

NITROGEN FLUORIDES AND THEIR ORGANIC DERIVATIVES¹

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I. INTRODUCTION

The study of liquid and solid rocket propellants has stimulated widespread interest in compounds containing nitrogen-fluorine bonds. The reasons for this interest are twofold. First, the nitrogen-fluorine bond is of low energy and easily broken. Second, nitrogen-fluorine compounds provide an alternative source of fluorine, obviating the necessity of handling the element itself. Apart from its importance to rocket technology, the subject is of interest in its own right, because the chemistry of nitrogen-fluorine compounds is comparatively new, the most significant advances having been made during the past decade.

This review covers binary and ternary inorganic nitrogen-fluorine compounds and organic compounds containing nitrogen-fluorine bonds. The chemistry of fluorine nitrate, FNO_3 , is not discussed, because this compound does not contain a nitrogen-fluorine bond. Ternary compounds of sulfur, nitrogen, and fluorine are not mentioned in this survey, even though some of them may contain a nitrogen-fluorine bond.

The literature of nitrogen-fluorine chemistry, which

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is widely scattered and often only accessible with difficulty, has been critically reviewed from the date of discovery of each inorganic nitrogen-fluorine compound through 1960. The literature of organic compounds containing the nitrogen-fluorine bond has been reviewed from 1900, when Moissan fluorinated several organic amines, through 1960. As no significant reference has been intentionally omitted, this article should be useful to readers seeking more detailed information on this subject than has hitherto appeared. Although alternative nomenclature is possible for most nitrogen-fluorine compounds, only the most commonly accepted names are employed in this review.

II. INORGANIC NITROGEN-FLUORINE COMPOUNDS

The number of compounds that can be predicted to form between nitrogen and fluorine is limited (159). Only four such binary compounds can be envisioned: nitrogen trifluoride, NF_3 ; tetrafluorohydrazine, N_2F_4 ; difluorodiazine, N_2F_2 ; azine fluoride, N_3F . Compounds of higher molecular weight require chains of three or more nitrogen atoms, and all attempts to prepare chains containing more than two nitrogen atoms have failed.

The search for methods to synthesize these binary compounds has received rather sporadic attention. Although numerous accounts relating to nitrogen trifluoride have been published since its discovery

(134), it was not until 1942 that the successful syntheses of two additional binary compounds of nitrogen and fluorine, N_2F_2 and N_3F , were reported (58). A nearly equal interval occurred before the subject was again investigated. Aided by modern developments in analytical and separation techniques, the discovery of new nitrogen fluorides was made possible and marked the beginning of a new era in inorganic chemistry. This era, initiated by the discovery of tetrafluorohydrazine, N_2F_4 (30), opens new vistas of investigation in the chemistry of fluorine.

Binary compounds formed by the combination of nitrogen and fluorine may be considered as fluorine analogs of ammonia, hydrazine, and other hydronitrogens (6, 7, 8). These analogs are usually styled N-F compounds by workers in this field (27).

The nitrogen fluorides may be classified into three series analogous to the hydronitrogens and the aliphatic hydrocarbons. A comparison of the nitrogen fluorides and the hydronitrogens is made in table 1. It will be noted that catenation, so prevalent in the chemistry of hydrocarbons, is limited in the hydronitrogen and nitrogen fluoride series. The nitrogen fluorides boil at lower temperatures than the corresponding hydronitrogens, although the molecular weights of the halogen compounds are higher. Without doubt, this is a result of hydrogen bonding which is, of course, nonexistent in the nitrogen fluorides.

The synthetic routes and reactions showing the relationship of the nitrogen fluorides and derivatives are depicted in figure 1.

A. BINARY NITROGEN FLUORIDES: SATURATED COMPOUNDS

1. Nitrogen trifluoride, NF_3

Nitrogen trifluoride, NF_3 , was first prepared in 1928

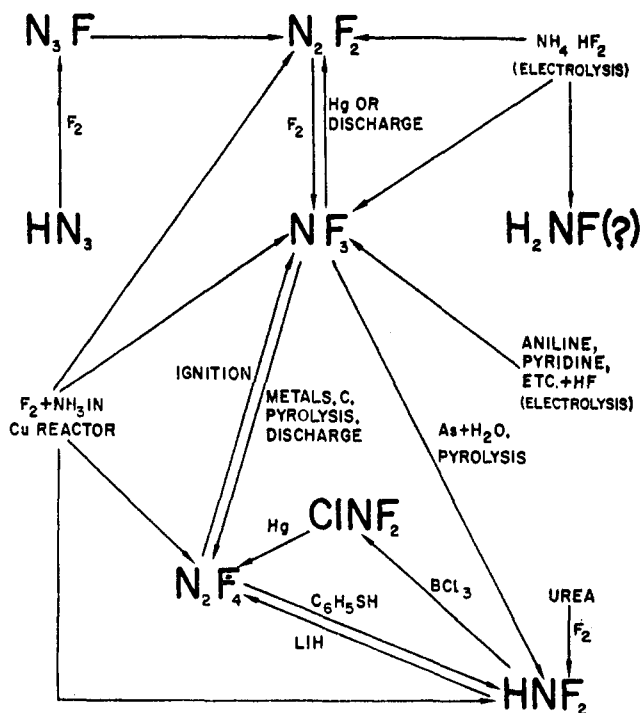


FIGURE 1.

by Ruff, Fischer, and Luft (134) by electrolyzing molten anhydrous ammonium bifluoride in an electrically heated copper cell, using a copper cathode and carbon anode. Electrolysis was carried out using a current of 10 amp. at 7-9 v. at an operating temperature of 125°C. Because of the presence of trace amounts of water in the electrolyte, the electrolysis gas contained ozone, oxygen, nitrous oxide, hydrogen, nitrogen, and hydrogen fluoride, in addition to nitrogen fluorides. The gaseous mixture was passed through a series of copper vessels filled with dry granular potassium fluoride to remove hydrogen fluoride and water and then passed over manganese dioxide, which catalyzed

TABLE 1

Comparison of hydronitrogens and nitrogen fluorides

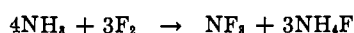
Hydronitrogens		Nitrogen Fluorides	
Structural formula	Name	Structural formula	Name
Saturated compounds: $N_n Y_{n+1}$			
NH_3 (normal boiling point, $-33.4^\circ C.$)	Ammonia	NF_3 (normal boiling point, $-129.0^\circ C.$)	Nitrogen trifluoride
H_2NNH_2 (normal boiling point, $113.5^\circ C.$)	Hydrazine	F_2NNF_2 (normal boiling point, $-73^\circ C.$)	Tetrafluorohydrazine, dinitrogen tetrafluoride, perfluorohydrazine
Unsaturated compounds: $N_n Y_n$			
$HN=NH$	Diimide*	$FN=NF$ cis isomer (normal boiling point, $-105.7^\circ C.$) trans isomer (normal boiling point, $-111.4^\circ C.$)	Difluorodiazine, difluorodiazene, dinitrogen difluoride
Unsaturated compounds: $N_n Y_{n-1}$			
HN_2 (normal boiling point, $37^\circ C.$)	Hydrazole acid, hydrogen azide, azoimide	NF (normal boiling point, $-82^\circ C.$)	Asine fluoride, fluorine azide

* Mass spectral evidence exists for diimide and higher hydronitrogens (44, 45).

the conversion of ozone to oxygen. Nitrogen trifluoride, nitrous oxide, and other gases were condensed in glass traps cooled by liquid air. The nitrogen trifluoride was then recovered by careful fractionation at -160°C . and further purified by allowing the gas to stand, in the absence of air, in contact with dilute sodium hydroxide solution, with which it does not react.

The electrolytic process for the preparation of nitrogen trifluoride has been improved by a number of workers (31, 74, 121, 129, 137, 140, 141) and has been patented (130).

Nitrogen trifluoride can also be formed by the direct fluorination of ammonia. The vapor-phase reaction of ammonia and fluorine was originally investigated by Ruff and Hanke (136), using an unpacked, T-shaped, copper reactor with either an excess of fluorine or an excess of ammonia. The products in all experiments were reported to be nitrogen trifluoride and ammonium fluoride:



although the presence of other nitrogen fluorides was postulated. This reaction has been investigated using a packed copper reactor (104, 105, 106). The results qualitatively confirmed the earlier work of Ruff for the reaction in which fluorine was in excess; however, with ammonia in excess, tetrafluorohydrazine, difluoroamine, and difluorodiazine, in addition to nitrogen trifluoride, were obtained (106). Direct burner combustion of ammonia in excess fluorine produces no nitrogen fluorides (2).

Haller (58) reports that the reaction of fluorine with difluorodiazine yields nitrogen trifluoride. The electrolysis of aniline, pyridine, and piperidine in anhydrous hydrogen fluoride also produces nitrogen trifluoride (163, 164).

The gas is now available commercially in the United States (146, 147).

The physical properties of nitrogen trifluoride have been investigated extensively. Its pyramidal molecular configuration was first proposed by Ruff (133). This basic structure is supported by studies of the infrared and Raman spectra (11, 55, 117, 149, 150, 151, 170, 177). Interpretation of these spectra led to a molecular model consisting of a slightly flattened pyramid with nitrogen at the apex, having a bond angle greater than 110° and a nitrogen-fluorine bond distance of 1.45 Å. (11). Electron-diffraction studies of the molecule indicate a more symmetrical configuration in which the F-N-F bond angles are 102.5° and the nitrogen-fluorine bond distances are 1.37 Å. (155). Microwave spectra (54, 75, 158) yield the values 1.371 Å. for the N-F distance and $102^{\circ}9'$ for the F-N-F angle, in agreement with electron-diffraction data.

