>SO<sub>4</sub> readily converts N,N'-bis(methanesulfonyl)-1,2-dihydroxyethylenediamine to the corresponding 1,2-bis(difluoramino)-substituted compound (270). Treatment of ammonium chloride with difluoramine in a 37% formalin solution resulted in the formation of 2,2',2''-tris(difluoramino)trimethylamine (code name: TMDA) (269).

The reaction of difluoramine with substituted piperazine compounds has been investigated. These results are summarized in Figure 1 (267a, 268, 269, 270). The underlined percentages indicate the yield for that reaction.

4-Difluoramino-4-difluoramino-methyl-1,3-dioxolane-2-one was produced by the treatment of a difluoramino-substituted tetraoxaspiro[2.2]nonane with difluoramine (453).



Tris(difluoramino)fluoraminomethane (code name: H-Delta) reacts with HNCO to yield multiple products as shown below (291):



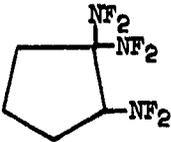
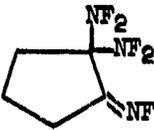
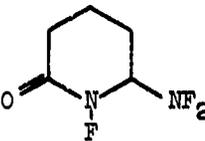
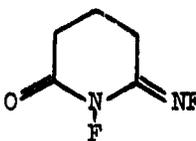
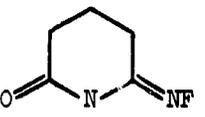
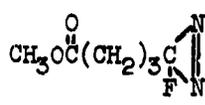
Dehydrofluorination of difluoramino-substituted compounds to produce the corresponding fluorimino- compounds has been reported for a number of materials. These reactions are summarized in Table I.



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TABLE I

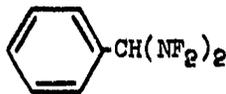
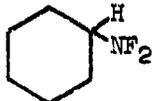
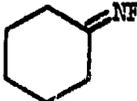
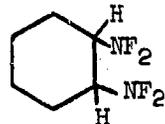
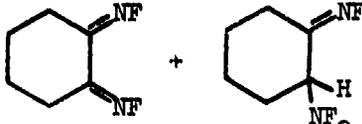
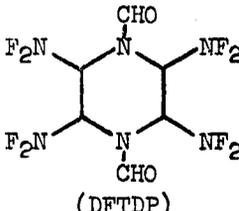
## DEHYDROFLUORINATION REACTIONS

<u>Starting Compound</u>	<u>Product</u>	<u>Conditions</u>	<u>Ref.</u>
		$\ominus$ OCH <sub>3</sub> in CH <sub>3</sub> OH	(441)
		"	(441)
		"	(441)
$\begin{array}{c} \text{NF}_2 \quad \text{NF}_2 \\   \quad   \\ \text{CH}_3\text{C} - \text{CHCH}_2\text{CH}_2\text{Cl} \\   \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{Cl} \quad \text{NF} \\   \quad   \\ \text{CH}_3\text{C} - \text{C} - \text{CH} = \text{CH}_2 \\   \\ \text{NF}_2 \end{array}$	Et <sub>3</sub> N in CH <sub>2</sub> Cl <sub>2</sub> at 0°C	(441, 447)
$\begin{array}{c} \text{NF}_2 \\   \\ \text{CH}_3\text{CCH}_2\text{NF}_2 \\   \\ \text{NF}_2 \end{array}$	$\begin{array}{c} \text{NF}_2 \\   \\ \text{CH}_3\text{CCN} \\   \\ \text{NF}_2 \end{array}$	Et <sub>3</sub> N in xylene at r.t.	(447)
$\begin{array}{c} \text{NF}_2 \\   \\ \text{n-C}_4\text{H}_9\text{OCHCH}_2\text{NF}_2 \\   \\ \text{NF}_2 \end{array}$	$\begin{array}{c} \text{NF} \\   \\ \text{n-C}_4\text{H}_9\text{OCCN} \end{array}$	Et <sub>3</sub> N	(449)
$\begin{array}{c} \text{NF}_2 \\   \\ \text{CH}_2\text{OCHCH}_2\text{NF}_2 \\   \quad   \\ \text{NF}_2 \quad \text{NF}_2 \\   \quad   \\ \text{CHOCHCH}_2\text{NF}_2 \\   \quad   \\ \text{NF}_2 \quad \text{NF}_2 \\   \quad   \\ \text{CH}_2\text{OCHCH}_2\text{NF}_2 \end{array}$	$\begin{array}{c} \text{NF} \\   \\ \text{CH}_2\text{OCCN} \\   \quad   \\ \text{NF} \quad \text{NF} \\   \quad   \\ \text{CHOCCN} \\   \quad   \\ \text{CH}_2\text{OCCN} \\   \\ \text{NF} \end{array}$	Norite-A in CH <sub>2</sub> Cl <sub>2</sub>	(449)

(code name: TVOPA)

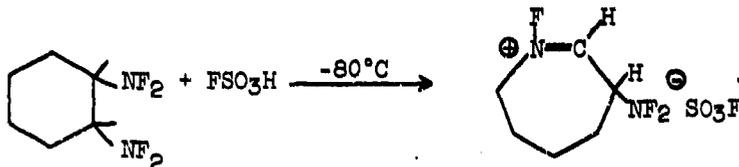
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TABLE I (Concluded)

<u>Starting Compound</u>	<u>Product</u>	<u>Conditions</u>	<u>Ref.</u>
	$\text{C}_6\text{H}_5\text{CNF}_2 + \text{C}_6\text{H}_5\text{CF}(\text{NF}_2)$ (tentative)	strong base	(354)
		strong base	(354)
	 (tentative)	Amberlite IR-45 in $\text{CH}_2\text{Cl}_2$	(354)
$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{NF}_2)_2$	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{C}(\text{NF}_2)\text{F}$	strong base	(354)
 (DFTDP)	no reaction	metal hydrides i.e.: $\text{LiAlH}_4$ also: $\text{NaBH}_4$ , $\text{PtO}_2$ , $\text{LiBH}_4$	(268)
$\text{FHNC}(\text{NF}_2)\text{NH}_2$	$\text{SiF}_4 + \text{HNF}_2 + \text{others}$	$\text{P}_2\text{O}_5$ at r.t.	(291)

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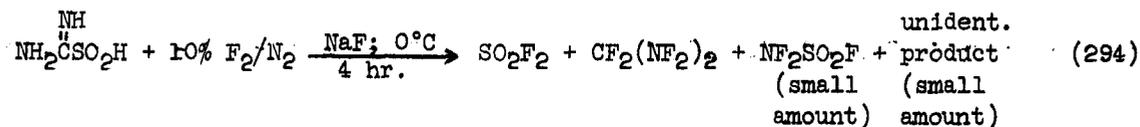
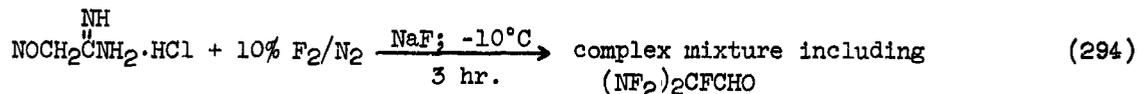
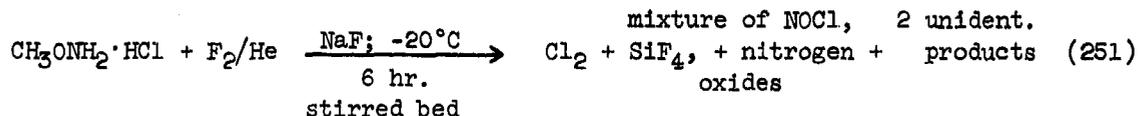
The reaction of 1,2-bis(difluoramino)cyclohexane with fluorsulfonic acid at  $-80^{\circ}\text{C}$  resulted in nitrogen insertion via a ring opening and closing process (46).



## I-B. Amine Fluorinations

Early attempts to fluorinate amine-N-oxides usually resulted in a vigorous reaction, but no stable NF or NOF compounds could be isolated (Crit. Rev. I, 284a). Recent investigations have shown that the room temperature reaction of difluoramine, using fuming  $\text{H}_2\text{SO}_4$  as a catalyst and  $\text{CH}_2\text{Cl}_2$  as a solvent, with 3,4-diacetyl-1,2,5-oxadiazole-2-N-oxide, produced 3,4-bis[1,1-bis(difluoramino)ethyl]-1,2,5-oxadiazole-2-N-oxide (451a). The same product was also obtained if chloroform was used as the solvent instead of methylene chloride (453). If Amberlyst-15 was added to the methylene chloride reaction mixture, the product formed was 4-acetyl-3-[1-difluoroamino-1-hydroxyethyl]-1,2,5-oxadiazole-2-N-oxide (451a).

The use of elemental fluorine, an effective fluorinating agent, very often resulted in degradation of the starting material and a complex mixture of products. This can be illustrated by the results of the reactions shown below.



Elemental fluorine has been utilized for the fluorination of some aromatic systems; however, the degree of fluorine substitution is often difficult to control. The reaction of 1,3,5-triamino-2,4-dinitrobenzene with fluorine in liquid hydrogen

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fluoride at  $-38^{\circ}\text{C}$  gave 1,2,3,4,5,6-hexafluoro-1,3,5-tris(difluoramino)-2,4-dinitro-cyclohexane as the major product with only small quantities of perfluoroaniline (497). With 2,3,4,5,6-pentafluoroaniline, a dimerization occurred upon treatment with fluorine in  $\text{CH}_3\text{CN}$  at  $-35^{\circ}\text{C}$  to yield  $\text{N,N}'$ -(perfluorophenyl)fluorohydrazine as the major product with only small quantities of perfluoroaniline (497). In liquid hydrogen fluoride, fluorination of 3,4-diamino-1,2,5-oxadiazole resulted in the formation of an unidentified polymeric material (497).

Cesium fluoride at  $90^{\circ}\text{C}$  was used to fluorinate  $\text{CF}_3\text{NHF}$  to a mixture of  $\text{CF}_2=\text{NF}$  and  $\text{CF}_3\text{N}(\text{F})\text{CF}_2$  (296).

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## CHAPTER II

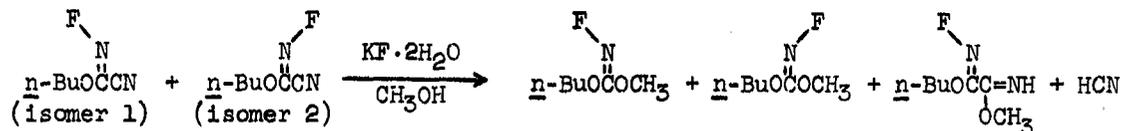
### CYANIDES (NITRILES) AND ISOCYANATES

#### II-A. Cyanides (Nitriles)

A large number of nitriles containing difluoramino groups have been prepared by reacting  $N_2F_4$  with the appropriate olefinic compound. The direct fluorination of nitriles and addition of selected nitriles to PFG have also been utilized as methods of preparation.

The photolysis of a mixture of cyanogen and  $N_2F_4$  proceeded at room temperature to yield a mixture of perfluoroethylenediamine and 2,2-difluoro-2-difluoroaminoacetonitrile (220a).

A detailed study of the kinetics of the reaction of the two isomers of *n*-butoxycyanoformamidine with potassium fluoride dihydrate in methanol has been studied (453).

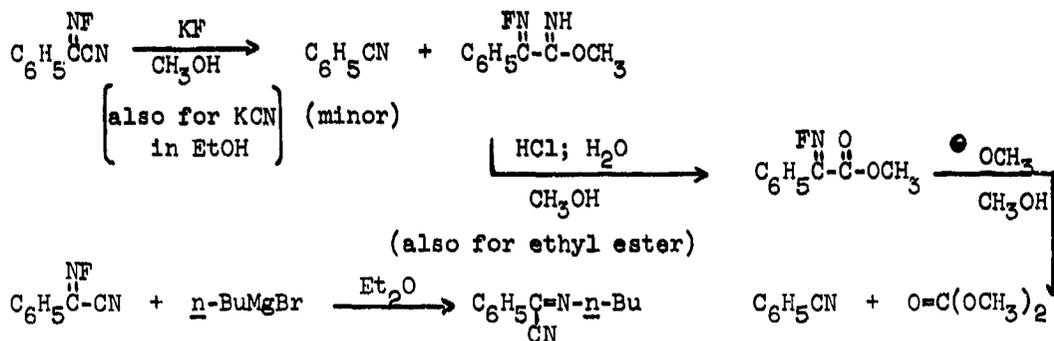


The rate of disappearance was found to be first order with respect to both isomer (1) and isomer (2). Graphical analysis of the change in rate constant as a function of temperature showed an activation energy for isomer (1) to be 15.9 Kcal/mole, while that for isomer (2) was found to be 14.2 Kcal/mole.

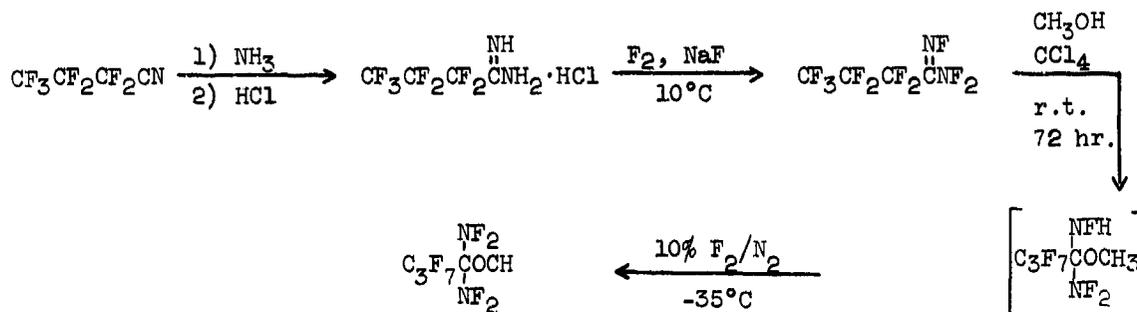
A number of studies on the reactions of substituted cyanofluoroformamidines (453, 455) have been conducted. Selected examples of these reactions are given below:



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Dimethylformamide has been found to decompose tris-(difluoramino)acetonitrile (code name: RN) in the presence of NaCN at room temperature to an unidentified compound, containing a tris-(difluoramino)methyl group (293). Recent studies have shown that the conversion of a perfluoronitrile to a difluoramino-substituted perfluoroether, via an amidine intermediate, can readily be made (497).



**II-B. Isocyanates**

In the synthesis of tetrakis(difluoramino)methane (code name: Delta) cyanic acid was condensed with perfluoroguanidine (code name: PFG) at  $-80^\circ\text{C}$  in the presence of 0.2 - 0.5% pyridine. The resulting compound  $(\text{NF}_2)_2\text{C}(\text{NFH})\text{NCO}$  (code name: Adduct) was then fluorinated under mild conditions to yield a mixture of tris-(difluoramino)acetone (code name: Tris-I) and Delta. In recent work, numerous studies have been conducted on the reaction of the two other products of this reaction: Adduct and Tris-I. Adduct was found to undergo a catalyzed rearrangement to yield trifluoroguanyl isocyanate (code name: TFGI) and difluoramine (85b). Several catalysts were utilized in this study and 100%  $\text{H}_2\text{SO}_4$  was found to produce the best yields. Among the other catalysts were NaF, a mixture of KCN and KOCN, and a mixture of KSCN in liquid  $\text{SO}_2$ . Sodium fluoride was unsuitable since it deactivated quickly and produced many side products. Neither of the two mixtures produced any appreciable conversion. A number of typical reactions of Adduct, TFGI, and Tris-I are shown in Table II.

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TABLE II

REACTIONS OF ADDUCT, TFGI, AND TRIS-I

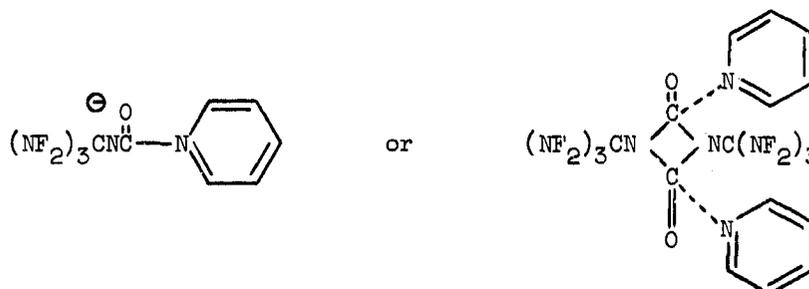
<u>Reactant</u>	<u>Products</u>	<u>Conditions</u>	<u>Reference</u>
1. $(\text{NF}_2)_3\text{CNCO}$	Code Name: Tris-I		
$\text{O}=\text{As}\phi_3$	$(\text{NF}_2)_3\text{CNH}_2$ + others	$\text{C}_6\text{H}_6$ , $\phi\text{NCO}$ , r.t., 1 day	85a
$\text{O}=\text{P}\phi_3$	no reaction	$\text{C}_6\text{H}_6$ , $\text{HCl}$ , r.t., 6 days	85b
$\text{NH}_3$	$(\text{NF}_2)_3\text{CNH}\overset{\text{O}}{\parallel}\text{NH}_2$	$\text{Et}_2\text{O}$ , 2 hr., r.t.	85b
$\text{CH}_2=\text{CHCH}_2\text{OH}$	$\text{CH}_2=\text{CHCH}_2\overset{\text{O}}{\parallel}\text{CNHC}(\text{NF}_2)_3$	r.t., 17 hr.	85b
$\text{H}_2\text{O}$	$(\text{NF}_2)_3\text{CNH}_2$	$\text{FC4-11}$ , r.t., 5 days	86
$\text{HF}$	$(\text{NF}_2)_3\text{CNH}\overset{\text{O}}{\parallel}\text{CF}$	$\text{CsF}$ , r.t., 7 days	293
2. $\text{NF}_2-\overset{\text{NF}}{\parallel}\text{C}-\text{NCO}$	Code Name: TFGI		
$\text{H}_2\text{O}$	$\text{NF}_2\overset{\text{NF}}{\parallel}\text{CNH}_2$ + $\text{CO}_2$	r.t.	85a
$\text{HNCO}$	N-F containing oil	$\text{KSCN}$ , $0^\circ\text{C}$ , 18 hr.	85b
$\text{NF}_2\overset{\text{NF}}{\parallel}\text{C}-\text{NH}_2$	$\text{NF}_2\overset{\text{NF}}{\parallel}\text{C}\overset{\text{O}}{\parallel}\text{NHC}\overset{\text{NF}}{\parallel}\text{CNF}$	$\phi_3\text{PO}$ , $\text{C}_6\text{H}_6$	85c
$\text{CH}_3\text{OH}$	$\text{NF}_2\overset{\text{NF}}{\parallel}\text{C}\overset{\text{O}}{\parallel}\text{NHCOCH}_3$	$0^\circ\text{C}$ , 1 day	85c
$\text{NF}_3$	$\text{NF}_2\overset{\text{NF}}{\parallel}\text{C}\overset{\text{O}}{\parallel}\text{NHCNH}_2$ (several isomers)	$\text{Et}_2\text{O}$ , $-78^\circ\text{C}$	85c

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TABLE II (Concluded)

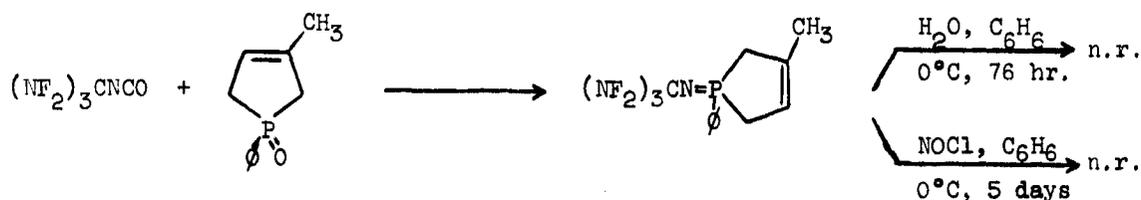
<u>Reactant</u>	<u>Products</u>	<u>Conditions</u>	<u>Reference</u>
3. $(\text{NF}_2)_2\overset{\text{NFH}}{\text{C}}\text{NCO}$	Code Name: Adduct		
$\text{NOCl}, \text{HCl}$	$(\text{NF}_2)_2\overset{\text{O}}{\text{C}}\text{FNHCCl} + (\text{NF}_2)_2\overset{\text{Cl}}{\text{C}}\text{NCO}$	Not stated	594
$\text{NOF}$	$(\text{NF}_2)_2\text{CFNCO}$ (50%)	r.t., 16 hr.	594

In addition to those reactions listed in Table II, the tris(difluoramino)-acetonitrile molecule has been the subject of numerous other studies. Reaction of Tris-I with pyridine led to the formation of a solid product which has not been positively identified (85a). A partial analysis of the solid material has shown that the Tris-I and pyridine are in a ratio of 1:1. The structure has been suggested to be one of the two shown below:



Further reaction of the Tris-I pyridine complex with acetic acid resulted in the formation of Tris-A, acetic anhydride, pyridine, and  $\text{CO}_2$  (85b). The products were identified by NMR and not isolated from the reaction mixture. Hydrolysis of Tris-I, using quinoline as a catalyst, leads to the formation of Tris-A, which upon further treatment with  $\text{OF}_2$  in Kel-F oil at room temperature for 22 hr. resulted in the decomposition of the Tris-A to perfluoroguanidine (code name: PFG) and silicon tetrafluoride (15a).

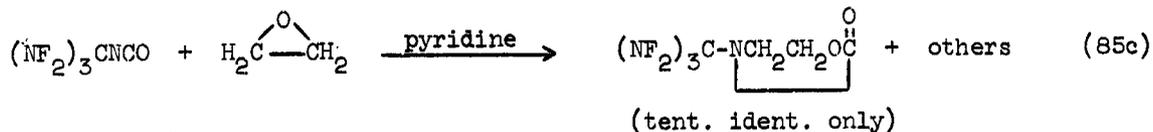
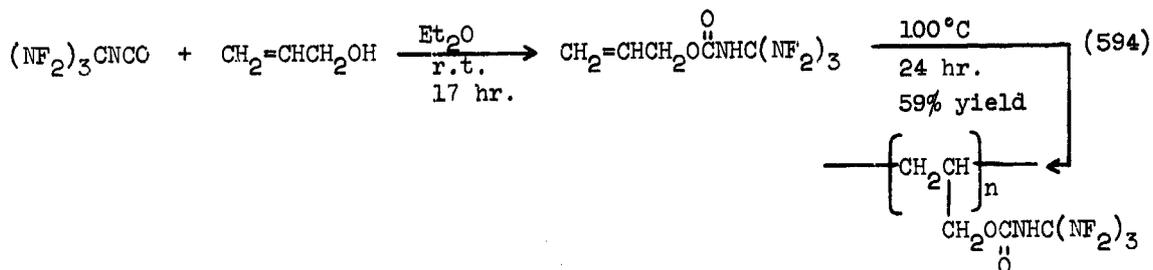
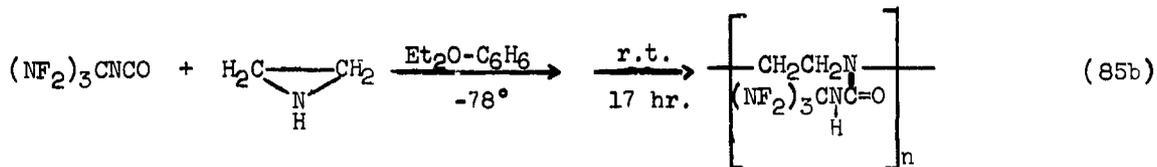
Although Tris-A does not react with triphenylphosphine oxide, it does undergo a condensation reaction with a similar molecule (85a).



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Attempts to further fluorinate Tris-I with HF, using trimethylamine as a catalyst, at room temperature for 5 days were unsuccessful (293). An explosive mixture is formed when Tris-I and *n*-BuSnOCH<sub>3</sub>, condensed together at low temperature, are allowed to warm to room temperature (86). Addition of methanol to Tris-I results in esterification to yield (NF<sub>2</sub>)<sub>3</sub>CNHCO<sub>2</sub>CH<sub>3</sub> (294). Fluorinations of the ester with either a 10% F<sub>2</sub>/N<sub>2</sub> mixture at 0°C or 100% F<sub>2</sub> at room temperature were unsuccessful.

The incorporation of Tris-I into polymeric materials has been the subject of a number of studies. Among the species utilized as potential prepolymers were ethylene oxide, ethylenimine, and allyl alcohol.

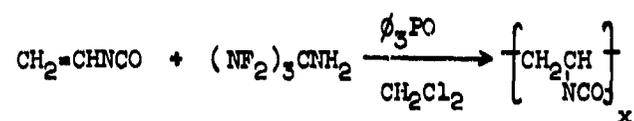


also for: TFGI

The polymeric material prepared by the second reaction, using allyl alcohol, was found to decompose at approximately 200°C and to have a molecular weight in the range of 429 - 1,165. Catalysts other than pyridine have been attempted in the reaction of Tris-I with ethylene oxide, with varying degrees of success. Sulfuric acid as a catalyst at -23°C produced no reaction, while fuming H<sub>2</sub>SO<sub>4</sub> at -23°C and SO<sub>3</sub> at -23°C yielded a nonvolatile unidentified oil. Without a catalyst, using dioxane as the solvent, heating the mixture to 45°C produced an unidentified oil. When tetraethylammonium bromide was added as a catalyst, no reaction occurred. If the ethylene oxide and Tris-I were allowed to react at room temperature without a catalyst, a cyclic condensation product was among the products (86).



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This reaction was also found to occur if quinoline was used as the catalyst in acetonitrile with the temperature maintained at  $-20^\circ\text{C}$  for 1 hr. (85c).

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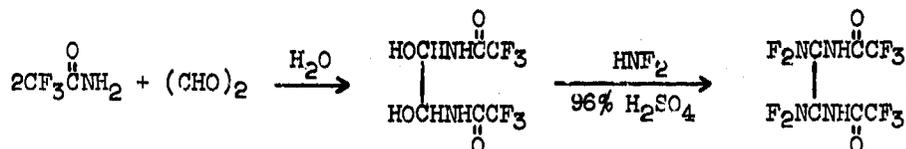
## CHAPTER III

### AMIDES, CARBAMATES AND UREAS

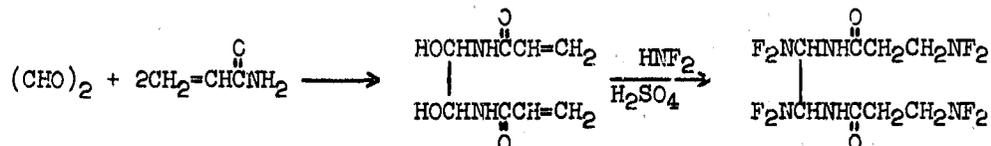
The various types of compounds which contain the  $-N-CO-$  (amide) group are discussed in this chapter; included also are those containing additional oxygen or nitrogen, e.g.,  $-N-CO-O-$  (carbamate) or  $-N-CO-N-$  (urea).

#### III-A. Amides

Glyoxal has been utilized as a condensation agent with amides to form amido-substituted diols. These diols can be subsequently reacted with difluoramine to yield the corresponding difluoramino-substituted compounds. In this manner, trifluoroacetamide was reacted with aqueous glyoxal to form 1,2-bis(trifluoroacetamido)-1,2-dihydroxyethane. Reaction of the diol with difluoramine in 96% sulfuric acid led to the replacement of the hydroxyl groups with difluoramino groups (269).

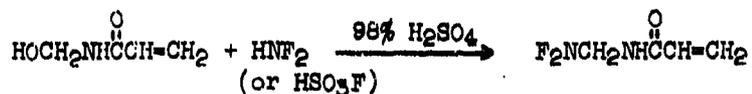


If the original amide contained unsaturation, such as acrylamide, the reaction with difluoramine also occurred with the unsaturated portion of the molecule (270).



The same reaction occurred if the intermediate diol was converted to the methoxy-substituted compound and then treated with  $\text{HN}\overset{\text{O}}{\parallel}\text{F}_2$  (270). Molecules containing acetylenic linkages, such as propiolamide, undergo reaction with  $(\text{CHO})_2$  and  $\text{HN}\overset{\text{O}}{\parallel}\text{F}_2$  in the same manner as those containing the carbon-carbon double bond (273). If the starting compound was a hydroxyl-substituted amide, which also contains unsaturation, reaction with difluoramine or fluosulfonic acid did not affect the unsaturated portion of the molecule (271).

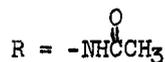
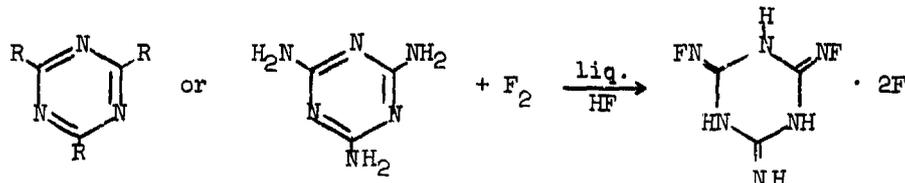
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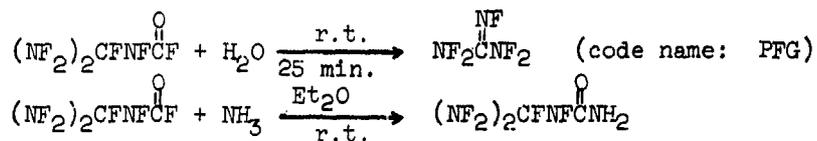
Direct fluorination of simple substituted amides with fluorine-nitrogen mixtures often results in decomposition and/or explosions. Reaction of N,N'-methylene-bis-formamide with 10% F<sub>2</sub>/N<sub>2</sub> over NaF at 0°C for 8 hr. resulted in severe decomposition of the starting material to a complex mixture containing NF<sub>3</sub>, COF<sub>2</sub>, CH<sub>2</sub>FNF<sub>2</sub> and others (292). Likewise, treatment of tris(difluoramino)acetamide with 3% F<sub>2</sub>/N<sub>2</sub> at 0°C resulted in an explosion (291).



The product of the above reaction could not be isolated from the reaction mixture; however, it was shown to contain a tris(difluoramino)methyl group. Fluorination with elemental fluorine using liquid hydrogen fluoride as the solvent has also been a successful method of preventing decomposition (497).

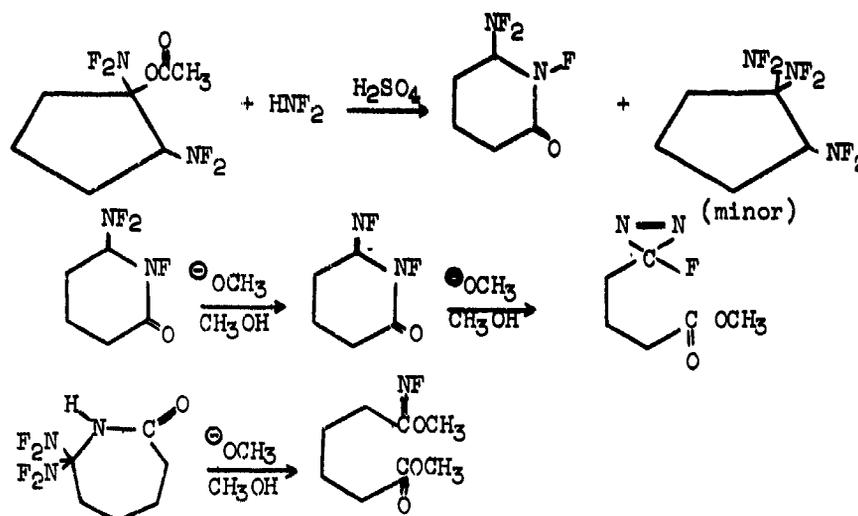


The product N<sup>2</sup>,N<sup>4</sup>-difluoro-isomelamine dihydrofluoride, hydrolyzed to give CO<sub>2</sub> and unidentified compounds (497). Hydrolysis and aminolysis of substituted perfluoroformamides led to the expected products (292).



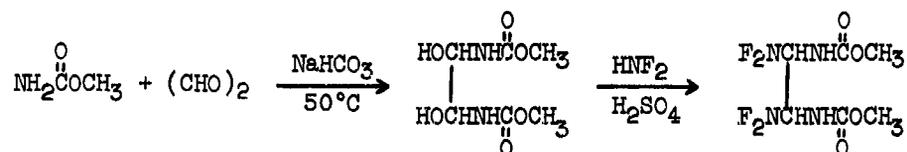
Cyclic compounds, containing difluoramino groups, undergo ring enlargement upon treatment with HNF<sub>2</sub> in sulfuric acid. Subsequent reaction of these cyclic amides with strong base resulted in ring opening (441, 451, 453, 455).

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**III-B. Carbamates**

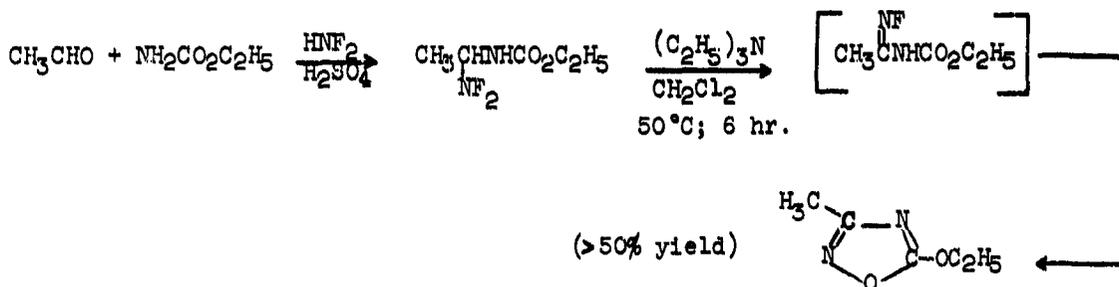
Carbamates, and related compounds, undergo condensation reactions with glyoxal in the same manner as the amides (268). Thus, oxamic acid, methyl carbamate, and ethyl carbamate reacted with glyoxal to form substituted diols, which were then further reacted with difluoramine in sulfuric acid.



Direct fluorination of N-substituted ethylcarbamates with elemental fluorine in either water or acetonitrile resulted in complete decomposition of the starting material (251). Treatment of N-tris(difluoramino)methyl allylcarbamate with 3% benzoyl peroxide at 88°C for 26 hr. produced an unidentified, brown, viscous syrup (85c). Acid hydrolysis of N-chloro-N-tris(difluoramino)methoxy-ethylcarbamate with 70% perchloric acid at room temperature resulted in the loss of the chlorine to form N-tris(difluoramino)methoxy-ethylcarbamate (291).

The formation of 3,5-substituted-1,2,4-oxadiazoles was readily accomplished by the reaction of ethylcarbamate with an aldehyde (451a).

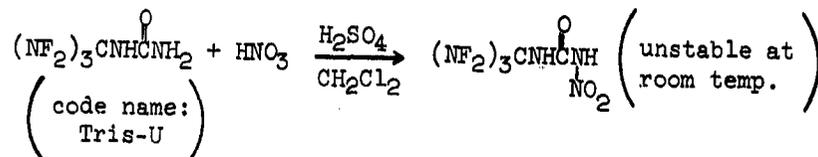
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**III-C. Ureas**

The reaction of glyoxal with numerous ureas has been shown to be analogous to the reaction with amides (see Section A). Substituted-2-imidazolidones were initially formed, and then further reacted with difluoramino in sulfuric acid to yield the corresponding difluoramino-substituted compounds. A brief survey of these reactions is presented in Table III.

Mono-substituted ureas: Nitration of ureas has been attempted, with nitric acid being used in the presence of sulfuric acid at room temperature. The resulting nitro-substituted compounds are usually unstable at ambient temperatures (85b).

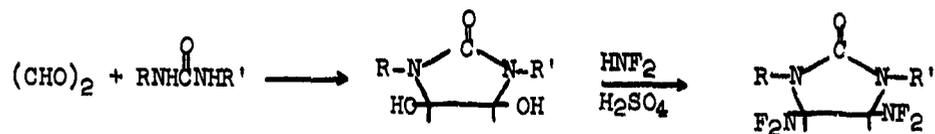


The above reaction has been attempted with trifluoroacetic anhydride as catalyst instead of sulfuric acid (85b). Within 1 hr. at ambient temperature, decomposition of the intermediate product resulted in the formation of Tris-I, nitrous oxide, and water. Reaction of Tris-U with trifluoroacetic anhydride in ether for 3 days at room temperature produced acylation on the unsubstituted  $\text{NH}_2$ -group (85c). At  $40^\circ\text{C}$ , trifluoroperoxyacetic acid in methylene chloride did not undergo reaction with Tris-U (85b), and the addition of boron trifluoride resulted only in the formation of a  $\text{BF}_3$ -Tris-U complex. Tris-U was found to react with triphenylphosphine oxide

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TABLE III

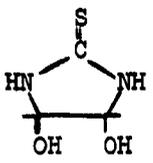
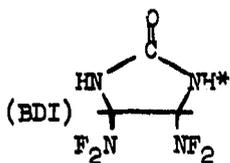
## REACTIONS OF GLYOXAL WITH SUBSTITUTED UREAS



<u>R,R'</u>	<u>Intermediate</u>	<u>Product</u>	<u>Reference</u>
H,H	unident. syrup	$\left[ \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \quad \text{N} \\ \diagup \quad \diagdown \\ \text{CH} \quad \text{CH} \\   \quad   \\ \text{NF}_2 \quad \text{NF}_2 \end{array} \right]_n$	tentative ident. 269
$\frac{i}{-}\text{Pr}, \frac{i}{-}\text{Pr}$ (or) $\text{CH}_3, \text{CH}_3$	$\left[ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{N} \quad \text{N}-\text{CH} \\ \diagup \quad \diagdown \\ \text{CH} \quad \text{OH} \\   \quad   \\ \text{OH} \quad \text{OH} \end{array} \right]_2$	$\left[ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{N} \quad \text{N}-\text{CH} \\ \diagup \quad \diagdown \\ \text{NF}_2 \quad \text{NF}_2 \\   \quad   \\ \text{NF}_2 \quad \text{NF}_2 \end{array} \right]_2$	269
H, $-\text{CNH}_2$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{N} \quad \text{N}-\text{R}' \\ \diagup \quad \diagdown \\ \text{OH} \quad \text{OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{N} \quad \text{N}-\text{R}' \\ \diagup \quad \diagdown \\ \text{NF}_2 \quad \text{NF}_2 \\   \quad   \\ \text{NF}_2 \quad \text{NF}_2 \end{array}$	270
$\text{HC}-, -\text{CH}$ (in basic sol'n) excess $(\text{CHO})_2$	$\left[ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{N} \quad \text{N}-\text{CH} \\ \diagup \quad \diagdown \\ \text{HO} \quad \text{OH} \\   \quad   \\ \text{OH} \quad \text{OH} \end{array} \right]_2$	$\left[ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{N} \quad \text{N}-\text{CH} \\ \diagup \quad \diagdown \\ \text{NF}_2 \quad \text{NF}_2 \\   \quad   \\ \text{NF}_2 \quad \text{NF}_2 \end{array} \right]_2$	271
$\text{HC}-, -\text{CH}$ (basic sol'n)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{N} \quad \text{N}-\text{H} \\ \diagup \quad \diagdown \\ \text{OH} \quad \text{OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{N} \quad \text{N}-\text{H} \\ \diagup \quad \diagdown \\ \text{NF}_2 \quad \text{NF}_2 \\   \quad   \\ \text{NF}_2 \quad \text{NF}_2 \end{array}$	268

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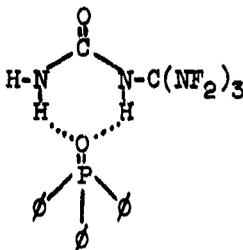
TABLE III (Concluded)

<u>R,R'</u>	<u>Intermediate</u>	<u>Product</u>	<u>Reference</u>
$\text{NH}_2\text{C}(=\text{S})\text{NH}_2$		 (BDI) (27% yield)	272

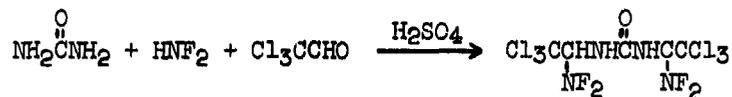
\* If HCHO is added in second step, S is retained 268.

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in methylene chloride at ambient temperature to produce a white solid, which was identified as the 1:1 complex shown below (85c).

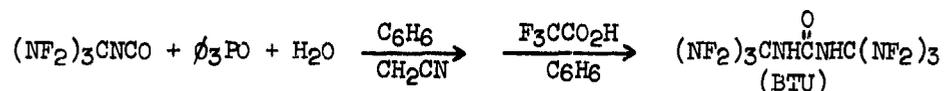


The fluorination of ureas has been attempted with urea, itself, and guanylurea. Fluorination of urea with  $\text{HNF}_2$  in the presence of sulfuric acid and trichloroacetaldehyde (or tribromoacetaldehyde) resulted in the formation of an intermediate product, which did not undergo further reaction with  $\text{HNF}_2$  (271).



The fluorination of guanylurea sulfate with 10%  $\text{F}_2/\text{N}_2$  over NaF at  $-7^\circ\text{C}$  for 8 hr. resulted in decomposition of the starting materials to PFG and  $\text{CF}(\text{NF}_2)_3$  plus small amounts of other products (292).

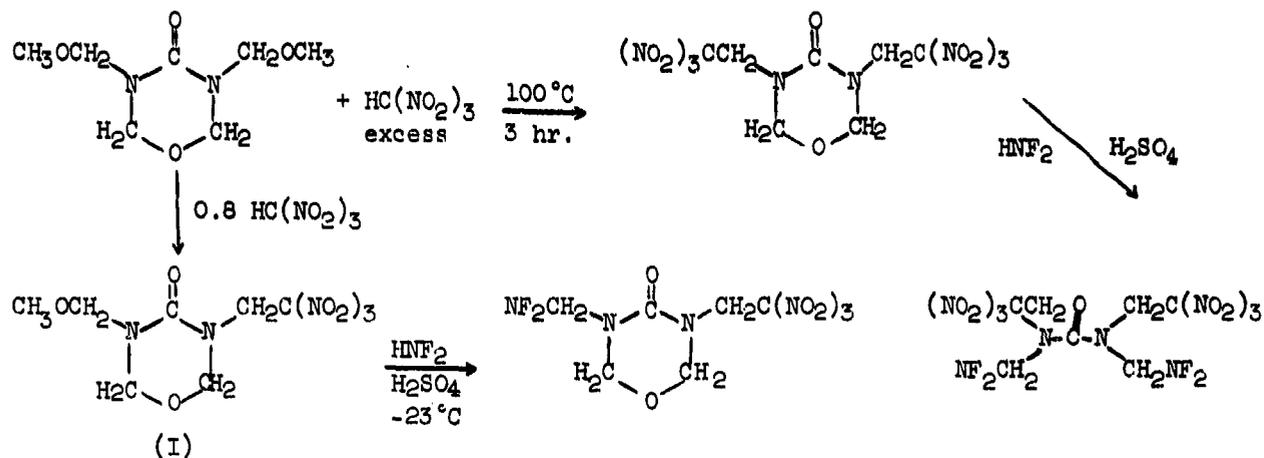
Disubstituted ureas: An improved method for the production of bis-[tris(difluoramino)methyl]-urea (code name: BTU) has been reported with an overall yield of 49% (162a).



The use of tri(*n*-butyl)phosphine oxide has been attempted. Preliminary results indicate it may provide a better yield than the triphenylphosphine oxide currently being used. Dimethylsulfoxide (DMSO) has been found to decompose BTU to produce Tris-A plus other products (85a).

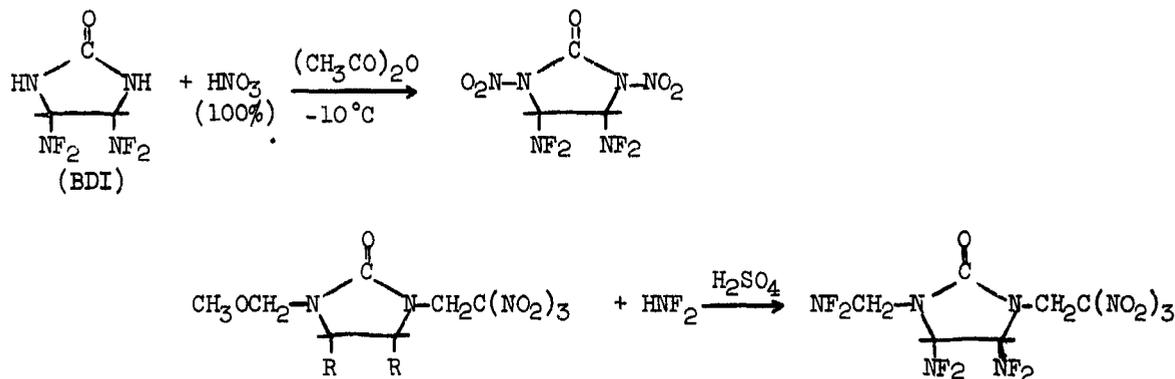
Cyclic ureas: Trinitromethane has been reacted with *N*-substituted cyclic ureas to produce the corresponding trinitromethyl-substituted compounds, which were then treated with difluoramine in  $\text{H}_2\text{SO}_4$ . The reaction products were highly dependent upon the initial purity of the cyclic urea and upon the quantity of trinitromethane used (271 and 272).

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If the starting material was not carefully purified, the reaction with excess trinitromethane, followed by reaction with difluoramine, resulted in the formation of N-difluoramino-methyl-N'-2,2,2-trinitroethyl-urea instead of the anticipated product (272). The reaction of compound (I) from above with difluoramine in H<sub>2</sub>SO<sub>4</sub> at ambient temperature and autogenous pressure yielded N,N'-tris(difluoramino-methyl)-N'-2,2,2-trinitroethyl-urea (272).

Nitric acid has been used with difluoramino-substituted 2-imidazolidones to produce the corresponding N-nitro-2-imidazolidones, which contain both a nitro and a difluoramino group (270, 272).



R = -OCH<sub>3</sub> or -CH<sub>2</sub>OH

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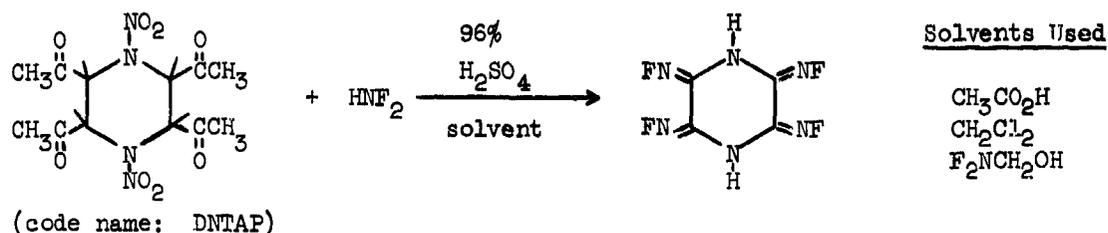
## CHAPTER IV

### IMINO COMPOUNDS

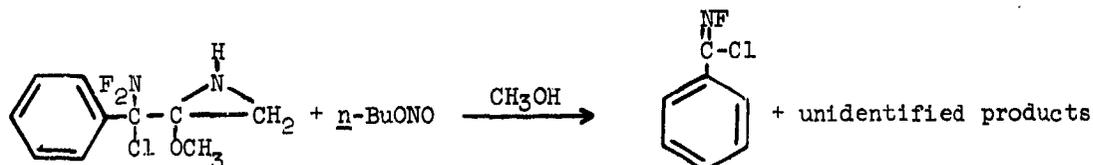
In this chapter, compounds containing the C=NF group could be considered. The first portion, fluorimines, will consider those molecules which contain groups other than -NF<sub>2</sub> attached to the carbon atom. The remainder of the chapter will be devoted to the discussion of compounds which contain the -NF<sub>2</sub> attached to the carbon atom.

#### IV-A. Fluorimines

The preparation of fluorimine compounds has utilized several methods, with one of the most general methods being the dehydrofluorination of difluoramino compounds (see Table I). 2,3,5,6-Tetra(fluorimino)piperazine (code name: TFP) has been produced by the reaction of HNF<sub>2</sub> with 1,4-dinitro-2,3,5,6-tetra(acetyl)piperazine in the presence of sulfuric acid (269).



Reaction of *n*-butylnitrite with substituted ethylenimines has also been found to yield fluorimines (451a).



Numerous studies have been conducted on the reaction of difluoramine with a wide variety of fluorimino compounds. A detailed discussion or listing of all reactions is precluded by the number of investigations in this area. A representative sample of the various types of fluorimino compounds which have been studied is given in Table IV. Additional examples of these reactions may be obtained from the work referenced in the table.

