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THE NITROGEN FLUORIDES AND SOME RELATED COMPOUNDS

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I. Introduction

The nitrogen fluorides were completely unknown until 1928, when Ruff, Fischer, and Luft prepared the trifluoride by electrolysis of molten acid ammonium fluoride, $NH_4F \cdot HF$ (*257*). Since then three other binary compounds of these two elements have been isolated, namely difluorodiazene (N_2F_2), tetrafluorohydrazine (N_2F_4), and fluorine azide (N_3F). In this article the chemistry of these four binary fluorides will be described, together with that of the related compounds difluoroamine (HNF_2), chloro- and bromodifluoroamine ($ClNF_2$, $BrNF_2$), and trifluoroamine oxide (NF_3O). Our aim has been to give the reader a broad picture of advances in this field, and no attempt has been made to cover the literature completely (*132*). This is particularly true of the earlier work on nitrogen trifluoride, which was reviewed in 1962 (*154*). The very extensive topic of organic compounds has also been excluded, except insofar as it relates to the use of tetrafluorohydrazine and HNF_2 and $ClNF_2$ as synthetic reagents.

II. Nitrogen Trifluoride, NF_3

In the original preparation of the trifluoride Ruff and his co-workers electrolyzed molten $NH_4F \cdot HF$, which was contained in a copper pot and held at 125°C, just at the melting point. The anode was a carbon rod and the cathode an open-ended copper bell inserted into the melt and surrounding the insulated anode. The gas evolved was a mixture of H_2 and NF_3 containing small amounts of fluorocarbons arising from attack on the anode and also oxides of nitrogen, oxygen, and ozone, due to the presence of water in the electrolyte. Some HF was also carried over. This was removed by means of KF, after which the trifluoride was isolated by vacuum fractionation. Ruff showed that electrolysis of the solution of $NH_4F \cdot HF$ in anhydrous hydrogen fluoride (AHF) gave only fluorine at the anode. He may have failed to detect NF_3. Ruff's method is still used in producing the trifluoride technically on a small scale, though it has been modified in detail, especially as regards cell design and the composition of the electrolyte. There is much information on this subject in the patent literature that will not be reviewed here.

At first sight the direct fluorination of ammonia might appear to be a useful alternative method for obtaining the trifluoride, but this reaction, if uncontrolled, yields mainly nitrogen and hydrogen fluoride with only about 6% of NF_3 (*258*). The yield is greatly improved when the fluorine is diluted with N_2 and this gas is allowed to mix with ammonia in a reactor packed with copper turnings (*212*). Under these conditions the reaction is moderated to such an extent that the temperature in the reactor may rise by as little as 20°C. With excess of fluorine, yields of NF_3 in the range 40–60% are obtained.

$$4NH_3 + 3F_2 \xrightarrow{N_2} NF_3 + 3NH_4F$$

When ammonia is in excess, yields of NF_3 are 10–25% and the product contains up to 10% of N_2F_4 and 5% of N_2F_2, together with a small amount of difluoroamine, HNF_2.

Closely related to the above is a new process (*301*) in which ammonia and fluorine are passed into a reactor containing $NH_4F \cdot HF$ at slightly above its melting point (125°C). Under these conditions the molten salt serves to moderate the reaction, which is essentially that between the two gases. It is claimed that the trifluoride produced is of high purity, and this appears to be an alternative to the electrolytic method for preparing the gas on a technical scale.

Direct synthesis of NF_3 from nitrogen and fluorine was not effected until 1964, when Maya obtained yields up to 30% on passing an N_2–F_2 mixture at a pressure of 20–40 mm through an electric discharge in a tube cooled to −196°C (*207*). This method is similar to that used in the synthesis of oxygen fluorides from the elements (*144, 259*), except that in the latter case different oxygen fluorides are produced by changing the stoichiometry of the mixture of reactants, whereas with N_2–F_2 mixtures only NF_3 results.

