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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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Air Force Rocket Propulsion Laboratory
Directorate of Laboratories
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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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TABLE OF CONTENTS

	Page No.
I. Introduction	1
Chapter I - Organic NF Compounds: Amines, Fluoramines, and Amine Fluorinations	2
I-A. Amines and Fluoramines	2
I-B. Amine Fluorinations	7
Chapter II - Cyanides (Nitriles) and Isocyanates	9
II-A. Cyanides (Nitriles)	9
II-B. Isocyanates	10
Chapter III - Amides, Carbamates and Ureas	16
III-A. Amides	16
III-B. Carbamates	18
III-C. Ureas	19
Chapter IV - Imino Compounds	24
IV-A. Fluorimines	24
IV-B. N,N,N'-Trifluoramidines	28
IV-C. Fluorinated Guanidines	29
IV-D. Perfluoroguanidines (Code Name: PFG)	30
Chapter V - NF Compounds which Contain NN Bonds	39
V-A. Hydrazine Derivatives	39
V-B. Diimide Derivatives	39
V-C. NNO and NNO ₂ Derivatives	44
Chapter VI - Inorganic Nitrogen Fluorides and Derivatives	46
VI-A. Nitrogen Trifluoride	46
VI-B. NF ₄ ⁺ Salts	46
VI-C. NH ₃ F ⁺ Salts	52
VI-D. Difluorodiazine	53
VI-E. N ₂ F ⁺ Salts	53
VI-F. Tetrafluorohydrazine	57
VI-G. N ₂ F ₃ ⁺ Salts	62
VI-H. Difluoramine	62
VI-I. Trifluoramine Oxide	65
VI-J. Complexes of NF ₃ O and the NF ₂ O ⁺ Salts	65
VI-K. Chlorodifluoramine and Dichlorofluoramine	70
VI-L. Miscellaneous N-O-F Compounds	71

CONFIDENTIAL

TABLE OF CONTENTS (Continued)

	<u>Page No.</u>
Chapter VII - Inorganic Halogen Fluorides and Derivatives	76
VII-A. Chlorine Pentafluoride	76
VII-B. ClF_5 - Lewis Acid Complexes	77
VII-C. Chlorine Trifluoride and Derivatives	85
VII-D. Chlorine Trifluoride Oxide and Related Compounds. .	85
VII-E. Miscellaneous Halogen Compounds	98
Chapter VIII - Oxygen Fluorides, O-F Derivatives and Miscellaneous Fluorinations	102
VIII-A. Oxygen Fluorides and Derivatives	102
VIII-B. Miscellaneous Fluorinations	107
Appendix A - Melting Points, Boiling Points, Densities and Refractive Indexes.	109
Appendix B - Thermodynamic Properties.	123
Appendix C - Mass, Infrared and Nuclear Magnetic Resonance Spectra	133
Bibliography	175
Open Literature References	221

List of Figures

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
1	Preparation and Reactions of Difluoramino-substituted Piperazine Compounds	4
2	Side Reactions in the Production of FA-TNEEG	37

List of Tables

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
I	Dehydrofluorination Reactions	5
II	Reactions of Adduct, TFGI, and TRIS-I	11
III	Reactions of Glyoxal with Substituted Ureas	20
IV	Reactions of Fluorimines with Difluoramine	25
V	Reactions of Perfluoroguanidine (PFG)	31
VI	Reactions of $(\text{NF}_2)_3\text{CON}=\text{CCl}_2$	38

v

CONFIDENTIAL

CONFIDENTIAL

TABLE OF CONTENTS (Continued)

List of Tables (Continued)

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
VII	Reactions of $F_{10}ADF$ and F_8ADF with CO	42
VIII	Reactions of NF_3	47
IX	Reactions of N_2F_2	54
X	Reactions of N_2F_4	58
XI	Reactions of $N_2F_3^+$ Salts	63
XII	Reactions of HNF_2 and $HNF_2 \cdot MF$ Complexes	66
XIII	Reactions of NF_3O	68
XIV	Reactions of Dichlorofluoramine	72
XV	Miscellaneous N-O-F Reactions	73
XVI	Reactions of ClF_5	78
XVII	Reactions of ClF_5 - Lewis Acid Complexes	84
XVIII	Reactions of ClF_3	86
XIX	Reactions of ClF_2^+ and ClF_4^- Salts	88
XX	Reactions of ClF_3O	92
XXI	Alternate Routes to ClF_3O	93
XXII	Other Efforts to Produce New Cl-F-O Compounds	94
XXIII	Reactions of ClO_2F	100
XXIV	Studies of ClO_3F	101
XXV	Studies of Oxygen Fluorides and Derivatives	102
XXVI	Miscellaneous Fluorinations	107
XXVII	Melting Points, Boiling Points, Densities and Refractive Indexes.	110
XXVIII	Thermodynamic Properties.	124
XXIX	Mass, Infrared and Nuclear Magnetic Resonance Spectra	134

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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 NF₂ 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 (NFH), fluorimine ($=\text{NF}$), guanidine ($>\text{NC}(=\text{N})\text{N}<$), imine ($>\text{C}=\text{N}$), isocyanate (NCO), or urea ($>\text{NC}(=\text{O})\text{N}<$); N-containing rings such as piperidine, pyrrolidine or triazine, N-N, N=N and N-NO₂. 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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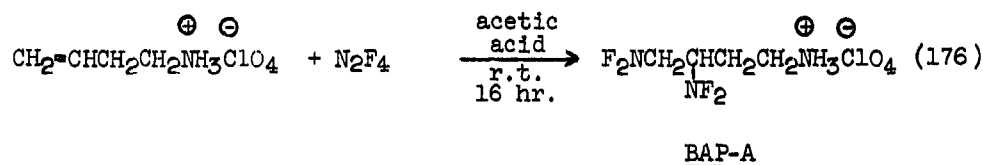
CHAPTER I

ORGANIC NF COMPOUNDS: AMINES, FLUORAMINES, AND AMINE FLUORINATIONS

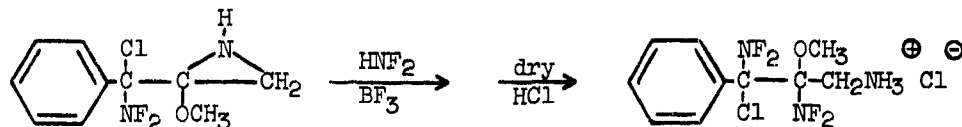
I-A. Amines and Fluoramines

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(difluoroamino)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 (HNF_2) has also been utilized in the preparation of fluorine-containing amine salts, as well as the free amines. The reaction of α,α,α -chloro-(difluoramino-(2-methoxy-2-aziridyl))-toluene with difluoramine in BF_3 , followed by treatment with dry HCl , produces the substituted propylamine hydrochloride (451a, 453).

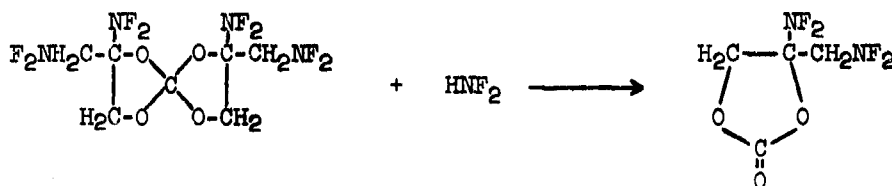


In a similar manner the reaction shown below resulted in hydrolysis instead of the anticipated product (449).

$$\text{X}-\text{C}_6\text{H}_4-\text{C}(\text{F})(\text{N}(\text{CH}_3)_2)=\text{N}-\text{C}(\text{CH}_3)(\text{N}(\text{CH}_3)_2) + \text{HNF}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{BF}_3} \text{X}-\text{C}_6\text{H}_4-\text{C}(\text{F})(\text{N}(\text{CH}_3)_2)-\text{N}(\text{CH}_3)-\text{C}(\text{CH}_3)(\text{N}(\text{CH}_3)_2) + \text{H}_2\text{N}-\text{C}(\text{CH}_3)(\text{N}(\text{CH}_3)_2) + \text{H}_2\text{O}$$

Using HNHF_2 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, HNHF_2 in 96% H_2SO_4 readily converts $\text{N,N}'$ -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).

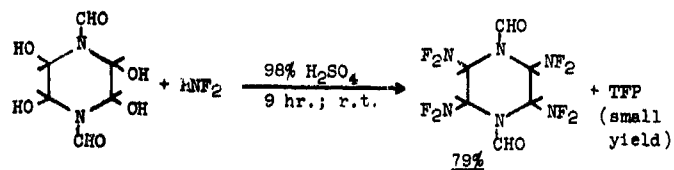
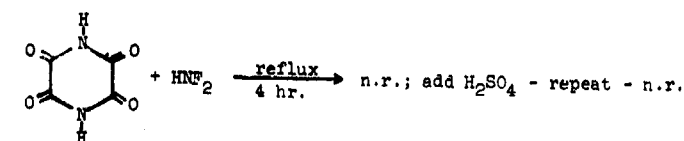
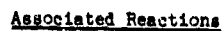
4-Difluoramino-4-difluoramino-methyl-1,3-dioxolane-2-one was produced by the treatment of a difluoramino-substituted tetraoxaspiro[2.2]nonane with difluoramine (453).


$$(\text{NF}_2)_3\text{CNFH} + \text{HNCO} \xrightarrow[-20^\circ\text{C}]{\text{urea}} \text{F}_2\text{N}(\text{CNF})\text{NF}_2 + \text{HNF}_2 + \text{C}_2\text{N}_2\text{H}_2\text{O}_2$$

(code name: PFG)

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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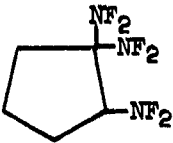
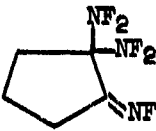
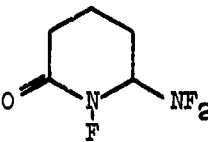
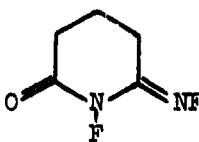
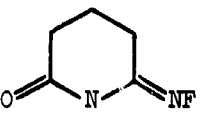
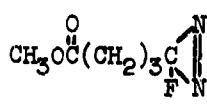


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TABLE I

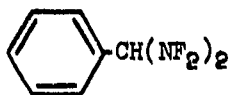
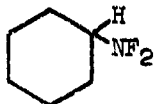
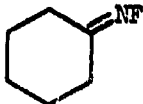
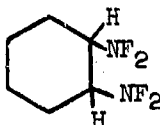
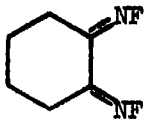
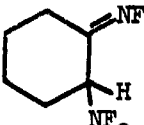
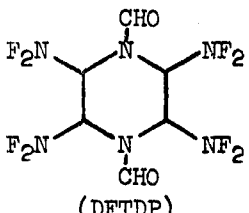
DEHYDROFLUORINATION REACTIONS

<u>Starting Compound</u>	<u>Product</u>	<u>Conditions</u>	<u>Ref.</u>
		$\ominus$ OCH ₃ in CH ₃ OH	(441)
		"	(441)
		"	(441)
$\text{CH}_3\text{C}(\text{Cl})(\text{NF}_2)\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	$\text{CH}_3\text{C}(\text{Cl})(\text{NF}_2)\text{CH}=\text{CH}_2$	Et ₃ N in CH ₂ Cl ₂ at 0°C	(441, 447)
$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CH}_2\text{NF}_2$	$\text{CH}_3\text{C}(\text{NF}_2)_2\text{CN}$	Et ₃ N in xylene at r.t.	(447)
$n\text{-C}_4\text{H}_9\text{OCH}(\text{NF}_2)\text{CH}_2\text{NF}_2$	$n\text{-C}_4\text{H}_9\text{OCCN}$	Et ₃ N	(449)
$\text{CH}_2\text{OCH}(\text{NF}_2)\text{CH}_2\text{NF}_2$ $\text{CHOCH}(\text{NF}_2)\text{CH}_2\text{NF}_2$ $\text{CH}_2\text{OCH}(\text{NF}_2)\text{CH}_2\text{NF}_2$	CH_2OCCN CHOCCN CH_2OCCN	Norite-A in CH ₂ Cl ₂	(449)

(code name: TVOPA)

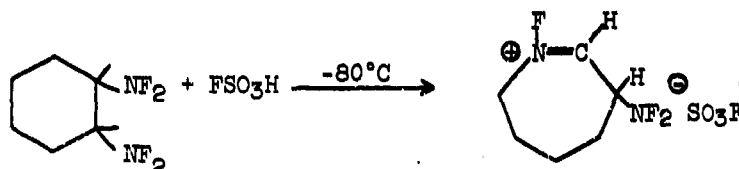
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TABLE I (Concluded)

Starting Compound	Product	Conditions	Ref.
	$\text{C}_6\text{H}_5\text{CNF}_2 + \text{C}_6\text{H}_5\text{CF}(\text{NF})$ (tentative)	strong base	(354)
		strong base	(354)
	 +  (tentative)	Amberlite IR-45 in CH_2Cl_2	(354)
$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{NF}_2)_2$	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{C}(\text{NF})_2$ 	strong base	(354)
 (DFTDP)	no reaction	metal hydrides i.e.: LiAlH_4 also: NaBH_4 , PtO_2 , LiBH_4	(268)
	$\text{SiF}_4 + \text{HNF}_2 + \text{others}$	P_2O_5 at r.t.	(291)

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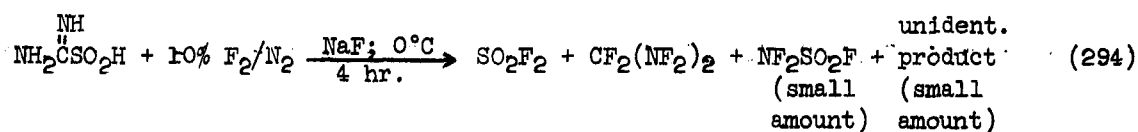
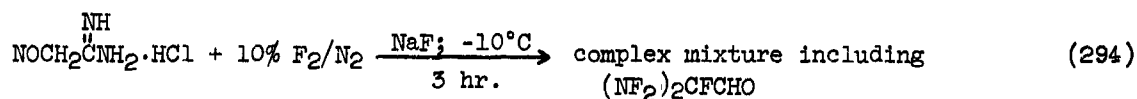
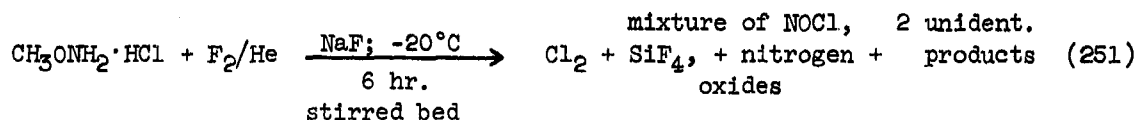
The reaction of 1,2-bis(difluoramino)cyclohexane with fluorsulfonic acid at -80°C resulted in nitrogen insertion via a ring opening and closing process (46).



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 H_2SO_4 as a catalyst and CH_2Cl_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-difluoro-amino-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°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 CH_3CN at -35°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°C was used to fluorinate CF_3NHF to a mixture of $\text{CF}_2=\text{NF}$ and $\text{CF}_3\text{N}-\text{CF}_2$ (296).



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CHAPTER II

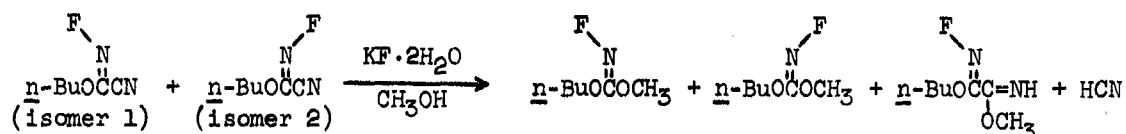
CYANIDES (NITRILES) AND ISOCYANATES

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).

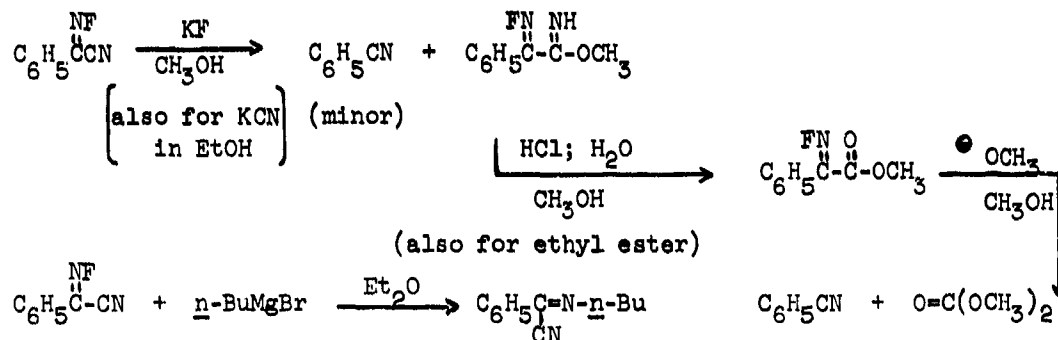


The rate of disappearance was found to be first order with respect to both isomer (1) and isomer (2). Graphical analysis of the change in rate constant as a function of temperature showed an activation energy for isomer (1) to be 15.9 Kcal/mole, while that for isomer (2) was found to be 14.2 Kcal/mole.

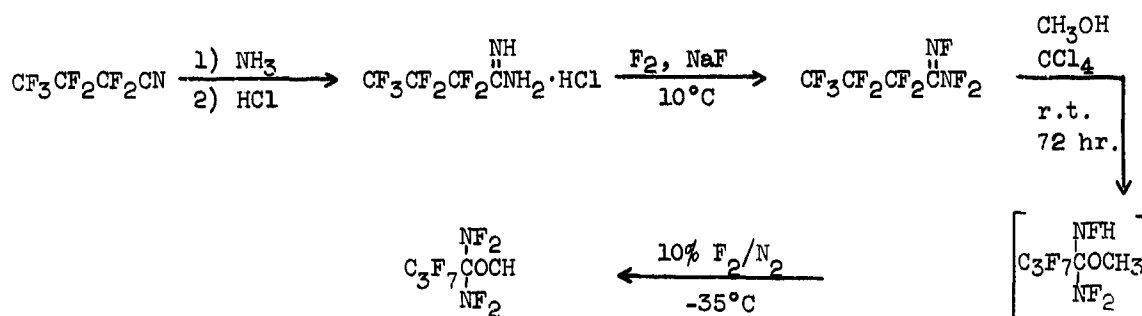
A number of studies on the reactions of substituted cyanofluoroformamidines (453, 455) have been conducted. Selected examples of these reactions are given below:



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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°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)acetonitrile (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% H_2SO_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 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

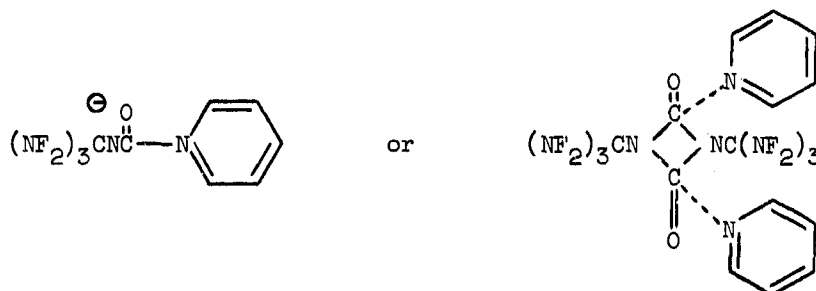
<u>Reactant</u>	<u>Products</u>	<u>Conditions</u>	<u>Reference</u>
1. $(\text{NF}_2)_3\text{CNCO}$	Code Name: Tris-I		
$\text{O}=\text{As}\phi_3$	$(\text{NF}_2)_3\text{CNH}_2$ + others	C_6H_6 , ϕNCO , r.t., 1 day	85a
$\text{O}=\text{P}\phi_3$	no reaction	C_6H_6 , HCl , r.t., 6 days	85b
NH_3	$(\text{NF}_2)_3\text{CNH}\overset{\text{O}}{\parallel}\text{CNH}_2$	Et_2O , 2 hr., r.t.	85b
$\text{CH}_2=\text{CHCH}_2\text{OH}$	$\text{CH}_2=\text{CHCH}_2\text{O}\overset{\text{O}}{\parallel}\text{CNHC}(\text{NF}_2)_3$	r.t., 17 hr.	85b
H_2O	$(\text{NF}_2)_3\text{CNH}_2$	FC4-11 , r.t., 5 days	86
HF	$(\text{NF}_2)_3\text{CNH}\overset{\text{O}}{\parallel}\text{CF}$	CsF , r.t., 7 days	293
2. $\text{NF}_2-\overset{\text{NF}}{\parallel}\text{C}-\text{NCO}$	Code Name: TFGI		
H_2O	$\text{NF}_2\overset{\text{NF}}{\parallel}\text{CNH}_2$ + CO_2	r.t.	85a
HNCO	N-F containing oil	KSCN , 0°C , 18 hr.	85b
$\text{NF}_2-\overset{\text{NF}}{\parallel}\text{C}-\text{NH}_2$	$\text{NF}_2\overset{\text{NF}}{\parallel}\text{C}\overset{\text{O}}{\parallel}\text{NHCNHCNF}$	$\phi_3\text{PO}$, C_6H_6	85c
CH_3OH	$\text{NF}_2\overset{\text{NF}}{\parallel}\text{C}\overset{\text{O}}{\parallel}\text{NHCOCH}_3$	0°C , 1 day	85c
NF_3	$\text{NF}_2\overset{\text{NF}}{\parallel}\text{C}\overset{\text{O}}{\parallel}\text{NHCNH}_2$ (several isomers)	Et_2O , -78°C	85c

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TABLE II (Concluded)

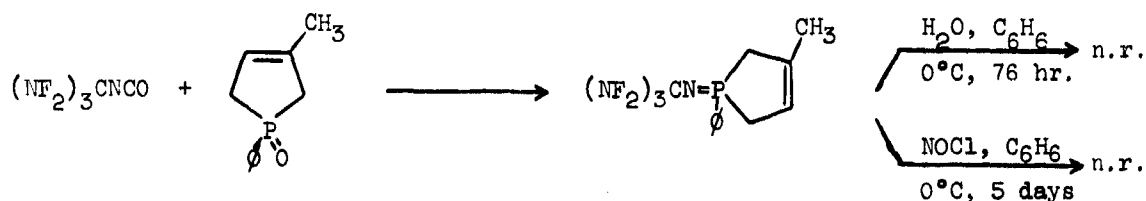
<u>Reactant</u>	<u>Products</u>	<u>Conditions</u>	<u>Reference</u>
3. $(\text{NF}_2)_2\overset{\text{NFH}}{\underset{ }{\text{C}}}\text{NCO}$	Code Name: Adduct		
NOCl, HCl	$(\text{NF}_2)_2\overset{\text{O}}{\underset{ }{\text{C}}}\text{FHNHCCl} + (\text{NF}_2)_2\overset{\text{Cl}}{\underset{ }{\text{C}}}\text{NCO}$	Not stated	594
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 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 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).

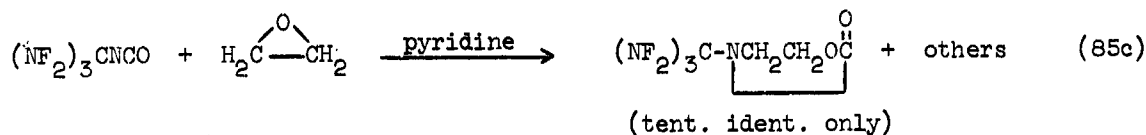
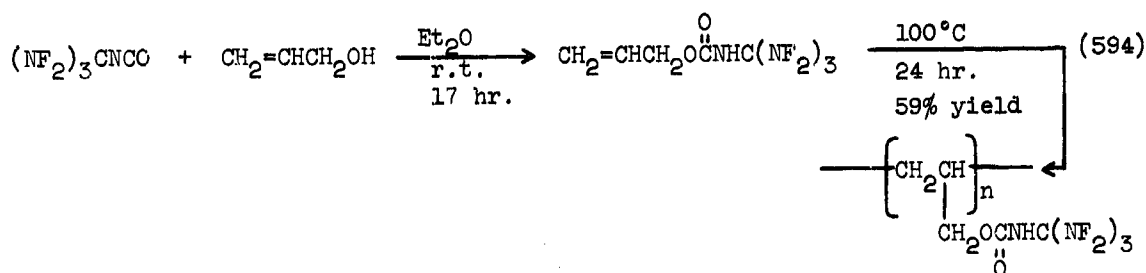
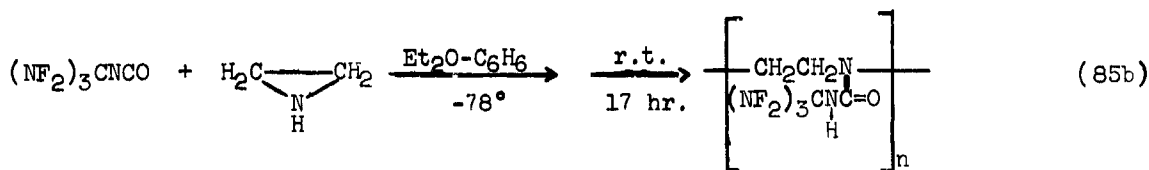
Although Tris-A does not react with triphenylphosphine oxide, it does undergo a condensation reaction with a similar molecule (85a).



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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 $n\text{-BuSnOCH}_3$, condensed together at low temperature, are allowed to warm to room temperature (86). Addition of methanol to Tris-I results in esterification to yield $(\text{NF}_2)_3\text{CNHCO}_2\text{CH}_3$ (294). Fluorinations of the ester with either a 10% F_2/N_2 mixture at 0°C or 100% F_2 at room temperature were unsuccessful.

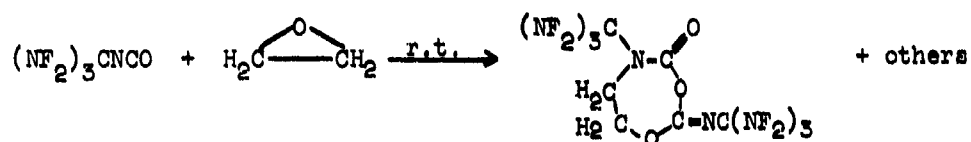
The incorporation of Tris-I into polymeric materials has been the subject of a number of studies. Among the species utilized as potential prepolymers were ethylene oxide, ethylenimine, and allyl alcohol.



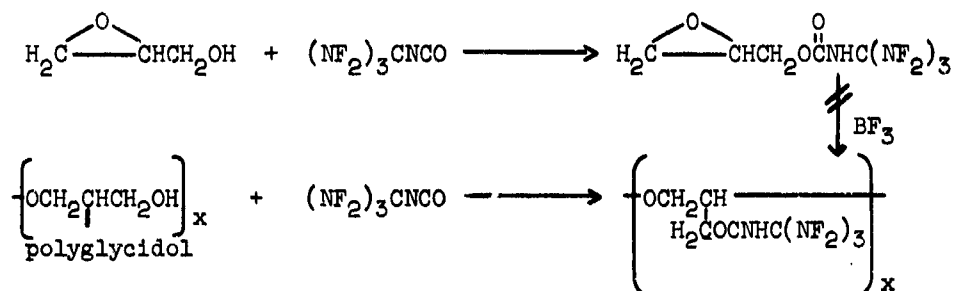
also for: TFGI

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_2SO_4 at -23°C and SO_3 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).

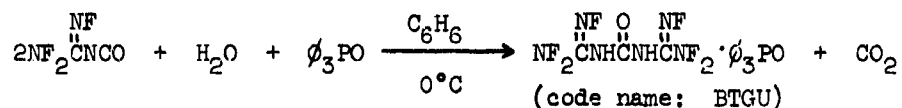
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Attempts to incorporate Tris-I into a polymeric material with polyvinylamine (PVAm) were unsuccessful (85c). A suspension of the two substances in $\text{SO}_2 + \text{Et}_2\text{O}$ yielded no reaction, while the mixture in DMSO at room temperature exploded after 1/2 hr. Reaction of Tris-I with 2,3-epoxy-1-propanol resulted in the formation of the corresponding epoxy-ester (594); however, further treatment of the ester with BF_3 did not produce the desired polymerization. The use of polyglycidol did result in the incorporation of Tris-I into a polymer (594).

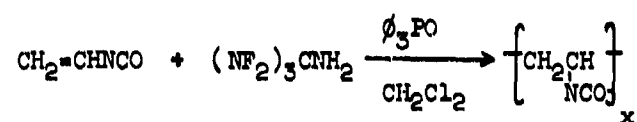


Considerably fewer studies have been conducted on the reactions of trifluoroguanyl isocyanate (code name: TFGI). Like Tris-I, TFGI did not react with triphenylphosphine oxide in benzene after 16 hr. at room temperature (85a). However, if water was added to the reaction mixture and the temperature maintained at 0°C , the TFGI underwent a dimerization, and the resulting product, N,N'-bis(trifluoroguanyl)-urea, formed a 1:1 complex with the triphenylphosphine oxide (85c).



No reaction was observed when vinyl isocyanate and Tris-A were mixed in methylene chloride and allowed to stand at room temperature for 3 days. If, however, triphenylphosphine oxide was added as a catalyst, a polymerization occurred after 3 days (85c).

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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°C for 1 hr. (85c).

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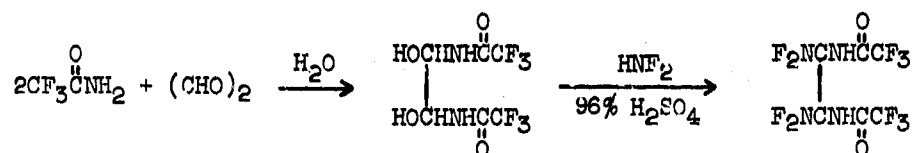
CHAPTER III

AMIDES, CARBAMATES AND UREAS

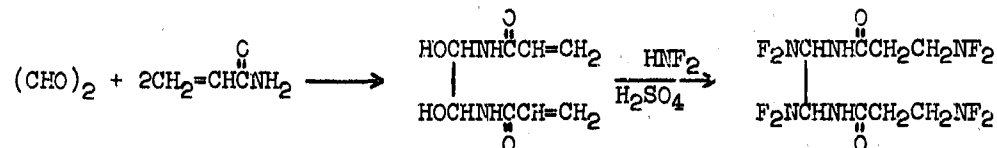
The various types of compounds which contain the $-N-CO-$ (amide) group are discussed in this chapter; included also are those containing additional oxygen or nitrogen, e.g., $-N-CO-O-$ (carbamate) or $-N-CO-N-$ (urea).

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).

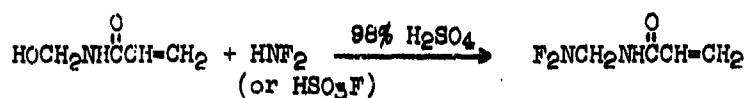


If the original amide contained unsaturation, such as acrylamide, the reaction with difluoramine also occurred with the unsaturated portion of the molecule (270).