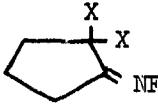
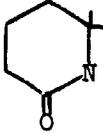
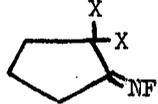
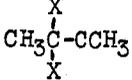
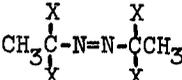
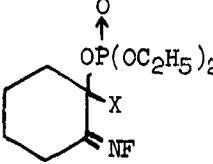
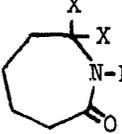
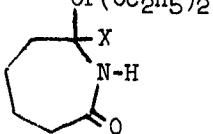
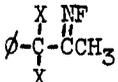
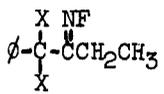
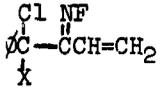
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TABLE IV

REACTIONS OF FLUORIMINES WITH DIFLUORAMINE

X = -NF<sub>2</sub>

φ = phenyl

<u>Reactant</u>	<u>Conditions</u>	<u>Product</u>	<u>Reference</u>
	FSO <sub>3</sub> H	NC(CH <sub>2</sub> ) <sub>3</sub> CX <sub>2</sub> OSO <sub>2</sub> F + 	447
NC(CH <sub>2</sub> ) <sub>3</sub> CX <sub>2</sub> OSO <sub>2</sub> F	H <sub>2</sub> SO <sub>4</sub>	X <sub>3</sub> C(CH <sub>2</sub> ) <sub>3</sub> CN	447
	BF <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub>	X <sub>3</sub> C(CH <sub>2</sub> ) <sub>3</sub> CN	447
	BF <sub>3</sub>		441
	HSO <sub>3</sub> F, CH <sub>2</sub> Cl <sub>2</sub>	 + 	447
	HSO <sub>3</sub> F, CH <sub>2</sub> Cl <sub>2</sub> or BF <sub>3</sub>	φ-CX <sub>3</sub> + φC=N-  (25%)	447
	H <sub>2</sub> SO <sub>4</sub>	φCO <sub>2</sub> H + φCN	451
	Amberlyst 15	no reaction	451

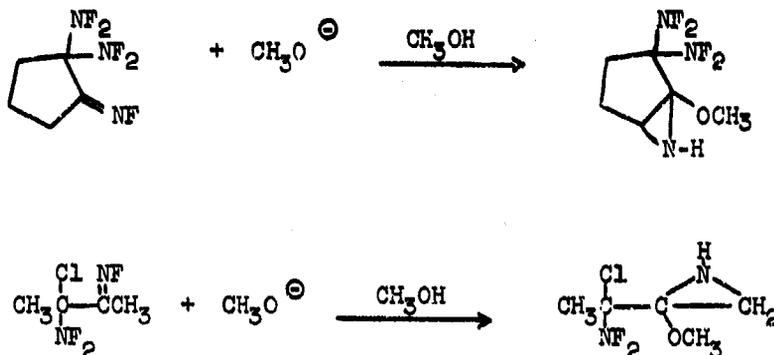
**CONFIDENTIAL**

TABLE IV (Concluded)

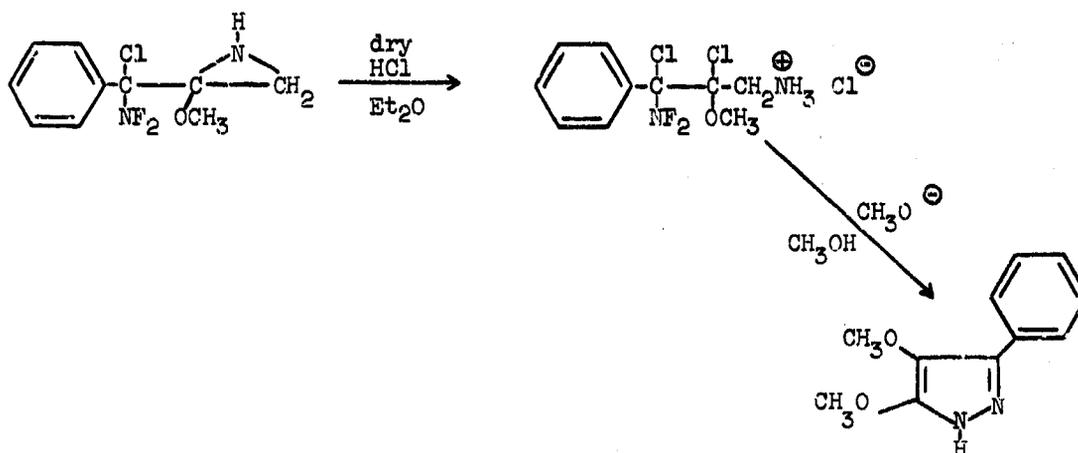
<u>Reactant</u>	<u>Conditions</u>	<u>Product</u>	<u>Reference</u>
$\begin{array}{c} \text{Cl} \quad \text{NF} \\   \quad   \\ \phi\text{C} - \text{C} = \text{CH} - \text{CH}_2 \\   \\ \text{X} \end{array}$	BF <sub>3</sub>	$\begin{array}{c} \text{Cl} \\   \\ \phi\text{C} - \text{X} \\   \\ \text{F} \end{array}$	451
$\text{CH}_3\text{O} - \text{C}_6\text{H}_4 - \begin{array}{c} \text{X} \\   \\ \text{C} = \text{N} \text{OCH}_3 \\   \quad   \\ \text{F} \quad \text{X} \end{array}$	BF <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub>	$\text{CH}_3\text{O} - \text{C}_6\text{H}_4 - \text{CN} + \text{CH}_3\text{CX}_3$	453
$\begin{array}{c} \text{X} \quad \text{NF} \\   \quad   \\ \text{CH}_3\text{C} - \text{C} - \text{CH}_3 \\   \\ \text{X} \end{array}$	H <sub>2</sub> SO <sub>4</sub>	$\begin{array}{c} \text{X} \quad \text{O} \\   \quad    \\ \text{CH}_3\text{C} - \text{NHC} - \text{CH}_3 \\   \\ \text{X} \end{array}$	501a
$\text{CH}_3(\text{CH}_2)_2\text{C} \begin{array}{c} \text{X} \quad \text{NF} \\   \quad   \\ \text{C} - \text{C} - \text{C}_2\text{H}_5 \\   \\ \text{X} \end{array}$	HSO <sub>3</sub> F	<p align="center">unident. product; not the expected 1,1,1-tris- difluoramino)butane</p>	501a

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Reaction of strong base, i.e., methoxide ion, with fluorimines has been shown to result in the formation of the three-membered ethylenimine ring (441, 451a, 455).



Similar reactions have also been found to occur for 1,1-bis(difluoramino)-2-fluorimino-cyclohexane, 1-chloro-1-difluoramino-2-fluorimino-cyclopentane, and 2,2-bis(difluoramino)-3-fluorimino-butane (441). If the ring compound was further treated with hydrogen chloride, ring cleavage occurred and the corresponding amine salt formed. Reaction of the amine salt with alkoxide ion resulted in recyclization to form a substituted pyrazole (451a).

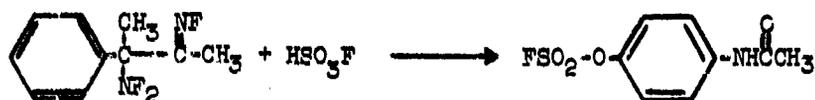


If the original fluorimino compound had been reacted with *i*-propoxide or *t*-butoxide, treatment with hydrogen chloride did not result in the formation of the amine salt (455).

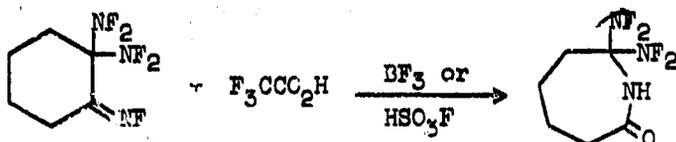
Attempts to oxidize fluorimines with peroxide have not been successful. Reaction of 1,2-bis(fluorimino)-cyclohexane with benzoyl peroxide in methylene chloride at room temperature for 4 hr. did not show any appreciable reaction (356).

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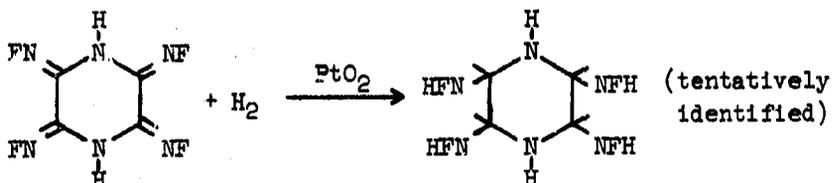
Fluosulfonic acid, often used as a catalyst in reactions of difluoramine, has been found to react with fluorimines via the Beckman Rearrangement (451a).



A similar type of reaction has been found to occur with 1,1-bis(difluoramino)-2-fluorimino-cyclohexane upon treatment with trifluoroacetic acid in  $\text{BF}_3$  in  $\text{HSO}_3\text{F}$  (447).

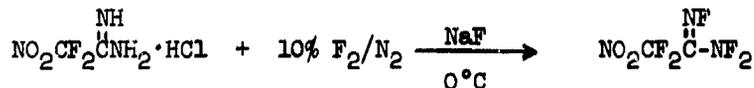
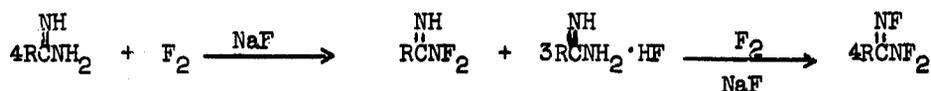


The hydrogenation of 2,3,5,6-tetra(fluorimino)-piperazine (code name: TFP) has been conducted with a platinum dioxide catalyst (269).



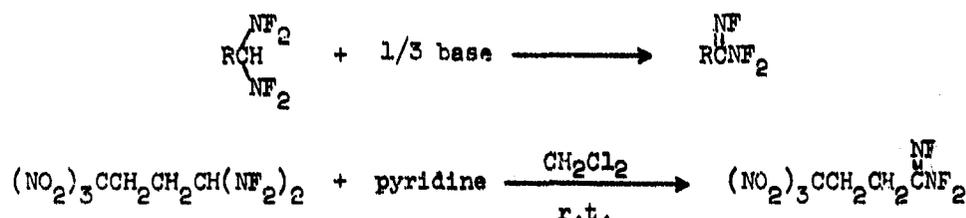
## IV-B. N,N,N'-Trifluoramidines

A general method for the preparation of fluorinated amidines by the reaction of elemental fluorine with the corresponding amidine has been developed (497).

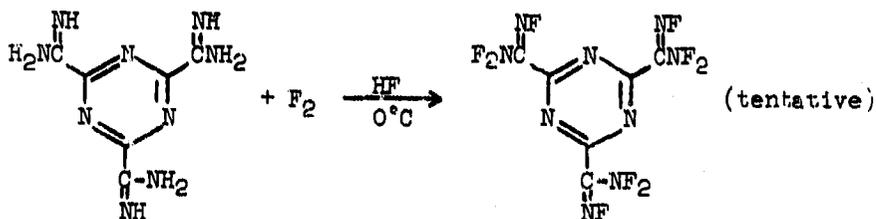


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The hydrolysis of gem-bis(difluoramino) compounds with base has also been utilized as a method for the preparation of fluorinated amidines (497).



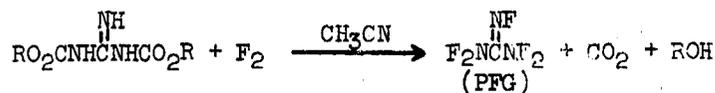
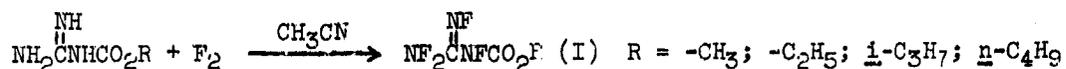
Fluorination with elemental fluorine in liquid hydrogen fluoride has been successful in converting amidines to fluoroamidines (497).



Reaction of 2-nitro-perfluoroacetamide with methanol in acetonitrile, followed by fluorination with elemental fluorine, resulted in the formation of methyl[2,2-difluoro-2-nitro-1,1-bis(difluoramino)] ethyl ether, presumably by a mechanism similar to the addition of methanol to perfluoroguanidine (code name: PFG) (497). However, the addition of n-butanol to N,N,N'-trifluorobenzamide did not show any reaction after 15 hr. at room temperature (354).

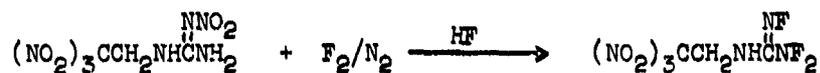
## IV-C. Fluorinated Guanidines

Fluorination of guanylcarbamate esters has been utilized as a convenient method for the preparation of fluorinated guanidines (46).



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Partially fluorinated guanidines have been obtained by the reaction of nitroguanidine or substituted nitroguanidines with elemental fluorine in liquid hydrogen fluoride (497, 501).



The attempted reduction of fluoro-bis(difluoramino) methyl perfluoroguanidine (code name: F<sub>6</sub>BG) with lithium amide resulted in the formation of two unidentified products: a tan solid and a colorless liquid (253).

#### IV-D. Perfluoroguanidine (Code Name: PFG)

The development of perfluoroguanidine has provided the propellant synthesis groups with an extremely prolific "building-block" material. This molecule has been utilized in numerous reactions, and shown to react with all compounds containing an active hydrogen. Since a detailed discussion of the various reactions involving PFG would be quite lengthy, a tabulation of the reactions reported during the review period is given in Table V. A few studies of PFG and PFG adducts, not listed in the table, will be discussed in the following paragraphs.

Battelle Institute (115) has conducted an investigation into the polymerization of PFG at high pressures. Thus far, the results have not been encouraging. A sample of PFG at 20 kilobars for 6 hr. in either a stainless steel or nickel capsule was shown to yield only metal fluorides. The use of a prefluorinated nickel capsule and 6 - 7 kilobars pressure led to an explosion. The use of solvents, such as acetonitrile, C<sub>3</sub>F<sub>8</sub>, CH<sub>3</sub>NO<sub>2</sub>, and C<sub>4</sub>F<sub>8</sub>, with 10 kilobars of compound has also been unsuccessful in producing any polymerization.

Many additional reactions of fluorinated adducts of PFG have been studied. The reaction of the fluorinated adduct of ethylglycolate (see Table V) with ammonia in methanol at room temperature for 2.5 hr. yielded tris(difluoramino)methoxyacetamide (code name: GA) (295). This compound is reported to be less sensitive to shock than many of the other tris-domino compounds, such as INFO. A similar molecule, the fluorinated adduct of N-ethyl-N-hydroxyethylcarbamate, underwent decomposition to a mixture of products when treated with ammonium hydroxide (292), but formed the N-chloro compound when reacted with (CH<sub>3</sub>)<sub>3</sub>COCl at ambient temperature.

TABLE V  
REACTIONS OF PERFLUOROGUANIDINE (PFG)

<u>Reactant</u>	<u>Conditions</u>	<u>Products</u>	<u>Reference</u>
<u>I. Inorganic Compounds</u>			
LiNH <sub>2</sub> + KCNO	Freon 113; -80 °C	$\text{NF}_2\text{C}(\text{NH}_2) + \text{N}_2\text{F}_2$ (F <sub>3</sub> G)	Hynes 1966 Prop. Ingrid. Conf.
LiCH <sub>3</sub>	Et <sub>2</sub> O; -196 °C	at 0 °C - explodes	250
LiN(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> ; R.T.	n.r.	250
O <sub>3</sub> /O <sub>2</sub>	CH <sub>3</sub> CN; 0 °C	n.r.	267a
H <sub>2</sub> S	acetone; R.T.	unident. prod.	267a
NH <sub>4</sub> ClO <sub>4</sub>	CH <sub>3</sub> CN	unident. prod.	267a
H <sub>2</sub> O <sub>2</sub>	1) urea, Et <sub>2</sub> O, R.T. 2) 10% F <sub>2</sub> /N <sub>2</sub> ; -50 °C	(NF <sub>2</sub> ) <sub>3</sub> COOH	292, 295
N <sub>2</sub> H <sub>4</sub>	CH <sub>3</sub> OCH <sub>3</sub> , -110 °C	$\text{H}_2\text{N}(\text{NHCF}_2)_2\text{NH}_2$ NF <sub>2</sub>	292
BF <sub>3</sub>	R.T.	n.r.	15a
<u>II. Organic Compounds</u>			
<u>A. Alcohols, Diols and Hydroxy Compounds</u>			
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N·HClO <sub>4</sub>	dimethylurea, CH <sub>3</sub> CN, R.T.	colorless oil	267a

TABLE V (Continued)

<u>Reactant</u>	<u>Conditions</u>	<u>Products</u>	<u>Reference</u>
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N	CH <sub>3</sub> CN	explodes	267a
CH <sub>3</sub> CH <sub>2</sub> NCO <sub>2</sub> Et OH	1) urea, CH <sub>3</sub> CN 2) 10% F <sub>2</sub> /N <sub>2</sub> , -30°C	(NF <sub>3</sub> )CONHCO <sub>2</sub> Et	292
ClCH <sub>2</sub> CH <sub>2</sub> OH (or) BrCH <sub>2</sub> CH <sub>2</sub> OH	1) urea, R.T. 2) 5% F <sub>2</sub> /N <sub>2</sub> , -45°C	ClCH <sub>2</sub> CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub> BrCH <sub>2</sub> CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub>	294
HOCH <sub>2</sub> CH <sub>2</sub> OH (excess)	1) R.T., 15 hr. 2) 5% F <sub>2</sub> /N <sub>2</sub> , -30°C	HOCH <sub>2</sub> CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub>	294
HOCH <sub>2</sub> CNH <sub>2</sub>	urea, CH <sub>3</sub> CN		294
C <sub>5</sub> H <sub>11</sub> OH	urea, r.t.	C <sub>5</sub> H <sub>11</sub> OC(NF <sub>2</sub> ) <sub>2</sub> NHF	354
	1) urea; CH <sub>3</sub> CN 2) 20% F <sub>2</sub> /N <sub>2</sub> ; -25°C		174
HOCH <sub>2</sub> CH <sub>2</sub> CN	1) urea; CH <sub>3</sub> CN 2) 20% F <sub>2</sub> /N <sub>2</sub> ; -25°C	(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> CN	175
(O <sub>2</sub> NOCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> OH	1) urea; CH <sub>3</sub> CN 2) 25% F <sub>2</sub> /N <sub>2</sub> ; -10°C	(O <sub>2</sub> NOCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub> (FA-PETRIN)	175

TABLE V (Continued)

Reactant	Conditions	Products	Reference
$(O_2NOCH_2)_2C(CH_2OH)_2$	1) urea; $CH_3CN$ 2) 25% $F_2/N_2$ ; $-10^\circ C$	$(O_2NOCH_2)_2C[CH_2OC(NF_2)_3]_2$ (FA-PEDIN)	175
$(NO_2)_3CCH_2CH(OH)CH_2OH$	1) $CH_3CN$ ; NaCN; pyridine 2) $F_2/N_2$ ; $-25^\circ C$	$(NO_2)_3CCH_2CHCH_2OC(NF_2)_3$ $OC(NF_2)_3$ (FA-TMEEG)	175
$(NO_2)_2CFCH_2CH_2OH$	1) $CH_3CN$ ; NaCN 2) 20% $F_2/N_2$ ; $-25^\circ C$	$(NO_2)_2CFCHCH_2OC(NF_2)_3$ $OC(NF_2)_3$ (FA-FDP)	175
$CH_2=CHCH_2OH$	1) urea; $CH_3CN$ 2) $F_2/N_2$ ; $-25^\circ C$	$CH_2=CHCH_2OC(NF_2)_3$ (FAG)	175
$C_2H_5O_2C-CH(OH)-CHCO_2C_2H_5$ (d-form)	1) urea; $CH_3CN$ 2) $F_2/N_2$ ; $-25^\circ C$	$OC(NF_2)_3$ $C_2H_5O_2C-CH_2CHCO_2C_2H_5$ $OC(NF_2)_3$ (FA-DET)	175
$(NO_2)_3CCH_2NCH(CH_2OH)_2$	1) urea; $CH_3CN$ 2) 20% $F_2/N_2$ ; $-10^\circ C$	$(NO_2)_3CCH_2NCH[CH_2OC(NF_2)_3]_2$ $NO_2$ (FA-TMEND)	176
$O_2NOCH_2C(CH_2OH)_3$	1) urea; $CH_3CN$ 2) 25% $F_2/N_2$ ; $-10^\circ C$	$O_2NOCH_2C[CH_2OC(NF_2)_3]_3$ (FA-PEMON)	176
$(HCCH_2CCH_2)_{NO_2}^{NO_2}$	1) urea; $CH_3CN$ 2) 25% $F_2/N_2$ ; $-10^\circ C$	$[ (NF_2)_3COCH_2CCH_2 ]_{NO_2}^{NO_2}$ (FA-TWH)	178

TABLE V (Continued)

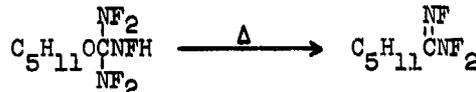
<u>Reactant</u>	<u>Conditions</u>	<u>Products</u>	<u>Reference</u>
$\left( \begin{array}{c} \text{NO}_2 \quad \text{NO}_2 \\   \quad   \\ \text{HOCH}_2\text{CCH}_2\text{NCH}_2 \\   \quad   \\ \text{NO}_2 \quad \text{NO}_2 \end{array} \right)_2$	1) urea; CH <sub>3</sub> CN 2) 25% F <sub>2</sub> /N <sub>2</sub> ; -10°C	$\left[ \begin{array}{c} \text{NO}_2 \quad \text{NO}_2 \\   \quad   \\ (\text{NF}_2)_3\text{COCH}_2\text{CCH}_2\text{NCH}_2 \\   \quad   \\ \text{NO}_2 \quad \text{NO}_2 \end{array} \right]_2$ (FA-HADD)	179
HOCH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> OH	1) urea; CH <sub>3</sub> CN 2) 20% F <sub>2</sub> /N <sub>2</sub> ; -10°C	(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub> (FA-OD)	179
HOCH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	1) urea; CH <sub>3</sub> CN 2) 5% F <sub>2</sub> /N <sub>2</sub> ; CFCl <sub>3</sub>	(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	293
<u>B. Miscellaneous Compounds</u>			
$\begin{array}{c} \text{HON}=\text{C}-\text{NH}_2 \\   \\ \text{HON}=\text{C}-\text{NH}_2 \end{array} \cdot 2\text{HClO}_4$	dimethylurea CH <sub>3</sub> CN	n.r.	267a
CH <sub>3</sub> NO <sub>2</sub>	urea; CH <sub>3</sub> CN	unident. product	267a
$\begin{array}{c} \text{NOH} \\   \\ \text{HCNH}_2 \end{array}$	CH <sub>3</sub> CN	NH <sub>2</sub> CH=NOC(NF <sub>2</sub> ) <sub>2</sub> NPH	292
CF <sub>2</sub> (OF) <sub>2</sub>	F <sub>2</sub> /N <sub>2</sub>	(NF <sub>2</sub> ) <sub>3</sub> CFCO	291
HON=CCl <sub>2</sub>	1) urea; CH <sub>3</sub> CN 2) 3% F <sub>2</sub> /N <sub>2</sub> ; CH <sub>3</sub> CN 3) CFCl <sub>3</sub> ; CF <sub>2</sub> (OF) <sub>2</sub>	$\begin{array}{c} (\text{NF}_2)_3\text{CON}=\text{CCl}_2 \\ (\text{NF}_2)_3\text{CON}=\text{CCl}_2 \\ + \\ (\text{NF}_2)_2\text{CFON}=\text{CCl}_2 \end{array}$	293

TABLE V (Concluded)

<u>Reactant</u>	<u>Conditions</u>	<u>Products</u>	<u>Reference</u>
CH <sub>3</sub> CHO	CH <sub>3</sub> CN; (CH <sub>3</sub> ) <sub>3</sub> N	n.r.	294
FHNC <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	urea; CH <sub>3</sub> CN	mixture of products	15a
HC(NO <sub>2</sub> ) <sub>3</sub>	KNCS	$\begin{array}{c} \text{NF}_2 \\   \\ \text{HFNC}-\text{C}(\text{NO}_2)_3 \\   \\ \text{NF}_2 \end{array}$	497

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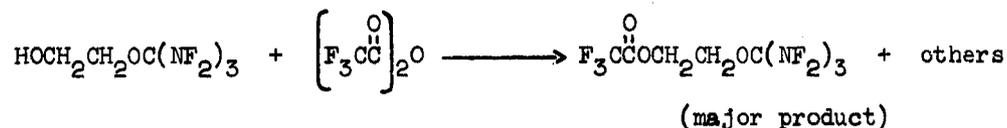
Heating the adduct of n-pentyl alcohol with PFG has been shown to yield the corresponding N,N,N'-trifluoroamidine (354).



The reaction of perfluoroguanidine with 2,2,2'-trinitroethylene glycol (code name: TNEEG) and subsequent fluorination to FA-TNEEG has also been shown to yield a number of side products (175), as shown in Figure 2.

The fluorinated adduct of phosgene oxime and perfluoroguanidine has received considerable study as a potential starting material for the formation of other tris-compounds. A survey of these reactions is given in Table VI.

Treatment of the fluorinated adduct of ethylene glycol (see Table V) with trifluoroacetic anhydride led to a mixture of products, with the major product being addition of the trifluoroacetyl group (294). This compound was found to undergo complete decomposition upon heating to 350°C. At 290°C partial decomposition occurred, while at 240°C no reaction was observed.



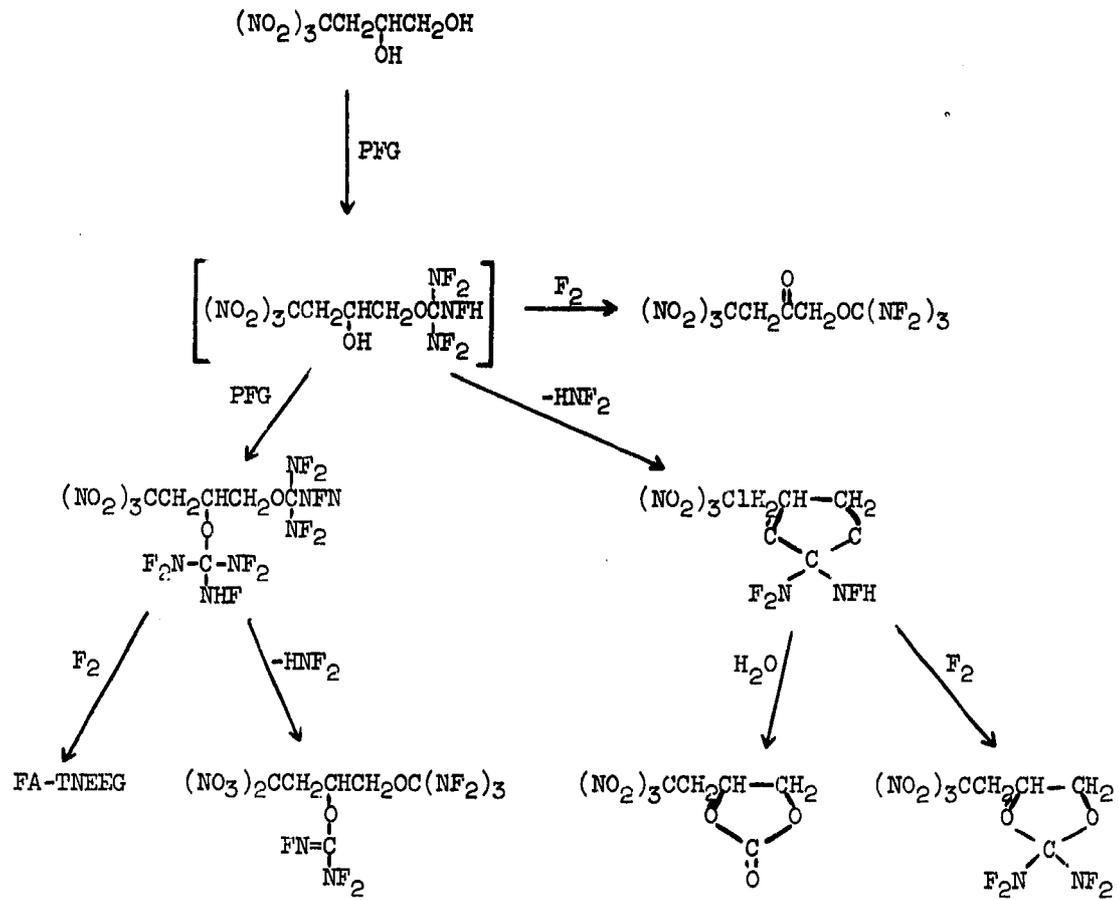
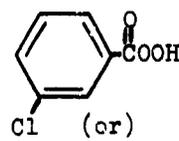


Figure 2 - Side Reactions in the Production of FA-TNEEG

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TABLE VI

REACTIONS OF  $(NF_2)_3CON=CCl_2$

<u>Reactant</u>	<u>Conditions</u>	<u>Products</u>	<u>Ref.</u>
CH <sub>3</sub> OH	NaOH; CFCl <sub>3</sub>	$(NF_2)_3CON=C(OCH_3)_2$	296
$(CH_3)_2NH$	CFCl <sub>3</sub>	$(NF_2)_3CON=C N(CH_3)_2$	296
Na <sub>2</sub> S·9H <sub>2</sub> O	CH <sub>3</sub> OH	decomposes	296
 (or)	CHCl <sub>3</sub> ) ) CH <sub>2</sub> Cl <sub>2</sub> H)	no reaction	295
CF <sub>2</sub> N <sub>2</sub> or N <sub>2</sub> F <sub>4</sub>	CFCl <sub>3</sub>	no reaction	296
NH <sub>3</sub>		$(NF_2)_3CON=C(NH_2)_2$	297
70% HClO <sub>4</sub>	CH <sub>3</sub> CN	no reaction	293
3% F <sub>2</sub> /N <sub>2</sub>	CH <sub>3</sub> CN; 0°C	no reaction	295
CsF	CH <sub>3</sub> CN	$(NF_2)_3CN-O-CF_2$ + others	298
		$\left[ (NF_2)_3CON=C-N \begin{array}{c} \diagup \diagdown \\ \text{Piperazine Ring} \end{array} N \right]_n$ tentative only	298

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## CHAPTER V

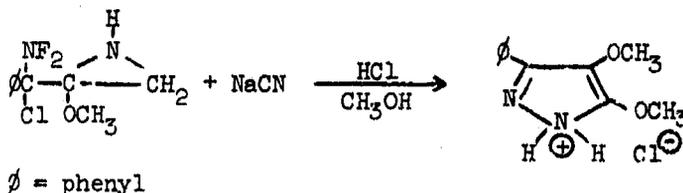
### NF COMPOUNDS WHICH CONTAIN NN BONDS

This chapter will be directed toward the preparation and reaction chemistries of those compounds which contain some type of nitrogen to nitrogen bond. Tetrafluorohydrazine and difluorodiazine can be regarded as the parent molecules for this group. The chapter can conveniently be divided into three parts: N-N, N=N, and N-NO<sub>2</sub> type compounds.

#### V-A. Hydrazine Derivatives

Only a few reactions have been reported for molecules containing the N-N bond. These reactions have been discussed in the preceding chapters and examples of their preparation and reactions can be found in the following parts: amine fluorinations, ureas, fluorimines, and perfluoroguanidine (Table V).

The formation of 3-phenyl-4,5-di(methoxy)pyrazolium chloride was found to occur by treatment of the appropriately substituted ethylenimine with sodium cyanide in methanol (453).



A second route to the same product was found by treating the original compound with dry hydrogen chloride, which resulted in ring opening and formation of the substituted ammonium chloride. Reaction of this material with strong base, methoxide ion, and then dry hydrogen chloride yielded the 3-phenyl-4,5-di(methoxy)pyrazolium chloride (453).

#### V-B. Diimide Derivatives

In addition to the work discussed below, other references to compounds containing a N=N bond can be found in the previous sections concerned with amides and fluorimines. Also included in this part are diazo compounds and molecules of higher N-content such as azides and tetrazoles.

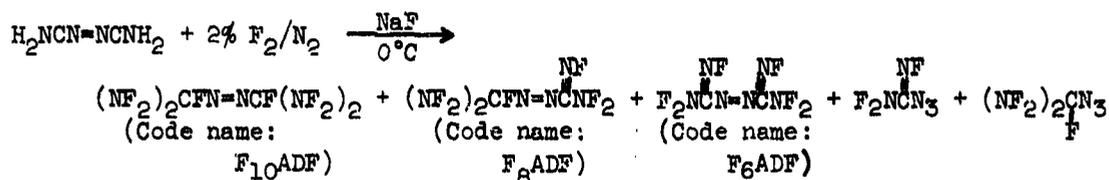
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Tris(difluoroamino)methyl chloride has been found to react with dimethyl sulfoxide (DMSO) at room temperature to yield two diazirines (85a).

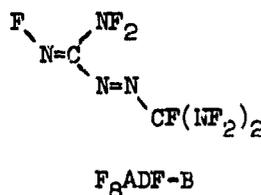
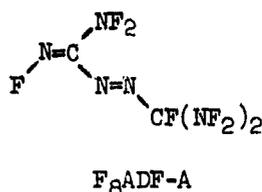


Reaction of acetamidine with sodium hypochlorite in DMSO has been reported to give chloromethyl diazirine (434).

The preparation and reactions of fluorinated azodiformamidines have received a considerable amount of study, principally by the workers at Hynes. Fluorination of azodiformamidine with elemental fluorine has resulted in the formation of a mixture of products (112a).

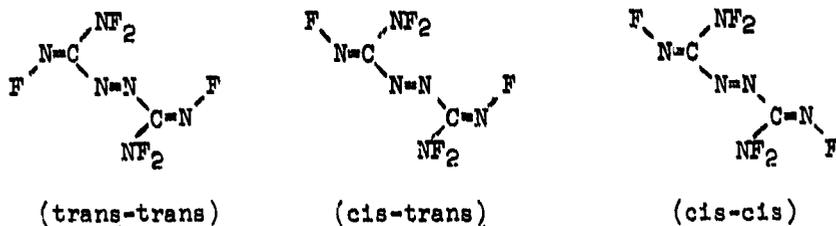


The compound  $\text{F}_8\text{ADF}$  has two isomers which have been designated A and B. Their structures are given below (255).

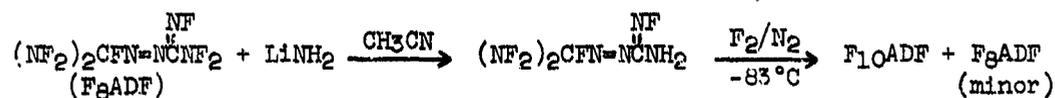


When the fluorination of azodiformamidine was carried out at  $-75^\circ\text{C}$  and then allowed to warm to  $0^\circ\text{C}$ , the compound designated  $\text{F}_8\text{ADF}$  was found to be the principal product (255). Like  $\text{F}_8\text{ADF}$ , the  $\text{F}_6\text{ADF}$  was found to be isomeric, and the three isomers have been identified.

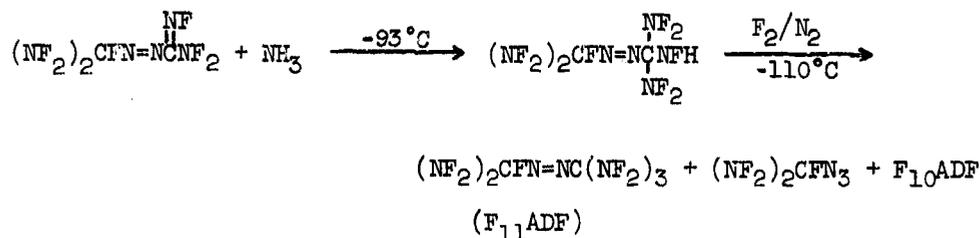
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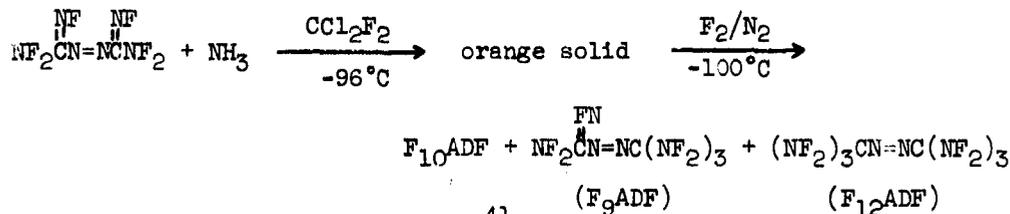
The reduction of several of the fluorinated azodiformamidines has been studied with lithium amide and ammonia. Reaction of F<sub>8</sub>ADF with LiNH<sub>2</sub> was found to produce the N-fluoroamidine, which upon fluorination yielded F<sub>10</sub>ADF (249,112a).



Similar treatment of F<sub>10</sub>ADF with LiNH<sub>2</sub> in Freon 113 resulted in no observable reaction (252,112a); however, F<sub>8</sub>ADF produced a mixture which was not resolved but did show the presence of N-H bonds (251,112a). Those results led to the conclusion that in order for the reaction to occur, the presence of a fluorimino group (C=NF) is required (112a). With ammonia, F<sub>8</sub>ADF-A reacted to form the addition compound. Fluorination of this compound with elemental fluorine led to the production of F<sub>11</sub>ADF and F<sub>10</sub>ADF (112a).



A similar reaction of ammonia with F<sub>6</sub>ADF yielded an orange solid, which upon fluorination resulted in the formation of F<sub>10</sub>ADF as the major product, with minor amounts of two materials tentatively identified as F<sub>9</sub>ADF and F<sub>12</sub>ADF (249,254,112a).



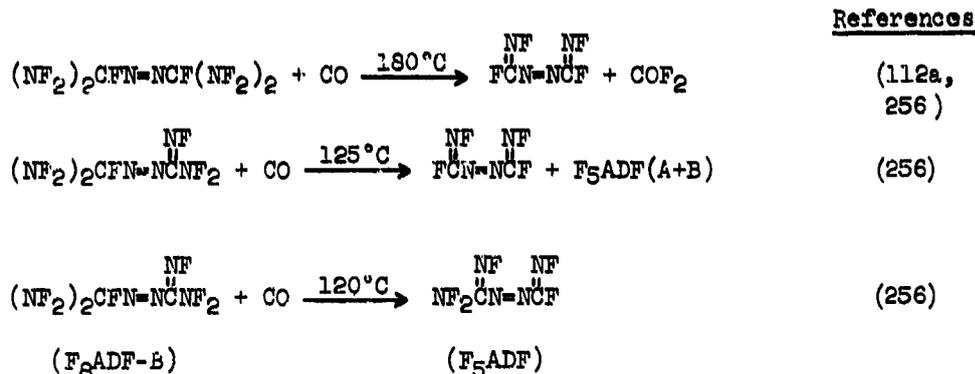
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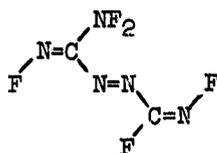
The reactions of  $F_{10}ADF$  and of the two isomers of  $F_8ADF$  with carbon monoxide at elevated temperatures have led to the formation of two new compounds,  $F_4ADF$  and  $F_5ADF$  as in Table VII.

TABLE VII

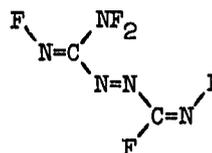
REACTIONS OF  $F_{10}ADF$  AND  $F_8ADF$  WITH CO



At 135°C no reaction occurs between the  $F_{10}ADF$  and carbon monoxide (256). The molecule,  $F_5ADF$ , has been found to have two isomers designated as A and B. (256).

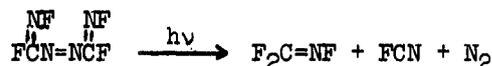
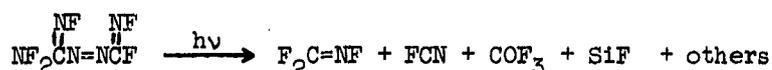


trans-isomer A



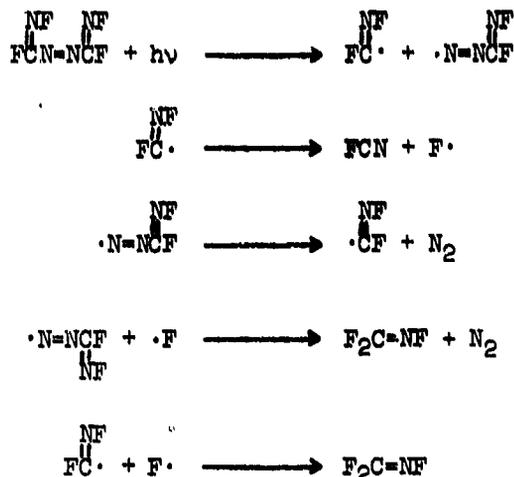
cis-isomer B

Isomer B of  $F_5ADF$  undergoes photolysis to yield perfluoroformimine plus other products (254,256). The same product has also been obtained as a result of the photolysis of  $F_4ADF$  (256).



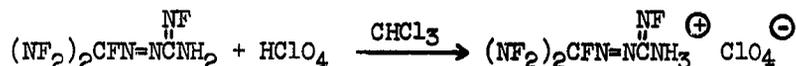
A mechanism for the formation of the products observed from the photolysis of the  $F_4ADF$  has been proposed (256).

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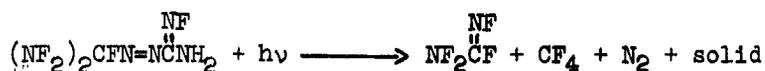


The reaction of F<sub>10</sub>ADF with nitrogen dioxide at 190°C resulted in decomposition of the starting material (250). Unsuccessful attempts were made to react hydrogen sulfide and monogermene with F<sub>10</sub>ADF (250,112a).

Several reactions have been attempted utilizing the partially hydrogenated intermediate formed in the reduction of F<sub>8</sub>ADF with lithium amide. Formation of the amidine salt was attempted with sulfuric, hydrochloric, 70% perchloric, and anhydrous perchloric acids (252). The only identified product was formed with anhydrous perchloric acid.

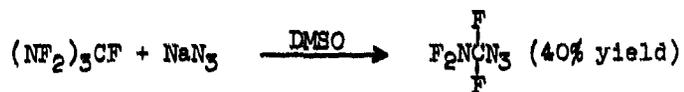


The solid salt was pale yellow and very hygroscopic. At 140°C, the free amidine was found to undergo complete decomposition within 24 hr. while at 110°C, in the presence of NaF, no decomposition was observed (251). Photolysis of the amidine led to the formation of perfluoroformamidine and an unidentified solid (251,112a).

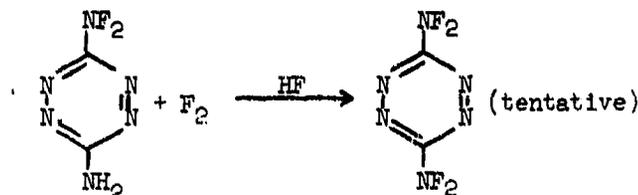


The reaction of tris(difluoramino)fluoromethane (code name: Compound R) with sodium azide in DMSO led to the formation of difluoro-fluoraminomethylazide (85c).

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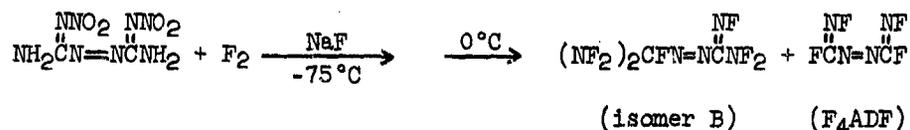
Fluorination of 3,6-diamino-1,2,4,5-tetrazine with elemental fluorine in liquid hydrogen fluoride led to a compound tentatively identified as the 3,6-bis-(difluoramino) substituted analog (497). Attempts to isolate the material resulted in a rapid decomposition.



### V-C. NNO and NNO<sub>2</sub> Derivatives

The preparation and reaction of the NNO- and NNO<sub>2</sub>-substituted compounds discussed in the ensuing paragraphs are only a portion of those reported. Additional citations of these molecules may be found in the sections relating to ureas, fluorinated guanidines, and perfluoroguanidine (see Table V).

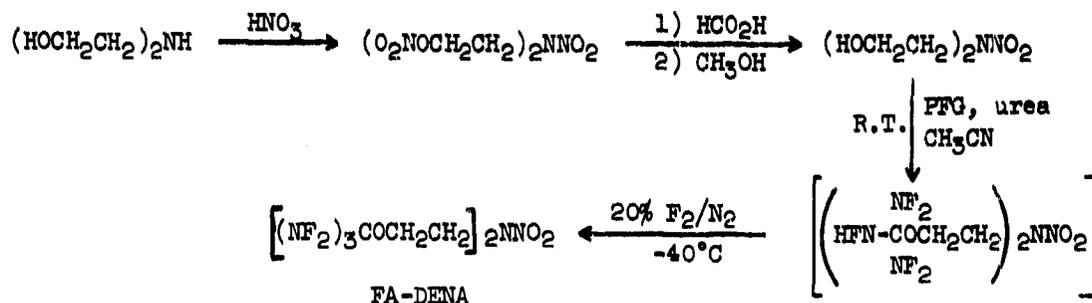
Fluorination of dinitroazodiformamide in the presence of sodium fluoride at low temperature has led to the formation of F<sub>3</sub>ADF-B, F<sub>4</sub>ADF, and two unidentified products (252).



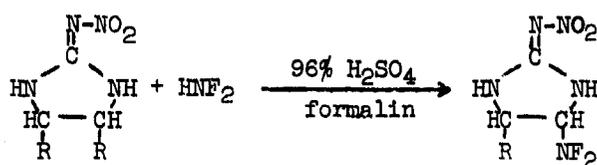
Attempts to conduct the same fluorination in aqueous solution in the presence of B<sub>2</sub>O<sub>3</sub> were unsuccessful and similar negative results were obtained by the use of a fluorine-helium mixture in the presence of sodium fluoride in Freon 113 at -22°C (252). The use of acetonitrile as a solvent resulted in an explosion.

FA-DENA has been prepared by a multistep process from 2,2'-dihydroxy-diethylamine (178).

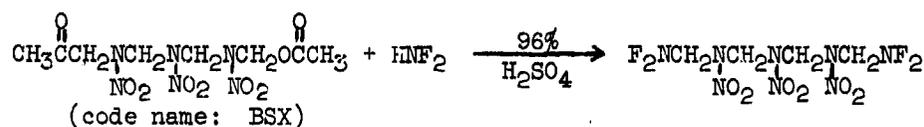
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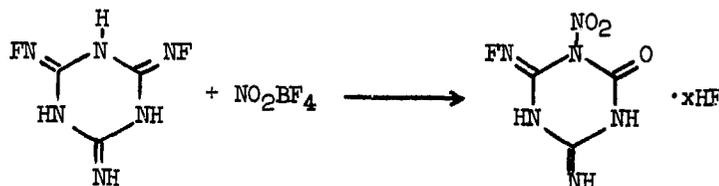
Difluoramine, in the presence of 96% sulfuric acid, has been used to replace alkoxy groups by difluoramino groups in substituted imidazolidine imines (270,272) and acetoxy groups from substituted amines (269).



R = -OCH<sub>3</sub> or -OC<sub>2</sub>H<sub>5</sub>



Nitryl tetrafluoroborate (NO<sub>2</sub>BF<sub>4</sub>) was reacted with 2,6-di(fluorimino)-4-imino-1,3,5-trihydrotriazine to yield a compound tentatively identified as N'-nitro-2-keto-4-imino-6-fluorimino-1,3,5-trihydrotriazine (497).



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## CHAPTER VI

### INORGANIC NITROGEN FLUORIDES AND DERIVATIVES

#### VI-A. Nitrogen Trifluoride

The heat of formation of  $\text{NF}_3$  has recently been redetermined by two methods: the direct reaction with sulfur (158) and via the dissociation of excess  $\text{NF}_3$  in the explosion with  $\text{H}_2$  (151a, 151, 151f, 155). The measured values were  $-31.75 \pm 0.2$  and  $-31.44 \pm 0.3$  kcal/mole, respectively. The former led to an average N-F bond energy of 67.1 kcal/mole and a derived  $D(\text{NF}_2\text{-F})$  of  $59.1 \pm 2$  kcal/mole, confirming the earlier conclusions that the dissociation of the first N-F bond (to give stable  $\text{NF}_2$  radicals) is lower than the average. The latter study was used to recalculate the heat of formation of aqueous HF (1:123  $\text{H}_2\text{O}$ ) as  $-77.0 \pm 0.2$  kcal/mole. The value of  $\Delta H_f = -30.60$  kcal/mole is then recommended in the use of  $\text{NF}_3$  as a calorimetric fluorinating agent.

Studies of the dipole moment of  $\text{NF}_3$  gave a tentative value of 0.17D (232) and from work at 48° and 80°C the value 0.20D (238).