The trifluoride is formed in various other reactions, though none appear to be of preparative value. Thus it results, together with OF_2 and NOF, in the electrolysis of a solution of N_2O in AHF (*248*). It has also been claimed that NF_3 and NOF are formed in the reaction between N_2O and F_2 at temperatures in excess of 100°C (*203*). The trifluoride is likewise produced in the reaction of many nitrogen-containing organic compounds with fluorine or a reactive fluoride such as CoF_3. Electrochemical fluorination may also be used, the electrochemical fluorination of pyridine in AHF, for example, yielding undecafluoropiperidine as the main product together with substantial amounts of fluorocarbons and of NF_3 resulting from breakdown of the pyridine molecule during reaction (*273*).

A. PHYSICAL PROPERTIES

The boiling point of nitrogen trifluoride is −129°C and its melting point −206.8°C. Because of its potential technical uses, thermal and other physical properties have been studied in detail (*300*), though they will not be considered here.

The molecule is pyramidal, having C_{3v} symmetry with the nitrogen atom at the apex. The molecular dimensions have been determined by electron diffraction (*266*) and by microwave spectroscopy (*161, 271*). The molecule with this symmetry will have four fundamental vibrations allowed, both in the infrared (IR) and the Raman spectra. The fundamental frequency assignments in the IR spectrum are 1031, ν_1 (A_1); 642, ν_2 (A_1); 907, ν_3 (E); and 497 cm^{-1}, ν_4 (E). The corresponding vibrations in the Raman spectrum appear at 1050, 667, 905, and 515 cm^{-1}, respectively (*8, 223, 293*). The vacuum ultraviolet spectrum has also been studied (*177*). The ^{19}F NMR spectrum of NF_3 shows a triplet at 145 ± 1 ppm relative to CCl_3F with $J_{NF} = 155$ Hz (*146, 216, 220, 249, 280*).

The dipole moment of nitrogen trifluoride (0.234 *D*) is much smaller than that of ammonia (1.42 *D*), though the structures are very similar. One explanation of this apparent anomaly is that in the trifluoride the moment associated with the positive nitrogen atom and its lone pair of electrons is opposite in direction to the moment along the same axis associated with the three N–F bonds. In ammonia the polarities are reversed and the moments due to the N–H bonds and to the electron pair on nitrogen operate in the same direction (*154*).

The heat of formation of NF_3 is -132.08 ± 1.13 kJ mol^{-1}, compared with 232 kJ mol^{-1} for NCl_3. The value for NF_3 was determined calorimetrically using the following two stoichiometric reactions (*5, 273*):

$$NF_3(g) + \tfrac{3}{2}H_2(g) = \tfrac{1}{2}N_2(g) + 3HF(aq)$$
$$NF_3(g) + 4NH_3(g) = 3NH_4F(c) + N_2(g)$$

In the first of the reactions, measured amounts of the trifluoride with excess of hydrogen were ignited over water in the bomb calorimeter. The mean N–F bond energy derived from the heat of formation was 277.8 ± 3.3 kJ mol^{-1}. From the heat of formation of NF_2 and the heat of atomization of F_2, together with the heat of formation of NF_3, the value of D (NF_2–F), i.e., the energy required to split off the first of the three fluorine atoms, was found to be 238.4 ± 10.5 kJ mol^{-1}. From this it follows that the mean dissociation energy for the remaining two N–F bonds must have the higher value of 297 kJ mol^{-1} (*69*).

B. CHEMICAL PROPERTIES

There has been a great revival of interest in nitrogen fluoride over the last decade because of its potential applications as a high-energy oxidizer for HF–DF chemical lasers, where it can replace elemental fluorine in the reaction with hydrogen. It has also been claimed as a potential rocket fuel, and there is also a growing interest in the oxidizing power of other compounds with N–F bonds in the same connection. At first sight this may appear inconsistent with the apparent chemical inertness of the trifluoride with substances such as H_2, CO, CH_4, H_2S, and a range of hydrocarbons, which has led to its classification with other inert fluorides such as CF_4 and SF_6. In all such cases reaction is in fact favored thermodynamically but is prevented at ambient temperatures by the kinetic stability of the system. Only when the necessary activation energy is provided by heating (or by an electric spark) does reaction occur for NF_3, and then it may be explosive. Temperatures in the range 200–350°C usually suffice to initiate such reactions; the trifluoride then behaves as a strong oxidizing and fluorinating agent.