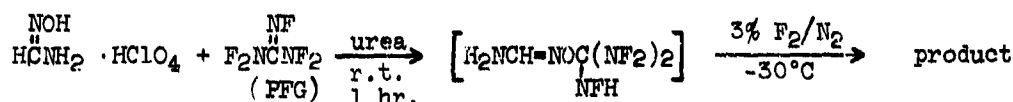


The same reaction occurred if the intermediate diol was converted to the methoxy-substituted compound and then treated with HNF_2 (270). Molecules containing acetylenic linkages, such as propiolamide, undergo reaction with $(CHO)_2$ and HNF_2 in the same manner as those containing the carbon-carbon double 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).

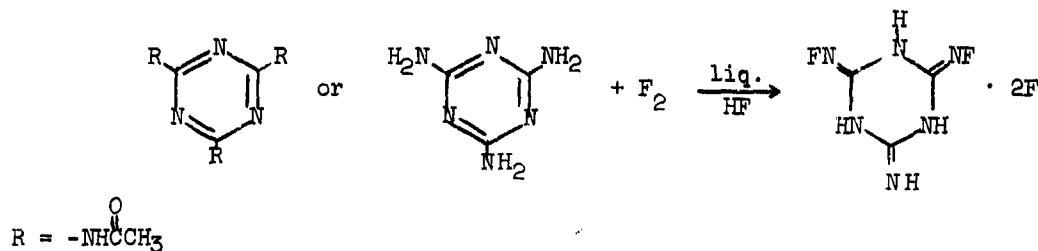
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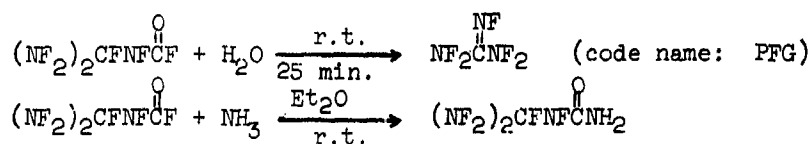
Direct fluorination of simple substituted amides with fluorine-nitrogen mixtures often results in decomposition and/or explosions. Reaction of N,N'-methylene-bis-formamide with 10% F₂/N₂ over NaF at 0°C for 8 hr. resulted in severe decomposition of the starting material to a complex mixture containing NF₃, COF₂, CH₂FNF₂ and others (292). Likewise, treatment of tris(difluoramino)acetamide with 3% F₂/N₂ 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).

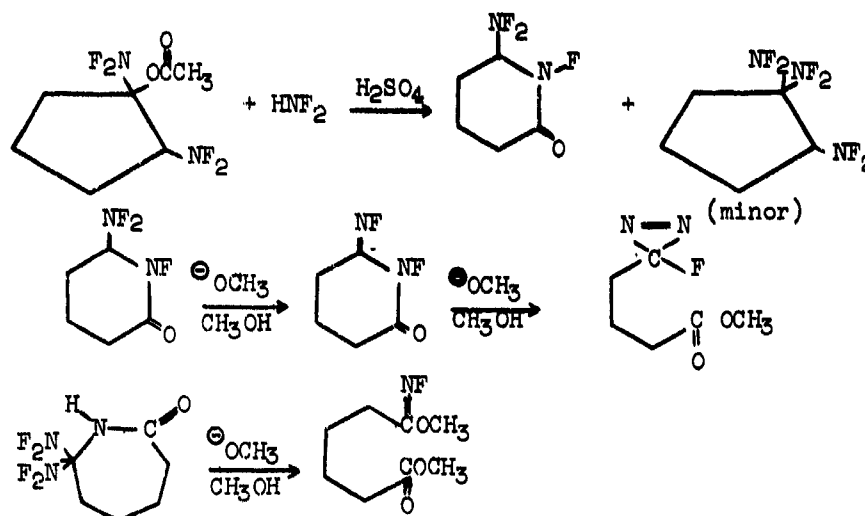


The product N²,N⁴-difluoro-isomelamine dihydrofluoride, hydrolyzed to give CO₂ and unidentified compounds (497). Hydrolysis and aminolysis of substituted perfluoro-formamides led to the expected products (292).



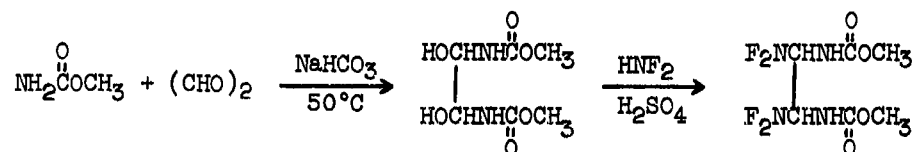
Cyclic compounds, containing difluoramino groups, undergo ring enlargement upon treatment with HNF₂ in sulfuric acid. Subsequent reaction of these cyclic amides with strong base resulted in ring opening (441, 451, 453, 455).

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III-B. Carbamates

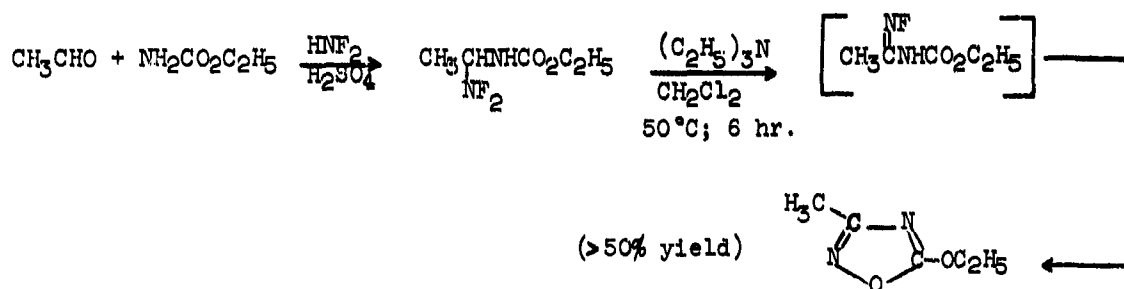
Carbamates, and related compounds, undergo condensation reactions with glyoxal in the same manner as the amides (268). Thus, oxamic acid, methyl carbamate, and ethyl carbamate reacted with glyoxal to form substituted diols, which were then further reacted with difluoramine in sulfuric acid.



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).

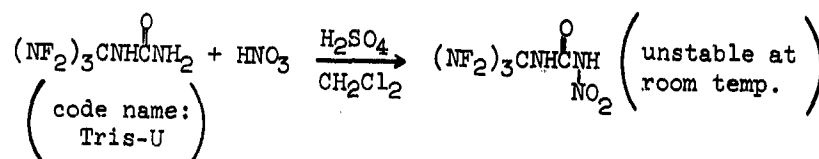
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III-C. Ureas

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 difluoramine 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).

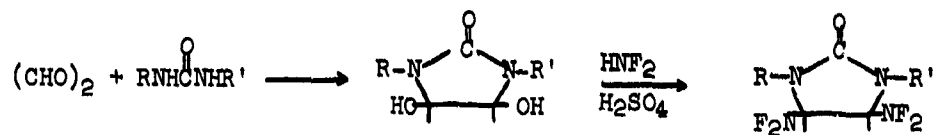


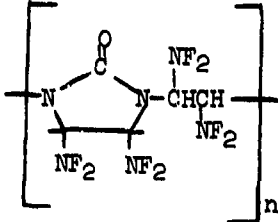
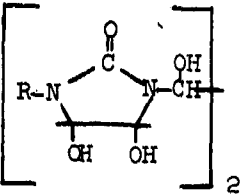
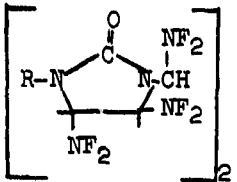
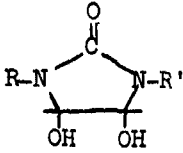
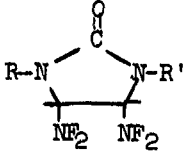
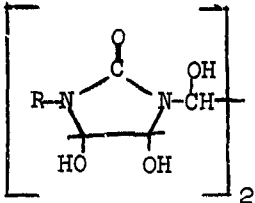
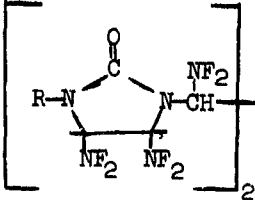
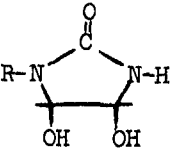
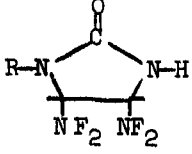
The above reaction has been attempted with trifluoroacetic anhydride as catalyst instead of sulfuric acid (85b). Within 1 hr. at ambient temperature, decomposition of the intermediate product resulted in the formation of Tris-I, nitrous oxide, and water. Reaction of Tris-U with trifluoroacetic anhydride in ether for 3 days at room temperature produced acylation on the unsubstituted NH_2 - group (85c). At 40°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 BF_3 -Tris-U complex. Tris-U was found to react with triphenylphosphine oxide

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TABLE III

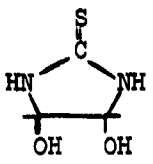
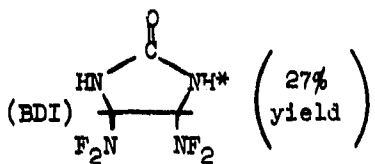
REACTIONS OF GLYOXAL WITH SUBSTITUTED UREAS



<u>R,R'</u>	<u>Intermediate</u>	<u>Product</u>	<u>Reference</u>
H,H	unident. syrup	 tentative ident.	269
$\frac{1}{2}\text{-Pr}$, $\frac{1}{2}\text{-Pr}$ (or) CH_3 , CH_3			269
H, $-\text{CNH}_2$			270
$\text{HC}-$, $-\text{CH}$ (in basic sol'n) excess $(\text{CHO})_2$			271
$\text{HC}-$, $-\text{CH}$ (basic sol'n)			268

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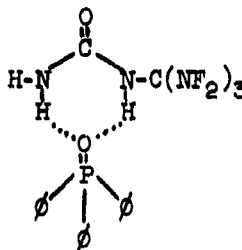
TABLE III (Concluded)

<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

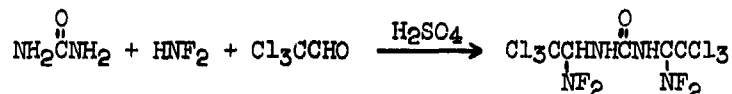
* If HCHO is added in second step, S is retained 268.

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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).

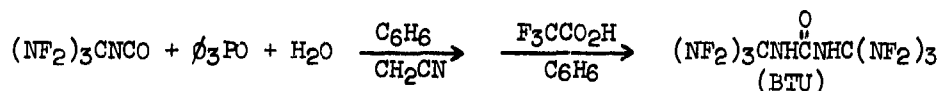


The fluorination of ureas has been attempted with urea, itself, and guanylurea. Fluorination of urea with HNF_2 in the presence of sulfuric acid and trichloroacetaldehyde (or tribromoacetaldehyde) resulted in the formation of an intermediate product, which did not undergo further reaction with HNF_2 (271).



The fluorination of guanylurea sulfate with 10% F_2/N_2 over NaF at -7°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).

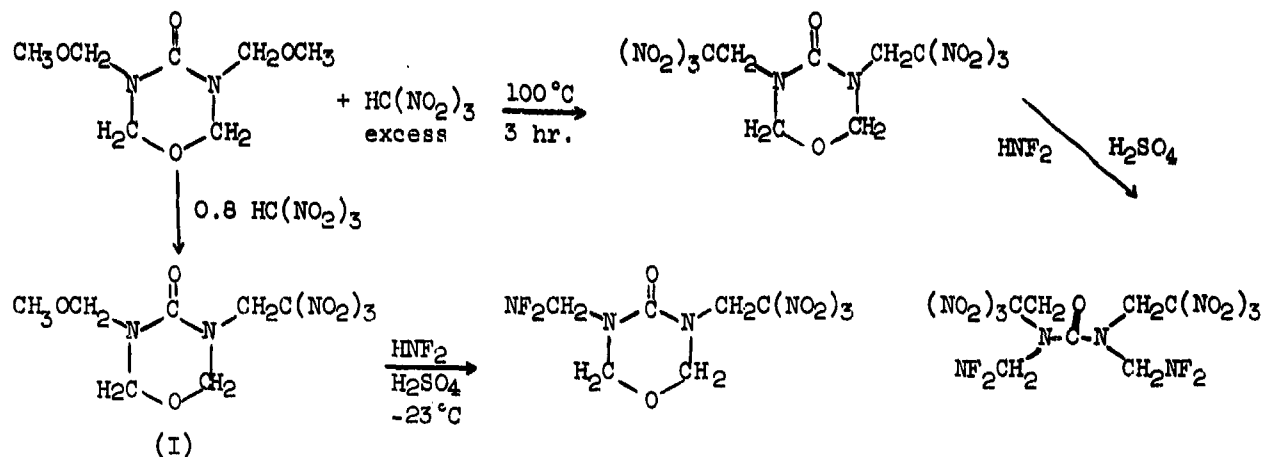
Disubstituted ureas: An improved method for the production of bis-[tris(difluoramino)methyl]-urea (code name: BTU) has been reported with an overall yield of 49% (162a).



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).

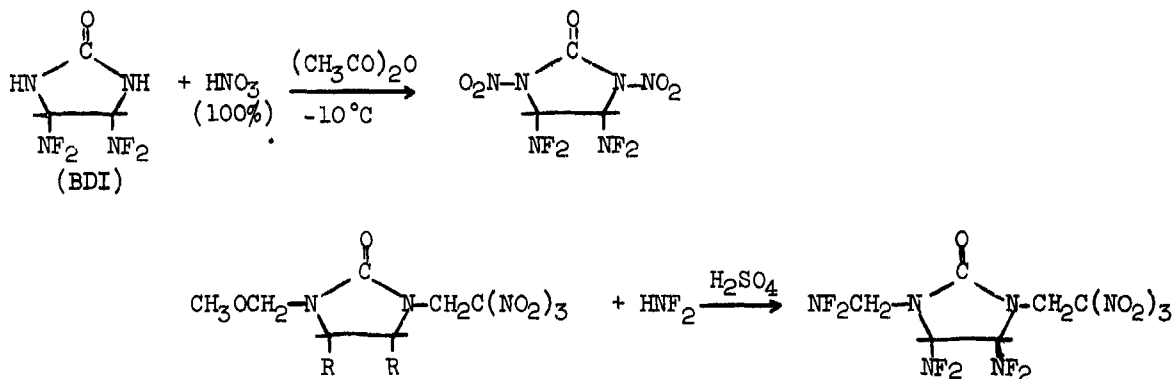
Cyclic ureas: Trinitromethane has been reacted with N-substituted cyclic ureas to produce the corresponding trinitromethyl-substituted compounds, which were then treated with difluoramine in H_2SO_4 . The reaction products were highly dependent upon the initial purity of the cyclic urea and upon the 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-difluoraminomethyl-N'-2,2,2-trinitroethyl-urea instead of the anticipated product (272). The reaction of compound (I) from above with difluoramine in H_2SO_4 at ambient temperature and autogenous pressure yielded N,N'-tris(difluoraminomethyl)-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 = $-\text{OCH}_3$ or $-\text{CH}_2\text{OH}$

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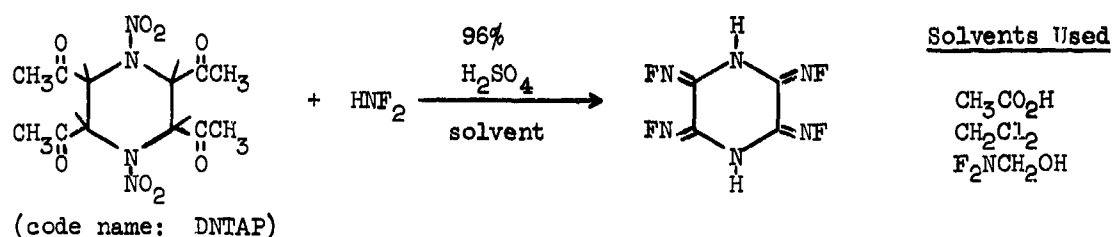
CHAPTER IV

IMINO COMPOUNDS

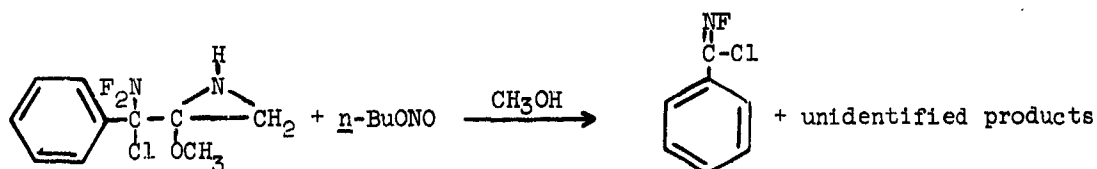
In this chapter, compounds containing the C=NF group could be considered. The first portion, fluorimines, will consider those molecules which contain groups other than -NF₂ attached to the carbon atom. The remainder of the chapter will be devoted to the discussion of compounds which contain the -NF₂ 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 HNF₂ 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.

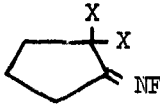
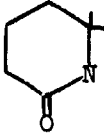
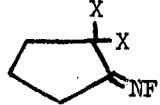
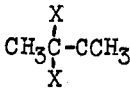
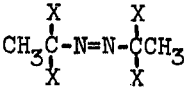
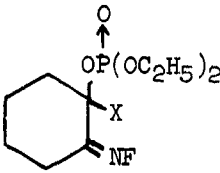
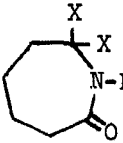
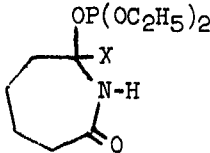
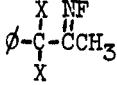
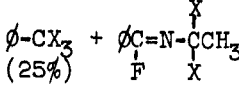
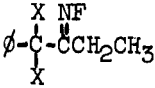
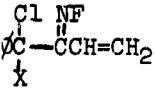
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TABLE IV

REACTIONS OF FLUORIMINES WITH DIFLUORAMINE

X = -NF₂

φ = phenyl

Reactant	Conditions	Product	Reference
	FSO ₃ H	NC(CH ₂) ₃ CX ₂ OSO ₂ F + 	447
NC(CH ₂) ₃ CX ₂ OSO ₂ F	H ₂ SO ₄	X ₃ C(CH ₂) ₃ CN	447
	BF ₃ , CH ₂ Cl ₂	X ₃ C(CH ₂) ₃ CN	447
	BF ₃		441
	HSO ₃ F, CH ₂ Cl ₂	 + 	447
	HSO ₃ F, CH ₂ Cl ₂ or BF ₃	 (25%)	447
	H ₂ SO ₄	φCO ₂ H + φCN	451
	Amberlyst 15	no reaction	451

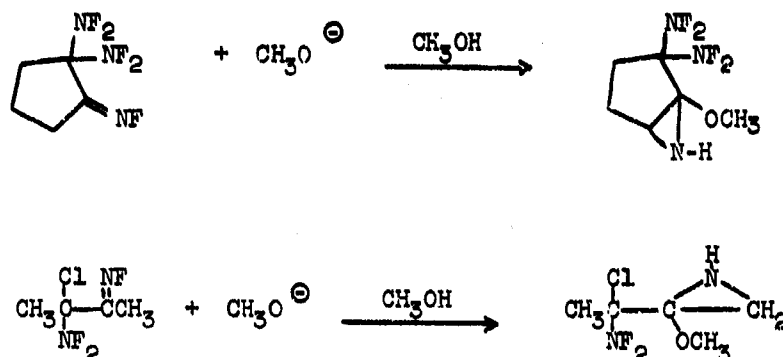
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TABLE IV (Concluded)

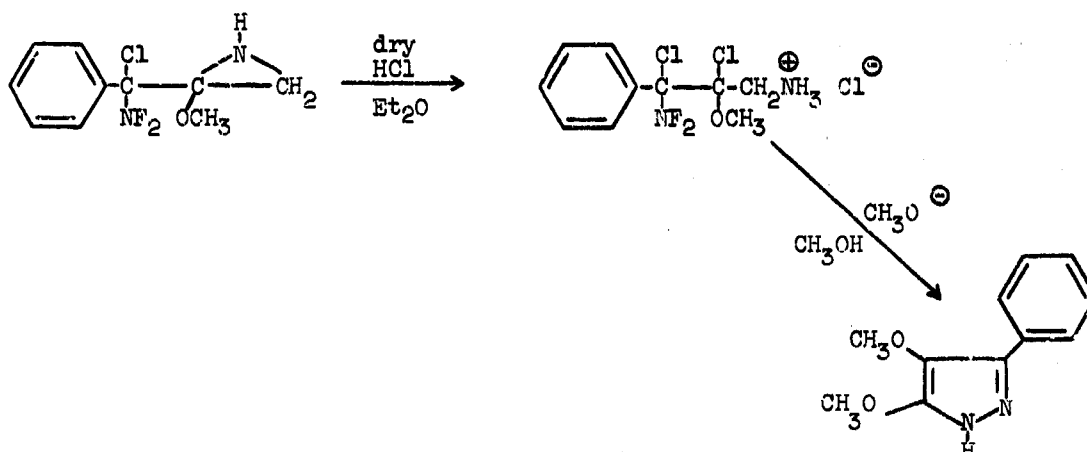
<u>Reactant</u>	<u>Conditions</u>	<u>Product</u>	<u>Reference</u>
$\begin{array}{c} \text{Cl} \quad \text{NF} \\ \quad \\ \phi\text{C}-\text{CCH}=\text{CH}_2 \\ \\ \text{X} \end{array}$	BF_3	$\begin{array}{c} \text{Cl} \\ \\ \phi\text{C}-\text{X} \\ \\ \text{F} \end{array}$	451
$\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{F})(\text{X})=\text{NCH}_3$	$\text{BF}_3, \text{CH}_2\text{Cl}_2$	$\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CN} + \text{CH}_3\text{CX}_3$	453
$\begin{array}{c} \text{X} \quad \text{NF} \\ \quad \\ \text{CH}_3\text{C}-\text{CCH}_3 \\ \\ \text{X} \end{array}$	H_2SO_4	$\begin{array}{c} \text{X} \quad \text{O} \\ \quad \\ \text{CH}_3\text{C}-\text{NHCCH}_3 \\ \\ \text{X} \end{array}$	501a
$\text{CH}_3(\text{CH}_2)_2\text{C}(\text{X})(\text{NF})\text{CC}_2\text{H}_5$	HSO_3F	unident. product; not the expected 1,1,1-tris-difluoramino)butane	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).

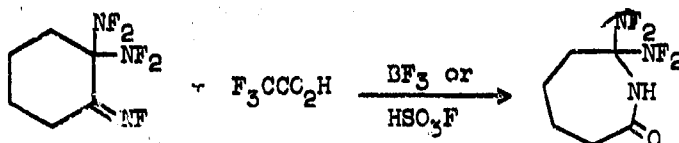
Attempts to oxidize fluorimines with peroxide have not been successful. Reaction of 1,2-bis(fluorimino)-cyclohexane with benzoyl peroxide in methylene chloride at room temperature for 4 hr. did not show any appreciable reaction (356).

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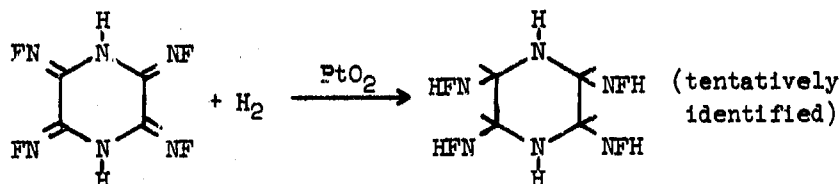
Fluosulfonic acid, often used as a catalyst in reactions of difluoramine, has been found to react with fluorimines via the Beckman Rearrangement (451a).



A similar type of reaction has been found to occur with 1,1-bis(difluoramino)-2-fluorimino-cyclohexane upon treatment with trifluoroacetic acid in BF_3 in HSO_3F (447).

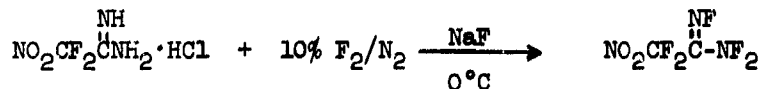
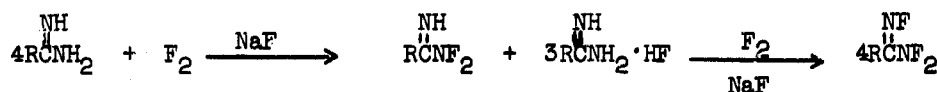


The hydrogenation of 2,3,5,6-tetra(flucrimino)-piperazine (code name: TFP) has been conducted with a platinum dioxide catalyst (269).



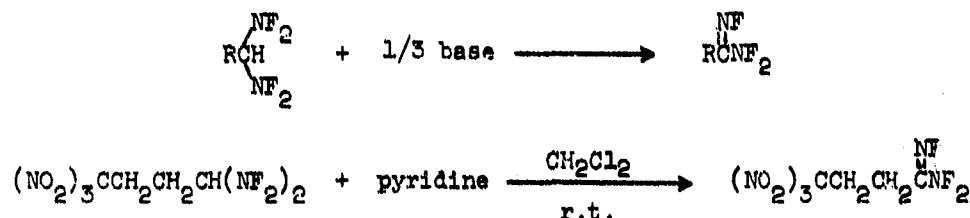
IV-B. N,N,N'-Trifluoramidines

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

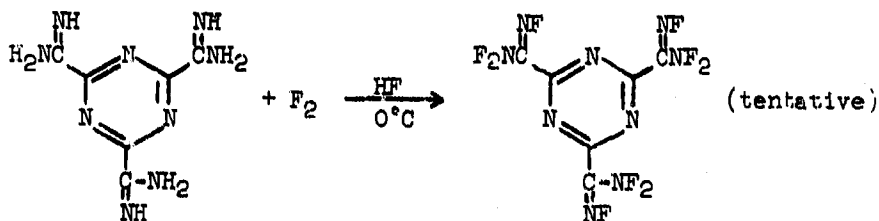


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The hydrolysis of gem-bis(difluoramino) compounds with base has also been utilized as a method for the preparation of fluorinated amidines (497).



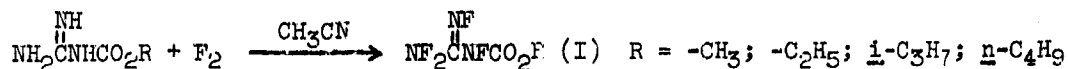
Fluorination with elemental fluorine in liquid hydrogen fluoride has been successful in converting amidines to fluoroamidines (497).



Reaction of 2-nitro-perfluoroacetamidine 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'-trifluorobenzamidine did not show any reaction after 15 hr. at room temperature (354).

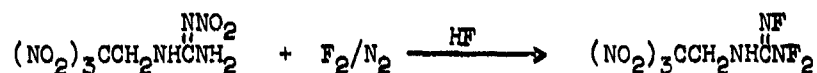
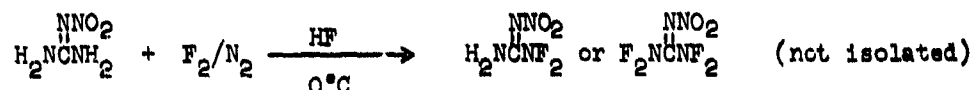
IV-C. Fluorinated Guanidines

Fluorination of guanylcabamate 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: F₆BG) 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, C₃F₈, CH₃NO₂, and C₄F₈, with 10 kilobars of compound has also been unsuccessful in producing any polymerization.

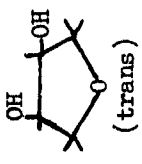
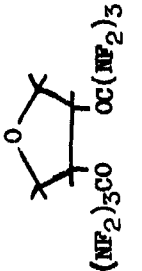
Many additional reactions of fluorinated adducts of PFG have been studied. The reaction of the fluorinated adduct of ethylglycolate (see Table V) with ammonia in methanol at room temperature for 2.5 hr. yielded tris(difluoramino)methoxyacetamide (code name: GA) (295). This compound is reported to be 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 (CH₃)₃COCl at ambient temperature.

