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CHEMISTRY OF DIFLUORAMINE

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1. INTRODUCTION

Until recently there had been very little investigation of difluoramine HNF_2. The main publications about it [1-3] related predominantly to its physical properties and to the history of the methods of its preparation, whereas its chemical properties remained almost uninvestigated, owing to the extreme hazard in working with it.

Of the three theoretically conceivable compounds in the series of fluoro-substituted ammonias only two are known at present: nitrogen trifluoride NF_3 and difluoramine HNF_2. The physical and chemical properties of nitrogen trifluoride are sufficiently well known [1-3]. The fluorine–nitrogen bond in NF_3 has a polar character, which determines the shift in the electron density towards the base of the regular pyramid with the nitrogen atom at the apex and the fluorine atoms in the base. It is also generally known that the ammonia molecule is extremely nucleophilic, owing to the unshared pair of electrons at the nitrogen atom. As the hydrogen atoms in it are replaced by fluorine atoms, an ever-increasing deficit in electron density is produced at the nitrogen atom (in compensation for which the electron lone pair of the nitrogen should play an ever-increasing part). Hence owing to the powerful inductive influence of the fluorine atoms there is a significant deactivation of this electron pair, increasing with the degree of substitution, and a sharp fall in the basic properties of the fluoro-substituted ammonias. This deactivation should be maximal in the nitrogen trifluoride molecule.

The same distribution of electron density along each nitrogen–fluorine bond in the NF_3 molecule and the almost complete absence of nucleophilic properties at the nitrogen atom confers on nitrogen trifluoride a high chemical inertness at temperatures up to 300–400° and explains the exclusively homolytic cleavage of the bonds under more intensive thermal action. Therefore all the reactions in which nitrogen trifluoride is at present known to participate are usually pyrolytic and have a radical character.

A feature of the structure of the difluoramine molecule gives it a reactivity which indicates the high degree of polarisation of the nitrogen–hydrogen bond $\overset{\delta+}{H}-\overset{\delta-}{NF_2}$, which under suitable conditions is capable of heterolysis with the formation of the difluoramide anion NF_2^-.

If the tervalent nitrogen atom in the ammonia molecule is considered to be in a reduced state and the tervalent nitrogen atom in nitrogen trifluoride is in an oxidised state, then the difluoramine molecule undergoes both oxidation and reduction.

Hence the difluoramine molecule, by allotting a rather active long pair of electrons to the nitrogen atom and with a hydrogen atom capable of loss as a proton, exhibits an amphoteric nature. The presence in it of an N–H bond capable of being oxidised, and of an N–F bond capable of being reduced, confers on it the dual character of reactivity in redox changes. The combination of such a variety of properties is usually responsible for the diversity of the chemical reactions in which difluoramine participates.

2. PHYSICAL PROPERTIES AND STRUCTURE OF THE DIFLUORAMINE MOLECULE

Difluoramine is a colourless gas with a characteristic sharp odour, reminiscent of the odour of nitrogen oxides, liquefying below -23° into a transparent, colourless, mobile liquid. The most important physical properties of difluoramine have been studied recently by Lawton and Weber [4,5] and by Kennedy and Colburn [6].

The microwave spectra of difluoramine and deuterated difluoramine have been investigated [7]. The HNF_2 molecule is characterised by the following parameters [7]:

length of nitrogen–fluorine bond	$r_{N-F} = 1.400 \pm 0.002$ Å,
length of nitrogen–hydrogen bond	$r_{N-H} = 1.026 \pm 0.002$ Å,
F–N–F bond angle	102.9°,
H–N–F bond angle	99.8° ± 0.2°.

The difluoramine molecule is thus an irregular triangular pyramid with the nitrogen atom at the apex.

The dissociation energy of the nitrogen–hydrogen bond in difluoramine $D(F_2N-H)$ is 72.5 kcal. [8]

The dipole moment of the HNF_2 molecule is 1.93 D, and its vector is directed at an angle of 19° to the direction of the nitrogen–hydrogen bond. This agrees well with the hypothesis of polarisation of the nitrogen–hydrogen bond and the tendency of difluoramine to dissociate according to the equation:

$$HNF_2 \rightleftharpoons H^+ + NF_2^-.$$

The infrared spectrum of gaseous difluoramine in the region 250–4000 cm^{-1} has been investigated; it includes strong doublets at 7.0, 7.8, and 10.2 μm and a triplet at 11.2 μm. [3]

The proton-NMR spectrum consists of a triplet, as should follow from proton spin–spin interaction with the two equivalent fluorine nuclei. The centre of the triplet is displaced by ~ 6 Hz to the side of fields of greater intensity in relation to benzene. The spin–spin splitting corresponds to ~ 24 Hz.

The ^{19}F-NMR spectrum consists of two broad bands arising from the spin–spin interaction of the fluorine nuclei with the proton. The peak of this doublet, which corresponds to a greater field strength, is located in the region 2100 Hz to the side of fields of lower intensity relative to trifluoroacetonitrile [3,6].

The mass spectra of difluoramine have also been studied in detail [4,6].

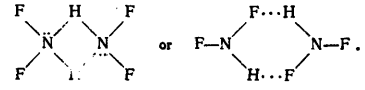
The anomalously high boiling point of difluoramine (-23.6°) compared with the value which could be expected starting from the boiling point of ammonia (-33.4°) and nitrogen trifluoride (-129°), the high dipole moment of the HNF_2 molecule, and other data given in Table 1 undoubtedly show that in the condensed phase difluoramine is a strongly associated liquid.

The difluoramine molecule is amphoteric and is capable of complex formation through hydrogen bonds with alkali metal fluorides [11–13] and Lewis basicity with several aprotic acids [14]. It is reasonable to assume that association

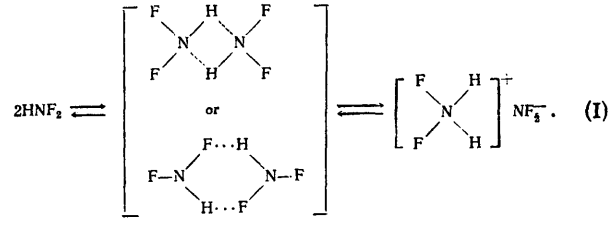
TABLE 1. Some properties of ammonia and several of its fluoro-derivatives.

Formula of compound / Characteristic	NH_3	HNF_2	$ClNF_2$	NF_3
Molecular weight	17	53	87	71
Boiling point, °C	−33	−23.6	−67	−129
Heat of vaporisation, kcal mole^{-1}	5581	5940	4350	2769
Trouton constant	23.3	23.7	21.0	19.94
Dipole moment, D	1.43	1.93	—	0.21
Solubility in water	very good	soluble	—	insoluble

in the liquid phase is effected by the formation of a hydrogen-bonded dimer, whose presence in solid difluoramine was shown by Craig by infrared spectroscopy [14]:



It is not ruled out that such an associate-dimer of difluoramine plays the part of an activated complex characterising the four- or six-membered transition state in equilibrium:



Difluoramine is rather readily soluble in several polar solvents, for example, in water [5,9,15,16] and, despite one assertion [2], is stable in deoxygenated aqueous and sulphuric acid solutions. Heating these solutions or non-hermetic storage leads to almost quantitative desorption of the difluoramine from them.

Preparations of 0.15 M solutions of difluoramine in 0.1 M sulphuric acid have been described [5]. On heating aqueous solutions acidified with sulphuric, nitric, phosphoric, sulphurous, or other mineral acids it can be completely expelled from them [15,17]. For example, the quantitative liberation of ~ 6.6 g HNF_2 from its solution in 100 ml 5% H_2SO_4 on heating the latter at 90° for 30 min has been described.

Difluoramine is sparingly soluble in concentrated sulphuric acid at reduced pressure and room temperature [18]. This property is utilised for its quantitative separation in preparation from triphenylmethyldifluoramine (tritylfluoramine). For example, by vacuum treatment 0.053 g HNF_2 was completely extracted from its solution in 10 ml concentrated sulphuric acid.