Values in the region of 0.21 and 0.25 Debye unit for the molecular dipole moment, obtained by the dielectric-

constant method, have been reported by Ramaswamy (123, 174). The more precise values, 0.234 ± 0.004 and 0.235 ± 0.007 Debye unit, were obtained using microwave techniques (51, 84, 85, 175). It has been postulated that the large atomic moment for nitrogen resulting from the lone pair of electrons is almost cancelled by the primary moment derived from the ionic character of the nitrogen-fluorine bonds (51). A similar interpretation also has been made by Schomaker and Lu (155). However, Kisliuk (85) has indicated that the amount of *s-p* hybridization (111) of the nitrogen-bonding orbitals is not simply related to the bond angles, but that nitrogen trifluoride has a multiple-bonded structure. Mashima (96) has suggested that the observed dipole moment may be explained in terms of hybridization of the nitrogen and fluorine parts of the bonding wave function, and that the hybrids of the nitrogen atom may be simply related to the observed bond angle.

The frequency of the intramolecular tunneling process for nitrogen trifluoride has been estimated to be approximately 1 reciprocal minute (16).

Measurements of the refractive index and dispersion have been made by Watson and Ramaswamy (123, 174). The nuclear magnetic shielding of fluorine in nitrogen trifluoride (57) and the temperature dependence of the ^{19}F spectrum have also been determined (108).

Ruff (137) and Menzel and Mohry (98) were the first to measure the vapor pressure of nitrogen trifluoride. Later, Pierce and Pace (122) carefully measured the vapor pressure from 86°K . to 144.5°K . and found the data to be closely represented by the equation:

$$\log P_{\text{mm.}} = \frac{-673.5828}{T} + 1.869858 \log T - 0.00783355T + 4.64615 \quad (T = ^{\circ}\text{K.})$$

Vapor-pressure measurements over the same temperature range have also been made by Jarry and Miller (74). The data follow the equation:

$$\log P_{\text{mm.}} = 6.77966 - \frac{501.913}{T - 15.37} \quad (T = ^{\circ}\text{K.})$$

The same authors extended the pressure measurements to the critical point and found that the data could be represented by

$$\log P_{\text{atm.}} = 4.27264 - (613.33/T) \quad (T = ^{\circ}\text{K.})$$

On being warmed from very low temperatures, opaque white solid nitrogen trifluoride becomes transparent at -216.54°C . but actually melts at -206.79°C . and boils at -129.01°C . (122).

Other values have been recorded for the transition point (138) and the melting and boiling points (38, 74, 98, 132, 137, 138, 140). Pierce and Pace (122) have

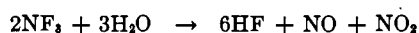
accurately determined the heat of transition at -216.54°C . as 361.8 cal./mole, the heat of fusion at -206.79°C . as 95.11 cal./mole, and the heat of vaporization at -129.01°C . as 2769 cal./mole, along with other important thermodynamic data. No transition in the adsorbed phase of nitrogen trifluoride on anatase corresponding to the solid transition has been observed (160). This result is of special interest, as the heat of transition of nitrogen trifluoride is approximately four times as great as its heat of fusion. The triple point, -206.79°C ., has been proposed as a possible calibration point (121). The critical temperature, -39.26°C ., and the critical pressure, 44.72 atm., have been reported (74). Values of the liquid density of nitrogen trifluoride are represented over the temperature range -195° to -103°C . by the equation (74):

$$d(\text{g./cm.}^3) = 2.103 - 3.294 \times 10^{-4}T - 4.675 \times 10^{-7}T^2$$

A mass-spectrometric study of nitrogen trifluoride has been made (126).

Ruff and Wallauer (143) have obtained a value of -26 ± 2 kcal./mole for the heat of formation of nitrogen trifluoride by the ignition of mixtures of nitrogen trifluoride and hydrogen in a steel bomb. The more precise value of -29.7 ± 1.8 kcal./mole, recently determined (4, 95), indicates that nitrogen trifluoride is slightly more stable than was suggested by the earlier value (1). Using this recent value, the mean bond energy, $E(\text{N}-\text{F})$, of the nitrogen-fluorine bond in the molecule of nitrogen trifluoride is calculated to be 66.4 ± 0.8 kcal./mole. Following Reese and Dibeler (126), the dissociation energies of the individual bonds are estimated to be, at 25°C .: $D(\text{NF}_2-\text{F}) = 74.0$; $D(\text{NF}-\text{F}) = 62.6$; $D(\text{N}-\text{F}) = 62.6$ kcal./mole.

Ruff (137) has reviewed the earliest aspects of the chemistry of nitrogen trifluoride, and a more recent review by Burg (22) has appeared. Compared with nitrogen trichloride, nitrogen trifluoride is remarkably stable, its heat of formation being negative. Nitrogen trifluoride does not react with dry glass, but dissolves slightly in water without chemical reaction. It is unaffected by dilute alkali solutions and, being nonbasic, does not react with dilute sulfuric acid. Gaseous mixtures of nitrogen trifluoride and water vapor, ignited by sparking, react according to the equation:



Explosion occurs when mixtures of nitrogen trifluoride with ammonia, hydrogen, methane, ethylene, carbon monoxide, or hydrogen sulfide are sparked or heated. Subjected to an electric discharge, mixtures of mercury vapor and nitrogen trifluoride react to form tetrafluorohydrazine and both isomers of difluorodiazine (46). The thermal reaction of nitrogen trifluoride with various metals such as stainless steel, copper, arsenic, antimony, and bismuth also produces tetra-

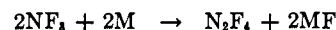
fluorohydrazine (30). Attempts to combine nitrogen trifluoride with diborane at room temperature have been unsuccessful (118); however, nitrogen trifluoride reacts with perfluoropropene (35, 37) and at 700°C . fluorinates phosphorus nitride (94).

Nitrogen trifluoride is odorless and toxic (74, 146, 147). Ruff reports that a 1 per cent concentration in air causes blood poisoning with fatal effect within 30 min. (137). However, Wilkinson (176) was unable to obtain evidence for the formation of a hemoglobin complex of nitrogen trifluoride and attributed Ruff's results to impurities in his sample.

Several materials have been used without serious difficulty in handling both nitrogen trifluoride and difluorodiazine in research production and storage (147). Hoses, valves, and other equipment recommended for handling oxygen have been used for the development of a hydrogen-nitrogen trifluoride torch (127).

2. Tetrafluorohydrazine, N_2F_4

Colburn and Kennedy (26, 30) have reported the isolation of tetrafluorohydrazine, made by the thermal reaction of nitrogen trifluoride with various metals such as stainless steel, copper, arsenic, antimony, and bismuth, according to the equation:



In a flow reactor packed with copper turnings at 375°C ., with a contact time of 13 min., tetrafluorohydrazine has been produced in 42-62 per cent conversion of nitrogen trifluoride and a yield of 62-71 per cent. Tetrafluorohydrazine has also been produced by the reaction of nitrogen trifluoride with mercury at $320-330^{\circ}\text{C}$. (36); at $400-500^{\circ}\text{C}$. nitrogen trifluoride reacts with carbon to produce tetrafluorohydrazine (23, 56).

Ruff and Hanke (136) have investigated the vapor-phase reaction of fluorine and ammonia in an unpacked copper reactor, using both an excess of fluorine and an excess of ammonia. In both cases the products were nitrogen trifluoride and ammonium fluoride, although the presence of other nitrogen fluorides was indicated. This reaction, in a packed T-shaped copper reactor to reduce the intensity of the reaction and to prevent conversion of ammonia to nitrogen and hydrogen fluoride, has been reinvestigated, using both an excess of fluorine and an excess of ammonia (104, 105, 106). With excess fluorine, results were similar to those obtained by Ruff, although yields of nitrogen trifluoride were higher; with excess ammonia, tetrafluorohydrazine also was obtained. When an excess of ammonia was used, the yields of tetrafluorohydrazine were as high as 11 per cent, while yields of nitrogen trifluoride ranged from 6 to 24 per cent, on the basis of the amount of fluorine converted.

Two alternative reactions resulting in the formation of tetrafluorohydrazine are noted subsequently in Sec-

tion II,C,1 and Section II,C,2 of this review.

Tetrafluorohydrazine, which recently has become commercially available in the United States, is a colorless gas possessing a musty odor. It condenses at -73°C . to a colorless liquid (146, 147). Most of the physical constants listed in table 2 were determined by Colburn and Kennedy (30). Additional characterizations by these workers included the determination of the

leads to the value -2.0 ± 2.5 kcal./mole for the heat of formation of tetrafluorohydrazine and a bond-dissociation energy $E(\text{N}-\text{F})$, of 66.4 ± 0.8 kcal./mole. The mean energies of the nitrogen-fluorine bond in nitrogen trifluoride (4, 95) and tetrafluorohydrazine (3) are the same within experimental error.