TABLE V
REACTIONS OF PERFLUOROGUANIDINE (PFG)

Reactant	Conditions	Products	Reference
<u>I. Inorganic Compounds</u>			
$\text{LiNH}_2 + \text{KCNO}$	Freon 113; -80°C	$\text{NF}_2\text{C}(\text{NH}_2) + \text{N}_2\text{F}_2$ (F ₃ G)	Hynes 1966 Prop. Ingred. Conf.
LiCH_3	Et_2O ; -196°C	at 0°C - explodes	250
$\text{LiN}(\text{CH}_3)_2$	C_6H_6 ; R.T.	n.r.	250
O_3/O_2	CH_3CN ; 0°C	n.r.	267a
H_2S	acetone; R.T.	unident. prod.	267a
NH_4ClO_4	CH_3CN	unident. prod.	267a
H_2O_2	1) urea, Et_2O , R.T. 2) 10% F_2/N_2 ; -50°C	$(\text{NF}_2)_3\text{COOH}$	292, 295
N_2H_4	CH_3OCH_3 , -110°C	$\text{H}_2\text{C}(\text{NH}_2)\text{CNFH}$ NF_2	292
BF_3	R.T.	n.r.	15a
<u>II. Organic Compounds</u>			
<u>A. Alcohols, Diols and Hydroxy Compounds</u>			
$(\text{HOCH}_2\text{CH}_2)_3\text{N}\cdot\text{HClO}_4$	dimethylurea, CH_3CN , R.T.	colorless oil	267a

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TABLE V (Continued)

<u>Reactant</u>	<u>Conditions</u>	<u>Products</u>	<u>Reference</u>
$(\text{HOCH}_2\text{CH}_2)_3\text{N}$	CH_3CN	explodes	267a
$\text{CH}_3\text{CH}_2\text{NCO}_2\text{Et}$ OH	1) urea, CH_3CN 2) 10% F_2/N_2 , -30°C	$(\text{NF}_2)_3\text{CONHCO}_2\text{Et}$	292
$\text{ClCH}_2\text{CH}_2\text{OH}$ (or) $\text{BrCH}_2\text{CH}_2\text{OH}$	1) urea, R.T. 2) 5% F_2/N_2 , -45°C	$\text{ClCH}_2\text{CH}_2\text{OC}(\text{NF}_2)_3$ $\text{BrCH}_2\text{CH}_2\text{OC}(\text{NF}_2)_3$	294
$\text{HOCH}_2\text{CH}_2\text{OH}$ (excess)	1) R.T., 15 hr. 2) 5% F_2/N_2 , -30°C	$\text{HOCH}_2\text{CH}_2\text{OC}(\text{NF}_2)_3$	294
$\text{HOCH}_2\text{CNH}_2$	urea, CH_3CN	$\text{NH}_2\text{CCH}_2\text{OC}(\text{NF}_2)_3$ NH	294
$\text{C}_5\text{H}_{11}\text{OH}$	urea, r. t.	$\text{C}_5\text{H}_{11}\text{OC}(\text{NF}_2)_2$ NFH	354
 (trans)	1) urea; CH_3CN 2) 20% F_2/N_2 ; -25°C	 $(\text{NF}_2)_3\text{CO}$ $\text{OC}(\text{NF}_2)_3$	174
$\text{HOCH}_2\text{CH}_2\text{CN}$	1) urea; CH_3CN 2) 20% F_2/N_2 ; -25°C	$(\text{NF}_2)_3\text{COCH}_2\text{CH}_2\text{CN}$	175
$(\text{O}_2\text{NOCH}_2)_3\text{CCH}_2\text{OH}$	1) urea; CH_3CN 2) 25% F_2/N_2 ; -10°C	$(\text{O}_2\text{NOCH}_2)_3\text{CCH}_2\text{OC}(\text{NF}_2)_3$ (FA-PETRIN)	175

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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
$(NO_2)_3CCH_2CHCH_2OH$ OH	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
$(NO_2)_2CFCHCH_2OH$ OH	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 ; $-25^\circ C$	$C_2H_5O_2C-CH(OC(NF_2)_3)-CHCO_2C_2H_5$ OC(NF ₂) ₃ (FA-DET)	175
$(NO_2)_3CCH_2NCH(CH_2OH)_2$ NO 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-TNEND)	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
$(NO_2)_3CCH_2C(CH_2OH)_2$ NO ₂	1) urea; CH_3CN 2) 25% F_2/N_2 ; $-10^\circ C$	$[(NO_2)_3CCH_2C(CH_2OH)_2]_2$ NO ₂ (FA-TWH)	178

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TABLE V (Continued)

Reactant	Conditions	Products	Reference
$\left(\begin{array}{c} \text{NO}_2 \quad \text{NO}_2 \\ \quad \\ \text{HOCH}_2\text{CCH}_2\text{NCH}_2 \\ \quad \\ \text{NO}_2 \quad \text{NO}_2 \end{array} \right)_2$	1) urea; CH_3CN 2) 25% F_2/N_2 ; -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
$\text{HOCH}_2(\text{CH}_2)_6\text{CH}_2\text{OH}$	1) urea; CH_3CN 2) 20% F_2/N_2 ; -10°C	$(\text{NF}_2)_3\text{COCH}_2(\text{CH}_2)_6\text{CH}_2\text{OC}(\text{NF}_2)_3$ (FA-OD)	179
$\text{HOCH}_2\text{CO}_2\text{C}_2\text{H}_5$	1) urea; CH_3CN 2) 5% F_2/N_2 ; CFCl_3	$(\text{NF}_2)_3\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5$	293
B. Miscellaneous Compounds			
$\text{HON}=\text{C}-\text{NH}_2 \cdot 2\text{HClO}_4$ $\text{HON}=\text{C}-\text{NH}_2$	dimethylurea CH_3CN	n.i.	267a
CH_3NO_2	urea; CH_3CN	unident. product	267a
NOH HCNH_2	CH_3CN	$\text{NH}_2\text{CH}=\text{NOC}(\text{NF}_2)_2\text{NPH}$	292
$\text{CF}_2(\text{OF})_2$	F_2/N_2	$(\text{NF}_2)_3\text{CFCO}$	291
$\text{HON}=\text{CCl}_2$	1) urea; CH_3CN 2) 3% F_2/N_2 ; CH_3CN 3) CFCl_3 ; $\text{CF}_2(\text{OF})_2$	$(\text{NF}_2)_3\text{CON}=\text{CCl}_2$ $(\text{NF}_2)_3\text{CON}=\text{CCl}_2$ $+$ $(\text{NF}_2)_2\text{CFON}=\text{CCl}_2$	293

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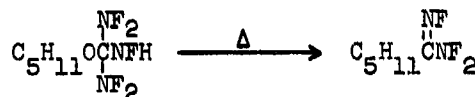
TABLE V (Concluded)

<u>Reactant</u>	<u>Conditions</u>	<u>Products</u>	<u>Reference</u>
CH_3CHO	$\text{CH}_3\text{CN}; (\text{CH}_3)_3\text{N}$	n.r.	294
$\text{FHNCO}_2\text{C}_2\text{H}_5$	urea; CH_3CN	mixture of products	15a
$\text{HC}(\text{NO}_2)_3$	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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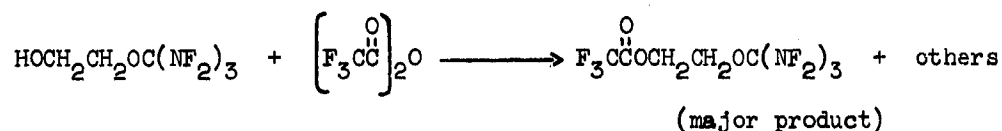
Heating the adduct of n-pentyl alcohol with PFG has been shown to yield the corresponding N,N,N'-trifluoroamidine (354).



The reaction of perfluoroguanidine with 2,2,2'-trinitroethylethylene 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.



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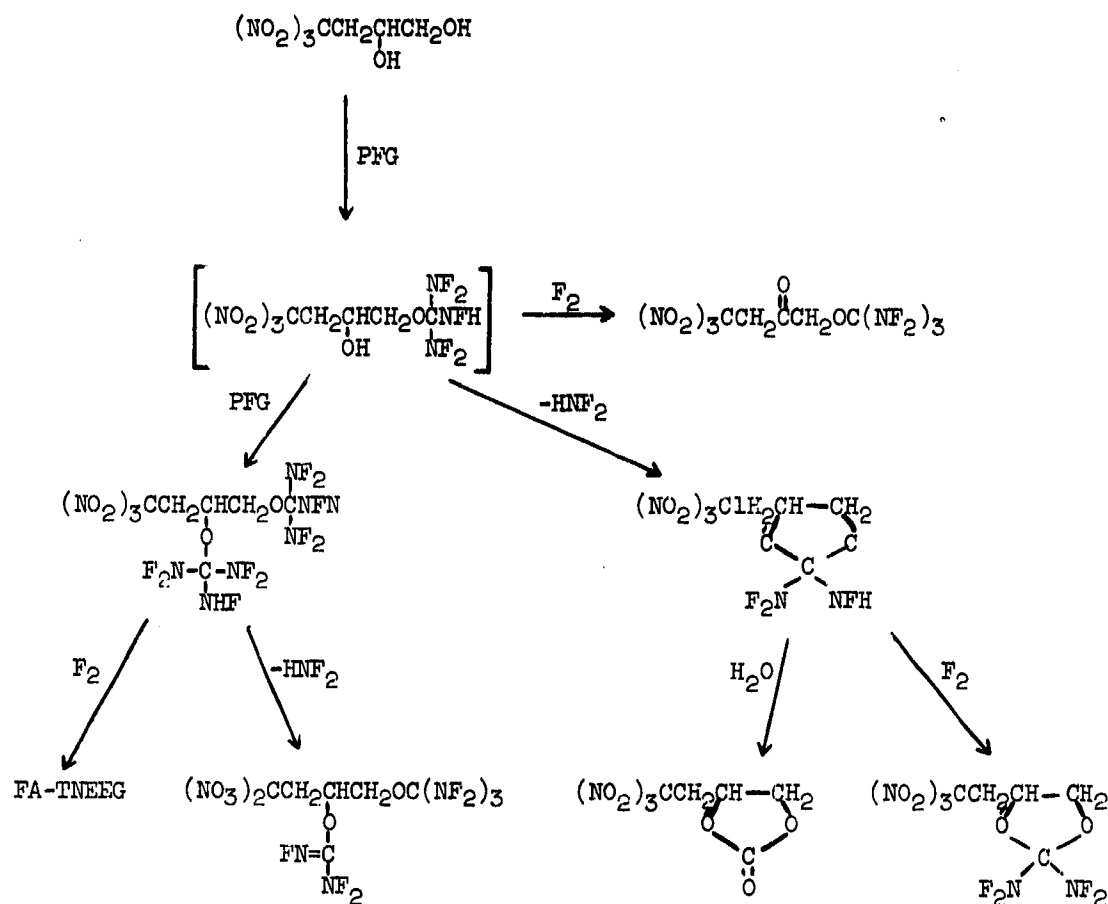


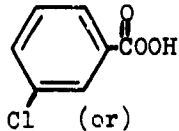
Figure 2 - Side Reactions in the Production of FA-TNEEG

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TABLE VI

REACTIONS OF $(\text{NF}_2)_3\text{CON}=\text{CCl}_2$

<u>Reactant</u>	<u>Conditions</u>	<u>Products</u>	<u>Ref.</u>
CH_3OH	$\text{NaOH}; \text{CFCl}_3$	$(\text{NF}_2)_3\text{CON}=\text{C}(\text{OCH}_3)_2$	296
$(\text{CH}_3)_2\text{NH}$	CFCl_3	$(\text{NF}_2)_3\text{CON}=\text{C} \text{N}(\text{CH}_3)_2$	296
$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	CH_3OH	decomposes	296
 Cl (or)	CHCl_3) CH_2Cl_2)	no reaction	295
CF_2N_2 or N_2F_4	CFCl_3	no reaction	296
NH_3		$(\text{NF}_2)_3\text{CON}=\text{C}(\text{NH}_2)_2$	297
70% HClO_4	CH_3CN	no reaction	293
3% F_2/N_2	$\text{CH}_3\text{CN}; 0^\circ\text{C}$	no reaction	295
CsF	CH_3CN	$(\text{NF}_2)_3\text{CN}-\overset{\text{O}}{\text{C}}\text{F}_2 + \text{others}$	298
		$\left[(\text{NF}_2)_3\text{CON}=\text{C}-\text{N} \begin{array}{c} \diagup \diagdown \\ \text{---} \text{---} \end{array} \text{N} \right]_n$ tentative only	298

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CHAPTER V

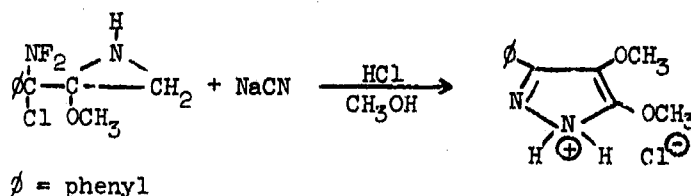
NF COMPOUNDS WHICH CONTAIN NN BONDS

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-NO₂ 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.

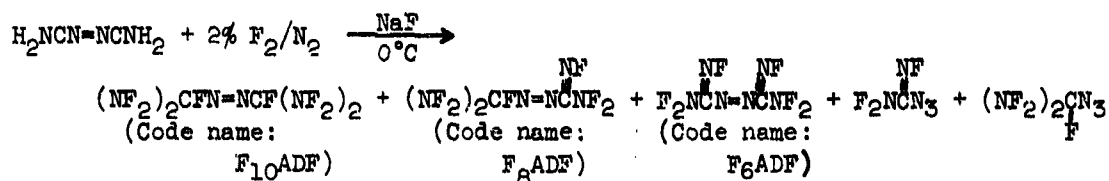
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Tris(difluoroamino)methyl chloride has been found to react with dimethyl sulfoxide (DMSO) at room temperature to yield two diazirines (85a).

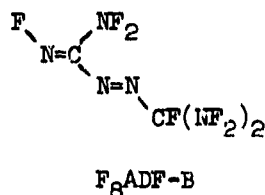
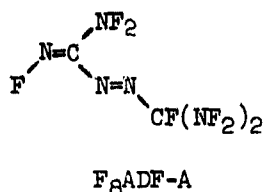


Reaction of acetamidine with sodium hypochlorite in DMSO has been reported to give chloromethyldiazirine (434).

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).

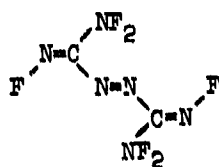


The compound F_8ADF has two isomers which have been designated A and B. Their structures are given below (255).

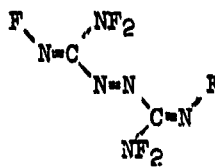


When the fluorination of azodiformamidine was carried out at -75°C and then allowed to warm to 0°C , the compound designated F_8ADF was found to be the principal product (255). Like F_8ADF , the F_6ADF was found to be isomeric, and the three isomers have been identified.

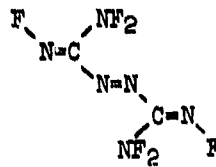
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(trans-trans)

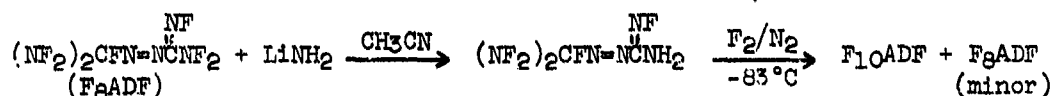


(cis-trans)

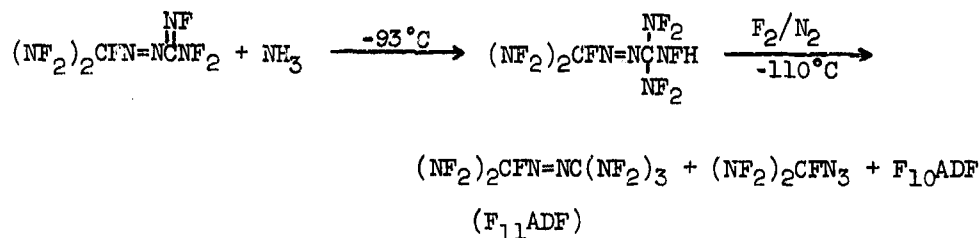


(cis-cis)

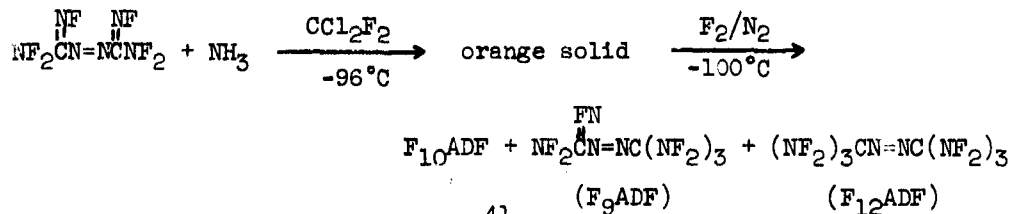
The reduction of several of the fluorinated azodiformamidines has been studied with lithium amide and ammonia. Reaction of F_8ADF with LiNH_2 was found to produce the N-fluoroamidine, which upon fluorination yielded F_{10}ADF (249,112a).



Similar treatment of F_{10}ADF with LiNH_2 in Freon 113 resulted in no observable reaction (252,112a); however, F_8ADF 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 ($\text{C}=\text{NF}$) is required (112a). With ammonia, F_8ADF -A reacted to form the addition compound. Fluorination of this compound with elemental fluorine led to the production of F_{11}ADF and F_{10}ADF (112a).



A similar reaction of ammonia with F_6ADF yielded an orange solid, which upon fluorination resulted in the formation of F_{10}ADF as the major product, with minor amounts of two materials tentatively identified as F_9ADF and F_{12}ADF (249,254,112a).



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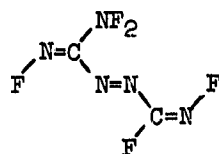
The reactions of $F_{10}ADF$ and of the two isomers of F_8ADF with carbon monoxide at elevated temperatures have led to the formation of two new compounds, F_4ADF and F_5ADF as in Table VII.

TABLE VII

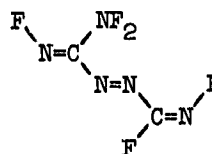
REACTIONS OF $F_{10}ADF$ AND F_8ADF WITH CO

	References
$(NF_2)_2CFN=NCF(NF_2)_2 + CO \xrightarrow{180^\circ C} \begin{array}{c} NF \quad NF \\ \quad \\ FCN=NCF \end{array} + COF_2$	(112a, 256)
$(NF_2)_2CFN=NCF_2 + CO \xrightarrow{125^\circ C} \begin{array}{c} NF \quad NF \\ \quad \\ FCN=NCF \end{array} + F_5ADF(A+B)$	(256)
$(NF_2)_2CFN=NCF_2 + CO \xrightarrow{120^\circ C} \begin{array}{c} NF \quad NF \\ \quad \\ NF_2CN=NCF \end{array}$ (F_8ADF-B) (F_5ADF)	(256)

At $135^\circ C$ 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).

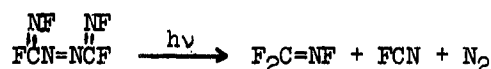
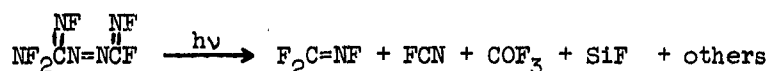


trans-isomer A



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).



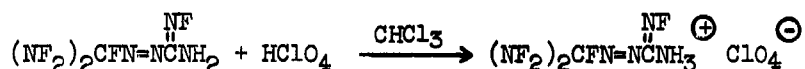
A mechanism for the formation of the products observed from the photolysis of the F_4ADF has been proposed (256).

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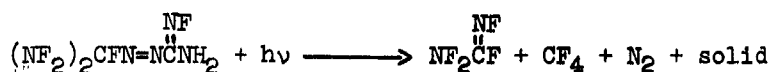


The reaction of F₁₀ADF with nitrogen dioxide at 190°C resulted in decomposition of the starting material (250). Unsuccessful attempts were made to react hydrogen sulfide and monogermene with F₁₀ADF (250,112a).

Several reactions have been attempted utilizing the partially hydrogenated intermediate formed in the reduction of F₈ADF 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).

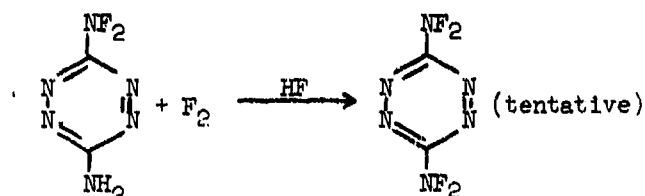


The reaction of tris(difluoramino)fluoromethane (code name: Compound R) with sodium azide in DMSO led to the formation of difluoro-fluoraminomethylazide (85c).

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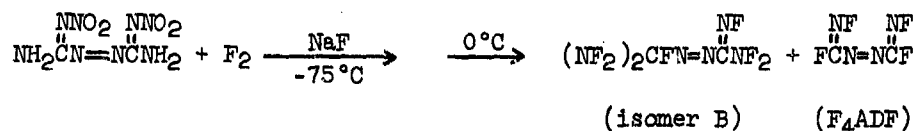
Fluorination of 3,6-diamino-1,2,4,5-tetrazine with elemental fluorine in liquid hydrogen fluoride led to a compound tentatively identified as the 3,6-bis-(difluoramino) substituted analog (497). Attempts to isolate the material resulted in a rapid decomposition.



V-C. NNO and NNO₂ Derivatives

The preparation and reaction of the NNO- and NNO₂-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).

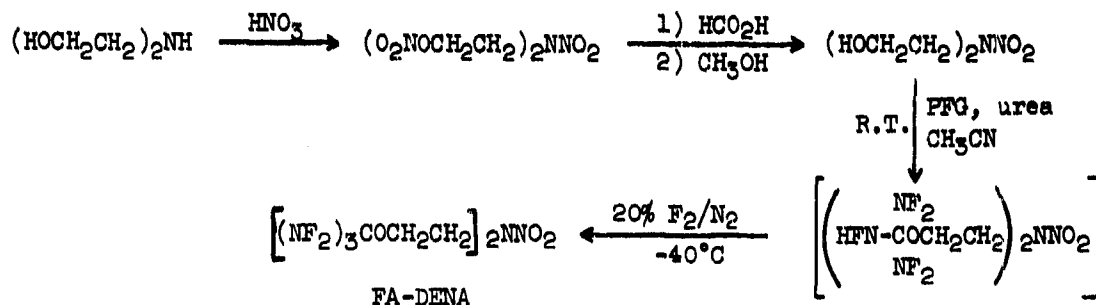
Fluorination of dinitroazodiformamidine in the presence of sodium fluoride at low temperature has led to the formation of F₃ADF-B, F₄ADF, and two unidentified products (252).



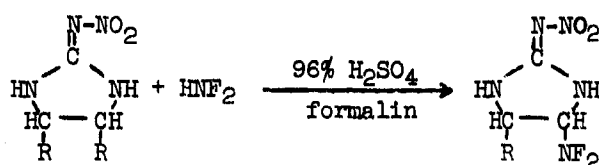
Attempts to conduct the same fluorination in aqueous solution in the presence of B₂O₃ were unsuccessful and similar negative results were obtained by the use of a fluorine-helium mixture in the presence of sodium fluoride in Freon 113 at -22°C (252). The use of acetonitrile as a solvent resulted in an explosion.

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

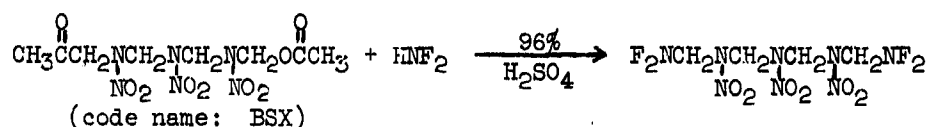
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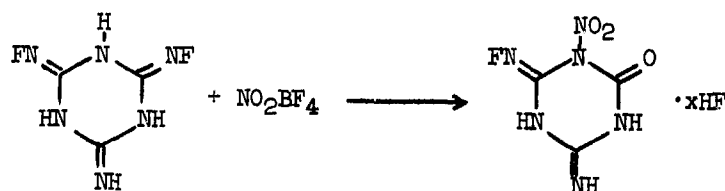
Difluoramine, in the presence of 96% sulfuric acid, has been used to replace alkoxy groups by difluoramino groups in substituted imidazolidine imines (270,272) and acetoxy groups from substituted amines (269).



R = -OCH₃ or -OC₂H₅



Nitryl tetrafluoroborate (NO₂BF₄) 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 NF_3 has recently been redetermined by two methods: the direct reaction with sulfur (158) and via the dissociation of excess NF_3 in the explosion with H_2 (151a, 151, 151f, 155). The measured values were -31.75 ± 0.2 and -31.44 ± 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 ± 2 kcal/mole, confirming the earlier conclusions that the dissociation of the first N-F bond (to give stable NF_2 radicals) is lower than the average. The latter study was used to recalculate the heat of formation of aqueous HF (1:123 H_2O) as -77.0 ± 0.2 kcal/mole. The value of $\Delta H_f^\circ = -30.60$ kcal/mole is then recommended in the use of NF_3 as a calorimetric fluorinating agent.

Studies of the dipole moment of NF_3 gave a tentative value of 0.17D (232) and from work at 48° and 80°C the value 0.20D (238).

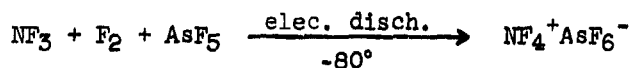
Efforts to observe the ion-molecule reaction



have not been successful to date (386, 402, 405). High energy radiation of mixtures of NF_3 and F_2 with AsF_5 at -196° gave (472) moderately stable solids which appeared to contain the salt $\text{NF}_4^+\text{AsF}_6^-$ (dec. 200°) together with $\text{N}_2\text{F}_3^+\text{AsF}_6^-$ (dec. $110 - 170^\circ$) and apparently a third salt which evolved N_2F_2 and AsF_5 at $20 - 50^\circ$ (N_2FAsF_6 is known to be much more stable than this). Radiation of $\text{NF}_3\text{-F}_2\text{-BF}_3$ mixture at -196° in a sapphire tube (oxygen-free fluorine) gave high purity NF_4BF_4 . The synthesis and properties of NF_4^+ salts are described in detail in section B of this chapter. Further reactions of NF_3 which have been studied or attempted are summarized in Table VIII.

VI-B. NF_4^+ Salts

The synthesis of salts of the long sought 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_3

<u>Reactant</u>	<u>Conditions</u>	<u>Results</u>	<u>References</u>
Cl_2	200 - 500°, 8000 - 10,000 psi	No reaction	75
NO	200 - 500°, 8000 - 10,000 psi	NO_2 , NOF	75
NO	Excess NF_3 , 300°, 8800 psia	NOF , NF_3	78
NO excess	200°	Exploded	78
$\text{NO/cis-N}_2\text{F}_2$	66°, 80,000 psi, 1 hr.	25% dec. of N_2F_2	89
OF_2	300°	Dec. of OF_2	339
OF_2	200°, 10,000 psi, 6 hr.	Unk. with IR abs. at 1225 and 2175 cm^{-1}	75
OF_2	Flash photolysis, liquid	O_3	88
CsF	500°, 8000 psi, 1 hr.	No reaction	78
CsF; NO	300°, 8800 psi, 18 hr.	Some NOF , probably N_2	78
BF_3 (or PF_5)	Tesla coil disch., 5 mm. pr. -196° quench	Some $\text{N}_2\text{F}^+\text{BF}_4^-$ (or PF_6^-) and SiF_6^{2-}	232
BF_3	1445 psi, 25°	No deviation from ideality	232
PF_5	1090 psi, 25°	No deviation from ideality	232
SbF_5	200°, 2400 psi, 50 hr.	~ 2% reaction of NF_3 to NF_4^+ ? and unidentified product	479

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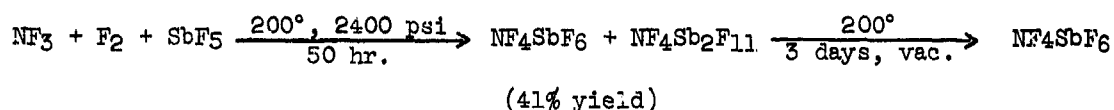
TABLE VIII (Concluded)

<u>Reactant</u>	<u>Conditions</u>	<u>Results</u>	<u>References</u>
AlCl_3	80° , 4 days (or 135° fast)	N_2Cl_2	227
Fe^{+2} , H_2aq^+	60° , fast	NH_4^+ , Fe^{+3} , F^-	227
c- or t- N_2F_2 , $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$	82° , 6, 100 atm., 4 hr.	Dec. of <u>cis</u> - N_2F_2	88
Xe	Flash photolysis, liquid	XeF compounds	88
ClF_3	425° , 1350 psig	No reaction	339
ClF_5	325° , 2125 psig, 20 hr.	Some ClF_3 and F_2	339
ClO_3F	475° , 2050 psig, 18 hr.	No reaction	339
ClF_2SbF_6	250° , 3 hr.	No reaction	339
ClF_2SbF_6	350° , 80 hr.	36%, dec. of NF_3 , hard pink solid	339
ClF_2SbF_6	350° , 23 hr.	No reaction	339
ClF_4SbF_6	200°	Some ClF_5 evolved	339
CsClF_4	200° , 24 hr.	No reaction	
CsClF_4	470°	Sl. dec. to CsF , ClF , ClF_3 , CuF_2 and NiF_2	340
ClO_2	110°	No reaction	340
t- N_2F_2	γ -Radiation, -196°	N_2 , F_2 , N_2F_4	471
N_2F_4	γ -Radiation, -196°	Inconcl. (Si contami- nation)	472
O_2	UV, liquid	Small amounts NO_2F , O_2F	532d

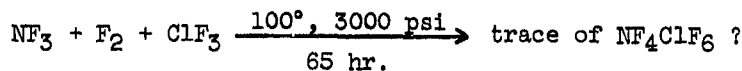
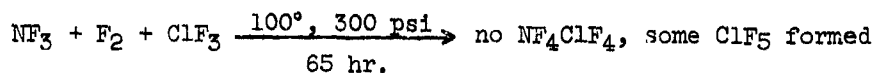
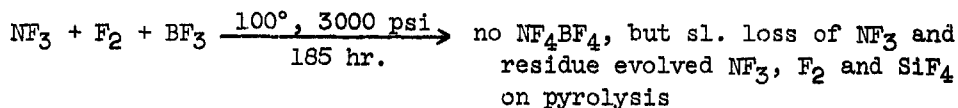
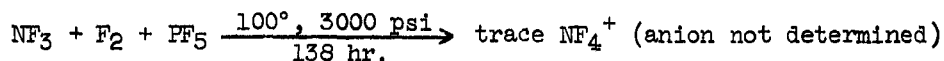
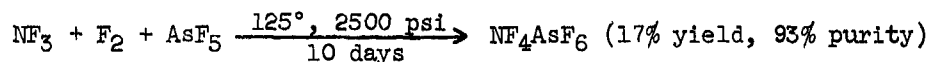
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The compound (apparently contaminated by N-O salts) was reasonably stable to 200° and gave an infrared spectrum showing bands at 1165 and 707 cm⁻¹ attributable to the NF₄⁺ and AsF₆⁻ ions. Publications describing the synthesis and properties (L11, L28) 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 ¹⁹F NMR (resonance of -215 ϕ) and thermal pyrolysis studies to be NF₄SbF₆ (476). The four component reaction system used, NF₃/F₂/SbF₅/HF, had in one run previously (475) given evidence of some reaction. The analogous reaction with AsF₆ 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 NF₄Sb₂F₁₁ was also demonstrated (477), but the excess SbF₅ could be removed. The final procedure is as follows:

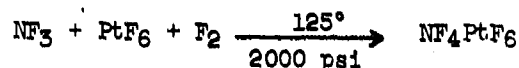


The synthesis and properties of NF₄SbF₆ and NF₄AsF₆ by similar methods have been described in the literature (156, 157), but applications of this method with weaker Lewis acids have been less successful as shown by the results (487) shown below:



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The identification of the ClF_5 reaction product was based only on the evolution of some NF_3 , F_2 , SiF_4 and ClF_5 when the reactor was heated above 225° , after prior evacuation at ambient. (In view of the dubious existence of the ClF_6^- anion the latter product appears unlikely.) As might be expected, however, PtF_6 forms a stable salt (559a).



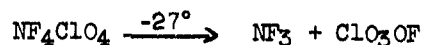
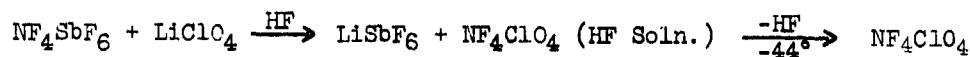
The direct reaction of NF_3 and SbF_5 (without F_2) at 200° and 2400 psi for 50 hr. appeared to give (479) a mixture of NF salts based on the reported hydrolysis products: NF_3 and O_2 from NF_4^+ , N_2O from N_2F^+ and NO and NO_2 from N_2F_3^+ .

In studies at Midwest Research Institute in early 1963, the formation of small amounts of NF_4AsF_6 was observed (248b) from the fluorination of $\text{N}_2\text{F}_3\text{AsF}_6$ at 115° , but the reaction route is not clear and may involve NF_3 as an intermediate. Results of studies at Shell (472) at about the same time suggested the formation of NF_4AsF_6 upon high energy radiation of a mixture of NF_3 , F_2 and AsF_5 at -196° . The resulting solid product evolved N_2F_2 and AsF_5 at $20 - 50^\circ$, N_2F_4 and AsF_5 at $110 - 170^\circ$ (i.e., from $\text{N}_2\text{F}_3\text{AsF}_6$) and NF_3 and AsF_5 at 200° (i.e., from NF_4AsF_6). Further studies with BF_3 in place of AsF_5 and oxygen free F_2 have led to good yields ($\sim 160 \text{ mg/hr}$) of high purity NF_4BF_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 NF_4ClF_4 .