The solubility of difluoramine in dimethyl, ethyl methyl, diethyl, di-isopropyl, and dibutyl ethers; methylal [diethoxymethane]; dimethoxyethane; anisole; tetrahydrofuran; tetrahydropyran; and ethylene oxide has been investigated [5,19]; it forms homogeneous solutions with these solvents over a rather wide range of ratios. Solutions containing up to 10 parts by weight were obtained for dimethyl and diethyl ethers and ethylene oxide, up to 5.8 parts by weight for methylal, and 5.2 parts by weight HNF_2 for dimethoxyethane per part by weight of solvent.

The solutions of difluoramine in ethers are quite stable over a rather wide range of temperature and were patented as mono-component and two-component liquid rocket propellents [15,19]. A mixture of dimethyl ether and difluoramine, for example, is stable at from -142° to room temperature. The order of mixing of the ethers with difluoramine and also the state of aggregation of the components of the mixture (except solid) are unimportant, but the rate of mixing should be rather slow, as there is a considerable exothermic effect during mixing. All the mixtures exhibit a marked negative departure from Raoult's law, which once again confirms the hypothesis concerning the association of difluoramine in the liquid phase.

The solutions of difluoramine in dimethyl ether, diethyl ether, and ethylene oxide have been studied most thoroughly [5]. It has been found that these ethers form molecular addition compounds with difluoramine in the ratio 1 : 1, giving the composition $R_2O.HNF_2$. However, at room temperature these addition products are completely dissociated into their constituent molecules.

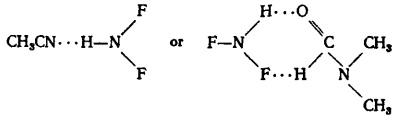
The solubility of difluoramine in methanol, ethanol, acetonitrile, dimethylformamide, and dimethyl sulphoxide has also been investigated [20]. It has been shown that equimolecular solutions of difluoramine in these solvents, like the solutions in ethers and ethylene oxide [5], behave as equilibrium systems of the form:

$$HNF_2 + X \underset{+\Delta}{\overset{-\Delta}{\rightleftharpoons}} X \cdot HNF_2$$

where X = H_2O, CH_3OH, C_2H_5OH, CH_3CN, $(CH_3)_2NCHO$, or $(CH_3)_2SO$, for which a fall in temperature favours a shift in the equilibrium to the right.

The stability of the complexes formed (adducts) depends on the nature of X. The most stable complexes are with dimethylformamide and dimethyl sulphoxide, whereas the complexes with water are distinguished by insignificant stability.

Infrared spectroscopy has shown that the complex formation in these examples is brought about by the formation of intermolecular hydrogen bonds, for example:



with the force of association falling in the sequence:

$$HNF_2 \cdot (CH_3)_2NCHO \sim HNF_2 \cdot (CH_3)_2SO > HNF_2 \cdot CH_3OH > HNF_2 \cdot H_2O$$

For some of these systems the equilibrium state is characterised as follows:

$$\ln K_{p_{HNF_2 \cdot CH_3OH}} = -\frac{4143.2}{T} + 23.22, \qquad \Delta H = 8.24 \text{ kcal mole}^{-1},$$

$$\ln K_{p_{HNF_2 \cdot CH_3CN}} = -\frac{6538.2}{T} + 31.464, \qquad \Delta H = 13.02 \text{ kcal mole}^{-1},$$

where $K_p = p^2/4$.

TABLE 2. Properties of some molecular adducts of difluoramine [5].

Ether	B.p., °C extrapolation	H_p, kcal mole^{-1}	Trouton constant	Dependence of vapour pressure on temperature. $\log p_{mmHg}$ =
Dimethyl	0	7.66	28.1	$-1674/T+9.005$
Diethyl	36	7.41	24.0	$-1619/T+8.124$
Ethylene oxide	22	6.92	23.5	$-1512/T+8.015$

The examples quoted of the reversible complex formation by difluoramine with water and various organic compounds undoubtedly show that its tendency to intermolecular interaction by the formation of hydrogen bonds is one of the most important prerequisites for understanding the character of the reactivity of this compound. In this, the difluoramine molecule can evidently act either as an acceptor (through the hydrogen atom) or as a donor (through the nitrogen or fluorine atoms).

3. METHODS OF MAKING DIFLUORAMINE

Despite Ruff and Staub's claim [21,22] to have made difluoramine by the electrolysis of fused ammonium hydrogen fluoride, it is quite clear [1-3] that this compound was first obtained by Kennedy and Colburn [6] in 1959. In studying the pyrolysis of nitrogen trifluoride over arsenic in the presence of water vapour with the aim of preparing tetrafluorohydrazine, they found [6] that at 250–300° a little difluoramine is formed in addition to N_2F_4.

It is impossible to support the suggestion [6] that the appearance of HNF_2 in this process is due to the intermediate formation of arsine. The oxidative nature of the interaction of nitrogen trifluoride with arsenic and of tetrafluorohydrazine with arsine [23] obviously excludes the possibility of the formation under these conditions of such a strong reductant as arsine. Most probably difluoramine is formed as a result of the difluoramine radicals which are produced in large amounts in the defluorination of nitrogen trifluoride by arsenic:

$$NF_3 + As \xrightarrow{300^\circ} {}^{\cdot}NF_2 + AsF_3,$$

reacting directly with water molecules:

$${}^{\cdot}NF_2 + HOH \longrightarrow HNF_2 + {}^{\cdot}OH.$$

The great ability of the difluoramine radical to detach a hydrogen atom, a reaction which is essentially an oxidation:

$$H^{\cdot} + {}^{\cdot}NF_2 \longrightarrow [H^+ + NF_2^-] \longrightarrow HNF_2,$$

forms the basis of a group of methods for obtaining difluoramine [23]. Thus, on heating mixtures of tetrafluorohydrazine with arsine in an autoclave (1 h at 50–60°), difluoramine can be obtained in 52% yield:

$$N_2F_4 + AsH_3 \longrightarrow HNF_2.$$

The reaction of tetrafluorohydrazine with thiols also leads to the formation of difluoramine:

$$2RSH + N_2F_4 \longrightarrow 2HNF_2 + R{-}S{-}S{-}R.$$

As a result of the reaction of tetrafluorohydrazine with thiophenol at 50° in a glass reactor, difluoramine is formed in 75% yield, whereas in reaction with butanethiol in a stainless steel autoclave it is obtained in only 9% yield.

In all these instances it was very difficult preparatively to isolate the difluoramine from the gaseous reaction mass and this was done by fractional condensation of the products in a vacuum with a series of traps at -80° and below.

One variety of this group of methods is the preparation of difluoramine by heating a mixture of tetrafluorohydrazine and acetaldehyde to 150°: [24]

$$CH_3CHO + N_2F_4 \xrightarrow{150^\circ} CH_3CONF_2 + HNF_2.$$

Evidently there is an unbranched chain reaction in which $^{\cdot}NF_2$ radicals play the initiating role:

(1) $$N_2F_4 \rightleftarrows 2{}^{\cdot}NF_2,$$

(2) $$RCHO + {}^{\cdot}NF_2 \longrightarrow R\dot{C}O + HNF_2,$$

(3) $$R\dot{C}O + N_2F_4 \longrightarrow RCONF_2 + \dot{N}F_2, \text{ etc.}$$
($^{\cdot}NF_2$)

This is the more probable in that the last stage has been successfully brought about after the homolytic photolysis of biacetyl in an atmosphere of tetrafluorohydrazine[24]:

$$CH_3COCOCH_3 \xrightarrow[N_2F_4]{h\nu} 2CH_3CONF_2.$$

We think that it is not accidental that not a single instance of the formation of difluoramine in the action of tetrahydrofluorohydrazine on alcohols, carboxylic acids, or amines has yet been described, though these compounds have labile hydrogen. Furthermore, it is known[16] that the action of tetrafluorohydrazine on dimethylamine at 80° for 2 h in the gas phase leads only to the production of small amounts of methyl azide, diazomethane, and azomethane and does not give difluoramine, and the action of chlorodifluoramine on an excess of dimethylamine in ethereal solution leads to quantitative formation of tetrafluorohydrazine and dimethylammonium chloride.