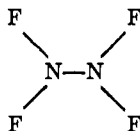
Tetrafluorohydrazine completely dissociates without detonation to nitrogen trifluoride and nitrogen when

TABLE 2
Physical properties of the nitrogen fluorides

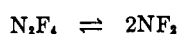
Physical Property	Nitrogen Trifluoride NF_3		Tetrafluorohydrazine N_2F_4		Difluorodiazine, N_2F_2				Azine fluoride N_2F	
	Value	Refer- ence	Value	Refer- ence	Cis isomer		Trans isomer		Value	Refer- ence
					Value	Refer- ence	Value	Refer- ence		
Boiling point, $^{\circ}\text{C}$	-129.01	(122)	-73	(30)	-105.7	(29)	-111.4	(29)	-82	(58)
Melting point, $^{\circ}\text{C}$	-206.79	(122)	—		<-195	(29)	-172	(29)	-154	(58)
Vapor-pressure equation constants:*										
A.....	6.77966	(74)	6.33	(30)	7.675	(29)	7.470	(29)	—	
B.....	—		-692	(30)	-803.0	(29)	-742.3	(29)	—	
C.....	501.913/($T - 15.37$)	(74)	—		—		—		—	
Heat of vaporization, cal./mole.....	2769	(122)	3170	(30)	3670	(29)	3400	(29)	—	
Trouton's constant.....	19.21	(122)	15.9†		21.9†		21.0†		—	
Critical temperature, $^{\circ}\text{C}$	-39.26	(74)	36	(30)	-1	(29)	-13	(29)	—	
Critical pressure, atm.....	44.72 \pm 0.17	(74)	77	(30)	70	(29)	55	(29)	—	
Heat of formation, kcal./mole.....	29.7 \pm 1.8	(4, 95)	-2.0 \pm 2.5	(3)	+48	(95)	+48	(95)	—	

* $\log P_{\text{mm.}} = A + B/T + C$, where T is in $^{\circ}\text{K}$. A more precise equation for nitrogen trifluoride is given in the text. † Computed using data from reference 30. ‡ Computed using data from reference 29.

infrared absorption spectrum, the mass spectrum, and the ^{19}F nuclear magnetic resonance spectrum. The triple point, -168°C ., and the value 1.65 g./cc. for the liquid density at the boiling point have been recorded (146). The microwave spectrum of tetrafluorohydrazine has been investigated (88) and the observed rotational constants found to be consistent with a hydrazine-like model:

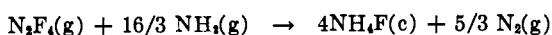


It is estimated that the internal rotation of the NF_2 groups is hindered by a barrier greater than 3 kcal./mole (88). The value 19.2 kcal. has been reported (28) for the heat of dissociation for the reaction:



Colburn and Johnson (28) suggest that the appearance potential measured by Loughran and Mader (89) is simply the ionization potential of the NF_2 fragment.

The heat of the reaction



has been determined (3). This datum, when combined with known heats of formation and bond energies,

ignited with a hot wire (147). It reacts slowly with water (146).

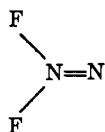
B. BINARY NITROGEN FLUORIDES: UNSATURATED COMPOUNDS

1. Difluorodiazine, N_2F_2

Difluorodiazine was first prepared by the thermal decomposition of azine fluoride, N_3F (58). Electron-diffraction studies by Bauer (14) of the difluorodiazine obtained by this method indicated a mixture of cis and trans isomers. Difluorodiazine was reported to be a minor gaseous product resulting from the electrolysis of molten ammonium bifluoride at $120-130^{\circ}\text{C}$. (29, 31, 154). The difluorodiazine obtained by this method also consisted of a mixture of cis and trans isomers. The trans isomer has been obtained in 99.7 per cent purity by chromatography and the cis isomer by low-temperature distillation in a minimum purity of 97.5 per cent (29). A small fraction of the reaction gases resulting from the fluorination of ammonia has been reported to be difluorodiazine (105, 106). However, the isolation of pure difluorodiazine by low-temperature distillation was not completely successful in this work. In an electric arc (46), or at $320-330^{\circ}\text{C}$. (36), small quantities of difluorodiazine and tetrafluoro-

hydrazine are produced by the reaction of nitrogen trifluoride with mercury.

Difluorodiazine is a colorless gas having an odor similar to that of nitrogen dioxide (14). The stable trans configuration has the more symmetrical charge distribution, and the trans isomer has the lower boiling point and higher melting point, as recorded in table 2. The cis isomer possesses a permanent dipole moment, which accounts for its higher boiling point. The electron-diffraction pattern is consistent with a mixture of cis and trans isomers of $\text{FN}=\text{NF}$, having an $\text{N}-\text{F}$ distance of 1.44 Å., an $\text{N}=\text{N}$ distance of 1.25 Å., and the $\text{N}=\text{N}-\text{F}$ bond angle of $115 \pm 5^\circ$ (14). Bauer (14) has also reported the possible existence of a third very unstable isomer, presumably 1,1-difluorodiazine.



From considerations of chemical dipole moment, mass spectroscopic, and infrared spectral evidence it has been proposed that the active form resembles 1,1-difluorodiazine rather than the cis isomer (148). The nuclear magnetic resonance spectrum has also been determined (29). The trans isomer shows a single absorption band, whereas the cis isomer exhibits a more complex infrared absorption spectrum. The two isomers of difluorodiazine react differently with glass at room temperature (29). Samples of the cis isomer react completely in two weeks with glass to form silicon tetrafluoride and nitrous oxide, whereas samples of the trans isomer are essentially unchanged after a month. The cis form is also more reactive toward mercury than the trans isomer. An equilibrium between the two isomers exists for which a heat of isomerization of 27.5 ± 5.0 kcal./mole has been estimated (29).

Difluorodiazine is inert to acidic and basic hydrolysis but is immediately decomposed by acid potassium iodide solution with precipitation of iodine and liberation of an equivalent amount of nitrogen (154). It can be saturated with fluorine to yield nitrogen trifluoride (58). Difluorodiazine markedly catalyzes certain vinyl polymerizations (29).

An estimated value of +43 kcal./mole for the heat of formation of difluorodiazine has been computed (95) from the approximate $\text{N}-\text{F}$ bond energy of 76.5 kcal./mole and the $\text{N}=\text{N}$ bond energy of 85.4 kcal./mole suggested by Glockler and Dawson (52).

2. Azine fluoride, N_3F

One of the gaseous products resulting from the action of fluorine upon nitrogen-diluted hydrogen azide has been interpreted (58) as being azine fluoride, a greenish-yellow gas (boiling point, -82°C .; melting point, -154°C .). Liquid azine fluoride is extremely sensitive

to shock and light, and usually explodes as it vaporizes. The gas may be handled up to a pressure of 200 mm.; however, at this pressure at 25°C . it slowly decomposes to difluorodiazine. Attempts to determine the structure of azine fluoride by electron diffraction have been unsuccessful (14).

C. TERNARY NITROGEN FLUORIDES

A number of substituted nitrogen fluorides which are not binary can be envisioned by the replacement of one or two of the fluorine atoms in the parent nitrogen trifluoride molecule (159). Only five substituted nitrogen fluorides are known with any degree of certainty: difluoroamine, monofluoroamine, chlorodifluoroamine, nitrosyl fluoride, and nitryl fluoride. The existence of monofluoroamine is still in doubt.

1. Difluoroamine, HNF_2

Although difluoroamine was reported by Ruff and Staub (140) as being one of the products obtained from the electrolysis of ammonium bifluoride, recent work on its synthesis and characterization (82, 87) has shown that the compound described by the original authors was not, in fact, HNF_2 . Kennedy and Colburn (82) have failed to obtain difluoroamine by the electrolysis of ammonium bifluoride, and Burg (22) has expressed doubts as to the certainty of the identification of this substance by Ruff.

Although the electrolysis of ammonium bifluoride did not produce difluoroamine, this compound has been prepared by several other routes. Kennedy and Colburn (26, 82) have obtained small amounts of the material, together with tetrafluorohydrazine, during the reaction of nitrogen trifluoride with arsenic and steam at $250-300^\circ\text{C}$. Direct fluorination of urea at 0°C . has yielded a complex corrosive liquid, which upon fractional distillation gave difluoroamine (87). The existence of difluoroamine in the products obtained by the reaction of fluorine with an excess of ammonia has recently been reported (105, 106). The synthesis of difluoroamine by the reaction of cyanuric acid with fluorine has been briefly mentioned (131), but this reaction is open to question (145).

Difluoroamine has been prepared in 75 per cent yield by the reduction of tetrafluorohydrazine with thiophenol and with other mercaptans (47). Table 3 lists the salient physical properties of difluoroamine. A difference in the melting points has been reported, and this variance can be attributed to experimental difficulties, since solid difluoroamine tends to detonate spontaneously when cooled to -196°C . (87). Kennedy and Colburn (82) state that the reported value of -131°C . is only approximate; hence the value $-116 \pm 3^\circ\text{C}$. has been selected for table 3. In addition to the physical properties listed in table 3, the gas density (87), infrared absorption bands (82), nuclear magnetic

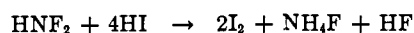
TABLE 3
Physical properties of substituted nitrogen fluorides

Physical Property	Difluoroamine, HNF ₂		Chlorodifluoroamine, ClNF ₂	
	Value	Reference	Value	Reference
Boiling point, °C.....	-23.6	(82, 87)	-67	(120)
Melting point, °C.....	-116 ± 3	(87)	-183 to -196	(120)
Constants of vapor-pressure equation:*				
A.....	8.072	(82)	7.478	(120)
B.....	-1298	(82)	-950	(120)
Heat of vaporization, cal./mole.....	5940	(82)	4350	(120)
Trouton's constant.....	23.7	(87)	21.0	(120)
Critical temperature, °C.....	130	(82)	—	—
Critical pressure, atm.....	93	(82)	—	—

* $\log p_{\text{mm.}} = A + (B/T)$, where T is in °K.

resonance absorption (82), and the mass spectrum (82, 87) have been determined.