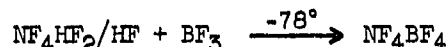
The synthesis of NF_4ClO_4 and other NF_4^+ salts by metathesis reactions have been studied extensively at Stanford, although previous calculations (474) had indicated that no oxyanions would be stable with NF_4^+ . The high solubilities of NF_4SbF_6 and NF_4AsF_6 , 2.6 and 1.2 g/g of anhydrous HF, respectively (157) make this an attractive solvent system. Preliminary studies (478) indicated that NF_4SbF_6 and KClO_4 were compatible as a solid mixture and in HF solution. The metathesis reaction with 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 NF_4ClO_4 which decomposed below room temperature:



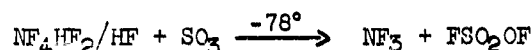
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This mode of decomposition, previously predicted (276a), is in contrast to the decomposition in all other reported systems involving fluorocations and the perchlorate ion, i.e., to give FClO_3 by the oxide-ion transfer mechanism (276a). A similar result was obtained when the metathesis reaction of NF_4SbF_6 and CsClO_4 was attempted in IF_5 solution, except the product NF_4ClO_4 decomposed at the melting point of the IF_5 , (559a) pure IF_5 melts at 10° .

Similarly, the metathesis reaction with LiF or HF gave a stable solution of NF_4HF_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 NF_3 , F_2 and HF at -44° (559a). However, the NF_4HF_2 solution is useful as an intermediate in the metathetical preparation of NF_4BF_4 (489).



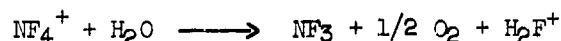
However, the salt of the oxyanion SO_3F^- could not be prepared by an analogous reaction as decomposition occurred:



Mixtures of the solid salts NF_4SbF_6 and LiClO_4 reacted at 55° similarly to give ClO_3OF while mixtures with KBr , KCl or KF evolved the corresponding halogen gases at 25° , 150° and 225° , respectively (488).

The thermal stabilities, of the known NF_4^+ salts containing perfluoroanions are (487, 593a) as follows: NF_4SbF_6 dec. $\sim 300^\circ$; NF_4AsF_6 , dec. $\sim 270^\circ$; NF_4BF_4 , dec. 236° . The good stability of the NF_4BF_4 is apparently kinetically derived (276a) since calculations indicate that the heat of decomposition to NF_3 , F_2 and BF_3 is $+3.6$ kcal/mole at 25° , although ΔH_f is -305.2 kcal/mole (593a). Differential thermal analysis on a sample of NF_4SbF_6 containing some $\text{Sb}_2\text{F}_{11}^-$ indicated a melting point of 170° (478). The density of single crystals of NF_4AsF_6 deposited from HF solution is 1.9225 g/ml.

All of the NF_4^+ salts are sensitive to moisture and appear to react with many organics (593a). The hydrolysis is described (478) by the equation

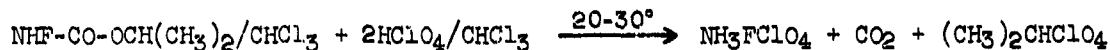


The NF_4SbF_6 reacts with traces of moisture in glass at ambient temperature and attacks glass at 85° to give SiF_4 , NF_3 and presumably O_2SbF_6 .

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VI-C. NH₃F⁺ 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 NH₃FClO₄ 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% HClO₄ caused partial hydrolysis of NH₃F⁺ and thus led to lower yield and purity. The use of anhydrous HClO₄ 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 CH₂Cl₂. 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 NH₃FClO₄ sample prepared from 70% HClO₄ 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 (NH₂ bend), i.e., shifted to shorter wavelengths by ~ 0.15 μ from NH₄ClO₄. The N-F band was not observed, and was assumed to be obscured by the ClO₄⁻ bands. The heat of formation of NH₃FClO₄ 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⁻, 1/3 NH₄⁺, 2-1/3 H⁺, 1/3 N₂ and ClO₄⁻. From the heat of formation and the assumption that the heat of vaporization of NH₃FClO₄ equals that of NH₄ClO₄ and that the N-H bond energy in NH₃F⁺ 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 NH₃FClO₄ with an aluminized butadiene fuel was calculated to be about 270 sec.

The NH₃FClO₄ 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 NH₃FClO₄ also occurs with the methanesulfonic acid salt, NH₃FSO₃CH₃, which undergoes a complex decomposition to give N₂H₄ along with N₂ and NH₃ (but no NO₂⁻, NO₃⁻ or NH₂OH).

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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° 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° 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_2F_2

Reactions and Results	Reference
$N_2F_2 + CsF \xrightarrow{25^\circ}$ 20 mole percent N_2F_2 absorbed ($Cs^+N_2F_3^-$?)	79
$N_2F_2 + CsF \xrightarrow[> 250 \text{ psi}]{60^\circ}$ dec. of N_2F_2	79
N_2F_2 (mostly <u>trans</u>) + $CsF \xrightarrow{-111^\circ}$ some solid "complex" $\xrightarrow{25^\circ}$ <u>cis</u> - N_2F_2	79
$N_2F_2 + CsF \xrightarrow{CFCl_3}$ no absorption, but one of two runs exploded	79
$N_2F_2 + OF_2 + CsF \xrightarrow[16 \text{ hr.}]{-50^\circ}$ No rxn. $\xrightarrow[20 \text{ hr.}]{25^\circ}$ unident. prod.	79
$N_2F_2 + OF_2 \xrightarrow[20 \text{ hr.}]{25^\circ}$ No rxn.	79
$N_2F_2 + OF_2 + CO_2 + CsF \longrightarrow (CF_3O)_2O$ (not obtained from ternary combinations)	79
$N_2F_2 + Cl_2 + CsF \longrightarrow$ unident. prod.: $N_2F_2Cl^+$ in mass spec. (two runs exploded)	79
N_2F_2 (<u>cis</u> or <u>trans</u>) + $CsF \xrightarrow{-80^\circ}$ some abs. of N_2F_2 (more <u>trans</u> abs.) $\xrightarrow{25^\circ}$ <u>cis</u> desorbs	80
$N_2F_2 + Cl_2 \xrightarrow[24 \text{ hr.}]{-80^\circ}$ No rxn.	80
<u>cis</u> - $N_2F_2 + OF_2 \xrightarrow[24 \text{ hr.}]{-80^\circ}$ unident. IR peaks	80
<u>cis</u> - $N_2F_2 \xrightarrow[4000 \text{ atm.}]{200^\circ}$ Detonation	88
<u>trans</u> - $N_2F_2 \xrightarrow[3400 \text{ atm.}]{82^\circ}$ No rxn.	88
$N_2F_2 + N_2F_4 \xrightarrow[6200 \text{ atm.}]{93-100^\circ}$ NF_3	88

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TABLE IX (Continued)

Reactions and Results	Reference
<u>cis</u> - or <u>trans</u> -N ₂ F ₂ + HClO ₄ ·2H ₂ O $\xrightarrow[4 \text{ hr. (NF}_3\text{)}]{82^\circ, 6100 \text{ atm.}}$ dec. of N ₂ F ₂	68
N ₂ F ₂ + Mg(ClO ₄) ₂ $\xrightarrow[\text{NF}_3]{10 - 52 \times 10^3 \text{ psig}}$ unident. rxn.; no N ₂ FCLO ₄	89
<u>cis</u> -N ₂ F ₂ + NO/NF ₃ $\xrightarrow[1 \text{ hr.}]{66^\circ, 8 \times 10^4 \text{ psig}}$ 25% dec. of NF ₃	89
<u>cis</u>-N₂F₂ + H₂O $\xrightarrow{74^\circ}$ <u>trans</u>-N₂F₂ + H₂O $\xrightarrow{89^\circ}$ $\searrow$ $\swarrow$ 1st order rate N₂ + 1/2 O₂ + 2 HF	227
(Note: no effect by OH ⁻ or surface on <u>cis</u> ; no N-O-F intermed. obsd.)	
N ₂ F ₂ + CO $\xrightarrow[\text{slow}]{\text{u.v. NR } 100^\circ}$ CF ₂ O	259
<u>t</u> -N ₂ F ₂ + ClO ₂ F $\xrightarrow{-78 \text{ to } 25^\circ}$ No rxn. $\xrightarrow{200^\circ}$ ClF ₃ + NF ₃ + N ₂ + O ₂	340
<u>t</u> -N ₂ F ₂ + ClO ₃ F $\xrightarrow{-78 \text{ to } 25^\circ} \sim$ No rxn. $\xrightarrow{> 150^\circ}$ dec. of N ₂ F ₂	340 341
<u>t</u> -N ₂ F ₂ + ClF ₅ $\xrightarrow{-78 \text{ to } 25^\circ}$ No rxn. (sl. dec. of N ₂ F ₂)	340
$\xrightarrow{> 150^\circ}$	341
dec. of N ₂ F ₂	
<u>t</u> -N ₂ F ₂ + OF ₂ $\xrightarrow{-78 \text{ to } 150^\circ}$ some dec. of both	342
<u>t</u> -N ₂ F ₂ + ClF $\xrightarrow{-78 \text{ to } 150^\circ}$ some dec. $\xrightarrow{150^\circ}$ ClF ₃ + N ₂	342
<u>t</u> -N ₂ F ₂ + ClF ₃ $\xrightarrow{-78 \text{ to } 150^\circ}$ some dec. $\xrightarrow{150^\circ}$ ClF ₅ + N ₂	342
N ₂ F ₂ + I ₂ $\xrightarrow{h\nu}$ IF ₅ (<u>trans</u> reacts faster than <u>cis</u>)	386
<u>t</u> -N ₂ F ₂ $\xrightarrow[\text{low temp.}]{\text{electron radiation}}$ N ₂ + NF ₃ + N ₂ F ₂	471
N ₂ F ₂ + NF ₃ $\xrightarrow[\text{low temp.}]{\text{electron radiation}}$ N ₂ + N ₂ F ₄ + F ₂	471

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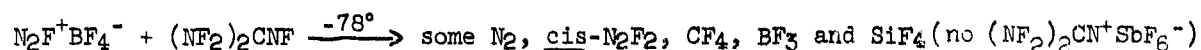
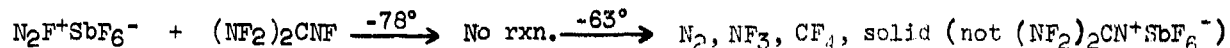
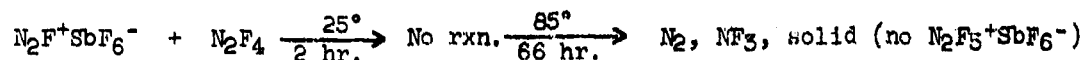
TABLE IX (Concluded)

<u>Reactions and Results</u>	<u>Reference</u>
$\text{N}_2\text{F}_2 \xrightarrow{\text{r.f. disch.}} \xrightarrow[\text{O}_2 \text{ Matrix}]{4^\circ\text{K quench}} \text{N}_2 + \text{F}\cdot \text{ (no N}_2\text{F obs.)}$	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° in a glass apparatus gave ambiguous results.

No reaction was observed between solid N_2FAsF_6 and 500 mm. pressure OF_2 at 25° to 112° , or at 25° 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 (129) and by Bohn and Bauer (16), the latter study also included the NF_2 radical. The ^{19}F NMR spectrum has been obtained at low temperatures by Colburn et al. (112a) 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 $N_2F_4 - C(NF_2)_4 - ClF_5$.

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TABLE X
REACTIONS OF N_2F_4

Reactant	Conditions	Result	Reference
$Hg(NFCOOR)_2$	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 μ (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 NOF and NO_2F with Δ ; 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 ₆		N ₂ F ₃ SbF ₆	152
C ₆ H ₅ Br	25 or 100°, 8 hr., Hg, Cl	C ₆ F ₆ , C ₆ F ₅ H	236
C ₆ H ₅ X	200°, Cu	C ₆ F ₆ , (C ₆ F ₅) ₂	236
H ₂ O	60°	NO, HF	227
H ₂ O	133°	N ₂ , NO ₃ ⁻ , HF	227
AlCl ₃	-78°	trans-N ₂ F ₂	227
Fe ⁺³ (aq.)	H ₂ SO ₄	HNF ₂ , Fe ⁺²	227
Cl ₂	H ₂ SO ₄	ClNF ₂	227
CH ₃ CN	As solvent	Good	227
SCL ₂ O, PCL ₃ O	As solvent	React very slowly at 60°	227
(CH ₃) ₂ SO	As solvent	Reacts slowly at 25°	227
CH ₃ COOH(glac.)	As solvent	Stable several days at 25°	227
H ₂ SO ₄	As solvent	Reacted slowly	227
HgO	25°, 30 min.	No rxn.	257a
HgO	96°, 1 hr.	NF ₃ , NO, no (NF ₂) ₂ O	257a
HgO	u.v., 8 hr.	NF ₃ , NO, no (NF ₂) ₂ O	257a
CF ₃ OF	u.v., 8 hr.	CF ₃ ONF ₂	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 ₂ CFO	259
C ₃ O ₂	25°	Unident. prods. with IR suggestive of NF ₂ O-C cpd. and a CFO cpd.	302
C ₃ O ₂	120°	Dec. of C ₃ O ₂ to polymer	302
O ₃	-196° and warmed	Exploded to NO ₂ , etc.	330
O· or O ₂	400°	No prods. of interest	330
KO ₂	25 to 40°	NF ₃ , NO ₂ F	330
OF ₂	Low temp., fast	NF ₃ , NOF, some NO ₂ F	336
ClF	250°	NF ₃ and Cl ₂	341
ClF ₃	250°	NF ₃ , ClF	341
ClF ₅	250°	NF ₃ , ClF ₃	341
ClO ₂	25°	NOCl and ClO ₂	341
HClO ₄	HF	No rxn.	354
AgClO ₄	HF	t-N ₂ F ₂ , NF ₃ , N ₂ O (from H ₂ O)	354
XeF ₆	HF	Inconcl.	355
(-CO ₂ F) ₂	hν	NF ₂ -CFO	298
(-CO ₂ F) ₂	BF ₃ cat.	FCO-CNF ₂	385
CF ₂ (OF) ₂		No CF ₂ (ONF ₂) ₂	402 and 405

60
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TABLE X (Concluded)

Reactant	Conditions	Result	Reference
ClF ₃ O	-80 to +60°	No rxn.	421
Cl ₂ O + MF·HNF ₂	-112°	NOF, ClNF ₂ , Cl ₂ (plus ClO ₂ , ClONO ₂ with excess Cl ₂ O), no (NF ₂) ₂ O	421
CF ₂ (OF) ₂ + SF ₄		Small amts. SF ₅ OCF ₂ OSF ₄ NF ₂	405
CF ₃ COONO ₂		CF ₃ CFO, NOF	405
(-OCF ₂ OF) ₂		No rxn.	405
(-OCF ₂ OF) ₂	Hg	Irreprod. amts. C ₂ F ₅ ONF ₂ , CF ₃ ONF ₂	405
K ₂ C ₂ O ₆		CO ₂ , NOF	405
CF ₃ COONa		CF ₃ -N(O)=NF	405
NF ₃	-196°, electron radiation	Inconclusive, Si contamination	472
SF ₂ O ₂	20-75°, 2.5 atm., 8 hr.	No N ₂ F ₂ SF ₃ O ₂	471
OF ₂	5 Å mol. sieve, -78° or 27°	Abs. of reactants, no NF ₂ OF	532d
NO	hv, low temperature	No (NF ₂) ₂ NO, (NF ₂) ₂ NONO or (NF ₂) ₂ NONF ₂	532d
(CF ₃) ₂ NO		(CF ₃) ₂ NONF ₂	532d
OF ₂	Elec. disch., -78°	NF ₃ , NO ₂ , SiF ₄ , no NF ₂ 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° . Further studies (352, 354, 355) led to the identification of the stable 1:1 adduct as $\text{N}_2\text{F}_3^+\text{AsF}_6^-$ according to the publication by Young and Moy (162). The reaction product at -80° approached the composition $\text{N}_2\text{F}_3\text{As}_2\text{F}_{11}$, but the excess AsF_5 was evolved on pumping at room temperature. Other studies (405) have also indicated a complex $(\text{N}_2\text{F}_4)_3(\text{AsF}_5)_2$ at -80° , 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 δ for $\text{N}_2\text{F}_3\text{AsF}_6$ in HF solution; NMR resonances at -189.9, -154.0 and -128.8 δ for $\text{N}_2\text{F}_3\text{Sb}_2\text{F}_{11}$ in SO_2 at -70° with the characteristic appearance of an ABX group. The latter salt in HF solution gave resonances at -180, -154 and -129 δ (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 $\text{F}_2\text{N}=\text{NF}^+$ ion, plus normally shaped anion bands have been observed for the AsF_6^- salt (276a). On the other hand, a tentative conclusion that $\text{N}_2\text{F}_4 \cdot 2\text{SbF}_5$ was not ionic was reached, based on NMR studies (477).

The $\text{N}_2\text{F}_3\text{AsF}_6$ is soluble without decomposition in BrF_5 at -60° and IF_5 at 25° , but is insoluble in SF_4 , CF_3OF , or $(\text{CF}_3)_2\text{CO}$ (357) and attacks CFCl_3 , $\text{C}_2\text{F}_3\text{Cl}_3$, 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 $1.93 \pm 0.02\text{D}$, 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 $\text{HNF}_2/\text{CD}_3\text{COOD}$ 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°	ClO_3FNF_3 , vigorous rxn.	357
$N_2F_3Sb_2F_{11} + CsClO_4$	Grinding, 25°	One sample deflagrated	357
$N_2F_4 (g) + CsClO_4 (s)$	SbF_5 suspension	White solid, dec. at 80° 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° , SO_2	Immed. rxn. to N_2F_4 , $N_2F_2?$, ϕ_3NAsF_6	357
$N_2F_3AsF_6 + F_2$	$115-120^\circ$	NF_3 , AsF_5 , traces NF_4AsF_6	276a

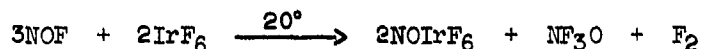
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The most important reaction of HNF_2 to be discovered recently is that (in the form of its KF complex) with fluoroxy compounds such as $\text{CF}_2(\text{OF})_2$ to give the very stable difluoroaminoxy analogues, e.g., $\text{CF}_2(\text{ONF}_2)_2$. 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° which is not shock sensitive and which is stable in concentrate H_2SO_4 at 25° for 40 hr. A number of other reactions of HNF_2 are summarized in Table XII. Publications are appearing in the literature on the reactions of HNF_2 with organic compounds. Results of studies of the hydrolysis (L15), electrochemical reduction (L60), and reaction with anions of HNF_2 (L61) have been published.

Studies of the miscibility, density and stability under storage and flow conditions for mixtures of HNF_2 and N_2F_2 were made at Aerojet (44).

VI-I. Trifluoramine Oxide

The independent discovery of NF_3O by Bartlett and co-workers has led to the declassification of much of its chemistry. Bartlett and co-workers first detected NF_3O (which they named nitrogen oxide trifluoride) as a trace by-product of the fluorination of NOF with PtF_6 (to give NOPtF_6 and F_2) (L185) or with OsF_6 to give NOOsF_6 and NOOsF_7 (L1a). Iridium hexafluoride on the other hand gave (L1a, L2) a stoichiometric amount of NF_3O of high purity according to the equation



the pyrolysis of $(\text{NO})_2\text{NiF}_6$ at 350° also gave NF_3O together with an approximately equal amount of NOF (L2). The synthesis and properties of NF_3O 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 NF_3O . The thermal decomposition NF_3O has been reported to begin at about 235° (76), while other reports state that it is stable in nickel or Monel at 300° and attacks glass or quartz only slowly at 400° .

The results of a number of other studies on NF_3O are summarized in Table XIII.

Vapor pressures were measured in the range $10 - 70^\circ$ for a 1:1 mixture of NF_3O 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 NF_3O with other components were studied at Rocketdyne (427, 395, 400).

VI-J. Complexes of NF_3O and the NF_2O^+ Salts

In the previous review (284a) the reactions of NF_3O to give complexes with weaker Lewis acids and ionic NF_2O^+ salts with very strong Lewis acids were described.

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TABLE XII
REACTIONS OF HNF_2 AND $\text{HNF}_2 \cdot \text{MF}$ COMPLEXES

Reactants	Conditions	Result	Reference
Cl_2NF	-78° , 25° , 65° or u.v.	No products of interest	18
$\text{OF}_2 + \text{HNF}_2 \cdot \text{CsF}$	-125° to 25°	N_2F_4 , NF_3 , NO_2 , NOF	78
$\text{OF}_2 + \text{CsF}$, $\text{KF} \cdot \text{HNF}_2$	-125° to 25° CFCl_3	Some expl. on warming	79
$\text{C}_6\text{F}_5\text{I}/\text{Hg}$	25° , 16 hr.; 100° , 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
AlCl_3	-78°	ClNF_2 , $\text{t-N}_2\text{F}_2$, N_2 , Cl_2 , HCl	227
HCl	-138° to -112°	No interaction	264
SO_3	0°	HOSO_2NF_2 (dec. 25°)	264
$\text{Al}(\text{CH}_3)_3$	Mixed rapidly	Exploded	264
$\text{Al}(\text{CH}_3)_3$	-80° , mixed slowly	$\text{NF}_2\text{Al}(\text{CH}_3)_2$?, CH_4	264
$\text{Al}(\text{CH}_3)_3$	25° , iso $-\text{C}_5\text{H}_{12}$, 2 days	$(\text{NF}_2)_2\text{AlCH}_3$?, CH_4	264
$\text{Al}(\text{CH}_3)_3$	-126°	$(\text{NF}_2)_2\text{AlCH}_3$?	264
$\text{Ga}(\text{CH}_3)_3$	-80° to 25°	Colorless liq., CH_4	264
CF_3COOH	-63° or -45°	Sl. sol.; ideal soln.	264
$(\text{CF}_3\text{CO})_2\text{O}$	-45°	Miscible	264
$\text{Al}(\text{CH}_3)_3$	$< -80^\circ$, 30 min.	$\text{HNF}_2 \cdot \text{Al}(\text{CH}_3)_3$? converts to $\text{NF}_2\text{Al}(\text{CH}_3)_2$? + CH_4 above -30°	266
B_2F_4	-78° , -63° , -45°	$\text{B}_2\text{F}_4 \cdot \text{HNF}_2$? some explosions	266

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TABLE XII (Concluded)

Reactants	Conditions	Result	Reference
$\text{CH}_2(\text{OF}_2) + \text{HNF}_2 \cdot \text{KF}$	-80°	$\text{CF}_2(\text{ONF}_2)_2$, $\text{FOCF}_2\text{ONF}_2$, NF_3 , N_2F_4 , CF_2O	789
$\text{CH}_2(\text{OF}_2) + \text{HNF}_2 \cdot \text{CsF}$		Only trace yields $\text{CF}_2(\text{ONF}_2)_2$	402
ClF		ClNF_2 , HF	420a
ClF_3		Fast rxn. to ClNF_2 , HF	420a
$\text{ClF}_3 + \text{HNF}_2 \cdot \text{BF}_3$	-80°	Slow rxn. to ClNF_2 , HF	420a
RbClF_4	-80°	Slow rxn. to ClNF_2 , N_2F_4	420a
KClF_4	-80°	One explosion	420a
ClF_5	-80°	ClNF_2 , N_2F_4 , NF_3	420a
IF_5	0°	I_2 , some N-F products	420a
NO_2OF		NO_2F , NO_2 , N_2F_4	420a
ClO_3OF		NOF , ClO_3F , some NO_2F , N_2F_4 , Cl_2	420a
$\text{cis-N}_2\text{F}_2 + \text{HNF}_2 \cdot \text{MF}$	-80°	$\text{NF}=\text{N}-\text{NF}_2$? 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°	NOF , ClNF_2 , Cl_2 (some ClNO_3 and ClC_2 with excess Cl_2O)	421

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TABLE XIII

REACTIONS OF NF_3O

Reactant	Conditions	Result	Reference
PF_3Cl_2	-78° , 8 hr.	No rxn. to $\text{NF}_2\text{OPF}_4\text{Cl}_2$	75
PF_3Cl_2	-20°	NOCl , NO_2Cl , PF_3O , Cl_2 , NOPF_6	75
LiClO_4 or $\text{Mg}(\text{ClO}_4)_2$		NO_2F , NOF , NOCl , NO_2 , ClO_3F	75
NaBH_4	BCl_3 , HF , AsF_3 or BrF_3	B_2H_6 , H_2 , (no NF_2OBH_4)	75
CF_3OF	u.v., 36 hr. fract. thru -110° trap	Unident. mat. with IR abs. at 5.0 - 5.5μ , 7.5 - 8.0μ , 8.6μ , 11.0 - 11.5μ , 12.2 - 12.7μ	76
CF_3OF	u.v., 235° , circ. system	Same unident. cpd. trapped at -110°	76
CF_3OF	u.v.	Inconclusive, numerous C-O-N-F fragments	77
ClO_3F	u.v.	NO_2F , NO_2 , ClO_2F , ClO_2	77
ClO_2F	u.v.	Similar to ClO_3F results	77
PF_3	100 mm.	NOPF_6	78
TiF_4	HF or BrF_5	No rxn.	78
PtF_6	25°	NF_2O^+ salt?	79
$\text{N}_2\text{O}_4/\text{CsF}$	0° , HF	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° , SO_2	ClO_3F , SiF_4	121
$\text{Li}_3\text{Al}(\text{ClO}_4)_6$			

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TABLE XIII (Concluded)

Reactant	Conditions	Result	Reference
NO	25°, glass	NO ₂ , NOF, SiF ₄ ?	122
NO	Low temperature	v.p. & IR suggest complex	121
NO/C ₂ F ₄	-78° or 25°	No rxn.	121
NO/N ₂ F ₄	-79	No NF ₂ NO formed; complex assumed	121
NO/CsCl	-78°, 16 hr.	No CsF or ClNF ₂ O	121
NaNO ₂	-78 to 25°	No rxn.	121
IF ₅	-78° or 25°	No NF ₂ OIF ₆	301
HF		No NF ₂ OHF ₂	301
SF ₄		No NF ₂ OSF ₅	301
SF ₂ O	-20°, 4 days	Small amts., 3NF ₃ O·2SF ₂ O	301
CF ₃ C(BF ₂)=CF ₂		CF ₃ C(O)CF ₂ NF ₂	386
CF ₃ C≡CF	BF ₃ or PF ₅ cat.	No CF ₃ C(NF ₂ O)=CF ₂	386
CH ₃ CH=C(CH ₃)CH ₃	BF ₃ or PF ₅ cat.	Explosion	386
PF ₂ (CF ₃) ₃		1:1 complex	386
BF ₂ Cl	-142° to -80°	2NF ₃ O·BF ₂ Cl, NF ₃ O, BF ₃ , Cl ₂ , NOFB ₄	420a
r.f. disch.	O ₂ /Ar matrix	NO ₂ F, NOF, NO ₃ F, O ₂ F ₂ , O ₂ F·	532a
r.f. disch.	Ar matrix	v.l. NO ₂ F, NOF, NO ₃ F	532a
O ₂	elec. disch., -196°	O ₃ , SiF ₄ , no NF ₂ OOF	532a
F ₂	v, -196°	No new products	
Cl ₂	-78° to 25°	No rxn.	122
4-(τ -C ₄ H ₉)C ₆ H ₄ SH		No HNF ₂ 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 NF_2O^+ salts have not been attained.

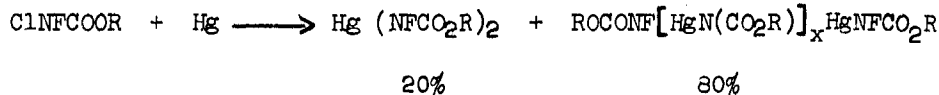
The ^{19}F NMR spectrum of the NF_2O^+ ion in BrF_5 solution shows a chemical shift which is dependent on the anion and apparently on the concentration, but essentially not on the temperature (75). The shift to higher field is in the order $\text{SbF}_6^- < \text{AsF}_6^- < \text{BF}_4^-$. At -60° the 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 NF_2OAsF_6 showed (78) that it was essentially insoluble in the following solvents at the temperatures listed: BrF_3 , 25° ; $(\text{CF}_3)_2\text{CO}$, 25° ; $(\text{CF}_3\text{CO})_2\text{O}$, 25° ; HSO_3F , 25° ; PF_3O , 0° ; ClO_3F , -10° ; SF_4O , -40° ; CF_2O , -40° . The vapor pressure of NF_2OAsF_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 NaClO with difluorourea appears to be one of the best methods for generating sizeable quantities of ClNF_2 (18).

Efforts to prepare $\text{Hg}(\text{NF}_2)_2$ from the reaction of ClNF_2 and Hg at -40° to 25° or in ethyl ether solution at 25° gave N_2F_4 and traces of N_2F_2 (17). In studies of the related compound ClNFCOOR ($\text{R} = \text{C}_2\text{H}_5$ or C_3H_7) the coupling reaction below was apparently observed (15, 17).

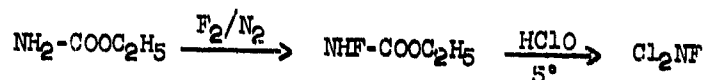


The $\text{Hg}(\text{NFCOOR})_2$ reacted with Cl_2 to give the starting material and with I_2 in CH_2Cl_2 to give INFCOOR (without solvent, FCOOR and N_2 were formed) rather than the desired coupled compound $(-\text{NFCOOR})_2$ which was envisioned as an intermediate to $\text{N}_2\text{F}_2\text{Cl}_2$ or N_3F_5 . Efforts to use sulfur of S_2Cl_2 as the coupling agent were inconclusive and Ca, Zn or Ag failed to give the Hg reaction.

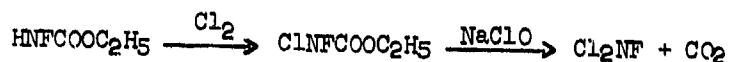
Another related compound $\text{C}(\text{NF}_2)_3\text{NFCl}$ (first prepared at 3M in 1964) was found (15) to lose ClNF_2 even at -196° in glass. An attempt to prepare $\text{C}(\text{NF}_2)_3\text{NFCIO}_3$ by the reaction of $\text{C}(\text{NF}_2)_3\text{NCO}$ with $\text{ClO}_3\text{F}/\text{NaF}$ was unsuccessful (15).