Few of the reactions of nitrogen trifluoride with inorganic substances have been described. The reaction with hydrogen is referred to above, and it has been found that the flammability limits for NF_3–H_2 mixtures are 9.4–95% NF_3 (*300*). The trifluoride oxidizes I_2 to IF_5 at 300°C and SbF_3 to SbF_5 at 250°C. The reaction with Cu to give N_2F_4 takes place at 450°C, while with As, Sb, and Bi somewhat lower temperatures suffice (see below). As already mentioned, the value of $D(NF_2{-}F)$, the energy required to break the first of the three N–F bonds, is about 238.5 kJ mol^{-1}, and this would be provided by heating to the temperatures at which reaction is observed. There have been several investigations of the thermal dissociation of the trifluoride over a wide temperature range (*87, 102, 200*).

When NF_3 is exposed to water vapor, there is no reaction, but on sparking the mixture a reaction takes place which is accompanied by a blue flame, the products being HF, NO, and NO_2. The fluoride also resists hydrolysis by aqueous acid or alkali at room temperature, but it is decomposed by the former at 130°C and by the latter at 100°C. Complete breakdown to NH_3, F^-, and N_2 occurs with aqueous KI solution.

A few other inorganic reactions have been investigated. At 700°C there is a reaction with P_4N_3 which yields $(PNF_2)_3$ and $(PNF_2)_4$ (*201*). In the reaction with P_4S_3 and P_4S_{10} at 330–360°C, the products are PF_3 and PSF_3, but at 180–215°C a mixture of phosphonitrilic fluorides $(PNF_2)_n$ ($n = 3$–9) is also obtained (*282*). Heating red phosphorus with NF_3 yields $[F_3P(NPF_2)_2NPF_3]PF_6$ as well as $(PNF_2)_3$, PF_3, and PF_5 (*282*). The donor properties of NF_3 are very weak, an unstable adduct being formed with BCl_3 below −100°C and with BF_3 at −125°C (*77*). NF_3 forms a clathrate hydrate with H_2O (*81*). Nitrogen trifluoride behaves as a powerful fluorinating agent when it reacts with organic substances, and only with perfluorinated molecules are products containing N–F bonds sometimes found. Thus, for example, in the reaction of NF_3 with hexafluoropropene at 510°C in the presence of NaF, the main products are *iso*-C_3 to C_6 fluorocarbons and fluorocarbon imines, while with C_3F_6 in presence of CsF at 320°C, $(CF_3)_2CFCF(CF_3)_2$, $(CF_3)_2CF(NF_2)$, and $(CF_3)_2C{=}NF$ are formed (*90*). With CF_3CN and NF_3 at 520°C in the presence of CsF the following reaction occurs (*21*):

$$NF_3 + CF_3CN \xrightarrow{520°C} CF_3NF_2 + (CF_3)_2NF + CF_3N{=}CF_2 + (CNF)_3$$

Such reactions occur only at elevated temperatures and, from the scanty evidence available, appear to yield mixtures of products so that their use in synthesis seems unlikely. The role of the alkali metal fluorides has not been explained.

With molten sulfur between 350 and 400°C, NF_3 gives good yields of NSF and SSF_2, demonstrating that it is a source of nitrogen as well as fluorine (*130*). At elevated temperatures either in a flow system or under pressure, its mode of behavior with nonmetal oxides is one of fluorination, e.g., $B_2O_3 \rightarrow BF_3$, $SiO_2 \rightarrow SiF_6$, $CO \rightarrow COF_2 \rightarrow CF_4$, $CO_2 \rightarrow CF_4$, $P_2O_5 \rightarrow POF_3 \rightarrow PF_5$, $SO_2 \rightarrow SOF_2$, or $SO_2F_2 \rightarrow SF_6$, $SO_3 \rightarrow SO_2F_2 \rightarrow S_2O_5F_2 \rightarrow (NO)_2(S_2O_5F_4)$, and $SeO_2 \rightarrow SeOF_2 \rightarrow SeF_6$. Depending on the stoichiometry, some N_2F_4 may form when NF_3 is reacted with SO_2 (*129*).