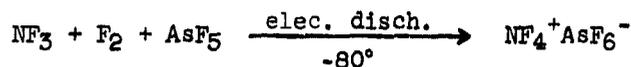
Efforts to observe the ion-molecule reaction



have not been successful to date (386, 402, 405). High energy radiation of mixtures of  $\text{NF}_3$  and  $\text{F}_2$  with  $\text{AsF}_5$  at  $-196^\circ$  gave (472) moderately stable solids which appeared to contain the salt  $\text{NF}_4^+\text{AsF}_6^-$  (dec.  $200^\circ$ ) together with  $\text{N}_2\text{F}_3^+\text{AsF}_6^-$  (dec.  $110 - 170^\circ$ ) and apparently a third salt which evolved  $\text{N}_2\text{F}_2$  and  $\text{AsF}_5$  at  $20 - 50^\circ$  ( $\text{N}_2\text{FAsF}_6$  is known to be much more stable than this). Radiation of  $\text{NF}_3\text{-F}_2\text{-BF}_3$  mixture at  $-196^\circ$  in a sapphire tube (oxygen-free fluorine) gave high purity  $\text{NF}_4\text{BF}_4$ . The synthesis and properties of  $\text{NF}_4^+$  salts are described in detail in section B of this chapter. Further reactions of  $\text{NF}_3$  which have been studied or attempted are summarized in Table VIII.

#### VI-B. $\text{NF}_4^+$ Salts

The synthesis of salts of the long sought  $\text{NF}_4^+$  ion has been well demonstrated since the previous review (284a). In October 1965, Stauffer Chemical Company chemists reported (507) the formation of  $\text{NF}_4\text{AsF}_6^-$  by a low temperature electric discharge method.



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TABLE VIII

## REACTIONS OF NF<sub>3</sub>

<u>Reactant</u>	<u>Conditions</u>	<u>Results</u>	<u>References</u>
Cl <sub>2</sub>	200 - 500°, 8000 - 10,000 psi	No reaction	75
NO	200 - 500°, 8000 - 10,000 psi	NO <sub>2</sub> , NOF	75
NO	Excess NF <sub>3</sub> , 300°, 8800 psia	NOF, NF <sub>3</sub>	78
NO excess	200°	Exploded	78
NO/ <u>cis</u> -N <sub>2</sub> F <sub>2</sub>	66°, 80,000 psi, 1 hr.	25% dec. of N <sub>2</sub> F <sub>2</sub>	89
OF <sub>2</sub>	300°	Dec. of OF <sub>2</sub>	339
OF <sub>2</sub>	200°, 10,000 psi, 6 hr.	Unk. with IR abs. at 1225 and 2175 cm <sup>-1</sup>	75
OF <sub>2</sub>	Flash photolysis, liquid	O <sub>3</sub>	88
CsF	500°, 8000 psi, 1 hr.	No reaction	78
CsF; NO	300°, 8800 psi, 18 hr.	Some NOF, probably N <sub>2</sub>	78
BF <sub>3</sub> (or PF <sub>5</sub> )	Tesla coil disch., 5 mm. pr. -196° quench	Some N <sub>2</sub> F <sup>+</sup> BF <sub>4</sub> <sup>-</sup> (or PF <sub>6</sub> <sup>-</sup> ) and SiF <sub>6</sub> <sup>=</sup>	232
BF <sub>3</sub>	1445 psi, 25°	No deviation from ideality	232
PF <sub>5</sub>	1090 psi, 25°	No deviation from ideality	232
SbF <sub>5</sub>	200°, 2400 psi, 50 hr.	~ 2% reaction of NF <sub>3</sub> to NF <sub>4</sub> <sup>+</sup> ? and unidentified product	479

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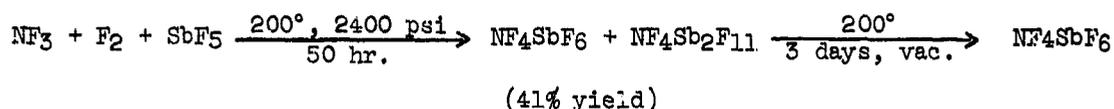
TABLE VIII (Concluded)

<u>Reactant</u>	<u>Conditions</u>	<u>Results</u>	<u>References</u>
$\text{AlCl}_3$	$80^\circ$ , 4 days (or $135^\circ$ fast)	$\text{N}_2\text{Cl}_2$	227
$\text{Fe}^{+2}$ , $\text{H}_2\text{aq}^+$	$60^\circ$ , fast	$\text{NH}_4^+$ , $\text{Fe}^{+3}$ , $\text{F}^-$	227
<u>c-</u> or <u>t-</u> $\text{N}_2\text{F}_2$ , $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$	$82^\circ$ , 6, 100 atm., 4 hr.	Dec. of <u>cis</u> - $\text{N}_2\text{F}_2$	88
Xe	Flash photolysis, liquid	XeF compounds	88
$\text{ClF}_3$	$425^\circ$ , 1350 psig	No reaction	339
$\text{ClF}_5$	$325^\circ$ , 2125 psig, 20 hr.	Some $\text{ClF}_3$ and $\text{F}_2$	339
$\text{ClO}_3\text{F}$	$475^\circ$ , 2050 psig, 18 hr.	No reaction	339
$\text{ClF}_2\text{SbF}_6$	$250^\circ$ , 3 hr.	No reaction	339
$\text{ClF}_2\text{SbF}_6$	$350^\circ$ , 80 hr.	36%, dec. of $\text{NF}_3$ , hard pink solid	339
$\text{ClF}_2\text{SbF}_6$	$350^\circ$ , 23 hr.	No reaction	339
$\text{ClF}_4\text{SbF}_6$	$200^\circ$	Some $\text{ClF}_5$ evolved	339
$\text{CsClF}_4$	$200^\circ$ , 24 hr.	No reaction	
$\text{CsClF}_4$	$470^\circ$	Sl. dec. to $\text{CsF}$ , $\text{ClF}$ , $\text{ClF}_3$ , $\text{CuF}_2$ and $\text{NiF}_2$	340
$\text{ClO}_2$	$110^\circ$	No reaction	340
<u>t-</u> $\text{N}_2\text{F}_2$	$\gamma$ -Radiation, $-196^\circ$	$\text{N}_2$ , $\text{F}_2$ , $\text{N}_2\text{F}_4$	471
$\text{N}_2\text{F}_4$	$\gamma$ -Radiation, $-196^\circ$	Inconcl. (Si contami- nation)	472
$\text{O}_2$	UV, liquid	Small amounts $\text{NO}_2\text{F}$ , $\text{O}_2\text{F}$ .	532d

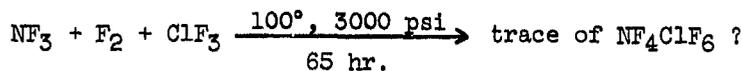
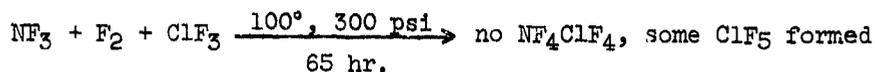
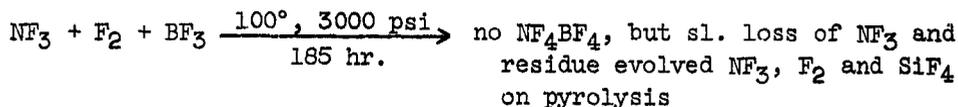
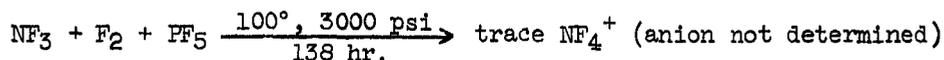
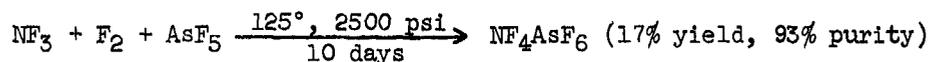
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The compound (apparently contaminated by N-O salts) was reasonably stable to 200° and gave an infrared spectrum showing bands at 1165 and 707 cm<sup>-1</sup> attributable to the NF<sub>4</sub><sup>+</sup> and AsF<sub>6</sub><sup>-</sup> ions. Publications describing the synthesis and properties (L11, L28) and the vibrational and NMR spectra (L12) have appeared.

In December 1965, Stanford Research Institute scientists reported the formation of a new N-F containing solid which was believed on the basis of <sup>19</sup>F NMR (resonance of -215  $\phi$ ) and thermal pyrolysis studies to be NF<sub>4</sub>SbF<sub>6</sub> (476). The four component reaction system used, NF<sub>3</sub>/F<sub>2</sub>/SbF<sub>5</sub>/HF, had in one run previously (475) given evidence of some reaction. The analogous reaction with AsF<sub>6</sub> was also demonstrated (477). The products of these early runs were badly contaminated with metal salts, but the elimination of the HF from the reaction mixture led to products of good purity (477). The formation (especially at short reaction times) of some of the salt NF<sub>4</sub>Sb<sub>2</sub>F<sub>11</sub> was also demonstrated (477), but the excess SbF<sub>5</sub> could be removed. The final procedure is as follows:

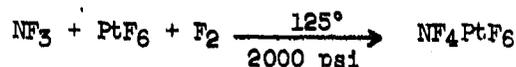


The synthesis and properties of NF<sub>4</sub>SbF<sub>6</sub> and NF<sub>4</sub>AsF<sub>6</sub> by similar methods have been described in the literature (156, 157), but applications of this method with weaker Lewis acids have been less successful as shown by the results (487) shown below:



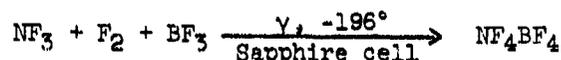
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The identification of the  $\text{ClF}_5$  reaction product was based only on the evolution of some  $\text{NF}_3$ ,  $\text{F}_2$ ,  $\text{SiF}_4$  and  $\text{ClF}_5$  when the reactor was heated above  $225^\circ$ , after prior evacuation at ambient. (In view of the dubious existence of the  $\text{ClF}_6^-$  anion the latter product appears unlikely.) As might be expected, however,  $\text{PtF}_6$  forms a stable salt (559a).



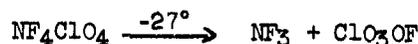
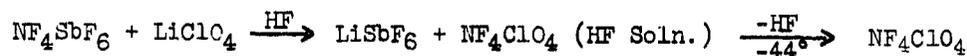
The direct reaction of  $\text{NF}_3$  and  $\text{SbF}_5$  (without  $\text{F}_2$ ) at  $200^\circ$  and 2400 psi for 50 hr. appeared to give (479) a mixture of NF salts based on the reported hydrolysis products:  $\text{NF}_3$  and  $\text{O}_2$  from  $\text{NF}_4^+$ ,  $\text{N}_2\text{O}$  from  $\text{N}_2\text{F}^+$  and  $\text{NO}$  and  $\text{NO}_2$  from  $\text{N}_2\text{F}_3^+$ .

In studies at Midwest Research Institute in early 1963, the formation of small amounts of  $\text{NF}_4\text{AsF}_6$  was observed (248b) from the fluorination of  $\text{N}_2\text{F}_3\text{AsF}_6$  at  $115^\circ$ , but the reaction route is not clear and may involve  $\text{NF}_3$  as an intermediate. Results of studies at Shell (472) at about the same time suggested the formation of  $\text{NF}_4\text{AsF}_6$  upon high energy radiation of a mixture of  $\text{NF}_3$ ,  $\text{F}_2$  and  $\text{AsF}_5$  at  $-196^\circ$ . The resulting solid product evolved  $\text{N}_2\text{F}_2$  and  $\text{AsF}_5$  at  $20 - 50^\circ$ ,  $\text{N}_2\text{F}_4$  and  $\text{AsF}_5$  at  $110 - 170^\circ$  (i.e., from  $\text{N}_2\text{F}_3\text{AsF}_6$ ) and  $\text{NF}_3$  and  $\text{AsF}_5$  at  $200^\circ$  (i.e., from  $\text{NF}_4\text{AsF}_6$ ). Further studies with  $\text{BF}_3$  in place of  $\text{AsF}_5$  and oxygen free  $\text{F}_2$  have led to good yields ( $\sim 160 \text{ mg/hr}$ ) of high purity  $\text{NF}_4\text{BF}_4$  according to Wilson (593a).



Application of this method to the  $\text{NF}_3/\text{F}_2/\text{ClF}_3$  system did not, however, lead to  $\text{NF}_4\text{ClF}_4$ .

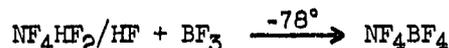
The synthesis of  $\text{NF}_4\text{ClO}_4$  and other  $\text{NF}_4^+$  salts by metathesis reactions have been studied extensively at Stanford, although previous calculations (474) had indicated that no oxyanions would be stable with  $\text{NF}_4^+$ . The high solubilities of  $\text{NF}_4\text{SbF}_6$  and  $\text{NF}_4\text{AsF}_6$ , 2.6 and 1.2 g/g of anhydrous HF, respectively (157) make this an attractive solvent system. Preliminary studies (478) indicated that  $\text{NF}_4\text{SbF}_6$  and  $\text{KClO}_4$  were compatible as a solid mixture and in HF solution. The metathesis reaction with  $\text{LiClO}_4$  (the lithium salt is preferred since the solubilities of the alkali fluorides and complex fluorosalts in HF increase with increasing size of the cation) followed by separation of the by-product and removal of solvent at low temperature gave (488) a white solid believed to be  $\text{NF}_4\text{ClO}_4$  which decomposed below room temperature:



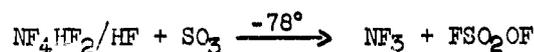
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This mode of decomposition, previously predicted (276a), is in contrast to the decomposition in all other reported systems involving fluorocations and the perchlorate ion, i.e., to give  $\text{FClO}_3$  by the oxide-ion transfer mechanism (276a). A similar result was obtained when the metathesis reaction of  $\text{NF}_4\text{SbF}_6$  and  $\text{CsClO}_4$  was attempted in  $\text{IF}_5$  solution, except the product  $\text{NF}_4\text{ClO}_4$  decomposed at the melting point of the  $\text{IF}_5$ , (559a) pure  $\text{IF}_5$  melts at  $10^\circ$ .

Similarly, the metathesis reaction with  $\text{LiF}$  or  $\text{HF}$  gave a stable solution of  $\text{NF}_4\text{HF}_2$  at low temperature (487) and a stable solid after evaporation of excess solvent (488). Most recently, however, this solid was described as a solvated material which decomposed to  $\text{NF}_3$ ,  $\text{F}_2$  and  $\text{HF}$  at  $-44^\circ$  (559a). However, the  $\text{NF}_4\text{HF}_2$  solution is useful as an intermediate in the metathetical preparation of  $\text{NF}_4\text{BF}_4$  (489).



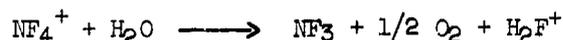
However, the salt of the oxyanion  $\text{SO}_3\text{F}^-$  could not be prepared by an analogous reaction as decomposition occurred:



Mixtures of the solid salts  $\text{NF}_4\text{SbF}_6$  and  $\text{LiClO}_4$  reacted at  $55^\circ$  similarly to give  $\text{ClO}_3\text{OF}$  while mixtures with  $\text{KBr}$ ,  $\text{KCl}$  or  $\text{KF}$  evolved the corresponding halogen gases at  $25^\circ$ ,  $150^\circ$  and  $225^\circ$ , respectively (488).

The thermal stabilities, of the known  $\text{NF}_4^+$  salts containing perfluoroanions are (487, 593a) as follows:  $\text{NF}_4\text{SbF}_6$  dec.  $\sim 300^\circ$ ;  $\text{NF}_4\text{AsF}_6$ , dec.  $\sim 270^\circ$ ;  $\text{NF}_4\text{BF}_4$ , dec.  $236^\circ$ . The good stability of the  $\text{NF}_4\text{BF}_4$  is apparently kinetically derived (276a) since calculations indicate that the heat of decomposition to  $\text{NF}_3$ ,  $\text{F}_2$  and  $\text{BF}_3$  is  $+3.6$  kcal/mole at  $25^\circ$ , although  $\Delta H_f$  is  $-305.2$  kcal/mole (593a). Differential thermal analysis on a sample of  $\text{NF}_4\text{SbF}_6$  containing some  $\text{Sb}_2\text{F}_{11}^-$  indicated a melting point of  $170^\circ$  (478). The density of single crystals of  $\text{NF}_4\text{AsF}_6$  deposited from  $\text{HF}$  solution is  $1.9225$  g/ml.

All of the  $\text{NF}_4^+$  salts are sensitive to moisture and appear to react with many organics (593a). The hydrolysis is described (478) by the equation

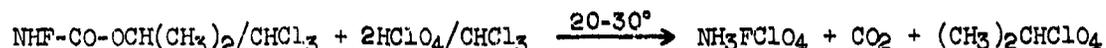


The  $\text{NF}_4\text{SbF}_6$  reacts with traces of moisture in glass at ambient temperature and attacks glass at  $85^\circ$  to give  $\text{SiF}_4$ ,  $\text{NF}_3$  and presumably  $\text{O}_2\text{SbF}_6$ .

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## VI-C. NH<sub>3</sub>F<sup>+</sup> Salts

The synthesis of fluoroammonium perchlorate by Grakauskas and Remanick at Aerojet-General was discussed in the previous review (284a). Early storage studies on the product available in 1965 showed (45) no reaction in nickel after three months at 25° and only very slight decomposition in Monel, but stainless steel and Teflon were unsatisfactory. Later studies on samples of higher purity showed no reaction with Teflon in 60 days at 25° (50) and no reaction with glass in 30 days at -20°, but slight reaction with nickel in 2 weeks at ambient temperature unless it was well passivated with HF. Electrostatic test (45) showed that NH<sub>3</sub>FClO<sub>4</sub> was only slightly more sensitive than RDX and scale-up studies were started. Thus 5 - 10 g. batches were prepared in 1965 (46) and 70 - 140 g. lots in 1966 (48). The preferred synthesis route was



The use of less than 70% HClO<sub>4</sub> caused partial hydrolysis of NH<sub>3</sub>F<sup>+</sup> and thus led to lower yield and purity. The use of anhydrous HClO<sub>4</sub> was introduced in late 1966 (49). The initial product appeared to be a less dense crystal form which rearranged on standing a few days to a more dense form. The latter form was obtained directly if the solvent was CH<sub>2</sub>Cl<sub>2</sub>. The fluorocarbamate was prepurified by removal of isopropylcarbamate on a silica gel column after N,N-difluorocarbamate was volatilized off. Traces of solvent must be carefully removed or they greatly reduce the stability.

Differential thermal analysis of a NH<sub>3</sub>FClO<sub>4</sub> sample prepared from 70% HClO<sub>4</sub> showed (46) an exotherm at 105°C and impact sensitivity tests showed ~50% detonations at 25 - 30 cm. compared to 25 cm for RDX. Infrared analysis of a sublimed sample (NaCl window) showed bonds at 3.05 μ (N-H st.) and 7.03 μ (NH<sub>2</sub> bend), i.e., shifted to shorter wavelengths by ~ 0.15 μ from NH<sub>4</sub>ClO<sub>4</sub>. The N-F band was not observed, and was assumed to be obscured by the ClO<sub>4</sub><sup>-</sup> bands. The heat of formation of NH<sub>3</sub>FClO<sub>4</sub> was determined by combustion calorimetry at Aerojet (50) to be -67.6 kcal/mole (-49.9 kcal/100 g.), in good agreement with the value -66.57 kcal/mole obtained from the heat of solution in water (-54.5 kcal/mole determined by Fasolino (302a) and the assumption that the hydrolysis products are F<sup>-</sup>, 1/3 NH<sub>4</sub><sup>+</sup>, 2-1/3 H<sup>+</sup>, 1/3 N<sub>2</sub> and ClO<sub>4</sub><sup>-</sup>. From the heat of formation and the assumption that the heat of vaporization of NH<sub>3</sub>FClO<sub>4</sub> equals that of NH<sub>4</sub>ClO<sub>4</sub> and that the N-H bond energy in NH<sub>3</sub>F<sup>+</sup> is 93.4 kcal/mole, a value of 57.1 kcal/mole was calculated for the N-F bond energy. This value is probably too low by 10 - 15 kcal. The theoretical specific impulse of NH<sub>3</sub>FClO<sub>4</sub> with an aluminized butadiene fuel was calculated to be about 270 sec.

The NH<sub>3</sub>FClO<sub>4</sub> is unusually soluble, for an inorganic perchlorate, in organic solvents such as nitriles and esters. Solutions in energetic solvents were being considered as liquid monopropellants. The very hygroscopic and moisture sensitive nature of NH<sub>3</sub>FClO<sub>4</sub> also occurs with the methanesulfonic acid salt, NH<sub>3</sub>FSO<sub>3</sub>CH<sub>3</sub>, which undergoes a complex decomposition to give N<sub>2</sub>H<sub>4</sub> along with N<sub>2</sub> and NH<sub>3</sub> (but no NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> or NH<sub>2</sub>OH).

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## VI-D. Difluorodiazine

The chromatographic purification of the two  $N_2F_2$  isomers has been studied at Rocketdyne (386). The cis- $N_2F_2$  is purified on a silica gel column while trans- $N_2F_2$  is purified on an activated alumina column on which the cis isomer is decomposed. Purified cis- $N_2F_2$  was found to be much less reactive than generally indicated in the published literature. Efforts to photosensitize the isomerization were not successful with  $NO_2$ ,  $C_6H_6$ ,  $C_6F_6$ ,  $Cl_2$ ,  $Br_2$  or  $I_2$  as agents. The thermal isomerization at  $74^\circ$  for 1 hr. gives good (93%) conversions of trans to cis according to studies at Harshaw (224). The trans- $N_2F_2$  is previously purified of  $N_2F_4$  and  $SF_6$  by treating with  $H_2O$  and subsequent distillation, then mixed with ~25% cis- $N_2F_2$  prior to isomerization. Flowing gaseous trans- $N_2F_2$  has been noted to ignite Kel-F needle valves (471) and hence should be handled with caution.

A number of reactions of cis- and trans- $N_2F_2$  have been attempted or studied as summarized in Table IX.

## VI-E. $N_2F^+$ Salts

The salt,  $N_2F^+AsF_6^-$ , (284a) has been estimated (386) from electronegativity considerations to be only ~35% ionic in the solid, although HF solutions might well be ionic. The shift of the  $AsF_6^-$  bond from ~700  $cm^{-1}$  in metal hexafluoroarsenates to 715  $cm^{-1}$  in  $N_2FAsF_6$  was considered indicative of partial covalency, but the similarity of the X-ray patterns of  $N_2FAsF_6$  and  $NO_2AsF_6$  was not considered significant. The use of HF as a solvent has been found satisfactory for crystal growth studies on  $N_2FAsF_6$  (472).

The reaction of either cis- or trans- $N_2F_2$  with  $SbF_5$  at  $40 - 50^\circ$  gives a 1:2 complex (m.p.  $82 - 84^\circ$ ) according to Ruff (152) which is apparently the salt  $N_2F^+Sb_2F_{11}^-$ . The infrared spectrum shows only a single band, 1054 ( $m$ )  $cm^{-1}$ , in the N-F region and no N-N bands were observed. No satisfactory NMR solvent was apparently found: the complex fluorinated  $AsF_3$  to  $AsF_5$  and reacted with  $SO_2$  to give  $N_2O$ ,  $N_2$ ,  $SF_2O$ ,  $SF_2O_2$  and  $SO_2SbF_5$ . The  $N_2FSb_2F_{11}$  decomposed readily at  $200^\circ$  with attack on glass. Only cis- $N_2F_2$  is evolved in the thermal decomposition or in the reaction of the complex with KF.

In another study of the infrared spectrum of  $N_2F^+SbF_6^-$  (87a) the N-F and SbF bands were again observed, but not the N-N bands. In  $SbF_5$  solutions of the salt, however, the N-F band was not observed (88, 89, 90). Interestingly enough, a transient royal blue color was repeatedly observed (89) at the interface of  $N_2F_2$  and  $SbF_5$ , or uniform blue solution was formed (90) when the  $N_2F_2$  was bubbled through the  $SbF_5$ . The blue solution, which soon changes to the final yellow color, was suspected of containing the intermediate product  $N_2F_2^+SbF_5^-$  based on the results of EPR studies. Even in the yellow solution, two distinct paramagnetic species could be observed at  $g=2.002$  and  $g=2.027$  using a Kel-F tube. In a glass tube, the 2.002 species (apparently the  $N_2$ -containing species) was not observed and absorption was probable.

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TABLE IX

REACTIONS OF N<sub>2</sub>F<sub>2</sub>

<u>Reactions and Results</u>	<u>Reference</u>
N <sub>2</sub> F <sub>2</sub> + CsF $\xrightarrow{25^\circ}$ 20 mole percent N <sub>2</sub> F <sub>2</sub> absorbed (Cs <sup>+</sup> N <sub>2</sub> F <sub>3</sub> <sup>-</sup> ?)	79
N <sub>2</sub> F <sub>2</sub> + CsF $\xrightarrow[> 250 \text{ psi}]{60^\circ}$ dec. of N <sub>2</sub> F <sub>2</sub>	79
N <sub>2</sub> F <sub>2</sub> (mostly <u>trans</u> ) + CsF $\xrightarrow{-111^\circ}$ some solid "complex" $\xrightarrow{25^\circ}$ <u>cis-N<sub>2</sub>F<sub>2</sub></u>	79
N <sub>2</sub> F <sub>2</sub> + CsF $\xrightarrow{\text{CFCl}_3}$ no absorption, but one of two runs exploded	79
N <sub>2</sub> F <sub>2</sub> + OF <sub>2</sub> + CsF $\xrightarrow[16 \text{ hr.}]{-50^\circ}$ No rxn. $\xrightarrow[20 \text{ hr.}]{95^\circ}$ unident. prod.	79
N <sub>2</sub> F <sub>2</sub> + OF <sub>2</sub> $\xrightarrow[20 \text{ hr.}]{25^\circ}$ No rxn.	79
N <sub>2</sub> F <sub>2</sub> + OF <sub>2</sub> + CO <sub>2</sub> + CsF $\longrightarrow$ (CF <sub>3</sub> O) <sub>2</sub> O (not obtained from ternary combinations)	79
N <sub>2</sub> F <sub>2</sub> + Cl <sub>2</sub> + CsF $\longrightarrow$ unident. prod.: N <sub>2</sub> F <sub>2</sub> Cl <sup>+</sup> in mass spec. (two runs exploded)	79
N <sub>2</sub> F <sub>2</sub> ( <u>cis</u> or <u>trans</u> ) + CsF $\xrightarrow{-80^\circ}$ some abs. of N <sub>2</sub> F <sub>2</sub> (more <u>trans</u> abs.) $\xrightarrow{25^\circ}$ <u>cis</u> desorbs	80
N <sub>2</sub> F <sub>2</sub> + Cl <sub>2</sub> $\xrightarrow[24 \text{ hr.}]{-80^\circ}$ No rxn.	80
<u>cis-N<sub>2</sub>F<sub>2</sub></u> + OF <sub>2</sub> $\xrightarrow[24 \text{ hr.}]{-80^\circ}$ unident. IR peaks	80
<u>cis-N<sub>2</sub>F<sub>2</sub></u> $\xrightarrow[4000 \text{ atm.}]{200^\circ}$ Detonation	88
<u>trans-N<sub>2</sub>F<sub>2</sub></u> $\xrightarrow[3400 \text{ atm.}]{82^\circ}$ No rxn.	88
N <sub>2</sub> F <sub>2</sub> + N <sub>2</sub> F <sub>4</sub> $\xrightarrow[6200 \text{ atm.}]{93-100^\circ}$ NF <sub>3</sub>	88

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TABLE IX (Continued)

Reactions and Results	Reference
$\text{cis- or trans-N}_2\text{F}_2 + \text{HClO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow[4 \text{ hr. (NF}_3\text{)}]{82^\circ, 6100 \text{ atm.}} \text{dec. of N}_2\text{F}_2$	68
$\text{N}_2\text{F}_2 + \text{Mg}(\text{ClO}_4)_2 \xrightarrow[\text{NF}_3]{10 - 52 \times 10^3 \text{ psig}} \text{unident. rxn.; no N}_2\text{FClO}_4$	89
$\text{cis-N}_2\text{F}_2 + \text{NO/NF}_3 \xrightarrow[1 \text{ hr.}]{66^\circ, 8 \times 10^4 \text{ psig}} 25\% \text{ dec. of NF}_3$	89
$\begin{array}{l} \text{cis-N}_2\text{F}_2 + \text{H}_2\text{O} \xrightarrow{74^\circ} \\ \text{trans-N}_2\text{F}_2 + \text{H}_2\text{O} \xrightarrow{89^\circ} \end{array} \begin{array}{l} \text{1st} \\ \text{order} \\ \text{rate} \end{array} \rightarrow \text{N}_2 + 1/2 \text{ O}_2 + 2 \text{ HF}$	227
(Note: no effect by OH <sup>-</sup> or surface on <u>cis</u> ; no N-O-F intermed. obsd.)	
$\text{N}_2\text{F}_2 + \text{CO} \xrightarrow[\text{slow}]{\text{u.v. NR } 100^\circ} \text{CF}_2\text{O}$	259
$\text{t-N}_2\text{F}_2 + \text{ClO}_2\text{F} \xrightarrow{-78 \text{ to } 25^\circ} \text{No rxn.} \xrightarrow{200^\circ} \text{ClF}_3 + \text{NF}_3 + \text{N}_2 + \text{O}_2$	340
$\text{t-N}_2\text{F}_2 + \text{ClO}_3\text{F} \xrightarrow{-78 \text{ to } 25^\circ} \sim \text{No rxn.} \xrightarrow{> 150^\circ} \text{dec. of N}_2\text{F}_2$	<div style="border-left: 1px solid black; border-right: 1px solid black; padding: 0 5px;">                     340 341                 </div>
$\text{t-N}_2\text{F}_2 + \text{ClF}_5 \xrightarrow{-78 \text{ to } 25^\circ} \text{No rxn. (sl. dec. of N}_2\text{F}_2)$	340
$\xrightarrow{> 150^\circ}$	341
dec. of N <sub>2</sub> F <sub>2</sub>	
$\text{t-N}_2\text{F}_2 + \text{OF}_2 \xrightarrow{-78 \text{ to } 150^\circ} \text{some dec. of both}$	342
$\text{t-N}_2\text{F}_2 + \text{ClF} \xrightarrow{-78 \text{ to } 150^\circ} \text{some dec.} \xrightarrow{150^\circ} \text{ClF}_3 + \text{N}_2$	342
$\text{t-N}_2\text{F}_2 + \text{ClF}_3 \xrightarrow{-78 \text{ to } 150^\circ} \text{some dec.} \xrightarrow{150^\circ} \text{ClF}_5 + \text{N}_2$	342
$\text{N}_2\text{F}_2 + \text{I}_2 \xrightarrow{h\nu} \text{IF}_5 \text{ (trans reacts faster than cis)}$	386
$\text{t-N}_2\text{F}_2 \xrightarrow[\text{low temp.}]{\text{electron radiation}} \text{N}_2 + \text{NF}_3 + \text{N}_2\text{F}_2$	471
$\text{N}_2\text{F}_2 + \text{NF}_3 \xrightarrow[\text{low temp.}]{\text{electron radiation}} \text{N}_2 + \text{N}_2\text{F}_4 + \text{F}_2$	471

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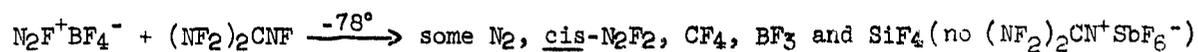
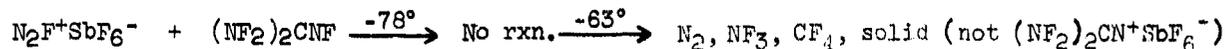
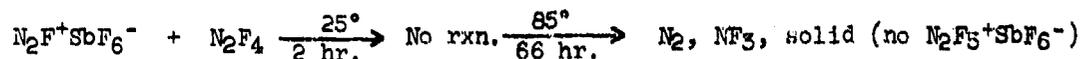
TABLE IX (Concluded)

<u>Reactions and Results</u>	<u>Reference</u>
$\text{N}_2\text{F}_2 \xrightarrow{\text{r.f. disch.}} \xrightarrow[\text{O}_2 \text{ Matrix}]{4^\circ\text{K quench}} \text{N}_2 + \text{F}\cdot$ (no $\text{N}_2\text{F}\cdot$ obs.)	532a
$\text{cis-N}_2\text{F}_2 + \text{OF}_2 \xrightarrow[-78^\circ]{\text{elec. disch.}} \text{N}_2, \text{F}_2, \text{O}_2$	532a
$\text{N}_2\text{F}_2 + \text{O}_2 \xrightarrow[-196^\circ]{\text{elec. disch.}} \text{some O}_3, \text{NO}_2, \text{SiF}_4$	532a

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Efforts to utilize the  $N_2F^+$  salts as reactants have not lead to the desired products.

The following results were obtained at Aerojet (17)



In studies at Reaction Motors (355) the mixing of solid  $N_2FAsF_6$  and  $CsClF_4$  at  $-78^\circ$  in a glass apparatus gave ambiguous results.

No reaction was observed between solid  $N_2FAsF_6$  and 500 mm. pressure  $OF_2$  at  $25^\circ$  to  $112^\circ$ , or at  $25^\circ$  in HF solution (532a). No products of interest were obtained from  $N_2FAsF_6$  and  $KNO_3$ ,  $AgNO_3$  or  $AgNO_2$ .

## VI-F. Tetrafluorohydrazine

Structural studies on  $N_2F_4$  have recently been reported by Hersh (L29) and by Bohn and Bauer (L6), the latter study also included the  $NF_2$  radical. The  $^{19}F$  NMR spectrum has been obtained at low temperatures by Colburn et al. (L12a) and shows the presence of rotational isomers.

Studies of the reaction chemistry of  $N_2F_4$  have continued since the previous review. An increased emphasis has been placed on reactions with inorganics since the reactions with organics had already been extensively explored. A large number of experimental studies with  $N_2F_4$  are summarized in Table X. Much of the chemistry of the C-N-F compounds is now appearing in the published literature.

Several studies have been concerned with the compatibility and properties of  $N_2F_4$  with other liquid oxidizers. Thus in a program at Aerojet (44), studies were made of the densities, vapor pressures and stabilities (thermal, adiabatic compression, flow conditions, and storage) for  $N_2F_4$  with  $C(NF_2)_4$ ,  $CF(NF_2)_3$ ,  $HNF_2$  and  $ClF_5$ . The  $N_2F_4 - ClF_5$  system was studied at Reaction Motors for thermal stability, pressurization and shock sensitivity (360-363). Homogeneous mixtures from the components  $N_2F_4$ ,  $NF_3O$ ,  $C(NO_2)_4$ ,  $CF(NF_2)_3$ ,  $ClO_3F$ ,  $ClF_3$ ,  $ClF_5$  were studied at Rocketdyne (387) and theoretical calculations made (393) for the ternary system  $N_2F_4 - C(NF_2)_4 - ClF_5$ .

TABLE X  
REACTIONS OF  $N_2F_4$

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$Hg(NFCOOR)_2$	25°, 4 days	No rxn.	18
$N_2F^+SbF_6^-$	85°, 66 hr.	$NF_3$ , $N_2$	17
$CF_2O/CsF$	135°	No rxn.	76
$CF_2O/CsF$	170°	$NF_3$ , $C_2F_6$ and unident. mat. abs. at 6.2 and 10.5 $\mu$ (no $-ONF_2$ )	76
$(CF_3O)_2O$	70°, 16 hr.	$CF_3ONF_2$ (30%), $(CF_3O)_2$ , $CF_2O$ , $NF_3$ , $NO_2$	79
$N_2F_2$	100°, 6200 atm.	$NF_3$	88
$F_2$	Kinetics study		136 and 98
$N_2O_4/CsF$	-78°	Solid containing N & F, but no N-F (solid fluorinates $SO_2$ )	121
$Cl_2O$	-78°, 3 days, Kel-F	$Cl_2$ and white solid (gives HOF and $NO_2F$ with $\Delta$ ; also $Cl_2$ with $F_2$ ) (no $ClONF_2$ formed)	123
$Cl_2O/CsF$		$Cl_2$ and white solid; x-ray suggests $CsNO_3-CsF$	123
$BF_3$	18°	v.p. lowering indicates complex	232
$PF_3$	20°	v.p. lowering indicates complex	232
$AsF_5$	-78° to 25°	$N_2F_3AsF_6$	162

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TABLE X (Continued)

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
SbF <sub>6</sub>		N <sub>2</sub> F <sub>3</sub> SbF <sub>6</sub>	152
C <sub>6</sub> H <sub>5</sub> Br	25 or 100°, 8 hr., Hg, Cl	C <sub>6</sub> F <sub>6</sub> , C <sub>6</sub> F <sub>5</sub> H	236
C <sub>6</sub> H <sub>5</sub> X	200°, Cu	C <sub>6</sub> F <sub>6</sub> , (C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	236
H <sub>2</sub> O	60°	NO, HF	227
H <sub>2</sub> O	133°	N <sub>2</sub> , NO <sub>3</sub> <sup>-</sup> , HF	227
AlCl <sub>3</sub>	-78°	trans-N <sub>2</sub> F <sub>2</sub>	227
Fe <sup>+3</sup> (aq.)	H <sub>2</sub> SO <sub>4</sub>	HNF <sub>2</sub> , Fe <sup>+2</sup>	227
Cl <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	ClNF <sub>2</sub>	227
CH <sub>3</sub> CN	As solvent	Good	227
SCL <sub>2</sub> O, PCl <sub>3</sub> O	As solvent	React very slowly at 60°	227
(CH <sub>3</sub> ) <sub>2</sub> SO	As solvent	Reacts slowly at 25°	227
CH <sub>3</sub> COOH(ϑlac.)	As solvent	Stable several days at 25°	227
H <sub>2</sub> SO <sub>4</sub>	As solvent	Reacted slowly	227
HgO	25°, 30 min.	No rxn.	257a
HgO	96°, 1 hr.	NF <sub>3</sub> , NO, no (NF <sub>2</sub> ) <sub>2</sub> O	257a
HgO	u.v., 8 hr.	NF <sub>3</sub> , NO, no (NF <sub>2</sub> ) <sub>2</sub> O	257a
CF <sub>3</sub> OF	u.v., 8 hr.	CF <sub>3</sub> ONF <sub>2</sub>	257a

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TABLE X (Continued)

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
CO	u.v.	15% NF <sub>2</sub> CFO	259
C <sub>3</sub> O <sub>2</sub>	25°	Unident. prods. with IR suggestive of NF <sub>2</sub> O-C cpd. and a CFO cpd.	302
C <sub>3</sub> O <sub>2</sub>	120°	Dec. of C <sub>3</sub> O <sub>2</sub> to polymer	302
O <sub>3</sub>	-196° and warmed	Exploded to NO <sub>2</sub> , etc.	330
O· or O <sub>2</sub>	400°	No prods. of interest	330
KO <sub>2</sub>	25 to 40°	NF <sub>3</sub> , NO <sub>2</sub> F	330
OF <sub>2</sub>	Low temp., fast	NF <sub>3</sub> , NOF, some NO <sub>2</sub> F	336
ClF	250°	NF <sub>3</sub> and Cl <sub>2</sub>	341
ClF <sub>3</sub>	250°	NF <sub>3</sub> , ClF	341
ClF <sub>5</sub>	250°	NF <sub>3</sub> , ClF <sub>3</sub>	341
ClO <sub>2</sub>	25°	NOCl and ClO <sub>2</sub>	341
HClO <sub>4</sub>	HF	No rxn.	354
AgClO <sub>4</sub>	HF	t-N <sub>2</sub> F <sub>2</sub> , NF <sub>3</sub> , N <sub>2</sub> O (from H <sub>2</sub> O)	354
XeF <sub>6</sub>	HF	Inconcl.	355
(-CO <sub>2</sub> F) <sub>2</sub>	hν	NF <sub>2</sub> -CFO	298
(-CO <sub>2</sub> F) <sub>2</sub>	BF <sub>3</sub> cat.	FCO-CNF <sub>2</sub>	385
CF <sub>2</sub> (OF) <sub>2</sub>		No CF <sub>2</sub> (ONF <sub>2</sub> ) <sub>2</sub>	402 and 405

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TABLE X (Concluded)

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
ClF <sub>3</sub> O	-80 to +60°	No rxn.	421
Cl <sub>2</sub> O + MF·HNF <sub>2</sub>	-112°	NOF, ClNF <sub>2</sub> , Cl <sub>2</sub> (plus ClO <sub>2</sub> , ClONO <sub>2</sub> with excess Cl <sub>2</sub> O), no (NF <sub>2</sub> ) <sub>2</sub> O	421
CF <sub>2</sub> (OF) <sub>2</sub> + SF <sub>4</sub>		Small amts. SF <sub>5</sub> OCF <sub>2</sub> OSF <sub>4</sub> NF <sub>2</sub>	405
CF <sub>3</sub> COONO <sub>2</sub>		CF <sub>3</sub> CFO, NOF	405
(-OCF <sub>2</sub> OF) <sub>2</sub>		No rxn.	405
(-OCF <sub>2</sub> OF) <sub>2</sub>	Hg	Irreprod. amts. C <sub>2</sub> F <sub>5</sub> ONF <sub>2</sub> , CF <sub>3</sub> ONF <sub>2</sub>	405
K <sub>2</sub> C <sub>2</sub> O <sub>6</sub>		CO <sub>2</sub> , NOF	405
CF <sub>3</sub> COONa		CF <sub>3</sub> -N(O)=NF	405
NF <sub>3</sub>	-196°, electron radiation	Inconclusive, Si contamination	472
SF <sub>2</sub> O <sub>2</sub>	20-75°, 2.5 atm., 8 hr.	No N <sub>2</sub> F <sub>2</sub> SF <sub>3</sub> O <sub>2</sub>	471
OF <sub>2</sub>	5 Å mol. sieve, -78° or 27°	Abs. of reactants, no NF <sub>2</sub> OF	532d
NO	hv, low temperature	No (NF <sub>2</sub> ) <sub>2</sub> NO, (NF <sub>2</sub> ) <sub>2</sub> NONO or (NF <sub>2</sub> ) <sub>2</sub> NONF <sub>2</sub>	532d
(CF <sub>3</sub> ) <sub>2</sub> NO		(CF <sub>3</sub> ) <sub>2</sub> NONF <sub>2</sub>	532d
OF <sub>2</sub>	Elec. disch., -78°	NF <sub>3</sub> , NO <sub>2</sub> , SiF <sub>4</sub> , no NF <sub>2</sub> OF	532a

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### VI-G. $N_2F_3^+$ Salts

The formation, properties and reactions of a product discovered at Rohm and Haas in 1961 and reported in 1965 (L49a) as  $NF_2SbF_5$  was previously reviewed (284a).

This material was obtained from the reaction of  $N_2F_4$  and  $SbF_5$  appeared to retain the N-N bond. Studies at Reaction Motors beginning in late 1964 of the  $N_2F_4$ - $AsF_5$  system indicated (351) the formation of one or more adducts at  $-80^\circ$ . Further studies (352, 354, 355) led to the identification of the stable 1:1 adduct as  $N_2F_3^+AsF_6^-$  according to the publication by Young and Moy (162). The reaction product at  $-80^\circ$  approached the composition  $N_2F_3As_2F_{11}$ , but the excess  $AsF_5$  was evolved on pumping at room temperature. Other studies (405) have also indicated a complex  $(N_2F_4)_3(AsF_5)_2$  at  $-80^\circ$ , according to the NMR of the solid. The earlier studies on the  $SbF_5$  system have been extended and published by Ruff (152). The  $^{19}F$  NMR data are consistent with the presence of the  $N_2F_3^+$  ion in both products: NMR resonances at  $-180$ ,  $-146$  and  $-122 \delta$  for  $N_2F_3AsF_6$  in HF solution; NMR resonances at  $-189.9$ ,  $-154.0$  and  $-128.8 \delta$  for  $N_2F_3Sb_2F_{11}$  in  $SO_2$  at  $-70^\circ$  with the characteristic appearance of an ABX group. The latter salt in HF solution gave resonances at  $-180$ ,  $-154$  and  $-129 \delta$  (476). The infrared spectra of the two materials also indicated the same cation and nine strong bands, corresponding to the expected nine fundamentals of the  $F_2N=NF^+$  ion, plus normally shaped anion bands have been observed for the  $AsF_6^-$  salt (276a). On the other hand, a tentative conclusion that  $N_2F_4 \cdot 2SbF_5$  was not ionic was reached, based on NMR studies (477).

The  $N_2F_3AsF_6$  is soluble without decomposition in  $BrF_5$  at  $-60^\circ$  and  $IF_5$  at  $25^\circ$ , but is insoluble in  $SF_4$ ,  $CF_3OF$ , or  $(CF_3)_2CO$  (357) and attacks  $CFCl_3$ ,  $C_2F_3Cl_3$ ,  $CCl_4$  and ignites organics (284b).

A number of attempted reactions of  $N_2F_3^+$  salts are summarized in Table XI.

### VI-H. Difluoramine

The structure of difluoramine has been determined recently by microwave (137) and electron diffraction (129) methods. The microwave study led to a dipole moment of  $1.93 \pm 0.02D$ , which was confirmed by the value  $2.01D$  in other studies (236). The infrared spectra of  $HNF_2$  and  $DNF_2$  (114) have been reported. The heat of formation of  $HNF_2$  was redetermined as  $-9$  kcal/mole (359a). The study of hydrogen exchange between  $HNF_2$  and  $D_2O$  or  $CF_3COOD$  was initially interpreted as showing evidence for the  $NF_2H_2^+$  ion, but cryoscopic studies of  $HNF_2-H_2SO_4$  did not give the same conclusion (184). An NMR study of the exchange between  $HNF_2$  and  $CF_3COOD$  showed second order behavior over a narrow range of stoichiometry (i.e., ratios of 0.5 to 2.0), but at higher  $HNF_2/CD_3COOD$  ratios the rate increased and no simple relationship was observed.

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TABLE XI

REACTIONS OF  $N_2F_3^+$  SALTS

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$N_2F_3AsF_6 + F^-$	$IF_5$	$t-N_2F_2, NF_3$	352
$N_2F_3AsF_6 + H_2O$		$N_2, NO, NF_3, N_2F_2$	355
$N_2F_3AsF_6 + NaIF_6$		28% $NF_3$ , 4% $t-N_2F_2$	355
$N_2F_3AsF_6 + KClO_4$	Ground solid mix., 25°	No rxn. in 10-15 min.	355
$N_2F_3AsF_6 + KSO_3F$	Ground solid mix., 25°	Complete loss of N-F	355
$N_2F_3AsF_6 + AgClO_4$	HF	No rxn. ( $AgClO_4$ too insol.)	355
$N_2F_3AsF_6 + KClO_4$	-80°, HF	Immed. rxn., $Cl_2$ , $N_2F_4$ , N-O cpds.	355
$N_2F_3AsF_6 + KClO_4$	-50°, $SO_2$	$NOAsF_6$ , attack on solvent	356
$N_2F_3AsF_6 + NH_4ClO_4$	-50°, $SO_2$	$NOAsF_6$ , attack on solvent	356
$N_2F_3AsF_6 + (CH_3)_4NClO_4$	-50°, $SO_2$	$NOAsF_6$ , attack on solvent	356
$N_2F_3AsF_6 + HSO_3F$	-50°, $SO_2$	Fast rxn.	356
$N_2F_3AsF_6 + NH_4ClO_4$	Solid	Compatible	356
$N_2F_3AsF_6 + (CH_3)NClO_4$	Solid	Compatible	356
$N_2F_3AsF_6 + BrF_5$	-60°	Sol. without dec.	357
$N_2F_3AsF_6 + IF_5$	25°	Sol. without dec.	357
$N_2F_3AsF_6 + KClO_4$	$IF_5$	Slow dec. to $ClO_3F$ , $NF_3, t-N_2F_2$	357

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TABLE XI (Concluded)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$N_2F_3AsF_6 + CsClO_4$	$IF_5$	very slow dec.	357
$N_2F_3Sb_2F_{11} + CsClO_4$	$90^\circ$	$ClO_3FNF_3$ , vigorous rxn.	357
$N_2F_3Sb_2F_{11} + CsClO_4$	Grinding, $25^\circ$	One sample deflagrated	357
$N_2F_4 (g) + CsClO_4 (s)$	$SbF_5$ suspension	White solid, dec. at $80^\circ$ to $ClO_3F, NF_3$	357
$N_2F_3AsF_6 + \phi_3CNF_2$	$SbF_5$ suspension	Deflagrated	357
$N_2F_3AsF_6 + \phi_3CNF_2$	$-70^\circ, SO_2$	Immed. rxn. to $N_2F_4, N_2F_2?, \phi_3NAsF_6$	357
$N_2F_3AsF_6 + F_2$	$115-120^\circ$	$NF_3, AsF_5$ , traces $NF_4AsF_6$	276a

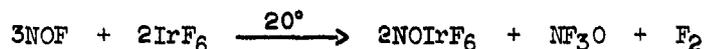
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The most important reaction of  $\text{HNf}_2$  to be discovered recently is that (in the form of its  $\text{KF}$  complex) with fluoroxy compounds such as  $\text{CF}_2(\text{OF})_2$  to give the very stable difluoroaminoxy analogues, e.g.,  $\text{CF}_2(\text{ONf}_2)_2$ . These studies have been pursued at Rocketdyne (385, 386, 402). The  $\text{CF}_2(\text{ONf}_2)_2$  for example is a stable liquid boiling at  $-9^\circ$  which is not shock sensitive and which is stable in concentrate  $\text{H}_2\text{SO}_4$  at  $25^\circ$  for 40 hr. A number of other reactions of  $\text{HNf}_2$  are summarized in Table XII. Publications are appearing in the literature on the reactions of  $\text{HNf}_2$  with organic compounds. Results of studies of the hydrolysis (L15), electrochemical reduction (L60), and reaction with anions of  $\text{MNF}_2$  (L61) have been published.