The research on the synthesis of dichlorofluoramine has been published (155a). 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):



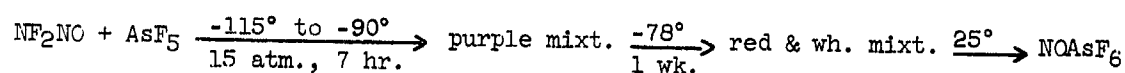
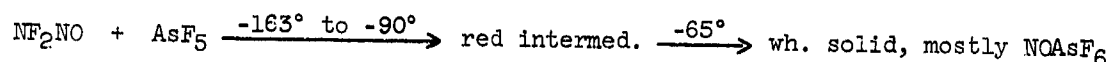
The pure Cl_2NF prepared at 5° was a colorless liquid, but reaction at -5 to -10° gave a yellowish product which contained CO_2 and organic matter. The Cl_2NF decomposed in glass at 25° . The presence of BF_3 accelerated the decomposition, but CsF appeared to stabilize it.

A number of reactions of Cl_2NF have been attempted as summarized in Table XIV. In general, the Cl_2NF appeared to act as a source of NF radicals (18). An attempt to react $\text{C}(\text{NF}_2)_4$ with $(\text{CH}_3)_3\text{COCl}$ gave ClNF_2 rather than the desired $\text{C}(\text{NF}_2)_3\text{NCl}_2$ (8).

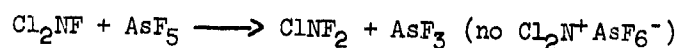
VI-L. Miscellaneous N-O-F Compounds

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 N_2F_2 , N_2F_4 and NF_3O 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 O_2F_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 NF_2NO led to degradation:



Arsenic pentafluoride acted as a fluorinating agent toward Cl_2NF (356).



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TABLE XIV

REACTIONS OF DICHLOROFUORAMINE

<u>Reactions and Results</u>	<u>Reference</u>
$\text{Cl}_2\text{NF} + \text{N}_2\text{F}_4 \xrightarrow{25^\circ} \text{NR} \xrightarrow[metal]{65^\circ} \text{ClNF}_2 + \text{N}_2\text{F}_2 \text{ (no } \text{N}_2\text{F}_3\text{Cl)}$	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 ₂ ; (no NF ₂ O ⁻)	76
NO ₂ F + CsF	3 hr. each at -78° & -45° 6 days at 25°	No rxn.	76
NO ₂ F + F ₂ /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 ₂	-78°, 2 hr. or 25°, 3 hr.	Some NO ₂ F	77
NOF + N ₂ F ₄ + CsF	200°, 8000 psi, 48 hr.	NF ₃ , NOF, NO, NF ₃ O, solid containing Cs, F, N (+O?)	79
NO ₂ F + CsF	-65°	No rxn.	77
NO ₂ + CsF	25°	Some abs.; solid stable at 200°	77
Solid above + F ₂	200°, 250 psi, 2 hr.	NO ₂ F	77
Excess NO ₂ + CsF	200°, 4700 psi, 18 hr.	1 mole NO ₂ abs/mole CsF	77
Solid above + F ₂	200°, 7100 psi, 4 hr.	NF ₃ O, NO ₂ F	77
NO ₂ + CsF + F ₂	25°, 3600 psi, 5 hr.	Some NO ₂ F, (no NF ₃ O)	77
NO ₂ F + CsF	-78°	Solid containing N, F	121
NO ₂ + (CF ₃ O) ₂ O	70°, 16 hr.	(CF ₃ O) ₂ , CF ₂ O, NO ₂	79
NOF + PtF	25°	F ₂ , NF ₃ O, NO ⁺ salt	79
NOF + IrF ₆	25°	NF ₃ O	79
N ₂ O + CsF	25-400°, 10,000 psi max.	No rxn.	76, 78
N ₂ O + F ₂ + CsF	200-400°, 9500 psi max., 15 hr.	Some NF ₃ , NF ₃ O two runs <u>exploded</u>	78
N ₂ O + PtF ₆	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 $N_2O_2 + F_2$, 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
$ClONC_2 + Me_4NBrCl_2$		$Me_4NBr(NO_3)_2$	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

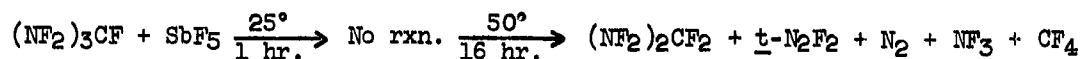
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TABLE XV (Concluded)

<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°	NF_3 , NO_2 , SiF_4	532a
NF_3 or $\text{N}_2\text{F}_4 + \text{H}_2$ or CS_2	flame	No :NF observed	537

The reaction of Cl_2NF with BF_3 reversibly formed a 1:1 complex at -78° which contained the BF_4^- according to infrared analysis (18). Neither AsF_5 nor BF_3 reacted with CF_3OF (356), but decomposition occurred with BF_3 and either N,N,N'-trifluoropentoxymformidine 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° , reaction was incomplete after 17 hr. but the gaseous products were the same. The unidentified solid product melted at $75 - 80^\circ$.

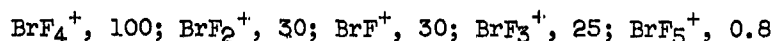
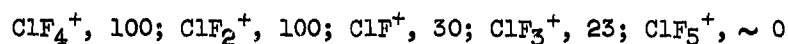
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CHAPTER VII

INORGANIC HALOGEN FLUORIDES AND DERIVATIVES

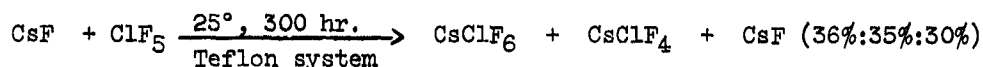
VII-A. Chlorine Pentafluoride

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 ClF_3 under ultraviolet radiation (L119) and by platinum hexafluoride (L120), on the thermal equilibrium of ClF_3 , F_2 , ClF_5 (L107) and a paper (L125) from the Rocketdyne Laboratories on the preparation and properties of 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 ClF_5 and ClF_3 , plus selected data on other interhalogens. The electrochemical preparation of 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}F NMR chemical shifts as -412δ (apical fluorine) and -247δ (basal fluorines). These values were previously reported (284a) as -428 and -258δ . The mass spectra of ClF_5 and BrF_5 have been rechecked (66b) and the following intensities observed:



A purification procedure reported (75) to give 99+% pure ClF_5 consists of adding excess BF_3 to trap ClO_2F (in the form, ClO_2BF_4) at -111° , followed by fractionation through traps at -130° (which retains ClF_5) and -196° .

Among the most interesting reactions involving 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° to 100° in 100 to 300 hr., in the absence of metal, with the best results as shown below:



The reaction with RbF at 70° was reported to give 28% yield of ClF_6^- while that with KF gave only a 6% yield. The identification was based entirely on elemental analyses of the mixtures, plus the observation that ClF_5 and ClF_3 were evolved and CsF remained upon pyrolysis at 200° . The actual existence of the 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 CsF_2^+ ion would be isoelectronic with the known stable 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 ClF_5 has been pursued vigorously, as illustrated by the results summarized in Table XVI.

Evaluations of the properties of 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 ClF_5 , ClF_3 , ClO_3F , $\text{CF}(\text{NF}_2)_3$, $\text{C}(\text{NO}_2)_4$, NF_3O and N_2F_4); properties determination and theoretical performance calculations with ClF_5 and N_2F_4 , $\text{C}(\text{NF}_2)_4$ or $\text{C}(\text{NO}_2)_4$ (392 - 394); and engineering properties studies of ClF_5 , ClF_3 , N_2O_4 and various fuels (396, 397). Aerojet General has also studied the physical properties, stability and storability of ClF_5 - N_2F_4 liquid mixtures and the gelling of ClF_5 with ~ 10 wt.% $\text{Ba}(\text{SbF}_6)_2$ (44), the passivation with ClF_5 and its behavior with selected fuels (51 - 53), including test firings with mixed hydrazines (56, 32) and the heat transfer characteristics of ClF_5 (44a). Reaction Motors has studied the viscosity, heat capacity and thermal stability of ClF_5 (359), properties of mixtures of ClF_5 with N_2F_4 (360 - 363), properties of dispersions of B_4C in ClF_5 (364), theoretical calculation of ClF_5 and ClF_3 with boron slurries (367), motor firings with ClF_5 and Borol 502 (368) and other studies with fuels (369).

VII-B. ClF_5 - Lewis Acid Complexes

The nature of the reaction products of ClF_5 with the Lewis acids AsF_5 and 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°) 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°) 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 SF_6 , gave a very weak NMR resonance at $\delta = 271$ ppm in AsF_5 and a red solution in BrF_5 which faded to pale yellow over several hours (76). One NMR sample in BrF_5 at -60 to -80° showed a weak doublet at $\delta = -265$ ppm (which tended to sharpen at lower temperature) plus a broadened BrF_5 signal. A second sample showed only BrF_5 as a pentet at -271 ppm and a doublet at -132 ppm. Some ClO_3F and BF_3 were observed in the gas phase. Neither pure ClF_5 nor AsF_5 had absorptions in the -265 ppm region, while $\text{BrF}_5 \cdot \text{AsF}_5$ mixture showed only a broad signal at -107 ppm. In further studies (77) the BrF_5 spectrum is reported as a doublet at -271 and a triplet at -132 ppm. When ClF_5 , BrF_5 and AsF_5 were combined and equilibrated at -45° , a doublet at -265 ppm was also observed and tentatively assigned to 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_3

<u>Reactants</u>	<u>Conditions</u>	<u>Results</u>	<u>Reference</u>
KIO_4		no new products	75
I_2O_5		no new products	75
$\text{I}_2\text{O}_5/\text{HF}$	-78°	ClO_3F , ClO_2F , IF_5	77
$\text{H}_2\text{O}/\text{HF}$	-78°	ClO_3F , ClO_2F , ClO_2	77
CsF	-30° , 12 hr.	no rxn.	77
CsF	-78° , 35 hr.	no rxn.	77
LiClO_4	-78°	4% Cl_2O_7 , trace unident. mat.?	76,77
KSO_3F	25°	no rxn.	80
KSO_3F	$140-170^\circ$	SF_2O_2 , O_2 , KClF_4 or KClF_2	80
SiO_2/CsF	25° , 16 hr.	SiF_4 , O_2 , unident. solid	80
PF_3O	-111° to -78°	some ClO_2F , ClO_3F	80
PF_3O	-78° to -30°	some PF_5 , unident. wh. solid which gave ClF_5 and PF_3O (5 mm. at 25°)	80
SO_3	-23° , 4 hr.	some $\text{S}_2\text{O}_5\text{F}_2$, SF_2O	80
SO_3	23° , 1 hr.	ClO_2F , ClO_3F , $\text{S}_2\text{O}_5\text{F}_2$, SF_2O_2	80
HSO_3F		slow reaction	79
O_2	$3-4 \times 10^4$ psi, $300-400^\circ$	no ClF_5O or ClF_7	117
OF_2	$3-4 \times 10^4$ psi, $300-400^\circ$	no ClF_5O or ClF_7	117
F_2	$3-4 \times 10^4$ psi, $300-400^\circ$	no ClF_7	117
F_2 (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_2	γ , 25,000 psi, 25°, 110 hr.	no ClF_7	119
O_2	120 to 420°, 44 - 108 hr.	ClF_5 , ClF_3 , Cl_2 , ClO_2F , MF, etc., unident. prod.	77
O_2	elec. disch. (static and flow)	complex mixture, unident. prod.	77
OF_2	elec. disch., -196° ($ClF_5(s)$)	complex mixture, unident. prod.	77
O_2F_2		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 $NOF \cdot ClF_5$	no $CsClF_6$	301
NO_2F	-78°	liquid complex stable <-35°	342
NO_2F	-60° to -80°	no evidence of interaction by NMR	420a
ClF_2AsF_6	~25°	no rxn.	301
KNO_3	25°	no rxn.	301
$CsNO_3$		NO_2F , ClO_2F	301
$KClO_4$		ClO_2F , KF	301
$KClO_3$		some ClO_2F	301
SbF_5/HF		1:1 adduct immediately	301
H_2O_2		violent rxn.	301
I_2O_5		IF_5 , IF_7 , ClO_3F , ClO_2 , O_2 (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
$Zn(SbF_6)_2$	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 ₂ , Cl-O-F mixtures	387
KClO ₃	25°	ClO ₂ F, ClO ₃ F, ClO ₂ , O ₂ , KClF ₄	387
KClO ₄	25° or 150°	no rxn.	387, 420a
KClO ₄	HF, 25°	KHF ₂ , ClO ₂ , FClO ₂ , FClO ₃	420a
NaNO ₂	25°	NO ₂ F, NOF, NO ₂ , ClO ₂ F, Cl ₂ , NaF	387
NaNO ₃	25°	NO ₂ F, ClO ₂ F, NaF	387
NaNO ₃	HF, 25°	NO ₂ F, ClO ₂ , ClO ₂ F, ClO ₃ F	420a
Na ₂ SO ₃	25°	no rxn.	387
Na ₂ SO ₃	150°	SF ₂ O ₂ , SF ₆ , ClO ₂ , Cl ₂ , O ₂ , NaF	387
Na ₂ S ₂ O ₃	25°	no rxn.	387
Na ₂ S ₂ O ₃	150°	same as with SO ₃ =	387
CsF or KF	25° or 150°	no rxn.	387
PF ₅	0°	no rxn.	387
BF ₃	-112°	no rxn.	387
(CF ₃) ₂ CO	25°	fluorination	387
(CF ₃ CO) ₂ O	25°	fluorination	387
CCl ₄	25°	Cl ₂ , CFCl ₃	387
CHCl ₃	25°	CHFCl ₂ , CF ₂ Cl, CF ₄ , Cl ₂ , CFCl ₃	387
XeF ₄	25°	solubility 5.5 g/100 g ClF ₅	393
XeF ₂		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 ₂ (g)	ClO ₂ F	420a
KBrO ₃		no BrF ₃ O	420a
HNF ₂	-80°	ClNF ₂ , N ₂ F ₄ , NF ₃	420a
2CsF·Cl ₂ O	0°	CsClF ₂ , ClF, ClO ₂ F	423
IO ₂ F		ClO ₂ F, some ClO ₃ F; no ClF ₃ O	426
I ₂ C ₅		ClO ₂ F, some ClO ₂ ; no ClF ₃ O	426
Pb(NO ₃) ₂	-30° to 25°; fast	O ₂ , NO ₂ F, ClO ₂ F, ClF ₃ , trace NO ₂ OClO ₂ ?	426
Pb(NO ₃) ₂	-50°, excess ClF ₅ , slow	NO ₂ F, ClO ₂ F, PbF ₂	426
NF ₃ , F ₂	100°, 3000 psi, 65 hr.	trace NF ₄ ClF ₆ ?	487
SbF ₅ , F ₂	Δ, press.	complex product	487
Ar, O ₃	h ν, 4°K	trace ClF ₅ O ?	532a
F ₂	γ, -196°	no new products	532a
ClF ₅	elec. disch., -80°	dec. of some ClO ₂ F, ClO ₃ F, no (ClF ₄) ₂	420a
ClF ₅	h ν, -190°	no EPR evidence of ClF ₄ ·	77
ClF ₅	h ν, -190°, CF ₄ , C ₂ F ₆ , SF ₆	no EPR evidence of ClF ₄ ·	77
ClF ₅	h ν, -190°, CF ₄ /CFCl ₃ liq.	no EPR evidence of ClF ₄ · or ClF ₂ ·	77, 78
ClF ₅	h ν, -190°, NF ₃ liq.	no EPR evidence of ClF ₄ · or ClF ₂ ·	78
ClF ₅	elec. disch., flow system	see only F· in EPR	78
CsF	25°, 300 hr. in Teflon	CsClF ₆ in mixture with CsClF ₄ , CsF	275a

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With more dilute samples (50 mole % 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 ClF_5 - BrF_5 mixture at -45°. A mixture of BrF_5 and AsF_5 gave a yellow solution at first, but this turned red on storage at -40°. 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 BrF_5 showed only a -107 peak. No paramagnetic species were observed in the red solutions. The combination of ClF_5 , BrF_5 and AsF_5 on the other hand gave a white solid at -40° and only weak, poorly resolved NMR peaks were observed. The -265 ppm peak was therefore tentatively assigned to ClF_4^+ . The ClF_5 - SbF_5 salt in 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 ClF_5 - AsF_5 in 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 BrF_5 alone. Thus ~1 M ClF_5 - AsF_5 in HF gave only one broad peak: +170 ppm at -30° or +188 ppm at -80°. On the other hand when excess ClF_5 was dissolved in excess SbF_5 , the resulting solution at 45° showed an NMR peak at -274 ppm. At 25° some solid precipitated and this peak was broadened, while at 0° or -60° only the Sb-F peak at +109 was observed. The ClF_5 - SbF_5 was not soluble in BrF_5 (79). However, when ClF_5 was added to a solution of SbF_5 in BrF_5 , a white solid which formed initially redissolved on standing at 25°. The ClF_5 was observed (NMR examination of six samples) when the ClF_5 / SbF_5 ratio was 4:1, but not when it was 2:1. With a 1:1 ratio (at -35°) the BrF_5 resonances were averaged at -154 δ and the SbF_5 at +121 δ , but with a 2:1 ratio (at -40°) the BrF_5 peak was unresolved at -167 δ in one sample but partially resolved at -276 and -138 δ in another. No evidence for BrF_4^+ was observed in the BrF_5 - SbF_5 system: at -40° only partially resolved BrF_5 was observed while at 25° the BrF_5 average was at -167 and the SbF species averaged at +109 ppm.

Efforts at Monsanto (301) to get the infrared spectrum of ClF_5 - SbF_5 product (formed by rapid reaction in HF) in KBr or KCl pellets, or KBr-F mulls gave inconclusive results because of the reactivity, but some differences from the spectrum of ClF_2SbF_6 were detected.

A lengthy research effort has been performed at Rocketdyne on the IR and NMR of ClF_5 - AsF_5 complex.

The 1:1 complex was formed at -80°, then warmed to 25° before being condensed at -196° 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 ClF_5 and AsF_5 were taken at -196° (the ClF_5 showed an anomalous strong band at 686 cm^{-1} which was attributed to ClF_4^- or ClF_2^-). The spectrum of the complex was relatively simple, suggesting C_{4v} symmetry. A band at 817 cm^{-1} was attributed to the Cl-F stretch and a band at 743 cm^{-1} to the As-F stretch. The latter is abnormally high for 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 cm^{-1} in the complex.) From correlations of the Hammett σ constants for a number of fluoro salts and the apparent shift of the 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: N_2F^+ , 2.05; NF_2O^+ , 2.25; ClF_4^+ , 2.2; AsF_5 , 3.2. (On this scale the O_2^+ ion was 1.76.) Although ClF_4^+ and NF_2O^+ have about the same electronegativity, the latter was judged to give a more ionic salt with AsF_6^- , because it does not have available orbitals to enter into fluorine bridging as the 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 ClF_4^+ ion (402). These studies included solid samples at -80° and 25° , solutions in 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 ClF_4SbF_6 salt or the $\text{ClF}_5 \cdot \text{AsF}_5$ complex as summarized in Table XVII.

TABLE XVII

REACTIONS OF ClF_5 - LEWIS ACID COMPLEXES

Additional reactions of ClF_5 ·Lewis acid complexes which have been attempted include:

$\text{ClF}_4\text{SbF}_6 + \text{NF}_3 \xrightarrow{200^\circ} \text{NF}_3, \text{ClF}_5 \text{ solid with } \text{SbF}_5:\text{ClF}_5 > 1$	339
$\text{ClF}_4\text{SbF}_6 + \text{OF}_2 \xrightarrow[18 \text{ hr.}]{200^\circ, 500 \text{ psig}} \text{some } \text{O}_2, \text{F}_2, \text{ClF}_5$	339
$\text{ClF}_4\text{SbF}_6 + \text{Na}_2\text{O}_2 \xrightarrow{75^\circ \text{ to } 250^\circ} \text{ClO}_3\text{F}, \text{ClO}_2\text{F}, \text{ClF}_3, \text{ClF}_5, \text{O}_2, \text{NaSbF}_6$	342
$\text{ClF}_5 \cdot \text{AsF}_5 + \text{H}_2\text{C(s)} \xrightarrow{0^\circ} \text{ClF}_5, \text{AsF}_3\text{O}, \text{HF}$	420a
$\text{ClF}_5 \cdot \text{AsF}_5 + \text{N}_2\text{O}_3 \xrightarrow{-23^\circ} \text{NOAsF}_6(?), \text{NO}_2\text{AsF}_6, \text{Cl}_2$	420a
$\text{ClF}_5 \cdot \text{AsF}_5 + \text{KNO}_3 \xrightarrow{25^\circ} \text{ClF}_5, \text{K}^+\text{AsF}_5\text{NO}_3^- (?)$	420a
$\text{ClF}_5 \cdot \text{AsF}_5 + \text{KNO}_3/\text{HF} \xrightarrow{25^\circ} \text{KHF}_2, \text{NO}_2\text{AsF}_6, \text{ClO}_2, \text{ClO}_2\text{F}, \text{ClO}_3\text{F}$	420a
$\text{ClF}_5 \cdot \text{AsF}_5 + (\text{CF}_3\text{CO})_2\text{O} \xrightarrow{0^\circ} \text{exploded}$	420a

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VII-C. Chlorine Trifluoride and Derivatives

The chemistry of 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 ClF_2AsF_6 and ClF_2BF_4 at -196° . The melting point of ClF_2SbF_6 has been established as $225 - 228^\circ$ (342). Christe, Sawodny and Guertin have concluded from analysis of vibrational spectra (L115) that the ClF_2^- ion (L109, L110) is linear. A paper by Christe and Guertin on spectra of salts of the ClF_4^- ion has also appeared (L111).

Electrical conductivity measurements on a solution containing ClF_3 , BrF_3 and BF_3 show (138) that it is an excellent conductor ($7.6 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$) at -60° . On the other hand, combination of ClF_3 with BrF_5 and AsF_5 gave a white sparingly soluble salt at -40° (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 BrF_5 was not changed significantly by the addition of 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 ClF_3 which have been studied are summarized in Table XVIII.

The results of a number of recent studies of the reactions of the ClF_3 derivatives, the ClF_2^+ and 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 ClO_3F and ClO_2F) have lead to the discovery at Rocketdyne of chlorine trifluoride oxide, ClF_3O , (also called oxychlorinetrifluoride and given the code name, Florox). Efforts to obtain ClF_3O_2 or ClF_5O have not been successful, but evidence has been obtained for an unstable FClO .

Discovery and properties: Chlorine trifluoride oxide was first detected in early 1965 (420) as an unidentified product of the fluorination of Cl_2O over CsF at -80° . The ClF_3O was evolved in low yields upon warming the residual solid. Positive identification of ClF_3O 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 Cs symmetry on the basis of the infrared spectrum (absorption bands at 1220, 680, 490, 320 and 280 cm^{-1}). The ^{19}F NMR spectrum was a single broad resonance at $\delta = -279 \text{ ppm}$ with either neat liquid or in CFCl_3 or Cl_2 solutions at -88° .

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TABLE XVIII

REACTIONS OF ClF_3

<u>Reactants</u>	<u>Conditions</u>	<u>Results</u>	<u>Reference</u>
OF_2/KF	25°, 48 hr., shaking	KClF_4 formed	79
$(\text{CF}_3\text{O})_2\text{O}$	25°	NR	80
OF_2	140 - 170°	SF_2O_2 , O_2 , KClF_2	80
KSO_3F	25°, 48 hr.	small amounts, SF_2O_2 , ClO_2F	80
KSO_3F	-78°	Cl_2 , ClO_2F (no ClONO_2)	122
CsSO_3F	70°, 16 hr.	$(\text{CF}_3\text{O})_2$, O_2 , unchanged ClF_3	79
ClONO_2	150°, 5500 psi, 18 hr.	some ClO_2F	80
OF_2	100 - 400°, static or flow	ClO_2F , ClO_3F , ClO_2	346
OF_2	elec. disch., -15° or -78°	ClF , ClO_2F , ClO_3F , ClO_2 , impurities	346
OF_2	elec. disch., -196°	as above plus some ClF_5 , O_2ClF_3 ?	346
O	-150°	ClO_2F , ClO_3F , ClO_2	346
O_3		inconclusive	330
NO_3^- , NO_2^- or $\text{N}_2\text{O}_2^=$	-110 to 350° 0.5 to 1200 atm.	no NFO anions in product	333
CsNO_3	25°	CsClF_4 + CsF	333
$\text{OF}_2/\text{CsClF}_4$	200 - 300°, 680 atm.	ClF_5 , ClO_2F , ClO_3F , O_2 , F_2	336
OF_2		ClF_5	336
O_2	elec. disch., 25°	ClF_5 , ClO_2 , ClO_3F , ClO_2F , impurities + unident. mat. abs. 6.2 μ	337
OF_2	280°, 1350 psig	some ClF_5 , O_2	339,341
O_3	-78°	ClO_3F , ClO_2F	339,341

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TABLE XVIII (Concluded)

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

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TABLE XIX

REACTIONS OF ClF_2^+ and ClF_4^- SALTS

	References
$\text{ClF}_2\text{SbF}_6 + \text{OF}_2 \xrightarrow[20 \text{ hr.}]{200^\circ, 850 \text{ psig}}$ some ClF_5 , O_2 and 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 ClF_3 , ClF , ClO_2F , O_2 , NaSbF_6	342
$\text{ClF}_2\text{SbF}_6 + \text{O}_3 \xrightarrow{-78^\circ/\text{ClF}_3}$ small amounts ClO_3F , ClO_2F from ClF_3	341
$\text{CsClF}_4 + \text{HF} \longrightarrow \text{CsHF}_2 + \text{ClF}_3$	489
$\text{MClF}_4 + \text{H}_2\text{O} \xrightarrow[50^\circ, 750 \text{ psi}]{}$ ClO_2 , Cl_2 (no MClF_2O or FCIO)	423
$\text{CsClF}_4 + \text{Na}_2\text{O}_2 \xrightarrow{300^\circ}$ CsF , NaF , O_2 , Cl_2	341
$\text{CsClF}_4 + \text{NF}_3 \xrightarrow[24 \text{ hr.}]{200^\circ}$ no rxn.	339
$\text{CsClF}_4 + \text{OF}_2 \xrightarrow[340-680 \text{ atm.}]{200-300^\circ}$ O_2 , F_2 , ClO_2F , ClO_3F , ClF_5 , Cs_2NiF_6	336
$\text{CsClF}_4 + \text{O}_2\text{AsF}_6 \xrightarrow{0^\circ}$ $\text{CsAsF}_6 + \text{O}_2$, Cl_2	354
$\text{RbClF}_4 + \text{O}_2\text{AsF}_6 \longrightarrow$ inconclusive	301
$\text{NOClF}_4 + \text{O}_2\text{AsF}_6 \xrightarrow{\text{CFCl}_3}$ NOAsF_6 , ClF_3 , NOF	301
$\text{ClF}_4^- + \text{NF}_2\text{O}^+ \longrightarrow$ no NF_2OClF_4	301
$\text{HNF}_2 + \text{RbClF}_4 \xrightarrow[\text{slow}]{-80^\circ}$ CNF_2 , N_2F_4 , HF , etc.	420a

More recently, Rocketdyne scientists (434a) have resolved the NMR spectrum of gaseous ClF_3O into two peaks at -300 and -262 ϕ in a 1:2 intensity ratio,* but the best

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

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samples of liquid ClF_3O still showed the collapsed singlet at -276° . (HF catalysis of the fluorine exchange was considered the cause.)

Allied Chemical (81) has since prepared a purified sample of ClF_3O and found a melting point of -44° and a boiling point of 30.1° , ΔH_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 ClO_2F , 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/cm³ at 20° , compared to the more dense value reported (421) previously of 1.90 at 25.5° . 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⁻¹. 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 ClF_3O is (425) as follows: $\text{ClFO}^+ > \text{ClF}_2\text{O}^+ > \text{Cl}^+ > \text{F}^+ > \text{ClF}^+ > \text{ClO}^+ > \text{O}^+$.

Rocketdyne reports that ClF_3O is stable at 284° (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 ClF_3O decomposes above 300° to ClF and ClO_2F (423).

The ClF_3O can be purified by pumping off ClO_2F , ClO_3F , ClF and some of the ClF_3 at -95° , and the remainder of the ClF_3 can be removed at -80° with a small loss of ClF_3O (423). Others have reported (80) that ClO_2F and ClF_3O could not be completely separated at -78° and -95° , nor by formation of the KF or CsF complexes at -78° , followed by removal of volatiles at 50° and redissociation of the complexes at 170° , i.e., ClF_3O , ClO_2F and ClO_3F were recovered. Alternatively, CsF can (423) be reacted with the ClF_3 - ClF_3O mixture. The CsClF_4O redissociates at 150° while the CsClF_4 remains nonvolatile (422). The chromatographic purification of ClF_3O using a halocarbon column has also been described (429).

Synthesis studies: In the early studies at Rocketdyne (420) the reaction of F_2 with Cl_2O at 125° had merely given ClF_3 and ClO_2F .* Thus, the nature of the CsF complex (a colorless solid at 0° which dissociates to Cl_2O at 25° (420a)) was considered to be very important and a search was made for modifications or another Cl-O reactant which would give greater efficiency or safety in handling. The Cl_2O (best prepared (421) by the reaction of Cl_2 with HgO) is a serious explosion hazard for scale-up studies. In mid-1965, Rocketdyne reported (421) that ClF_3O could also be made by fluorination of the CsF complex of ClONO_2 . However, the best method then known for making ClONO_2 was the reaction of Cl_2O with N_2O_4 (424).

* Efforts to fluorinate Cl_2O with F_2 in CCl_4 solution at Allied Chemical (1960) and with OF_2 and ultraviolet light at Imperial Chemical (1961) had also been unsuccessful.

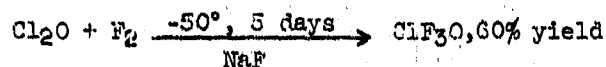
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Cesium fluoride was found (421) to absorb ClF_3O at 25° to give the 1:1 salt $\text{Cs}^+\text{ClF}_4\text{O}^-$ (422), although this salt redissociated on heating (421) to 150° (423). While fluorination of the CsF complex of Cl_2O ,* i.e., $2 \text{CsF} \cdot 3 \text{Cl}_2\text{O}$ (423), gives mostly free ClF_3O , fluorination of the CsF complex of ClONO_2 yields CsClF_4O (346b).

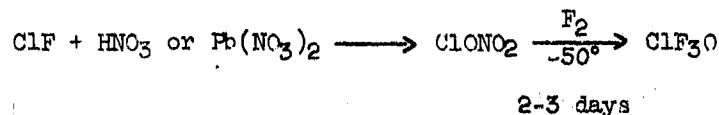
The KF complex of Cl_2O gave (422) up to 44% yields of ClF_3O and the work-up was easier since the KClF_4O dissociated appreciably at room temperature. Some ClF_3O was also formed in the fluorination of Cl_2O plus NaF (423) and $\text{HgCl}_2 \cdot \text{Cl}_2\text{O}$ (383), the latter being generated *in situ* from HgO and Cl_2 and thus eliminating the need for handling Cl_2O . In early 1966, the direct reaction of Cl_2O with F_2 was found (423,346b) to give ClF_3O 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 Cl_2O and F_2 for three days at -78° was preferable** to the use of the 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 ClF_3O in the reaction of Cl_2O with F_2 at 155° or with OF_2 at 130° .