NF_3 on thermal activation with F_2 and Lewis acids is a source of NF_4^+ salts (see below).

III. The Tetrafluoroammonium Ion, NF_4^+

The terms "tetrafluoroammonium," "perfluoroammonium," "tetrafluoronitrogen(V)," and "tetrafluoronitronium" have been used to describe NF_4^+. Most authors prefer to call this the tetrafluoroammonium ion. The polarity of the bond is NF_4^+ is different from that in NH_4^+; for NF_4^+ the nitrogen atom has a formal oxidation state of +5. NF_4^+ salts are important for solid propellant NF_3–F_2 gas generators or reagents for the electrophilic fluorination of aromatic compounds.

The isolation for the first time in 1966/1967 of salts of the coordinatively saturated fluorocation NF_4^+ has proved to be a milestone in this branch of fluorine chemistry. Other fluorocations of this type are ClF_6^+ (*38, 245*) and BrF_6^+ (*128*). All can be prepared from the appropriate lower fluoride (NF_3, ClF_5, or BrF_5) by oxidation under conditions which will be described more fully later in the case of NF_3. Nitrogen pentafluoride, from which the NF_4^+ cations could, in principle, be formed by reaction with a fluoride ion acceptor, is unknown and unlikely to exist, as the nitrogen atom lacks the orbitals necessary for its formation. An early theoretical discussion of the possible existence of NF_4^+ also led to the conclusion that the ionization potential of nitrogen is too high and the size of the carbon is likely to be too large to provide the lattice energy necessary for stable salt formation (*240*). This does not, however, exclude the possibility that such a salt might exist under certain conditions because of its kinetic stability, even if it were thermodynamically unstable, and this has proved to be the case.

Two independent groups were responsible for the original discovery of tetrafluoroammonium salts, both basing the synthesis on the reaction of NF_3 with fluorine in the presence of a strong Lewis acid, which acts as a fluoride ion acceptor:

$$NF_3 + F_2 + xF_n \longrightarrow NF_4^+[xF_{n+1}]^-$$

The activation energy was provided in one case by heating the reactants and in the other by passing them through a glow discharge.

The thermal reaction was discovered by Tolberg, Rewick, Stringham, and Hill in 1966 (*283*). Equimolar quantities of NF_3, F_2, and SbF_5, together with AHF, were heated in a Monel metal tube reactor at 200°C/150 atm, the reactor having been previously exposed to ClF_3 to passivate its surface against attack by fluorine. At the conclusion of the reaction, residual volatile material (NF_3, F_2, HF) was removed and a hygroscopic white crystalline solid, NF_4SbF_6, remained, the yield, based on the SbF_5 taken, being almost quantitative.

$$NF_3 + F_2 + SbF_5 \xrightarrow[\text{AHF}]{200^\circ\text{C}} NF_4SbF_6$$

It was shown later that the reaction took place equally well in the absence of HF and that SbF_5 could be replaced by SbF_3, which is easier to handle (*295*). The hexafluoroarsenate, NF_4AsF_6, was prepared similarly using a reaction temperature of 125°C. In the reaction with SbF_3, a polyfluoroantimonate with the approximate composition $NF_4Sb_2F_{11}$ is formed if lower reaction temperatures are employed, but it is readily converted to NF_4SbF_6 by heating at 250–260°C under a dynamic vacuum (*57*). In these preparations the product may be contaminated by $Ni(SbF_6)_2$ and $Cu(SbF_6)_2$, which result from attack on the reactor. These two salts can be removed by dissolving the tetrafluoroammonium salt in AHF, in which the metal salts are very sparingly soluble, and by filtering through a Teflon filter of special design. The difficulty of synthesizing NF_4^+ salts from NF_3, F_2, and Lewis acid increases with decreasing strength of Lewis acid.