Studies of the miscibility, density and stability under storage and flow conditions for mixtures of  $\text{MNF}_2$  and  $\text{N}_2\text{F}_2$  were made at Aerojet (44).

### VI-I. Trifluoramine Oxide

The independent discovery of  $\text{NF}_3\text{O}$  by Bartlett and co-workers has led to the declassification of much of its chemistry. Bartlett and co-workers first detected  $\text{NF}_3\text{O}$  (which they named nitrogen oxide trifluoride) as a trace by-product of the fluorination of  $\text{NOF}$  with  $\text{PtF}_6$  (to give  $\text{NOPtF}_6$  and  $\text{F}_2$ ) (L185) or with  $\text{OsF}_6$  to give  $\text{NOOsF}_6$  and  $\text{NOOsF}_7$  (L1a). Iridium hexafluoride on the other hand gave (L1a, L2) a stoichiometric amount of  $\text{NF}_3\text{O}$  of high purity according to the equation



the pyrolysis of  $(\text{NO})_2\text{NiF}_6$  at  $350^\circ$  also gave  $\text{NF}_3\text{O}$  together with an approximately equal amount of  $\text{NOF}$  (L2). The synthesis and properties of  $\text{NF}_3\text{O}$  have been summarized in a note published by scientists at Allied Chemical (L25) and Rocketdyne scientists have published (L17) a paper on the infrared spectrum, structure and thermodynamic properties of  $\text{NF}_3\text{O}$ . The thermal decomposition  $\text{NF}_3\text{O}$  has been reported to begin at about  $235^\circ$  (76), while other reports state that it is stable in nickel or Monel at  $300^\circ$  and attacks glass or quartz only slowly at  $400^\circ$ .

The results of a number of other studies on  $\text{NF}_3\text{O}$  are summarized in Table XIII.

Vapor pressures were measured in the range  $10 - 70^\circ$  for a 1:1 mixture of  $\text{NF}_3\text{O}$  and  $\text{C}(\text{NF}_2)_4$  and the stability over a 41-day period at the higher temperature was established at Aerojet (44). Properties of homogeneous oxidizer mixtures of  $\text{NF}_3\text{O}$  with other components were studied at Rocketdyne (427, 395, 400).

### VI-J. Complexes of $\text{NF}_3\text{O}$ and the $\text{NF}_2\text{O}^+$ Salts

In the previous review (284a) the reactions of  $\text{NF}_3\text{O}$  to give complexes with weaker Lewis acids and ionic  $\text{NF}_2\text{O}^+$  salts with very strong Lewis acids were described.

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TABLE XII  
 REACTIONS OF  $\text{HNF}_2$  AND  $\text{HNF}_2 \cdot \text{MF}$  COMPLEXES

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$\text{Cl}_2\text{NF}$	$-78^\circ$ , $25^\circ$ , $65^\circ$ or u.v.	No products of interest	18
$\text{OF}_2 + \text{HNF}_2 \cdot \text{CsF}$	$-125^\circ$ to $25^\circ$	$\text{N}_2\text{F}_4$ , $\text{NF}_3$ , $\text{NO}_2$ , $\text{NOF}$	78
$\text{OF}_2 + \text{CsF}$ , $\text{KF} \cdot \text{HNF}_2$	$-125^\circ$ to $25^\circ$ $\text{CFCl}_3$	Some expl. on warming	79
$\text{C}_6\text{F}_5\text{I}/\text{Hg}$	$25^\circ$ , 16 hr.; $100^\circ$ , 8 hr.	No rxn. to $\text{C}_6\text{F}_5\text{NF}_2$	236
$\text{C}_6\text{F}_4\text{ISO}_3\text{OH}$	Hg	No rxn.	236
$\text{AlCl}_3$	$-78^\circ$	$\text{ClNF}_2$ , $\text{t-N}_2\text{F}_2$ , $\text{N}_2$ , $\text{Cl}_2$ , $\text{HCl}$	227
$\text{HCl}$	$-138^\circ$ to $-112^\circ$	No interaction	264
$\text{SO}_3$	$0^\circ$	$\text{HOSO}_2\text{NF}_2$ (dec. $25^\circ$ )	264
$\text{Al}(\text{CH}_3)_3$	Mixed rapidly	Exploded	264
$\text{Al}(\text{CH}_3)_3$	$-80^\circ$ , mixed slowly	$\text{NF}_2\text{Al}(\text{CH}_3)_2$ ?, $\text{CH}_4$	264
$\text{Al}(\text{CH}_3)_3$	$25^\circ$ , iso $-\text{C}_5\text{H}_{12}$ , 2 days	$(\text{NF}_2)_2\text{AlCH}_3$ ?, $\text{CH}_4$	264
$\text{Al}(\text{CH}_3)_3$	$-126^\circ$	$(\text{NF}_2)_2\text{AlCH}_3$ ?	264
$\text{Ga}(\text{CH}_3)_3$	$-80^\circ$ to $25^\circ$	Colorless liq., $\text{CH}_4$	264
$\text{CF}_3\text{COOH}$	$-63^\circ$ or $-45^\circ$	Sl. sol.; ideal soln.	264
$(\text{CF}_3\text{CO})_2\text{O}$	$-45^\circ$	Miscible	264
$\text{Al}(\text{CH}_3)_3$	$< -80^\circ$ , 30 min.	$\text{HNF}_2 \cdot \text{Al}(\text{CH}_3)_3$ ? converts to $\text{NF}_2\text{Al}(\text{CH}_3)_2$ ? + $\text{CH}_4$ above $-30^\circ$	266
$\text{B}_2\text{F}_4$	$-78^\circ$ , $-63^\circ$ , $-45^\circ$	$\text{B}_2\text{F}_4 \cdot \text{HNF}_2$ ? some explosions	266

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TABLE XII (Concluded)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$\text{CH}_2(\text{OF}_2) + \text{HNF}_2 \cdot \text{KF}$	$-80^\circ$	$\text{CF}_2(\text{ONF}_2)_2$ , $\text{FOCF}_2\text{ONF}_2$ , $\text{NF}_3$ , $\text{N}_2\text{F}_4$ , $\text{CF}_2\text{O}$	789
$\text{CH}_2(\text{OF}_2) + \text{HNF}_2 \cdot \text{CsF}$		Only trace yields $\text{CF}_2(\text{ONF}_2)_2$	402
$\text{ClF}$		$\text{ClNF}_2$ , HF	420a
$\text{ClF}_3$		Fast rxn. to $\text{ClNF}_2$ , HF	420a
$\text{ClF}_3 + \text{HNF}_2 \cdot \text{BF}_3$	$-80^\circ$	Slow rxn. to $\text{ClNF}_2$ , HF	420a
$\text{RbClF}_4$	$-80^\circ$	Slow rxn. to $\text{ClNF}_2$ , $\text{N}_2\text{F}_4$	420a
$\text{KClF}_4$	$-80^\circ$	One explosion	420a
$\text{ClF}_5$	$-80^\circ$	$\text{ClNF}_2$ , $\text{N}_2\text{F}_4$ , $\text{NF}_3$	420a
$\text{IF}_5$	$0^\circ$	$\text{I}_2$ , some N-F products	420a
$\text{NO}_2\text{OF}$		$\text{NO}_2\text{F}$ , $\text{NO}_2$ , $\text{N}_2\text{F}_4$	420a
$\text{ClO}_3\text{OF}$		$\text{NOF}$ , $\text{ClO}_3\text{F}$ , some $\text{NO}_2\text{F}$ , $\text{N}_2\text{F}_4$ , $\text{Cl}_2$	420a
$\text{cis-N}_2\text{F}_2 + \text{HNF}_2 \cdot \text{MF}$	$-80^\circ$	$\text{NF}=\text{N}-\text{NF}_2$ ? or $(\text{NF}_2-\text{N}=\text{N})_2$ ?	420a
$\text{Cl}_2\text{O} + \text{N}_2\text{F}_4 + \text{HNF}_2 \cdot \text{MF}$	$-112^\circ$	$\text{NOF}$ , $\text{ClNF}_2$ , $\text{Cl}_2$ (some $\text{ClNO}_3$ and $\text{Cl}_2\text{O}$ with excess $\text{Cl}_2\text{O}$ )	421

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TABLE XIII

REACTIONS OF  $\text{NF}_3\text{O}$

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$\text{PF}_3\text{Cl}_2$	-78°, 8 hr.	No rxn. to $\text{NF}_2\text{O}(\text{PF}_4)\text{Cl}_2$	75
$\text{PF}_3\text{Cl}_2$	-20°	$\text{NOCl}$ , $\text{NO}_2\text{Cl}$ , $\text{PF}_3\text{O}$ , $\text{Cl}_2$ , $\text{NO}(\text{PF}_6)$	75
$\text{LiClO}_4$ or $\text{Mg}(\text{ClO}_4)_2$		$\text{NO}_2\text{F}$ , $\text{NOF}$ , $\text{NOCl}$ , $\text{NO}_2$ , $\text{ClO}_3\text{F}$	75
$\text{NaBH}_4$	$\text{BCl}_3$ , $\text{HF}$ , $\text{AsF}_3$ or $\text{BrF}_3$	$\text{B}_2\text{H}_6$ , $\text{H}_2$ , (no $\text{NF}_2\text{OBH}_4$ )	75
$\text{CF}_3\text{OF}$	u.v., 36 hr. fract. thru -110° trap	Unident. mat. with IR abs. at 5.0-5.5 $\mu$ , 7.5-8.0 $\mu$ , 8.6 $\mu$ , 11.0-11.5 $\mu$ , 12.2-12.7 $\mu$	76
$\text{CF}_3\text{OF}$	u.v., 255°, circ. system	Same unident. cpd. trapped at -110°	76
$\text{CF}_3\text{OF}$	u.v.	Inconclusive, numerous C-O-N-F fragments	77
$\text{ClO}_3\text{F}$	u.v.	$\text{NO}_2\text{F}$ , $\text{NO}_2$ , $\text{ClO}_2\text{F}$ , $\text{ClO}_2$	77
$\text{ClO}_2\text{F}$	u.v.	Similar to $\text{ClO}_3\text{F}$ results	77
$\text{PF}_3$	100 mm.	$\text{NO}(\text{PF}_6)$	78
$\text{TlF}_4$	$\text{HF}$ or $\text{BrF}_5$	No rxn.	78
$\text{PtF}_6$	25°	$\text{NF}_2\text{O}^+$ salt?	79
$\text{N}_2\text{O}_4/\text{CsF}$	0°, $\text{HF}$	$\text{CsNO}_3$	121
$(\text{NO}_2)_3\text{Al}(\text{ClO}_4)_6$	-78°	No rxn.	121
$\text{NO}_2\text{Al}(\text{ClO}_4)_4$	-50°, $\text{SO}_2$	$\text{ClO}_3\text{F}$ , $\text{SiF}_4$	121
$\text{Li}_3\text{Al}(\text{ClO}_4)_6$			

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TABLE XIII (Concluded)

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
NO	25°, glass	NO <sub>2</sub> , NOF, SiF <sub>4</sub> ?	122
NO	Low temperature	v.p. & IR suggest complex	121
NO/C <sub>2</sub> F <sub>4</sub>	-78° or 25°	No rxn.	121
NO/N <sub>2</sub> F <sub>4</sub>	-79	No NF <sub>2</sub> NO formed; complex assumed	121
NO/CsCl	-78°, 16 hr.	No CsF or ClNF <sub>2</sub> O	121
NaN <sub>2</sub> O	-78 to 25°	No rxn.	121
IF <sub>5</sub>	-78° or 25°	No NF <sub>2</sub> OIF <sub>6</sub>	301
HF		No NF <sub>2</sub> OHF <sub>2</sub>	301
SF <sub>4</sub>		No NF <sub>2</sub> OSF <sub>5</sub>	301
SF <sub>2</sub> O	-20°, 4 days	Small amts., 3NF <sub>3</sub> O·2SF <sub>2</sub> O	301
CF <sub>3</sub> C(BF <sub>2</sub> )=CF <sub>2</sub>		CF <sub>3</sub> C(O)CF <sub>2</sub> NF <sub>2</sub>	386
CF <sub>3</sub> C≡CF	BF <sub>3</sub> or PF <sub>5</sub> cat.	No CF <sub>3</sub> C(NF <sub>2</sub> O)=CF <sub>2</sub>	386
CH <sub>3</sub> CH=C(CH <sub>3</sub> )CH <sub>3</sub>	BF <sub>3</sub> or PF <sub>5</sub> cat.	Explosion	386
PF <sub>2</sub> (CF <sub>3</sub> ) <sub>3</sub>		1:1 complex	386
BF <sub>2</sub> Cl	-142° to -80°	2NF <sub>3</sub> O·BF <sub>2</sub> Cl, NF <sub>3</sub> O, BF <sub>3</sub> , Cl <sub>2</sub> , NOFB <sub>4</sub>	420a
r.f. disch.	O <sub>2</sub> /Ar matrix	NO <sub>2</sub> F, NOF, NO <sub>3</sub> F, O <sub>2</sub> F <sub>2</sub> , O <sub>2</sub> F·	532a
r.f. disch.	Ar matrix	v.l. NO <sub>2</sub> F, NOF, NO <sub>3</sub> F	532a
O <sub>2</sub>	elec. disch., -196°	O <sub>3</sub> , SiF <sub>4</sub> , no NF <sub>2</sub> OOF	532a
F <sub>2</sub>	v, -196°	No new products	
Cl <sub>2</sub>	-78° to 25°	No rxn.	122
4-(τ-C <sub>4</sub> H <sub>9</sub> )C <sub>6</sub> H <sub>4</sub> SH		No HNF <sub>2</sub> O	122

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Further studies of the  $\text{NF}_3\text{O}-\text{BF}_3$  system at Rocketdyne concluded (386) that the product can be either "ionic" or "covalent" depending on the preparatory route, but the  $\text{NF}_3\text{O}-\text{AsF}_5$  product was estimated from electronegativity considerations and Hammel calculations to be at least 20% ionic. Studies of these materials have continued, but useful  $\text{NF}_2\text{O}^+$  salts have not been attained.

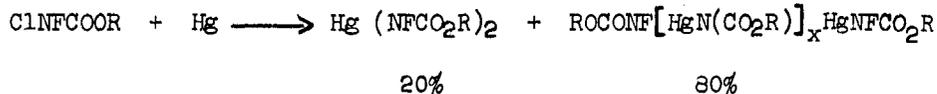
The  $^{19}\text{F}$  NMR spectrum of the  $\text{NF}_2\text{O}^+$  ion in  $\text{BrF}_5$  solution shows a chemical shift which is dependent on the anion and apparently on the concentration, but essentially not on the temperature (75). The shift to higher field is in the order  $\text{SbF}_6^- < \text{AsF}_6^- < \text{BF}_4^-$ . At  $-60^\circ$  the  $\text{SbF}_6^-$  salt appears to be two singlets, one broad and one narrow but at room temperature a triplet is observed. The  $\text{NF}_3\text{O}-\text{AsF}_5$  product also gave varying NMR shifts with different HF samples (386).

Solubility studies on  $\text{NF}_2\text{OAsF}_6$  showed (78) that it was essentially insoluble in the following solvents at the temperatures listed:  $\text{BrF}_3$ ,  $25^\circ$ ;  $(\text{CF}_3)_2\text{CO}$ ,  $25^\circ$ ;  $(\text{CF}_3\text{CO})_2\text{O}$ ,  $25^\circ$ ;  $\text{HSO}_3\text{F}$ ,  $25^\circ$ ;  $\text{PF}_3\text{O}$ ,  $0^\circ$ ;  $\text{ClO}_3\text{F}$ ,  $-10^\circ$ ;  $\text{SF}_4\text{O}$ ,  $-40^\circ$ ;  $\text{CF}_2\text{O}$ ,  $-40^\circ$ . The vapor pressure of  $\text{NF}_2\text{OAsF}_6$  was determined to be 10 - 20 mm. at room temperature.

### VI-K. Chlorodifluoramine and Dichlorofluoramine

The chemical properties of chlorodifluoramine have been summarized by Petry (146). The reaction of an aqueous  $\text{NaClO}$  with difluorourea appears to be one of the best methods for generating sizeable quantities of  $\text{ClNF}_2$  (18).

Efforts to prepare  $\text{Hg}(\text{NF}_2)_2$  from the reaction of  $\text{ClNF}_2$  and  $\text{Hg}$  at  $-40^\circ$  to  $25^\circ$  or in ethyl ether solution at  $25^\circ$  gave  $\text{N}_2\text{F}_4$  and traces of  $\text{N}_2\text{F}_2$  (17). In studies of the related compound  $\text{ClNF}_2\text{COOR}$  ( $\text{R} = \text{C}_2\text{H}_5$  or  $\text{C}_3\text{H}_7$ ) the coupling reaction below was apparently observed (15, 17).

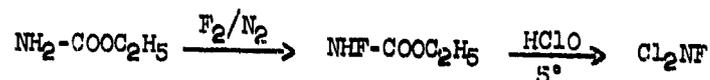


The  $\text{Hg}(\text{NFCOOR})_2$  reacted with  $\text{Cl}_2$  to give the starting material and with  $\text{I}_2$  in  $\text{CH}_2\text{Cl}_2$  to give  $\text{INFCOOR}$  (without solvent,  $\text{FCOOR}$  and  $\text{N}_2$  were formed) rather than the desired coupled compound  $(-\text{NFCOOR})_2$  which was envisioned as an intermediate to  $\text{N}_2\text{F}_2\text{Cl}_2$  or  $\text{N}_3\text{F}_5$ . Efforts to use sulfur of  $\text{S}_2\text{Cl}_2$  as the coupling agent were inconclusive and  $\text{Ca}$ ,  $\text{Zn}$  or  $\text{Ag}$  failed to give the  $\text{Hg}$  reaction.

Another related compound  $\text{C}(\text{NF}_2)_3\text{NFCl}$  (first prepared at 3M in 1964) was found (15) to lose  $\text{ClNF}_2$  even at  $-196^\circ$  in glass. An attempt to prepare  $\text{C}(\text{NF}_2)_3\text{NFCO}_3$  by the reaction of  $\text{C}(\text{NF}_2)_3\text{NCO}$  with  $\text{ClO}_3\text{F}/\text{NaF}$  was unsuccessful (15).

The research on the synthesis of dichlorofluoramine has been published (L55a). This compound has been synthesized in good yield and purity at Aerojet (15) from N-fluoroethylcarbamate:

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This method (which strangely did not work with the propyl carbamate) was an improved version of a 1961 Aerojet method not included in the previous review (see ref. 27 in bibliography of ref. 284a):



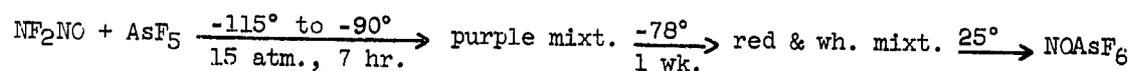
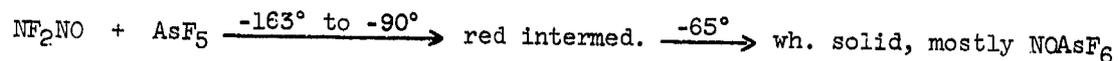
The pure  $\text{Cl}_2\text{NF}$  prepared at  $5^\circ$  was a colorless liquid, but reaction at  $-5$  to  $-10^\circ$  gave a yellowish product which contained  $\text{CO}_2$  and organic matter. The  $\text{Cl}_2\text{NF}$  decomposed in glass at  $25^\circ$ . The presence of  $\text{BF}_3$  accelerated the decomposition, but  $\text{CsF}$  appeared to stabilize it.

A number of reactions of  $\text{Cl}_2\text{NF}$  have been attempted as summarized in Table XIV. In general, the  $\text{Cl}_2\text{NF}$  appeared to act as a source of  $\text{NF}$  radicals (18). An attempt to react  $\text{C}(\text{NF}_2)_4$  with  $(\text{CH}_3)_3\text{COCl}$  gave  $\text{ClNF}_2$  rather than the desired  $\text{C}(\text{NF}_2)_3\text{NCl}_2$  (8).

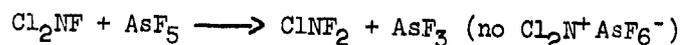
## VI-L. Miscellaneous N-O-F Compounds

A large number of reactions have been attempted on various compounds which contain nitrogen with fluorine, oxygen, or both as summarized in Table XV.

Although  $\text{N}_2\text{F}_2$ ,  $\text{N}_2\text{F}_4$  and  $\text{NF}_3\text{O}$  readily undergo the fluoride abstraction reaction with Lewis acids (e.g., to give  $\text{N}_2\text{F}^+\text{AsF}_6^-$ ) and similar reactions are readily entered into by the halogen fluorides, some of the sulfur fluorides and  $\text{O}_2\text{F}_2$ , this type reaction could not be effected with a number of other N-F or likely C-F compounds. Thus, the attempted (355) reaction with  $\text{NF}_2\text{NO}$  led to degradation:



Arsenic pentafluoride acted as a fluorinating agent toward  $\text{Cl}_2\text{NF}$  (356).



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TABLE XIV

## REACTIONS OF DICHLOROFUORAMINE

<u>Reactions and Results</u>	<u>Reference</u>
$\text{Cl}_2\text{NF} + \text{N}_2\text{F}_4 \xrightarrow{25^\circ} \text{NR} \xrightarrow[\text{metal}]{65^\circ} \text{ClNF}_2 + \text{N}_2\text{F}_2 \text{ (no } \text{N}_2\text{F}_3\text{Cl)}$	18
$\text{Cl}_2\text{NF} + \text{N}_2\text{F}_2 \xrightarrow{\text{u.v.}} \text{N}_2, \text{N}_2\text{F}_2, \text{NF}_3, \text{Cl}_2, \text{NOF}$	18
$\text{Cl}_2\text{NF} + \text{NO} \xrightarrow{-132^\circ} \text{ClNF}_2 + \text{N}_2\text{O} + \text{NOF}$	15
$\text{Cl}_2\text{NF} + \text{HNF}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{ClNF}_3\text{N}_2\text{F}_4, \text{HCl}, \text{H}_2\text{O}, \text{SiF}_4$	17
$\text{Cl}_2\text{NF} + \text{HNF}_2 \xrightarrow[\text{Pyrex}]{-78^\circ, 35 \text{ min.}} \text{NR} \xrightarrow[\text{Pyrex}]{25^\circ, 15 \text{ min.}} \text{SiF}_4, \text{N}_2\text{F}_4?$	18
$\text{Cl}_2\text{NF} + \text{HNF}_2 \xrightarrow[\text{S.S.}]{25^\circ, 2 \text{ hr.}} \text{NR} \xrightarrow{70-80^\circ, 30 \text{ min.}} \text{N}_2\text{F}_4, \text{cis-N}_2\text{F}_2, \text{trace NOCl}$	18
$\text{Cl}_2\text{NF} + \text{HNF}_2 \xrightarrow[\text{metal flow system}]{70-80^\circ, \text{quench}} \text{cis- and trans-N}_2\text{F}_2, \text{ClNF}_2, \text{NOCl} \text{ (some } \text{N}_2\text{F}_4, \text{SiF}_4, \text{NO}_2)$	18
$\text{Cl}_2\text{NF} + \text{F}_2/\text{CsF} \xrightarrow{-78^\circ} \text{ClNF}_2, \text{NF}_3, \text{N}_2\text{F}_2 \text{ (no } \text{ClF}_3\text{NF)}$	356
$\text{Cl}_2\text{NF} + \text{AsF}_5 \longrightarrow \text{ClNF}_2 + \text{AsF}_3$	356
$\text{Cl}_2\text{NF} + \text{SbF}_3 \xrightarrow{25^\circ} \text{N}_2, \text{Cl}_2$	18
$\text{Cl}_2\text{NF} + \text{BCl}_3 \xrightarrow{-78^\circ} \text{N}_2, \text{Cl}_2, \text{BF}_3$	18
$\text{Cl}_2\text{NF} + \text{BF}_3 \xrightleftharpoons[25^\circ]{-78^\circ} \text{HCl}_2^+\text{BF}_4^-?$	18
$\text{Cl}_2\text{NBF}_4 + \text{HNF}_2 \longrightarrow \text{ClNF}_2, \text{Cl}_2, \text{BF}_3, \text{HF}$	18

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TABLE XV

## MISCELLANEOUS N-O-F REACTIONS

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
NOF + CsF	25-300°, 1400-3140 psi	NO <sub>2</sub> ; (no NF <sub>2</sub> O <sup>-</sup> )	76
NO <sub>2</sub> F + CsF	3 hr. each at -78° & -45° 6 days at 25°	No rxn.	76
NO <sub>2</sub> F + F <sub>2</sub> /CsF	-78°, -45°, 25°, 150°	No rxn. in 1 hr. each	76
NOF + CsF	25°, 3 hr. or -78°, 16 hr.	No rxn.	77
NOF + CsF + F <sub>2</sub>	-78°, 2 hr. or 25°, 3 hr.	Some NO <sub>2</sub> F	77
NOF + N <sub>2</sub> F <sub>4</sub> + CsF	200°, 8000 psi, 48 hr.	NF <sub>3</sub> , NOF, NO, NF <sub>3</sub> O, solid containing Cs, F,N (+O?)	79
NO <sub>2</sub> F + CsF	-65°	No rxn.	77
NO <sub>2</sub> + CsF	25°	Some abs.; solid stable at 200°	77
Solid above + F <sub>2</sub>	200°, 250 psi, 2 hr.	NO <sub>2</sub> F	77
Excess NO <sub>2</sub> + CsF	200°, 4700 psi, 18 hr.	1 mole NO <sub>2</sub> abs/mole CsF	77
Solid above + F <sub>2</sub>	200°, 7100 psi, 4 hr.	NF <sub>3</sub> O, NO <sub>2</sub> F	77
NO <sub>2</sub> + CsF + F <sub>2</sub>	25°, 3600 psi, 5 hr.	Some NO <sub>2</sub> F, (no NF <sub>3</sub> O)	77
NO <sub>2</sub> F + CsF	-78°	Solid containing N,F	121
NO <sub>2</sub> + (CF <sub>3</sub> O) <sub>2</sub> O	70°, 16 hr.	(CF <sub>3</sub> O) <sub>2</sub> , CF <sub>2</sub> O, NO <sub>2</sub>	79
NOF + PtF	25°	F <sub>2</sub> , NF <sub>3</sub> O, NO <sup>+</sup> salt	79
NOF + IrF <sub>6</sub>	25°	NF <sub>3</sub> O	79
N <sub>2</sub> O + CsF	25-400°, 10,000 psi max.	No rxn.	76, 78
N <sub>2</sub> O + F <sub>2</sub> + CsF	200-400°, 9500 psi max., 15 hr.	Some NF <sub>3</sub> , NF <sub>3</sub> O two runs <u>exploded</u>	78
N <sub>2</sub> O + PtF <sub>6</sub>	25°	No rxn.	28

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TABLE XV (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$N_2O + IrF_6$	25°	No rxn.	79
$NO + SF_4$	25 or 125°	No rxn.	259
$NO_2 + O_2F_2$	-130°	$NO_2F$	266
$NO + OF_2$		$NO_2F$ , $NOF$	284
$NO_2 + ClF_3$	liq.	No evidence of ions	301
$Na_2N_2O_2 + F_2$	$CCl_4$	$NaF$ , no $NFO$ anion	335, 333
$NO_3^-$ , $NO_2^-$ or $N_2O_2^{2-} + F_2$ , $OF_2$ or $ClF_3$	-110° to 350° 0.5 to 1200 atm.	No $NFO$ anion	335
$CsNO_3 + F_2$	-40°, 25°	$CsF$ at 25° only	335
$NO_2 + CsF$	25, 100, 200°; 10-72 hr. each	$CsNO_3$ (no N-F)	335
$N_2O + CsF$	300°, 24 hr.; 100°, 4 hr.	No rxn.	335
$NOF + CsF$	25°, 20 atm., 72 hr. 150°, 30 atm., 12 hr. 80°, 1,200 atm., 1 wk. } }	No rxn.	335
$NO_2F + CsF$	25°, 20 atm., 72 hr. 150°, 30 atm., 12 hr. 25°, 825 atm., 1 wk. } }	No rxn.	335
$NO_2 + AsF_5$		$NO_2AsF_6$ , $NOAsF_6$ (not $NO_2 \cdot AsF_5$ as in Lit.)	354
$ClONCl_2 + Me_4NBrCl_2$		$Me_4NBr(NO_3)_2$	437
$AgNO_3 + Me_4NICl_4$		$Me_4NI(NO_3)_4$	436
$(CF_3)_2NO + F_2$		$(CF_3)_2NOF$	532d
$(CF_3)_2NO + NO_2$	25°	$(CF_3)_2NONO_2$ , $(CF_3)_2NONO$ , $(CF_3)_2NOONO?$	532d
$(CF_3)_2NO + N_2F_4$		$(CF_3)_2NONF_2$	532d

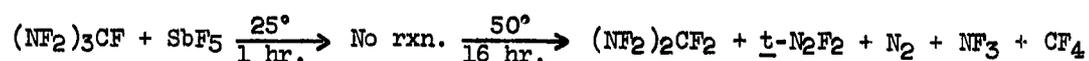
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TABLE XV (Concluded)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$\text{NO}_2\text{OF} + \text{N}_2\text{F}_4$	elec. disch., $-40^\circ$	$\text{NF}_3$ , $\text{NO}_2$ , $\text{SiF}_4$	532a
$\text{NF}_3$ or $\text{N}_2\text{F}_4 +$ $\text{H}_2$ or $\text{CS}_2$	flame	No :NF observed	537

The reaction of  $\text{Cl}_2\text{NF}$  with  $\text{BF}_3$  reversibly formed a 1:1 complex at  $-78^\circ$  which contained the  $\text{BF}_4^-$  according to infrared analysis (18). Neither  $\text{AsF}_5$  nor  $\text{BF}_3$  reacted with  $\text{CF}_3\text{OF}$  (356), but decomposition occurred with  $\text{BF}_3$  and either N,N,N'-trifluoropentoxyformamidine or 1,2-bis(difluoramino)cyclohexane.

The attempted fluoride abstraction reaction on  $(\text{NF}_2)_3\text{CF}$  to give  $(\text{NF}_2)_3\text{C}^+\text{SbF}_6^-$  led only to degradation (17):



At  $35^\circ$ , reaction was incomplete after 17 hr. but the gaseous products were the same. The unidentified solid product melted at  $75 - 80^\circ$ .

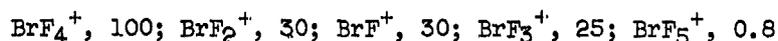
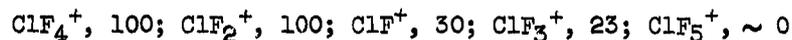
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## CHAPTER VII

### INORGANIC HALOGEN FLUORIDES AND DERIVATIVES

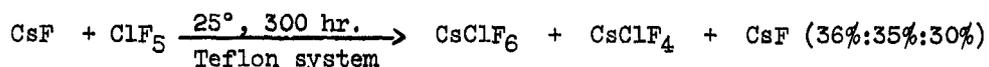
#### VII-A. Chlorine Pentafluoride

Several publications on the preparation and properties of chlorine pentafluoride have appeared in the literature since the previous review (284a). Included are publications on the fluorination of  $\text{ClF}_3$  under ultraviolet radiation (L119) and by platinum hexafluoride (L120), on the thermal equilibrium of  $\text{ClF}_3$ ,  $\text{F}_2$ ,  $\text{ClF}_5$  (L107) and a paper (L125) from the Rocketdyne Laboratories on the preparation and properties of  $\text{ClF}_5$ . Rocketdyne has issued recently a Chlorine Pentafluoride Handbook (415) as well as an Interhalogen Handbook (415a) which is primarily a compilation of engineering properties, handling characteristics and design criteria for  $\text{ClF}_5$  and  $\text{ClF}_3$ , plus selected data on other interhalogens. The electrochemical preparation of  $\text{ClF}_5$  has been studied (417) and an evaluation made for the use of this method in a large scale (0.1 - 1 million lb/yr) manufacturing process (409, 410). Chlorine pentafluoride has been made available commercially in laboratory quantities by Allied Chemical Corporation (Industrial Chemicals Division). The publication from Rocketdyne (L125) gives the  $^{19}\text{F}$  NMR chemical shifts as  $-412 \delta$  (apical fluorine) and  $-247 \delta$  (basal fluorines). These values were previously reported (284a) as  $-428$  and  $-258 \delta$ . The mass spectra of  $\text{ClF}_5$  and  $\text{BrF}_5$  have been rechecked (66b) and the following intensities observed:



A purification procedure reported (75) to give 99+% pure  $\text{ClF}_5$  consists of adding excess  $\text{BF}_3$  to trap  $\text{ClO}_2\text{F}$  (in the form,  $\text{ClO}_2\text{BF}_4$ ) at  $-111^\circ$ , followed by fractionation through traps at  $-130^\circ$  (which retains  $\text{ClF}_5$ ) and  $-196^\circ$ .

Among the most interesting reactions involving  $\text{ClF}_5$  to be reported is that from the Olin Mathieson Laboratories (275a) to give  $\text{Cs}^+\text{ClF}_6^-$ . The reaction was observed from  $25^\circ$  to  $100^\circ$  in 100 to 300 hr., in the absence of metal, with the best results as shown below:



The reaction with  $\text{RbF}$  at  $70^\circ$  was reported to give 28% yield of  $\text{ClF}_6^-$  while that with  $\text{KF}$  gave only a 6% yield. The identification was based entirely on elemental analyses of the mixtures, plus the observation that  $\text{ClF}_5$  and  $\text{ClF}_3$  were evolved and  $\text{CsF}$  remained upon pyrolysis at  $200^\circ$ . The actual existence of the  $\text{ClF}_6^-$  ion would be most interesting since it would be a pseudoheptacoordinate structure which is without

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precedence in the second row elements. The  $\text{CsF}_2^+$  ion would be isoelectronic with the known stable  $\text{XeF}_2$  molecule, and the presence of the salt  $\text{CsF}_2^+\text{ClF}_4^-$  as an alternate possibility for  $\text{Cs}^+\text{ClF}_3^-$  has been suggested (276b). Spectral data are obviously needed.

The reaction chemistry of  $\text{ClF}_5$  has been pursued vigorously, as illustrated by the results summarized in Table XVI.

Evaluations of the properties of  $\text{ClF}_5$  as an advanced propellant ingredient have included: Rocketdyne's physicochemical characterization studies (387, 388) (compatibility with metals and metalloids, properties of homogeneous liquid mixtures among the components  $\text{ClF}_5$ ,  $\text{ClF}_3$ ,  $\text{ClO}_3\text{F}$ ,  $\text{CF}(\text{NF}_2)_3$ ,  $\text{C}(\text{NO}_2)_4$ ,  $\text{NF}_3\text{O}$  and  $\text{N}_2\text{F}_4$ ); properties determination and theoretical performance calculations with  $\text{ClF}_5$  and  $\text{N}_2\text{F}_4$ ,  $\text{C}(\text{NF}_2)_4$  or  $\text{C}(\text{NO}_2)_4$  (392 - 394); and engineering properties studies of  $\text{ClF}_5$ ,  $\text{ClF}_3$ ,  $\text{N}_2\text{O}_4$  and various fuels (396, 397). Aerojet General has also studied the physical properties, stability and storability of  $\text{ClF}_5$ - $\text{N}_2\text{F}_4$  liquid mixtures and the gelling of  $\text{ClF}_5$  with ~ 10 wt.%  $\text{Ba}(\text{SbF}_6)_2$  (44), the passivation with  $\text{ClF}_5$  and its behavior with selected fuels (51 - 53), including test firings with mixed hydrazines (56, 32) and the heat transfer characteristics of  $\text{ClF}_5$  (44a). Reaction Motors has studied the viscosity, heat capacity and thermal stability of  $\text{ClF}_5$  (359), properties of mixtures of  $\text{ClF}_5$  with  $\text{N}_2\text{F}_4$  (360 - 363), properties of dispersions of  $\text{B}_4\text{C}$  in  $\text{ClF}_5$  (364), theoretical calculation of  $\text{ClF}_5$  and  $\text{ClF}_3$  with boron slurries (367), motor firings with  $\text{ClF}_5$  and Borol 502 (368) and other studies with fuels (369).

### VII-B. $\text{ClF}_5$ - Lewis Acid Complexes

The nature of the reaction products of  $\text{ClF}_5$  with the Lewis acids  $\text{AsF}_5$  and  $\text{SbF}_5$  has been the subject of considerable research. As reported in the previous review (284a) the  $\text{ClF}_5 \cdot \text{AsF}_5$  product is a solid with a high dissociation pressure (150 mm. at  $0^\circ$ ) and the  $\text{ClF}_5 \cdot \text{SbF}_5$  product was a low melting ( $34 - 36^\circ$ ) solid with a low dissociation pressure (apparently nonvolatile at  $100^\circ$ ) which gave evidence of being ionic, i.e.,  $\text{ClF}_4^+\text{SbF}_6^-$ . The previously inconclusive NMR and IR studies on both complexes have been pursued.

In studies at Allied Chemical, the  $\text{ClF}_5 \cdot \text{AsF}_5$  complex\* was insoluble in  $\text{SF}_6$ , gave a very weak NMR resonance at  $\delta = 271$  ppm in  $\text{AsF}_5$  and a red solution in  $\text{BrF}_5$  which faded to pale yellow over several hours (76). One NMR sample in  $\text{BrF}_5$  at  $-60$  to  $-80^\circ$  showed a weak doublet at  $\delta = -265$  ppm (which tended to sharpen at lower temperature) plus a broadened  $\text{BrF}_5$  signal. A second sample showed only  $\text{BrF}_5$  as a pentet at  $-271$  ppm and a doublet at  $-132$  ppm. Some  $\text{ClO}_3\text{F}$  and  $\text{BF}_3$  were observed in the gas phase. Neither pure  $\text{ClF}_5$  nor  $\text{AsF}_5$  had absorptions in the  $-265$  ppm region, while  $\text{BrF}_5$ - $\text{AsF}_5$  mixture showed only a broad signal at  $-107$  ppm. In further studies (77) the  $\text{BrF}_5$  spectrum is reported as a doublet at  $-271$  and a triplet at  $-132$  ppm. When  $\text{ClF}_5$ ,  $\text{BrF}_5$  and  $\text{AsF}_5$  were combined and equilibrated at  $-45^\circ$ , a doublet at  $-265$  ppm was also observed and tentatively assigned to  $\text{ClF}_4^+$ . (The relative rates of formation of  $\text{ClF}_5 \cdot \text{AsF}_5$  and  $\text{BrF}_5 \cdot \text{AsF}_5$  would appear to be an important consideration here.)

\* Efforts to get an elemental analysis on  $\text{ClF}_5 \cdot \text{AsF}_5$  were unsatisfactory (76).

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TABLE XVI

## REACTIONS OF ClF<sub>3</sub>

<u>Reactants</u>	<u>Conditions</u>	<u>Results</u>	<u>Reference</u>
KIO <sub>4</sub>		no new products	75
I <sub>2</sub> O <sub>5</sub>		no new products	75
I <sub>2</sub> O <sub>5</sub> /HF	-78°	ClO <sub>3</sub> F, ClO <sub>2</sub> F, IF <sub>5</sub>	77
H <sub>2</sub> O/HF	-78°	ClO <sub>3</sub> F, ClO <sub>2</sub> F, ClO <sub>2</sub>	77
CsF	-30°, 12 hr.	no rxn.	77
CsF	-78°, 35 hr.	no rxn.	77
LiClO <sub>4</sub>	-78°	4% Cl <sub>2</sub> O <sub>7</sub> , trace unident. mat.?	76,77
KSO <sub>3</sub> F	25°	no rxn.	80
KSO <sub>3</sub> F	140-170°	SF <sub>2</sub> O <sub>2</sub> , O <sub>2</sub> , KClF <sub>4</sub> or KClF <sub>2</sub>	80
SiO <sub>2</sub> /CsF	25°, 16 hr.	SiF <sub>4</sub> , O <sub>2</sub> , unident. solid	80
PF <sub>3</sub> O	-111° to -78°	some ClO <sub>2</sub> F, ClO <sub>3</sub> F	80
PF <sub>3</sub> O	-78° to -30°	some PF <sub>5</sub> , unident. wh. solid which gave ClF <sub>5</sub> and PF <sub>3</sub> O (5 mm. at 25°)	80
SO <sub>3</sub>	-23°, 4 hr.	some S <sub>2</sub> O <sub>5</sub> F <sub>2</sub> , SF <sub>2</sub> O	80
SO <sub>3</sub>	23°, 1 hr.	ClO <sub>2</sub> F, ClO <sub>3</sub> F, S <sub>2</sub> O <sub>5</sub> F <sub>2</sub> , SF <sub>2</sub> O <sub>2</sub>	80
HSO <sub>3</sub> F		slow reaction	79
O <sub>2</sub>	3-4 x 10 <sup>4</sup> psi, 300-400°	no ClF <sub>5</sub> O or ClF <sub>7</sub>	117
OF <sub>2</sub>	3-4 x 10 <sup>4</sup> psi, 300-400°	no ClF <sub>5</sub> O or ClF <sub>7</sub>	117
F <sub>2</sub>	3-4 x 10 <sup>4</sup> psi, 300-400°	no ClF <sub>7</sub>	117
F <sub>2</sub> (9.3X)	43,800 psi, 440°, 48 hr.	mass spec. peaks in 147-150 range	119

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TABLE XVI (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Results</u>	<u>Reference</u>
F <sub>2</sub>	γ, 25,000 psi, 25°, 110 hr.	no ClF <sub>7</sub>	119
O <sub>2</sub>	120 to 420°, 44 - 108 hr.	ClF <sub>5</sub> , ClF <sub>3</sub> , Cl <sub>2</sub> , ClO <sub>2</sub> F, MF, etc., unident. prod.	77
O <sub>2</sub>	elec. disch. (static and flow)	complex mixture, unident. prod.	77
OF <sub>2</sub>	elec. disch., -196° (ClF <sub>5</sub> (s))	complex mixture, unident. prod.	77
O <sub>2</sub> F <sub>2</sub>		complex mixture, unident. prod.	77
NOF	-78°	~1:1 complex stable <-20°	301, 337
NOF	-108°	no evidence of interaction by NMR	420a
NOF/CsF	<-20°; preformed NOF·ClF <sub>5</sub>	no CsClF <sub>6</sub>	301
NO <sub>2</sub> F	-78°	liquid complex stable <-35°	342
NO <sub>2</sub> F	-60° to -80°	no evidence of interaction by NMR	420a
ClF <sub>2</sub> AsF <sub>6</sub>	~25°	no rxn.	301
KNO <sub>3</sub>	25°	no rxn.	301
CsNO <sub>3</sub>		NO <sub>2</sub> F, ClO <sub>2</sub> F	301
KClO <sub>4</sub>		ClO <sub>2</sub> F, KF	301
KClO <sub>3</sub>		some ClO <sub>2</sub> F	301
SbF <sub>5</sub> /HF		1:1 adduct immediately	301
H <sub>2</sub> O <sub>2</sub>		violent rxn.	301
I <sub>2</sub> O <sub>5</sub>		IF <sub>5</sub> , IF <sub>7</sub> , ClO <sub>3</sub> F, ClO <sub>2</sub> , O <sub>2</sub> (sudden rxn. after ~5 min. delay)	301

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TABLE XVI (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Results</u>	<u>Reference</u>
$O_2AsF_6$		$ClF_2AsF_6?$	301
$Ba(SbF_6)_2$		no gel formation	301
$Ba(BiF_6)_2$		no gel formation	301
$Ba(SbF_6)_2$	10 wt. %	gel	44
$O_2$	elec. disch., 10 mm., -40 to -10°	$ClF_3$ , $ClO_3F$ , $ClO_2F$ , $ClO_2$ , HF	338
$NF_3$	325°, 2125 psig, 20 hr.	some $ClF_3$ and $F_2$	339
$OF_2$	300°, 2950 psig	dec. of $OF_2$	339
$NiF_2 \cdot 4H_2O$	200°	$ClO_2F$ , $ClO_3F$ , HF	339
$ClO_2/N_2$	110°	$ClO_2F$ , $Cl_2$	339
5% $O_3$ in $O_2$	-78°, $CF_2Cl_2$	$ClO_3F$ , $ClO_2F$ , $ClF_3$	339
$Na_2O_2$	150°	$NaF$ , $O_2$ , $ClF_3$ , $ClF$ , $Cl_2$	341
<u>cis</u> - $N_2F_2$	-78 to 150°	v. sl. dec.	342
$Cl_2$	25°	no rxn.	387
$ClO_2$	25°	no rxn.	387
Graphite	25°	10 wt. % $ClF_5$ absorbed	387
NO	25°	$NOF$ + $Cl_2$	387
CO		$CF_2O$ , $ClFCO$	387
$H_2O$ or metal hydrates		$ClO_2F$ or $ClO_3F$ , $ClO_2$	387
$NO_2$		$ClO_2F$ , $ClO_2$ , $NO_2F$ , $NOF$	387
$P_2O_5$		$PF_3O$ , $O_2$ , $Cl_2$	387
$SO_3$		$SF_2O_2$ , $Cl_2$ , $O_2$	387

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TABLE XVI (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Results</u>	<u>Reference</u>
Misc. hydroxides		HF, O <sub>2</sub> , Cl-O-F mixtures	387
KClO <sub>3</sub>	25°	ClO <sub>2</sub> F, ClO <sub>3</sub> F, ClO <sub>2</sub> , O <sub>2</sub> , KClF <sub>4</sub>	387
KClO <sub>4</sub>	25° or 150°	no rxn.	387, 420a
KClO <sub>4</sub>	HF, 25°	KHF <sub>2</sub> , ClO <sub>2</sub> , FClO <sub>2</sub> , FClO <sub>3</sub>	420a
NaNO <sub>2</sub>	25°	NO <sub>2</sub> F, NOF, NO <sub>2</sub> , ClO <sub>2</sub> F, Cl <sub>2</sub> , NaF	387
NaNO <sub>3</sub>	25°	NO <sub>2</sub> F, ClO <sub>2</sub> F, NaF	387
NaNO <sub>3</sub>	HF, 25°	NO <sub>2</sub> F, ClO <sub>2</sub> , ClO <sub>2</sub> F, ClO <sub>3</sub> F	420a
Na <sub>2</sub> SO <sub>3</sub>	25°	no rxn.	387
Na <sub>2</sub> SO <sub>3</sub>	150°	SF <sub>2</sub> O <sub>2</sub> , SF <sub>6</sub> , ClO <sub>2</sub> , Cl <sub>2</sub> , O <sub>2</sub> , NaF	387
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	25°	no rxn.	387
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	150°	same as with SO <sub>3</sub> <sup>=</sup>	387
CsF or KF	25° or 150°	no rxn.	387
PF <sub>5</sub>	0°	no rxn.	387
BF <sub>3</sub>	-112°	no rxn.	387
(CF <sub>3</sub> ) <sub>2</sub> CO	25°	fluorination	387
(CF <sub>3</sub> CO) <sub>2</sub> O	25°	fluorination	387
CCl <sub>4</sub>	25°	Cl <sub>2</sub> , CFC <sub>3</sub>	387
CHCl <sub>3</sub>	25°	CHFCl <sub>2</sub> , CF <sub>2</sub> Cl, CF <sub>4</sub> , Cl <sub>2</sub> , CFCl <sub>3</sub>	387
XeF <sub>4</sub>	25°	solubility 5.5 g/100 g ClF <sub>5</sub>	393
XeF <sub>2</sub>		low solubility	394

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TABLE XVI (Concluded)

<u>Reactants</u>	<u>Conditions</u>	<u>Results</u>	<u>Reference</u>
HgO	0°, N <sub>2</sub> (g)	ClO <sub>2</sub> F	420a
KBrO <sub>3</sub>		no BrF <sub>3</sub> O	420a
HNF <sub>2</sub>	-80°	ClNF <sub>2</sub> , N <sub>2</sub> F <sub>4</sub> , NF <sub>3</sub>	420a
2CsF·Cl <sub>2</sub> O	0°	CsClF <sub>2</sub> , ClF, ClO <sub>2</sub> F	423
IO <sub>2</sub> F		ClO <sub>2</sub> F, some ClO <sub>3</sub> F; no ClF <sub>3</sub> O	426
I <sub>2</sub> O <sub>5</sub>		ClO <sub>2</sub> F, some ClO <sub>2</sub> ; no ClF <sub>3</sub> O	426
Pb(NO <sub>3</sub> ) <sub>2</sub>	-30° to 25°; fast	O <sub>2</sub> , NO <sub>2</sub> F, ClO <sub>2</sub> F, ClF <sub>3</sub> , trace NO <sub>2</sub> OClO <sub>2</sub> ?	426
Pb(NO <sub>3</sub> ) <sub>2</sub>	-50°, excess ClF <sub>5</sub> , slow	NO <sub>2</sub> F, ClO <sub>2</sub> F, PbF <sub>2</sub>	426
NF <sub>3</sub> , F <sub>2</sub>	100°, 3000 psi, 65 hr.	trace NF <sub>4</sub> ClF <sub>6</sub> ?	487
SbF <sub>5</sub> , F <sub>2</sub>	Δ, press.	complex product	487
Ar, O <sub>3</sub>	h ν, 4°K	trace ClF <sub>5</sub> O ?	532a
F <sub>2</sub>	γ, -196°	no new products	532a
ClF <sub>5</sub>	elec. disch., -80°	dec. of some ClO <sub>2</sub> F, ClO <sub>3</sub> F, no (ClF <sub>4</sub> ) <sub>2</sub>	420a
ClF <sub>5</sub>	h ν, -190°	no EPR evidence of ClF <sub>4</sub> ·	77
ClF <sub>5</sub>	h ν, -190°, CF <sub>4</sub> , C <sub>2</sub> F <sub>6</sub> , SF <sub>6</sub>	no EPR evidence of ClF <sub>4</sub> ·	77
ClF <sub>5</sub>	h ν, -190°, CF <sub>4</sub> /CFCl <sub>3</sub> liq.	no EPR evidence of ClF <sub>4</sub> · or ClF <sub>2</sub> ·	77,78
ClF <sub>5</sub>	h ν, -190°, NF <sub>3</sub> liq.	no EPR evidence of ClF <sub>4</sub> · or ClF <sub>2</sub> ·	78
ClF <sub>5</sub>	elec. disch., flow system	see only F· in EPR	78
CsF	25°, 300 hr. in Teflon	CsClF <sub>6</sub> in mixture with CsClF <sub>4</sub> , CsF	275a

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With more dilute samples (50 mole %  $\text{BrF}_5$ ), a broad peak at  $-80$  ppm and a peak at  $-226$  ppm were observed. In a 1:1:1 sample a broad peak at  $-100$  ppm was observed in the three component system, but normal spectra were obtained in a  $\text{ClF}_5$  -  $\text{BrF}_5$  mixture at  $-45^\circ$ . A mixture of  $\text{BrF}_5$  and  $\text{AsF}_5$  gave a yellow solution at first, but this turned red on storage at  $-40^\circ$ . The NMR of the latter was a broad peak at  $-106$  ppm and a small unexplained peak at  $-90$  ppm. A second, more concentrated sample using less pure  $\text{BrF}_5$  showed only a  $-107$  peak. No paramagnetic species were observed in the red solutions. The combination of  $\text{ClF}_5$ ,  $\text{BrF}_5$  and  $\text{AsF}_5$  on the other hand gave a white solid at  $-40^\circ$  and only weak, poorly resolved NMR peaks were observed. The  $-265$  ppm peak was therefore tentatively assigned to  $\text{ClF}_4^+$ . The  $\text{ClF}_5 \cdot \text{SbF}_5$  salt in  $\text{SbF}_5$  gave only a  $-274$  ppm peak downfield plus a broad peak above  $100$  ppm from the fluorines on antimony.