Extreme caution must be used when working with difluoroamine, because explosions with both the solid and the liquid compound have been reported (82, 87). Difluoroamine reacts instantaneously and quantitatively with 0.15 *N* hydriodic acid according to the equation (87):



Gaseous difluoroamine loses hydrogen on contact with various solids to form tetrafluorohydrazine, and with lithium hydride as catalyst 70 per cent yields of this compound have been achieved (87).

2. Monofluoroamine, H₂NF

A colorless unstable gas, possibly monofluoroamine, is reported to be one of the by-products in the preparation of nitrogen trifluoride by the electrolysis of molten ammonium bifluoride (140, 154). The synthesis of monofluoroamine by the reaction of fluorine with cyanuric acid (131) has been questioned (145). The pure compound has not been obtained, and its formula has not been confirmed by analysis (22). The impure compound is very explosive. Recent attempts to synthesize monofluoroamine by the reaction of ammonia and fluorine under stoichiometric conditions were unsuccessful (105, 106). Little work has been done with this fluoroamine since its discovery. Ruff and Staub (140) report a boiling point of -77°C., and a measured molecular weight of 34.3 (theory, 35.0) for monofluoroamine, but these data are unconfirmed and, at best, tentative.

Employing the isoelectronic principle, a value of -5 kcal./mole was calculated for the standard heat of formation of monofluoroamine (166).

The only chemical properties reported are those recorded by the original workers (140). Monofluoroamine reduces Fehling's solution at once to copper, but liberates very little iodine from aqueous hydriodic acid, in which it dissolves.

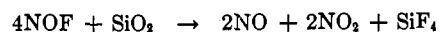
3. Chlorodifluoroamine, ClNF₂

The successful synthesis of the colorless, air-stable gas chlorodifluoroamine, ClNF₂, in yields up to 50 per cent, by the reaction of equimolar quantities of boron trichloride and difluoroamine, has been reported by Petry (120). The vapor-pressure equation gives an extrapolated boiling point of -67°C. for chlorodifluoroamine. The other physical constants entered in table 3, as well as the mass spectrum, infrared absorption spectrum, and nuclear magnetic resonance absorption spectrum have also been determined by Petry (120). The gas, which has been kept at room temperature in Pyrex vessels without decomposition, reacts with mercury to form tetrafluorohydrazine and mercurous chloride. Experiments with chlorodifluoroamine have occasionally resulted in explosions (120).

4. Nitrosyl fluoride, NOF

Brief reviews on the preparation, properties, and chemical reactions of nitrosyl fluoride have appeared elsewhere (12, 22, 49, 83, 97, 99, 142, 145, 167, 172).

The compound was first prepared by Ruff and Stäuber (142), who passed nitrosyl chloride over silver(I) fluoride contained in a long platinum tube heated at 200-250°C. The gaseous products were condensed in a platinum flask cooled in liquid air, and on fractionation nitrosyl fluoride was obtained as a colorless solid, melting point -132.5°C., which melted to a colorless liquid, boiling point -59.9°C. Nitrosyl fluoride has also been prepared in a copper tube by the direct vapor-phase fluorination of nitric oxide with fluorine (139). Attempts to purify the crude product by distillation in a quartz apparatus were not entirely successful, since the reaction of nitrosyl fluoride with silicon dioxide furnishes the contaminants silicon tetrafluoride, nitric oxide, and nitrogen dioxide:

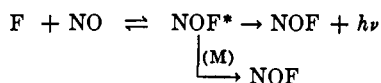
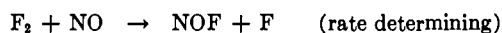


Using a Fluorothene vessel Faloon and Kenna (42) conducted a smooth reaction between fluorine and nitric oxide to produce nitrosyl fluoride in 90 per cent

yield, with no contamination by silicon tetrafluoride. Rapp and Johnston (124) recently have investigated the kinetics of the reaction



using the dilute diffusion flame method for measuring the rates of fast gas reactions. Although the interpretation of results is somewhat ambiguous, the following mechanism is proposed:



A spectroscopic study of this reaction has also been made (17).

Nitrosyl fluoride has also been prepared by the action of heat on nitrosyl complexes. For example, nitrosyl fluoroborate, NOBF_4 , prepared by the reaction of N_2O_3 with HBF_4 , on being heated at 300°C . with sodium fluoride reacts to yield nitrosyl fluoride (12). Ruff (128) treated nitrosyl chloride with arsenic trifluoride to produce NOAsF_6 , and this complex on being heated at 320°C . with powdered potassium fluoride in a platinum tube gave nitrosyl fluoride. The complex with antimony pentafluoride, NOSbF_6 , behaved similarly. By themselves NOAsF_6 and NOSbF_6 are very stable and can be sublimed above 200°C . in a vacuum (156). The nitrosyl complexes of silicon and selenium fluorides, $(\text{NO})_2\text{SiF}_6$ and $(\text{NO})_2\text{SeF}_6$, respectively, are quite unstable and lose nitrosyl fluoride even at room temperature (156). Haszeldine (63) has shown that the pyrolysis of trifluoronitromethane, CF_3NO_2 , at 500°C .

in a platinum tube produces nitrosyl fluoride, carbon dioxide, and carbonyl fluoride. Heptafluoronitropropane, $\text{CF}_3\text{CF}_2\text{CF}_2\text{NO}_2$, under similar conditions gives the same products, together with small amounts of $\text{C}_2\text{F}_6\text{COF}$ and C_3F_6 . In view of the inaccessibility of the starting materials and the number of by-products formed, this pyrolytic procedure is only of academic interest.

The physical constants of nitrosyl fluoride are listed in table 4. Nitrosyl fluoride is colorless in the solid, liquid, and gaseous states. The relationship of the saturated vapor pressure to the temperature of liquid nitrosyl fluoride is given by the equation (139):

$$\log P_{\text{mm.}} = -\frac{7234}{4.573T} + 1.75 \log T - \frac{0.0742T}{4.573} + 9.6840$$

The calculated heat of vaporization at the normal boiling point is 4607 cal./mole, and the Trouton constant is 21.6. The density of gaseous nitrosyl fluoride at room temperature exceeds the theoretical value by 2 per cent, possibly owing to a slight amount of association (139). The density of liquid nitrosyl fluoride between -125°C . and -67°C . is given by the relationship (139) $d = 1.919 - 0.0278T$.

The structure of the nitrosyl fluoride molecule has been determined from studies of the infrared (77, 92, 93, 178) and microwave (91, 92) spectra. Nitrosyl fluoride is a bent unsymmetrical molecule with three fundamental modes of vibration.

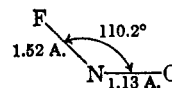


TABLE 4

Physical properties of nitrosyl fluoride and nitryl fluoride

Physical Property	Nitrosyl Fluoride		Nitryl Fluoride	
	Value	Reference	Value	Reference
Melting point, $^\circ\text{C}$	-132.5	(49)	-166	(72)
Boiling point, $^\circ\text{C}$	-59.9	(49)	-72.5	(72)
Critical temperature, $^\circ\text{C}$	—	—	76.3	(72)
Liquid density, g./cc.....	1.326 (-59.9°C .)	(49)	1.571 (-101°C .)	(72)
			1.494 (-73°C .)	(49)
Vapor density (air = 1.00).....	1.683	(97)	2.17-2.31 (calculated, 2.26)	(172)
	1.701	(172)	2.24	(103)
Molar volume at boiling point, cc.....	37.0	(139)	43.5	(139)
Molar volume at 0°C ., cc.....	25.9	(139)	30.8	(139)
Vapor pressure, mm.....	—	—	113.8 (-101°C .)	(72)
Surface tension, dynes/cm.....	—	—	27.6 (-104.5°C .)	(72)
Viscosity, poises.....	—	—	0.00572 (-101°C .)	(72)
	—	—	0.00460 (-72.5°C .)	(72)
Parachor.....	—	—	94.3	(145)
Trouton's constant.....	21.3	(22)	21.2	(22)
Dipole moment, Debyes.....	1.81	(91)	—	—
F—N bond distance, Å.....	1.52	(49)	1.35	(49)
O—N bond distance, Å.....	1.13	(49)	1.23	(49)
F—N—O bond angle, degrees.....	110	(49)	—	—
O—N—O bond angle, degrees.....	—	—	125 (assumed)	(49)
Heat of dissociation of the N—F bond, kcal.....	55.4	(76)	—	—
Heat of hydrolysis kcal./mole.....	—	—	31	(72)
Heat of formation, kcal./mole.....	-15.8	(49, 76)	26	(72)
Heat of vaporization, kcal./mole.....	4.6	(49)	4.3	(49)

The dissociation energy of the nitrogen-fluorine bond in nitrosyl fluoride has been computed to be 55.4 kcal. (76), about 11 kcal. less than the value for the single bond in nitrogen trifluoride (4, 95) and tetrafluorohydrazine (3). The nitrogen-fluorine bond in nitrosyl fluoride is anomalously long (91, 92).

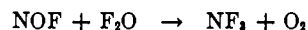
Force constants for nitrosyl fluoride have been calculated (161, 169) from infrared absorption spectral data. Similarly, a set of potential constants has been calculated from infrared spectral data, using the Wilson FG matrix method and assuming a valence force field (81). The calculated and observed values of the wave numbers of the fundamentals agree fairly well for nitrosyl chloride and nitrosyl bromide but diverge somewhat in the case of nitrosyl fluoride. A correlation between the electronegativities and infrared spectral frequencies has been made (116) for the nitrosyl frequencies in RNO, where R = F, Cl, Br, CH₃CO, HO, CH₃O, C₂H₅O, and C₆H₅. The frequencies and the electron-withdrawing power of the substituents are linearly related and in close agreement.