The second of the original preparations of a tetrafluoroammonium salt was also described in 1966 by Christe and his co-workers (*46*). A 1:1:2 mixture of NF_3, F_2, and AsF_5 at a pressure of not greater than 80 mm was allowed to stream through a glow discharge in a tube cooled to −78°C, and it was found that a white solid deposited on the cold surface as the reaction proceeded. That this was a hexafluoroarsenate was first shown from bands in the infrared spectrum, and it was later fully characterized as NF_4AsF_6. The properties of the salts isolated in these early investigations are described more fully later.

Subsequent preparative work in this field has been of two types, the first involving oxidative fluorination of NF_3 by fluorine and other reagents and the second involving the use of metathetical or replacement reactions, i.e., the preparation from one salt of a second containing a different anion. Several new compounds have been prepared by the method used originally for NF_4SbF_6. Thus, when NF_3, F_2, and TiF_4 were heated together at 190°C under an autogeneous pressure of 160 atm, a polyfluorotitanate with the approximate composition $NF_4Ti_6F_2$ resulted (*48*). Similar polyfluorotitanates, and also $(NF_4)_2TiF_6$, may be prepared by metathetical or displacement reactions (see later), and it has also been shown that salts of the polyanion may be obtained from the reaction between $(NF_4)_2TiF_6$ and TiF_4. The hexafluorobismuthate, NF_4BiF_6, was prepared similarly from BiF_5 (*57*). At 175°C a polyfluorobismuthate results, and this loses BiF_5 at a higher temperature, giving NF_4BiF_6:

$$NF_3 + F_2 + (n+1)BiF_5 \xrightarrow{175^\circ C} NF_4BiF_6 \cdot nBiF_5$$

$$NF_4BiF_6 \cdot nBiF_5 \xrightarrow{280^\circ C} NF_4BiF_6 + nBiF_5$$

An alternative preparative method is available in this instance also (see later). The hexafluoroplatinate NF_4PtF_6 is formed in high yield when PtF_6 is treated with a large excess of NF_3 and F_2 at 125°C under an autogeneous pressure of about 140 atm (*65*). A less pure sample was obtained by oxidizing a mixture of NF_3 and PtF_6 with a KrF^+ salt (see later).

PHOTOCHEMICAL SYNTHESIS OF NF_4^+ SALTS

Several tetrafluoroammonium salts have been prepared by irradiating a mixture of NF_3, F_2, and a Lewis acid with ultraviolet light, which effects the activation process needed for reaction to occur. The mechanism is believed to involve initial cleavage of the fluorine molecule to atoms, which then undergo the following sequence of reactions (*55*):

$$\begin{aligned} F_2 &\xrightarrow{h\nu} 2F\cdot \\ F\cdot + NF_3 &\rightleftharpoons \cdot NF_4 \\ \cdot NF_4 + MF_n &\rightleftharpoons NF_3^+[MF_{n+1}]^- \\ NF_3^+[MF_{n+1}]^- + F\cdot &\rightleftharpoons NF_4MF_{n+1} \end{aligned}$$

Thermal dissociation of the weak F–F bond in F_2 [$D°(F_2) = 153.97$ kJ mol^{-1}] (*287*) can be brought about equally well by heating to temperatures above roughly 120°C, so that a similar mechanism could operate in those reactions where purely thermal activation is used. The N–F bond in NF_3 is considerably stronger [$D°(NF_2{-}F) = 238.5$ kJ mol^{-1}], and for it to be involved in the thermal activation process considerably higher temperatures would be required. There is strong electron spin resonance (ESR) evidence for the intermediate formation of the NF_3^+ radical cation (*45, 134, 211*).

Photolysis by ultraviolet light has been used in the synthesis of NF_4SbF_6, NF_4AsF_6, NF_4BF_4, NF_4PF_6, and NF_4GeF_5 from mixtures of NF_3 and F_2 with SbF_5, AsF_5, BF_3, PF_5, and GeF_4, respectively (*50, 54*). Some of these compounds may be prepared by other methods, but use of the thermal activation method may be restricted by the low thermal stability of the required product, whereas ultraviolet irradiation can be carried out at a low temperature. In the case of NF_4BF_4, for example, the salt is stable only to about 150°C, and it cannot be prepared by the thermal reaction between NF_3, F_2, and BF_3. The photochemical method is very similar to that used in the synthesis of some dioxygenyl salts, the compound $O_2^+GeF_5^-$, for example, being formed when a mixture of O_2, F_2, and GeF_4 is irradiated with ultraviolet light at −78°C (*56*).