By late 1966, Rocketdyne had prepared 1 lb. of ClF_3O by the batch fluorination of Cl_2O :



Rocketdyne also found that the direct fluorination of ClONO_2 at -78° gave up to 80% yield of ClF_3O (423). The development of an alternate route (405,1178) to ClONO_2 together with its more favorable handling properties may make this the method of choice. This route (429) consists of the reactions:



* The $\text{CsF} \cdot \text{ClONO}_2$ complex completely dissociates at -78° upon prolonged vacuum pumping as also does the $\text{RbF} \cdot \text{Cl}_2\text{O}$ complex, but the $\text{CsF} \cdot 1.5\text{Cl}_2\text{O}$ does not (426). Cl_2O also forms a complex with BF_3 which is unstable at room temperature (123). The complex formed between Cl_2O and AsF_5 , reported in the literature to be Cl_2OAsF_5 at -80° and ClOAsF_5 above -50° , has been shown (425,424) to be $\text{ClO}_2^+\text{AsF}_6^-$. The infrared spectrum showed ClO_2^+ at 1283 db. and 1040 w. and the AsF_6^- at 690 cm^{-1} .

** At 0° , however, only ClO_2F and ClO_3F were obtained.

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Rocketdyne workers have reported (346b) the possible detection of ClF_3O as an unstable by-product while working up mixtures containing ClF_3O . The low temperature infrared spectrum (-196°) showed bands at 1260, 1225 and $645\text{--}630\text{--}610\text{ cm}^{-1}$ and a possible band at 490 cm^{-1} deduced from an overtone at 930 cm^{-1} . 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_2F_2 with NaClO_2 at -160° . A tentative IR band at 1258 cm^{-1} 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_4O^- ion, ClF_3O also acts as a fluoride donor toward strong Lewis acids to form ClF_2O^+ ions. The acid base behavior, then is analogous to that of the isoelectronic molecule SF_4 which forms SF_5^- and SF_3^+ ions. The $\text{ClF}_3\text{O} - \text{AsF}_5$ reaction product is nonvolatile at 50° (381) and can be assumed to have the ionic structure $\text{ClF}_2\text{O}^+\text{AsF}_6^-$. The $\text{ClF}_3\text{O} - \text{BF}_3$ product, which forms more rapidly (20 min.) at -80° than the analogous ClF_3 or ClO_2F 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 $\text{ClF}_3\text{O} - \text{PF}_5$ complex has a slightly higher dissociation pressure than the BF_3 complex. A sample of $\text{ClF}_3\text{O} \cdot \text{PF}_5$ was sublimed onto the window of a low temperature infrared cell (424). Bands attributed to PF_6^- were observed and two other strong bands at 1315 cm^{-1} and 1465 cm^{-1} were suggestive of ClO_2^+ (from ClO_2F impurities) and a ClF_2O^+ ion respectively, but assignments could not be made with certainty. (At this low temperature the Cl=O bands of solid ClO_2F and ClF_3O were observed at 1280 cm^{-1} and 1250 cm^{-1} , respectively.) Silicon tetrafluoride formed a complex $2\text{ClF}_3\text{O} \cdot \text{SiF}_4$ 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 $+14^\circ\text{C}$) a heat of reaction of -2 kcal/mole was calculated.

Complexes are also formed between ClF_3O and NO_2F (421) and NOF (424). From the dissociation pressure of the $\text{NOF} \cdot \text{ClF}_3\text{O}$, $\log P_{\text{mm}} = 8.47 - 1625/T$ (-80° to 0°C) (i.e., about 1 atm. at 25°), a heat of reaction of -5 kcal/mole was calculated. A ^{19}F NMR study of this complex from -77° to 26° showed only a broad line 40 ppm downfield from ClF_3O , i.e., about -316 ppm . 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^{-1} and a N=O stretch at 2050 cm^{-1} . At this low temperature ClF_3O has Cl-F and Cl=O stretches at 685 and 1250 cm^{-1} , respectively and NOF has an N=O stretch at 1990 cm^{-1} (compared to 1850 cm^{-1} at 25°). No N-F stretch was observed in either the complex or in NOF at -196° , (normally 765 cm^{-1} at 25°). The structure of the $\text{NOF} \cdot \text{ClF}_3\text{O}$ complex is thus uncertain. The NMR data indicate fluorine exchange between N and Cl, but very little contribution from ClF_4O^- (424). In fact, a tendency toward the formation of $\text{ClF}_2\text{O}^+\text{NF}_2\text{O}^-$ is indicated, but the transfer may be

* Thus ClF_3O is a stronger fluoride donor than ClF_3 or ClO_2F . This method can be used as a basis of purification, the ClF_3O 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° or 25°	$NO_2F + NOF$	81
NO_2F		ClO_2F , $NOCIO_4$ or NO_2ClO_4	81
NO_2		as with NO_2F	81
$NaClO_2$	-196 to -20°	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° , 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°	no rxn., misc.	422, 426
Br_2	-80° to 25°	some ClO_2F , Cl_2 ; no BrF_3	422
N_2F_4	25°	no rxn.	425
N_2F_4	100°	v. slow rxn.	425
NF_3	130° , 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°	no rxn.	423

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Alternate synthesis approaches: A host of other synthesis routes to ClF_3O (and/or ClF_3O_2 or ClF_5O) have been attempted since the previous review (284a) and a number of these have led to ClF_3O . 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_3O

	<u>References</u>
$\text{Cl}_2\text{O} + \text{F}_2 \xrightarrow{\text{elec. disch.}}$ 45% ClF_5 , some ClF_3 , ClF_3O , ClO_2F	346b, 424
$\text{NaClO}_2 + \text{F}_2 \xrightarrow[-196^\circ \text{ or } -78^\circ]{\text{exothermic}}$ ClO_2F , NaF , Cl_2 , O_2 , traces ClF_3O , ClFO (?)	424
$\text{ClF}_3 + \text{OF}_2 \xrightarrow[\text{Pyrex}]{h\nu}$ ClO_2F , $\text{ClO}_2^+\text{BF}_4^-$, SiF_4 , plus some ClO_3F , ClO_2 and apparently ClF_3O and $\text{ClF}_2\text{O}^+\text{BF}_4^-$.	276a
$\text{ClF} + \text{OF}_2 \xrightarrow[18 \text{ hr.}, 5500 \text{ psi}]{150^\circ}$ ClF_3 , + 2% ClF_3O (CsF had no effect)	80
$\text{Cl}_2 + \text{OF}_2 \xrightarrow[18 \text{ hr.}, 5500 \text{ psi}]{150^\circ}$ ClF_3 , ClF , ClO_2F , traces ClF_3O	80
$\text{ClO}_2\text{F} + \text{ClF}_5 \xrightarrow{h\nu}$ ClF_3O	426a
$\text{ClO}_3\text{F} + \text{ClF}_5 \xrightarrow{h\nu}$ ClF_3O	426a
$\text{ClO}_2\text{F} + \text{ClF}$, ClF_3 , OF_2 , $\xrightarrow{h\nu}$ ClF_3O	346a
$\text{ClO}_2\text{F} + \text{BrF}_5 \xrightarrow{h\nu}$ some ClF_3O	346a
$\text{ClO}_2\text{F} \xrightarrow[-40^\circ]{h\nu}$ 86% ClF_3O	346a
$\text{ClO}_3\text{F} \xrightarrow[-40^\circ]{h\nu}$ ClF_3O	346a
$\text{ClO}_2\text{F} + \text{F}_2 \xrightarrow{h\nu}$ $\text{ClF}_3\text{O} + \text{ClF}_5$	346a
$\text{Cl}_2\text{O} + \text{F}_2 \xrightarrow{155^\circ}$ ClF_3O	342
$\text{Cl}_2\text{O} + \text{F}_2 \xrightarrow{130^\circ}$ ClF_3O	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 ClF₅O 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 ₅ + metal or metalloid oxides, oxygen, or ozone		usually ClO ₂ F or ClO ₃ F	see Table XVI
ClF ₅ + H ₂ O or hydrates		usually ClO ₂ F or ClO ₃ F	see Table XVI
ClF ₃ + various agents			see Table XVI
CsF-ClO ₂ F complex + F ₂	25°, 2900 psi	some ClF ₅ , ClO ₃ F, ClO ₂ F	75
NaClO ₂ + BrF ₅	-50°, then AsF ₅ at -20°	some Cl ₂ + solid	75
solid from NaClO ₂ above	CsF, -20°	ClO ₂ F (25%), no FClO	75
LiClO ₄ + ClF ₅	-78°	Cl ₂ O ₇ (4%) + trace unk. w/IR similar to Cl ₂ O ₇ and ClO ₃ OF, mass spec. similar to ClO ₃ F, and ¹⁹ F resonance at -369 ϕ (unk. + H ₂ O gave ClO ₃ F and F ⁻)	76 77
ClO ₂ F + PtF ₆	25°	ClO ₂ PtF ₆ , ClF ₅ , ClO ₃ F, O ₂ PtF ₆ ?	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°	ClO_2PtF_6 , Cl_2 , O_2	79
$\text{CsF} \cdot \text{Cl}_2\text{O} + \text{PtF}_6$	25°	solids, Cl_2 , O_2	79
$\text{Cl}_2\text{O} + \text{ClF}_3 + \text{PtF}_6$	25°	ClF_5 , Cl_2 , O_2	79
$\text{KClO}_3 + 48\% \text{ aq. HF}$	evap.	no rxn. to KClF_2O_2	79
$\text{ClOSO}_2\text{F} + \text{F}_2$	-78°, 5 days	some SF_2O_2 and ClO_2	79
$\text{CsSO}_3\text{F} + \text{ClF}_3$	25° or 170°	SF_2O_2 , ClO_2F , CsClF_2-4	79
$\text{KSO}_3\text{F} + \text{ClF}_3$	25°	no rxn.	79
$\text{KSO}_3\text{F} + \text{ClF}_3$	140-170°	SF_2O_2 , O_2 , KClF_2-4	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
$\text{Mg}(\text{ClO}_4)_2 + \text{F}_2$	NF_3 , -196°	No rxn. (no ClO_3OF)	89
$\text{LiClO} + \text{F}_2$	Low temp.	ClO_2F , ClO_3F , possibly ClF_3-50	346
$\text{O} + \text{ClF}_x$	-150°	ClO_2F , ClO_3F , 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 ClF_3O	346
$\text{ClF}_5(\text{s}) + \text{OF}_2$	elec. disch., -196°	Apparently small amounts ClF_3O	346

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TABLE XXII (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
$\text{CsF} + \text{Cl}_2\text{O} + \text{N}_2\text{F}_4$		Cl_2 + unident. solid	123
$\text{ClONO}_2 + \text{ClF}_3$	-78°	mostly Cl_2 , some ClO_2F	123
$\text{ClONO}_2 + \text{NF}_3\text{O}$	-78°	No rxn.	123
$\text{OF}_2 + \text{ClF}$	-160 to -196°	No rxn. indicated by v.p. and elec. cond. measurements	333
$\text{CsClF}_4 + \text{OF}_2$	$175-300^\circ$, 580 atm.	O_2 , $\text{F}_2\text{ClO}_2\text{F}$, ClO_3F , some ClF_5	334, 336
$\text{OF}_2 + \text{ClF}_3$		ClF_3	336
$\text{OF}_2 + \text{ClF}_3$	280° , 1350 psig	O_2 , F_2 , ClF_5	339
$\text{OF}_2 + \text{CsCl}$	200°	CsF , O_2 , Cl_2 , some ClF , ClO_2F	339
$\text{OF}_2 + \text{ClO}_2\text{F}$	250° , 825 psig	some dec. of OF_2 + formation of ClO_3F	339
$\text{OF}_2 + \text{ClO}_3\text{F}$	200° , 1110 psig, 20 hr.	No rxn.	339
$\text{OF}_2 + \text{ClO}_2$	110°	ClF_5 , ClO_3F , ClO_2F	340
$\text{NF}_3 + \text{ClO}_2$	110°	No rxn.	340
$\text{CF}_3\text{OCl} + \text{F}_2$	-78°	CF_3OF (no ClFO)	356
$\text{O}_2\text{AsF}_6 + \text{CsClF}_4$	0°	O_2 , Cl_2 , CsAsF_6	354
$\text{Cl}_2\text{-O}_2\text{AsF}_6$ complex + F_2	-78° , 5 days	ClO_2 , Cl_2 , O_2 , unident. solid	356
$\text{Cl}_2\text{-O}_2\text{AsF}_6$ complex + F_2	higher press. than above	O_2 , Cl_2 , ClO_3F , ClO_2	357
$\text{Cl}_2 + 6\text{F}_2 + \text{O}_2$	elec. disch., -80°	ClO_2 , ClO_2F , ClO_3F , ClF_3 , ClF_5 + NOF compounds	420a
$\text{ClO}_2\text{F} + \text{ClO}_2$ + F .	elec. disch., -196°	ClO_3F , (ClO_2 unaffected)	420a
$\text{HNF}_2 + \text{ClO}_3\text{OF}$		NOF, ClO_3F , some N_2F_4 , NO_2F , Cl_2	420a

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TABLE XXII (Continued)

<u>Reactants</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
NOF	25°	NO ₂ F, ClO ₂ F, (ClO ₂ w/excess ClF ₃) + unk. w/IR abs. at 5.8 db., 7.2 hr., 8.4, 9.7 FQR	420a
Cl ₂ O + ClF ₃	-50°, NaF	ClO ₂ F + ClF	423
Cl ₂ O + AgF ₂	flow system -76° to 100°	ClO ₂ F, Cl ₂	424
CsClF ₄ O + F ₂	50-160°, 750-1200 psi, 16 hr.	ClF ₃ O recovered	424
ClF ₃ O + F ₂	70 to 284°	no ClF ₅ O	421
ClF ₃ O + N ₂ F ₄	-80° to +60°	no rxn. to ClFO	421
ClF ₃ O + KrF ₂		no ClF ₅ O	421
Ca(OCl) ₂ + F ₂	-80°	ClO ₂ F, ClO ₃ F	423
Cl ₂ O + CF ₂ (OF) ₂	-60°, 15 days	dec. of Cl ₂ O	425
ClO ₂ + F ₂		explosive rxn. to ClF ₃ , ClO ₂ F, (+O ₂ with excess F ₂ or Cl ₂ with excess ClO ₂)	425
CsF + ClO ₂	-23° or -45°	no obvious complex	425
KClO ₄ + F ₂		ClO ₂ F + ClO ₃ F	424
MClF ₄ + H ₂ O		MHF ₂ , ClO ₂ , Cl ₂ , ClFO, KClF ₄ ·H ₂ O	425, 426
ClF ₃ O + H ₂ O	-16 to +25°	HF, ClO ₂ , trace ClFO	425
ClF ₃ + O ₂	elec. disch., -196°	ClO ₂	532a
ClF + O ₂	r.f. disch., 4°K	Cl ₂ , O ₂ , F ₂	532a
ClF ₅ + Ar + O ₃	hν (filtered), 4°K	unident. cpd; possibly ClF ₅ O, which dec. on warming to ClF ₃ , OF ₂ (IR bands at 1220, 1210, 664, 657, 646 cm ⁻¹)	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 O_2ClF_3 of (284a)). IR bands at 1026, 751, 675, 668 cm^{-1}	535b
$\text{ClF}_3 + \text{Ar} + \text{O}_2$	4°K	as with O_3 above	535b
$\text{ClF}_3 + \text{Ar} + \text{O}_3$	hv, 4°K	ClO_2F , ClFO	535b
$\text{ClNF}_2 + \text{O}_2$, O_3 or ClO_2	hv	no evidence of desired product	535b
$\text{Cl}_2\text{O}-\text{CsF} + \text{ClF}_5$		no ClF_3O	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 Cl_2 and F_2 in argon at 4°K led only to ClF_3 and ClF upon warming (535b). The pressure-temperature relation of the ClF_5-F_2 (1:9) system was studied up to 440° and 43,800 psi and was essentially linear (119).

Purification of BrF_5 can be accomplished by storing it over KF at 25° (386) or NaF at 100° followed by distillation (78). The complex formed with CsF , i.e., CsBrF_6 decomposed only at 320° with extensive decomposition of the BrF_5 .

No evidence was observed for the conversion of solid BrF_5 (-196°) to BrF_7 upon exposure to excited F_2 from an electric discharge (420,420a). Again BrF_7 was not produced when a BrF_5-F_2 mixture was radiated with u.v. light at -40° to -60° (346a). Similar negative results had been obtained in efforts to react F_2 with BrF_5 or CsBrF_6 with heat and pressure. In another study (77) no BrF_7 was observed after fluorination of BrF_5 over CsF at 250° and 1700 psi for 16 hr. Extensive efforts to prepare BrF_7 by fluorination of BrF_5 at very high pressures and temperatures (up to 48,800 psi at 508°C) or under radiation at 25°, or of CsBrF_6 (at 400°, and 6630 psi) gave inconclusive results (118-120).

An effort to react BrF_5 with ClO_3OF to give $\text{BrF}_6^+\text{ClO}_4^-$ resulted only in partial degradation of ClO_3OF to ClO_3F (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 BrF_3 and the presence of the BF_4^- band (1020 - 1000 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 NO_2BrF_4 (426). It melts at 27°, has a dissociation pressure of 1 atm. at 45° and a ΔH dissociation of 11.7 kcal/mole. The infrared spectrum of NO_2BrF_4 shows the NO_2^+ band at 2385 cm^{-1} and the BrF_4^- band at 665 cm^{-1} (346a).

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The vapor pressure of IF_7 is described (426a) by the equation: $\log P_{\text{mm}} = 7.6939 - 1356.6/T$. 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 -329δ (78) and -321δ (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° and 100 atm. with an $\text{O}_2 - \text{F}_2$ mixture for 8 weeks (333). The reaction of BrF_3 with O_3 in the range -196 to -95° gave an unidentified compound which decomposed at -35° (330). Fluorination of the complex $\text{CsF} \cdot \text{Br}_2\text{O}$ has not yielded BrF_3O or BrF_5O (421), nor did fluorination of BrONO_2 which appeared to give a complex of the type $\text{NO}_2\text{F} \cdot \text{BrF}_x\text{O}$ (425). An attempt to prepare BrO_2NF_2 by reaction of BrNF_2 with O_3 in CFCl_3 at -78° 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 $\text{IO}_2^+\text{IF}_6^-$ (420a). The ^{19}F NMR of the IF_6^- ion was established at -18δ (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_2F

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
CsF	-22° , 3 hr.	50% ClO_2F absorbed, unident. component in product by X-ray	75
$\text{CsF}-\text{ClO}_2\text{F}$ "complex"	$80-100^\circ$	ClO_2F evolved	75
CsF	-22° , 19 hr.; 25° , 72 hr.	82% ClO_2F absorbed, couldn't obtain IR of solid or ^{19}F NMR in ClO_2F (liq.)	76
CsF	HF	no NMR evidence of rxn.; don't see ClO_2F , but see HF exchanging	77
CsF , ClF_5		" " " "	77
CsF	25° , 4 hr., shaking; and 16 hr., static	Cs/F/Cl ratio of 1:5.4:2.3 in solid	77
NO_2F	-20°	no NMR evidence of interaction (see ClO_2F at -329 and NO_2F at -390 ϕ)	78
PtF_6	25°	ClF_5 , $\text{ClO}_2^+\text{PtF}_6^-$, ClO_3F , O_2PtF_6 ?	79
IrF_6	25°	ClO_2IrF_6 ?	80
NOF	-78°	"wet" solid with v.p. of 15 mm. at -78° ; solid gave two liq. phases at -20 to -15°	337
OF_2	250° , 825 psig	some dec. of OF_2 and formation of ClO_3F	339
$\text{t-N}_2\text{F}_2$	-78° to 25°	no rxn.	340
HNF_2	as ClO_2BF_4 , -80°	Deflagration; unident. prod. w/IR abs. at 7.6 & 7.7 μ	420a
ClF	liq.	equilibrium amt. ClFO ?	424

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TABLE XXIII (Concluded)

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

TABLE XXIV

STUDIES OF ClO₃F

<u>Reactant</u>	<u>Conditions</u>	<u>Result</u>	<u>Reference</u>
SbF ₅	-51°	no reaction noted by elec. cond.	337
SbF ₅	1 hr. each at: 25°, 7000; 100°, 8900; 200°, 11,300 psi	no reaction detected by NMR	75
ClF ₃	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 ₂ + CsF	200°, 5900 psi, 18 hr.	some F ₂ absorbed which did not revolatilize at 500°. Solid contained Cs:Cl:F ratio of 2.2:1:3	77
F ₂ w/w.o. CsF	200°, 6400 psi, 15 hr.	inconsistent results, apparently rxn. w/equipment	78
PtF ₆	25°	no reaction	60
NF ₃	475°, 18 hr.	no reaction	339
t-N ₂ F ₂	-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 SF_2O_2 formed at 25°)	77
$\text{OF}_2 + \text{SF}_4\text{O} + \text{CsF}$	-78° to 100°	no rxn. except to form CsSF_5O	77
$\text{OF}_2 + \text{SF}_4 + \text{CsF}$	25°	SF_6 , SF_2O_2 , S_2F_{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	CF_3OF , CsSF_5O , CsCF_3O	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	SF_2O_2 , CF_3OF , $(\text{CF}_3\text{O})_2$	78
$\text{OF}_2 + \text{SF}_4\text{O}$	25°, KF	no rxn.	78
$\text{OF}_2 + \text{SF}_4\text{O}$	175°, NaF	SF_2O_2 , O_2	78
$\text{CF}_2(\text{OF})_2 + \text{SO}_2$	CsF	SF_2O_2 , CF_3OF , $(\text{CF}_3\text{O})_2$	78
$\text{CF}_2(\text{OF})_2 + \text{CF}_2\text{O}$	25°, CsF	$(\text{CF}_3\text{O})_2\text{O}$, CF_3OF , O_2	78
$\text{CF}_2(\text{OF})_2 + \text{CF}_3\text{O}$	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	CF_2C , O_2	78
$\text{CF}_3\text{OF} + \text{CO}$	100°, 16 hr.	CF_3OCFO	78
$\text{SF}_5\text{OF} + \text{CO}$	95°	SF_4O , CF_2O , SF_6 , CO_2	78
$\text{SF}_5\text{OF} + \text{CO}$	$h\nu$, 0 to -35°	SF_4O , CF_2O , SF_6 , CO_2	78
$\text{CF}_2(\text{OF})_2 + \text{CO}$	CsF	CF_4 , CF_2O , 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, CCl_4	SF_6 , SF_2O_2	79
$\text{OF}_2 + \text{SO}_2$	CsF, CCl_4	SF_2O_2 , unk. abs. 14μ	79
$\text{OF}_2 + \text{ClF}_3 + \text{KF}$	25° , 48 hr.	KClF_4	79
$\text{OF}_2 + \text{MF} \cdot \text{HNF}_2$	CFCl_3	explosions on warming	79
$\text{OF}_2 + \text{CsN}_3$	-196 to -40° , 20 hr.	dark blue solid (reactants explode if warmed too rapidly)	79
$\text{OF}_2 + \text{ClF}$ (w/wo CsF)	150° , 5500 psi, 18 hr.	ClF_3 and 2% ClF_3O	80
$\text{OF}_2 + \text{Cl}_2$ (w/wo CsF)	150° , 5500 psi, 18 hr.	ClF_3 , ClF , ClO_2F , trace ClF_3O	80
$\text{OF}_2 + \text{Cl}_2\text{O}$	150° , 5500 psi, 18 hr.	ClF_5 , ClO_2F	80
$\text{OF}_2 + \text{ClF}_3$	150° , 5500 psi, 18 hr.	some ClO_2F	80
$\text{CF}_3\text{OF} + \text{NH}_2\text{CFC}$		CF_3ONF_3 (38%)	259
$\text{O}_2\text{F}_2 + (\text{NaOCO})_2\text{O}$	-111°	CF_4 , CF_2O , CO_2	264
$\text{F}_2/\text{CsF} + "$	-183° , 1 wk.	sl. rxn. as above	264
$\text{O}_2\text{F}_2 + \text{C}_6\text{F}_6$	-183°	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 Mg		no rxn.	264
$\text{O}_3\text{F}_2 + \text{Li}$, Na or K		react smoothly	264
$\text{O}_2\text{F}_2 + \text{SO}_2$		SF_2O_2 , O_2 ; side rxn. to FSO_2OF and FSO_2OOF	266
$\text{O}_2\text{F}_2 + \text{SF}_2\text{O}$	-160	SF_4O	266

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TABLE XXV (Continued)

Reactants	Conditions	Result	Reference
$O_2AsF_6 + CsClF_4$	0°	$O_2, Cl_2, CsAsF_6$	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°)	355
$O_2AsF_6 + CsClO_4$	IF5	Cl_2O_6 , etc.	355
$O_2AsF_6 + CsClF_4$	-78° (solids)	3:1 ratio $Cl_2:O_2$	355
$O_2AsF_6 + CsBrF_4$	-78°	F_2, O_2, Br_2, SiF_4	355
$O_2AsF_6 + Cl_2$	-78°	purple 1:1 complex	356
$O_2AsF_6 \cdot Cl_2 + F_2$	-78°	ClO_3F, ClO_2, Cl_2, O_2	355
$O_2AsF_6 \cdot Cl_2 + NOCl$		O_2 , trace NO_2OF , $NOAsF_6?$	355
$CF_2(OF)_2 + N_2F_4$		no $-ONF_2$ cpds.	405
$CF_2(OF)_2 + KF \cdot HNF_2$		$CF_2(ONF_2)_2$	405
$CF_2(OF)_2 +$ $CsCF(CF_3)_2O$		extens. rearrang. to CF_4 , $(CF_3)_2CFOOCF_3$ and ex- plosive oxides	436
$OF_2 + CsCF(CF_3)_2O$		as with $CF_2(OF)_2$ above	436
$OF_2 + BF_3$	hv, -196°	O_2BF_4	472
$O_2PtF_6 + F_2$	62° , 1 atm., Teflon	some C-F cpds. (no OF_4)	532d
$N_2O + OF_2$ + CsF	350° , 2700 psi, 4 hr.	no rxn., but exploded on cooling to 315° to NF_3 , NF_3O , HNO_3 , unident. products	532d
$OF_2 + SbF_5$	-30°	NMR suggests $OF_2 \cdot SbF_5$	532d
$OF_2 + N_2F_4$	elec. disch., -78°	NF_3, NO_2, SiF_4	532a
$OF_2 + \text{cis-}N_2F_2$	elec. disch., -78°	N_2, F_2, O_2	532a
$OF_2 + N_2FAsF_6$	$25-112^\circ$ or HF, 25°	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°	no rxn.	266
$O_2F_2 + SF_2O_2$	-160°	no rxn.	266
$O_2F_2 + NO_2$	-130°	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°	elec. cond. shows no rxn.	333, 335
$OF_2 + AsF_5$	200° , 130 atm., 1 wk.	O_2AsF_6 (97%)	335
$OF_2 + AsF_5$	25° , 6 wk.	only 3% O_2AsF_6	335
$OF_2 + SbF_5$	130° , 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°	ClF_5	336
$OF_2 + SbF_5$ or AsF_5	IF_5 , 25°	$IF_5 \cdot SbF_5$ (or $IF_5 \cdot AsF_5$)	335
$OF_2 + SbF_5$	200° , 760 psig, 16 hr.	no rxn.	339
$OF_2 + SF$	200°	no rxn.	339
$OF_2 + CsClF_4$		ClF_5	336, 339
$OF_2 + ClF_4SbF_6$	200° , 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 ₂ + CsCl	200°	CsF, O ₂ , Cl ₂ , ClF, ClO ₂ F	339
OF ₂ + ClO ₂	110°	ClF ₅ , ClO ₂ F, ClO ₃ F	340
OF ₂ + Cl ₂ O	130°	ClF ₃ O	340
OF ₂ + <u>cis</u> -N ₂ F ₂	-78° to 150°	some dec. of both	340
OF ₂ + Cl ₂ (or ClF)	25°	no rxn.	340
OF ₂ + Cl ₂ (or ClF)	150°	ClF, (ClF ₃), ClO ₂ F	340
O ₂ AsF ₆ + NO ₂ ClO ₄	0°, solids	NO ₂ AsF ₆ , O ₂ (Cl ₂ O ₆ dec.)	351
O ₂ AsF ₆ + CsBrF ₄		CsAsF ₆ + O ₂ , F ₂ , Br ₂	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 ₃ /O ₂ /F ₂	8.5% F	miscible and stabilized	72,73
CsCF ₃ O + F ₂	-80°	CF ₃ OF (quantatively)	75
CsCF(CF ₃) ₂ O + F ₂	-80°	CF ₃ OF + CF ₄	75
NOClF ₄ + F ₂	high press. -45 to 300°	NF ₃ O, ClF ₅ , NO ₂ F	75
COS + F ₂ /CsF	-78°	CF ₂ O + SF ₆	76
N ₂ O + F ₂ /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>
$\text{SF}_2\text{O} + \text{CsF}$	130° , 7 hr.	no rxn.	76
$\text{SF}_2\text{O} + \text{CsF}$	-78° or -40° , CH_3CN	sl. abs., unident. ^{19}F peak at -51δ	78
$\text{PF}_3\text{O} + \text{CsF}$	40° , 24 hr.	some abs. of PF_3O	77
$\text{PF}_3\text{O} + \text{CsF}$	-30° , CH_3CN	inconclusive	78
$\text{SF}_2\text{O}_2 + \text{CsF}$	-78°	no rxn.	78
$\text{CsNO}_3 + \text{F}_2$	200° , 7100 psi, 4 hr.	NF_3O , NO_2F	77
$\text{CsF} + \text{NOCl}$	25°	CsCl	77
$\text{CsF} + \text{Cl}_2$	25° , 24 hr.	$\text{CsFCl}_2?$	77
$\text{CsF} + \text{CO}_2$	25° , 120 psi, CH_3OH	$\text{Cs}^+\text{CFO}_2^-?$	77
$\text{KNO}_3 + \text{F}_2$	-196°	no rxn.	89
$\text{CF}_3\text{NO} + \text{F}_2$	125° , AgF_2	$(\text{CF}_3)_2\text{NOCF}_3$	259
$\text{Cl}_2 \cdot \text{O}_2\text{AsF}_6 + \text{F}_2$	-78°	ClO_3F , ClO_2 , Cl_2 , O_2	356, 357
$\text{CF}_3\text{OCl} + \text{F}_2$		CF_3OF	356
$\text{CsF} \cdot \text{FC}(\text{O})\text{NF}_2 + \text{F}_2$		CF_3OF , NF_3	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 ³)	refractive index	ref.
Empirical	Structural					
Ag ₁ C ₂ H ₄ N ₄ O ₆	AgN(NO ₂)CH ₂ CH ₂ N(NO ₂) ₂	130				4
AsF ₁₀ N	NF ₄ AsF ₆			2.70		489
B ₁ C ₅ F ₄ H ₅ N ₄ O ₄	CHCHC(NHNO ₂)CHCHN(NO ₂) ⁺ BF ₄ ⁻	93-94				5
B ₁ C ₅ F ₄ H ₄ N ₅ O ₆	CHCHC(N(NO ₂) ₂)CHCHN(NO ₂) ⁺ BF ₄ ⁻	78				5
BC ₆ F ₄ H ₇ N ₃ O ₄	CHCHC(N(NO ₂) ₂)CHCHN(CH ₃) ⁺ BF ₄ ⁻	95 dec.				6
BrCF ₆ N ₃	(NF ₂) ₃ C-Br		71 est.			142
BrFO ₂ S	SO ₂ BrF	-86±0.5	40	2.12 (20°)		52
BrF ₃	BrF ₃			2.8		52
BrF ₅	BrF ₅	-61.3	+40.5			137 359
CFN ₃ O ₆	CF(NO ₂) ₃	-29	88	2.465 (25°)		52
CF ₄ O ₂	CF ₂ (OF) ₂	-196	-64	1.20 (20°)		52
CF ₄ O ₄	C(OF) ₄			1.60 est.		294
CF ₅ NO ₂	F ₂ COF(ONF ₂)		-29			386