The dipole moment of the nitrosyl fluoride molecule has been determined by Magnuson (91). The moments of the N-F and N-O bonds are 1.75×10^{-18} and -0.17×10^{-18} e.s.u., respectively, and of the nitrosyl fluoride molecule itself, 1.81×10^{-18} e.s.u.

Stephenson and Jones (169) have calculated the standard thermodynamic functions of nitrosyl fluoride for temperatures ranging from 273.16°K. to 1500°K. From the heat of the reaction $2\text{NO} + \text{F}_2 \rightarrow 2\text{NOF}$ at 298°K. the standard heat of formation has been computed as $\Delta H^\circ = -15.8$ kcal. (76).

Although far less reactive than elementary fluorine, nitrosyl fluoride reacts with incandescence on contact with cold boron, silicon, red phosphorus, and arsenic (97, 145, 172). On heating, sodium and antimony react readily with it, the fluoride and nitric oxide being formed (145, 172). In the cold, copper, aluminum, lead, and bismuth are only slowly attacked by nitrosyl fluoride; tin reacts slowly when heated (145, 172). In reactions with metals nitric oxide is produced and in other reactions nitrogen dioxide is formed. Even on heating carbon, sulfur, and iodine do not react (172), but Ruff (139) states that sulfur, selenium, and tungsten(VI) oxide form white vapors on treatment with nitrosyl fluoride at 300°C. Powdered magnesium, zinc, iron, and tungsten react with nitrosyl fluoride only at red heat (145). Phosphorus pentoxide gives POF₃ and N₂O₅ at ordinary temperatures. Liquid sulfur dioxide reacts with nitrosyl fluoride, but the products have not been characterized. On contact with solid potassium iodide iodine is rapidly liberated. Many organic compounds are decomposed by nitrosyl fluoride with formation of hydrogen fluoride (142). A mixture of solid nitrosyl fluoride and oxygen difluoride (F₂O) explodes on melt-

ing, and the gaseous compounds burn on mixing (145):



With water nitrosyl fluoride forms a blue solution which decomposes to yield nitric oxide, nitrous acid, nitric acid, and hydrofluoric acid; with sodium hydroxide it forms nitric oxide, sodium nitrite, sodium nitrate, and sodium fluoride (139). Knunyants and coworkers (86) recently have studied the reaction of nitrosyl fluoride with fluoroolefins, and NOF and NOBF₄ have been used for the preparation of nitrosoamines, alkyl nitrites, and alkyl nitrates (113).

Seel and Sauer (157) have shown that solutions of nitrosyl fluoride in liquid hydrogen fluoride contain the salt NO⁺(FHF)⁻, which gives a violet color with nitric oxide. The properties of nitrosyl fluoride are those expected for the fluoroanhydride of nitrous acid. Nitrosyl fluoride forms addition compounds with a large number of fluorides, e.g., NOAsF₆, NOSbF₆, NOVF₆, NONbF₆, NOTaF₆, and NOBF₄ (12, 41, 97), but as these compounds do not contain nitrogen-fluorine bonds they are not discussed in this review. Concentrated sulfuric acid absorbs nitrosyl fluoride with evolution of heat to form nitrosylsulfuric acid and hydrogen fluoride (139). Liquid sulfur trioxide has been stabilized against polymerization during storage by the addition of 0.1-2.0 per cent of NOF or NOPF₆ (78).

Nitrosyl fluoride has been considered as a possible oxidant in rocket fuels, and the maximum theoretical exhaust velocities have been calculated for its reaction with various elements and their hydrides (20).

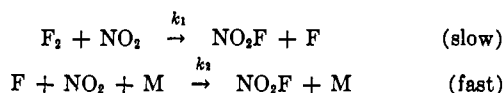
5. Nitryl fluoride, NO₂F

Several reviews on the preparation, physical and chemical properties, and uses of nitryl fluoride have appeared elsewhere (15, 22, 40, 49, 66, 72, 83, 97, 145, 172).

As long ago as 1905 Moissan and Lebeau (102, 103) caused nitric oxide to react with an excess of fluorine at the temperature of liquid oxygen. Excess fluorine was removed by distillation, and nitryl fluoride was obtained in an impure form as a white solid which melted at -139°C. to a colorless liquid of boiling point -63.5°C. Moissan and Lebeau described nitryl fluoride as a colorless gas which fumes in moist air and strongly attacks the mucous membranes, producing painful and persistent irritation. More than a quarter of a century later Ruff and his coworkers (139), in attempting to repeat Moissan's work, obtained principally nitrosyl fluoride, not nitryl fluoride, in the reaction of nitric oxide with fluorine. According to Ruff any nitryl fluoride in Moissan's preparation was due to the fortuitous presence of oxygen in the fluorine. In 1929 Ruff (129) successfully prepared nitryl fluoride by the reaction of fluorine with nitrogen dioxide. Hetherington and

Robinson (72) report that this is not a good method for preparing nitryl fluoride, because the reaction is so highly exothermic that it is often accompanied by flame. The product is a mixture of nitrogen oxyfluorides contaminated with silicon tetrafluoride formed by reaction with the quartz vessels. To eliminate such contamination the reaction of fluorine with nitrogen dioxide has been conducted in a Fluorothene vessel (42). Under these conditions the reaction proceeds smoothly and a 90 per cent yield of nitryl fluoride is obtained.

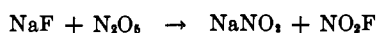
The kinetic behavior of the reaction between fluorine and nitrogen dioxide has been studied (119), using the light absorption of the dioxide to follow the reaction. By employing low concentrations of reactants ($0.5\text{--}20 \times 10^{-8}$ mole/cm.³) the extremely fast reaction has been reduced to a convenient value for taking kinetic measurements. Between 27.7° and 70.2°C. the rate is first order in each reactant and shows no dependence on nitryl fluoride. The mechanism proposed is:



In these equations M represents a molecule of any species present. The empirical second-order rate constant k_1 is that of an elementary bimolecular reaction, and if the rate constant is written as $Ae^{-E/RT}$ the value of A is 1.6×10^{12} cm.³/mole⁻¹ sec.⁻¹ and E is 10.5 kcal. The Arrhenius preexponential factor, A , has been calculated and compared for a number of bimolecular gas-phase reactions involving nitrogen dioxide and other simple molecules (fluorine, ozone, carbon monoxide) (68).

A one-stage preparation of nitryl fluoride has been described recently (10) in which slightly warm anhydrous sodium nitrite reacts with gaseous fluorine in glass equipment. The nitrite is almost quantitatively converted to nitryl fluoride, but the reaction temperature must be carefully controlled to prevent the nitrogen dioxide, formed as intermediate, from burning in the fluorine. If combustion occurs the hot yellow flame corrodes the glass, and the resulting nitryl fluoride becomes contaminated with silicon tetrafluoride.

Nitryl fluoride may also be prepared without the agency of elementary fluorine. By passing a stream of nitryl chloride, NO_2Cl , over silver fluoride in a platinum tube heated at 240°C. a 5 per cent yield of nitryl fluoride has been obtained (153). When nitrogen pentoxide is condensed onto dry sodium fluoride in a closed system and the mixture is alternately warmed and cooled in liquid nitrogen (to remove oxygen formed as by-product by the decomposition of nitrogen pentoxide), nitryl fluoride is produced according to the reaction (110):



Addition of hydrogen fluoride to nitrogen pentoxide in nitromethane at -20°C ., followed by saturation with boron trifluoride, results in a 94 per cent yield of NO_2BF_4 (112). On being heated to about 170°C . this nitronium derivative decomposes, without melting, to produce nitryl fluoride. Schmeisser (152) has described a similar reaction in which nitryl complexes, e.g., NO_2BF_4 , are heated at 200°C . with sodium fluoride in a platinum crucible *in vacuo*. Nitryl fluoride passes off and is frozen out in a trap cooled by liquid nitrogen.

The physical constants of nitryl fluoride have recently been redetermined by Hetherington and Robinson (71), who have corrected some of the data previously reported by Ruff and his coworkers (139). The best data at present available are presented in table 4. The vapor-tension curve of nitryl fluoride is represented by the equation (139):

$$\log p_{\text{mm}} = -(5692/4.573T) + 1.75 \log T - (0.051606T/4.573) + 7.3187$$

Over the temperature range -103.8° to -64.6°C . the density of liquid nitryl fluoride follows the equation (71):

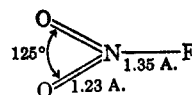
$$d_L = 2.046 - 0.00276T \text{ g./cc.}$$

The coefficient of cubical expansion over this temperature range is 0.00118 cc./cc. degree (71). Measurements of viscosity (η) from -118.5° to -84.2°C . indicate that for the relation

$$\eta_t = \eta_0(1 + At + Bt^2)$$

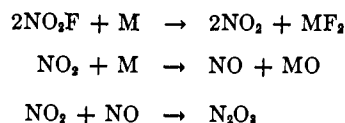
$A = -0.000759$ and $B = -0.0000384$ (71). The critical temperature of nitryl fluoride, evaluated from the surface tension (γ) and density (d_L), is 76.3°C ., in good agreement with the experimentally observed value of $75\text{--}76^\circ\text{C}$.

The structure of nitryl fluoride has been deduced from a study of the infrared and Raman spectra (34), and from considerations of microwave spectrum analysis (165) and nuclear magnetic resonance measurements (110). The nuclear magnetic resonance data show large separations between outside peaks, which preclude the possibility that the splitting caused by the ^{14}N nucleus could be transferred through an intermediate oxygen atom.