On the other hand, Grzechowiak and coworkers have reported that heating certain alkanes[8] or acetone[26] with tetrafluorohydrazine leads to the removal by the $^{\cdot}NF_2$ radical of a hydrogen atom from the alkane and the formation of difluoramine and the corresponding alkyldifluoramines:

$$RH + {}^{\cdot}NF_2 \longrightarrow R^{\cdot} + HNF_2,$$
$$R^{\cdot} + N_2F_4 \longrightarrow RNF_2,$$
($^{\cdot}NF_2$)

where R = CH_3COCH_2 or a hydrocarbon radical.

The authors evidently did not succeed in isolating alkyldifluoramines in the pure state, since under the conditions of the reaction they decompose into a complex mixture of resinous products.

Bumgardner[26] observed the formation of alkyl-, alkenyl-, and alkynyl-difluoramines in the photochemical reaction between tetrafluorohydrazine and certain saturated and unsaturated hydrocarbons:

$$2CH_4 + 2N_2F_4 \xrightarrow[30\ min]{h\nu} 2CH_3NF_2 + 2N_2F_2 + 2HF \quad (50\%),$$

$$CH_3CH{=}CHCH_3 \xrightarrow[h\nu]{N_2F_4} CH_3CH{=}CHCH_2NF_2 + CH_3CHFCH(NF_2)CH_3 \quad (74\%),$$

$$CH_3C{\equiv}CCH_3 + N_2F_4 \xrightarrow{h\nu} \begin{cases} CH_3C{\equiv}CCH_2NF_2 \\ CH_3CF_2C(=NF)CH_3, \\ CH_3CF{=}C(NF_2)CH_3 \end{cases}$$

Chromatographic analysis of the products of the reaction on Chromosorb impregnated with silicone oil showed the absence of difluoramine from them. The initiating role in this process on account of the loss of the hydrogen atom from the hydrocarbon was ascribed by Bumgardner solely to a fluorine atom formed in the decomposition of the excited radical $^{\cdot}NF_2$†:

$$^{\cdot}NF_2 + h\nu \longrightarrow [{}^{\cdot}NF_2^*] \longrightarrow F^{\cdot} + F\dot{N},$$
$$RH + F^{\cdot} \longrightarrow R^{\cdot} + HF.$$

† Bumgardner believed the reaction to be initiated by F· (instead of $^{\cdot}NF_2^*$) as no HNF_2 or bisdifluoramino-compounds are observed (Ed. of Translation).

However, considering the ease with which difluoramine in contact with solid materials undergoes dehydrofluorination to form fluorazene [or fluoronitrene (Ed. of Translation)], then giving difluorodiazine [dinitrogen difluoride (Ed. of Translation)][5]:

$$HNF_2 \longrightarrow HF + \dot{N}F,$$
$$2\dot{N}F \longrightarrow N_2F_2,$$

and the probability that this change can occur in the chromatographic column, then once again the chromatographic data cannot be considered completely adequate for concluding the absence of difluoramine from this process due to the removal of a hydrogen atom by the radical $^{\cdot}NF_2$.

These facts show that the formation of difluoramine can be expected in by no means all instances of the interaction of tetrafluorohydrazine with substances bearing a labile hydrogen, as has been stated[2], but only when the substance is capable of easily losing not a proton, but an atom of hydrogen, which subsequently recombines with the $^{\cdot}NF_2$ radical.

Until recently the most acceptable method for making difluoramine[4] consisted in the action of elemental fluorine diluted with nitrogen on urea at 0°. Other investigators[5,27] have often used this method. It provides difluoramine in yields which, although moderate (up to 30% on the fluorine used[5]), are evidently sufficiently stable. Taking into account that the *NN*-difluorourea being formed in this process in high yield can be almost quantitatively decomposed on heating its aqueous solutions to 90° with sulphuric acid according to the equation[15,17,27]:

$$2NH_2CONF_2 + 2H_2O + H_2SO_4 \longrightarrow 2CO_2 + 2HNF_2 + (NH_4)_2SO_4,$$

the overall practical yield of difluoramine should be considered to be considerably higher.

In a modification of this method[11] it is proposed to isolate difluoramine from the liquid which is obtained by the fluorination of urea after Lawton and Weber in a single stage by acidifying it with sulphuric acid. With this reaction a continuous process for the production of difluoramine becomes possible[15].

To obtain difluoramine by acidic hydrolytic decomposition it is possible to use the products of the fluorination of biuret, aminoguanidine, diaminourea, 5-aminotetrazole, guanidinium chloride[28], and also almost any derivative of the type:

$$RR'NCXNF_2,$$

where R and R′ can be aryl, nitroaryl, or alkyl; and X is a sulphur or oxygen atom or an NH group. These products are readily obtainable according to the equation[15]:

$$RR'NCXNH_2 + 2F_2 \longrightarrow RR'NCXNF_2 + 2HF.$$

Evidently the ability of *NN*-difluoroamido-derivatives to give difluoramine when aqueous solutions of acids act on them is one of the most important features of the reactivity of this class of compound. Mono- and di-*N*-fluorocarbamates are formed in good yield in the fluorination of alkyl carbamates with elemental fluorine in water or acetonitrile[29]:

$$H_2NCOOR \xrightarrow[H_2O \text{ or } CH_3CN]{F_2} [FHNCOOR] \xrightarrow{F_2} F_2NCOOR,$$

where R = methyl, ethyl, n-propyl, isopropyl, or n-butyl.

Like *NN*-difluorourea, the esters of *NN*-difluorocarbamic acid give difluoramine quantitatively on heating with aqueous solutions of acids:

$$F_2NCOOR \xrightarrow{H_3O^+} HNF_2 + CO_2 + ROH.$$

Difluoramine can be obtained in good yield by hydrolysis of *NN*-difluoroaminocarbonyl fluoride[30], obtained in the ultraviolet irradiation of a mixture of carbon monoxide and tetrafluorohydrazine:

(1) $$CO + N_2F_4 \xrightarrow{h\nu} F_2NCOF + COF_2 + CO_2 + NF_3,$$

(2) $$F_2NCOF + H_2O \longrightarrow HNF_2 + HF + CO_2.$$

Difluoroaminocarbonyl fluoride is hydrolysed immediately even by the action of traces of moisture; therefore on reacting with other substances in aqueous solution it behaves like difluoramine[4-6,9,11], for example:

$$2F_2NCOF + 8OH^- \longrightarrow N_2F_2 + 2CO_3^{2-} + 4F^- + 4H_2O \text{ (see Refs. 9 and 11),}$$

$$F_2NCOF + 6I^- + 5H_3O^+ \longrightarrow 2I_3^- + NH_4^+ + 3HF + 4H_2O + CO_2 \text{ (see Refs. 4 and 5).}$$

Difluoramine can be made in good yield by acid hydrolytic decomposition of *NN*-difluorosulphonyl diamide[31], which can be obtained by the fluorination of an aqueous solution of sulphonyl diamide with fluorine below -5°:

$$2F_2 + H_2NSO_2NH_2 \longrightarrow 2HF + F_2NSO_2NH_2,$$
$$F_2NSO_2NH_2 + H_2O \xrightarrow[t^\circ]{H^+} HNF_2 + HOSO_2NH_2.$$

Acidification may be effected with phosphoric or sulphuric acid of a concentration not above 1 *N*: the use of concentrated sulphuric acid is said to decrease the yield of difluoramine and increase that of tetrafluorohydrazine.

Difluoramine can be obtained just as successfully by the acid hydrolysis of some complexes of *NN*-difluorosulphonyl diamide, for example:

$$(C_6H_5)_3PO \cdot H_2NSO_2NF_2,$$

complexes which, unlike *NN*-difluorosulphonyl diamide, can be isolated pure.

The "sulphamide" method of obtaining difluoramine can be considered to be more preferable than the "carbamide", since in the final stage it does not give any gaseous products other than difluoramine, whereas in the preparation from *NN*-difluorourea it is liberated from solution as an equimolecular mixture with carbon dioxide, the separation of which presents known preparative difficulties.