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TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm ³)	refractive index	ref.
Empirical	Structural					
CF ₅ N ₃	(NF ₂) ₂ C=NF	-160	-2	1.70		115
CF ₆ N ₂ O ₂	F ₂ C(ONF ₂) ₂	-196	-9.0 (ext.)	2.01-1.52x 10 ⁻³ T		386
CF ₇ N	CF(NF ₂) ₃			1.56		51
CF ₇ N ₃	CF(NF ₂) ₃	-135	5.6	1.58 (20)		52
CF ₈ N ₄	C(NF ₂) ₄	-13.5	40	1.63 (20) 1.748 1.60		52 51 294
C ₂ ClF ₆ H ₄ N ₅ O ₅	CN ₃ F ₆ ONCHNH ₃ ClO ₄			1.80 est.		292
C ₂ F ₂ H ₄ N ₄ O ₃	O ₂ NNHC ₂ ONHCH ₂ NF ₂	83-7				274
C ₂ F ₂ H ₆ N ₂ O ₂ S	CH ₃ SO ₂ NHCH ₂ NF ₂	74-76				274
C ₂ F ₄ H ₄ N ₄ O ₂	(F ₂ NCH ₂) ₂ NNC ₂		159 est.			274
C ₂ F ₄ O ₂	CF ₃ COOF		-22			90
C ₂ F ₆ H ₂ N ₂ O	CN ₃ F ₆ CONH ₂			1.41 est.		291
C ₂ F ₆ H ₂ N ₄ O	(NF ₂) ₃ CCNH ₂			1.41		293
C ₂ F ₆ H ₂ N ₆ O ₃	(NF ₂) ₃ C-NH-CO-NH-NO ₂	55-58				86
C ₂ F ₆ O ₄	FOCF ₂ OOCF ₂ OF		9			403
C ₂ F ₇ H ₂ N ₅ O	CN ₃ F ₆ NFCONH ₂			1.80		291

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TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm ³)	refractive index	ref.
Empirical	Structural					
C ₂ F ₇ NO	(CF ₃) ₂ NOF or (CF ₃) ₂ $\overset{\text{F}}{\text{N}} \rightarrow 0$	-69	25 (ext.)			532a
C ₂ F ₁₂ N ₆ O ₂	CN ₃ F ₆ OOCN ₃ F ₆			1.60 est.		291
C ₂ H ₄ K ₁ N ₅ O ₆	KN(NO ₂)CH ₂ CH ₂ N(NO ₂) ₂	130				4
C ₂ H ₈ N ₂	(CH ₃) ₂ NNH ₂	-57.2	63	0.786 (25°)		56
C ₃ ClF ₆ H ₇ N ₄ O ₅	CN ₃ F ₆ OC ₂ H ₄ NH ₃ ClO ₄	221	218			291 241 152
C ₃ F ₂ H ₆ N ₂ O ₂	CH ₃ ON(OH)CH ₂ NF ₂	93-94				274
C ₃ F ₄ H ₂ N ₆ O ₅	F ₂ NCHN(NO ₂)CON(NO ₂)CHNF ₂	69-70				274
C ₃ F ₄ H ₃ N ₆ O ₃	F ₂ NCHN(NO ₂)CONHCHNF ₂	85-89 dec.				274
C ₃ F ₄ H ₆ N ₄ O	F ₂ NCH ₂ NHCONHCH ₂ NF ₂	162				274
C ₃ F ₄ H ₆ N ₆ O ₄	CH ₂ [N(CH ₂ NF)NO ₂] ₂	89				274, 179
C ₃ F ₄ H ₇ N ₃ O ₂ S	CH ₃ SO ₂ N(CH ₂ NF ₂) ₂	44-46				274
C ₃ F ₆ H ₂ N ₆ O	NF ₂ C(NF)NHCONHC(NF)NF ₂	95-97 dec.				86
C ₃ F ₆ H ₂ N ₆ O ₇	(NF ₂) ₃ COCH ₂ C(NO ₂) ₃		25 (0.4 mm.)	1.54		174
C ₃ F ₆ H ₄ N ₄ O ₂	(NF ₂) ₃ COCH ₂ CO(NH ₂)			1.65 est.		293
C ₃ F ₆ H ₆ N ₄	N(CH ₂ NF ₂) ₃		166		1.378 (18)	274

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TABLE XXVII (Continued)

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

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TABLE XXVII (Continued)

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

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TABLE XXVII (Continued)

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

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TABLE XXVII (Continued)

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

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TABLE XXVII (Continued)

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

117
CONFIDENTIAL

CONFIDENTIAL

TABLE XXVII (Continued)

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

CONFIDENTIAL

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TABLE XXVII (Continued)

Formula		m.p. (°C)	b.p. (°C)	density (g/cm ³)	refractive index	ref.
Empirical	Structural					
C ₁₂ H ₆ N ₆ O ₈	CHC(NO ₂)CHC(NO ₂)CHCN=NCCHC(NO ₂)CHC(NO ₂)CH	230-232 dec.				5
C ₁₆ H ₁₆ F ₁₂ N ₁₀ O ₂	[CH(NF ₂)CH(NF ₂)N(C ₂ H ₅)CON(CHNF ₂)] ₂	178 dec.				
(C ₆ F ₁₂ H ₄ N ₆ O ₃) _x	[O-(CHCH ₂ OC(NF ₂) ₃) ₂] _x					
ClFO ₃	ClO ₃ F	-146	-46.8	1.712		274
ClF ₃	ClF ₃	-76.3	11.75	1.434 (25°)		174
ClF ₃ O	ClF ₃ O	-66±	29.4±1	1.8094 (25°)		56
		-37.2±0.5		1.90± 0.05 (25.5°)		421
ClF ₄ NO ₂	NO ₂ ClF ₄		+30±5			429 420a
ClF ₅	ClF ₅	-103± 4	9.5	2.696-3.08 x10 ⁻³ T		342
			-14			359
			-18.1	1.75		56 51
ClF ₈ Sb	ClF ₂ SbF ₆	225-228				342
ClF ₁₀ Sb	ClF ₄ SbF ₆	34-35				342
ClH ₄ NO ₄	NH ₄ ClO ₄					
ClH ₅ N ₂ O ₄	N ₂ H ₅ ClO ₄			1.95		174, 51
				1.94		174

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TABLE XXVII (Continued)

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

120

CONFIDENTIAL

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TABLE XXVII (Concluded)

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

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APPENDIX B

THERMODYNAMIC PROPERTIES

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TABLE XXVIII
THERMODYNAMIC PROPERTIES

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

124
CONFIDENTIAL

CONFIDENTIAL

TABLE XXVIII (Continued)

Formula		ΔH_f	ΔF_f	S°	C_p°	H_v	S_v	ref.
Empirical	Structural	kcal/mole	kcal/mole	E.U.	cal/°mole	kcal/mole	E.U.	
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
$C_2ClF_6H_5N_6O_5$	$(NF_2)_3-C-O-N \begin{array}{c} NH_2 \\ \\ C \\ \\ NH_3^+ ClO_4^- \end{array}$	-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
$C_2F_2H_4N_4O_3$	$O_2NNHCONHCH_2NF_2$	-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
$C_2F_6H_2N_4O$	$(NF_2)_3C \begin{array}{c} O \\ \\ CNH_2 \end{array}$	-53 est.						293
$C_2F_6O_4$	$FOCF_2OOCF_2OF$					6.6		403
$C_2F_7H_2N_5O$	$CN_3F_6NFCONH_2$	-35 est.						291
C_2F_7NO	$(CF_3)_2NOF$ or $(CF_3)_2N \begin{array}{c} F \\ \\ N \rightarrow O \end{array}$					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	63°	56

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TABLE XXVIII (Continued)

Formula		ΔH_f kcal/mole	ΔF_f kcal/mole	S° E.U.	C_p° cal/mole	H_y kcal/mole	S_y E.U.	ref.
Empirical	Structural							
$C_3Cl_1F_4H_6N_3O_4$	$NF_2CH_2CHNF_2CH_2NH_3ClO_4$	-90.45						176
$C_3ClF_6H_7N_4O_5$	$CN_3F_6OC_2H_4NH_2ClO_4$	-103 $\pm$ 3 -89.3 113.6 $\pm$ 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 $\pm$ 2.2 -73.7 $\pm$ 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
$C_4F_8H_4N_4O$	$C_4H_4(NF_2)_4O$	-73.24 -68.3 $\pm$ 3.2						166

CONFIDENTIAL

CONFIDENTIAL

TABLE XXVIII (Continued)

Empirical	Formula		ΔH_f kcal/mole	ΔF_f kcal/mole	S° E.U.	C_p° cal/mole	H_v kcal/mole	S_v E.U.	ref.
	Structural								
$C_4F_8H_4N_4O_2$	$[-(CH(NF_2)_2O-)]_2$		-91.4 calc.					166	
$C_4F_8H_6N_4$	$C_4H_6(NF_2)_4$		-57.49					174	
$C_5Cl_{11}F_{12}H_8N_7O_6$	$[(NF_2)_3COCH_2]_2CHNF_2 \cdot HClO_4$		-113.0					174	
$C_5F_6H_4N_6O$	$[-C(NF_2)-N(CH_2NF_2)-]_2CO$		-32.7 calc.					274	
$C_5F_6H_6N_8O_9$	$(F_2N)_3COCH_2CH_2N(NO_2)CH_2C(NO_2)_3$		-54.9					179 178a	
$C_5F_7H_6N_7O_7$	$(NO_2)_2CFCH_2N(NO_2)CH_2CH_2OC(NF_2)_3$		-95.0			25.3		174	
$C_5F_8H_6N_6O$	$[-CHNF_2-N(CH_2NF_2)-]_2CO$		-163.4 calc.					274	
$C_5F_8H_8N_6O$	$(F_2NCH_2)_2NCON(CH_2NF_2)_2$		-114.8 calc.					274	
$C_5H_4N_4O_4$	$(NO_2)NCHCHC(NNO_2)CHCH$		+26.3 $\pm$ 2.5					7	
$C_6F_6H_6N_8O_7$	$CON(CH_2NF_2)CH(NF_2)CH(NF_2)N[CH_2C(NO_2)_3]$		-150.0 calc.					274	
$C_6F_6H_8N_4O_{10}$	$(O_2NOCH_2)_3CCH_2OC(NF_2)_3$		-139.3 $\pm$ 2.7				21.5	178	
$C_6F_8H_6N_6O_2$	$[K-CHNF_2-]_2N(CHO-)_2$		-71.2 calc.					274	
$C_6F_8H_8N_4$	$[-C(NF_2)_2C_2H_4-]_2$		-55.4 calc.				2	274	
$C_6F_{12}H_6N_8O_8$	$[(NF_2)_3COCH_2CHNO_3]_2$		-119.7					174	
$C_6F_{12}H_8N_6O_1$	$(H_2CNF_2CHNF_2CHNF_2)_2O$		-114.26 -128.4 $\pm$ 8.7					174 174,293	

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TABLE XXVIII (Continued)

Formula		ΔH_f° kcal/mole	ΔF_f° kcal/mole	S° E.U.	C_p° cal/°/mole	H_v kcal/mole	S_v E.U.	ref.
Empirical	Structural							
$C_6F_{14}H_5N_7O_3$	$(NF_2)_3COCH_2CH[OC(NF_2)_3]CH_2OC(NF_2)_3$	-147.4						174
$C_7Cl_1F_{18}H_9N_{10}O_7$	$(NF_2)_3(COCH_2)_3CNH_2 \cdot HClO_4$	-136.0						174
$C_7F_4H_8N_{10}O_{13}$	$[(O_2N)_3CCH_2N(CH_2NF_2)]_2CO$	-111.5 calc.						274
$C_7F_{12}H_7N_{11}O_{10}$	$(NO_2)_3CCH_2N(NO_2)CH[CH_2OC(NF_2)_3]_2$	-93.0						176
$C_7F_{12}H_8N_6O_4$	$[(NF_2)_3COCH_2]CHOCH_2OCH[CH_2OC(NF_2)_3]$	-150.0						176
$C_7F_{12}H_8N_8O_8$	$(NF_2)_3(COCH_2)_2C(CH_2ON_2)_2$	-126.7						174
$C_7F_{18}H_6N_{10}O_6$	$(NF_2)_3COCH_2CH[OC(OC(NF_2)_3)CH(ON_2)CH_2OC(NF_2)_3]$	-133.6			23.3			178
$C_8F_8H_{10}N_8O_2$	$HC[-N(CH_2NF_2)CO-N(CH_2NF_2)-]_2CH$	-20.0 calc.						174
$C_8F_{12}H_8N_{10}O_2$	$[CH(NF_2)CH(NF_2)NHCON(CH_2NF_2)]_2$	-301.2 calc.						274
$C_8F_{18}H_8N_{10}O_6$	$O_2NOCH_2-C-(CH_2CO[NF_2]_2)_3$	-186.4 $\pm$ 4.7						178a
$C_9F_{12}H_{12}N_{12}$	$NCN(CH_2NF_2)_2NCN(CH_2NF_2)_2NCN(CH_2NF_2)_2$	-47.9 calc.			22.3			178
								274

CONFIDENTIAL

CONFIDENTIAL

TABLE XXVIII (Continued)

Formula		ΔH_f kcal/mole	ΔF_f kcal/mole	S° E.U.	C_p° 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
$ClFO_3$	ClO_3F	-51.2 $\pm$ 0.68			0.261 (1)	4.6 (-46.8°)		56
		-10.91						44
ClF_3	ClF_3	-45.37 (1)			27.92 (1) (0°)	6.58 (11.75°)		56
			-21.9					137
ClF_3O	ClF_3O					7.7		421
ClF_4O_2	O_2ClF_4	-21 est.						351
ClF_5	ClF_5	-55.8 $\pm$ 6 -60		87.6				387
				42.3 $\pm$ 1.8 calc.	(0.00114) +0.318 (g)	5.330		387, 359 359

CONFIDENTIAL

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TABLE XXVIII (Continued)

Formula		ΔH_f° kcal/mole	ΔF_f° kcal/mole	S° E.U.	C_p° cal/mole	H_v kcal/mole	S_v E.U.	ref.
Empirical	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 $\pm$ 0.5						364
F_3N	$NF_3(g)$	31.44						151f

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TABLE XXVIII (Concluded)

Formula		ΔH_f kcal/mole	ΔF_f kcal/mole	S° E.U.	C_p° cal/°/mole	H_v kcal/mole	S_v E.U.	ref.
Empirical	Structural							
F_3NO	NF_3O	-36 ± 3 -35.0 -35.5 ± 2.2						52 44 142
F_4N_2	N_2F_4	-5.2				3.170		52 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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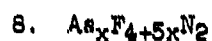
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TABLE XXIX

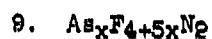
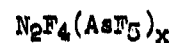
MASS, INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRA

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. AsClF_{10}	$\text{ClF}_5 \cdot \text{AsF}_5$
IR: (385)	
Mass:	
NMR:	
3. AsF_8NO	$\text{F}_3\text{NO} \cdot \text{AsF}_5$
IR:	
Mass:	
NMR: (386)	
4. AsF_9N_2	$\text{N}_2\text{F}_3\text{AsF}_6$
IR: (357)	
Mass:	
NMR:	
5. AsF_9N_2	$\text{N}_2\text{F}_4 : \text{AsF}_5$
IR: (352)	
Mass:	
NMR: (352)	
6. AsF_{10}N	NF_4AsF_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:	

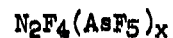
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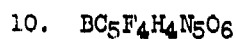
IR: (353)
Mass:
NMR: (353)



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

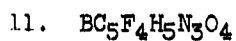
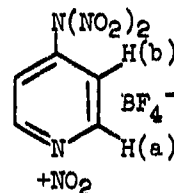


F^{19} : $\left. \begin{array}{l} -67 \delta \\ -95 \delta \\ -134 \delta \end{array} \right\} 3 \text{ broad resonances}$



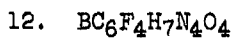
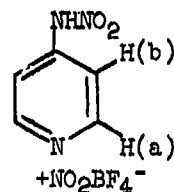
IR: (5)
Mass:
NMR: (5)

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



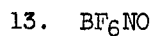
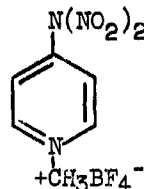
IR:
Mass:
NMR: (5)

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

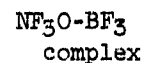


IR:
Mass:
NMR: (6)

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. BrCF_6N_3

$(\text{NF}_2)_3\text{C-Br}$

IR: (142)
Mass: (142)
NMR: (142)

15. $\text{BrC}_4\text{FH}_7\text{NO}_2$

$(\text{CH}_3)_2\text{CHOOCCNBr}$

IR: (17)
Mass:
NMR:

16. BrF_4NO_2

NO_2BrF_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. CCsF_3O

$\text{Cs}^+\text{OCF}_3^-$

IR: (75)
Mass:
NMR: (75)

F^{19} : +107.5 ppm, singlet, $-\text{OCF}_3^-$

19. $\text{CF}_2\text{H}_3\text{N}$

CH_3NF_2

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

20. CF_4O

CF_3OF

IR:
Mass:
NMR: (284)

F^{19} : 72.5 ppm, doublet, downfield - CF_3
142 $\pm$ 10 ppm, quartet, downfield - OF

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21. CF_5N

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

CF_3NF_2

22. CF_5NO_2

IR: (386)
Mass:
NMR:

$\text{CF}_2(\text{OF})\text{ONF}_2$

23. $\text{CF}_5\text{NO}_6\text{S}_2$

IR: (440)
Mass:
NMR:

$\text{CF}(\text{NF}_2)(\text{OSO}_2\text{F})_2$

24. CF_5N_2

IR: (115)
Mass:
NMR:

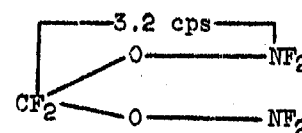
$(\text{NF}_2)_2\text{C}=\text{NF}$

25. $\text{CF}_6\text{N}_6\text{O}$

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

$\text{CF}_2(\text{ONF}_2)_2$

F19: 126.6 ppm, broad, $-\text{ONF}_2$
66.2 ppm, pentet, $>\text{CF}_2$



26. $\text{CF}_6\text{N}_2\text{O}_2$

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

$\text{F}_2\text{C}(\text{ONF}_2)_2$

27. CF_6N

IR:
Mass: (146a)
NMR:

$\text{C}(\text{NF}_2)_4$

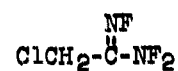
28. $\text{CF}_{13}\text{NO}_2\text{S}_2$

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

$\text{SF}_5\text{OCF}_2\text{OSF}_4\text{NF}_2$

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29. $C_2ClF_5H_2N_2$



IR:

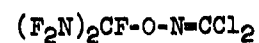
Mass:

NMR: (292)

F19: -46.9 ppm

-21.4 ppm

30. $C_2Cl_2F_5N_3O$



IR:

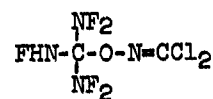
Mass:

NMR: (293)

F19: -20.9 ppm, $-NF_2$

116.3 ppm, $>CF$

31. $C_2Cl_2F_5HN_4O$



IR:

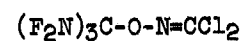
Mass:

NMR: (293)

F19: -23.4 ppm, $-NF_2$

137.5 ppm, $-NHF$

32. $C_2Cl_2F_6N_4O$



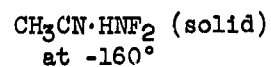
IR: (293)

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)



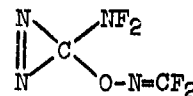
F19: -6.9 ppm, =NF
79.6 ppm, >CF

38. $C_2F_4N_4O$

IR: (299)

Mass:

NMR:

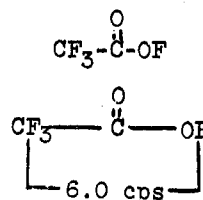


39. $C_2F_4O_2$

IR: (294)

Mass:

NMR: (294)



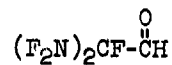
F19: -188.0 ppm, quartet, OF
70.8 ppm, doublet, CF₃

40. $C_2F_5HN_2O$

IR: (294)

Mass: (294)

NMR: (294)



H¹: 0.34 τ, -C(=O)H
F19: -22.6 ppm, -NF₂
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)

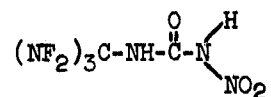
F19:
Trans -11.4 ppm F

$$\begin{array}{c} NF_2 -45.4 \text{ ppm} \\ | \\ N=C \\ | \quad \backslash \\ F \quad N=N \quad F -9.1 \text{ ppm} \\ | \quad \quad | \\ F \quad C=N \\ | \quad \quad | \\ F \quad 80.8 \text{ ppm} \end{array}$$

Cis -18.3 ppm F

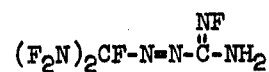
$$\begin{array}{c} NF_2 -41.2 \text{ ppm} \\ | \\ N=C \\ | \quad \backslash \\ F \quad N=N \quad F -8.9 \text{ ppm} \\ | \quad \quad | \\ F \quad C=N \\ | \quad \quad | \\ F \quad 80.4 \text{ ppm} \end{array}$$

43. $C_2F_6H_2N_2O_3$



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

44. $C_2F_6H_2N_6$



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

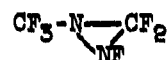
H¹: 4.69 τ , $-NH_2$
F19: -20.8 ppm, $-NF_2$
+9.2 ppm, $=NF$
137.6 ppm, $\geq CF$

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45. $C_2F_6N_2$

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

F^{19} : 12.4 ppm, >NF
62.5 ppm, -CF₃
112.5 ppm, >CF₂



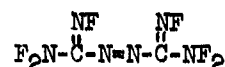
46. $C_2F_6N_4O$

IR: (164)
Mass:
NMR:

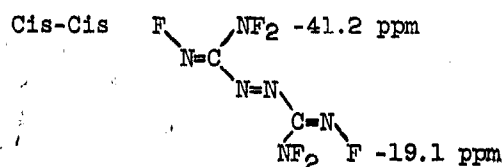
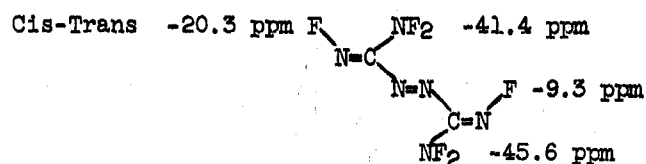
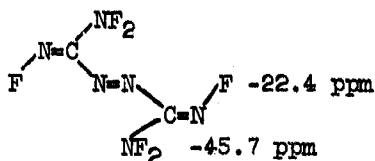


47. $C_2F_6N_6$

IR: (255)
Mass:
NMR: (255)



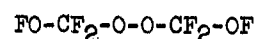
F^{19} : Trans-Trans



48. $C_2F_6O_4$

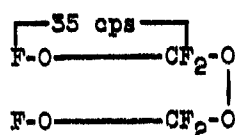
IR: (403)
Mass:
NMR: (403)(435)

F^{19} : -158 ϕ , triplet, -OF
81 ϕ , doublet, >CF₂

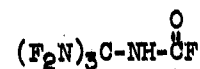


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48. $C_2F_6O_4$ (Concluded)



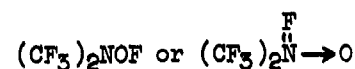
49. $C_2F_7HN_4O$



IR:
Mass:
NMR: (295)

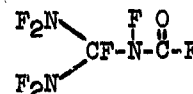
Flg: -27.6 ppm, $-NF_2$
+1.5 ppm, $-C(=O)F$

50. C_2F_7NO



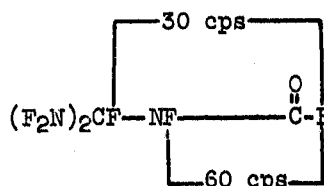
IR:
Mass:
NMR: (532a)

51. $C_2F_7N_2O$

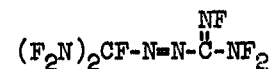


IR: (292)
Mass:
NMR: (292)

Flg: -23.6 ppm, $-NF_2$
9.6 ppm, doublet of doublets, $-C(=O)F$
72.4 ppm, $>NF$
132.9 ppm, $\geq CF$



52. $C_2F_8N_6$



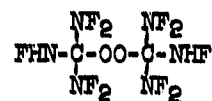
IR:
Mass: (249)
NMR:

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53. $C_2F_{10}H_2N_6O_2$

IR:
Mass:
NMR: (296)

F^{19} : -22.2 ppm, $-NF_2$
+138.6 ppm, $-NHF$

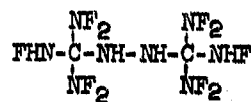


54. $C_2F_{10}H_4N_8$

IR:
Mass:
NMR: (291)

H^1 : 4.3 τ , singlet, $>NH$
0.8 τ , doublet, $-NHF$

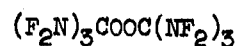
F^{19} : -21.3 ppm, doublet, $-NF_2$



55. $C_2F_{12}N_6O_2$

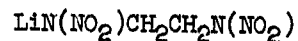
IR:
Mass:
NMR: (296)

F^{19} : -25.2 ppm, $-C(NF_2)_3$



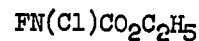
56. $C_2H_4LiN_4O_4$

IR: (4)
Mass:
NMR:



57. $C_3ClF_5H_5NO_2$

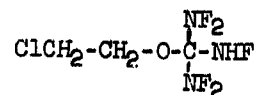
IR: (18)
Mass:
NMR:



58. $C_3ClF_5H_5N_3O$

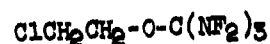
IR:
Mass:
NMR: (293)

F^{19} : -21.5 ppm, $-NF_2$
141.3 ppm, $-NHF$



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59. $C_3ClF_6H_4N_3O$



IR: (293)

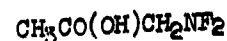
Mass:

NMR: (293)

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

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

60. $C_3F_2H_6N_2O_2$

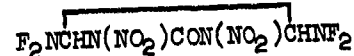


IR: (274)

Mass:

NMR:

61. $C_3F_4H_2N_6O_5$



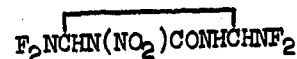
IR: (274)

Mass:

NMR: (274,

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

62. $C_3F_4H_3N_5O_3$



IR: (274)

Mass:

NMR: (274)

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

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

63. $C_3F_4H_4N_4O$



IR: (274)

Mass:

NMR: (274)

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

F^{19} : Triplet at -31.6 δ , $J = 15$ 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:

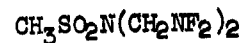


66. $C_3F_4H_7N_3O_2S$

IR: (274)

Mass:

NMR:

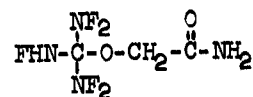


67. $C_3F_5H_5N_9O_2$

IR:

Mass:

NMR: (85c)



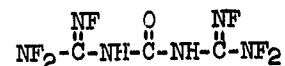
F^{19} : -21.0 ppm, $-NF_2$
142.6 ppm, $-NHF$

68. $C_3F_6H_2N_6O$

IR: (86)

Mass:

NMR: (86)

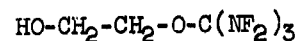


69. $C_3F_6H_5N_3O_2$

IR: (294)

Mass:

NMR: (294)



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

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

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70. $C_3F_6H_6N_4$

$N(CH_2NF_2)_3$

IR: (274)

Mass:

NMR: (274)

H1: 5.43 τ , triplet, $J = 24$ cps

F19: -42.7 δ , triplet, $J = 24$ cps

71. $C_3F_6O_3$

$CF_3CF_2-O-O-\overset{O}{\parallel}C-F$

IR: (296)

Mass: (296)

NMR: (296)

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

83.0 ppm, $-CF_3$

95.8 ppm, $>CF_2$

72. $C_3F_6O_3$

$CF_3-\overset{O}{\parallel}C-OO-CF_3$

IR: (296)

Mass: (296)

NMR: (296)

F19: 68.9 ppm, singlet, $-OCF_3$

72.0 ppm, singlet, $CF_3C(=O)-$

73. C_3F_8HN

$(CF_3)_2CF-NHF$

IR:

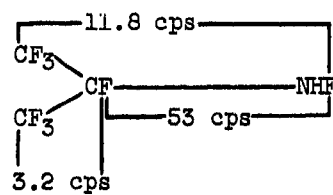
Mass:

NMR: (296)

F19: 76.1 ppm, $-CF_3$

134.9 ppm, $-NHF$

151.2 ppm, $\geq CF$

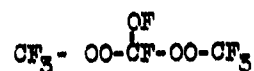
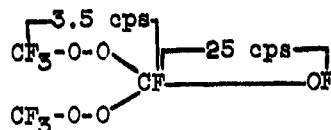


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74. $C_3F_8O_5$

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

τ 19: -168.0 ppm, doublet, -OF
68.7 ppm, doublet, -CF₃
90.6 ppm, complex, $\geq$ CF



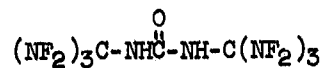
75. $C_3F_9N_3$

IR: (235)
Mass:
NMR:



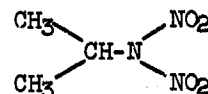
76. $C_3F_{12}H_2N_8O$

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



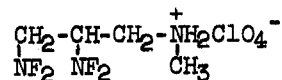
77. $C_3H_7N_3O_4$

IR: (6)
Mass:
NMR:



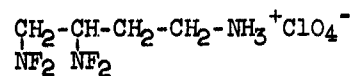
78. $C_4ClF_4H_{10}N_3O_4$

IR: (176)
Mass:
NMR:



79. $C_4ClF_4H_{10}N_3O_4$

IR: (176)
Mass:
NMR:

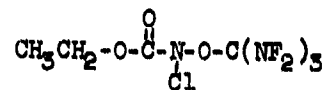


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80. $C_4ClF_6H_5N_4O_4$

IR:
Mass:
NMR: (292)

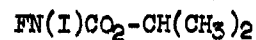
τ_{19} : -26.9 ppm, $-C(NF_2)_3$



81. $C_4FH_7INO_2$

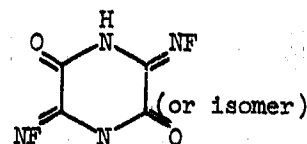
IR:
Mass:
NMR: (17)

τ_{19} : +25 ppm



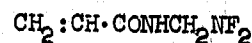
82. $C_4F_2H_2N_4O_2$

IR: (274)
Mass:
NMR:



83. $C_4F_2H_6N_2O$

IR: (274)
Mass:
NMR:



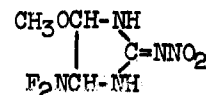
84. $C_4F_2H_6N_6O_7$

IR: (274)
Mass:
NMR:



85. $C_4F_2H_7N_5O_3$

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



H^1 : Complex series (ring CH) region
CH₃ peaks obscured by solvent
NH absorptions 0.72 and 1.21 τ C_2H_5

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

86. $C_4F_2H_8N_2O_2$

IR: (274)
Mass:
NMR:



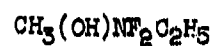
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87. $C_4F_2H_9NO$

IR: (274)

Mass:

NMR:

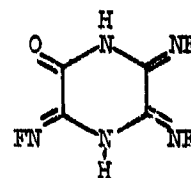


88. $C_4F_3H_2N_5O$

IR: (274)

Mass:

NMR:



89. $C_4F_3H_5N_2O_2$

IR: (10)

Mass:

NMR: (10)



F19: 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. $C_4F_4H_2N_6$

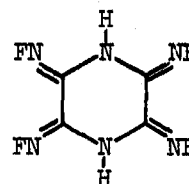
IR: (274)

Mass:

NMR: (274)

H¹: 6.41 τ (solvent)
-0.30 τ (solvent)
6.35 τ (MeCN?)