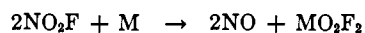
Chemically nitryl fluoride is extremely reactive. Quartz glass is attacked less strongly by it than by nitrosyl fluoride (145), but softer glasses containing less silica are attacked by nitryl fluoride at ordinary temperatures (97). Hetherington and Robinson (72) have classified metals into three groups according to their reactivity with nitryl fluoride. The first and largest

group comprises those metals which form both an oxide and a fluoride by reaction with nitryl fluoride. The reaction must occur in at least two stages, because N_2O_3 , of characteristic blue color, can be isolated from the gaseous products. The mechanism postulated is as follows, where M is the reacting metal:



Metals of this group include sodium, potassium, silver, zinc, cadmium, aluminum, titanium, zirconium, thorium, tin, lead, manganese, iron, and nickel.

The second group consists of those metals (chromium, molybdenum, tungsten, uranium) which form oxyfluorides on reaction with nitryl fluoride. Since the oxides of these metals react with nitryl fluoride to give oxyfluorides, the metal itself probably reacts first to give the oxide and then the oxyfluoride. The overall reaction is expressed by the equation:



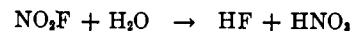
The third group includes those metals (beryllium, magnesium, calcium, gold) which do not react with nitryl fluoride below about 300°C.

With the exception of tellurium and bromine, almost all nonmetals react with nitryl fluoride to give nitronium complex salts, e.g., NO_2BF_4 , $(NO_2)_2SiF_6$, NO_2PF_6 , NO_2SbF_6 , etc. The reactions of nitryl fluoride with many elements and with nonmetallic fluorides and oxides have been described (10), and a number of new nitronium compounds reported. Hetherington and Robinson (72) have discussed the preparation and properties of these compounds in some detail, but as nitronium complexes do not contain nitrogen-fluorine bonds their inclusion in the present review is inappropriate. When heated alone (112), or with anhydrous sodium fluoride (152, 153), nitronium complexes evolve nitryl fluoride.

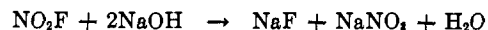
Nitryl fluoride does not combine in the cold with hydrogen (97, 103, 172) or sulfur (97, 103, 145, 172), and does not react with carbon (97, 103, 172) even at a dull red heat, but Ruff and his coworkers (139) state that some reaction does occur.

In contact with most elements and their compounds nitryl fluoride is chemically more reactive than nitrosyl fluoride. Reaction of nitryl fluoride with boron, silicon, germanium, phosphorus, arsenic, antimony, selenium, and iodine, or with the fluorides of these elements, and also with the oxides of silicon, vanadium, sulfur, selenium, and tellurium, produces nitronium salts of fluoro complexes, e.g., NO_2VOF_4 , NO_2VF_6 , NO_2SO_3F , NO_2BF_4 (24, 145). With water nitryl fluoride is immediately and quantitatively decomposed to an equimolar mixture of hydrofluoric and nitric acids, a re-

action that has been employed for the analysis of the compound (15, 97, 103, 172).



Sodium hydroxide reacts quantitatively with nitryl fluoride to yield sodium fluoride and sodium nitrate (139, 145):



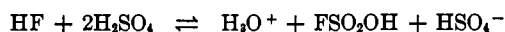
Bromine or iodine is liberated when bromides or iodides are treated with nitryl fluoride (97).

Nitryl fluoride is a powerful nitrating agent for organic compounds. This subject has been reviewed recently (72). Because nitryl fluoride usually produces a higher yield of nitrated product than when nitryl chloride is employed, it has been suggested (72) that nitryl fluoride is a more powerful nitrating agent than nitryl chloride, owing to the greater electron affinity of the fluorine atom. Nitryl fluoride is without action on aliphatic hydrocarbons and deactivated aromatic compounds (e.g., nitrobenzene). Compounds which are normally nitrated by "nitrating acid" produce nitro derivatives on treatment with nitryl fluoride. Activated aromatic compounds (e.g., amines) rapidly give tars. Hetherington and Robinson (70) have passed nitryl fluoride through several organic compounds or their solutions in an inert solvent. Pentane, chloroform, carbon tetrachloride, and benzoic acid do not react. Carbon disulfide reacts slightly. Benzene gives 65 per cent nitrobenzene and less than 5 per cent *m*-dinitrobenzene. Naphthalene yields 35 per cent 1-nitronaphthalene, and anthracene produces 9-nitroanthracene. Toluene yields 55 per cent 2,4-dinitrotoluene, and bromobenzene gives 60 per cent 4-nitrobromobenzene together with a trace of the ortho derivative. Nitrobenzene is essentially unreactive, only traces of *m*-dinitrobenzene being formed. Similarly, benzaldehyde yields only a trace of benzoic acid. Phenol gives only traces of *o*- and *p*-nitrophenols. Salicylic acid yields 5-nitrosalicylic acid. Ethyl alcohol gives ethyl nitrate and the oxidation products acetaldehyde and acetic acid. Aniline, quinoline, furan, anisole, diphenyl ether, and *m*-cresol give tars with nitryl fluoride.

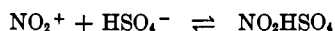
Oláh and his coworkers (113) have prepared nitrosoamines, alkyl nitrites, and alkyl nitrates using $NOBF_4$ and NO_2BF_4 . Benzene, toluene, fluorobenzene, chlorobenzene, and nitrobenzene have been nitrated in good yield, using either NO_2BF_4 or NO_2F in the presence of boron trifluoride (112, 113, 114). Benzotrifluoride, nitryl fluoride, and boron trifluoride form a 1:1:1 complex which is stable to $-50^\circ C$. On being warmed above this temperature the complex decomposes, giving an almost 100 per cent yield of *m*-nitrobenzotrifluoride (114). A study has been made of the reaction mechanism involved in the ionic polymerization of

α -olefins in the presence of nitryl fluoride and boron trifluoride (115).

The behavior of solutions of nitryl fluoride in concentrated mineral acids has been reviewed recently (69, 72). Electrical conductivity, density, viscosity, cryoscopic, and Raman spectral measurements have been carried out using solutions of nitryl fluoride in concentrated sulfuric, selenic, and orthophosphoric acids. At concentrations not exceeding 1 mole per cent, nitryl fluoride dissociates to nitronium and bisulfate ions:



Between 1 and 9.6 mole per cent concentration of nitryl fluoride (where maximum conductivity occurs) the first reaction is accompanied by the reversible equilibrium:



At about 22 mole per cent nitryl fluoride maximum viscosity is reached. At 68 mole per cent nitryl fluoride, solid $\text{NO}_2\text{SO}_3\text{F}$ separates and the supernatant liquid turns yellow, owing to the presence of nitrogen dioxide (72).

Nitrosyl fluoride and nitryl fluoride have been considered as components of rocket fuels (48), and maximum theoretical exhaust velocities have been calculated for the reaction between these compounds and various hydrides [N_2H_4 , LiH , LiAlH_4 , $\text{Al}(\text{BH}_4)_3$, SiH_4 , B_2H_6 , $\text{Be}(\text{CH}_3)_2$, $\text{B}(\text{C}_2\text{H}_5)_3$, $\text{Si}(\text{CH}_3)_4$], organic compounds (diacetylene, octane, ethyl alcohol, aniline), and elements (hydrogen, lithium, sodium, beryllium, magnesium, aluminum, carbon, silicon) (20).

III. ORGANIC NITROGEN-FLUORINE COMPOUNDS

Brief references to the subject of organic nitrogen-fluorine compounds have appeared elsewhere (18, 32, 39, 43, 64, 65, 66, 90, 145, 168).

Moissan (100) reported in 1900 that dimethylamine, aniline, or pyridine reacts with incandescence on contact with fluorine. Although he isolated carbon, hydrogen fluoride, and carbon tetrafluoride, Moissan was unable to demonstrate the presence of organic nitrogen-fluorine compounds, and it is unlikely that compounds containing nitrogen-fluorine bonds were produced under such severe conditions.

Ruff and Giese (135) were the first to describe organic compounds containing N—F groups. By directly fluorinating solid silver cyanide, mixed with calcium fluoride, these workers obtained several gaseous products including CF_4 , CF_3NF_2 mixed with C_2F_6 , and compounds of the empirical formula $(\text{CNF}_3)_2$ believed to be $\text{CF}_3\text{N}=\text{NCF}_3$, $\text{CF}_2\text{NFCF}_2\text{NF}$, $\text{CF}_2=\text{NCF}_2\text{NF}_2$, and other isomers. Under somewhat different conditions (144) direct fluorination of silver

cyanide produced hexafluoroazomethane, $\text{CF}_3\text{N}=\text{NCF}_3$, a compound also studied by Bigelow and coworkers (50). Trifluoromethyldifluoroamine, CF_3NF_2 , uncontaminated with perfluoroethane (*cf.* Ruff's work), has been isolated by Coates and coworkers (25) by the action of gaseous fluorine (diluted with nitrogen) on solid potassium ferricyanide and ferrocyanide. The vapor pressure of CF_3NF_2 , measured from -135°C . to -75°C ., is represented by the equation:

$$\log P_{\text{mm.}} = 7.474 - (901.0/T)$$

which gives the latent heat of vaporization as 4.12 kcal./mole and Trouton's constant as 21.0. The vapor pressure of the solid, melting point -122.1°C ., is represented by the equation

$$\log P_{\text{mm.}} = 7.95 - \frac{970}{T}$$

Fluorination of anhydrous hydrogen cyanide by cobalt trifluoride at $200\text{--}250^\circ\text{C}$. gives CF_4 , CF_3NF_2 (contaminated with C_2F_6), fractions of the empirical formulas $(\text{CNF}_3)_2$ and $(\text{CNF}_4)_2$ (*cf.* Ruff's work), and a mixture of compounds of high molecular weight containing carbon, nitrogen, and fluorine, which is unreactive to all reagents tested except hot potassium (25).