The attempt to bring about the preparation of difluoramide by the vapour-phase fluorination of ammonia with elemental fluorine[32] cannot be considered successful, since this results in the formation of a complex, difficultly separable mixture of reaction products:

$$NH_3 + F_2 \longrightarrow NF_3 + N_2F_4 + HNF_2 + N_2F_2 + NH_4F.$$

A small quantity of difluoramine in a high degree of purity under laboratory conditions can be easily obtained by the decomposition of trityldifluoramine with concentrated sulphuric acid at room temperature[18]:

$$(C_6H_5)_3CNF_2 + H_2SO_4 \longrightarrow HNF_2 + (C_6H_5)_3C^+ \cdot HSO_4^-$$
$$\xrightarrow{H_2O} (C_6H_5)_3COH + H_2SO_4.$$

The method ensures a 99% yield of almost pure difluoramine, which in combination with the relative accessibility of trityldifluoramine makes it extremely attractive. Trityldifluoramine in turn can be readily made from trityl chloride by reaction with tetrafluorohydrazine in the presence of mercury[18]. However, the method is of little use for technical purposes, since (as an example) 0.30 g (0.001 M) trityldifluoramine were spent in decomposition and a total of 23 cm^3 gaseous difluoramine was obtained.

The use of concentrated sulphuric acid does not prevent the quantitative formation and isolation of difluoramine and does not result in a redox reaction with the formation of tetrafluorohydrazine, as happens in the decomposition of *NN*-difluorosulphonyl amide or its complexes[31]. Probably the reason for the contradiction in these two observations lies in the different temperature conditions.

The ability of trityldifluoramine to give difluoramine with concentrated sulphuric acid is still unique among the difluoroaminoalkane series. The action of sulphuric acid on ethyl, t-isobutyl, n-butyl-, and s-butyl-*NN*-difluoramines does not lead to the formation of difluoramine[33]: these reactions are considered in detail in Section 4.

Mention must also be made of a single instance of the formation of difluoramine: ethanol acts on *NN*-difluoroacetamide to give the products ethyl acetate and difluoramine[24]:

$$CH_3CONF_2 + HOC_2H_5 \longrightarrow CH_3COOC_2H_5 + HNF_2.$$

This example, like the many instances of the hydrolytic instability of the *NN*-difluoroamido-derivatives described above, suggests that they possess the properties of acid halides and that the NF_2 group has a pseudo-halogen character.

4. CHEMICAL PROPERTIES AND REACTIVITY OF DIFLUORAMINE

It is desirable to start the review of the chemical properties of difluoramine by considering its capability for complex formation with different reagents.

The amphoteric nature of the HNF_2 molecule enables difluoramine to form coordination complexes either through the acceptor properties of the hydrogen atom or through the donor ability of the nitrogen and fluorine atoms, which have sufficiently active lone electron pairs.

In investigating the interaction of a series of organic and inorganic difluoramine derivatives of the type XNF_2, including some alkyldifluoramines, difluoramine, chlorodifluoramine, and nitrogen trifluoride, with such Lewis acids as BF_3, BCl_3, PF_5, and SO_2, Craig[14] found that the reactivity of these difluoramine derivatives is determined mainly by the donor properties of the nitrogen atom, which has a lone pair of electrons.

The activity of this pair depends directly on the electronegativity of the substituents X at the nitrogen atom. The greater the electronegativity of X, the greater the deficiency of electron density which is formed at the nitrogen atom and the greater the extent to which the lone pair of electrons takes part in the compensation of this deficit, the more the electron-donor properties of the molecule appear, and their Lewis basicity falls.

Craig showed experimentally that the basic properties of the compounds of type XNF_2 fall in the sequence:

$$C_2H_5NF_2 > CH_3NF_2 \sim CD_3NF_2 > HNF_2 > ClNF_2 > N_2F_4 \sim CF_3NF_2 \sim NF_3.$$

The most stable complexes of the type $HNF_2.A$, where A is a Lewis acid, are formed by difluoramine with BF_3, BCl_3, and SO_2. When these complexes, which are quite stable at low temperatures (< -78°), are heated they either

undergo irreversible changes – for example, $HNF_2.BCl_3$, which decomposes to give chlorodifluoramine [34]:

$$BCl_3 \cdot HNF_2 \longrightarrow ClNF_2 + BF_3 + HCl + BCl_3,$$

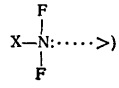
– or form equilibrium systems:

$$HNF_2.A(solid) \rightleftharpoons HNF_2(gas) + A(gas).$$

On the basis of kinetic measurements, Craig found the enthalpies of the processes and the equations which describe the temperature dependence of the pressure in the system (see Table 3).

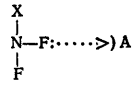
In investigating the mechanism of formation of complexes of difluoramine derivatives of the type $X-NF_2$ with Lewis acids, Craig started from the assumption of four theoretically conceivable possibilities for complex formation, due to:

(a) donor–acceptor interaction of the partners with participation of the lone pair of electrons of the nitrogen atom:

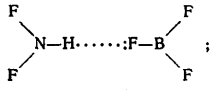


(II)

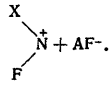
(b) donor–acceptor interaction of the partners with participation of the lone pair of electrons of the fluorine atoms, that is, by the formation of "fluorine bridges":



(c) hydrogen bonds between the hydrogen atom of the difluoramine and a nucleophilic atom of the Lewis acid:



(d) the formation of ions:

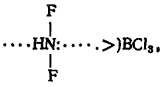


From infrared investigations Craig concluded that structure (II) best corresponds to the entire set of experimental results he obtained.

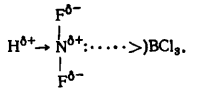
The absence from both the liquid and solid phases of difluoramine of association between the partner molecules of complex formation due to $XFN \rightarrow F \ldots A$ fluorine bridges [14] indicates greater activity by the lone pair of electrons at the nitrogen atom than by that at a fluorine atom.

Hence, although also acting as a weak base, difluoramine is capable of forming donor–acceptor bonds. The complexes thus formed are probably capable of sometimes acting as activated complexes, the formation of which can follow irreversible reactions between donor and acceptor atoms (for example, in the formation of $ClNF_2$).

According to Craig, the initial stage in the formation of chlorodifluoramine from difluoramine and boron trichloride is either the formation of a hydrogen bond:



or simple weakening of the NH bond, owing to a decrease in the electron density at the nitrogen atom:



Craig's results about the capability of difluoramine to give complexes with Lewis acids disagree with the statement of Lawton and Weber [5], who formulated their conclusions without reference to temperature interval. Craig's careful investigation showed that Lawton and Weber's conclusion about the absence of complex formation between difluoramine and Lewis acids can be correct apparently only at temperatures above 0°.

The activating role of the complex formation stage between difluoramine derivatives and Lewis acids is also shown in the dehydrofluorinations of alkyldifluoramines with BF_3, BCl_3, and PF_5. [14]

According to Craig, the first stage of the process here is the formation of complexes of the type $RNF_2.BX_3$, where R = CH_3 or C_2H_5, and X = F or Cl:

$$R'CH_2NF_2 + BX_3 \rightleftharpoons R'CH_2NF_2 \cdot BX_3, \quad \text{(III)}$$

$$R'CH_2NF_2 \cdot BX_3 \longrightarrow R'CH{=}NF + HF + BX_3,$$

$$R'CH{=}NF + BX_3 \rightleftharpoons R'CH{=}NF \cdot BX_3,$$

$$R'CH{=}NF \cdot BX_3 \longrightarrow R'C{\equiv}N + HF + BX_3. \quad \text{(IV)}$$

In citing this scheme of dehydrofluorination and unambigously considering that complex formation is brought about by the lone electron pair of the nitrogen atom, Craig contradicts some of his own observations and conclusions. The infrared spectra of the complexes of the alkyldifluoramines with Lewis acids, according to Craig's own statement, are quite complex and he did not succeed in interpreting them with sufficient certainty. In assuming that the complexes have the structure $RF_2N:BX_3$ he relied to a great extent on argument by analogy, and not on the infrared spectroscopic data.