In further studies (78) of  $\text{ClF}_5 \cdot \text{AsF}_5$  in  $\text{BrF}_5$  a very broad NMR peak ( $-150$  to  $-87$  ppm) was observed but these, as well as the previous results, were considered inconclusive because of HF impurities in the solvent, i.e., the HF promotes fluorine exchange with dissolved salt although it does not with  $\text{BrF}_5$  alone. Thus  $\sim 1$  M  $\text{ClF}_5 \cdot \text{AsF}_5$  in HF gave only one broad peak:  $+170$  ppm at  $-30^\circ$  or  $+188$  ppm at  $-80^\circ$ . On the other hand when excess  $\text{ClF}_5$  was dissolved in excess  $\text{SbF}_5$ , the resulting solution at  $45^\circ$  showed an NMR peak at  $-274$  ppm. At  $25^\circ$  some solid precipitated and this peak was broadened, while at  $0^\circ$  or  $-60^\circ$  only the Sb-F peak at  $+109$  was observed. The  $\text{ClF}_5 \cdot \text{SbF}_5$  was not soluble in  $\text{BrF}_5$  (79). However, when  $\text{ClF}_5$  was added to a solution of  $\text{SbF}_5$  in  $\text{BrF}_5$ , a white solid which formed initially redissolved on standing at  $25^\circ$ . The  $\text{ClF}_5$  was observed (NMR examination of six samples) when the  $\text{ClF}_5/\text{SbF}_5$  ratio was 4:1, but not when it was 2:1. With a 1:1 ratio (at  $-35^\circ$ ) the  $\text{BrF}_5$  resonances were averaged at  $-154 \delta$  and the  $\text{SbF}_5$  at  $+121 \delta$ , but with a 2:1 ratio (at  $-40^\circ$ ) the  $\text{BrF}_5$  peak was unresolved at  $-167 \delta$  in one sample but partially resolved at  $-276$  and  $-138 \delta$  in another. No evidence for  $\text{BrF}_4^+$  was observed in the  $\text{BrF}_5$  -  $\text{SbF}_5$  system: at  $-40^\circ$  only partially resolved  $\text{BrF}_5$  was observed while at  $25^\circ$  the  $\text{BrF}_5$  average was at  $-167$  and the SbF species averaged at  $+109$  ppm.

Efforts at Monsanto (301) to get the infrared spectrum of  $\text{ClF}_5$ - $\text{SbF}_5$  product (formed by rapid reaction in HF) in KBr or KCl pellets, or Kel-F mulls gave inconclusive results because of the reactivity, but some differences from the spectrum of  $\text{ClF}_2\text{SbF}_6$  were detected.

A lengthy research effort has been performed at Rocketdyne on the IR and NMR of  $\text{ClF}_5 \cdot \text{AsF}_5$  complex.

The 1:1 complex was formed at  $-80^\circ$ , then warmed to  $25^\circ$  before being condensed at  $-196^\circ$  onto a AgCl window of the IR cell (385). (This method raises the question of whether the complex reformed normally upon condensing.) The spectra of the complex and of solid  $\text{ClF}_5$  and  $\text{AsF}_5$  were taken at  $-196^\circ$  (the  $\text{ClF}_5$  showed an anomalous strong band at  $686 \text{ cm}^{-1}$  which was attributed to  $\text{ClF}_4^-$  or  $\text{ClF}_2^-$ ). The spectrum of the complex was relatively simple, suggesting  $C_{4v}$  symmetry. A band at  $817 \text{ cm}^{-1}$  was attributed to the Cl-F stretch and a band at  $743 \text{ cm}^{-1}$  to the As-F stretch. The latter is abnormally high for  $\text{AsF}_6^-$  and was therefore taken to indicate a fluorine bridged structure,  $\text{F}_4\text{Cl-F} \cdots \text{AsF}_5$ . (Bending vibrations were at  $586$  and  $514 \text{ cm}^{-1}$  in the complex.) From correlations of the Hammett  $\sigma$  constants for a number of fluoro salts and the apparent shift of the  $\text{AsF}_6^-$  band an estimate of 20% ionic character was made for

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$\text{ClF}_5 \cdot \text{AsF}_6^-$  (386). The calculated electronegativities of some of the fluoro species were:  $\text{N}_2\text{F}^+$ , 2.05;  $\text{NF}_2\text{O}^+$ , 2.25;  $\text{ClF}_4^+$ , 2.2;  $\text{AsF}_5$ , 3.2. (On this scale the  $\text{O}_2^+$  ion was 1.76.) Although  $\text{ClF}_4^+$  and  $\text{NF}_2\text{O}^+$  have about the same electronegativity, the latter was judged to give a more ionic salt with  $\text{AsF}_6^-$ , because it does not have available orbitals to enter into fluorine bridging as the  $\text{ClF}^+$  does.

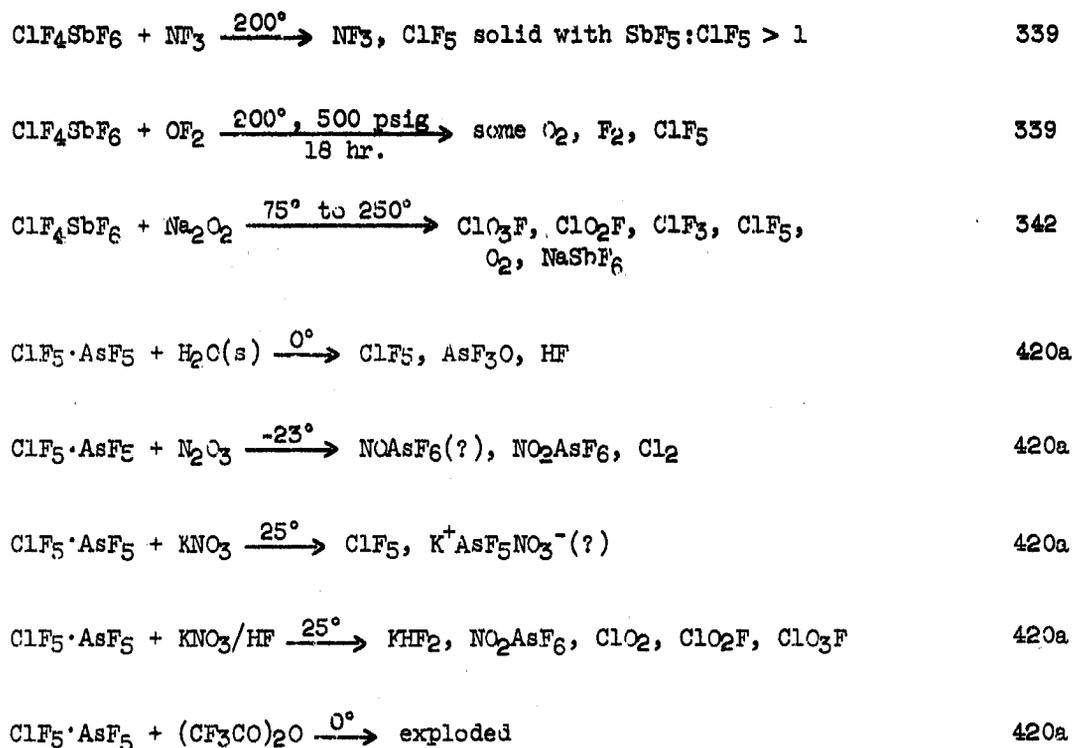
NMR studies also gave evidence for the covalent and ionic forms  $\text{F}_5\text{As} \leftarrow \text{ClF}_4^+\text{AsF}_6^-$  and  $\text{F}_5\text{As} \leftarrow \text{ClF}_4\text{-F-AsF}_5$  in addition to the 1:1 complex, but no evidence for the free  $\text{ClF}_4^+$  ion (402). These studies included solid samples at  $-80^\circ$  and  $25^\circ$ , solutions in  $\text{BrF}_5$  (changes with aging in these solutions were attributed to precipitation of the more ionic forms) and the gases. No reference standards were used unfortunately.

A few reactions have been attempted with the  $\text{ClF}_4\text{SbF}_6$  salt or the  $\text{ClF}_5 \cdot \text{AsF}_5$  complex as summarized in Table XVII.

TABLE XVII

REACTIONS OF  $\text{ClF}_5$  - LEWIS ACID COMPLEXES

Additional reactions of  $\text{ClF}_5$ ·Lewis acid complexes which have been attempted include:



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## VII-C. Chlorine Trifluoride and Derivatives

The chemistry of  $\text{ClF}_3$  has not been extended appreciably since the previous review (284a). A publication by Christe and Pavlath (L112) gives evidence that the  $\text{ClF}_3\text{-AsF}_5$  reaction product is  $\text{ClF}_2^+\text{AsF}_6^-$ , but infrared assignments in this paper have been retracted by Christe and Sawodny (L115) who observed new bands in  $\text{ClF}_2\text{AsF}_6$  and  $\text{ClF}_2\text{BF}_4$  at  $-196^\circ$ . The melting point of  $\text{ClF}_2\text{SbF}_6$  has been established as  $225 - 228^\circ$  (342). Christe, Sawodny and Guertin have concluded from analysis of vibrational spectra (L115) that the  $\text{ClF}_2^-$  ion (L109, L110) is linear. A paper by Christe and Guertin on spectra of salts of the  $\text{ClF}_4^-$  ion has also appeared (L111).

Electrical conductivity measurements on a solution containing  $\text{ClF}_3$ ,  $\text{BrF}_3$  and  $\text{BF}_3$  show (158) that it is an excellent conductor ( $7.6 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) at  $-60^\circ$ . On the other hand, combination of  $\text{ClF}_3$  with  $\text{BrF}_5$  and  $\text{AsF}_5$  gave a white sparingly soluble salt at  $-40^\circ$  (77). Conductivity data on the  $\text{ClF}_3\text{-KNO}_3$  system were inconclusive, regarding the presence of ions, but no evidence for ions was observed with the  $\text{ClF}_3\text{-N}_2\text{O}_4$  system (301). Conductivity measurements on the systems  $\text{ClF}_3\text{-IF}_5$  or  $\text{ClF}_3\text{-ClO}_3\text{F}$  did not give evidence of any ions while the system  $\text{ClF}_3\text{-ClO}_3\text{F-CsF}$  appeared to have the ions (337)  $\text{ClF}_2^+\text{CsF}_2^-$  thought to be present in  $\text{ClF}_3\text{-CsF}$  mixture. The conductivity of  $\text{BrF}_3$  was not changed significantly by the addition of  $\text{ClF}_3$  (337). The mixture  $\text{ClF}_3 \cdot 2\text{BrF}_5 \cdot \text{BrF}_3$  was successfully gelled with  $\text{Ba}(\text{SbF}_6)_2$  (302) in studies of potential incendiary agents.

A number of reactions of  $\text{ClF}_3$  which have been studied are summarized in Table XVIII.

The results of a number of recent studies of the reactions of the  $\text{ClF}_3$  derivatives, the  $\text{ClF}_2^+$  and  $\text{ClF}_4^-$  ions are summarized in Table XIX.

## VII-D. Chlorine Trifluoride Oxide and Related Compounds

The numerous efforts to prepare higher chlorine fluoride oxides (i.e., in addition to the well known  $\text{ClO}_3\text{F}$  and  $\text{ClO}_2\text{F}$ ) have led to the discovery at Rocketdyne of chlorine trifluoride oxide,  $\text{ClF}_3\text{O}$ , (also called oxychlorinetrifluoride and given the code name, Florox). Efforts to obtain  $\text{ClF}_3\text{O}_2$  or  $\text{ClF}_5\text{O}$  have not been successful, but evidence has been obtained for an unstable  $\text{FClO}$ .

Discovery and properties: Chlorine trifluoride oxide was first detected in early 1965 (420) as an unidentified product of the fluorination of  $\text{Cl}_2\text{O}$  over  $\text{CsF}$  at  $-80^\circ$ . The  $\text{ClF}_3\text{O}$  was evolved in low yields upon warming the residual solid. Positive identification of  $\text{ClF}_3\text{O}$  soon followed (420a), the boiling point and melting points fixed at  $30 \pm 5^\circ\text{C}$  and  $-68 \pm 3^\circ\text{C}$ , respectively, and the structure suggested to be  $\text{Cs}$  symmetry on the basis of the infrared spectrum (absorption bands at 1220, 680, 490, 320 and  $280 \text{ cm}^{-1}$ ). The  $^{19}\text{F}$  NMR spectrum was a single broad resonance at  $\delta = -279 \text{ ppm}$  with either neat liquid or in  $\text{CFCl}_3$  or  $\text{Cl}_2$  solutions at  $-88^\circ$ .

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TABLE XVIII

REACTIONS OF ClF<sub>3</sub>

<u>Reactants</u>	<u>Conditions</u>	<u>Results</u>	<u>Reference</u>
OF <sub>2</sub> /KF	25°, 48 hr., shaking	KClF <sub>4</sub> formed	79
(CF <sub>3</sub> O) <sub>2</sub> O	25°	NR	80
OF <sub>2</sub>	140 - 170°	SF <sub>2</sub> O <sub>2</sub> , O <sub>2</sub> , KClF <sub>2</sub>	80
KSO <sub>3</sub> F	25°, 48 hr.	small amounts, SF <sub>2</sub> O <sub>2</sub> , ClO <sub>2</sub> F	80
KSO <sub>3</sub> F	-78°	Cl <sub>2</sub> , ClO <sub>2</sub> F (no ClONF <sub>2</sub> )	122
CsSO <sub>3</sub> F	70°, 16 hr.	(CF <sub>3</sub> O) <sub>2</sub> , O <sub>2</sub> , unchanged ClF <sub>3</sub>	79
ClONO <sub>2</sub>	150°, 5500 psi, 18 hr.	some ClO <sub>2</sub> F	80
OF <sub>2</sub>	100 - 400°, static or flow	ClO <sub>2</sub> F, ClO <sub>3</sub> F, ClO <sub>2</sub>	346
OF <sub>2</sub>	elec. disch., -15° or -78°	ClF, ClO <sub>2</sub> F, ClO <sub>3</sub> F, ClO <sub>2</sub> , impurities	346
OF <sub>2</sub>	elec. disch., -196°	as above plus some ClF <sub>5</sub> , O <sub>2</sub> ClF <sub>3</sub> ?	346
O	-150°	ClO <sub>2</sub> F, ClO <sub>3</sub> F, ClO <sub>2</sub>	346
O <sub>3</sub>		inconclusive	330
NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> or N <sub>2</sub> O <sub>2</sub> <sup>=</sup>	-110 to 350° 0.5 to 1200 atm.	no NFO anions in product	333
CsNO <sub>3</sub>	25°	CsClF <sub>4</sub> + CsF	333
OF <sub>2</sub> /CsClF <sub>4</sub>	200 - 300°, 680 atm.	ClF <sub>5</sub> , ClO <sub>2</sub> F, ClO <sub>3</sub> F, O <sub>2</sub> , F <sub>2</sub>	336
OF <sub>2</sub>		ClF <sub>5</sub>	336
O <sub>2</sub>	elec. disch., 25°	ClF <sub>5</sub> , ClO <sub>2</sub> , ClO <sub>3</sub> F, ClO <sub>2</sub> F, impurities + unident. mat. abs. 6.2 μ	337
OF <sub>2</sub>	280°, 1350 psig	some ClF <sub>5</sub> , O <sub>2</sub>	339,341
O <sub>3</sub>	-78°	ClO <sub>3</sub> F, ClO <sub>2</sub> F	339,341

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TABLE XVIII (Concluded)

<u>Reactants</u>	<u>Conditions</u>	<u>Results</u>	<u>Reference</u>
O <sub>3</sub> (5% in O <sub>2</sub> )	CF <sub>2</sub> Cl <sub>2</sub> , -78°	small amounts ClO <sub>3</sub> F, ClO <sub>2</sub> F	340
O <sub>3</sub> (5% in O <sub>2</sub> )	-78°	as above plus ClO <sub>2</sub>	340
BiF <sub>3</sub> , F <sub>2</sub>	250°, 1000 psi	ClF <sub>6</sub> <sup>+</sup> BiF <sub>6</sub> <sup>-</sup> ?	276a
O <sub>3</sub>		attacked Kel-F IR cell rxn. vessel	420a
HNF <sub>2</sub>	fast rxn. on warming	ClNF <sub>2</sub> + N <sub>2</sub> F <sub>4</sub> + HF	420a
HNF <sub>2</sub> ·BF <sub>3</sub>	-80°, slow	ClNF <sub>2</sub> , etc.	420a
CsClF <sub>4</sub> O		CsClF <sub>4</sub> + ClF <sub>3</sub> O	424
KClO <sub>3</sub>	25°, 16 hr.	ClO <sub>2</sub> F + ClO <sub>2</sub>	420
H <sub>2</sub> O	-18° to +25°	trace ClFO?, HF, ClO <sub>2</sub>	425
Cl <sub>2</sub> O	-50°, NaF	ClO <sub>2</sub> F + ClF (ClFO intermed.?)	423
NF <sub>3</sub> + F <sub>2</sub>	100°, 3000 psi, 65 hr. small amounts	NF <sub>4</sub> <sup>+</sup> ClF <sub>6</sub> <sup>-</sup> ?	487
F <sub>2</sub> + BF <sub>3</sub>		ClF <sub>2</sub> BF <sub>4</sub>	593a
O <sub>2</sub>	elec. disch., -196°	ClO <sub>2</sub> ?	537

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TABLE XIX

REACTIONS OF  $\text{ClF}_2^+$  and  $\text{ClF}_4^-$  SALTS

	<u>References</u>
$\text{ClF}_2\text{SbF}_6 + \text{OF}_2 \xrightarrow[20 \text{ hr.}]{200^\circ, 850 \text{ psig}}$ some $\text{ClF}_5$ , $\text{O}_2$ and $\text{Cl}_2$	339
$\text{ClF}_2\text{SbF}_6 + \text{Na}_2\text{O}_2 \xrightarrow[24 \text{ hr.}]{125^\circ}$ NR $\xrightarrow[30 \text{ min.}]{250^\circ}$ sudden reaction to $\text{ClF}_3$ , $\text{ClF}$ , $\text{ClO}_2\text{F}$ , $\text{O}_2$ , $\text{NaSbF}_6$	342
$\text{ClF}_2\text{SbF}_6 + \text{O}_3 \xrightarrow{-78^\circ/\text{ClF}_3}$ small amounts $\text{ClO}_3\text{F}$ , $\text{ClO}_2\text{F}$ from $\text{ClF}_3$	341
$\text{CsClF}_4 + \text{HF} \longrightarrow \text{CsHF}_2 + \text{ClF}_3$	489
$\text{MClF}_4 + \text{H}_2\text{O} \xrightarrow[750 \text{ psi}]{50^\circ}$ $\text{ClO}_2$ , $\text{Cl}_2$ (no $\text{MClF}_2\text{O}$ or $\text{FClO}$ )	423
$\text{CsClF}_4 + \text{Na}_2\text{O}_2 \xrightarrow{300^\circ}$ $\text{CsF}$ , $\text{NaF}$ , $\text{O}_2$ , $\text{Cl}_2$	341
$\text{CsClF}_4 + \text{NF}_3 \xrightarrow[24 \text{ hr.}]{200^\circ}$ no rxn.	339
$\text{CsClF}_4 + \text{OF}_2 \xrightarrow[340-680 \text{ atm.}]{200-300^\circ}$ $\text{O}_2$ , $\text{F}_2$ , $\text{ClO}_2\text{F}$ , $\text{ClO}_3\text{F}$ , $\text{ClF}_5$ , $\text{Cs}_2\text{NlF}_6$	336
$\text{CsClF}_4 + \text{O}_2\text{AsF}_6 \xrightarrow{0^\circ}$ $\text{CsAsF}_6 + \text{O}_2$ , $\text{Cl}_2$	354
$\text{RbClF}_4 + \text{O}_2\text{AsF}_6 \longrightarrow$ inconclusive	301
$\text{NOClF}_4 + \text{O}_2\text{AsF}_6 \xrightarrow{\text{CFCl}_3}$ $\text{NOAsF}_6$ , $\text{ClF}_3$ , $\text{NOF}$	301
$\text{ClF}_4^- + \text{NF}_2\text{O}^+ \longrightarrow$ no $\text{NF}_2\text{OClF}_4$	301
$\text{HNF}_2 + \text{RbClF}_4 \xrightarrow[\text{slow}]{-80^\circ}$ $\text{CNF}_2$ , $\text{N}_2\text{F}_4$ , $\text{HF}$ , etc.	420a

More recently, Rocketdyne scientists (434a) have resolved the NMR spectrum of gaseous  $\text{ClF}_3\text{O}$  into two peaks at  $-300$  and  $-262 \phi$  in a 1:2 intensity ratio,\* but the best

\* A recent Rocketdyne report (426) gives the gaseous resonances at  $-317$  and  $-276 \phi$ .

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samples of liquid  $\text{ClF}_3\text{O}$  still showed the collapsed singlet at  $-276^\circ$ . (HF catalysis of the fluorine exchange was considered the cause.)

Allied Chemical (81) has since prepared a purified sample of  $\text{ClF}_3\text{O}$  and found a melting point of  $-44^\circ$  and a boiling point of  $30.1^\circ$ ,  $\Delta H_f$  of  $-7.06$  kcal./mole, entropy of 23.3 e.u., and vapor pressure in the range  $-23$  to  $+19^\circ$  described by the equation  $\log P_{\text{mm}} = 7.965 - 1543/T$ . Rocketdyne had previously (421) derived the equation:  $\log P_{\text{mm}} = 8.433 - 1680/T$ . The melting point was found at Allied to be quite sensitive to small amounts of  $\text{ClO}_2\text{F}$ , accounting for the much higher value than previously observed. Most recently, Rocketdyne workers have reported (429,276c) that the true melting point is  $-37.2 \pm 0.5^\circ\text{C}$ , and the density is  $1.863$  g/cm<sup>3</sup> at  $20^\circ$ , compared to the more dense value reported (421) previously of 1.90 at  $25.5^\circ$ . The Allied group also reported a more detailed infrared spectrum as follows: 1229-1225-1219 (PQR) m; 684, 675, 666 (sh.) all v.s.; 502-490-483 (PQR) m; and 311 and 281 v.w. cm<sup>-1</sup>. The spectrum indicated, but did not prove that the structure was of  $C_s$  symmetry (a trigonal bipyramid derivative) with two apical fluorines and one fluorine and the oxygen in the equatorial plane. The mass spectrum of  $\text{ClF}_3\text{O}$  is (425) as follows:  $\text{ClFO}^+ > \text{ClF}_2\text{O}^+ > \text{Cl}^+ > \text{F}^+ > \text{ClF}^+ > \text{ClO}^+ > \text{O}^+$ .

Rocketdyne reports that  $\text{ClF}_3\text{O}$  is stable at  $284^\circ$  (421), but reacts with stainless steel to the extent that pyrolysis is an analytical method:  $\text{ClF}_3\text{O} + \text{S.S.} \xrightarrow{\Delta} \text{Cl}_2 + \text{O}_2 + \text{MF}_6$ . The  $\text{ClF}_3\text{O}$  decomposes above  $300^\circ$  to  $\text{ClF}$  and  $\text{ClO}_2\text{F}$  (423).

The  $\text{ClF}_3\text{O}$  can be purified by pumping off  $\text{ClO}_2\text{F}$ ,  $\text{ClO}_3\text{F}$ ,  $\text{ClF}$  and some of the  $\text{ClF}_3$  at  $-95^\circ$ , and the remainder of the  $\text{ClF}_3$  can be removed at  $-80^\circ$  with a small loss of  $\text{ClF}_3\text{O}$  (423). Others have reported (80) that  $\text{ClO}_2\text{F}$  and  $\text{ClF}_3\text{O}$  could not be completely separated at  $-78^\circ$  and  $-95^\circ$ , nor by formation of the  $\text{KF}$  or  $\text{CsF}$  complexes at  $-78^\circ$ , followed by removal of volatiles at  $50^\circ$  and redissociation of the complexes at  $170^\circ$ , i.e.,  $\text{ClF}_3\text{O}$ ,  $\text{ClO}_2\text{F}$  and  $\text{ClO}_3\text{F}$  were recovered. Alternatively,  $\text{CsF}$  can (423) be reacted with the  $\text{ClF}_3 - \text{ClF}_3\text{O}$  mixture. The  $\text{CsClF}_4\text{O}$  redissociates at  $150^\circ$  while the  $\text{CsClF}_4$  remains nonvolatile (422). The chromatographic purification of  $\text{ClF}_3\text{O}$  using a halocarbon column has also been described (429).

Synthesis studies: In the early studies at Rocketdyne (420) the reaction of  $\text{F}_2$  with  $\text{Cl}_2\text{O}$  at  $125^\circ$  had merely given  $\text{ClF}_3$  and  $\text{ClO}_2\text{F}$ .\* Thus, the nature of the  $\text{CsF}$  complex (a colorless solid at  $0^\circ$  which dissociates to  $\text{Cl}_2\text{O}$  at  $25^\circ$  (420a)) was considered to be very important and a search was made for modifications or another  $\text{Cl-O}$  reactant which would give greater efficiency or safety in handling. The  $\text{Cl}_2\text{O}$  (best prepared (421) by the reaction of  $\text{Cl}_2$  with  $\text{HgO}$ ) is a serious explosion hazard for scale-up studies. In mid-1965, Rocketdyne reported (421) that  $\text{ClF}_3\text{O}$  could also be made by fluorination of the  $\text{CsF}$  complex of  $\text{ClONO}_2$ . However, the best method then known for making  $\text{ClONO}_2$  was the reaction of  $\text{Cl}_2\text{O}$  with  $\text{N}_2\text{O}_4$  (424).

\* Efforts to fluorinate  $\text{Cl}_2\text{O}$  with  $\text{F}_2$  in  $\text{CCl}_4$  solution at Allied Chemical (1960) and with  $\text{OF}_2$  and ultraviolet light at Imperial Chemical (1961) had also been unsuccessful.

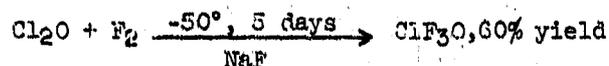
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Cesium fluoride was found (421) to absorb  $\text{ClF}_3\text{O}$  at  $25^\circ$  to give the 1:1 salt  $\text{Cs}^+\text{ClF}_4\text{O}^-$  (422), although this salt redissociated on heating (421) to  $150^\circ$  (423). While fluorination of the  $\text{CsF}$  complex of  $\text{Cl}_2\text{O}$ ,\* i.e.,  $2 \text{CsF} \cdot 3 \text{Cl}_2\text{O}$  (423), gives mostly free  $\text{ClF}_3\text{O}$ , fluorination of the  $\text{CsF}$  complex of  $\text{ClONO}_2$  yields  $\text{CsClF}_4\text{O}$  (346b).

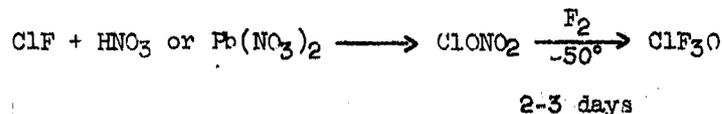
The  $\text{KF}$  complex of  $\text{Cl}_2\text{O}$  gave (422) up to 44% yields of  $\text{ClF}_3\text{O}$  and the work-up was easier since the  $\text{KClF}_4\text{O}$  dissociated appreciably at room temperature. Some  $\text{ClF}_3\text{O}$  was also formed in the fluorination of  $\text{Cl}_2\text{O}$  plus  $\text{NaF}$  (423) and  $\text{HgCl}_2 \cdot \text{Cl}_2\text{O}$  (383), the latter being generated in situ from  $\text{HgO}$  and  $\text{Cl}_2$  and thus eliminating the need for handling  $\text{Cl}_2\text{O}$ . In early 1966, the direct reaction of  $\text{Cl}_2\text{O}$  with  $\text{F}_2$  was found (423,346b) to give  $\text{ClF}_3\text{O}$  according to the equation:  $\text{Cl}_2\text{O} + 2\text{F}_2 \xrightarrow{-78^\circ} \text{ClF}_3\text{O} + \text{ClF}$ .

Allied Chemical independently discovered (80) that reaction of  $\text{Cl}_2\text{O}$  and  $\text{F}_2$  for three days at  $-78^\circ$  was preferable\*\* to the use of the  $\text{CsF}$  complex. This reaction was first discovered at Picatinny Arsenal in 1964 (346), but the product was not positively identified. On the other hand, workers at Pennsalt Chemical observed (342) the formation of  $\text{ClF}_3\text{O}$  in the reaction of  $\text{Cl}_2\text{O}$  with  $\text{F}_2$  at  $155^\circ$  or with  $\text{OF}_2$  at  $130^\circ$ .

By late 1966, Rocketdyne had prepared 1 lb. of  $\text{ClF}_3\text{O}$  by the batch fluorination of  $\text{Cl}_2\text{O}$ :



Rocketdyne also found that the direct fluorination of  $\text{ClONO}_2$  at  $-78^\circ$  gave up to 80% yield of  $\text{ClF}_3\text{O}$  (423). The development of an alternate route (405,1178) to  $\text{ClONO}_2$  together with its more favorable handling properties may make this the method of choice. This route (429) consists of the reactions:



\* The  $\text{CsF}-\text{ClONO}_2$  complex completely dissociates at  $-78^\circ$  upon prolonged vacuum pumping as also does the  $\text{RbF}-\text{Cl}_2\text{O}$  complex, but the  $\text{CsF} \cdot 1.5\text{Cl}_2\text{O}$  does not (426).  $\text{Cl}_2\text{O}$  also forms a complex with  $\text{BF}_3$  which is unstable at room temperature (123). The complex formed between  $\text{Cl}_2\text{O}$  and  $\text{AsF}_5$ , reported in the literature to be  $\text{Cl}_2\text{OAsF}_5$  at  $-80^\circ$  and  $\text{ClOAsF}_5$  above  $-50^\circ$ , has been shown (425,424) to be  $\text{ClO}_2^+\text{AsF}_6^-$ . The infrared spectrum showed  $\text{ClO}_2^+$  at 1283  $\text{cm}^{-1}$  and 1040  $\text{cm}^{-1}$  and the  $\text{AsF}_6^-$  at 690  $\text{cm}^{-1}$ .

\*\* At  $0^\circ$ , however, only  $\text{ClO}_2\text{F}$  and  $\text{ClO}_3\text{F}$  were obtained.

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Rocketdyne workers have reported (346b) the possible detection of ClFO as an unstable by-product while working up mixtures containing ClF<sub>3</sub>O. The low temperature infrared spectrum (-196°) showed bands at 1260, 1225 and 645-630-610 cm<sup>-1</sup> and a possible band at 490 cm<sup>-1</sup> deduced from an overtone at 930 cm<sup>-1</sup>. The new species was partially trapped at -142° or -160°. The same compound was apparently observed by Lawless (276a) as a very volatile (partially trapped at -136°) glass-reactive product from the reaction of O<sub>2</sub>F<sub>2</sub> with NaClO<sub>2</sub> at -160°. A tentative IR band at 1258 cm<sup>-1</sup> was reported for the gas, but the possibility of C-F impurities from Kel-F grease was not eliminated.

Reactions: In addition to its reaction as a strong oxidizer and its reaction as a Lewis acid with fluoride ion to give the ClF<sub>4</sub>O<sup>-</sup> ion, ClF<sub>3</sub>O also acts as a fluoride donor toward strong Lewis acids to form ClF<sub>2</sub>O<sup>+</sup> ions. The acid base behavior, then is analogous to that of the isoelectronic molecule SF<sub>4</sub> which forms SF<sub>5</sub><sup>-</sup> and SF<sub>3</sub><sup>+</sup> ions. The ClF<sub>3</sub>O - AsF<sub>5</sub> reaction product is nonvolatile at 50° (381) and can be assumed to have the ionic structure ClF<sub>2</sub>O<sup>+</sup>AsF<sub>6</sub><sup>-</sup>. The ClF<sub>3</sub>O - BF<sub>3</sub> product, which forms more rapidly (20 min.) at -80° than the analogous ClF<sub>3</sub> or ClO<sub>2</sub>F products,\* was reported to sublime slowly at 100° under vacuum (381) and to have a dissociation pressure of 20 mm. at room temperature (424). The ClF<sub>3</sub>O - PF<sub>5</sub> complex has a slightly higher dissociation pressure than the BF<sub>3</sub> complex. A sample of ClF<sub>3</sub>O·PF<sub>5</sub> was sublimed onto the window of a low temperature infrared cell (424). Bands attributed to PF<sub>6</sub><sup>-</sup> were observed and two other strong bands at 1315 cm<sup>-1</sup> and 1465 cm<sup>-1</sup> were suggestive of ClO<sub>2</sub><sup>+</sup> (from ClO<sub>2</sub>F impurities) and a ClF<sub>2</sub>O<sup>+</sup> ion respectively, but assignments could not be made with certainty. (At this low temperature the Cl=O bands of solid ClO<sub>2</sub>F and ClF<sub>3</sub>O were observed at 1280 cm<sup>-1</sup> and 1250 cm<sup>-1</sup>, respectively.) Silicon tetrafluoride formed a complex 2ClF<sub>3</sub>O·SiF<sub>4</sub> of high (340 mm. at 25°) dissociation pressure, but the infrared spectrum of a sublimed sample showed only the starting materials. From the vapor pressure equation,  $\log P_{\text{mm}} = 7.75 - 1545/T$ , (-80 to +14°C) a heat of reaction of -2 kcal/mole was calculated.

Complexes are also formed between ClF<sub>3</sub>O and NO<sub>2</sub>F (421) and NOF (424). From the dissociation pressure of the NOF·ClF<sub>3</sub>O,  $\log P_{\text{mm}} = 8.47 - 1625/T$  (-80° to 0°C) (i.e., about 1 atm. at 25°), a heat of reaction of -5 kcal/mole was calculated. A <sup>19</sup>F NMR study of this complex from -77° to 26° showed only a broad line 40 ppm downfield from ClF<sub>3</sub>O, i.e., about -316  $\delta$ . An infrared study showed only the starting materials at 25°, but at -196° the complex showed a broad band in the Cl-F region, a Cl=O stretch at 1230 cm<sup>-1</sup> and a N=O stretch at 2050 cm<sup>-1</sup>. At this low temperature ClF<sub>3</sub>O has Cl-F and Cl=O stretches at 685 and 1250 cm<sup>-1</sup>, respectively and NOF has an N=O stretch at 1990 cm<sup>-1</sup> (compared to 1850 cm<sup>-1</sup> at 25°). No N-F stretch was observed in either the complex or in NOF at -196°, (normally 765 cm<sup>-1</sup> at 25°). The structure of the NOF·ClF<sub>3</sub>O complex is thus uncertain. The NMR data indicate fluorine exchange between N and Cl, but very little contribution from ClF<sub>4</sub>O<sup>-</sup> (424). In fact, a tendency toward the formation of ClF<sub>2</sub>O<sup>+</sup>NF<sub>2</sub>O<sup>-</sup> is indicated, but the transfer may be

\* Thus ClF<sub>3</sub>O is a stronger fluoride donor than ClF<sub>3</sub> or ClO<sub>2</sub>F. This method can be used as a basis of purification, the ClF<sub>3</sub>O regenerated by displacement with NaF.

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incomplete. The IR data probably indicate the presence of bridged fluorine  $F_2ClO-F---NFC$  and  $ON-F---ClF_3O$  as well as the presence of fluorine bridging in solid  $NOF$  alone.

A number of other studies of the reactions of  $ClF_3O$  are summarized in Table XX.

TABLE XX  
REACTIONS OF  $ClF_3O$

<u>Reactants</u>	<u>Conditions</u>	<u>Results</u>	<u>Reference</u>
$ClF_3$		no adduct	81
$NF_3O$		no adduct	81
$N_2F_4$	$-78^\circ$ or $25^\circ$	$NO_2F + NOF$	81
$NO_2F$		$ClO_2F$ , $NOClO_4$ or $NO_2ClO_4$	81
$NO_2$		as with $NO_2F$	81
$NaClO_2$	$-196$ to $-20^\circ$	$ClO_2$ , $NaF$ ; one explosion	81
$CF_2=CF_2$		explosion	81
$N_2F_4$	$-80$ to $+60^\circ$	no rxn.	421
$KrF_2$		no $ClF_5O$	424
$Cl_2O$	$25^\circ$ , 3 days	$ClO_2F$ , some $ClF$	422
$SO_2$	$-80$ to $+45^\circ$	$ClO_2F$ , $SF_2O$ , some $SF_2O_2$ , possibly some $SF_4(SO_3F)_2$	422
$BrF_3$ , $BrF_5$	$25^\circ$	no rxn., misc.	422, 426
$Br_2$	$-80^\circ$ to $25^\circ$	some $ClO_2F$ , $Cl_2$ ; no $BrF_3$	422
$N_2F_4$	$25^\circ$	no rxn.	425
$N_2F_4$	$100^\circ$	v. slow rxn.	425
$NF_3$	$130^\circ$ , 65 hr.	some $NF_3O$ , $NO_2F$ , $NOF$ , $ClF$	425
$Cl_2$	$71-200^\circ$	$ClO_2F$ , $ClF_3$ at low temp.; $O_2$ , $ClF$ at higher temp.	425
$O_2$	$-196$ to $25^\circ$	no rxn.	423

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Alternate synthesis approaches: A host of other synthesis routes to ClF<sub>3</sub>O (and/or ClF<sub>3</sub>O<sub>2</sub> or ClF<sub>5</sub>O) have been attempted since the previous review (284a) and a number of these have led to ClF<sub>3</sub>O. However, the successful methods have generally given low yields or are not suited to scale-up. A number of the successful methods are summarized in Table XXI.

TABLE XXI

ALTERNATE ROUTES TO ClF<sub>3</sub>O

	<u>References</u>
Cl <sub>2</sub> O + F <sub>2</sub> $\xrightarrow{\text{elec. disch.}}$ 45% ClF <sub>5</sub> , some ClF <sub>3</sub> , ClF <sub>3</sub> O, ClO <sub>2</sub> F	346b, 424
NaClO <sub>2</sub> + F <sub>2</sub> $\xrightarrow[\text{exothermic}]{-196^\circ \text{ or } -78^\circ}$ ClO <sub>2</sub> F, NaF, Cl <sub>2</sub> , O <sub>2</sub> , traces ClF <sub>3</sub> O, ClFO (?)	424
ClF <sub>3</sub> + OF <sub>2</sub> $\xrightarrow[\text{Pyrex}]{h\nu}$ ClO <sub>2</sub> F, ClO <sub>2</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup> , SiF <sub>4</sub> , plus some ClO <sub>3</sub> F, ClO <sub>2</sub> and apparently ClF <sub>3</sub> O and ClF <sub>2</sub> O <sup>+</sup> BF <sub>4</sub> <sup>-</sup> .	276a
ClF + OF <sub>2</sub> $\xrightarrow[18 \text{ hr.}, 5500 \text{ psi}]{150^\circ}$ ClF <sub>3</sub> , + 2% ClF <sub>3</sub> O (CsF had no effect)	80
Cl <sub>2</sub> + OF <sub>2</sub> $\xrightarrow[18 \text{ hr.}, 5500 \text{ psi}]{150^\circ}$ ClF <sub>3</sub> , ClF, ClO <sub>2</sub> F, traces ClF <sub>3</sub> O	80
ClO <sub>2</sub> F + ClF <sub>5</sub> $\xrightarrow{h\nu}$ ClF <sub>3</sub> O	426a
ClO <sub>3</sub> F + ClF <sub>5</sub> $\xrightarrow{h\nu}$ ClF <sub>3</sub> O	426a
ClO <sub>2</sub> F + ClF, ClF <sub>3</sub> , OF <sub>2</sub> , $\xrightarrow{h\nu}$ ClF <sub>3</sub> O	346a
ClO <sub>2</sub> F + BrF <sub>5</sub> $\xrightarrow{h\nu}$ some ClF <sub>3</sub> O	346a
ClO <sub>2</sub> F $\xrightarrow[-40^\circ]{h\nu}$ 86% ClF <sub>3</sub> O	346a
ClO <sub>3</sub> F $\xrightarrow[-40^\circ]{h\nu}$ ClF <sub>3</sub> O	346a
ClO <sub>2</sub> F + F <sub>2</sub> $\xrightarrow{h\nu}$ ClF <sub>3</sub> O + ClF <sub>5</sub>	346a
Cl <sub>2</sub> O + F <sub>2</sub> $\xrightarrow{155^\circ}$ ClF <sub>3</sub> O	342
Cl <sub>2</sub> O + F <sub>2</sub> $\xrightarrow{130^\circ}$ ClF <sub>3</sub> O	342

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A number of efforts to produce new Cl-F-O compounds which gave negative or inconclusive results are summarized in Table XXII. Evidence has been obtained for an unstable ClFO (346b), but ClF<sub>5</sub>O has not been prepared.