Craig (32) has made a systematic study of the fluorination of cyanogen chloride, cyanogen bromide, and cyanogen iodide, using silver(II) fluoride. Although numerous products are formed, the major product being $\text{CF}_3\text{N}=\text{NCF}_3$, little evidence was found for the presence of organic compounds containing nitrogen-fluorine bonds. The indirect fluorination of fluorocarbon nitrogen compounds by silver(II) fluoride under mild conditions has been studied (179, 181). Reactions with this reagent were determined for the following functional groups: $-\text{N}=\text{C}=\text{}$, $\text{N}\equiv\text{C}-$, $\text{C}(\text{C}\equiv\text{N})_3$, $=\text{NH}$, $=\text{NCOF}$, $-\text{N}=\text{C}=\text{O}$, $-\text{NHCOF}$, and $-\text{CONH}_2$. Most of these groups react between 20° and 100°C ., and the results usually can be explained in the following manner. Fluorine attacks carbon where possible. Formation of a free radical containing nitrogen next occurs. The radical can then react with fluorine, or couple with another radical, or undergo internal rearrangement. Of these possibilities coupling usually predominates.

Concurrently with work on purely inorganic compounds other investigators have studied the reactions of fluorine and fluorinating agents with organic compounds. By far the largest number of organic nitrogen-fluorine compounds are prepared by fluorinating compounds of related structure containing hydrogen. The organic compound is dissolved in anhydrous hydrogen fluoride contained in a specially designed cell, and a minimum voltage (usually less than 5–6 v.) is applied (168). Under these circumstances elementary fluorine is not formed, and the organic compound is converted

to the perfluoro derivative together with fluorinated fission products by an anodic process as yet imperfectly understood. Only rarely are incompletely fluorinated compounds formed. Perfluoro derivatives are usually more volatile than the parent organic material and are carried out of the electrolysis cell by the cathodic hydrogen to traps cooled by liquid nitrogen. Subsequent fractionation generally results in a sharp separation of the various perfluoro products. Occasionally the perfluoro compound is insoluble in anhydrous hydrogen fluoride and forms a lower layer which can be drained off and fractionally distilled. Low yields of perfluoroamines have been obtained by fluorination of amines in the vapor phase, using cobalt trifluoride (60, 61), but in general electrochemical fluorination is the preferred method, as it gives superior yields of perfluoro compounds.

Replacement of carbon by nitrogen in a fluorocarbon does not bring about an appreciable change in physicochemical properties (59, 64, 66). A strong peak near $10\ \mu$ is very common in the infrared spectra of nitrogen-fluorine compounds (183). It is both interesting and significant that perfluoroamines are completely non-basic, are stable to 5 per cent sodium hydroxide solution, are not absorbed by 5 *N* hydrochloric acid, are very inert to chemical attack, and are thus to be regarded as derivatives of nitrogen trifluoride rather than as derivatives of ammonia and amines. Perfluoroamines possess a characteristic musty odor.

Organic compounds which have been fluorinated to produce nitrogen-fluorine derivatives fall into the following broad categories: amines (aliphatic, aromatic, heterocyclic), amides, nitriles, perfluoroolefins, and methyl thiocyanate.

A. PREPARATION FROM AMINES

Haszeldine (60, 61, 62) has shown that vapor-phase fluorination of tertiary amines, using cobalt trifluoride, produces only low yields of the corresponding perfluoro compounds. The behavior of aromatic and heterocyclic amines when fluorinated by the cobalt trifluoride and electrolytic methods has been studied extensively (7, 59, 79, 80, 163, 168). Thus, pyridine and aniline give perfluoropiperidine and perfluorocyclohexylamine, respectively, together with perfluorinated fission products. Dimethylaniline produces a mixture of perfluorocyclohexane, perfluorodimethylamine, and possibly perfluorodimethylcyclohexylamine. Perfluorodimethylamine has also been prepared by the fluorination of trimethylamine (171). Methylaniline gives perfluorocyclohexane and perfluoromethylamine, the latter compound also being obtained by the passage of methylamine over cobalt trifluoride. In all cases, yields of the perfluoroamines are very low.

Direct fluorination of a series of amines has been carried out by Bigelow and coworkers (50), who have

shown that mono-, di-, and trimethylamines under a variety of conditions are not only fluorinated but undergo alkylation, dealkylation, and dimerization. Dimethylamine, for example, yields CF_3NF_2 , $(\text{CF}_3)_2\text{NF}$, $(\text{CF}_3)_3\text{N}$, $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$, and other products. Trimethylamine gives CF_3NF_2 , $(\text{CF}_3)_2\text{NF}$, $\text{CF}_3\text{CF}_2\text{NF}_2$, and a volatile dimer fraction possibly containing $\text{CF}_3\text{NFNFCF}_3$ or isomers, $\text{CF}_3\text{NFN}(\text{CF}_3)_2$ and $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$. Ethylenediamine and ethylenimine produce significant amounts of $\text{CF}_3\text{N}=\text{NCF}_3$, a compound remarkable in that it is stable at 500°C . and is even stable to fluorine at 400°C ., showing that fluorine does not add readily to the nitrogen-nitrogen double bond in a perfluorocarbon derivative. Ethylenimine also yields $(\text{CF}_3)_2\text{NF}$.

Extensive studies have been made on the fluorination of various heterocyclic nitrogen compounds. Simons (164) has found that electrolysis of pyridine in anhydrous hydrogen fluoride gives nitrogen trifluoride and perfluoropentane, not perfluoropiperidine (*cf.* 59), but a later report (125) states that perfluoropentane and perfluoropiperidine are formed, and these gases have been separated using a 2-meter chromatographic column. Employing the catalytic (fluorine and gold- or silver-plated copper catalyst) and cobalt trifluoride methods, Haszeldine (59) has shown that fluorination of 2,6-dimethylpyridine gives a 5 per cent yield of a solid, m.p. $94\text{--}95^\circ\text{C}$., possessing a characteristic musty odor and believed to be perfluoro-2,6-dimethylpiperidine. Quinoline has also been fluorinated (66). Attempts have been made to determine the energy of the nitrogen-fluorine bond from data obtained by the combustion of perfluoropiperidine (53). When Burdon and coworkers (21) passed perfluoropiperidine at 560°C . through a nickel tube packed with nickel gauze, they found that a defluorination reaction occurred, perfluoropiperidine giving pentafluoropyridine. The latter compound has also been prepared by passing perfluoropiperidine, at $< 1\ \text{mm.}$, over iron wire at $580^\circ\text{--}610^\circ\text{C}$. (13).

Fluorination of some secondary and tertiary cyclic amines in anhydrous hydrogen fluoride, using the Simons electrofluorination cell (164), has demonstrated that pyridine, *C*-substituted pyridines, and morpholine give the corresponding perfluorinated cyclic compounds, whereas *N*-substituted piperidines and 1-methylmorpholine give the corresponding tertiary perfluoroamines (162). In all cases considerable cleavage occurs, nitrogen trifluoride being the principal product.

Melamine on fluorination yields only CF_4 , crude FCN , CF_3NF_2 , $(\text{CF}_3)_2\text{NF}$, and other known products, but none of the expected $\text{F}_2\text{NCF}_2\text{NF}_2$, nor any fluorinated product containing the triazine nucleus (19). Cyanuric fluoride is very unreactive toward fluorine, even under drastic conditions, and the products when formed consist of an inseparable mixture of CF_4 ,

$(\text{CF}_3)_2\text{NF}$, CF_3NF_2 , and sublimable solid (19).

The nuclear magnetic resonance spectra of a number of aliphatic and cyclic perfluoramines have been reported by Muller and coworkers (107).

Hückel (73) and Nerdel (109) have treated mercury (II) fluoride with perfluoro-2-azapropene, $\text{CF}_2\text{N}=\text{CF}_2$, and claimed to have added fluorine across the carbon-nitrogen double bond to produce organic nitrogen-fluorine compounds. However, when this reaction was attempted by other workers (182), the sole product was the mercury derivative of bis(perfluoromethyl)amine, $(\text{CF}_3)_2\text{NHgN}(\text{CF}_3)_2$. Thus it appears that fluorine does not add readily to the azomethine linkage.

A study (180) made on the reaction of a series of metallic fluorides with the double bond of $\text{CF}_3\text{N}=\text{CF}_2$ shows that silver(II) fluoride, for example, at room temperature gives the azomethine dimer, $(\text{CF}_3)_2\text{NCF}=\text{NCF}_3$, and the hydrazine, $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$. At higher temperatures both the monomer, $\text{CF}_3\text{N}=\text{CF}_2$, and the dimer, $(\text{CF}_3)_2\text{NCF}=\text{NCF}_3$, are converted to $(\text{CF}_3)_2\text{NF}$. The hydrazine, $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$, does not react further. Cobalt trifluoride and $\text{CF}_3\text{N}=\text{CF}_2$ give $(\text{CF}_3)_2\text{NF}$ and the hydrazine, but no dimer.