The ease with which the complexes of the alkyldifluoramines with Lewis acids undergo irreversible decomposition with loss of hydrogen fluoride from the alkyldifluoramine molecule and the absence of a capacity for dehydrofluorination from the complexes of these Lewis acids with difluoramine enables the following propositions to be advanced.

Where difluoramine is concerned, the complexes with Lewis acids are, as Craig has shown sufficiently conclusively, formed by the lone electron pair of the nitrogen atom, but the dissociation of these complexes at elevated temperatures leads to the establishment of the reversible equilibrium considered above (with the exception of the special example of that with boron trichloride).

According to Craig's own results, the complexes of methyldifluoramine and ethyldifluoramine with boron halides and phosphorus pentafluoride are stable at temperatures below -100° and at higher temperatures "decompose irreversibly"

TABLE 3. Some characteristics of the equilibria $HNF_2.A(solid) \rightleftharpoons HNF_2(gas) + A(gas)$.

A	Expression for $\ln K_{equil}$	ΔH, kcal mole^{-1}	Note
BF_3	$-\frac{10566}{T} + 54286$	20.97	$K_p = \frac{p^2}{4}$
SO_2	$-\frac{6291.2}{T} + 35978$	12.50	

with the formation of hydrogen fluoride and the corresponding nitrile. Hence the use in Eqns. (III) and (IV) of the equilibrium sign between the left and right sides is incorrect. It is more logical to assume that in the alkyldifluoramines, when R is a hydrocarbon radical, owing to the electron donor properties of the latter the electron density at the nitrogen atom rises, as Craig observed, which naturally activates the lone electron pair at the nitrogen atom and also favours an increase in the Lewis basicity of the fluorine atom:

$$R\rightarrow\overset{\cdot\cdot}{N}F\rightarrow F:.$$

Together with steric hindrance which the alkyl radical of the Lewis acid molecule inevitably creates in its tendency to bind the lone pair of electrons of the nitrogen atom, this circumstance apparently leads to the formation of alkyldifluoramine complexes, due to fluoride bridges:

$$RCH_2\rightarrow\underset{F}{N}\rightarrow F:\ +\ )BF_3\longrightarrow RCH_2{-}NF{-}F:)BF_3,$$

and not due to the lone pair of electrons of the nitrogen atom, as occurs with difluoramine.

The decomposition of this complex when the temperature is raised leads to loss of a fluorine as a BF_4^- ion from the Lewis acid:

$$RCH_2{-}FN\rightarrow F:BF_3\longrightarrow RCH_2{-}\overset{+}{N}F+BF_4^-.$$

The cation which is formed is stabilised by the elimination of a proton and conversion into a molecule of an *N*-fluoroimine:

$$R{-}\underset{H}{\overset{H}{C}}{-}\overset{+}{N}F\longrightarrow RCH{=}NF+H^+.$$

Subsequently, this process is repeated using hydrogen atoms at the α carbon atom, leading eventually to the formation of nitriles. The presence of hydrogen atoms at the carbon atom next to the difluoramine group is evidently proof of the condition of dehydrofluorination of the alkyldifluoramines by the Lewis acids, so that trifluoromethyldifluoramine, for example, is only very weakly associated with boron halides and no chemical reaction occurs between them [14].

The above treatment of the mechanism of dehydrofluorination is confirmed by Baum's results [33]. By studying the interaction of certain alkyldifluoramines with concentrated sulphuric acid and boron trifluoride, he showed that the process passes through the stage of formation of an *N*-fluoroiminium ion owing to the initial loss of a fluoride ion from the molecule of the difluoramine derivative:

$$R'CH_2NF_2+H_2SO_4\longrightarrow\left[RCH{=}\overset{+}{N}\begin{matrix}H\\F\end{matrix}\right]\cdot HSO_4^-+HF.$$

When R′ = CH_3, Baum observed the intermediate stabilisation of the *N*-fluoroiminium ion by conversion into a molecule of an *N*-fluoroimine, which, on undergoing further dehydrofluorination by the same mechanism, was converted finally into acetonitrile:

$$\left[CH_3CH{=}\overset{+}{N}\begin{matrix}H\\F\end{matrix}\right]\xrightarrow{-H^+}CH_3CH{=}NF\xrightarrow{-HF}CH_3C{\equiv}N.$$

Baum also observed the formation of an *N*-fluoroiminium ion in other examples. When the number of carbon atoms in the radical exceeded two, a rearrangement occurred instead:

$$(CH_3)_3CNF_2+BF_3\longrightarrow\left[\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!=\!\overset{+}{N}\!<\!\begin{matrix}F\\CH_3\end{matrix}\right]\cdot BF_4^-,$$

$$C_3H_7CH_2NF_2\xrightarrow{H_2SO_4}\left[CH_2{=}\overset{+}{N}\begin{matrix}F\\C_3H_7\end{matrix}\right],$$

$$C_2H_5(CH_3)CHNF_2\xrightarrow{H_2SO_4}\left[CH_3CH{=}\overset{+}{N}\begin{matrix}F\\C_2H_5\end{matrix}\right].$$

It is also necessary to note that complex formation with Lewis acids should bring about a redistribution of the electron density in the molecule of the difluoramine derivative in the direction of its depletion at the atoms which do not participate in complex formation and increase at the atom responsible for the formation of the complex. Consequently the formation of complexes with alkyldifluoramines due to the electron lone pair of the nitrogen atom should be not facilitated, but hindered by the loss of the fluoride ion, that is, dehydrofluorination, and on the contrary, complex formation due to a fluorine bridge should promote this process, as Craig also observed.

If difluoramine could form complexes with Lewis acids through fluorine bridges, then it is probable that the ready formation of fluorazene and subsequently difluorodiazine also, would be observed, which is not so:

$$HNF_2+BF_3\longrightarrow\begin{matrix}H\\F\end{matrix}\!\!>\!N\rightarrow F:)BF_3\longrightarrow\overset{+}{H}NF+BF_4^-,$$

$$H\rightarrow\overset{+}{N}F\longrightarrow\overset{+}{H}+\overset{\cdot}{N}F\longrightarrow N_2F_2$$

The complex formation by difluoramine with alkali metal fluorides, established by Lawton and coworkers [11], is well known. These investigators found that potassium, rubidium, and caesium fluorides (with an activity rising from potassium to caesium) form with difluoramine molecular complexes of 1 : 1 composition, $MF.HNF_2$ (similar to the complexes of difluoramine with the dialkyl ethers [5,19]), which decompose at even low temperatures to form the two isomers of difluorodiazine and hydrogen fluoride:

$$MF+HNF_2\longrightarrow MF\cdot HNF_2\longrightarrow MF\cdot HF+\tfrac{1}{2}N_2F_2.$$

On the basis of this reaction they have patented [35] what is perhaps the simplest and most convenient of the known methods for obtaining N_2F_2, in which the difluorodiazine is formed in almost quantitative yield and almost without impurities.

The activity of the alkali metal fluorides in this reaction rises in the sequence:

$$LiF\ll NaF<KF<RbF<CsF.$$

Careful investigation by the same authors [11] of the ability of metal fluorides to form complexes with difluoramine showed that NaF, CaF_2, and NiF_2 do not form complexes with difluoramine at -80° and below, but the complexes $KF.HNF_2$ and $RbF.HNF_2$ dissociate reversibly at elevated temperatures (from -60° to -30°). The equilibria for complexes with potassium and rubidium fluorides are characterised by the data given in Table 4.

The complex $CsF.HNF_2$ readily exploded at elevated temperatures; therefore none of the investigators has studied it in detail [11,13].

TABLE 4. Some characteristics of the equilibria[11] $MF.HNF_2$(solid) ⇌ MF(solid) + HNF_2(gas).