TABLE XXII

OTHER EFFORTS TO PRODUCE NEW Cl-F-O COMPOUNDS

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
ClF <sub>5</sub> + metal or metalloid oxides, oxygen, or ozone		usually ClO <sub>2</sub> F or ClO <sub>3</sub> F	see Table XVI
ClF <sub>5</sub> + H <sub>2</sub> O or hydrates		usually ClO <sub>2</sub> F or ClO <sub>3</sub> F	see Table XVI
ClF <sub>3</sub> + various agents			see Table XVI
CsF-ClO <sub>2</sub> F complex + F <sub>2</sub>	25°, 2900 psi	some ClF <sub>5</sub> , ClO <sub>3</sub> F, ClO <sub>2</sub> F	75
NaClO <sub>2</sub> + BrF <sub>5</sub>	-50°, then AsF <sub>5</sub> at -20°	some Cl <sub>2</sub> + solid	75
solid from NaClO <sub>2</sub> above	CsF, -20°	ClO <sub>2</sub> F (25%), no FClO	75
LiClO <sub>4</sub> + ClF <sub>5</sub>	-78°	Cl <sub>2</sub> O <sub>7</sub> (4%) + trace unk. w/IR similar to Cl <sub>2</sub> O <sub>7</sub> and ClO <sub>3</sub> OF, mass spec. similar to ClO <sub>3</sub> F, and <sup>19</sup> F resonance at -369 $\phi$ (unk. + H <sub>2</sub> O gave ClO <sub>3</sub> F and F <sup>-</sup> )	76 77
ClO <sub>2</sub> F + PtF <sub>6</sub>	25°	ClO <sub>2</sub> PtF <sub>6</sub> , ClF <sub>5</sub> , ClO <sub>3</sub> F, O <sub>2</sub> PtF <sub>6</sub> ?	79

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TABLE XXII (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$\text{Cl}_2\text{O} + \text{PtF}_6$	25°	$\text{ClO}_2\text{PtF}_6$ , $\text{Cl}_2$ , $\text{O}_2$	79
$\text{CsF} \cdot \text{Cl}_2\text{O} + \text{PtF}_6$	25°	solids, $\text{Cl}_2$ , $\text{O}_2$	79
$\text{Cl}_2\text{O} + \text{ClF}_3 + \text{PtF}_6$	25°	$\text{ClF}_5$ , $\text{Cl}_2$ , $\text{O}_2$	79
$\text{KClO}_3 + 48\% \text{ aq. HF}$	evap.	no rxn. to $\text{KClF}_2\text{O}_2$	79
$\text{ClOSO}_2\text{F} + \text{F}_2$	-78°, 5 days	some $\text{SF}_2\text{O}_2$ and $\text{ClO}_2$	79
$\text{CsSO}_3\text{F} + \text{ClF}_3$	25° or 170°	$\text{SF}_2\text{O}_2$ , $\text{ClO}_2\text{F}$ , $\text{CsClF}_2\text{-4}$	79
$\text{KSO}_3\text{F} + \text{ClF}_3$	25°	no rxn.	79
$\text{KSO}_3\text{F} + \text{ClF}_3$	140-170°	$\text{SF}_2\text{O}_2$ , $\text{O}_2$ , $\text{KClF}_2\text{-4}$	79
$\text{ClO}_3\text{F} + \text{PtF}_6$	25°	No rxn.	79
$\text{ClO}_2\text{F} + \text{IrF}_6$	25°	No rxn.	79
$\text{Cl}_2\text{O} + \text{IrF}_6$	25°	$\text{ClO}_2\text{IrF}_6?$	79
$\text{Mg}(\text{ClO}_4)_2 + \text{F}_2$	$\text{NF}_3$ , -196°	No rxn. (no $\text{ClO}_3\text{OF}$ )	89
$\text{LiClO} + \text{F}_2$	Low temp.	$\text{ClO}_2\text{F}$ , $\text{ClO}_3\text{F}$ , possibly $\text{ClF}_3\text{-5O}$	346
$\text{O} \cdot + \text{ClF}_x$	-150°	$\text{ClO}_2\text{F}$ , $\text{ClO}_3\text{F}$ , $\text{ClO}_2$	346
$\text{ClF}_3 + \text{OF}_2$	100°-400°, static and flow systems	Cl-F-O mixtures	346
$\text{ClF}_3 + \text{OF}_2$	elec. disch., -15, -78 and -196°	Cl-F-O mixtures	346
$\text{ClF}_5 + \text{O}_2$	elec. disch. (static and flow)	Apparently small amounts $\text{ClF}_3\text{O}$	346
$\text{ClF}_5(\text{s}) + \text{OF}_2$	elec. disch., -196°	Apparently small amounts $\text{ClF}_3\text{O}$	346

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TABLE XXII (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
CsF + Cl <sub>2</sub> O + N <sub>2</sub> F <sub>4</sub>		Cl <sub>2</sub> + unident. solid	123
ClONO <sub>2</sub> + ClF <sub>3</sub>	-78°	mostly Cl <sub>2</sub> , some ClO <sub>2</sub> F	123
ClONO <sub>2</sub> + NF <sub>3</sub> O	-78°	No rxn.	123
OF <sub>2</sub> + ClF	-160 to -196°	No rxn. indicated by v.p. and elec. cond. measurements	333
CsClF <sub>4</sub> + OF <sub>2</sub>	175-300°, 580 atm.	O <sub>2</sub> , F <sub>2</sub> ClO <sub>2</sub> F, ClO <sub>3</sub> F, some ClF <sub>5</sub>	334, 336
OF <sub>2</sub> + ClF <sub>3</sub>		ClF <sub>3</sub>	336
OF <sub>2</sub> + ClF <sub>3</sub>	280°, 1350 psig	O <sub>2</sub> , F <sub>2</sub> , ClF <sub>5</sub>	339
OF <sub>2</sub> + CsCl	200°	CsF, O <sub>2</sub> , Cl <sub>2</sub> , some ClF, ClO <sub>2</sub> F	339
OF <sub>2</sub> + ClO <sub>2</sub> F	250°, 825 psig	some dec. of OF <sub>2</sub> + formation of ClO <sub>3</sub> F	339
OF <sub>2</sub> + ClO <sub>3</sub> F	200°, 1110 psig, 20 hr.	No rxn.	339
OF <sub>2</sub> + ClO <sub>2</sub>	110°	ClF <sub>5</sub> , ClO <sub>3</sub> F, ClO <sub>2</sub> F	340
NF <sub>3</sub> + ClO <sub>2</sub>	110°	No rxn.	340
CF <sub>3</sub> OCl + F <sub>2</sub>	-78°	CF <sub>3</sub> OF (no ClFO)	356
O <sub>2</sub> AsF <sub>6</sub> + CsClF <sub>4</sub>	0°	O <sub>2</sub> , Cl <sub>2</sub> , CsAsF <sub>6</sub>	354
Cl <sub>2</sub> -O <sub>2</sub> AsF <sub>6</sub> complex + F <sub>2</sub>	-78°, 5 days	ClO <sub>2</sub> , Cl <sub>2</sub> , O <sub>2</sub> , unident. solid	356
Cl <sub>2</sub> -O <sub>2</sub> AsF <sub>6</sub> complex + F <sub>2</sub>	higher press. than above	O <sub>2</sub> , Cl <sub>2</sub> , ClO <sub>3</sub> F, ClO <sub>2</sub>	357
Cl <sub>2</sub> + 6F <sub>2</sub> + O <sub>2</sub>	elec. disch., -80°	ClO <sub>2</sub> , ClO <sub>2</sub> F, ClO <sub>3</sub> F, ClF <sub>3</sub> , ClF <sub>5</sub> + NOF compounds	420a
ClO <sub>2</sub> F + ClO <sub>2</sub> + F.	elec. disch., -196°	ClO <sub>3</sub> F, (ClO <sub>2</sub> unaffected)	420a
HNF <sub>2</sub> + ClO <sub>3</sub> OF		NOF, ClO <sub>3</sub> F, some N <sub>2</sub> F <sub>4</sub> , NO <sub>2</sub> F, Cl <sub>2</sub>	420a

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TABLE XXII (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
NOF	25°	NO <sub>2</sub> F, ClO <sub>2</sub> F, (ClO <sub>2</sub> w/excess Cl <sub>2</sub> ) + unk. w/IR abs. at 5.8 db., 7.2 hr., 8.4, 9.7 FQR	420a
Cl <sub>2</sub> O + ClF <sub>3</sub>	-50°, NaF	ClO <sub>2</sub> F + ClF	423
Cl <sub>2</sub> O + AgF <sub>2</sub>	flow system -76° to 100°	ClO <sub>2</sub> F, Cl <sub>2</sub>	424
CsClF <sub>4</sub> O + F <sub>2</sub>	50-160°, 750-1200 psi, 16 hr.	ClF <sub>3</sub> O recovered	424
ClF <sub>3</sub> O + F <sub>2</sub>	70 to 284°	no ClF <sub>5</sub> O	421
ClF <sub>3</sub> O + N <sub>2</sub> F <sub>4</sub>	-80° to +60°	no rxn. to ClFO	421
ClF <sub>3</sub> O + KrF <sub>2</sub>		no ClF <sub>5</sub> O	421
Ca(OCl) <sub>2</sub> + F <sub>2</sub>	-80°	ClO <sub>2</sub> F, ClO <sub>3</sub> F	423
Cl <sub>2</sub> O + CF <sub>2</sub> (OF) <sub>2</sub>	-60°, 15 days	dec. of Cl <sub>2</sub> O	425
ClO <sub>2</sub> + F <sub>2</sub>		explosive rxn. to ClF <sub>3</sub> , ClO <sub>2</sub> F, (+O <sub>2</sub> with excess F <sub>2</sub> or Cl <sub>2</sub> with excess ClO <sub>2</sub> )	425
CsF + ClO <sub>2</sub>	-23° or -45°	no obvious complex	425
KClO <sub>4</sub> + F <sub>2</sub>		ClO <sub>2</sub> F + ClO <sub>3</sub> F	424
MClF <sub>4</sub> + H <sub>2</sub> O		MHF <sub>2</sub> , ClO <sub>2</sub> , Cl <sub>2</sub> , ClFO, KClF <sub>4</sub> ·H <sub>2</sub> O	425, 426
ClF <sub>3</sub> O + H <sub>2</sub> O	-16 to +25°	HF, ClO <sub>2</sub> , trace ClFO	425
ClF <sub>3</sub> + O <sub>2</sub>	elec. disch., -196°	ClO <sub>2</sub>	532a
ClF + O <sub>2</sub>	r.f. disch., 4°K	Cl <sub>2</sub> , O <sub>2</sub> , F <sub>2</sub>	532a
ClF <sub>5</sub> + Ar + O <sub>3</sub>	hv (filtered), 4°K	unident. cpd; possibly ClF <sub>5</sub> O, which dec. on warming to ClF <sub>3</sub> , OF <sub>2</sub> (IR bands at 1220, 1210, 664, 657, 646 cm <sup>-1</sup> )	532a

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TABLE XXII (Concluded)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$\text{ClF}_3 + \text{Ar} + \text{O}_3$	4°K	unident. cpd. (possibly $\text{O}_2\text{ClF}_3$ of (284a)). IR bands at 1026, 751, 675, 668 $\text{cm}^{-1}$	535b
$\text{ClF}_3 + \text{Ar} + \text{O}_2$	4°K	as with $\text{O}_3$ above	535b
$\text{ClF}_3 + \text{Ar} + \text{O}_3$	hv, 4°K	$\text{ClO}_2\text{F}$ , $\text{ClFO}$	535b
$\text{ClNF}_2 + \text{O}_2, \text{O}_3$ or $\text{ClO}_2$	hv	no evidence of desired product	535b
$\text{Cl}_2\text{O}-\text{CsF} + \text{ClF}_5$		no $\text{ClF}_3\text{O}$	123
$\text{ClO}_2\text{AsF}_6 + \text{F}_2$	25°	no rxn.	424

## VII-E. Miscellaneous Halogen Compounds

New halogen fluorides: Attempts to generate  $\text{F}_2\text{Cl}-\text{ClF}_2$  by u.v. irradiation of  $\text{Cl}_2$  and  $\text{F}_2$  in argon at 4°K led only to  $\text{ClF}_3$  and  $\text{ClF}$  upon warming (535b). The pressure-temperature relation of the  $\text{ClF}_5-\text{F}_2$  (1:9) system was studied up to 440° and 43,800 psi and was essentially linear (119).

Purification of  $\text{BrF}_5$  can be accomplished by storing it over  $\text{KF}$  at 25° (386) or  $\text{NaF}$  at 100° followed by distillation (78). The complex formed with  $\text{CsF}$ , i.e.,  $\text{CsBrF}_6$  decomposed only at 320° with extensive decomposition of the  $\text{BrF}_5$ .

No evidence was observed for the conversion of solid  $\text{BrF}_5$  (-196°) to  $\text{BrF}_7$  upon exposure to excited  $\text{F}_2$  from an electric discharge (420,420a). Again  $\text{BrF}_7$  was not produced when a  $\text{BrF}_5-\text{F}_2$  mixture was radiated with u.v. light at -40° to -60° (346a). Similar negative results had been obtained in efforts to react  $\text{F}_2$  with  $\text{BrF}_5$  or  $\text{CsBrF}_6$  with heat and pressure. In another study (77) no  $\text{BrF}_7$  was observed after fluorination of  $\text{BrF}_5$  over  $\text{CsF}$  at 250° and 1700 psi for 16 hr. Extensive efforts to prepare  $\text{BrF}_7$  by fluorination of  $\text{BrF}_5$  at very high pressures and temperatures (up to 48,800 psi at 508°C) or under radiation at 25°, or of  $\text{CsBrF}_6$  (at 400°, and 6630 psi) gave inconclusive results (118-120).

An effort to react  $\text{BrF}_5$  with  $\text{ClO}_3\text{OF}$  to give  $\text{BrF}_6^+\text{ClO}_4^-$  resulted only in partial degradation of  $\text{ClO}_3\text{OF}$  to  $\text{ClO}_3\text{F}$  (421). The complex  $\text{BrF}_3 \cdot \text{BF}_3$  has been shown (138) to be in the ionic form  $\text{BrF}_2^+\text{BF}_4^-$  by its high electrical conductivity in  $\text{BrF}_3$  and the presence of the  $\text{BF}_4^-$  band (1020 - 1000  $\text{cm}^{-1}$ ) in the infrared spectrum. It melts at 180° with decomposition. The complex  $\text{NO}_2\text{F} \cdot \text{BrF}_3$  has also been characterized as an ionic material  $\text{NO}_2\text{BrF}_4$  (426). It melts at 27°, has a dissociation pressure of 1 atm. at 45° and a  $\Delta H$  dissociation of 11.7 kcal/mole. The infrared spectrum of  $\text{NO}_2\text{BrF}_4$  shows the  $\text{NO}_2^+$  band at 2385  $\text{cm}^{-1}$  and the  $\text{BrF}_4^-$  band at 665  $\text{cm}^{-1}$  (346a).

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The vapor pressure of  $IF_7$  is described (426a) by the equation:  $\log P_{mm} = 7.6939 - 1356.6/T$ . The mass spectrum of  $IF_7$  shows the  $IF_4^+$  peak as the most intense and no parent peak is observed (346a).

Halogen fluoride oxides: Studies of chloryl fluoride and perchloryl fluoride have not lead to new compounds of interest except, as noted previously, they have been photochemically converted to  $ClF_3O$ . The  $^{19}F$  NMR of  $ClO_2F$  has been more firmly established by independent observations of the resonance at  $-329 \delta$  (78) and  $-321 \delta$  (420a). The results of a number of studies of  $ClO_2F$  reactions are summarized in Table XXIII and of a few studies of  $ClO_3F$  in Table XXIV.

No reaction was observed when either  $BrF_5$  or  $IF_5$  was held at  $25^\circ$  and 100 atm. with an  $O_2 - F_2$  mixture for 8 weeks (333). The reaction of  $BrF_3$  with  $O_3$  in the range  $-196$  to  $-95^\circ$  gave an unidentified compound which decomposed at  $-35^\circ$  (330). Fluorination of the complex  $CsF \cdot Br_2O$  has not yielded  $BrF_3O$  or  $BrF_5O$  (421), nor did fluorination of  $BrONO_2$  which appeared to give a complex of the type  $NO_2F \cdot BrF_xO$  (425). An attempt to prepare  $BrO_2NF_2$  by reaction of  $BrNF_2$  with  $O_3$  in  $CFCl_3$  at  $-78^\circ$  was apparently unsuccessful (123).

Studies on the compound reported in the literature as being  $IF_3O$  have shown it to be in the ionic form  $IO_2^+IF_6^-$  (420a). The  $^{19}F$  NMR of the  $IF_6^-$  ion was established at  $-18 \delta$  (420a).

The vapor pressure and mass spectrum of  $IF_5O$  has been determined (346a). A parent  $IF_5O^+$  peak is observed at an intensity of 32 compared to  $IF_4^+$  at 100. The  $IF_5O$  did not enter into acid-base reactions with either  $CsF$  or  $AsF_5$ . Efforts to convert  $IF_5O$  to  $IF_3O$  or  $IF_3O_2$  by pyrolysis or reaction with  $SiO_2$  were unsuccessful.

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TABLE XXIII

REACTIONS OF ClO<sub>2</sub>F

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
CsF	-22°, 3 hr.	50% ClO <sub>2</sub> F absorbed, unident. component in product by X-ray	75
CsF-ClO <sub>2</sub> F "complex"	80-100°	ClO <sub>2</sub> F evolved	75
CsF	-22°, 19 hr.; 25°, 72 hr.	82% ClO <sub>2</sub> F absorbed, couldn't obtain IR of solid or <sup>19</sup> F NMR in ClO <sub>2</sub> F (liq.)	76
CsF	HF	no NMR evidence of rxn.; don't see ClO <sub>2</sub> F, but see HF exchanging	77
CsF, ClF <sub>5</sub>		" " " "	77
CsF	25°, 4 hr., shaking; and 16 hr., static	Cs/F/Cl ratio of 1:5.4:2.3 in solid	77
NO <sub>2</sub> F	-20°	no NMR evidence of interaction (see ClO <sub>2</sub> F at -329 and NO <sub>2</sub> F at -390 $\phi$ )	78
PtF <sub>6</sub>	25°	ClF <sub>5</sub> , ClO <sub>2</sub> <sup>+</sup> PtF <sub>6</sub> <sup>-</sup> , ClO <sub>3</sub> F, O <sub>2</sub> PtF <sub>6</sub> ?	79
IrF <sub>6</sub>	25°	ClO <sub>2</sub> IrF <sub>6</sub> ?	80
NOF	-78°	"wet" solid with v.p. of 15 mm. at -78°; solid gave two liq. phases at -20 to -15°	337
OF <sub>2</sub>	250°, 825 psig	some dec. of OF <sub>2</sub> and formation of ClO <sub>3</sub> F	339
<u>t</u> -N <sub>2</sub> F <sub>2</sub>	-78° to 25°	no rxn.	340
HNF <sub>2</sub>	as ClO <sub>2</sub> BF <sub>4</sub> , -80°	Deflagration; unident. prod. w/IR abs. at 7.6 & 7.7 $\mu$	420a
ClF	liq.	equilibrium amt. ClFO?	424

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TABLE XXXIII (Concluded)

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
F <sub>2</sub>	elec. disch.	ClF <sub>5</sub> , ClF <sub>3</sub> , ClF, ClO <sub>3</sub> F, SiF <sub>4</sub>	425
F <sub>2</sub>	u.v., 70° or 24°	ClF <sub>3</sub> , ClF <sub>5</sub> (trace ClF <sub>3</sub> O?)	425

TABLE XXXIV

STUDIES OF ClO<sub>3</sub>F

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
SbF <sub>5</sub>	-51°	no reaction noted by elec. cond.	337
SbF <sub>5</sub>	1 hr. each at: 25°, 7000; 100°, 8900; 200°, 11,300 psi	no reaction detected by NMR	75
ClF <sub>3</sub>	w/w.o. CsF	no reaction noted by elec. cond.	337
CsF	25°, 5 hr. or 200° 3200 psi, 6 hr.	no reaction	77
F <sub>2</sub> + CsF	200°, 5900 psi, 18 hr.	some F <sub>2</sub> absorbed which did not revolatilize at 500°. Solid contained Cs:Cl:F ratio of 2.2:1:3	77
F <sub>2</sub> w/w.o. CsF	200°, 6400 psi, 15 hr.	inconsistent results, apparently rxn. w/equipment	78
PtF <sub>6</sub>	25°	no reaction	60
NF <sub>3</sub>	475°, 18 hr.	no reaction	339
<u>t</u> -N <sub>2</sub> F <sub>2</sub>	-78° to 25°	no reaction	340

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## CHAPTER VIII

### OXYGEN FLUORIDES, O-F DERIVATIVES AND MISCELLANEOUS FLUORINATIONS

#### VIII-A. Oxygen Fluorides and Derivatives

The structures of the oxygen fluorides have been studied extensively during the last few years and references to many recent publications are in the bibliography. The existence of the  $O_2F$  radical in liquid  $OF_2$  after exposure to light, and in all of the higher oxygen fluorides has been well demonstrated. It is, of course, iso-electronic with the known  $O_3^-$  ion which forms stable salts. The existence of  $O_3F_2$  as a separate entity has become very doubtful except possibly as a very unstable material.

The reaction chemistry of  $OF_2$ ,  $O_2F_2$ , the C-OF compounds and the  $O_2^+$  salts have been studied at length. The results of most of these studies are summarized in Table XXV.

TABLE XXV

#### STUDIES OF OXYGEN FLUORIDES AND DERIVATIVES

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
liq. $O_3-O_2-OF_2$	4.5% $OF_2$	miscible and stabilized	72,73
liq. $O_3 + OF_2$	v.p. measurements	nonideal soln.	262
$OF_2 + CO_2 + CsF$	-80° to 100°	no rxn.	75
	180°	$CF_3OF$	75
$OF_2 + (CF_3)_2CO$	-50°	slow rxn. to $CF_4$ , $CF_3CFO$	75
$OF_2 + CF_2O + MF$	25° w/ $CsF$ , $RbF$ or $KF$	$(CF_3O)_2O$	76
$OF_2 + SF_4 + CsF$	25°	$SF_6$ , $SF_2O_2$ , some unident. cpd.	76
$OF_2 + CF_3CN + CsF$	140° only	$C_2F_6$ , $CF_3CFO$ , $CO_2$	76
$OF_2 + CsSO_2F$		no rxn.	27
$OF_2 + SF_2O_2 + CsF$	108°	no rxn.	27

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TABLE XXV (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$\text{OF}_2 + \text{SF}_2\text{O} + \text{CsF}$	140°	no rxn. (traces $\text{SF}_2\text{O}_2$ formed at 25°)	77
$\text{OF}_2 + \text{SF}_4\text{O} + \text{CsF}$	-78° to 100°	no rxn. except to form $\text{CsSF}_5\text{O}$	77
$\text{OF}_2 + \text{SF}_4 + \text{CsF}$	25°	$\text{SF}_6$ , $\text{SF}_2\text{O}_2$ , $\text{S}_2\text{F}_{10}$ , ( $\text{SF}_5$ ) $_2\text{O}_2$	77
$\text{OF}_2 + \text{CsSF}_5$		no rxn.	77
$\text{SF}_5\text{OF} + \text{CF}_2\text{O}$	25°, CsF	$\text{CF}_3\text{OF}$ , $\text{CsSF}_5\text{O}$ , $\text{CsCF}_3\text{O}$	77
$\text{CF}_3\text{OF} + \text{SF}_4\text{O}$	100°, CsF	no rxn.	77
$\text{CF}_2(\text{OF})_2 + \text{SF}_4\text{O}$	CsF	$\text{SF}_2\text{O}_2$ , $\text{CF}_3\text{OF}$ , ( $\text{CF}_3\text{O}$ ) $_2$	78
$\text{OF}_2 + \text{SF}_4\text{O}$	25°, KF	no rxn.	78
$\text{OF}_2 + \text{SF}_4\text{O}$	175°, NaF	$\text{SF}_2\text{O}_2$ , $\text{O}_2$	78
$\text{CF}_2(\text{OF})_2 + \text{SO}_2$	CsF	$\text{SF}_2\text{O}_2$ , $\text{CF}_3\text{OF}$ , ( $\text{CF}_3\text{O}$ ) $_2$	78
$\text{CF}_2(\text{OF})_2 + \text{CF}_2\text{O}$	25°, CsF	( $\text{CF}_3\text{O}$ ) $_2\text{O}$ , $\text{CF}_3\text{OF}$ , $\text{O}_2$	78
$\text{CF}_2(\text{OF})_2 + \text{CF}_3\text{CFO}$	25°, CsF	C-C cleavage	78
$\text{OF}_2 + \text{CF}_3\text{CFO}$	115°, NaF	no rxn.	78
$\text{OF}_2 + \text{CF}_3\text{CFO}$	175°, NaF	$\text{CF}_2\text{C}$ , $\text{O}_2$	78
$\text{CF}_3\text{OF} + \text{CO}$	100°, 16 hr.	$\text{CF}_3\text{OCFO}$	78
$\text{SF}_5\text{OF} + \text{CO}$	95°	$\text{SF}_4\text{O}$ , $\text{CF}_2\text{O}$ , $\text{SF}_6$ , $\text{CO}_2$	78
$\text{SF}_5\text{OF} + \text{CO}$	hv, 0 to -35°	$\text{SF}_4\text{O}$ , $\text{CF}_2\text{O}$ , $\text{SF}_6$ , $\text{CO}_2$	78
$\text{CF}_2(\text{OF})_2 + \text{CO}$	CsF	$\text{CF}_4$ , $\text{CF}_2\text{O}$ , $\text{CO}_2$	78
$\text{C}_2\text{F}_5\text{OF} + \text{CO}$	100°	$\text{CF}_4 + \text{CF}_2\text{O}$	78
$\text{OF}_2 + \text{CF}_3\text{CFO}$	25°, CsF	$\text{C}_2\text{F}_5\text{OOF}$ (5%)	79
$\text{OF}_2 + \text{F}_2 + \text{CO}_2$	CsF	$\text{CF}_2(\text{OF})_2$	79

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TABLE XXV (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$\text{OF}_2 + \text{SF}_4$	CsF, $\text{CCl}_4$	$\text{SF}_6$ , $\text{SF}_2\text{O}_2$	79
$\text{OF}_2 + \text{SO}_2$	CsF, $\text{CCl}_4$	$\text{SF}_2\text{O}_2$ , unk. abs. $14 \mu$	79
$\text{OF}_2 + \text{ClF}_3 + \text{KF}$	$25^\circ$ , 48 hr.	$\text{KClF}_4$	79
$\text{OF}_2 + \text{MF} \cdot \text{HNF}_2$	$\text{CFCl}_3$	explosions on warming	79
$\text{OF}_2 + \text{CsN}_3$	$-196$ to $-40^\circ$ , 20 hr.	dark blue solid (reactants explode if warmed too rapidly)	79
$\text{OF}_2 + \text{ClF}$ (w/wo CsF)	$150^\circ$ , 5500 psi, 18 hr.	$\text{ClF}_3$ and 2% $\text{ClF}_3\text{O}$	80
$\text{OF}_2 + \text{Cl}_2$ (w/wo CsF)	$150^\circ$ , 5500 psi, 18 hr.	$\text{ClF}_3$ , $\text{ClF}$ , $\text{ClO}_2\text{F}$ , trace $\text{ClF}_3\text{O}$	80
$\text{OF}_2 + \text{Cl}_2\text{O}$	$150^\circ$ , 5500 psi, 18 hr.	$\text{ClF}_5$ , $\text{ClO}_2\text{F}$	80
$\text{OF}_2 + \text{ClF}_3$	$150^\circ$ , 5500 psi, 18 hr.	some $\text{ClO}_2\text{F}$	80
$\text{CF}_3\text{OF} + \text{NH}_2\text{CFC}$		$\text{CF}_3\text{ONF}_3$ (38%)	259
$\text{O}_2\text{F}_2 + (\text{NaOCO})_2\text{O}$	$-111^\circ$	$\text{CF}_4$ , $\text{CF}_2\text{O}$ , $\text{CO}_2$	264
$\text{F}_2/\text{CsF} + "$	$-183^\circ$ , 1 wk.	sl. rxn. as above	264
$\text{O}_2\text{F}_2 + \text{C}_6\text{F}_6$	$-183^\circ$	vigorous rxn.; explosive solid	264
$\text{O}_3\text{F}_2 + \text{NaOH}$	$-183$ , 24 hr.	v. little rxn.	264
$\text{O}_3\text{F}_2 + \text{NaNO}_3$	$-183$ , 24 hr.	v. little rxn.	264
$\text{O}_3\text{F}_2 + \text{NaNO}_2$	$-183$ , 24 hr.	v. little rxn.	264
$\text{O}_3\text{F}_2 + \text{Ca}$ or $\text{Mg}$		no rxn.	264
$\text{O}_3\text{F}_2 + \text{Li}$ , $\text{Na}$ or $\text{K}$		react smoothly	264
$\text{O}_2\text{F}_2 + \text{SO}_2$		$\text{SF}_2\text{O}_2$ , $\text{O}_2$ ; side rxn. to $\text{FSO}_2\text{OF}$ and $\text{FSO}_2\text{OOF}$	266
$\text{O}_2\text{F}_2 + \text{SF}_2\text{O}$	$-160$	$\text{SF}_4\text{O}$	266

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TABLE XXV (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$O_2AsF_6 + CsClF_4$	$0^\circ$	$O_2, Cl_2, CsAsF_6$	354
$O_2AsF_6 + NO_2ClO_4$	IF5?	$NO_2AsF_6, ClO_3F, Cl_2O_6$ (dec. to $ClO_2, O_2, Cl_2$ at $25^\circ$ )	355
$O_2AsF_6 + CsClO_4$	IF5	$Cl_2O_6$ , etc.	355
$O_2AsF_6 + CsClF_4$	$-78^\circ$ (solids)	3:1 ratio $Cl_2:O_2$	355
$O_2AsF_6 + CsBrF_4$	$-78^\circ$	$F_2, O_2, Br_2, SiF_4$	355
$O_2AsF_6 + Cl_2$	$-78^\circ$	purple 1:1 complex	356
$O_2AsF_6 \cdot Cl_2 + F_2$	$-78^\circ$	$ClO_3F, ClO_2, Cl_2, O_2$	355
$O_2AsF_6 \cdot Cl_2 + NOCl$		$O_2$ , trace $NO_2OF$ , $NOAsF_6?$	355
$CF_2(O_2F)_2 + N_2F_4$		no $-ONF_2$ cpds.	405
$CF_2(O_2F)_2 + KF \cdot HNF_2$		$CF_2(ONF_2)_2$	405
$CF_2(O_2F)_2 + CsCF(CF_3)_2O$		extens. rearrang. to $CF_4$ , $(CF_3)_2CFOOCF_3$ and ex- plosive oxides	436
$OF_2 + CsCF(CF_3)_2O$		as with $CF_2(O_2F)_2$ above	436
$OF_2 + BF_3$	hv, $-196^\circ$	$O_2BF_4$	472
$O_2PtF_6 + F_2$	$62^\circ$ , 1 atm., Teflon	some C-F cpds. (no $OF_4$ )	532d
$N_2O + OF_2 + CsF$	$350^\circ$ , 2700 psi, 4 hr.	no rxn., but exploded on cooling to $315^\circ$ to $NF_3$ , $NF_3O$ , $HNO_3$ , unident. products	532d
$OF_2 + SbF_5$	$-30^\circ$	NMR suggests $OF_2 \cdot SbF_5$	532d
$OF_2 + N_2F_4$	elec. disch., $-78^\circ$	$NF_3, NO_2, SiF_4$	532a
$OF_2 + cis-N_2F_2$	elec. disch., $-78^\circ$	$N_2, F_2, O_2$	532a
$OF_2 + N_2FAsF_6$	$25-112^\circ$ or HF, $25^\circ$	no rxn.	532a

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TABLE XXV (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$O_2F_2 + SF_4O$	$-140^\circ$	no rxn.	266
$O_2F_2 + SF_2O_2$	$-160^\circ$	no rxn.	266
$O_2F_2 + NO_2$	$-130^\circ$	$NO_2F$	266
$OF_2 + HCF_3$	spark	$CF_3OF$	284
$OF_2 + CH_4 + N_2$		some $NO_2OF$	284
$O_3F_2 + SbF_5$		deep purple explosive solid	301
$OF_2 + BF_3, PF_5,$ $AsF_5$ or $SbF_5$	liq. or gases	v.p. studies show no interaction	333
$OF_2 + BF_3, AsF_5$ or $ClF$	$-160$ to $-196^\circ$	elec. cond. shows no rxn.	333, 335
$OF_2 + AsF_5$	$200^\circ$ , 130 atm., 1 wk.	$O_2AsF_6$ (97%)	335
$OF_2 + AsF_5$	$25^\circ$ , 6 wk.	only 3% $O_2AsF_6$	335
$OF_2 + SbF_5$	$130^\circ$ , 200 atm., 3 wk.	$O_2SbF_6$ (98%)	335
$OF_2 + BF_3,$ $PF_5$ or $SiF_4$		no rxn.	335
$OF_2 + ClF_3$	$200^\circ$	$ClF_5$	336
$OF_2 + SbF_5$ or $AsF_5$	$IF_5$ , $25^\circ$	$IF_5 \cdot SbF_5$ (or $IF_5 \cdot AsF_5$ )	335
$OF_2 + SbF_5$	$200^\circ$ , 760 psig, 16 hr.	no rxn.	339
$OF_2 + SF$	$200^\circ$	no rxn.	339
$OF_2 + CsClF_4$		$ClF_5$	336, 339
$OF_2 + ClF_4SbF_6$	$200^\circ$ , 500 psig, 18 hr.	some $O_2, F_2, ClF_5$	339

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TABLE XXV (Concluded)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
OF <sub>2</sub> + CsCl	200°	CsF, O <sub>2</sub> , Cl <sub>2</sub> , ClF, ClO <sub>2</sub> F	339
OF <sub>2</sub> + ClO <sub>2</sub>	110°	ClF <sub>5</sub> , ClO <sub>2</sub> F, ClO <sub>3</sub> F	340
OF <sub>2</sub> + Cl <sub>2</sub> O	130°	ClF <sub>3</sub> O	340
OF <sub>2</sub> + <u>cis</u> -N <sub>2</sub> F <sub>2</sub>	-78° to 150°	some dec. of both	340
OF <sub>2</sub> + Cl <sub>2</sub> (or ClF)	25°	no rxn.	340
OF <sub>2</sub> + Cl <sub>2</sub> (or ClF)	150°	ClF, (ClF <sub>3</sub> ), ClO <sub>2</sub> F	340
O <sub>2</sub> AsF <sub>6</sub> + NO <sub>2</sub> ClO <sub>4</sub>	0°, solids	NO <sub>2</sub> AsF <sub>6</sub> , O <sub>2</sub> (Cl <sub>2</sub> O <sub>6</sub> dec.)	351
O <sub>2</sub> AsF <sub>6</sub> + CsBrF <sub>4</sub>		CsAsF <sub>6</sub> + O <sub>2</sub> , F <sub>2</sub> , Br <sub>2</sub>	352

## VIII-B. Miscellaneous Fluorinations

Table XXVI summarizes the results of a number of studies employing elemental fluorine or CsF.

TABLE XXVI

### MISCELLANEOUS FLUORINATIONS

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
liq. O <sub>3</sub> /O <sub>2</sub> /F <sub>2</sub>	8.5% F	miscible and stabilized	72,73
CsCF <sub>3</sub> O + F <sub>2</sub>	-80°	CF <sub>3</sub> OF (quantatively)	75
CsCF(CF <sub>3</sub> ) <sub>2</sub> O + F <sub>2</sub>	-80°	CF <sub>3</sub> OF + CF <sub>4</sub>	75
NOClF <sub>4</sub> + F <sub>2</sub>	high press. -45 to 300°	NF <sub>3</sub> O, ClF <sub>5</sub> , NO <sub>2</sub> F	75
COS + F <sub>2</sub> /CsF	-78°	CF <sub>2</sub> O + SF <sub>6</sub>	76
N <sub>2</sub> O + F <sub>2</sub> /CsF	200°, 12,000 psi, 4 hr.	no rxn.	76

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TABLE XXVI (Concluded)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
SF <sub>2</sub> O + CsF	150°, 7 hr.	no rxn.	76
SF <sub>2</sub> O + CsF	-78° or -40°, CH <sub>3</sub> CN	sl. abs., unident. IR peak at -51 $\mu$	78
PF <sub>3</sub> O + CsF	40°, 24 hr.	some abs. of PF <sub>3</sub> O	77
PF <sub>3</sub> O + CsF	-30°, CH <sub>3</sub> CN	inconclusive	78
SF <sub>2</sub> O <sub>2</sub> + CsF	-78°	no rxn.	78
CsNO <sub>3</sub> + F <sub>2</sub>	200°, 7100 psi, 4 hr.	NF <sub>3</sub> O, NO <sub>2</sub> F	77
CsF + NOCl	25°	CsCl	77
CsF + Cl <sub>2</sub>	25°, 24 hr.	CsFCl <sub>2</sub> ?	77
CsF + CO <sub>2</sub>	25°, 120 psi, CH <sub>3</sub> OH	Cs <sup>+</sup> CFO <sub>2</sub> <sup>-</sup> ?	77
KNO <sub>3</sub> + F <sub>2</sub>	-196°	no rxn.	89
CF <sub>3</sub> NO + F <sub>2</sub>	125°, AgF <sub>2</sub>	(CF <sub>3</sub> ) <sub>2</sub> NOCF <sub>3</sub>	259
Cl <sub>2</sub> ·O <sub>2</sub> AsF <sub>6</sub> + F <sub>2</sub>	-78°	ClO <sub>3</sub> F, ClO <sub>2</sub> , Cl <sub>2</sub> , O <sub>2</sub>	356, 357
CF <sub>3</sub> OC1 + F <sub>2</sub>		CF <sub>3</sub> OF	356
CsF·FC(O)NF <sub>2</sub> + F <sub>2</sub>		CF <sub>3</sub> OF, NF <sub>3</sub>	436

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APPENDIX A

MELTING POINTS, BOILING POINTS, DENSITIES  
AND REFRACTIVE INDEXES

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TABLE XXVII

MELTING POINTS, BOILING POINTS, DENSITIES  
AND REFRACTIVE INDEXES

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
Ag <sub>1</sub> C <sub>2</sub> H <sub>4</sub> N <sub>4</sub> O <sub>6</sub>	AgN(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> N(NO <sub>2</sub> ) <sub>2</sub>	130				4
AsF <sub>10</sub> N	NF <sub>4</sub> AsF <sub>6</sub>			2.70		489
B <sub>1</sub> C <sub>5</sub> F <sub>4</sub> H <sub>5</sub> N <sub>4</sub> O <sub>4</sub>	CHCHC(NHNO <sub>2</sub> )CHCHN(NO <sub>2</sub> ) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	93-94				5
B <sub>1</sub> C <sub>5</sub> F <sub>4</sub> H <sub>4</sub> N <sub>5</sub> O <sub>6</sub>	CHCHC(N(NO <sub>2</sub> ) <sub>2</sub> )CHCHN(NO <sub>2</sub> ) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	78				5
BC <sub>6</sub> F <sub>4</sub> H <sub>7</sub> N <sub>5</sub> O <sub>4</sub>	CHCHC(N(NO <sub>2</sub> ) <sub>2</sub> )CHCHN(CH <sub>3</sub> ) <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	95 dec.				6
BrCF <sub>6</sub> N <sub>3</sub>	(NF <sub>2</sub> ) <sub>3</sub> C-Br		71 est.			142
BrFO <sub>2</sub> S	SO <sub>2</sub> BrF	-86±0.5	40	2.12 (20°)		52
BrF <sub>3</sub>	BrF <sub>3</sub>			2.8		52
BrF <sub>5</sub>	BrF <sub>5</sub>	-61.3	+40.5			137 359
CFN <sub>3</sub> O <sub>6</sub>	CF(NO <sub>2</sub> ) <sub>3</sub>	-29	88	2.465 (25°)		52
CF <sub>4</sub> O <sub>2</sub>	CF <sub>2</sub> (OF) <sub>2</sub>	-196	-64	1.20 (20°)		52
CF <sub>4</sub> O <sub>4</sub>	C(OF) <sub>4</sub>					294
CF <sub>5</sub> NO <sub>2</sub>	F <sub>2</sub> COF(ONF <sub>2</sub> )		-29	1.60 est.		386

TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
CF <sub>5</sub> N <sub>3</sub>	(NF <sub>2</sub> ) <sub>2</sub> C=NF	-160	-2	1.70		115
CF <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	F <sub>2</sub> C(ONF <sub>2</sub> ) <sub>2</sub>	-196	-9.0 (ext.)	2.01-1.52x 10 <sup>-3</sup> T		386
CF <sub>7</sub> N	CF(NF <sub>2</sub> ) <sub>3</sub>			1.56		51
CF <sub>7</sub> N <sub>3</sub>	CF(NF <sub>2</sub> ) <sub>3</sub>	-135	5.6	1.58 (20)		52
CF <sub>8</sub> N <sub>4</sub>	C(NF <sub>2</sub> ) <sub>4</sub>	-13.5	40	1.68 (20) 1.748 1.60		52 51 294
C <sub>2</sub> ClF <sub>6</sub> H <sub>4</sub> N <sub>5</sub> O <sub>5</sub>	CN <sub>3</sub> F <sub>6</sub> ONCHNH <sub>3</sub> ClO <sub>4</sub>			1.80 est.		292
C <sub>2</sub> F <sub>2</sub> H <sub>4</sub> N <sub>4</sub> O <sub>3</sub>	O <sub>2</sub> NNHC <sub>2</sub> ONHCH <sub>2</sub> NF <sub>2</sub>	83-7				274
C <sub>2</sub> F <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> S	CH <sub>3</sub> SO <sub>2</sub> NHCH <sub>2</sub> NF <sub>2</sub>	74-76				274
C <sub>2</sub> F <sub>4</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	(F <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> NNC <sub>2</sub>		159 est.			274
C <sub>2</sub> F <sub>4</sub> O <sub>2</sub>	CF <sub>3</sub> COOF		-22			90
C <sub>2</sub> F <sub>6</sub> H <sub>2</sub> N <sub>2</sub> O	CN <sub>3</sub> F <sub>6</sub> CONH <sub>2</sub>			1.41 est.		291
C <sub>2</sub> F <sub>6</sub> H <sub>2</sub> N <sub>4</sub> O	(NF <sub>2</sub> ) <sub>3</sub> CCNH <sub>2</sub> <sup>O</sup>			1.41		295
C <sub>2</sub> F <sub>6</sub> H <sub>2</sub> N <sub>6</sub> O <sub>3</sub>	(NF <sub>2</sub> ) <sub>3</sub> C-NH-CO-NH-NO <sub>2</sub>	55-58				86
C <sub>2</sub> F <sub>6</sub> O <sub>4</sub>	FOCF <sub>2</sub> OOCF <sub>2</sub> OF		9			403
C <sub>2</sub> F <sub>7</sub> H <sub>2</sub> N <sub>6</sub> O	CN <sub>3</sub> F <sub>6</sub> NFCONH <sub>2</sub>			1.80		291

TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
C <sub>2</sub> F <sub>7</sub> NO	(CF <sub>3</sub> ) <sub>2</sub> NOF or (CF <sub>3</sub> ) <sub>2</sub> $\overset{\text{F}}{\text{N}} \rightarrow 0$	-69	25 (ext.)			532a
C <sub>2</sub> F <sub>12</sub> N <sub>6</sub> O <sub>2</sub>	CN <sub>3</sub> F <sub>6</sub> OOCN <sub>3</sub> F <sub>6</sub>			1.60 est.		291
C <sub>2</sub> H <sub>4</sub> K <sub>1</sub> N <sub>5</sub> O <sub>6</sub>	KN(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> N(NO <sub>2</sub> ) <sub>2</sub>	130				4
C <sub>2</sub> H <sub>8</sub> N <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> NNH <sub>2</sub>	-57.2	63	0.786 (25)		56
C <sub>3</sub> ClF <sub>6</sub> H <sub>7</sub> N <sub>4</sub> O <sub>5</sub>	CN <sub>3</sub> F <sub>6</sub> OC <sub>2</sub> H <sub>4</sub> NH <sub>3</sub> ClO <sub>4</sub>	221	218			291 241 152
C <sub>3</sub> F <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> ON(OH)CH <sub>2</sub> NF <sub>2</sub>	93-94				274
C <sub>3</sub> F <sub>4</sub> H <sub>2</sub> N <sub>6</sub> O <sub>5</sub>	F <sub>2</sub> NCHN(NO <sub>2</sub> )CON(NO <sub>2</sub> )CHNF <sub>2</sub>	69-70				274
C <sub>3</sub> F <sub>4</sub> H <sub>3</sub> N <sub>6</sub> O <sub>3</sub>	F <sub>2</sub> NCHN(NO <sub>2</sub> )CONHCHNF <sub>2</sub>	85-89 dec.				274
C <sub>3</sub> F <sub>4</sub> H <sub>6</sub> N <sub>4</sub> O	F <sub>2</sub> NCH <sub>2</sub> NHCONHCH <sub>2</sub> NF <sub>2</sub>	162				274
C <sub>3</sub> F <sub>4</sub> H <sub>6</sub> N <sub>6</sub> O <sub>4</sub>	CH <sub>2</sub> [N(CH <sub>2</sub> NF) <sub>2</sub> NO <sub>2</sub> ] <sub>2</sub>	89				274, 179
C <sub>3</sub> F <sub>4</sub> H <sub>7</sub> N <sub>3</sub> O <sub>2</sub> S	CH <sub>3</sub> SO <sub>2</sub> N(CH <sub>2</sub> NF <sub>2</sub> ) <sub>2</sub>	44-46				274
C <sub>3</sub> F <sub>6</sub> H <sub>2</sub> N <sub>6</sub> O	NF <sub>2</sub> C(NF)NHCNHC(NF)NF <sub>2</sub>	95-97 dec.				86
C <sub>3</sub> F <sub>6</sub> H <sub>2</sub> N <sub>6</sub> O <sub>7</sub>	(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> C(NO <sub>2</sub> ) <sub>3</sub>	25 (0.4 mm.)		1.54		174
C <sub>3</sub> F <sub>6</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> CO(NH <sub>2</sub> )			1.65 est.		293
C <sub>3</sub> F <sub>6</sub> H <sub>6</sub> N <sub>4</sub>	N(CH <sub>2</sub> NF <sub>2</sub> ) <sub>3</sub>		166			274

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TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
C <sub>3</sub> F <sub>6</sub> O <sub>5</sub>	(CF <sub>3</sub> OO) <sub>2</sub> CO		60-65 est.			238
C <sub>3</sub> F <sub>7</sub> H <sub>2</sub> N <sub>5</sub> O <sub>5</sub>	(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> CF(NO <sub>2</sub> ) <sub>2</sub>		110			174
C <sub>3</sub> F <sub>12</sub> H <sub>2</sub> N <sub>8</sub> O	[ (NF <sub>2</sub> ) <sub>3</sub> C-NH ] <sub>2</sub> CO			1.88		86
C <sub>3</sub> H <sub>7</sub> N <sub>5</sub> O <sub>6</sub>	CH <sub>3</sub> N(NO <sub>2</sub> )CH <sub>2</sub> CF <sub>2</sub> N(NO <sub>2</sub> ) <sub>2</sub>	29-30				3
C <sub>4</sub> ClF <sub>4</sub> H <sub>7</sub> N <sub>2</sub>	CH <sub>3</sub> C(NF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl		46 (2 mm.)			315
C <sub>4</sub> ClF <sub>4</sub> H <sub>10</sub> N <sub>5</sub> O <sub>4</sub>	NF <sub>2</sub> CH <sub>2</sub> CHNF <sub>2</sub> CH <sub>2</sub> NF <sub>2</sub> CH <sub>2</sub> ClO <sub>4</sub> <sup>⊖</sup>	95 dec.				176
C <sub>4</sub> F <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>2</sub>	[ -C(NF)CONH- ] <sub>2</sub>	156-157				274
C <sub>4</sub> F <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O	CH <sub>2</sub> :CHCONHCH <sub>2</sub> NF <sub>2</sub>	46-48				274
C <sub>4</sub> F <sub>2</sub> H <sub>6</sub> N <sub>6</sub> O <sub>7</sub>	F <sub>2</sub> NCH <sub>2</sub> NHCONHCH <sub>2</sub> C(NO <sub>2</sub> ) <sub>3</sub>	170-171				274
C <sub>4</sub> F <sub>2</sub> H <sub>7</sub> N <sub>5</sub> O <sub>3</sub>	NHC(NNO <sub>2</sub> )NHCH(NF <sub>2</sub> )CH(OCH <sub>3</sub> )	152				274
C <sub>4</sub> F <sub>2</sub> H <sub>8</sub> N <sub>1</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH(NF <sub>2</sub> )		36 (62 mm.)			315
C <sub>4</sub> F <sub>3</sub> H <sub>2</sub> N <sub>5</sub> O	NHC(NF) <sub>2</sub> C(NF)NHC(NF)CO	206-207				274
C <sub>4</sub> F <sub>4</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	N(CHO)CONHCH(NF <sub>2</sub> )CH(NF <sub>2</sub> )	105-107				274
C <sub>4</sub> F <sub>4</sub> H <sub>5</sub> N <sub>5</sub> O <sub>2</sub>	N(CONH <sub>2</sub> )CONHCH(NF <sub>2</sub> )CH(NF <sub>2</sub> )	159-163				274
C <sub>4</sub> F <sub>4</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>	(F <sub>2</sub> NCHNCHO) <sub>2</sub>	184-185				274

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TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
C <sub>4</sub> F <sub>4</sub> H <sub>8</sub> N <sub>2</sub>	CH <sub>3</sub> C(NF <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>		35-36 (56 mm.)			315
C <sub>4</sub> F <sub>4</sub> H <sub>8</sub> N <sub>6</sub> O <sub>6</sub>	F <sub>2</sub> NCH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> NF <sub>2</sub>	166-167				274
C <sub>4</sub> F <sub>6</sub> H <sub>6</sub> N <sub>6</sub> O <sub>9</sub>	(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> C(NO <sub>2</sub> ) <sub>3</sub> (subl.)	106-107 (subl.)				177
C <sub>4</sub> F <sub>6</sub> H <sub>7</sub> N <sub>3</sub>	CH <sub>3</sub> C(NF <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> NF <sub>2</sub>		39 (10 mm.)			315
C <sub>4</sub> F <sub>6</sub> H <sub>7</sub> N <sub>5</sub> O	(F <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> NCNHCH <sub>2</sub> NF <sub>2</sub>	70-74				274
C <sub>4</sub> F <sub>6</sub> H <sub>4</sub> N <sub>4</sub> O	C <sub>4</sub> H <sub>4</sub> (NF <sub>2</sub> ) <sub>4</sub> O			1.604		166
C <sub>4</sub> F <sub>8</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	[-(CH(NF <sub>2</sub> ) <sub>2</sub> O)-] <sub>2</sub>		78-82 (5 mm.) 100-110 (10 mm.)		1.3960 (78)	166
C <sub>4</sub> F <sub>8</sub> H <sub>6</sub> N <sub>4</sub>	C <sub>4</sub> H <sub>6</sub> (NF <sub>2</sub> ) <sub>4</sub>			1.54		174
C <sub>4</sub> F <sub>9</sub> H <sub>2</sub> N <sub>5</sub> O <sub>2</sub>	(NF <sub>2</sub> ) <sub>3</sub> CNHCNHCOCF <sub>3</sub>	81-82				86
C <sub>4</sub> H <sub>7</sub> N <sub>3</sub> O <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CCH <sub>2</sub> N(NO <sub>2</sub> ) <sub>2</sub>	27.5-28.0				3
C <sub>4</sub> H <sub>8</sub> N <sub>5</sub> O <sub>6</sub>	NO <sub>2</sub> -N[CH <sub>2</sub> CH <sub>2</sub> ] <sub>2</sub> N(NO <sub>2</sub> ) <sub>2</sub>	71-72				3
C <sub>4</sub> H <sub>8</sub> N <sub>10</sub> N <sub>11</sub> O <sub>12</sub>	NI[N(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> N(NO <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub>	130				4
C <sub>4</sub> H <sub>9</sub> N <sub>7</sub> O <sub>8</sub>	CH <sub>3</sub> N(NO <sub>2</sub> )CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> N(NO <sub>2</sub> ) <sub>2</sub>	66-67				3
C <sub>5</sub> BrF <sub>4</sub> H <sub>4</sub> N <sub>4</sub> O	(CBr <sub>3</sub> CHNF <sub>2</sub> NH) <sub>2</sub> CO	145				274
C <sub>5</sub> Cl <sub>1</sub> F <sub>12</sub> H <sub>8</sub> N <sub>7</sub> O <sub>6</sub>	[(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> ] <sub>2</sub> CHNH <sub>2</sub> ·HClO <sub>4</sub>	221-222				174

TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
C <sub>5</sub> Cl <sub>4</sub> H <sub>4</sub> N <sub>5</sub> O <sub>10</sub>	$\overline{\text{CHCH}(\text{NHNO}_2)\text{C}(\text{NO}_2)\text{CHN}(\text{NO}_2)^+\text{ClO}_4^-}$	163-164				7
C <sub>5</sub> Cl <sub>4</sub> H <sub>5</sub> N <sub>4</sub> O <sub>8</sub>	$\overline{\text{CHCH}(\text{NHNO}_2)\text{C}_2\text{H}_2\text{N}(\text{NO}_2)^+\text{ClO}_4^-}$	100-102				6
C <sub>5</sub> Cl <sub>3</sub> F <sub>4</sub> H <sub>4</sub> N <sub>4</sub> O	$(\text{CCl}_3\text{CHNF}_2\text{NH})_2\text{CO}$	160				274
C <sub>5</sub> F <sub>2</sub> H <sub>9</sub> NO	$\overline{\text{HOC}(\text{NF}_2)\text{C}_3\text{H}_6\text{CH}_2}$	10				274
C <sub>5</sub> F <sub>2</sub> H <sub>9</sub> N <sub>5</sub> O <sub>3</sub>	$\overline{\text{NHC}(\text{NNO}_2)\text{NHCH}(\text{NF}_2)\text{CH}(\text{OC}_2\text{H}_5)}$	173 dec.				274
C <sub>5</sub> F <sub>4</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>	$\overline{\text{N}(\text{CHO})\text{CH}_2\text{N}(\text{CHO})\text{CH}(\text{NF}_2)\text{CHNF}_2}$	118				274
C <sub>5</sub> F <sub>4</sub> H <sub>6</sub> N <sub>7</sub> O <sub>9</sub>	$(\text{NF}_2)_3\text{COCH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{C}(\text{NO}_2)_3$	109-110				175
C <sub>5</sub> F <sub>4</sub> H <sub>7</sub> N <sub>5</sub> O <sub>6</sub>	$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NO}_2)_3$	39-40				315
C <sub>5</sub> F <sub>4</sub> H <sub>10</sub> N <sub>4</sub> O	$\text{CH}_3\text{CH}(\text{NF}_2)\text{NHCNHCH}(\text{NF}_2)\text{CH}_3$	125 dec.				274
C <sub>5</sub> F <sub>4</sub> H <sub>10</sub> N <sub>4</sub> O	$\text{F}_2\text{NCH}_2\text{NC}_2\text{H}_5\text{CONHCH}_2\text{NF}_2$	52-53				274
C <sub>5</sub> F <sub>5</sub> H <sub>7</sub> N <sub>4</sub> O <sub>4</sub>	$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{F}$		70-72 (4 mm.)			315
C <sub>5</sub> F <sub>6</sub> H <sub>4</sub> N <sub>6</sub> O	$[-\text{C}(\text{NF})-\text{N}(\text{CH}_2\text{NF}_2)-]_2\text{CO}$	162-164				274
C <sub>5</sub> F <sub>6</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>	$\text{CH}_2\text{CHCH}_2\text{CCONHC}(\text{NF}_2)_3$	11.6-12.6				86
C <sub>5</sub> F <sub>6</sub> H <sub>6</sub> N <sub>6</sub> O <sub>9</sub>	$(\text{F}_2\text{N})_3\text{COCH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{C}(\text{NO}_2)_3$	106-108				179
C <sub>5</sub> H <sub>3</sub> N <sub>5</sub> O <sub>6</sub>	$\overline{\text{NCHC}(\text{NO}_2)\text{C}(\text{NHNO}_2)\text{C}(\text{NO}_2)\text{CH}}$	173 dec.				6
C <sub>5</sub> H <sub>3</sub> N <sub>5</sub> O <sub>6</sub>	$(\text{NO}_2)\overline{\text{NCHC}(\text{NO}_2)\text{C}(\text{NNO}_2)\text{CHCH}}$	105				6
C <sub>5</sub> H <sub>3</sub> N <sub>5</sub> O <sub>6</sub>	$\overline{\text{NC}(\text{NHNO}_2)\text{C}(\text{NO}_2)\text{CHC}(\text{NO}_2)\text{CH}}$	163 dec.				5

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TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
C <sub>5</sub> H <sub>4</sub> N <sub>4</sub> O <sub>4</sub>	NC(NHNO <sub>2</sub> )CHCHC(NO <sub>2</sub> )CH	155 dec.				5
C <sub>5</sub> H <sub>4</sub> N <sub>4</sub> O <sub>4</sub>	NCHC(NO <sub>2</sub> )C(NHNO <sub>2</sub> )CHCH	197 dec.				6
C <sub>5</sub> H <sub>4</sub> N <sub>4</sub> O <sub>4</sub>	(NO <sub>2</sub> )NCHCHC(NNO <sub>2</sub> )CHCH	134 (deflagrates)				7
C <sub>5</sub> H <sub>11</sub> N <sub>7</sub> O <sub>8</sub>	C <sub>2</sub> H <sub>5</sub> N(NO <sub>2</sub> )CHN(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> N(NO <sub>2</sub> ) <sub>3</sub>	60-61				3
C <sub>6</sub> F <sub>2</sub> H <sub>8</sub> N <sub>6</sub> O <sub>8</sub>	OCH <sub>2</sub> N[CH <sub>2</sub> C(NO <sub>2</sub> ) <sub>3</sub> ]CON(CH <sub>2</sub> NF <sub>2</sub> )CH <sub>2</sub>	83-85				274
C <sub>6</sub> F <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>	[-C <sub>2</sub> H <sub>4</sub> -CNF <sub>2</sub> (OH)] <sub>2</sub>	145				274
C <sub>6</sub> F <sub>4</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	(F <sub>2</sub> NCHNCOCH <sub>3</sub> ) <sub>2</sub>	194				274
C <sub>6</sub> F <sub>4</sub> H <sub>6</sub> N <sub>4</sub> O <sub>6</sub>	(F <sub>2</sub> NCHNCOCOOH) <sub>2</sub>	160 dec.				274
C <sub>6</sub> F <sub>4</sub> H <sub>10</sub> N <sub>2</sub>	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> C(NF <sub>2</sub> ) <sub>2</sub>		45 (6 mm.)			315
C <sub>6</sub> F <sub>4</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub>	CH <sub>3</sub> C(NF <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(NO <sub>2</sub> )CH <sub>3</sub>	43-45				315
C <sub>6</sub> F <sub>4</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub>	(F <sub>2</sub> NCHNCOOCH <sub>3</sub> ) <sub>2</sub>	222-224 dec.				274
C <sub>6</sub> F <sub>4</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub> S <sub>2</sub>	(CH <sub>3</sub> SO <sub>2</sub> )NCHOCHN(F <sub>2</sub> )N(SO <sub>2</sub> CH <sub>3</sub> )CHOCHN(F <sub>2</sub> )	188 dec.				274
C <sub>6</sub> F <sub>5</sub> H <sub>4</sub> N <sub>3</sub> O <sub>2</sub>	C <sub>6</sub> F <sub>5</sub> (NNO <sub>2</sub> NH <sub>4</sub> )	120 dec.				6
C <sub>6</sub> F <sub>6</sub> H <sub>6</sub> N <sub>6</sub> O <sub>7</sub>	CON(CH <sub>2</sub> NF <sub>2</sub> )CH(NF <sub>2</sub> )CH(NF <sub>2</sub> )N[CH <sub>2</sub> C(NO <sub>2</sub> ) <sub>3</sub> ]	86-87				274
C <sub>6</sub> F <sub>6</sub> H <sub>11</sub> N <sub>3</sub>	CH <sub>3</sub> C(NF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> CNF <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub>	39 (2 mm.)				315
C <sub>6</sub> F <sub>8</sub> H <sub>6</sub> N <sub>6</sub> O <sub>2</sub>	[-(CHNF <sub>2</sub> -) <sub>2</sub> N(CHO)] <sub>2</sub>	171-172				274

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TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
C <sub>6</sub> F <sub>8</sub> H <sub>8</sub> N <sub>4</sub>	[ -C(NF <sub>2</sub> ) <sub>2</sub> C <sub>2</sub> H <sub>4</sub> - ] <sub>2</sub>	107-108 101-103		1.7		274 315
C <sub>6</sub> F <sub>8</sub> H <sub>10</sub> N <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	[ -N(SO <sub>2</sub> CH <sub>3</sub> )(CH(NF <sub>2</sub> )) <sub>2</sub> - ] <sub>2</sub>	235-240 dec.				274
C <sub>6</sub> F <sub>10</sub> H <sub>4</sub> N <sub>4</sub> C <sub>2</sub>	(F <sub>2</sub> NCHNHCOCF <sub>3</sub> ) <sub>2</sub>	183-186				274
C <sub>6</sub> F <sub>12</sub> H <sub>6</sub> N <sub>8</sub> O <sub>8</sub>	[ (NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> CHNO <sub>2</sub> ] <sub>2</sub>			1.709		174
C <sub>6</sub> F <sub>12</sub> H <sub>8</sub> N <sub>6</sub> O <sub>1</sub>	(H <sub>2</sub> CNF <sub>2</sub> CHNF <sub>2</sub> CHNF <sub>2</sub> ) <sub>2</sub> O			1.65		174, 293
C <sub>6</sub> H <sub>4</sub> Li <sub>1</sub> N <sub>5</sub> O <sub>6</sub>	LiN(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> N(NO <sub>2</sub> ) <sub>2</sub>	130				4
C <sub>6</sub> H <sub>4</sub> N <sub>4</sub> O <sub>6</sub>	C(NHNO <sub>2</sub> )CHC(NO <sub>2</sub> )CHC(NO <sub>2</sub> )CH	115-116 dec.				5
C <sub>6</sub> H <sub>12</sub> N <sub>6</sub> O <sub>6</sub>	C[N(NO <sub>2</sub> )H]CH <sub>2</sub> C[N(NO <sub>2</sub> )H]CH <sub>2</sub> C[N(NO <sub>2</sub> )H]CH <sub>2</sub>	210 dec.				3
C <sub>7</sub> F <sub>4</sub> H <sub>5</sub> N <sub>3</sub> O <sub>2</sub>	NO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CH(NF <sub>2</sub> ) <sub>2</sub>	47-49				315
C <sub>7</sub> F <sub>4</sub> H <sub>6</sub> N <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH(NF <sub>2</sub> ) <sub>2</sub>		36 (1 mm.)			315
C <sub>7</sub> F <sub>4</sub> H <sub>8</sub> N <sub>6</sub> O <sub>12</sub>	[ (NO <sub>2</sub> ) <sub>3</sub> CC <sub>2</sub> H <sub>4</sub> ] <sub>2</sub> C(NF <sub>2</sub> ) <sub>2</sub>	81-82				315
C <sub>7</sub> F <sub>4</sub> H <sub>8</sub> N <sub>10</sub> O <sub>13</sub>	[ (O <sub>2</sub> N) <sub>3</sub> CC <sub>2</sub> H <sub>2</sub> N(CH <sub>2</sub> NF <sub>2</sub> ) ] <sub>2</sub> CO	108-109				274
C <sub>7</sub> F <sub>6</sub> H <sub>5</sub> N <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> C(NF <sub>2</sub> ) <sub>3</sub>		48 (1 mm.)			315
C <sub>7</sub> F <sub>12</sub> H <sub>7</sub> N <sub>11</sub> O <sub>10</sub>	(NO <sub>2</sub> ) <sub>3</sub> CC <sub>2</sub> H <sub>2</sub> N(NO <sub>2</sub> )CH[CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	97-98				176
C <sub>8</sub> F <sub>2</sub> H <sub>14</sub> He <sub>1</sub> N <sub>2</sub> O <sub>4</sub>	He[NFCO <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	105-108				16
C <sub>8</sub> F <sub>4</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub>	(F <sub>2</sub> NCHNHCOC≡CH) <sub>2</sub>	160 dec. with- out melting				274

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TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
C <sub>8</sub> F <sub>4</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub>	(F <sub>2</sub> NCHNHCOC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	200-205				274
C <sub>8</sub> F <sub>8</sub> H <sub>10</sub> N <sub>8</sub> O <sub>2</sub>	HC[-N(CH <sub>2</sub> NF <sub>2</sub> )CO-N(CH <sub>2</sub> NF <sub>2</sub> )-] <sub>2</sub> CH	155				274
C <sub>8</sub> F <sub>8</sub> H <sub>12</sub> N <sub>6</sub> O <sub>2</sub>	(F <sub>2</sub> NCHNHCOC <sub>2</sub> H <sub>5</sub> CH <sub>2</sub> NF <sub>2</sub> ) <sub>2</sub>	185 dec.				274
C <sub>8</sub> F <sub>12</sub> H <sub>6</sub> N <sub>10</sub> O <sub>2</sub>	[CH(NF <sub>2</sub> )CH(NF <sub>2</sub> )NHCON(CHNF <sub>2</sub> )-] <sub>2</sub>	~180 dec.				274
C <sub>8</sub> F <sub>12</sub> H <sub>8</sub> N <sub>10</sub> O <sub>10</sub>	[-CH <sub>2</sub> C(NO <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	119-127				178
C <sub>8</sub> F <sub>16</sub> H <sub>10</sub> N <sub>8</sub> O <sub>2</sub>	[NF <sub>2</sub> CH <sub>2</sub> C(NF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OCH(NF <sub>2</sub> )] <sub>2</sub>			1.713 (25)	1.3881 (25)	450
C <sub>9</sub> F <sub>12</sub> H <sub>12</sub> N <sub>12</sub>	NCN(CH <sub>2</sub> NF <sub>2</sub> ) <sub>2</sub> NCN(CH <sub>2</sub> NF <sub>2</sub> ) <sub>2</sub> NCN(CH <sub>2</sub> NF <sub>2</sub> ) <sub>2</sub>	138-140				274
C <sub>9</sub> F <sub>12</sub> H <sub>14</sub> N <sub>6</sub> O <sub>3</sub>	NF <sub>2</sub> CH <sub>2</sub> CHNF <sub>2</sub> OCH <sub>2</sub> CH(OCHNF <sub>2</sub> CH <sub>2</sub> NF <sub>2</sub> )CH <sub>2</sub> OCHNF <sub>2</sub> CH <sub>2</sub> NF <sub>2</sub>			1.535		174
C <sub>10</sub> F <sub>4</sub> H <sub>14</sub> N <sub>4</sub> O <sub>6</sub>	(F <sub>2</sub> NCHNHCOCOC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	200-230 dec.				274
C <sub>10</sub> F <sub>4</sub> H <sub>16</sub> N <sub>4</sub> O <sub>8</sub> S <sub>2</sub>	(CH <sub>3</sub> O <sub>2</sub> S)NC(OAc)C(NF <sub>2</sub> )N(SO <sub>2</sub> CH <sub>3</sub> )C(OAc)CNF <sub>2</sub>	210-220 dec.				274
C <sub>10</sub> F <sub>10</sub> H <sub>14</sub> N <sub>6</sub> O <sub>6</sub>	[HFN(NF <sub>2</sub> ) <sub>2</sub> CO-CH(COOC <sub>2</sub> H <sub>5</sub> )-] <sub>2</sub>	133-135				175
C <sub>10</sub> F <sub>12</sub> H <sub>8</sub> N <sub>10</sub> O <sub>4</sub>	[CH(NF <sub>2</sub> )CH(NF <sub>2</sub> )N(OCH)CON(CHNF <sub>2</sub> )-] <sub>2</sub>	125 dec.				274
C <sub>10</sub> F <sub>12</sub> H <sub>12</sub> N <sub>10</sub> O <sub>2</sub>	[CON(CHNF <sub>2</sub> )CH(NF <sub>2</sub> )CH(NF <sub>2</sub> )N(CH <sub>3</sub> )] <sub>2</sub>	208				274
C <sub>10</sub> F <sub>12</sub> H <sub>12</sub> N <sub>14</sub> O <sub>14</sub>	[-CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> C(NO <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	133-136				179
C <sub>10</sub> F <sub>12</sub> H <sub>16</sub> N <sub>6</sub> O <sub>2</sub>	(NF <sub>2</sub> ) <sub>3</sub> CO-(CH <sub>2</sub> ) <sub>8</sub> -OC(NF <sub>2</sub> ) <sub>3</sub>	100 (0.005 mm.)				179
C <sub>11</sub> F <sub>2</sub> H <sub>10</sub> N <sub>4</sub> O <sub>6</sub>	(C <sub>2</sub> H <sub>5</sub> OOCNH) <sub>2</sub> CHCH(NF <sub>2</sub> )NHCOC <sub>2</sub> H <sub>5</sub>	194-195				274

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TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
C <sub>12</sub> H <sub>6</sub> N <sub>6</sub> O <sub>8</sub>	CHC(NO <sub>2</sub> )CHC(NO <sub>2</sub> )CHCN=NCCHC(NO <sub>2</sub> )CHC(NO <sub>2</sub> )CH					5
C <sub>16</sub> H <sub>16</sub> F <sub>12</sub> N <sub>10</sub> O <sub>2</sub>	[CH(NF <sub>2</sub> )CH(NF <sub>2</sub> )N(C <sub>2</sub> H <sub>5</sub> )CON(CHNF <sub>2</sub> )] <sub>2</sub>	178 dec.				
(C <sub>6</sub> F <sub>12</sub> H <sub>4</sub> N <sub>6</sub> O <sub>3</sub> ) <sub>x</sub>	[O-(CHCH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub> ) <sub>2</sub> ] <sub>x</sub>					
ClFO <sub>3</sub>	ClO <sub>3</sub> F	-146	-46.8	1.712		274
ClF <sub>3</sub>	ClF <sub>3</sub>	-76.3	11.75	1.434 (20°)		174
ClF <sub>3</sub> O	ClF <sub>3</sub> O	-66±	29.4±1	1.8094 (25°)		56
ClF <sub>4</sub> NO <sub>2</sub>	NO <sub>2</sub> ClF <sub>4</sub>	-37.2±0.5	+30±5	1.90± 0.05 (25.5°)		421
ClF <sub>5</sub>	ClF <sub>5</sub>	-103± 4	9.5			429 420a
ClF <sub>8</sub> Sb	ClF <sub>2</sub> SbF <sub>6</sub>	225-228	-14	2.696-3.08 x10 <sup>-3</sup> T		342
ClF <sub>10</sub> Sb	ClF <sub>4</sub> SbF <sub>6</sub>	34-35	-18.1	1.75		359
ClH <sub>4</sub> NO <sub>4</sub>	NH <sub>4</sub> ClO <sub>4</sub>					56 51
ClH <sub>5</sub> N <sub>2</sub> O <sub>4</sub>	N <sub>2</sub> H <sub>5</sub> ClO <sub>4</sub>					342
						342
						174,51
						174

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TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
ClNO <sub>3</sub>	ClNO <sub>3</sub>		+22.3			425
ClNO <sub>6</sub>	NO <sub>2</sub> ClO <sub>4</sub>			2.22		174, 52
Cl <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O <sub>8</sub>	N <sub>2</sub> H <sub>4</sub> (2HClO <sub>4</sub> )			2.20 1.86		174
FNO <sub>2</sub>	NC <sub>2</sub> F	-166	-72.5	1.216 (20)		52
F <sub>2</sub>	F <sub>2</sub>			1.472 (-185)		71
F <sub>2</sub> Kr	KrF <sub>2</sub>	-157				528
F <sub>2</sub> O	OF <sub>2</sub> (77.2° K)			1.755		261
F <sub>2</sub> O	OF <sub>2</sub> (90° K)			1.695		261
F <sub>2</sub> O	OF <sub>2</sub> (120° K)			1.558		261
F <sub>2</sub> O	OF <sub>2</sub> (140° K)			1.466		261
F <sub>2</sub> O	OF <sub>2</sub>	-223.8	-145			301 261 71
F <sub>2</sub> O <sub>3</sub>	O <sub>3</sub> F <sub>2</sub>					263
F <sub>2</sub> O <sub>4</sub>	O <sub>4</sub> F <sub>2</sub>	82.2° K	-79			527
				2.104-0.00455 T 1.694 (-185)		
				1.75		

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TABLE XXVII (Concluded)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm <sup>3</sup> )	refractive index	ref.
Empirical	Structural					
F <sub>3</sub> N	NF <sub>3</sub>	-206.8	-129			301
F <sub>3</sub> NO	NF <sub>3</sub> O	-161.5	-89.1	1.24 (0°)		52
F <sub>3</sub> NS	NSF <sub>3</sub>	-81	-23	1.92 (80°)		52
F <sub>4</sub> N <sub>2</sub>	N <sub>2</sub> F <sub>4</sub>	-168 -163	-74	1.34 (0°)		52 301
F <sub>6</sub> OS	F <sub>5</sub> SOF	-86	-35.1	1.70 (20°)		52
F <sub>6</sub> Xe	XeF <sub>6</sub>			3.0		348
O <sub>3</sub>	O <sub>3</sub>			1.573 (-185°)		71

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APPENDIX B

THERMODYNAMIC PROPERTIES

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TABLE XXVIII

## THERMODYNAMIC PROPERTIES

Formula		$\Delta H_f$ kcal/mole	$\Delta F_f$ kcal/mole	$S^\circ$ E.U.	$C_p^\circ$ cal/°/mole	$H_v$ kcal/mole	$S_v$ E.U.	ref.
Empirical	Structural							
BF <sub>4</sub> O <sub>2</sub>	O <sub>2</sub> BF <sub>4</sub>	-273 est.					351	
BrF	BrF		18.7				137	
BrF <sub>3</sub>	BrF <sub>3</sub>	-72.5	-57				52 137	
CCLF <sub>6</sub> H <sub>3</sub> N <sub>4</sub> O <sub>5</sub>	(NF <sub>2</sub> ) <sub>3</sub> -C-OHF <sub>3</sub> <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	-82					299	
CFN <sub>3</sub> O <sub>6</sub>	CF(NO <sub>2</sub> ) <sub>3</sub>	-37.3 ± 2					52	
CF <sub>2</sub>	CF <sub>2</sub> (g)	-41.00 ± 2.00					159	
CF <sub>4</sub> O <sub>2</sub>	CF <sub>2</sub> (OF) <sub>2</sub>	-130.5 ± 5 -135					52 44	
CF <sub>4</sub> O <sub>4</sub>	C(OF) <sub>4</sub>	-46.6 est.					294	
CF <sub>5</sub> NO	CF <sub>3</sub> ONF <sub>2</sub>	-188.4 ± 2.0 est.					160	
CF <sub>5</sub> N <sub>3</sub>	(NF <sub>2</sub> ) <sub>2</sub> C=NF	+28.2					174	
CF <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	F <sub>2</sub> C(ONF <sub>2</sub> ) <sub>2</sub>				6.3		386	
CF <sub>7</sub> N	CF(NF <sub>2</sub> ) <sub>3</sub>	-50					51	
CF <sub>7</sub> N <sub>3</sub>	CF(NF <sub>2</sub> ) <sub>3</sub>	-46.5 ± 2 -50.0 -48.6 est. -43.3					52 44 294 179	

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TABLE XXVIII (Continued)

Formula		$\Delta H_f$ kcal/mole	$S^\circ$ E.U.	$C_p^\circ$ cal/°/mole	$H_v$ kcal/mole	$S_v$ E.U.	ref.
Empirical	Structural						
$CF_8N_4$	$C(NF_2)_4$	2.6-2.8					151
		+ 6.5					151f
		+6.0					44
$C_2ClF_6H_5N_6O_6$	$CN_3F_6ONCHNH_3ClO_4$	-86 est.					292
$C_2ClF_6H_5N_6O_5$	$(NF_2)_3-C-O-N \begin{matrix} NH_2 \\   \\ C \\   \\ NH_3^+ ClO_4^- \end{matrix}$	-71 est.					295
$C_2Cl_2F_3H_6N_6O_9$	$(F_2N)_3-C-O-N=C-(NH_3^+ClO_4^-)_2$	-98 est.					299
$C_2F_2H_4N_4O_3$	$O_2NNHCNHC_2NF_2$	-134.4 calc.					274
$C_2F_4H_4N_4O_2$	$(F_2NCH_2)_2NNO_2$	-30.1 calc.					274
$C_2F_6H_2N_2O$	$CN_3F_6CONH_2$	-53 est.					291
$C_2F_6H_2N_4O$	$(NF_2)_3CCNH_2$	-53 est.					295
$C_2F_6O_4$	$FOCF_2OOCF_2OF$				6.6		403
$C_2F_7H_2N_5O$	$CN_3F_6NFCONH_2$	-35 est.					291
$C_2F_7NO$	$(CF_3)_2NOF$ or $(CF_3)_2\overset{F}{N} \rightarrow O$				5.5		532a
$C_2F_{12}N_6O_2$	$CN_3F_6OOCN_3F_6$	+12 est.					291
$C_2H_6N_2$	$(CH_3)_2NNH_2$	+12.74 (1)	(1) 39.21		8.37		56
						63°	

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TABLE XXVIII (Continued)

Empirical	Formula	Structural	$\Delta H_f$ kcal/mole	$\Delta F_f$ kcal/mole	$S^\circ$ E.U.	$C_p^\circ$ cal/mole	$H_y$ kcal/mole	$S_y$ E.U.	ref.
$C_3Cl_1F_4H_6N_3O_4$	$NF_2CH_2CHNF_2CH_2NH_3ClO_4$		-90.45					176	
$C_3ClF_6H_7N_4O_5$	$CN_3F_6OC_2H_4NH_2ClO_4$		-103 ± 3 -89.3 113.6 ± 10					291 174 152	
$C_3F_4H_6N_4O$	$F_2NCH_2NHCONHCH_2NF_2$		-128.7 calc.					274	
$C_3F_4H_4N_4O$	$F_2NCHNHCONHCHNF_2$		-153.8					274	
$C_3F_4H_4N_4O_6$	$O_3NCH_2C(NF_2)_2CH_2NO_3$		-60.7 -74.0					174	
$C_3F_6H_2N_6O_7$	$(NF_2)_3COCH_2C(NO_2)_3$		-48.44					174	
$C_3F_6H_4N_4O_2$	$(NF_2)_3COCH_2CO(NF_2)$		-60 est.					295	
$C_3F_6H_6N_4$	$N(CH_2NF_2)_3$		-25.3 calc.					274	
$C_3F_7H_2N_5O_5$	$(NF_2)_3COOH_2CF(NO_2)_2$		-88.4					174	
$C_3F_{12}H_2N_8O$	$[(NF_2)_3C-NH]_2CO$		-82.7 ± 2.2 -73.7 ± 4					152, 86 152	
$C_4ClF_4H_9N_3O_4$	$NF_2CH_2CHNF_2CH_2CH_2NH_3ClO_4$		-97.0					176	
$C_4F_6H_5N_5O_7$	$(NF_2)_3COCH_2CH(ONO_2)CH_2ONO_2$						18.7	178	
$C_4F_8H_4N_4O$	$C_4H_4(NF_2)_4O$		-75.24 -68.5 ± 3.2					166	

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TABLE XXVIII (Continued)

Empirical	Formula Structural	$\Delta H_f$ kcal/mole	$\Delta F_f$ kcal/mole	$S^\circ$ E.U.	$C_p^\circ$ cal/mole	$H_v$ kcal/mole	$S_v$ E.U.	ref.
C <sub>4</sub> F <sub>8</sub> H <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	$[-(CH(NF_2)_2O)]_2$	-91.4 calc.					166	
C <sub>4</sub> F <sub>8</sub> H <sub>6</sub> N <sub>4</sub>	C <sub>4</sub> H <sub>6</sub> (NF <sub>2</sub> ) <sub>4</sub>	-57.49					174	
C <sub>5</sub> Cl <sub>1</sub> F <sub>12</sub> H <sub>8</sub> N <sub>7</sub> O <sub>6</sub>	$[(NF_2)_3COCH_2]_2CHNF_2 \cdot HClO_4$	-113.0					174	
C <sub>5</sub> F <sub>6</sub> H <sub>4</sub> N <sub>6</sub> O	$[-C(NF_2)-N(CH_2NF_2)-]_2CO$	-32.7 calc.					274	
C <sub>5</sub> F <sub>6</sub> H <sub>6</sub> N <sub>8</sub> O <sub>9</sub>	(F <sub>2</sub> N) <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> C(NO <sub>2</sub> ) <sub>3</sub>	-54.9					179	178a
C <sub>5</sub> F <sub>7</sub> H <sub>6</sub> N <sub>7</sub> O <sub>7</sub>	(NO <sub>2</sub> ) <sub>2</sub> CFCH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub>	-95.0			25.3		174	
C <sub>5</sub> F <sub>8</sub> H <sub>6</sub> N <sub>6</sub> O	$[-CHNF_2-N(CH_2NF_2)-]_2CO$	-163.4 calc.					274	
C <sub>5</sub> F <sub>8</sub> H <sub>8</sub> N <sub>6</sub> O	(F <sub>2</sub> NCH <sub>2</sub> ) <sub>2</sub> NCN(CH <sub>2</sub> NF <sub>2</sub> ) <sub>2</sub>	-114.8 calc.					274	
C <sub>5</sub> H <sub>4</sub> N <sub>4</sub> O <sub>4</sub>	(NO <sub>2</sub> )NCH <sub>2</sub> C(NNO <sub>2</sub> )CHCH	+26.3 ± 2.5					7	
C <sub>6</sub> F <sub>6</sub> H <sub>6</sub> N <sub>8</sub> O <sub>7</sub>	CON(CH <sub>2</sub> NF <sub>2</sub> )CH(NF <sub>2</sub> )CH(NF <sub>2</sub> )N[CH <sub>2</sub> C(NO <sub>2</sub> ) <sub>3</sub> ]	-150.0 calc.					274	
C <sub>6</sub> F <sub>6</sub> H <sub>8</sub> N <sub>4</sub> O <sub>10</sub>	(O <sub>2</sub> NOCH <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub>	-139.3 ± 2.7				21.5	178	
C <sub>6</sub> F <sub>8</sub> H <sub>6</sub> N <sub>6</sub> O <sub>2</sub>	$[-CHNF_2-]_2N(CHO)_2$	-71.2 calc.					274	
C <sub>6</sub> F <sub>8</sub> H <sub>8</sub> N <sub>4</sub>	$[-C(NF_2)_2C_2H_4-]_2$	-55.4 calc.				2	274	
C <sub>6</sub> F <sub>12</sub> H <sub>6</sub> N <sub>8</sub> O <sub>8</sub>	$[(NF_2)_3COCH_2CHNO_2]_2$	-119.7					174	
C <sub>6</sub> F <sub>12</sub> H <sub>8</sub> N <sub>6</sub> O <sub>1</sub>	(H <sub>2</sub> CNF <sub>2</sub> CHNF <sub>2</sub> CHNF <sub>2</sub> ) <sub>2</sub> O	-114.26					174	174, 295
		-128.4 ± 8.7						

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TABLE XXVIII (Continued)

Empirical Formula	Structural Formula	$\Delta H_f^\circ$ kcal/mole	$\Delta F_f^\circ$ kcal/mole	$S^\circ$ E.U.	$C_p^\circ$ cal/°/mole	$H_v$ kcal/mole	$S_v$ E.U.	ref.
C <sub>6</sub> F <sub>14</sub> H <sub>5</sub> N <sub>7</sub> O <sub>3</sub>	(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> CH[OC(NF <sub>2</sub> ) <sub>3</sub> ]CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub>	-147.4						174
C <sub>7</sub> Cl <sub>1</sub> F <sub>18</sub> H <sub>9</sub> N <sub>10</sub> O <sub>7</sub>	(NF <sub>2</sub> ) <sub>3</sub> (COCH <sub>2</sub> ) <sub>3</sub> CNF <sub>2</sub> ·HClO <sub>4</sub>	-136.0						174
C <sub>7</sub> F <sub>4</sub> H <sub>8</sub> N <sub>10</sub> O <sub>13</sub>	[(O <sub>2</sub> N) <sub>3</sub> CCH <sub>2</sub> N(CH <sub>2</sub> NF <sub>2</sub> ) <sub>2</sub> ]CO	-111.5 calc.						274
C <sub>7</sub> F <sub>12</sub> H <sub>7</sub> N <sub>11</sub> O <sub>10</sub>	(NO <sub>2</sub> ) <sub>3</sub> CCH <sub>2</sub> N(NO <sub>2</sub> )CH[CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	-93.0						176
C <sub>7</sub> F <sub>12</sub> H <sub>8</sub> N <sub>6</sub> O <sub>4</sub>	[(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> ]CHOCH <sub>2</sub> OCH[CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	-150.0						176
C <sub>7</sub> F <sub>12</sub> H <sub>8</sub> N <sub>8</sub> O <sub>8</sub>	(NF <sub>2</sub> ) <sub>3</sub> (COCH <sub>2</sub> ) <sub>2</sub> C(CH <sub>2</sub> ONF <sub>2</sub> ) <sub>2</sub>	-126.7				23.3		174 178
C <sub>7</sub> F <sub>18</sub> H <sub>6</sub> N <sub>10</sub> O <sub>6</sub>	(NF <sub>2</sub> ) <sub>3</sub> COCH <sub>2</sub> CH[OC(NF <sub>2</sub> ) <sub>3</sub> ]CH(ONO <sub>2</sub> )CH <sub>2</sub> OC(NF <sub>2</sub> ) <sub>3</sub>	-133.6						174
C <sub>8</sub> F <sub>8</sub> H <sub>10</sub> N <sub>6</sub> O <sub>2</sub>	HC[-N(CH <sub>2</sub> NF <sub>2</sub> )CO-N(CH <sub>2</sub> NF <sub>2</sub> )-] <sub>2</sub> CH	-20.0 calc.						274
C <sub>8</sub> F <sub>12</sub> H <sub>8</sub> N <sub>10</sub> O <sub>2</sub>	[CH(NF <sub>2</sub> )CH(NF <sub>2</sub> )NHCN(CH <sub>2</sub> NF <sub>2</sub> )] <sub>2</sub>	-301.2 calc.						274
C <sub>8</sub> F <sub>16</sub> H <sub>8</sub> N <sub>10</sub> O <sub>6</sub>	O <sub>2</sub> NOCH <sub>2</sub> -C-(CH <sub>2</sub> CO[NF <sub>2</sub> ] <sub>2</sub> ) <sub>3</sub>	-186.4 ± 4.7				22.3		178a 178
C <sub>9</sub> F <sub>12</sub> H <sub>12</sub> N <sub>12</sub>	NCN(CH <sub>2</sub> NF <sub>2</sub> ) <sub>2</sub> NCN(CH <sub>2</sub> NF <sub>2</sub> ) <sub>2</sub> NCN(CH <sub>2</sub> NF <sub>2</sub> ) <sub>2</sub>	-47.9 calc.						274

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TABLE XXVIII (Continued)

Formula		$\Delta H_f$ kcal/mole	$\Delta F_f$ kcal/mole	$S^\circ$ E.U.	$C_p^\circ$ cal/mole	$H_v$ kcal/mole	$S_v$ E.U.	ref.
Empirical	Structural							
$C_9F_{12}H_{14}N_6O_3$	$NF_2CH_2CHNF_2OCH_2CH(OCHNF_2CH_2NF_2)CH_2OCHNF_2CH_2NF_2$ -119.45				20.9			174 178
$C_{10}F_{12}H_{12}N_{10}O_2$	$[CON(CHNF_2)CH(NF_2)CH(NF_2)N(CH_3)]_2$ -298.2 calc.							274
$C_{10}F_{16}H_{10}N_{12}O_2$	$[CH(NF_2)CH(NF_2)N(CH_2NF_2)CON(CHNF_2)]_2$ -311.2 calc.							274
$(C_6F_{12}H_4N_6O_3)_n$	$\{O-(CHCH_2OC(NF_2)_3)_2\}_n$	-112.74						174
ClF	ClF		-12.6					137
ClFO <sub>3</sub>	ClO <sub>3</sub> F	-51.2 ± 0.68			0.261 (1)	4.6 (-46.8°)		56
		-10.91						44
ClF <sub>3</sub>	ClF <sub>3</sub>	-45.37 (1)			27.92 (1) (0°)	6.58 (11.75°)		56
			-21.9					137
ClF <sub>3</sub> O	ClF <sub>3</sub> O					7.7		421
ClF <sub>4</sub> O <sub>2</sub>	O <sub>2</sub> ClF <sub>4</sub>	-21 est.						351
ClF <sub>5</sub>	ClF <sub>5</sub>	-55.8±6 -60		87.6				387
				42.3 ± 1.8 calc.	(0.00114) +0.318 (g)	5.330		387, 359 359

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TABLE XXVIII (Continued)

Empirical	Formula		$\Delta H_f$ kcal/mole	$\Delta F_f$ kcal/mole	$S^\circ$ E.U.	$C_p^\circ$ cal/mole	$H_v$ kcal/mole	$S_v$ E.U.	ref.
	Structural								
$ClH_4NO_4$	$NH_4ClO_4$		-70.74					174,51	
$ClH_5N_2O_4$	$N_2H_5ClO_4$		-42.0					174	
$ClNO_3$	$ClNO_3$					6.9		425	
$ClNO_6$	$NO_2ClO_4$		+8.89 +8.0					174 44	
$ClO$	$ClO$		24.2					104	
$ClO_6$	$O_2ClO_4$		+6.4 est.					351	
$ClO_6N$	$NO_2ClO_4$		-8					52	
$Cl_2H_6N_2O_8$	$N_2H_4(2HClO_4)$		-71.82 -77.0 -92.55					174	
$FNO$	$NOF(1)$		-19.7					44	
$FNO_2$	$NO_2F$		-25.8 -22.5					52 44	
$FNO_3$	$NO_3F(1)$		-1.5					44	
$F_2HN$	$HNF_2$		-5.0 ± 0.5					364	
$F_3N$	$NF_3(g)$		31.44					151f	

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TABLE XXVIII (Concluded)

Formula		$\Delta H_f$ kcal/mole	$\Delta F_f$ kcal/mole	$S^\circ$ E.U.	$C_p^\circ$ cal/mole	$H_v$ kcal/mole	$S_v$ E.U.	ref.
Empirical	Structural							
$F_3NO$	$NF_3O$	-36 ± 3						52
		-35.0						44
		-35.5 ± 2.2						142
$F_4N_2$	$N_2F_4$	-5.2						52
					3.170			56
$H_2O_4$	$H_2O_4$	-27.9						330
$NO_3$	$NO_3^-$	-84.2 ± 2.0						469
$NO_5$	$O_2NO_3$	+44 est.						351

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APPENDIX C

MASS, INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRA

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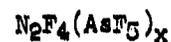
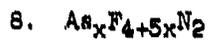
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## TABLE XXIX

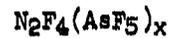
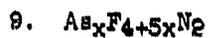
### MASS, INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRA

1. $\text{AgC}_2\text{H}_2\text{N}_5\text{O}_6$	$\text{AgN}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{N}(\text{NO}_2)_2$
IR: (3)	
Mass:	
NMR:	
2. $\text{AsClF}_{10}$	$\text{ClF}_5 \cdot \text{AsF}_5$
IR: (385)	
Mass:	
NMR:	
3. $\text{AsF}_8\text{NO}$	$\text{F}_3\text{NO} \cdot \text{AsF}_5$
IR:	
Mass:	
NMR: (386)	
4. $\text{AsF}_9\text{N}_2$	$\text{N}_2\text{F}_3\text{AsF}_6$
IR: (357)	
Mass:	
NMR:	
5. $\text{AsF}_9\text{N}_2$	$\text{N}_2\text{F}_4 : \text{AsF}_5$
IR: (352)	
Mass:	
NMR: (352)	
6. $\text{AsF}_{10}\text{N}$	$\text{NF}_4\text{AsF}_6$
IR:	
Mass:	
NMR: (477)	
7. $\text{As}_4\text{F}_{26}\text{N}_4\text{O}_7$	$\text{N}_4\text{O}_7\text{F}_2(\text{AsF}_6)_4$
IR: (137)	
Mass:	
NMR:	

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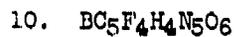


IR: (353)  
Mass:  
NMR: (353)



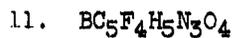
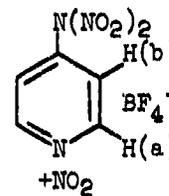
IR: (351)  
Mass:  
NMR: (351)

$F^{19}$ :  $\left. \begin{array}{l} -67 \delta \\ -95 \delta \\ -134 \delta \end{array} \right\} 3 \text{ broad resonances}$



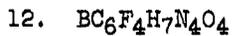
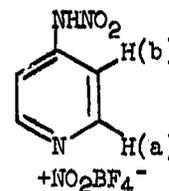
IR: (5)  
Mass:  
NMR: (5)

$H^1$ : (a) 9.64 ppm, doublet  
(b) 8.18 ppm, doublet



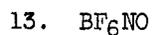
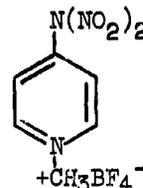
IR:  
Mass:  
NMR: (5)

$H^1$ : (a) 8.62 ppm, doublet  
(b) 8.17 ppm, doublet

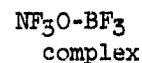


IR:  
Mass:  
NMR: (6)

$H^1$ :  $\nu_{3,5} = 7.55 \text{ ppm}$ ,  $\nu_{2,6} = 8.13 \text{ ppm}$ ,  $J_{2,3} = 7.45 \text{ cps}$



IR: (36)  
Mass:  
NMR:



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14.  $\text{BrCF}_6\text{N}_3$   $(\text{NF}_2)_3\text{C-Br}$   
IR: (142)  
Mass: (142)  
NMR: (142)
15.  $\text{BrC}_4\text{FH}_7\text{NO}_2$   $(\text{CH}_3)_2\text{CHOO}^{\text{F}}\text{C}^{\text{F}}\text{NBr}$   
IR: (17)  
Mass:  
NMR:
16.  $\text{BrF}_4\text{NO}_2$   $\text{NO}_2\text{BrF}_4$   
IR: (426)  
Mass:  
NMR:
17.  $\text{Br}_6\text{C}_5\text{F}_4\text{H}_4\text{N}_4\text{O}$   $(\text{CBr}_3\text{CHNF}_2\text{NH})_2\text{CO}$   
IR: (274)  
Mass:  
NMR:
18.  $\text{CCsF}_3\text{O}$   $\text{Cs}^+\text{OCF}_3^-$   
IR: (75)  
Mass:  
NMR: (75)  
 $\text{F}^{19}$ : +107.5 ppm, singlet,  $-\text{OCF}_3^-$
19.  $\text{CF}_2\text{H}_3\text{N}$   $\text{CH}_3\text{NF}_2$   
IR: (232)  
Mass: (232)  
NMR:
20.  $\text{CF}_4\text{O}$   $\text{CF}_3\text{OF}$   
IR:  
Mass:  
NMR: (284)  
 $\text{F}^{19}$ : 72.5 ppm, doublet, downfield -  $\text{CF}_3$   
142  $\pm$  10 ppm, quartet, downfield - OF

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21.  $CF_5N$

IR: (233)  
Mass: (232)  
NMR:



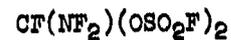
22.  $CF_5NO_2$

IR: (386)  
Mass:  
NMR:



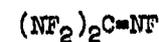
23.  $CF_5NO_6S_2$

IR: (440)  
Mass:  
NMR:



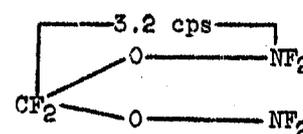
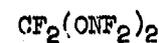
24.  $CF_5N_2$

IR: (115)  
Mass:  
NMR:



25.  $CF_6N_6O$

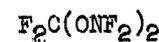
IR: (293)  
Mass: (293)  
NMR: (293)



F19: 126.6 ppm, broad,  $-ONF_2$   
66.2 ppm, pentet,  $>CF_2$

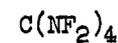
26.  $CF_6N_2O_2$

IR: (385)  
Mass: (385)  
NMR: (385)



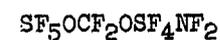
27.  $CF_6N$

IR:  
Mass: (146a)  
NMR:



28.  $CF_{13}NO_2S_2$

IR: (405)  
Mass: (405)  
NMR:



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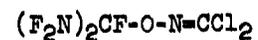
29.  $C_2Cl_2F_3H_2N_2$



IR:  
Mass:  
NMR: (292)

F19: -46.9 ppm  
-21.4 ppm

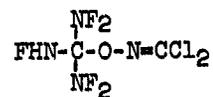
30.  $C_2Cl_2F_5N_3O$



IR:  
Mass:  
NMR: (293)

F19: -20.9 ppm,  $-NF_2$   
116.3 ppm,  $>CF$

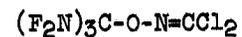
31.  $C_2Cl_2F_5HN_4O$



IR:  
Mass:  
NMR: (293)

F19: -23.4 ppm,  $-NF_2$   
137.5 ppm,  $-NHF$

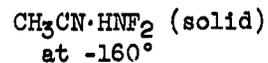
32.  $C_2Cl_2F_6N_4O$



IR: (293)  
Mass: (293)  
NMR: (293)

F19: -25.3 ppm, singlet,  $-NF_2$

33.  $C_2F_2H_4N$



IR: (232)  
Mass:  
NMR:

34.  $C_2F_2H_4N_4O_3$



IR: (274)  
Mass:  
NMR:

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35.  $C_2F_2H_6N_2O_2S$



IR: (274)  
Mass:  
NMR:

36.  $C_2F_4H_6N_4O_2S$



IR: (274)  
Mass:  
NMR:

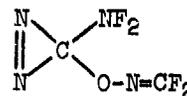
37.  $C_2F_4N_4$



IR: (249)  
Mass: (249)  
NMR: (249)

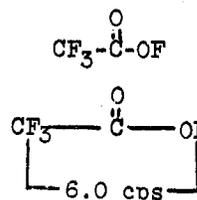
F19: -6.9 ppm, =NF  
79.6 ppm, >CF

38.  $C_2F_4N_4O$



IR: (299)  
Mass:  
NMR:

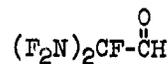
39.  $C_2F_4O_2$



IR: (294)  
Mass:  
NMR: (294)

F19: -188.0 ppm, quartet, OF  
70.8 ppm, doublet, CF<sub>3</sub>

40.  $C_2F_5HN_2O$



IR: (294)  
Mass: (294)  
NMR: (294)

H<sup>1</sup>: 0.34 τ, -C(=O)H  
F19: -22.6 ppm, -NF<sub>2</sub>  
158.0 ppm, >CF

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41.  $C_2F_5H_2N_4O$



IR:  
Mass:  
NMR: (291)

F19: -24.8 ppm,  $-NF_2$   
74.2 ppm,  $\geq NF$   
132.1 ppm,  $\geq CF$

42.  $C_2F_5N_5$



IR: (256)  
Mass:  
NMR: (256)

F19:

Trans -11.4 ppm F

$N=C$   $NF_2$  -45.4 ppm

$N=N$  F -9.1 ppm

$C=N$  F 80.8 ppm

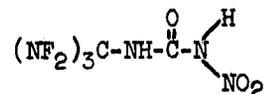
Cis -18.3 ppm F

$N=C$   $NF_2$  -41.2 ppm

$N=N$  F -8.9 ppm

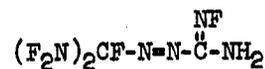
$C=N$  F 80.4 ppm

43.  $C_2F_6H_2N_2O_3$



IR: (86)  
Mass:  
NMR: (86)

44.  $C_2F_6H_2N_6$



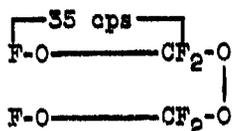
IR: (251)  
Mass:  
NMR: (251)

H<sup>1</sup>: 4.69  $\tau$ ,  $-NH_2$   
F19: -20.8 ppm,  $-NF_2$   
+9.2 ppm,  $=NF$   
137.6 ppm,  $\geq CF$

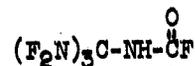


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48. C<sub>2</sub>F<sub>6</sub>O<sub>4</sub> (Concluded)



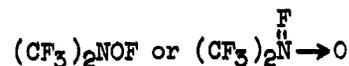
49. C<sub>2</sub>F<sub>7</sub>HN<sub>4</sub>O



IR:  
Mass:  
NMR: (295)

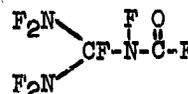
Fl<sub>9</sub>: -27.6 ppm, -NF<sub>2</sub>  
+1.5 ppm, -C(=O)F

50. C<sub>2</sub>F<sub>7</sub>NO



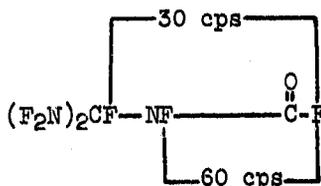
IR:  
Mass:  
NMR: (532a)

51. C<sub>2</sub>F<sub>7</sub>N<sub>2</sub>O

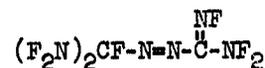


IR: (292)  
Mass:  
NMR: (292)

Fl<sub>9</sub>: -23.6 ppm, -NF<sub>2</sub>  
9.6 ppm, doublet of doublets, -C(=O)F  
72.4 ppm, >NF  
132.9 ppm, >CF



52. C<sub>2</sub>F<sub>8</sub>N<sub>6</sub>

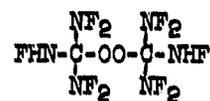


IR:  
Mass: (249)  
NMR:

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53.  $C_2F_{10}H_2N_6O_2$

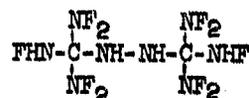
IR:  
Mass:  
NMR: (296)



F<sup>19</sup>: -22.2 ppm, -NF<sub>2</sub>  
+138.6 ppm, -NHF

54.  $C_2F_{10}H_4N_8$

IR:  
Mass:  
NMR: (291)

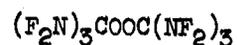


H<sup>1</sup>: 4.3 τ, singlet, >NH  
0.8 τ, doublet, -NHF

F<sup>19</sup>: -21.3 ppm, doublet, -NF<sub>2</sub>

55.  $C_2F_{12}N_6O_2$

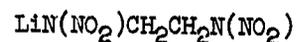
IR:  
Mass:  
NMR: (296)



F<sup>19</sup>: -25.2 ppm, -C(NF<sub>2</sub>)<sub>3</sub>

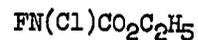
56.  $C_2H_4LiN_4O_4$

IR: (4)  
Mass:  
NMR:



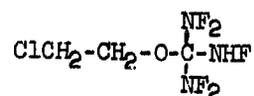
57.  $C_3ClF_5H_5NO_2$

IR: (18)  
Mass:  
NMR:



58.  $C_3ClF_5H_5N_3O$

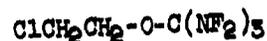
IR:  
Mass:  
NMR: (293)