B. PREPARATION FROM AMIDES

At 0°C. direct fluorination of urea yields a yellow corrosive liquid containing up to 16 per cent of fluorine active to hydrogen iodide and about 45–55 per cent of total fluorine (87). Distillation of this mixture gives difluoroamine, HNF_2 , but no organic compounds containing the N—F group. Bigelow and coworkers (5) have studied the action of fluorine on dimethylformamide, methylformamide, and acetamide. When relatively mild conditions are used (9), dimethylformamide gives good yields of $(\text{CF}_3)_2\text{NF}$, but under more vigorous conditions a mixture of $(\text{CF}_3)_2\text{NF}$, $(\text{CF}_3)_3\text{N}$, $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$, and a small amount of $\text{CHF}_2\text{NFCF}_3$ is produced. Vigorous fluorination of methylformamide gives $\text{CF}_2=\text{NF}$, CF_3NF_2 , and $(\text{CF}_3)_2\text{NF}$, but even mild fluorination of acetamide causes cleavage before substitution of hydrogen, giving acetyl fluoride and nitrogen.

C. PREPARATION FROM NITRILES

Fluorination of acetonitrile (62) or trifluoroacetonitrile (5, 19, 25) gives $\text{C}_2\text{F}_5\text{NF}_2$; fluorination of $\text{C}_2\text{H}_5\text{CN}$ produces $\text{CF}_3(\text{CF}_2)_2\text{NF}_2$ (19); and fluorination of $\text{C}_3\text{H}_7\text{CN}$ yields $\text{C}_3\text{F}_9\text{NF}_2$ (64). The interesting compound trifluoromethylenimine, $\text{CF}_2=\text{NF}$, a colorless gas of nauseating odor, is a by-product of the fluorination of acetonitrile. Craig (32) has shown that $\text{CF}_2=\text{NF}$ can be dimerized by ultraviolet light and by heat. The compound is very reactive, attacks metallic mercury, liberates iodine from potassium iodide solution, is completely absorbed by alkaline bisulfite solution, and has been considered as a possible monomer leading

to perfluorinated polymers of the type $-(\text{CF}_2\text{NF})_n-$ (62, 64). Only carbon tetrafluoride and other fluorocarbons are formed in the vapor-phase fluorination of acetonitrile over a copper metal catalyst at low concentrations of fluorine in helium (33). A nitrogen-containing polymeric material is also formed. At higher concentrations of fluorine CF_4 , C_2F_6 , $\text{CF}_2=\text{NF}$, $\text{CF}_3\text{CF}_2\text{NF}_2$, and a highly fluorinated polymeric nitrogenous material (stable to 475°C.) are formed. Under very mild conditions of fluorination (5) trifluoroacetonitrile or pentafluoropropionitrile gives $\text{CF}_3\text{CF}_2\text{N}=\text{NCF}_2\text{CF}_3$ and $\text{CF}_3(\text{CF}_2)_2\text{N}=\text{N}(\text{CF}_2)_2\text{CF}_3$, whereas vigorous fluorination of $\text{CF}_3\text{CF}_2\text{CN}$ produces $\text{CF}_3(\text{CF}_2)_2\text{NF}_2$. Malononitrile, $\text{CH}_2(\text{CN})_2$, has been fluorinated over a metal packing under a variety of conditions (9, 125); the cyclic five-membered compound, $\text{CF}_2\text{CF}_2\text{CF}_2\text{NFNF}$, was obtained, together with com-

pletely fluorinated malononitrile: namely, perfluoro-1,3-diaminopropane, $\text{F}_2\text{NCF}_2\text{CF}_2\text{CF}_2\text{NF}_2$. Trifluoroacetonitrile has been fluorinated with nitrogen trifluoride, using cesium fluoride as catalyst at 520°C. (37). The products are CF_3NF_2 , $\text{CF}_3\text{N}=\text{CF}_2$, $(\text{CF}_3)_2\text{NF}$, $(\text{CNF})_3$, and CF_4 .

D. PREPARATION FROM PERFLUOROOLEFINS

The use of nitrogen trifluoride as a fluorinating agent for perfluoroolefins has been reported (35, 37). No appreciable reaction occurs between perfluoropropene ($\text{CF}_3\text{CF}=\text{CF}_2$) and nitrogen trifluoride below 450°C. when sodium fluoride is used as catalyst, but at 520°C. with an estimated contact time of 103 sec., 87 per cent of the perfluoropropene reacts to produce fluorinated products in the following relative molar amounts: $\text{CF}_3\text{CF}_2\text{CF}_3$ (10.0); $\text{CF}_3\text{CF}=\text{NCF}_3$ (4.1); $(\text{CF}_3)_2\text{CFCF}_3$ (3.1); $(\text{CF}_3)_2\text{C}=\text{CF}_2$ (2.8); $\text{CF}_3\text{N}=\text{CF}_2$ (2.7); $(\text{CF}_3)_2\text{CFCF}_2\text{CF}_3$ (2.5); $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_2\text{CF}_3$ (1.4); $(\text{CF}_3)_2\text{CFCF}(\text{CF}_3)_2$ (1.0). On substituting cesium fluoride for sodium fluoride and using about the same contact time, nitrogen trifluoride reacts with perfluoropropene at 320°C. Under these milder reaction conditions only a small amount of cleavage of the fluoroolefin occurs and compounds containing nitrogen-fluorine bonds in the following relative molar amounts could be isolated: $(\text{CF}_3)_2\text{C}=\text{NF}$ (3.0); $(\text{CF}_3)_2\text{CFNF}_2$ (2.5); $(\text{CF}_3)_2\text{CFCF}(\text{CF}_3)_2$ (2.0); C_6F_{12} (2.0); $\text{C}_4\text{F}_8\text{N}$ (1.0); and C_3F_8 (<1.0). The reaction apparently proceeds via the formation of radicals resulting from attack of nitrogen trifluoride on the olefin. The major reaction products may be accounted for by combination of the radicals in the following manner:

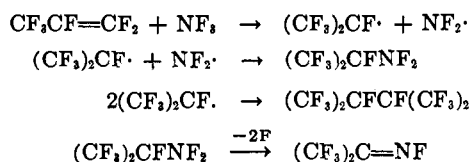
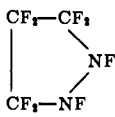
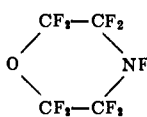
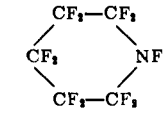
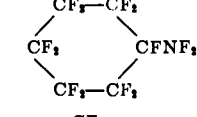
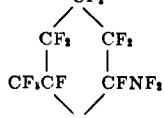
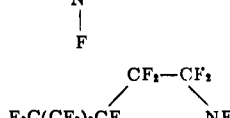
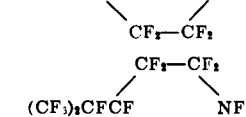


TABLE 5

Physical properties of the substituted organic nitrogen-fluorine derivatives

Empirical Formula	Structural Formula	Freezing Point or Melting Point	Boiling Point*	Other Data†	References
		°C.	°C.		
CF ₂ NO	FCONF ₂	-152.5	-82.4		(18, 135)
CF ₂ N	CF ₂ =NF		-101 to -95		(5, 9, 33, 62, 64)
CF ₄ N	CF ₃ NF ₂	-122.1	-78 to -75		(25, 50, 59, 135, 163)
CF ₃ NS	SF ₅ CF ₂ NF ₂	-153	9.5	r	(5, 19)
C ₂ F ₇ N	CF ₂ CF ₂ NF ₂	Glass	-40 to -37		(25, 33, 50, 62)
C ₂ F ₇ N	(CF ₂) ₂ NF	-171	-38 to -37	i	(5, 9, 25, 33, 59, 64, 163, 171, 180, 183)
C ₂ F ₇ HN ₃	CHF ₂ NFNFCF ₂	-123	-15		(9)
C ₂ F ₈ N ₂	CF ₂ -CF ₂ 	-124	-35.5/203 mm.		(9, 19)
C ₂ F ₉ N	CF ₂ (CF ₂) ₂ NF ₂	-168	0.0	r	(5, 19, 62)
C ₂ F ₁₀ N ₂	F ₂ N(CF ₂) ₂ NF ₂		-8 to -1/207 mm.		(9)
C ₂ F ₉ NO	O 		15/356 mm.	r	(107, 162)
C ₂ F ₁₁ N	CF ₂ -CF ₂ 		49 to 50	n, d, r, a, m	(18, 59, 107, 125, 162, 163)
C ₂ F ₁₂ N	CF ₂ -CF ₂ 		75 to 76	n, d	(59, 66, 163)
C ₂ F ₁₃ N	CF ₂ 	94 to 95			(59)
C ₂ F ₁₇ N	F ₂ C(CF ₂) ₂ CF 		123.5	n, d, a, m	(162)
C ₂ F ₁₇ N	(CF ₂) ₂ CFCF 		124.5	n, d, a, m	(162)

* Boiling point is at 760 mm. unless otherwise stated. † a = AR_f (calculated atomic refraction for fluorine); d = d₂₅²⁵; i = infrared data; m = MRD (calculated from Lorentz-Lorenz equation); n = n_D²⁵; r = nuclear magnetic resonance data.

E. PREPARATION FROM METHYL THIOCYANATE

Vapor-phase fluorination of a methyl thiocyanate and nitrogen mixture (5) (F₂=CH₃SCN=N₂=4:1:100) at 90°C. gives SF₅CN under mild conditions. More vigorous conditions (F₂=CH₃SCN=N₂=6:1:90) at 95°C. bring about fluorination of SF₅CN and a low-boiling liquid, SF₅CF₂NF₂ (boiling point 9.5°C.) is produced, which slowly decomposes on standing. In addition to the foregoing compounds, CF₄, SF₆, CF₃SF₅, C₂F₁₀, and CF₂=NF are also formed.

Table 5 lists some of the organic, nitrogen-fluorine-

containing compounds that have been definitely characterized.

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