MF	Expression for $\log K_{equil}$	ΔH, kcal mole^{-1}
KF	$-\frac{1467}{T}+7784$	6.7
RbF	$-\frac{2166}{T}+10338$	9.9

Dubb and coworkers have made a detailed study of the structure of the complexes $MF.HNF_2$ by infrared spectroscopy[13]. They found that potassium and rubidium fluorides form complexes with difluoramine mainly by hydrogen bonds set up between the hydrogen atom of the difluoramine molecule and the nucleophilic atom of the fluorine atom of the alkali metal fluoride (complex of type A):

$$M^+F^- \cdots \overset{\delta+}{H}\text{—}\overset{\delta-}{NF_2}.$$

Such a structure for the complexes of difluoramine with the alkali metal fluorides agrees well with the above series[11,35] for their relative tendencies to complex formation; it can also be taken as the series for the relative nucleophilicity of the fluorine atom in the fluorides, or the series for increasing electropositivity of the alkali metals.

Dubb and coworkers[13] consider that the explosive nature of the complex of caesium fluoride with difluoramine is due to the formation of the difluoramide anion NF_2^- in the complex, the existence of which they have demonstrated quite thoroughly. They think that caesium fluoride forms two types of complexes with difluoramine, one of which is identical in structure with the complexes which are formed by potassium and rubidium fluorides (type A) and the other is an ionic complex (type B): $Cs^+FH.NF_2^-$, which is responsible for the explosive nature of the adduct.

Unfortunately the authors were unable to obtain quantitative relations between the forms A and B. Possibly the explosive nature of this complex is due not only to the existence of form B, but also to the energy effect of the change of the adduct from form A to form B, that is, by the heat of the reaction:

$$\underset{\text{form A}}{Cs^+F^-\cdots\overset{\delta+}{H}\text{—}\overset{\delta-}{NF_2}} \xrightarrow{t^\circ} \underset{\text{form B}}{Cs^+\cdot HF\cdot NF_2^-} + Q.$$

For the complexes with potassium and rubidium fluorides, because of the lower electropositivities of the potassium and rubidium atoms compared with the caesium atom the nucleophilicity of the fluorine atom is insufficient for the realisation of the transformation of form A into form B.

Lawton and coworkers[11] found that the dehydrofluorination of difluoramine with formation of N_2F_2 isomers can be successfully effected also by aqueous solutions of potassium fluoride.

Thus when a 25% aqueous solution of potassium fluoride with pH 8.6 is used at room temperature, difluorodiazine can be obtained in 75% yield. The authors express the process by the equation:

$$2F^- + 2HNF_2 \longrightarrow 2HF_2^- + N_2F_2.$$

When the nucleophile is not F^- but OH^- in the form of standard buffer solutions with pH 8.0 and 9.0, difluorodiazine is formed in 25% yield.

There is a basis for supposing that this equation can be considered as the overall expression for a difluorodiazine formation process from difluoramine of at least four stages in which the nucleophilic attack:

$$B: + \overset{\delta+}{H}\text{—}\overset{\delta-}{NF_2} \longrightarrow B: \cdots HNF_2,$$

is equivalent to the formation of a type A complex in the solid phase as a result of this attack, that is, the formation of the anion NF_2^-:

$$B:\cdots H\text{—}NF_2 \longrightarrow NF_2^- + B\cdot H^+,$$

is equivalent to the transformation of a type A complex into a type B complex, with the sole difference that in the solid phase the latter is rigidly fixed, but in water it is completely dissociated into its constituent ions. Subsequent decomposition of the difluoroamide anion leads to the formation of difluorodiazine:

$$F\leftarrow\bar{N}F \longrightarrow F^- + \dot{N}F,$$

$$(\text{or } M^+ + F\text{—}\bar{N}F \longrightarrow M^+\cdots F\text{—}\bar{N}F \longrightarrow MF + \dot{N}F),$$

$$2\dot{N}F \longrightarrow N_2F_2.$$

Here M^+ is an alkali metal cation, for example potassium, etc., and B^- an anion, for example F^-, OH^-, etc.

Such a treatment is the more firmly based in that the existence of the NF_2^- anion in aqueous solutions was shown quite distinctly first by Word and Wright[36] and then by Martin[9] in their electrochemical and polarographic investigations. The latter also showed that the stability of aqueous buffer solutions of difluoramine falls with rise in temperature and pH and the decomposition products are difluorodiazine and nitrogen monoxide, the appearance of which should precede the formation of fluorazene $\dot{N}F$ due to the destruction of the anion NF_2^-:

$$NF_2^- \longrightarrow F^- + \dot{N}F.$$

Johnson[37] made analogous observations on the decomposition of aqueous solutions of *NN*-difluorourea by aqueous alkalis below 0°, when he obtained difluorodiazine, tetrafluorohydrazine, dinitrogen monoxide, etc. By using ^{15}N-labelled urea he showed that difluorodiazine is formed by an intermolecular process, the decomposition of the difluoroamide anion playing an important part:

$$NF_2^- \longrightarrow NF + F^-,$$
$$NF + NF \longrightarrow N_2F_2,$$
$$NF + NF_2^- \longrightarrow N_2F_2 + F^-,$$
$$NF + H_2NCONF_2 \longrightarrow N_2F_2 + CO_2 + NH_4^+ + F^-$$

The facts of the formation of fluorazene or fluoronitrene $\dot{N}F$ were discussed both in the investigations of the decomposition of the electron-excited radical $^*NF_2$[26,33,38-41] and also in studying the reaction of difluoramine with primary and secondary amines[40,42,43], which we will discuss below.

The promoting action of alkali metal fluorides (potassium, rubidium) in the chlorination of difluoramine by elemental chlorine is also known[12]:

$$MF:\cdots \overset{\delta+}{H}\text{—}\overset{\delta-}{NF_2} + Cl_2 \longrightarrow ClNF_2 + MF\cdot HCl.$$

Complexes of difluoramine with alkali metal fluorides, just like the complexes with Lewis acids, can evidently play the part of activated precursors in the reaction of the difluoramine.

These facts show that the polarisation of the nitrogen–hydrogen bond in the difluoramine molecule is sufficiently

strong for the hydrogen atom in it to be capable not only of complex formation with certain nucleophilic reagents due to hydrogen bonds, but also to be lost as a proton, so that difluoramine in aqueous solutions is a weak acid[9,36], but one which does not give salts with silver and copper nitrates even in alkaline media[5].

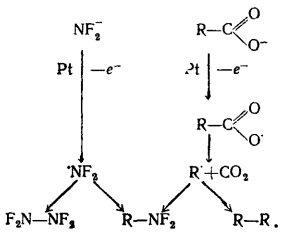
As well as complex formation, and often because of it in more complex reactions, difluoramine is capable of entering into a whole series of redox reactions.

The tendency of difluoramine (or more precisely, the difluoramide ion) to be oxidised is most clearly seen in the electrochemical preparation of tetrafluorohydrazine from it[36], when the process is localised at the stage of transfer of one electron from the anion to the platinum electrode:

$$NF_2^- \xrightarrow[\text{Pt anode}]{-e^-} \cdot NF_2.$$

Further oxidation in the electrochemical process seems impossible, thanks to the ready recombination of the difluoramine radicals to give the stable tetrafluorohydrazine molecule[36], which slowly leaves the electrolyte. This process was investigated in detail by Word and Wright[36]. It was found that the oxidation of difluoramine is possible only in acidified solutions (perchloric, sulphuric, or acetic acids) and is essentially inhibited by the presence of an oxide film on the electrode surface.

The electrochemical oxidation of difluoramine at a platinum anode can be successfully combined with the electrochemical (anodic) generation of free radicals[36]. Here, in the vicinity of the electrode, various radicals are formed in ratios which depend on the concentrations of the initial substances, and the recombination of which leads to the formation of organic difluoramine derivatives:



In the electrolysis of aqueous solutions of difluoramine in acetic, propionic, or completely deuterated acetic acids in the presence of sodium acetate, yields not below 60% of the methyl-, ethyl-, and trideuteromethyl-difluoramines were obtained in this way.

The chemical oxidation of difluoramine to tetrafluorohydrazine is easily effected by the action on aqueous solutions of HNF_2 of such oxidants as bromine, perchloryl fluoride, and oxygen[5], and also by iron(III).[9] However, the oxidation of difluoramine by an excess of oxygen-containing oxidants goes further and nitrogen oxides appear among the reaction products.