F<sup>19</sup>: -21.5 ppm, -NF<sub>2</sub>  
141.3 ppm, -NHF

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59.  $C_3ClF_6H_4N_3O$

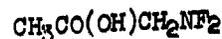


IR: (293)  
Mass:  
NMR: (293)

$H^1$ : 5.40  $\tau$ , triplet,  $-CH_2O-$   
6.29  $\tau$ , triplet,  $ClCH_2-$

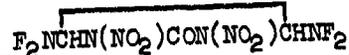
$F^{19}$ : -23.1 ppm,  $-NF_2$

60.  $C_3F_2H_6N_2O_2$



IR: (274)  
Mass:  
NMR:

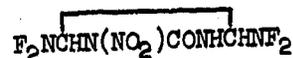
61.  $C_3F_4H_2N_6O_5$



IR: (274)  
Mass:  
NMR: (274,

$H^1$ : Triplet centered at 3.1  $\tau$ ,  $J = 16$  cps

62.  $C_3F_4H_3N_5O_3$



IR: (274)  
Mass:  
NMR: (274)

$H^1$ : Triplet 4.35  $\tau$  ( $J = 18$  cps)  
3.45  $\tau$  ( $J = 18$  cps)  
Broad singlet 1.74  $\tau$  (NH)

$F^{19}$ : Triplet at -32.5  $\delta$  ( $J = 18$  cps)

63.  $C_3F_4H_4N_4O$



IR: (274)  
Mass:  
NMR: (274)

$H^1$ : Triplet at 4.39  $\tau$ ,  $J = 18$  cps (CH) each peak split by  $^{14}N$   $J = 1.8$  cps  
Broad singlet at 2.12  $\tau$  (NH)

$F^{19}$ : Triplet at -31.6  $\delta$ ,  $J = 15$  cps

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64.  $C_3F_4H_6N_4O$

IR: (274)

Mass:

NMR:



65.  $C_3F_4H_6N_6O_4$

IR: (274)

Mass:

NMR:

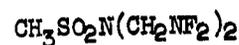


66.  $C_3F_4H_7N_3O_2S$

IR: (274)

Mass:

NMR:

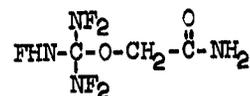


67.  $C_3F_5H_5N_9O_2$

IR:

Mass:

NMR: (85c)



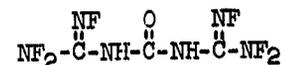
$F^{19}$ : -21.0 ppm,  $-NF_2$   
142.6 ppm,  $-NHF$

68.  $C_3F_6H_2N_6O$

IR: (86)

Mass:

NMR: (86)

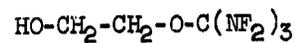


69.  $C_3F_6H_5N_3O_2$

IR: (294)

Mass:

NMR: (294)

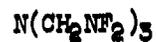


$H^1$ : 5.49  $\tau$ , triplet,  $-CH_2-O-C$   
6.10  $\tau$ , triplet,  $-CH_2OH$   
5.97  $\tau$ ,  $-OH$

$F^{19}$ : -23.3 ppm,  $-NF_2$

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70.  $C_3F_6H_6N_4$



IR: (274)

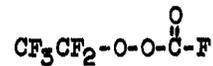
Mass:

NMR: (274)

H1: 5.43  $\tau$ , triplet, J = 24 cps

F19: -42.7  $\delta$ , triplet, J = 24 cps

71.  $C_3F_6O_3$



IR: (296)

Mass: (296)

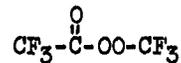
NMR: (296)

F19: 33 ppm, -C(=O)F

83.0 ppm, -CF<sub>3</sub>

95.8 ppm, >CF<sub>2</sub>

72.  $C_3F_6O_3$



IR: (296)

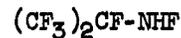
Mass: (296)

NMR: (296)

F19: 68.9 ppm, singlet, -OCF<sub>3</sub>

72.0 ppm, singlet, CF<sub>3</sub>C(=O)-

73.  $C_3F_8HN$



IR:

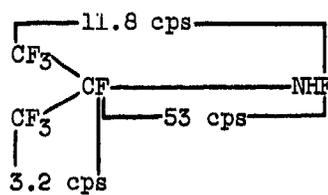
Mass:

NMR: (296)

F19: 76.1 ppm, -CF<sub>3</sub>

134.9 ppm, -NHF

151.2 ppm, >CF

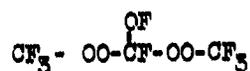
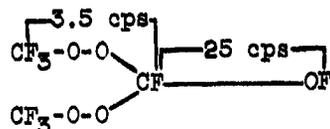


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74.  $C_3F_8O_5$

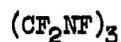
IR: (296)  
Mass: (296)  
NMR: (296)

F19: -168.0 ppm, doublet, -OF  
68.7 ppm, doublet, -CF<sub>3</sub>  
90.6 ppm, complex, >CF



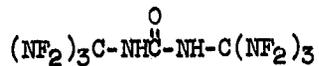
75.  $C_3F_9N_3$

IR: (235)  
Mass:  
NMR:



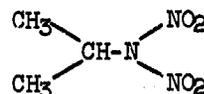
76.  $C_3F_{12}H_2N_2O$

IR: (86)(164)  
Mass:  
NMR: (86)(164)



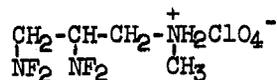
77.  $C_3H_7N_3O_4$

IR: (6)  
Mass:  
NMR:



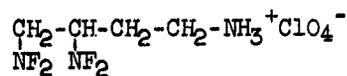
78.  $C_4ClF_4H_{10}N_3O_4$

IR: (176)  
Mass:  
NMR:



79.  $C_4ClF_4H_{10}N_3O_4$

IR: (176)  
Mass:  
NMR:

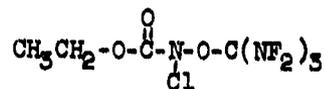


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80.  $C_4ClF_6H_5N_4O_4$

IR:  
Mass:  
NMR: (292)

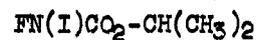
$\tau_{19}$ : -26.9 ppm,  $-C(NF_2)_3$



81.  $C_4FH_7INO_2$

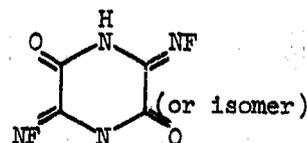
IR:  
Mass:  
NMR: (17)

$\tau_{19}$ : +25 ppm



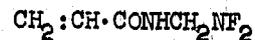
82.  $C_4F_2H_2N_4O_2$

IR: (274)  
Mass:  
NMR:



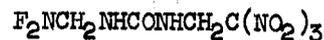
83.  $C_4F_2H_6N_2O$

IR: (274)  
Mass:  
NMR:



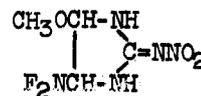
84.  $C_4F_2H_6N_6O_7$

IR: (274)  
Mass:  
NMR:



85.  $C_4F_2H_7N_5O_3$

IR: (274)  
Mass:  
NMR: (274)



$H^1$ : Complex series (ring CH) region  
CH<sub>3</sub> peaks obscured by solvent  
NH absorptions 0.72 and 1.21  $\tau$   $C_2H_5$

$\tau_{19}$ : Two doublets centered at -38.8  $\delta$  ( $J = 27$  cps) and -41.6  $\delta$   
( $J = 18$  cps)

86.  $C_4F_2H_8N_2O_2$

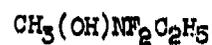
IR: (274)  
Mass:  
NMR:



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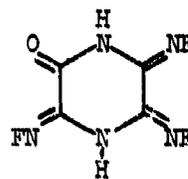
87.  $C_4F_2H_9NO$

IR: (274)  
Mass:  
NMR:



88.  $C_4F_3H_2N_5O$

IR: (274)  
Mass:  
NMR:



89.  $C_4F_3H_5N_2O_2$

IR: (10)  
Mass:  
NMR: (10)



$F^{19}$ : 15.0, singlet, broad,  $NF = CF$   
53.2, doublet,  $-NFCO-$ ,  $J = \sim 26$  cps  
63.4, doublet of doublets,  $=CF-$ , fluorimino fluorine coupled with  $-CF-$ , 13 cps

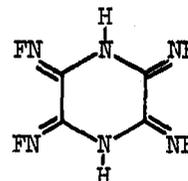
90.  $C_4F_3H_7N_2O_2$

IR: (274)  
Mass:  
NMR:



91.  $C_4F_4H_2N_6$

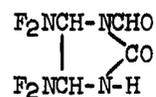
IR: (274)  
Mass:  
NMR: (274)



$H^1$ : 6.41  $\tau$  (solvent)  
-0.30  $\tau$  (solvent)  
6.35  $\tau$  (MeCN?)  
 $F^{19}$ : +24.0  $\delta$

92.  $C_4F_4H_4N_4O_2$

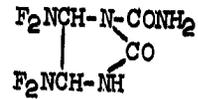
IR: (274)  
Mass:  
NMR:



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93.  $C_4F_4H_5O_2$

IR: (274)  
Mass:  
NMR: (274)

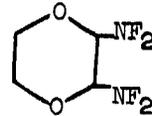


$H^1$ : 2.45  $\tau$ , 3.18  $\tau$ , (NH), broad peaks  
3.98  $\tau$ , quadruplet,  $J = 17$  cps  
4.05  $\tau$ , doublet,  $J = 24$  cps (CH)

$F^{19}$ : -28.7  $\delta$ , doublet  $J = 27$  cps  
-30.8  $\delta$ , quintuplet,  $J = 17$  cps

94.  $C_4F_4H_6N_2O_2$

IR: (274)  
Mass:  
NMR:



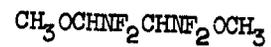
95.  $C_4F_4H_6N_4O_2$

IR: (274)  
Mass:  
NMR:



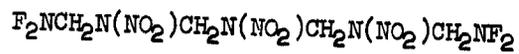
96.  $C_4F_4H_8N_2O_2$

IR: (274)  
Mass:  
NMR:



97.  $C_4F_4H_8N_8O_6$

IR: (274)  
Mass:  
NMR:

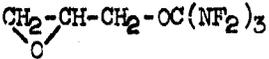
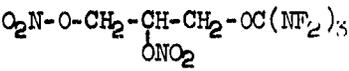


98.  $C_4F_4H_{10}N_4O_4S_2$

IR: (274)  
Mass:  
NMR:

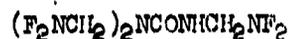


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99.  $C_4F_5H_5O_2$   $NF_2CF_2NFCO_2C_2H_5$
- IR: (46)  
Mass:  
NMR: (46)
- F19: -19.8 ppm, singlet, broadened,  $NF_2$   
+77.4 ppm, singlet  $NFCO$   
+97.9 ppm, doublet ( $J = 12$  cps)  $-CF_2$
100.  $C_4F_6H_5N_3O_2$   $CH_2-CH-CH_2-OC(NF_2)_3$   

- IR: (175)  
Mass:  
NMR:
101.  $C_4F_6H_5N_5O_7$   $O_2N-O-CH_2-CH-CH_2-OC(NF_2)_3$   

- IR: (177)  
Mass:  
NMR: (177)
- H<sup>1</sup>: 4.42  $\tau$ ,  $\text{>CH}$   
5.20  $\tau$ ,  $\text{>CH}_2$
102.  $C_4F_6H_6N_4O_3$   $(F_2N)_3CON=C(OCH_3)_2$
- IR: (296)  
Mass:  
NMR: (296)
- H<sup>1</sup>: 6.12  $\tau$  }  $-CH_3$   
6.16  $\tau$  }
- F19: -24.0 ppm,  $-NF_2$
103.  $C_4F_6H_6N_4O_3$   $CH_2CH_3-O-\overset{O}{\parallel}C-NH-O-C(NF_2)_3$
- IR:  
Mass:  
NMR: (292)
- H<sup>1</sup>: 8.7  $\tau$ , triplet,  $CH_3^-$   
5.71  $\tau$ , quartet,  $\text{>CH}_2$   
0.55  $\tau$ , singlet,  $\text{>NH}$
- F19: -24.5 ppm,  $-NF_2$

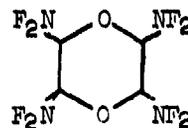
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104. C<sub>4</sub>F<sub>8</sub>H<sub>7</sub>N<sub>5</sub>O



IR: (274)  
Mass:  
NMR:

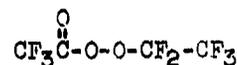
105. C<sub>4</sub>F<sub>8</sub>H<sub>4</sub>N<sub>4</sub>O<sub>2</sub>



IR: (274)  
Mass:  
NMR: (274)

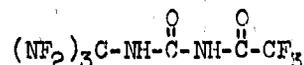
$\text{H}^1$ : 4.49  $\tau$ , triplet, J = 19 cps  
 $\text{F}^{19}$ : -34.3  $\delta$ , doublet, J = 20 cps  
-33.6  $\delta$ , doublet, J = 20 cps  
31.2  $\delta$ , broad band (Impurity ?)

106. C<sub>4</sub>F<sub>8</sub>O<sub>3</sub>



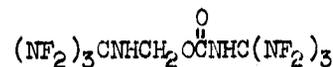
IR: (296)  
Mass: (296)  
NMR:

107. C<sub>4</sub>F<sub>9</sub>H<sub>2</sub>N<sub>5</sub>O<sub>2</sub>



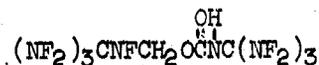
IR: (86)  
Mass:  
NMR: (86)

108. C<sub>4</sub>F<sub>12</sub>H<sub>4</sub>N<sub>8</sub>O<sub>2</sub>



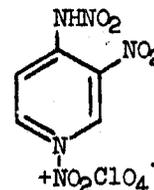
IR: (163)  
Mass:  
NMR: (163)

109. C<sub>4</sub>F<sub>13</sub>H<sub>3</sub>N<sub>7</sub>O<sub>2</sub>



IR: (163)  
Mass:  
NMR: (163)

110. C<sub>5</sub>ClH<sub>4</sub>N<sub>4</sub>O<sub>10</sub>



IR: (6)  
Mass:  
NMR: (6)

$\text{H}^1$ :  $\nu_2 = 8.89$  ppm,  $\nu_5 = 7.53$  ppm,  $\nu_6 = 8.13$  ppm  
 $J_{5,6} = 7.22$  cps,  $J_{2,6} \sim 0.3$  cps

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111.  $C_5ClH_5N_4O_8$

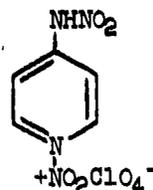
IR: (6)

Mass:

NMR: (6)

$H^1$ : singlet,  $\nu_{NH} = 9.89$

two doublets:  $\begin{cases} \nu_{2,6} = 8.91 \text{ ppm} \\ \nu_{3,5} = 6.75 \text{ ppm} \end{cases} J_{2,3} = 6.08 \text{ cps}$



112.  $C_5Cl_6F_4H_4N_4O$

IR: (274)

Mass:

NMR:

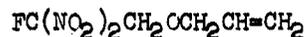


113.  $C_5FH_7N_2O_5$

IR: (49)

Mass:

NMR: (49)



$H^1$ :  $\delta = 5.56 - 6.20$  (12 line pattern, doublet of doublet of triplets)

$J_{cis} = 9 \text{ cps}$ ,  $J_{trans} = 17.5 \text{ cps}$ ,  $J_{allyl} = 5.5 \text{ cps}$

Internal olefin proton at a terminal vinyl group

$\delta = 5.06 - 5.51$  superposition of multiplets (external olefin protons of vinyl group)

$\delta = 4.58$ , doublet ( $J_{HF} = 18 \text{ cps}$ )  $CH_2$  in the fluorodinitroethyl moiety

$\delta = 4.15$ , doublet ( $J = 5.5 \text{ cps}$ ) allylic  $CH_2$

$F^{19}$ :  $\delta = 111.0$ , triplet,  $J_{HF} \approx 15 \text{ cps}$ , fluorine in the fluorodinitro-methyl moiety

114.  $C_5FH_{10}NO_4S$

IR:

Mass:

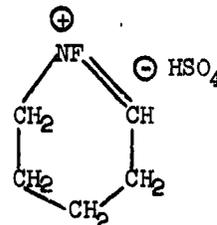
NMR: (45)

$H^1$ : 116, 137 cps, multiplet

3.13, 3.10 ppm (TMH)

4.28,  $J_{doublet} = 2.8 \pm 0.3 \text{ cps}$

8.83,  $J_{doublet}$ ,  $25.2 \pm 0.4 \text{ cps}$ ,  $J_{triplet} \approx 3 \text{ cps}$  pair of unresolved triplets



$F^{19}$ :  $-157.53 \pm 0.03 \text{ ppm}$ , broad doublet (NF),  $J = 24.1 \pm 0.5 \text{ cps}$

115.  $C_5F_2H_9NO$

IR: (274)

Mass:

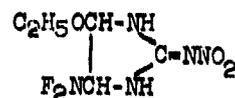
NMR:



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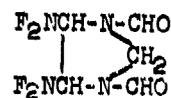
116.  $C_5F_2H_9N_5O_3$

IR: (274)  
Mass:  
NMR:



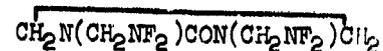
117.  $C_5F_4H_6N_4O_2$

IR: (274)  
Mass:  
NMR:



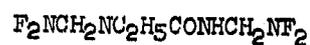
118.  $C_5F_4H_8N_4O$

IR: (274)  
Mass:  
NMR:



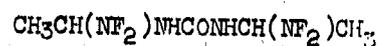
119.  $C_5F_4H_{10}N_4O$

IR: (274)  
Mass:  
NMR:



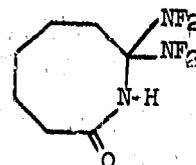
120.  $C_5F_4H_{10}N_4O$

IR: (274)  
Mass:  
NMR:



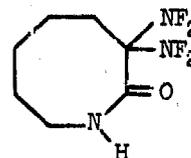
121.  $C_5F_4H_{11}N_3O$

IR: (451)  
Mass:  
NMR: (451)



122.  $C_5F_4H_{11}N_3O$

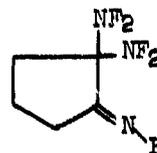
IR: (451)  
Mass:  
NMR: (451)



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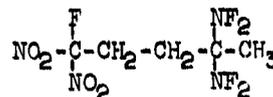
123. C<sub>5</sub>F<sub>5</sub>H<sub>6</sub>N<sub>3</sub>

IR: (440)  
Mass:  
NMR: (440)



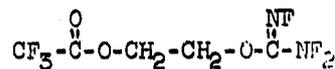
124. C<sub>5</sub>F<sub>5</sub>H<sub>7</sub>N<sub>4</sub>O<sub>4</sub>

IR: (315)  
Mass:  
NMR:



125. C<sub>5</sub>F<sub>6</sub>H<sub>4</sub>N<sub>2</sub>O<sub>3</sub>

IR: (294)  
Mass:  
NMR: (294)

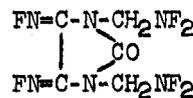


H<sup>1</sup>: 5.5 τ, >CH<sub>2</sub>, mixture of isomers

F <sup>19</sup> :	Isomer	Peak	Assignment
	A, B	75.7 ppm	CF <sub>3</sub>
	A	-43.0 ppm	-NF <sub>2</sub>
		40.8 ppm	=NF
	B	-37.7 ppm	-NF <sub>2</sub>
		49.0 ppm	=NF

126. C<sub>5</sub>F<sub>6</sub>H<sub>4</sub>N<sub>6</sub>O

IR: (274)  
Mass:  
NMR: (274)

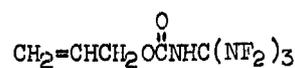


H<sup>1</sup>: 4.41 τ, triplet (J = 24 cps)

F<sup>19</sup>: +31.4 δ, single peak (C:NF)  
-44.0 δ, triplet (J = 24 cps)(CH<sub>2</sub>NF<sub>2</sub>)

127. C<sub>5</sub>F<sub>6</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub>

IR: (86)  
Mass:  
NMR: (86)

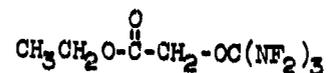


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128.  $C_5F_6H_7N_3O_3$

IR:  
Mass:  
NMR: (294)

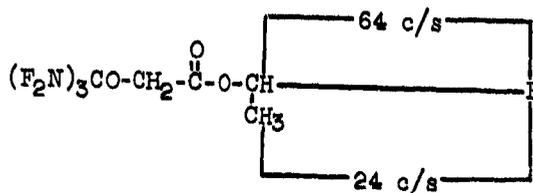
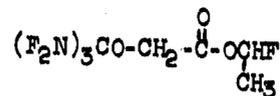
F19: -22.8 ppm,  $-NF_2$



129.  $C_5F_7H_6N_3O_3$

IR:  
Mass:  
NMR: (294)

F19: -23 ppm,  $-NF_2$   
+123.1 ppm, doublet of quartets,  $>CF$

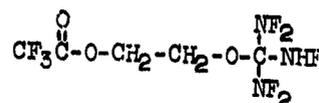


130.  $C_5F_8H_5N_3O_3$

IR: (294)  
Mass:  
NMR: (294)

H1: 1.25  $\tau$ ,  $-NHF$   
5.4  $\tau$ ,  $-CH_2$

F19: -21.3 ppm,  $-NF_2$   
76.0 ppm,  $-CF_3$   
139.1 ppm,  $-NHF$

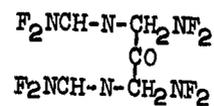


131.  $C_5F_8H_6N_6O$

IR: (274)  
Mass:  
NMR: (274)

H1: 15 peaks (triplet and pair of sextuplets) 4.15 - 5.72  $\tau$   
 $CH_2$  groups and nonequivalent ring CH-rings

F19: -30.5  $\delta$ , doublet,  $J = 18$  cps,  $CHNF_2$   
-43.2  $\delta$ , triplet,  $J = 21$  cps,  $CH_2NF_2$   
Doublet:triplet in 1:1 ratio



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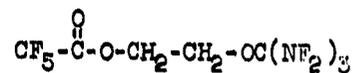
132.  $C_5F_8H_8N_6O$

IR: (274)  
Mass:  
NMR:



133.  $C_5F_9H_4N_3O_3$

IR: (294)  
Mass:  
NMR: (294)

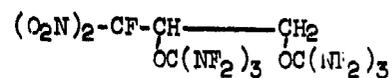


$H^1$ : 5.37  $\tau$ ,  $>CH_2$

$F^{19}$ : -23.0 ppm,  $-NF_2$   
75.8 ppm,  $-CF_3$

134.  $C_5F_{13}H_3N_6O_6$

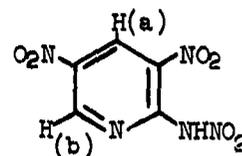
IR: (175)  
Mass:  
NMR: (175)



$F^{19}$ : -23.9,  $-NF_2$   
+118,  $-CF$

135.  $C_5H_3N_5O_6$

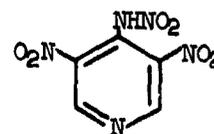
IR:  
Mass:  
NMR: (5)



$H^1$ : a = 8.97 ppm, doublet,  
b = 9.19 ppm, doublet,  $J_{4,6} = 2.50$  cps

136.  $C_5H_3N_5O_6$

IR: (6)  
Mass:  
NMR: (6)

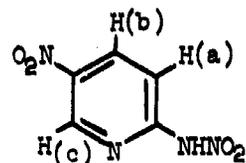


$H^1$ :  $\nu_{NHNO_2} = 11.07$  ppm  
 $\nu_{2,6} = 9.02$  ppm

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137.  $C_5H_4N_4O_4$

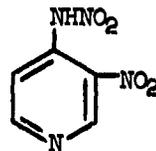
IR:  
Mass:  
NMR: (5)



$H^1$ : (a) 8.00 ppm, doublet, J: between protons in 5 and 6 position  
4.8 cps  
(b) 8.74 ppm, quartet  
(c) 9.24 ppm, doublet, J: protons 3 and 5 position 1.4 cps

138.  $C_5H_4N_4O_4$

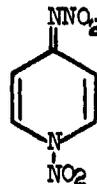
IR:  
Mass:  
NMR: (6)



$H^1$ : Protons 5 and 6 position  $J_{5,6} = 8.16$   
 $\nu_5 = 7.64$  ppm,  $\nu_6 = 8.26$  (two doublets)  
proton number 2 position  $\nu_2 = 9.04$  ppm  
 $J_{2,6} \sim 0.3$  cps

139.  $C_5H_4N_4O_4$

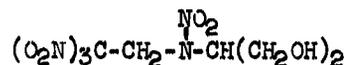
IR: (5)  
Mass:  
NMR: (7)



$H^1$ :  $\nu_{2,6} = 9.19$  ppm  
 $\nu_{3,5} = 7.10$  ppm

140.  $C_5H_9N_5O_{10}$

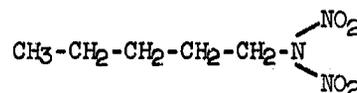
IR: (176)  
Mass:  
NMR: (175)



$H^1$ : 4.40  $\tau$ ,  $-CH_2-C(NO_2)_3$   
5.25  $\tau$ ,  $\text{>}CH$   
6.25  $\tau$ ,  $-CH_2OH$   
6.78  $\tau$ ,  $-CH_2OH$

141.  $C_5H_{11}N_3O_4$

IR:  
Mass:  
NMR: (2)



$H^1$ :  $\alpha$ -methylene protons  
 $\delta = 4.15$  ppm from TMS

158

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142.  $C_6F_8H_{10}NO_3$

$CH_3CONFCO_2CH(CH_3)_2$

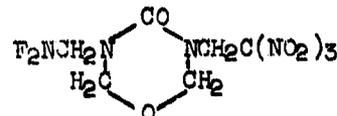
IR:

Mass:

NMR: (17)

$\tau_{19}$ : +68.8 ppm (relative to internal Freon-11)

143.  $C_6F_2H_8N_6O_8$



IR: (274)

Mass:

NMR: (274)

$\tau_{19}$ : 5.08  $\tau$ , triplet,  $J_{CH_2-NF_2} = 24$  cps  
 5.01  $\tau$ , peak  
 4.88  $\tau$ , peak  $[CH_2C(NO_2)_3]$ , ratio 1:2:1

$\tau_{19}$ : -44.5  $\delta$ , triplet,  $J_{NF_2-CH_2} = 24$  cps

144.  $C_6F_2H_{10}HgN_2O_4$

$Hg(NFCO_2C_2H_5)_2$

IR:

Mass:

NMR: (16)

$\tau_{19}$ :  $CHCl_3$  solvent, broad absorption at 97.8 ppm  
 $CH_3CN$  " " " " 92 ppm

145.  $C_6F_4H_6N_4O_6$

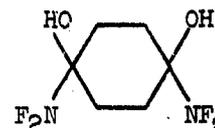
$(F_2NCHNHCOCOOH)_2$

IR: (274)

Mass:

NMR:

146.  $C_6F_4H_{10}N_2O_2$



IR: (274)

Mass:

NMR:

147.  $C_6F_4H_{10}N_4O_2$

$(F_2NCHNHCOCH_3)_2$

IR: (274)

Mass:

NMR:

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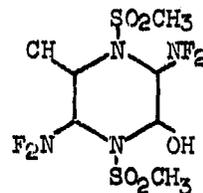
148.  $C_6F_4H_{10}N_4O_4$



IR: (274)  
Mass:  
NMR:

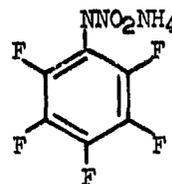
149.  $C_6F_4H_{12}N_4O_6S_2$

IR: (274)  
Mass:  
NMR:



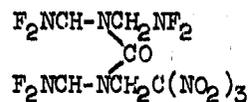
150.  $C_6F_5H_4N_3O_2$

IR: (6)  
Mass:  
NMR:



151.  $C_6F_6H_6N_6O_7$

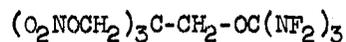
IR: (274)  
Mass:  
NMR: (274)



H<sup>1</sup>: 16 peaks, 4.03 - 5.68  $\tau$   
consisting of singlet  $CH_2C(NO_2)_3$   
triplet  $CH_2NF_2$   
and pair sextuplets, magnetically nonequivalent ring CH-rings

F<sup>19</sup>:  $\left. \begin{array}{l} -28.8 \delta, \text{ triplet, } J = 21 \text{ cps} \\ -31.0 \delta, \text{ doublet, } J = 12 \text{ cps} \\ -43.6 \delta, \text{ triplet, } J = 24 \text{ cps} \end{array} \right\}$  NF<sub>2</sub> positions 5, 4, and 1 resp.  
ratio 1:1:1

152.  $C_6F_8H_8N_6O_{10}$

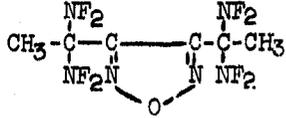
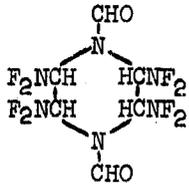


IR: (174)  
Mass:  
NMR: (174)

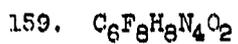
H<sup>1</sup>: 6.05  $\tau$ , singlet,  $-CH_2-O-C-$   
6.15  $\tau$ , singlet,  $-CH_2-O-NO_2$

F<sup>19</sup>: -24.7, singlet,  $-NF_2$

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153.  $C_6F_6H_6N_8O_7$   $(F_2NCH_2)_2NCON(CH_2NF_2)CH_2C(NO_2)_3$   
 IR: (274)  
 Mass:  
 NMR:
154.  $C_6F_6H_{11}N_3O_3$   $C_2H_5OCH_2-\underset{OH}{\underset{|}{CH}}-CH_2OC(NF_2)_3$   
 IR:  
 Mass:  
 NMR: (178a)
155.  $C_6F_6H_{12}N_6O$   $(F_2N)_3CON=C[N(CH_3)_2]_2$   
 IR:  
 Mass:  
 NMR: (297)  
 H<sup>1</sup>: 6.87  $\tau$ ,  $-CH_3$   
 F<sup>19</sup>: -24.5 ppm,  $-NF_2$
156.  $C_6F_6H_6N_6O$    
 IR: (453)  
 Mass:  
 NMR:
157.  $C_6F_6H_6N_6O_2$    
 IR: (274)  
 Mass:  
 NMR: (274)  
 H<sup>1</sup>: 1.09  $\tau$ , singlet (CHO)  
 3.68  $\tau$ , triplet, J = 23 cps (Ring CH),  
 each peak split into doublet J = 4 cps  
 F<sup>19</sup>: Complex spectrum between -40.9  $\delta$  and -36.3  $\delta$
158.  $C_6F_8H_8N_4$    
 IR: (274)  
 Mass:  
 NMR: (274)  
 H<sup>1</sup>: 7.61  $\tau$ , single peak  
 F<sup>19</sup>: -27.4  $\delta$ , single peak

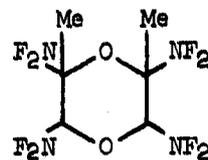
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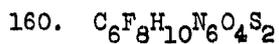
IR: (274)

Mass:

NMR:



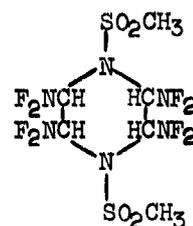
or isomer



IR: (274)

Mass:

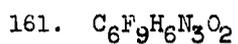
NMR: (274)



$H^1$ : 3.95  $\tau$ , triplet,  $J = 21$  cps (Ring CH)

$F^{19}$ : -41.3  $\delta$ , doublet,  $J = 12$  cps

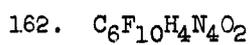
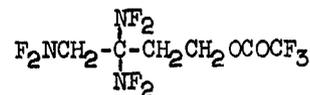
-38.7  $\delta$ , doublet,  $J = 12$  cps



IR:

Mass:

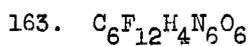
NMR: (440)



IR: (274)

Mass:

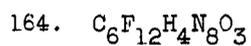
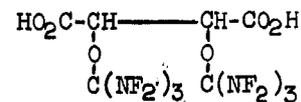
NMR:



IR: (174)

Mass:

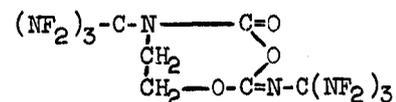
NMR:



IR: (86)

Mass:

NMR: (86)

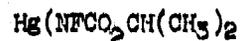
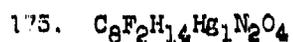


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165.  $C_6F_{12}H_5N_9O_8$   $(NO_2)_3C-CH_2-\underset{\substack{| \\ OC(NF_2)_3}}{CH}-CH_2-C(NF_2)_3$   
 IR: (175)  
 Mass:  
 NMR: (175)  
 F19: -23.8,  $-NF_2$
166.  $C_6F_{12}H_6N_6O_3$   $(F_2N)_3CO-\underset{\substack{| \\ CH_2}}{CH}-\underset{\substack{| \\ CH_2}}{CH}-OC(NF_2)_3$   
 IR: (174)  
 Mass:  
 NMR: (174)  
 H<sup>1</sup>: 5.5  $\tau$ ,  $CH_2$  (Cis)  
 4.28  $\tau$ , CH  
 F19: -24.0,  $-NF_2$   
 H<sup>1</sup>: 5.5  $\tau$ ,  $CH_2$  (trans)  
 4.45  $\tau$ , CH  
 F19: -24.0,  $NF_2$
167.  $C_6F_{12}H_8N_8O_4$   $(F_2N)_3CO-CH_2-CH_2-\underset{\substack{| \\ NO_2}}{N}-CH_2-CH_2-OC(NF_2)_3$   
 IR: (178)  
 Mass:  
 NMR: (178)  
 F19: -27.0,  $-NF_2$
168.  $C_7F_2H_{15}NO_3$   $(C_2H_5)_2CHC(OH)NF_2CH_3$   
 IR: (274)  
 Mass:  
 NMR:
169.  $C_7F_4H_6N_2$   $\begin{array}{c} C_6H_5 \\ | \\ HC-NF_2 \\ | \\ NF_2 \end{array}$   
 IR: (315)  
 Mass:  
 NMR:

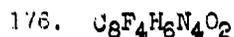


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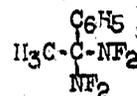
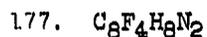


IR:  
Mass:  
NMR: (16)

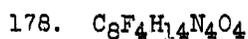
$\tau_{19}$ : +90.8  $\phi$



IR: (274)  
Mass:  
NMR:



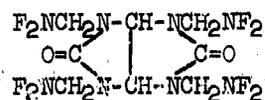
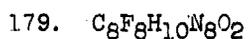
IR: (315)  
Mass:  
NMR:



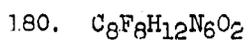
IR: (274)  
Mass:  
NMR: (274)

$\tau_{19}$ : 5.83  $\tau$ , quadruplet,  $J = 7.2$  cps ( $CH_2$ )  
2.17, 2.30  $\tau$ , broad doublet,  $J = 7.8$  cps (NH)  
3.8 - 4.8  $\tau$ , complex multiplet (CH)

$\tau_{19}$ : -26.9  $\delta$ , doublet,  $J = 27$  cps  
-31.0  $\delta$ , singlet  
-35.2  $\delta$ , doublet,  $J = 12$  cps



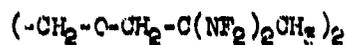
IR: (274)  
Mass:  
NMR:



IR: (274)  
Mass:  
NMR:

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181.  $C_6F_{14}H_{14}N_4O_2$



IR:  
Mass:  
NMR: (455)

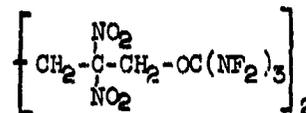


182.  $C_8F_{12}H_8N_{10}O_2$

IR: (274)  
Mass:  
NMR:

183.  $C_8F_{12}H_8N_{10}O_{10}$

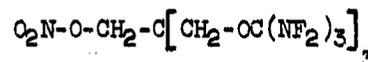
IR:  
Mass:  
NMR: (178)



H<sup>1</sup>: 4.50  $\tau$ , singlet,  $-\text{CH}_2-\text{OC}(\text{NF}_2)_3$   
7.02  $\tau$ ,  $-\text{CH}_2-\text{CH}_2-$

F<sup>19</sup>: -25.1 ppm, singlet,  $-\text{NF}_2$

184.  $C_8F_{18}H_8N_{10}O_6$

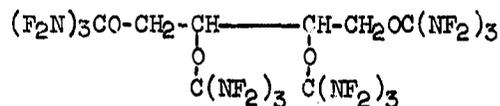


IR: (176)  
Mass:  
NMR: (176)

H<sup>1</sup>: 6.04  $\tau$ , singlet,  $-\text{CH}_2-\text{OC}(\text{NF}_2)_3$   
6.07  $\tau$ ,  $-\text{CH}_2-\text{ONO}_2$

F<sup>19</sup>: -24.5 ppm, singlet,  $-\text{NF}_2$

185.  $C_8F_{24}H_6N_{12}O_4$



IR: (174)  
Mass:  
NMR: (174)

F<sup>19</sup>: -23.6, singlet,  $-\text{NF}_2$

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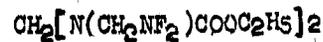
186.  $C_9F_2H_{11}N_3$

IR:  
Mass:  
NMR: (49)

$H^1$ : 7.4 - 9.0  $\delta$ , complex aromatic multiplet  
1.5  $\delta$ , sym. triplet,  $J = 1.8$  cps  
1.2  $\delta$ , small singlet, acetone contaminant

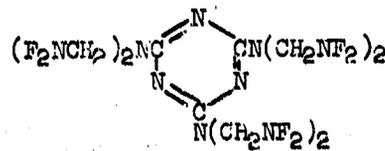
$F^{19}$ : -25.3  $\phi$ , broad singlet

187.  $C_9F_4H_{16}N_4O_4$



IR: (274)  
Mass:  
NMR:

188.  $C_9F_{12}H_{12}N_{12}$



IR: (274)  
Mass:  
NMR: (274)

$H^1$ : 4.4  $\tau$ , triplet,  $J = 24$  cps

$F^{19}$ : -45.6  $\tau$ , triplet,  $J = 24$  cps

189.  $C_{10}F_4H_{12}N_2$

IR:  
Mass:  
NMR: (455)



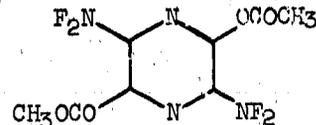
190.  $C_{10}F_4H_{14}N_4O_6$



IR: (274)  
Mass:  
NMR:

191.  $C_{10}F_4H_{16}N_4O_8S_2$

IR: (274)  
Mass:  
NMR:



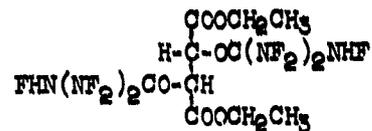
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192.  $C_{10}F_{10}H_{14}N_6O_6$

IR: (175)

Mass:

NMR:

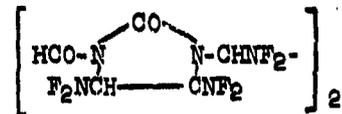


193.  $C_{10}F_{12}H_8N_{10}O_4$

IR: (274)

Mass:

NMR:

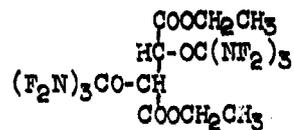


194.  $C_{10}F_{12}H_{12}N_6O_6$

IR: (175)

Mass:

NMR: (175)



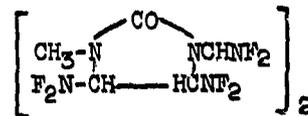
$F^{19}$ : -24.7,  $-\text{NF}_2$

195.  $C_{10}F_{12}H_{12}N_{10}O_2$

IR: (274)

Mass:

NMR:



$H^1$ : 4.02  $\tau$ , triplet,  $J = 18$  cps  
5.50  $\tau$ , doublet,  $J = 12$  cps

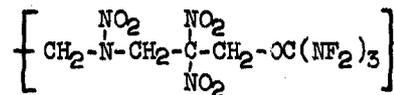
$F^{19}$ : -26.7, -30.2, -32.5, -33.7, -34.2, -37.3  $\delta$ ,

196.  $C_{10}F_{12}H_{12}N_{14}O_{14}$

IR: (179)

Mass:

NMR: (179)



$H^1$ : 4.50  $\tau$ , singlet,  $-\text{CH}_2\text{OC}(\text{NF}_2)_2$   
4.90  $\tau$ , singlet,  $-\text{C}(\text{NO}_2)_2-\text{CH}_2-\text{N}(\text{NO}_2)-$   
5.88  $\tau$ , singlet,  $-\text{CH}_2-\text{CH}_2-$

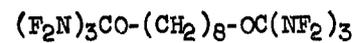
$F^{19}$ : -25.0 ppm, singlet,  $-\text{NF}_2$

197.  $C_{10}F_{12}H_{16}N_6O_2$

IR: (179)

Mass:

NMR: (179)



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197. (Concluded)

$H^1$ : 8.0 - 8.7  $\tau$ , internal  $-CH_2-$   
5.5  $\tau$ ,  $-CH_2-OC(NF_2)_3$

198.  $C_{11}F_2H_2O_4N_6$



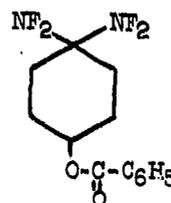
IR: (274)  
Mass:  
NMR:

199.  $C_{12}F_{12}H_{10}N_{16}O_{14}$



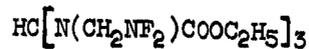
IR: (274)  
Mass:  
NMR:

200.  $C_{13}F_4H_{14}N_2O_2$



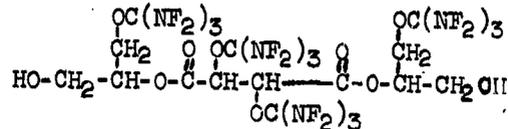
IR:  
Mass:  
NMR: (453)

201.  $C_{13}F_6H_{22}N_6O_6$



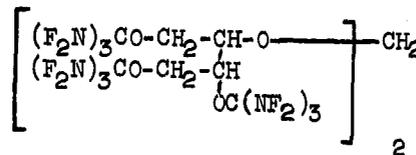
IR: (274)  
Mass:  
NMR:

202.  $C_{14}F_{24}H_{14}N_{12}O_{10}$



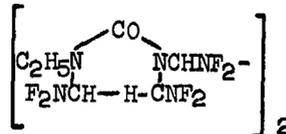
IR: (175)  
Mass:  
NMR:

203.  $C_{15}F_{36}H_{14}N_{18}O_8$



IR: (166)  
Mass:  
NMR:

204.  $C_{16}F_{12}H_{16}N_{10}O_2$



IR: (274)  
Mass:  
NMR:

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204.  $C_{16}F_{12}H_{16}N_{10}O_2$  (Concluded)

$H^1$ : 3.95  $\tau$ , triplet,  $J = 19$  cps (CH)  
6.4  $\tau$ , quintuplet,  $J = 6$  cps (CH<sub>2</sub>)

$F^{19}$ : Indistinct spectrum due to solubility difficulties peak -29.9  $\delta$

205.  $C_{18}F_{19}H_{25}N_6O_2$

$(NF_2)_3CO(CH_2)_{16}CO(NF_2)_3$   $C_2H_5$

IR: (180)

Mass:

NMR:

206.  $Cl_2D_3NO_{11}$

$DNO_3 \cdot 2OClO_4$

IR: (121)

Mass:

NMR:

207.  $ClF_2N$

$NF_2Cl$

IR: (518)

Mass:

NMR:

208.  $ClF_3O$

$ClF_3O$

IR:

Mass: (425)

NMR: (425)

209.  $ClF_4^+(?)$

$ClF_4^+$

IR:

Mass:

NMR: (76)

$F^{19}$ : -271 ppm, in  $AsF_5$  soln, broad  
-265 ppm, in  $BrF_5$  soln, doublet

210.  $ClF_4NO_2$

$FNO-ClF_3O$

IR: (423)

Mass:

NMR: (423)

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211.  $\text{ClF}_5$   $\text{ClF}_5$   
IR: (359)  
Mass:  
NMR: (420a)
212.  $\text{ClH}_4\text{NO}_4$   $\text{NH}_4\text{ClO}_4$   
IR: (100)  
Mass:  
NMR:
213.  $\text{ClO}_2$   $\text{ClOCl}$   
IR: (534)  
Mass:  
NMR:
214.  $\text{Cl}_2\text{H}_3\text{NO}_{11}$   $\text{HNO}_3 \cdot 2\text{HClO}_4$   
IR: (121)  
Mass:  
NMR:
215.  $\text{Cl}_2\text{O}_2$   $\text{Cl}_2\text{O}_2$   
IR: (533a)  
Mass:  
NMR:
216.  $\text{FNO}$   $\text{FNO}$   
IR:  
Mass:  
NMR: (420a)
217.  $\text{FNO}_2$   $\text{FNO}_2$   
IR:  
Mass:  
NMR: (420a)
218.  $\text{F}^{18}\text{NO}_3$   $\text{NO}_3\text{F}^{18}$   
IR: (284)  
Mass:  
NMR: (284)

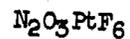
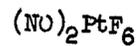
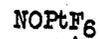
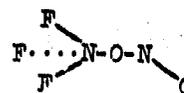
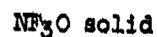
$\text{F}^{19}$ : 221.5 ppm downfield from  $\text{CFCl}_3$

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219.  $\text{FO}_2$   $\text{O}_2\text{F}$   
IR: (532b)  
Mass:  
NMR:
220.  $\text{FO}_3$   $\text{O}_3\text{F}$   
IR: (532b)  
Mass:  
NMR:
221.  $\text{FO}_4$   $\text{O}_4\text{F}$   
IR: (532b)  
Mass:  
NMR:
222.  $\text{F}_2\text{HN}$   $\cdot\text{HNF}_2(\text{solid})$  at  $-160^\circ$   
IR: (232)  
Mass:  
NMR:
223.  $\text{F}_2\text{H}_3\text{NO}$   $\text{H}_2\text{O}\cdot\text{HNF}_2$  solid at  $-160^\circ$   
IR: (232)  
Mass:  
NMR:
224.  $\text{F}_2\text{O}_2$   $\text{O}_2\text{F}_2$   
IR: (263)  
Mass:  
NMR:
225.  $\text{F}_2\text{O}_3$   $\text{O}_3\text{F}_2$   
IR: (532b)(263)  
Mass:  
NMR:
226.  $\text{F}_2\text{O}_4$   $\text{O}_4\text{F}_2$   
IR: (532b)  
Mass:  
NMR:

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- 227.  $F_2Si$   
IR: (379)  
Mass:  
NMR:
- 228.  $F_3NO$   
IR: (121)  
Mass:  
NMR:
- 229.  $F_3N_2O_2$   
IR: (121)  
Mass:  
NMR:
- 230.  $F_5Sb$   
IR: (89)  
Mass:  
NMR:
- 231.  $F_6NOPt$   
IR: (571)  
Mass:  
NMR:
- 232.  $F_6NO_2Pt$   
IR: (571)  
Mass:  
NMR:
- 233.  $F_6N_2O_2Pt$   
IR: (517)(513)  
Mass:  
NMR:
- 234.  $F_6N_2O_3Pt$   
IR: (571)  
Mass:  
NMR:



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235. F<sub>7</sub>NOPT<sub>7</sub>

IR: (570)  
Mass:  
NMR:

NOPT<sub>7</sub>  
(570) : IR  
: MASS  
: NMR

236. F<sub>10</sub>NSb

IR: (477)  
Mass:  
NMR: (477)

NF<sub>4</sub>SbF<sub>6</sub>  
(477) : IR  
: MASS  
: NMR

237. F<sub>11</sub>Sb<sub>2</sub>

IR:  
Mass:  
NMR: (479)

Sb<sub>2</sub>F<sub>11</sub>  
(479) : IR  
: MASS  
: NMR

238. F<sub>14</sub>N<sub>2</sub>Sb<sub>2</sub>

IR:  
Mass:  
NMR: (490)

N<sub>2</sub>F<sub>4</sub>·2SbF<sub>5</sub> complex  
(490) : IR  
: MASS  
: NMR

239. H<sub>2</sub>O<sub>2</sub>

IR: (330)  
Mass:  
NMR:

H<sub>2</sub>O<sub>2</sub>  
(330) : IR  
: MASS  
: NMR

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13. ABSTRACT This review summarizes much of the chemistry of advanced oxidizers which have been reported since the completion of the previous MRI report, "A Critical Review of the Chemistry of Advanced Oxidizers," Volumes I and II, 31 December 1965, which was prepared for the Advanced Research Projects Agency under Contract DA-31-ARO(D)-19, Mod. No. 2 & 3. The present review covers the areas of inorganic N-F, Cl-F and O-F oxidizers and organic NF oxidizers with N-containing functional groups, or N-N bonds. Other advanced oxidizers and advanced fuels which were described in the previous review could not be covered in detail in the present review because of contract termination, but properties data and literature references are tabulated for all types of advanced oxidizers. These tabulations include physical properties data on 170 compounds, thermodynamic data on 93 compounds and spectral information on 239 compounds. The review contains 29 tables, 595 references to technical reports or papers presented at symposia, 210 references to open literature publications, and 236 pages.		

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