F19: +24.0 δ

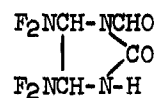


92. $C_4F_4H_4N_4O_2$

IR: (274)

Mass:

NMR:



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93. $C_4F_4H_5O_2$

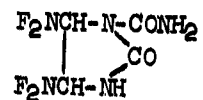
IR: (274)

Mass:

NMR: (274)

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

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

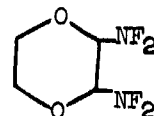


94. $C_4F_4H_6N_2O_2$

IR: (274)

Mass:

NMR:



95. $C_4F_4H_6N_4O_2$

IR: (274)

Mass:

NMR:

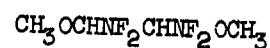


96. $C_4F_4H_8N_2O_2$

IR: (274)

Mass:

NMR:

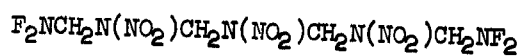


97. $C_4F_4H_8N_8O_6$

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. $C_4F_6H_5N_3O_2$

$CH_2-CH-CH_2-OC(NF_2)_3$
|
O

IR: (175)
Mass:
NMR:

101. $C_4F_6H_5N_5O_7$

$O_2N-O-CH_2-CH-CH_2-OC(NF_2)_3$
|
ONO₂

IR: (177)
Mass:
NMR: (177)

H¹: 4.42 τ , $>CH$
5.20 τ , $>CH_2$

102. $C_4F_6H_6N_4O_3$

$(F_2N)_3CON=C(OCH_3)_2$

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

H¹: 6.12 τ } $-CH_3$
6.16 τ }

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)

H¹: 8.7 τ , triplet, CH_3^-
5.71 τ , quartet, $>CH_2$
0.55 τ , singlet, $>NH$

F19: -24.5 ppm, $-NF_2$

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104. $C_4F_6H_7N_3O$

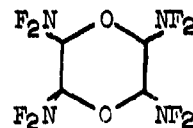


IR: (274)

Mass:

NMR:

105. $C_4F_8H_4N_4O_2$



IR: (274)

Mass:

NMR: (274)

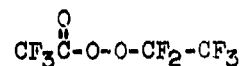
H^1 : 4.49 τ , triplet, $J = 19$ cps

F^{19} : -34.3 δ , doublet, $J = 20$ cps

-33.6 δ , doublet, $J = 20$ cps

31.2 δ , broad band (Impurity ?)

106. $C_4F_8O_3$

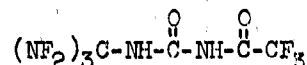


IR: (296)

Mass: (296)

NMR:

107. $C_4F_9H_2N_5O_2$

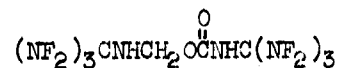


IR: (86)

Mass:

NMR: (86)

108. $C_4F_{12}H_4N_8O_2$

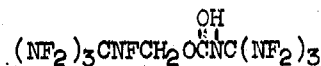


IR: (163)

Mass:

NMR: (163)

109. $C_4F_{13}H_3N_7O_2$

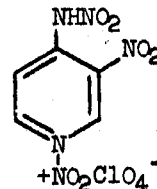


IR: (163)

Mass:

NMR: (163)

110. $C_5ClH_4N_4O_{10}$



IR: (6)

Mass:

NMR: (6)

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. $C_5ClH_5N_4O_8$

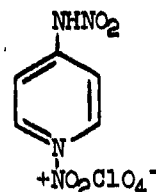
IR: (6)

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:

$(CCl_3CHNF_2NH)_2CO$

113. $C_5FH_7N_2O_5$

IR: (49)

Mass:

NMR: (49)

$FC(NO_2)_2CH_2OCH_2CH=CH_2$

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:

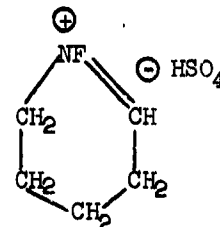
NMR: (45)

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:



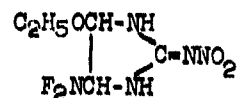
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116. $C_5F_2H_9N_5O_3$

IR: (274)

Mass:

NMR:

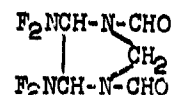


117. $C_5F_4H_6N_4O_2$

IR: (274)

Mass:

NMR:

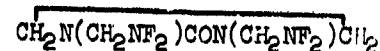


118. $C_5F_4H_8N_4O$

IR: (274)

Mass:

NMR:

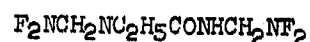


119. $C_5F_4H_{10}N_4O$

IR: (274)

Mass:

NMR:

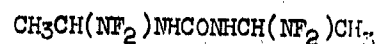


120. $C_5F_4H_{10}N_4O$

IR: (274)

Mass:

NMR:

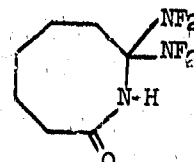


121. $C_5F_4H_{11}N_3O$

IR: (451)

Mass:

NMR: (451)

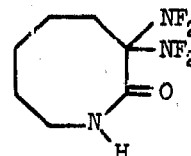


122. $C_5F_4H_{11}N_3O$

IR: (451)

Mass:

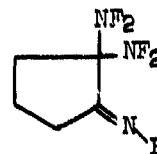
NMR: (451)



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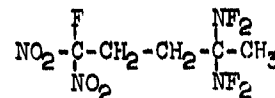
123. $C_5F_5H_6N_3$

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



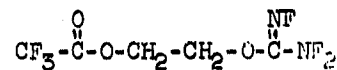
124. $C_5F_5H_7N_4O_4$

IR: (315)
Mass:
NMR:



125. $C_5F_6H_4N_2O_3$

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

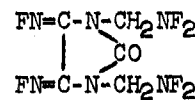


H^1 : 5.5 τ , $>CH_2$, mixture of isomers

F^{19}	Isomer	Peak	Assignment
	A, B	75.7 ppm	CF_3
	A	-43.0 ppm	$-NF_2$
		40.8 ppm	$=NF$
	B	-37.7 ppm	$-NF_2$
		49.0 ppm	$=NF$

126. $C_5F_6H_4N_6O$

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

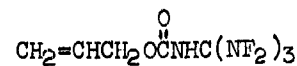


H^1 : 4.41 τ , triplet ($J = 24$ cps)

F^{19} : +31.4 δ , single peak (C:NF)
-44.0 δ , triplet ($J = 24$ cps) (CH_2NF_2)

127. $C_5F_6H_6N_4O_2$

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

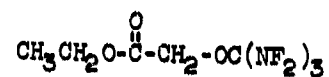


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128. $C_5F_6H_7N_3O_3$

IR:
Mass:
NMR: (294)

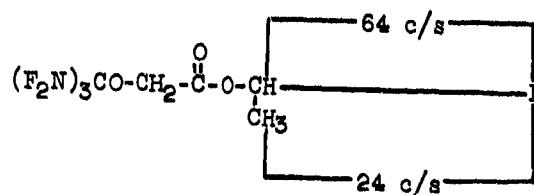
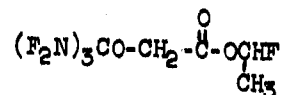
F19: -22.8 ppm, $-NF_2$



129. $C_5F_7H_6N_3O_3$

IR:
Mass:
NMR: (294)

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

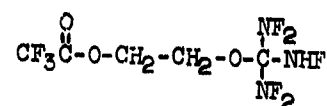


130. $C_5F_8H_5N_3O_3$

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

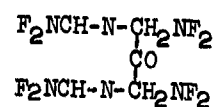
H1: 1.25 τ , $-NHF$
5.4 τ , $-CH_2$

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 τ
 CH_2 groups and nonequivalent ring CH-rings

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

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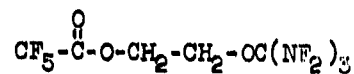
132. $C_5F_8H_8N_6O$

IR: (274)
Mass:
NMR:



133. $C_5F_9H_4N_3O_3$

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

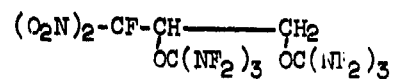


H^1 : 5.37 τ , $>CH_2$

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

134. $C_5F_{13}H_3N_8O_6$

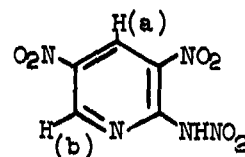
IR: (175)
Mass:
NMR: (175)



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

135. $C_5H_3N_5O_6$

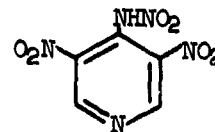
IR:
Mass:
NMR: (5)



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)

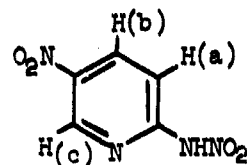


H^1 : $\nu_{NHNO_2} = 11.07$ ppm
 $\nu_{2,6} = 9.02$ ppm

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137. $C_5H_4N_4O_4$

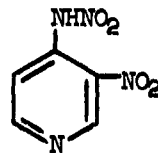
IR:
Mass:
NMR: (5)



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. $C_5H_4N_4O_4$

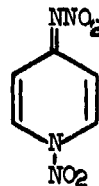
IR:
Mass:
NMR: (6)



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. $C_5H_4N_4O_4$

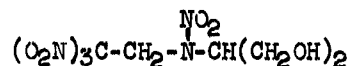
IR: (5)
Mass:
NMR: (7)



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

140. $C_5H_9N_5O_{10}$

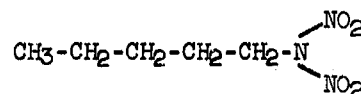
IR: (176)
Mass:
NMR: (175)



H^1 : 4.40 τ , $-\text{CH}_2-\text{C}(\text{NO}_2)_3$
5.25 τ , $-\text{CH}$
6.25 τ , $-\text{CH}_2\text{OH}$
6.78 τ , $-\text{CH}_2\text{OH}$

141. $C_5H_{11}N_3O_4$

IR:
Mass:
NMR: (2)



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

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142. $C_6F_9H_{10}NO_3$

$CH_3CONFCO_2CH(CH_3)_2$

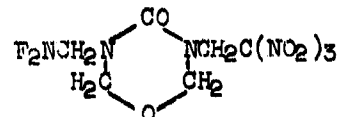
IR:

Mass:

NMR: (17)

τ_{19} : +68.8 ppm (relative to internal Freon-11)

143. $C_6F_2H_8N_6O_8$



IR: (274)

Mass:

NMR: (274)

H^1 : 5.08 τ , triplet, $J_{CH_2-NF_2} = 24$ cps
 5.01 τ , peak
 4.88 τ , peak $[CH_2C(NO_2)_3]$, ratio 1:2:1

τ_{19} : -44.5 δ , 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)

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

145. $C_6F_4H_6N_4O_6$

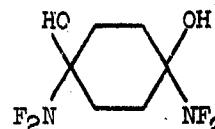
$(F_2NCHNHCOCOOH)_2$

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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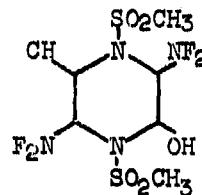
148. $C_6F_4H_{10}N_4O_4$



IR: (274)
Mass:
NMR:

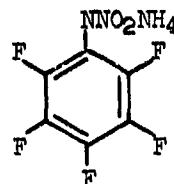
149. $C_6F_4H_{12}N_4O_6S_2$

IR: (274)
Mass:
NMR:



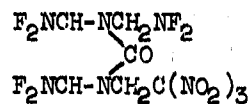
150. $C_6F_5H_4N_3O_2$

IR: (6)
Mass:
NMR:



151. $C_6F_6H_6N_8O_7$

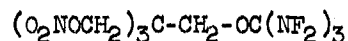
IR: (274)
Mass:
NMR: (274)



H¹: 16 peaks, 4.03 - 5.68 τ
consisting of singlet $CH_2C(NO_2)_3$
triplet CH_2NF_2
and pair sextuplets, magnetically nonequivalent ring CH-rings

F¹⁹: $\left. \begin{array}{l} -28.8 \delta, \text{ triplet, } J = 21 \text{ cps} \\ -31.0 \delta, \text{ doublet, } J = 12 \text{ cps} \\ -43.6 \delta, \text{ triplet, } J = 24 \text{ cps} \end{array} \right\} \begin{array}{l} NF_2 \text{ positions 5, 4, and 1 resp.} \\ \text{ratio 1:1:1} \end{array}$

152. $C_6F_8H_8N_6O_{10}$



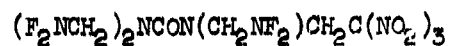
IR: (174)
Mass:
NMR: (174)

H¹: 6.05 τ , singlet, $-CH_2-O-C-$
6.15 τ , singlet, $-CH_2-O-NO_2$

F¹⁹: -24.7, singlet, $-NF_2$

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153. $C_6F_6H_6N_8O_7$

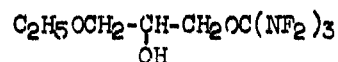


IR: (274)

Mass:

NMR:

154. $C_6F_6H_{11}N_3O_3$

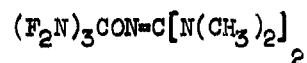


IR:

Mass:

NMR: (178a)

155. $C_6F_6H_{12}N_6O$



IR:

Mass:

NMR: (297)

H^1 : 6.87 τ , $-CH_3$

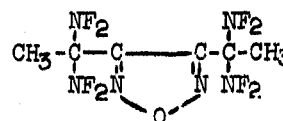
F^{19} : -24.5 ppm, $-NF_2$

156. $C_6F_6H_6N_6O$

IR: (453)

Mass:

NMR:

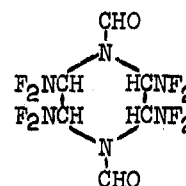


157. $C_6F_6H_6N_6O_2$

IR: (274)

Mass:

NMR: (274)



H^1 : 1.09 τ , singlet (CHO)

3.68 τ , triplet, $J = 23$ cps (Ring CH),
each peak split into doublet $J = 4$ cps

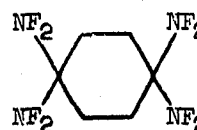
F^{19} : Complex spectrum between -40.9 δ and -36.3 δ

158. $C_6F_6H_8N_4$

IR: (274)

Mass:

NMR: (274)



H^1 : 7.61 τ , single peak

F^{19} : -27.4 δ , single peak

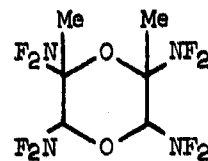
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159. $C_6F_8H_8N_4O_2$

IR: (274)

Mass:

NMR:



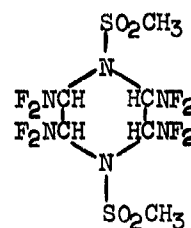
or isomer

160. $C_6F_8H_{10}N_6O_4S_2$

IR: (274)

Mass:

NMR: (274)



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

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

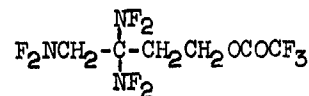
-38.7 δ , doublet, $J = 12$ cps

161. $C_6F_9H_6N_3O_2$

IR:

Mass:

NMR: (440)



162. $C_6F_{10}H_4N_4O_2$

IR: (274)

Mass:

NMR:

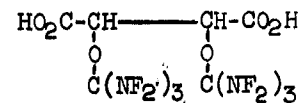


163. $C_6F_{12}H_4N_6O_6$

IR: (174)

Mass:

NMR:

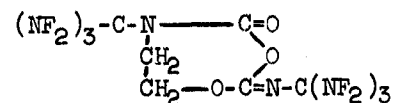


164. $C_6F_{12}H_4N_8O_3$

IR: (86)

Mass:

NMR: (86)



CONFIDENTIAL

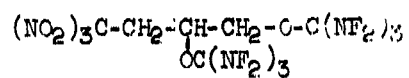
165. $C_6F_{12}H_5N_9O_8$

IR: (175)

Mass:

NMR: (175)

F19: -23.8, $-NF_2$



166. $C_6F_{12}H_6N_6O_3$

IR: (174)

Mass:

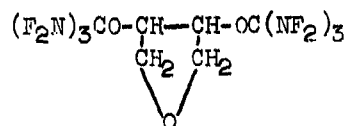
NMR: (174)

H¹: 5.5 τ , CH_2 (Cis)
4.28 τ , CH

F19: -24.0, $-NF_2$

H¹: 5.5 τ , CH_2 (trans)
4.45 τ , CH

F19: -24.0, NF_2



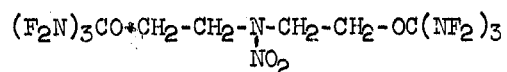
167. $C_6F_{12}H_8N_8O_4$

IR: (178)

Mass:

NMR: (178)

F19: -27.0, $-NF_2$

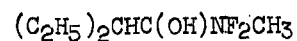


168. $C_7F_2H_{15}NO_3$

IR: (274)

Mass:

NMR:



169. $C_7F_4H_6N_2$

IR: (315)

Mass:

NMR:



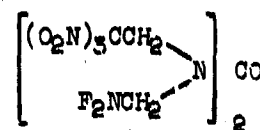
CONFIDENTIAL

170. $C_7F_4H_8N_{10}O_{13}$

IR: (274)

Mass:

NMR: (274)



H^1 : 4.70 τ , triplet, $J = 23$ cps (CH_2CF_2)

3 peaks 4.84, 4.62, 4.35 τ , steric hindrance of $CH_2C(NO_2)_3$

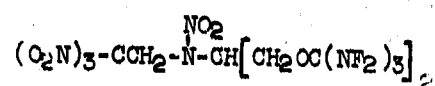
F^{19} : 45.2 δ , triplet, $J = 23$ cps ($N-CH_2NF_2$)

171. $C_7F_{12}H_7N_{11}O_{10}$

IR: (176)

Mass:

NMR: (175)



H^1 : 4.30 τ , $-CH_2-C(NO_2)_3$

5.08 τ , $>CH$, $-CH_2OC(NF_2)_3$

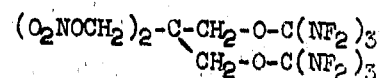
F^{19} : -24.2 ppm, $-NF_2$

172. $C_7F_{12}H_8N_8O_8$

IR: (174)(175)

Mass:

NMR: (174)



H^1 : 6.11 τ , singlet, $-CH_2-O-C(NF_2)_3$

6.22 τ , singlet, $-CH_2-ONO_2$

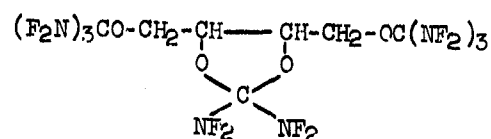
F^{19} : -24.4, singlet, $-NF_2$

173. $C_7F_{16}H_6N_8O_4$

IR: (174)

Mass:

NMR: (174)



F^{19} : -23.6 ϕ , singlet, $-OC(NF_2)_3$

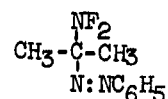
-20.8 ϕ , singlet, $>C(NF_2)_2$

174. $C_8F_2H_{12}N_3$

IR: (49)

Mass:

NMR:



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175. $C_8F_2H_{14}Hg_1N_2O_4$

$Hg(NFCO_2CH(CH_3)_2)_2$

IR:
Mass:
NMR: (16)

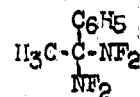
τ_{19} : +90.8 ϕ

176. $C_8F_4H_6N_4O_2$

$(F_2NCH_2NHCOCH_3)_2$

IR: (274)
Mass:
NMR:

177. $C_8F_4H_8N_2$



IR: (315)
Mass:
NMR:

178. $C_8F_4H_{14}N_4O_4$

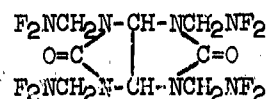
$(F_2NCH_2NHCOOC_2H_5)_2$

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

H^1 : 5.83 τ , quadruplet, $J = 7.2$ cps (CH_2)
2.17, 2.30 τ , broad doublet, $J = 7.8$ cps (NH)
3.8 - 4.8 τ , complex multiplet (CH)

τ_{19} : -26.9 δ , doublet, $J = 27$ cps
-31.0 δ , singlet
-35.2 δ , doublet, $J = 12$ cps

179. $C_8F_8H_{10}N_6O_2$



IR: (274)
Mass:
NMR:

180. $C_8F_8H_{12}N_6O_2$

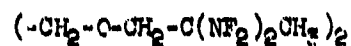
$(F_2NCH_2NHCOCH_2CH_2NF_2)_2$

IR: (274)
Mass:
NMR:

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181. $C_6F_6H_{14}N_4O_2$

IR:
Mass:
NMR: (455)



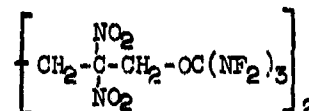
182. $C_8F_{12}H_8N_{10}O_2$

IR: (274)
Mass:
NMR:



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

IR:
Mass:
NMR: (178)

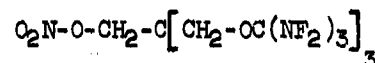


H¹: 4.50 τ , singlet, $-CH_2-OC(NF_2)_3$
7.02 τ , $-CH_2-CH_2-$

τ_{19} : -25.1 ppm, singlet, $-NF_2$

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

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

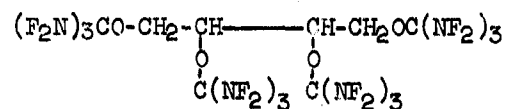


H¹: 6.04 τ , singlet, $-CH_2-OC(NF_2)_3$
6.07 τ , $-CH_2-ONO_2$

τ_{19} : -24.5 ppm, singlet, $-NF_2$

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

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



τ_{19} : -23.6, singlet, $-NF_2$

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186. $C_9F_2H_{11}N_3$

IR:
Mass:
NMR: (49)

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

F^{19} : -25.3 ϕ , broad singlet

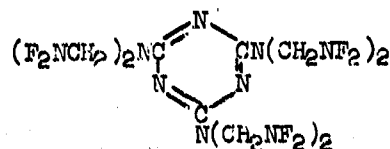
187. $C_9F_4H_{16}N_4O_4$



IR: (274)
Mass:
NMR:

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

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

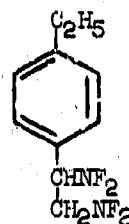


H^1 : 4.4 τ , triplet, $J = 24$ cps

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

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

IR:
Mass:
NMR: (455)



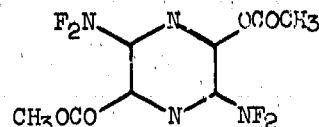
190. $C_{10}F_4H_{14}N_4O_6$

IR: (274)
Mass:
NMR:



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

IR: (274)
Mass:
NMR:



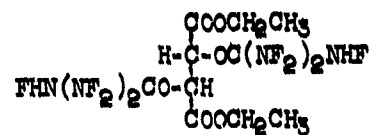
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192. $C_{10}F_{10}H_{14}N_6O_8$

IR: (175)

Mass:

NMR:

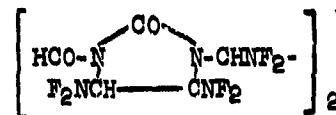


193. $C_{10}F_{12}H_8N_{10}O_4$

IR: (274)

Mass:

NMR:

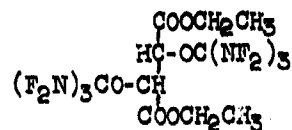


194. $C_{10}F_{12}H_{12}N_6O_6$

IR: (175)

Mass:

NMR: (175)



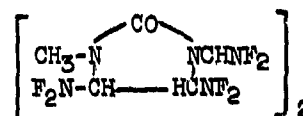
F^{19} : -24.7, $-\text{NF}_2$

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

IR: (274)

Mass:

NMR:



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

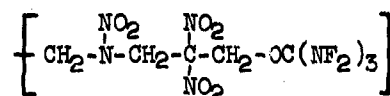
F^{19} : -26.7, -30.2, -32.5, -33.7, -34.2, -37.3 δ ,

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

IR: (179)

Mass:

NMR: (179)



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

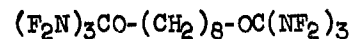
F^{19} : -25.0 ppm, singlet, $-\text{NF}_2$

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

IR: (179)

Mass:

NMR: (179)



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197. (Concluded)

H¹: 8.0 - 8.7 τ , internal -CH₂-
5.5 τ , -CH₂-OC(NF₂)₃

198. C₁₁F₂H₂₀N₄O₆

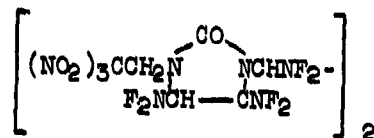
(C₂H₅COONH)₂CHCH(NF₂)NHCOOEt

IR: (274)

Mass:

NMR:

199. C₁₂F₁₂H₁₀N₁₆O₁₄

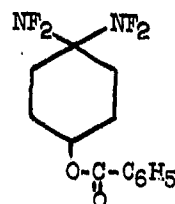


IR: (274)

Mass:

NMR:

200. C₁₃F₄H₁₄N₂O₂



IR:

Mass:

NMR: (453)

201. C₁₃F₆H₂₂N₆O₆

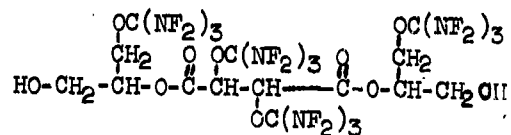
HC[N(CH₂NF₂)COOC₂H₅]₃

IR: (274)

Mass:

NMR:

202. C₁₄F₂₄H₁₄N₁₂O₁₀

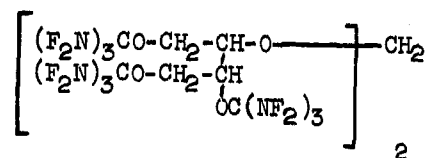


IR: (175)

Mass:

NMR:

203. C₁₅F₃₆H₁₄N₁₈O₈

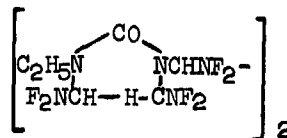


IR: (166)

Mass:

NMR:

204. C₁₆F₁₂H₁₆N₁₀O₂



IR: (274)

Mass:

NMR:

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

H^1 : 3.95 τ , triplet, $J = 19$ cps (CH)
6.4 τ , quintuplet, $J = 6$ cps (CH₂)

F^{19} : Indistinct spectrum due to solubility difficulties peak -29.9 δ

205. $C_{16}F_{19}H_{25}N_6O_2$

$(NF_2)_3CO(CH_2)_{16}OC(NF_2)_3$ 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. ClF_5

IR: (359)
Mass:
NMR: (420a)

ClF_5

212. ClH_4NO_4

IR: (100)
Mass:
NMR:

NH_4ClO_4

213. ClO_2

IR: (534)
Mass:
NMR:

ClOCl

214. $\text{Cl}_2\text{H}_3\text{NO}_{11}$

IR: (121)
Mass:
NMR:

$\text{HNO}_3 \cdot 2\text{HClO}_4$

215. Cl_2O_2

IR: (533a)
Mass:
NMR:

Cl_2O_2

216. FNO

IR:
Mass:
NMR: (420a)

FNO

217. FNO_2

IR:
Mass:
NMR: (420a)

FNO_2

218. F^{18}NO_3

IR: (284)
Mass:
NMR: (284)

NO_3F^{18}

F^{19} : 221.5 ppm downfield from CFCl_3

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219. FO_2 O_2F
IR: (532b)
Mass:
NMR:
220. FO_3 O_3F
IR: (532b)
Mass:
NMR:
221. FO_4 O_4F
IR: (532b)
Mass:
NMR:
222. F_2HN $\text{HNF}_2(\text{solid})$ at -160°
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°
IR: (232)
Mass:
NMR:
224. F_2O_2 O_2F_2
IR: (263)
Mass:
NMR:
225. F_2O_3 O_3F_2
IR: (532b)(263)
Mass:
NMR:
226. F_2O_4 O_4F_2
IR: (532b)
Mass:
NMR:

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227. F_2Si

IR: (379)
Mass:
NMR:

SiF_2

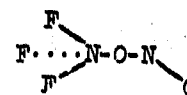
228. F_3NO

IR: (121)
Mass:
NMR:

NOF_3 solid

229. $F_3N_2O_2$

IR: (121)
Mass:
NMR:



230. F_5Sb

IR: (89)
Mass:
NMR:

SbF_5

231. F_6NOPt

IR: (571)
Mass:
NMR:

$NOPtF_6$

232. F_6NO_2Pt

IR: (571)
Mass:
NMR:

NO_2PtF_6

233. $F_6N_2O_2Pt$

IR: (517)(513)
Mass:
NMR:

$(NO)_2PtF_6$

234. $F_6N_2O_3Pt$

IR: (571)
Mass:
NMR:

$N_2O_3PtF_6$

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235. F_7NOPt

IR: (570)
Mass:
NMR:

$NOPtF_7$

(670) IR
Mass
NMR

236. $F_{10}NSb$

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

NF_4SbF_6

(477) IR
Mass
NMR

237. $F_{11}Sb_2$

IR:
Mass:
NMR: (479)

Sb_2F_{11}

(479) IR
Mass
NMR

238. $F_{14}N_2Sb_2$

IR:
Mass:
NMR: (490)

$N_2F_4 \cdot 2SbF_5$ complex

(490) IR
Mass
NMR

239. H_2O_2

IR: (330)
Mass:
NMR:

H_2O_2

(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)-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, 595 references to technical reports or papers presented at symposia, 210 references to open literature publications, and 236 pages.			

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