The oxidation of difluoramine to tetrafluorohydrazine with iron(III) or electrochemically seemed so effective that these processes were recommended by the authors as the best means for obtaining completely pure N_2F_4 in high yields ($\lesssim$ 70%[9,35]).

The electrochemical reduction of difluoramine at a dropping mercury electrode at various pH was first studied by Martin[9] polarographically: the reduction of difluoramine proceeds only in acid medium at potentials more negative than -1.0 V relative to the standard calomel electrode. He established that in aqueous solutions there is a single-stage, four-electron process.

Subsequently Ward and coworkers[20] showed that the electrochemical reduction of difluoramine at a dropping mercury electrode in water, methanol, ethanol, acetonitrile, dimethylformamide, and dimethyl sulphoxide goes to ammonia at potentials from -1.23 to -1.64 V relative to the standard calomel electrode, depending on the nature of the solvent and base electrolyte, for which various perchlorates were used:

$$HNF_2 + 4e^- + 2H^+ \longrightarrow NH_3 + 2F^-.$$

The authors proposed a mechanism for this process and considered the influence of solvation on the half-wave potential for the reduction of difluoramine.

The typical and most studied example of the chemical reduction of difluoramine is its reaction with acidified aqueous solutions of hydrogen iodide and potassium iodide, which goes instantly and quantitatively according to the equation[4,5]:

$$HNF_2 + 4HI = 2I_2 + NH_4F + HF,$$

and is therefore used analytically for the quantitative determination of difluoramine. Nitrogenous products of the reaction (other than ammonia) are not formed in this reaction.

The capacity of the difluoramine molecule for both oxidation and reduction evidently governs its ready disproportionation under the action of various agents, according to the equation[4,5]:

$$5HNF_2 \longrightarrow 2N_2F_4 + NH_4F + HF.$$

The process is catalysed by various solid substances, among which copper, stainless steel, urea, and lithium hydride[5] can be singled out for special activity, the reaction often going explosively.

The reaction between difluoramine and hydrogen chloride in the gas phase evidently proceeds by the same mechanism[16,44]

$$3HNF_2 + 3HCl \longrightarrow 2ClNF_2 + NH_4Cl + 2HF,$$

as does that between difluoramine and carbonyl dichloride[5]:

$$3HNF_2 + COCl_2 \longrightarrow 2ClNF_2 + \text{side products}.$$

The temperature interval 100–200° is optimal for the last reaction, but even at a high temperature tens of hours are needed for the reaction. Thus at 110° $>$ 40 h are needed to complete the reaction, and at 200° $\lesssim$ 6 h. It is emphasised[44] that the ratio of reagents must be in accordance with the above equation. The use of an excess of carbonyl dichloride favours the completion of the reaction and increases the yield of chlorodifluoramine.

The authors note[5] that despite the production of chlorodifluoramine by this means in 80% yield, the reaction is not always reproducible and is accompanied by the formation of tetrafluorohydrazine. Although the mechanism of this reaction remains unexplained, it is suggested that in the first stage hydrogen chloride is formed, which on being further contacted with difluoramine forms chlorodifluoramine by the above equation for gas-phase reaction.

The liquid-phase modification of the reaction of difluoramine with hydrogen chloride is important in practical respects[16]; it makes it easy to obtain chlorodifluoramine in yields of up to 67%. The ability of difluoramine to form complexes with water sharply reduces the explosion hazard

of the process. The reaction is carried out in aqueous solution using an alkali metal chloride and elemental chlorine, and undoubtedly proceeds by an ionic mechanism in which the decisive role belongs to the difluoramide ion on the one hand, and to chlorine or a residue of hypochlorous acid on the other:

$$NF_2^- + Cl_2 \longrightarrow ClNF_2 + Cl^-, \text{ or}$$
$$NF_2^- + OCl^- \longrightarrow ClNF_2 + O^{2-}.$$

This is the more correct in that the reaction of aqueous solutions of hypochlorous acid and sodium hypochlorite with *NN*-difluorosulphonyl diamide react quite vigorously even in the cold and this is accompanied by the formation of chlorodifluoramine in 71% yield[31]:

$$H_2N{-}SO_2{-}NF_2 + ClO^- \longrightarrow ClNF_2 + \bar{O}SO_2NH_2.$$

An analogous reaction has been described[15] in which aqueous solutions of sodium hypochlorite react with aqueous solutions of *NN*-difluorourea, when the oxidation products are chlorodifluoramine and tetrafluorohydrazine:

$$H_2N{-}CO{-}NF_2 + ClO^- \longrightarrow ClNF_2 + N_2F_4.$$

There is also an example[29] of the production of dichlorofluoramine and chlorodifluoramine by the oxidation of mono- and di-*N*-fluoroalkyl carbamates by aqueous solutions of sodium hypochlorite:

$$FHN{-}COOR \xrightarrow[H_2O]{NaClO} \left[\begin{matrix} F \\ \diagdown \\ N{-}COOR \\ \diagup \\ Cl \end{matrix}\right] \xrightarrow{NaClO} Cl_2NF,$$

$$F_2N{-}COOR \xrightarrow[0-5^\circ]{NaClO} ClNF_2 + R{-}COONa.$$

Most of the known reactions of difluoramine cited above are reactions with inorganic substances. For almost all of these, reaction at high rates under conditions which favour the formation of the difluoramide anion are characteristic.

Considering difluoramine as a possible raw material for the preparation of various nitrogen fluorides it is easy to note that to obtain the desired result it is not always necessary to isolate the free difluoramine in a pure form. Either pure difluoramine or its aqueous solutions can be used for this purpose with the same success, and so also can aqueous solutions of difluoramine derivatives in which the NF_2 group has the character of an acid halide. On this basis, tetrafluorohydrazine, difluorodiazine, and chlorodifluoramine can be prepared with high yields.

There are only two examples of the interaction of difluoramine with organic compounds. Stevens and Freeman found[17] that gaseous difluoramine with solutions of alkyl or aryl nitroso-compounds in a mixture of pyridine and methylene chloride (15 : 75 ml) at 0–20° gave the corresponding alkyl- or aryl-*N'*-fluorodi-imide *N*-oxides:

$$RNO + HNF_2 \xrightarrow[0-20^\circ]{\text{pyridine} + CH_2Cl_2} R{-}\overset{\uparrow O}{N}{=}NF.$$

This reaction has been carried out on a series of nitroso--compounds, where R = phenyl; *o*-, *m*-, and *p*-tolyl; *o*- and *p*-chlorophenyl; *p*-bromophenyl; *p*-nitrophenyl; t-butyl; 2-nitro-2-propyl; 2-chloro-2-propyl; trifluoromethyl; benzyl; 2-phenylethyl; and cyclohexyl.

Simultaneously Stevens and Freeman showed that the same result can be obtained when gaseous tetrafluorohydrazine is used instead of difluoramine to react with solutions of nitroso-compounds in methylene dichloride, chlorobenzene, or carbon tetrachloride.

The last circumstance, with the known fact of tetrafluorohydrazine formation during the action of pyridine on difluoramine[5], led the authors to conclude that in both instances the formation of *N'*-fluorodi-imide *N*-oxides occurs by the very same mechanism proposed earlier by Frazer and coworkers[45] who effected a gas-phase photochemical reaction between trifluoronitrosomethane and tetrafluorohydrazine and first isolated trifluoromethyl--*N'*-fluorodi-imide *N*-oxide:

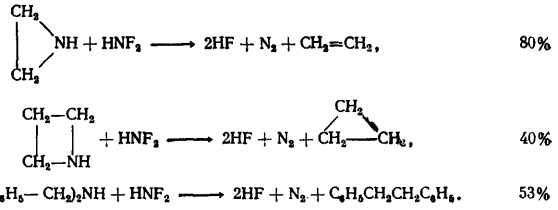
$$CF_3{-}\overset{\uparrow O}{N}{=}NF$$

Bumgardner and coworkers[42] showed that difluoramine, when condensed in a glass apparatus with an excess of an aromatic or aliphatic primary or secondary amine, deaminates the latter and gives the corresponding alkanes:

$$3RNH_2 + HNF_2 \longrightarrow 2RNH_2{\cdot}HF + N_2 + R{-}H.$$

The yield of RH reaches 77%.

With some secondary amines the reactions are:



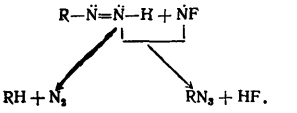
The authors explain the reaction with primary amines by the intermediate formation of a mono-substituted di-imide RN=NH. They consider that initially the amine promotes the α-elimination of hydrogen fluoride by the difluoramine, with formation of fluorazene:

$$RNH_2 + HNF_2 \longrightarrow RNH_2{\cdot}HF + \dot{N}F.$$

The electrophilic fluorazene in the excess of amine attacks the latter to form monosubstituted di-imide:

$$RNH_2 + \dot{N}F \longrightarrow RN{=}NH + HF,$$

which, by eliminating the nitrogen, gives an alkane, or by acting as a "trap" for the fluorazene, eliminates hydrogen fluoride and gives an alkyl azide, which was also found among the reaction products:



With t-butylamine only ammonia and 2-methylpro-1-ene were found in the reaction products; they are formed also by the action of hydrogen chloride on this amine, which the authors take to be evidence of the acidic nature of difluoramine in relation to the amines.

Bumgardner and Freeman investigated the same reaction with certain allyl- and cyclopropylcarbinyl-amines‡ [43]. Here they observed some novelty in the reaction due rather to the unsaturated nature of the hydrocarbon radicals than to the specific effects introduced by the difluoramine. As in the previous investigation, difluoramine mainly acted as a deaminating agent.

‡ Sic. Diallyl-, allyl-, crotyl-, and 1-cyclopropylethyl-amine were studied (Ed. of Translation).

The summary of the facts given in the present review covers those reactions of difluoramine which were known up to the end of 1966. There is no doubt that the diverse reaction capabilities of difluoramine have hardly been investigated, for completely understandable reasons; in relation to different organic substances it will have many unexpected and interesting reactions, which will give a deeper understanding of the nature of this extremely interesting compound and enable the nature of the processes in which it takes part to be formulated more reliably.

5. EXPLOSIVE PROPERTIES OF DIFLUORAMINE

All the authors cited in this review without exception consider it their duty to warn readers about the extreme hazard of working with nitrogen fluorides in general and with difluoramine in particular. This danger consists in the fact that independently of the state of aggregation, difluoramine tends to spontaneous explosive decomposition for unknown reasons. Mixtures of difluoramine, like other nitrogen fluorides, with the vapours of organic substances also form explosive hazards. It is difficult to state which of the states of aggregation of difluoramine is the most dangerous but there are many indications that difluoramine itself is particularly dangerous in the solid form.

Lawton and Weber [5] note that: "... Difluoramine is extremely shock sensitive as a liquid, and even more so as a solid. The liquid is at least as detonable as nitroglycerine. The solid will detonate spontaneously when a large quantity is frozen by liquid nitrogen".

In special experiments Lawton and Weber observed over ten instances of explosion following condensation of difluoramine in quantities of 50 mg or less by liquid nitrogen, that is, at temperatures of ~ -196°. The explosions took place in the first few seconds after the trap with the difluoramine was removed from the bath of liquid nitrogen. However, they were successful more than 100 times in condensing without explosion more than 1 g difluoramine at -142° with a melting methylcyclohexane bath.

All the investigators think that at temperatures down to -142° difluoramine is comparatively harmless; they are all unanimous in the inadmissability of cooling it below this temperature and categorically forbid the use of liquefied gases (particularly liquid nitrogen) as cooling agents.

It has also been maintained [16,19] that aqueous solutions of difluoramine [16] or its solutions in ethers [19] have considerably less tendency to explode and are comparatively harmless. Nevertheless, Word and Wright [36] observed some instances of the explosion of electrolysers when the space above the aqueous electrolyte containing dissolved difluoramine communicated freely with the atmosphere. When the free space was purged with dry inert gas, they succeeded in subsequently avoiding the troubles associated with the explosion of the cells. Apparently there is also a hazard from explosions on contact of the purge gas from concentrated solutions of difluoramine with the air.

The reason for the high tendency of difluoramine to spontaneous explosive decomposition probably lies in the wholly amphoteric nature of its molecule and the dual nature of its reactivity to redox interaction. This opens a path to intermolecular disproportionation, which is also accompanied by such highly exothermic processes as the formation of hydrogen fluoride, elemental nitrogen, and nitrogen trifluoride. The activation of this process is apparently very small and can be greatly reduced by the catalytic action of various solid substances. The initial impulse can be produced either inside the system by effective catalysis, or externally by an action of accidental origin. Subsequent processes probably develop autothermically and possibly also autocatalytically.

Instances of the remarkable explosive decomposition of difluoramine after cooling below -196° should be placed in a special category. Undoubtedly such behaviour of difluoramine is connected with some energetic effects which take place inside or on the surface of the crystals of solid difluoramine. It is not ruled out that the reason for this phenomenon lies in the ionic structure of the crystal lattice of solid HNF_2, although Craig [14] also did not succeed in observing any essential difference in the infrared spectra of gaseous and solid difluoramine at -196°.

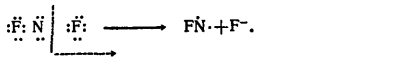
Here infrared spectroscopy cannot give the necessary information for a categorical decision as to the absence of ionisation from solid difluoramine. Just the fact of the similarity of the absorption frequencies for gaseous and solid difluoramine in the infrared region cannot serve as sufficient proof of the absence of a change of difluoramine into an ionic state at ~ -196°. One of the explanations of this important phenomenon can be a useful subsequent approach, which follows logically from the discussion in Section 2 of the present review.

In the liquid state equilibrium (I) is apparently almost wholly displaced to the left, that is, to the side of the molecular form of the dimer. The rigid fixation of the ions NF_2^- and $[H_2NF_2]^+$ at the nodes of the crystal lattice which is a consequence of deep cooling rules out the possibility of a change of the ionic form of the dimer into the molecular form and greatly facilitates the displacement of equilibrium (I) to the right. This change, under a suitable regime of cooling and crystallisation (which is evidently realised at -196° and below, but more correctly in attaining these temperatures) ends the almost complete fixation of the difluoramine as an ionic dimer. On raising the temperature the change of the difluoramine into the liquid state should be accompanied by intensive association of the ions into the molecular form of the dimer with a perceptible thermal effect.

The energy liberated is evidently sufficient to surmount the low activation barrier and start the process of rapid autothermal (possibly, also autocatalytic) decomposition of difluoramine, which is explosive in nature.

The many statements of various authors on the instability of the difluoroamide anion and the ease with which it decomposes into fluoronitrene and the fluoride anion have been given above. In all the instances of such decomposition conditions were created for suppressing the dissociation of difluoramine with formation of the NF_2^- ion (increase in the pH of the aqueous difluoramine solutions above 7, heating them, the action of ionising complex-forming agents, such as potassium fluoride, rubidium fluoride, and especially caesium fluoride, etc.). Therefore there are grounds for assuming that explosion in the processes in which difluoramine participates (because of the explosive decomposition of the latter) should be expected in those instances when conditions are created for the formation of high concentrations of difluoramido-anions in the absence of conditions for their recombination into stable molecules of the $X-NF_2$ type, in which the X–N bond will have a more covalent character than the H–N bond in difluoramine.

The NF_2^- ion is a species limitingly saturated with electrons, which should stimulate its tendency to stabilisation, leading to a decrease in this saturation, by the elimination of a fluoride anion:



Depending upon the conditions (the presence or absence of solvents and catalysts) the temperature, the difluoramine concentration, pH of the medium or basicity of the reagent, etc.) the process can proceed either quietly (for example, in aqueous alkaline solutions or under the action of potassium and rubidium fluorides) or explosively (for example, in pure difluoramine or upon reaction with caesium fluoride).

It cannot be excluded that the existence of the difluoramide anion for a sufficiently prolonged period outside the molecule of difluoramine, adducts, transition states, etc. (that is, not in a bound state) is impossible in general.

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ACIDITY FUNCTIONS OF AQUEOUS SOLUTIONS OF STRONG ACIDS

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