There is a single report of the use of 3-MeV bremsstrahlung from a Van de Graff source for preparing the tetrafluoroborate, which, in fact, was first obtained in this way (*133*) from NF_3, F_2, and BF_3. These were irradiated at −196°C and, after removing any excess of the volatile reactants, NF_4BF_4 remained as a white crystalline solid. The compound is, however, much more conveniently prepared by the glow discharge method (as already described) or, better, by irradiation of the reactants with ultraviolet light as already described. A metathetical reaction may also be used (see p. 150).

In the course of this investigation a suspension of 4 mmol of NF_3 and 24 mmol of F_2 was also irradiated at −196°C without the addition of BF_3. When material volatile at −160°C was subsequently pumped away, a small amount of white residue remained which disappeared as soon as the temperature was raised to −130°C. Nitrogen trifluoride was evolved at this stage. The white residue also reacted with added BF_3 to form NF_4BF_4. Hydrogen fluoride was rigorously excluded from the system and the authors suggested that the unstable material might be the ionic fluoride $NF_4^+F^-$, which is much more likely to form than the covalent pentafluoride NF_5. Later experiments on the ultraviolet photolysis of NF_3–F_2 mixtures at −196°C did not confirm the result, but the observation has not been checked with bremsstrahlung (*50*).

IV. Use of KrF^+ and PtF_6 as Oxidative Fluorinating Reagents

The oxidative fluorination of NF_3 with a KrF^+ salt in place of elemental fluorine was first reported by Artyukhov and Khoroshev in 1977 (*6*). Stoichiometric amounts of NF_3, KrF_2, and Lewis acid (SbF_5, NbF_5, PF_5, TiF_4, or BF_3) were allowed to react at room temperature. Alternatively, the preformed solid salt $KrF^+SbF_6^-$ was reacted with NF_3 at a pressure of 1 atm. In each instance the corresponding tetrafluoroammonium salt resulted, though yields were not reported. The products were identified by their vibrational spectra and also by chemical analysis. Krypton was liberated in the reaction, e.g.,

$$NF_3 + KrF_2 + AsF_5 \longrightarrow NF_4AsF_6 + Kr$$

The formation of NF_4^+ salts by this method was discovered independently by Christe and his co-workers, though their results were first published considerably later (*65*). Mixtures of NF_3, KrF_2, and either AsF_5 or BF_3 in stainless-steel cylinders were allowed to warm from −196 to 55°C and, after 2 days at the higher temperature under an autogenous pressure of ~75 atm, the yields of NF_4AsF_6 and NF_4BF_4 were 97 and 30%, respectively. These authors also studied some of the other reactions reported earlier. With solid $KrF^+SbF_6^-$ and NF_3, or with these two reactants in HF solution, $NF_4Sb_2F_{11}$ was also formed and conditions were found under which the hexafluoroantimonate was the sole product. Salts of a polyanion rather than of TiF_6^{2-} were also obtained from the reaction of NF_3, KrF_2, and TiF_4.

The KrF^+ cation is the most powerful oxidizer known, and attempts were made to fluorinate CF_3NF_2 by means of KrF^+ to produce a salt of the $CF_3NF_3^+$ cation, exactly the same procedure being as is used in the reaction with NF_3. There was, however, no evidence for the formation of $CF_3NF_3^+AsF_6^-$ (AsF_5 being the Lewis acid employed). Instead, the main volatile products were NF_3 and CF_4, the excess CF_3NF_2 decomposing to CF_4 and a mixture of *cis*- and *trans*-N_2F_2. The former reacted further with AsF_5, forming $N_2F^+AsF_6^-$ (see below).

The same authors showed that platinum hexafluoride, which is a somewhat weaker oxidative fluorinating agent than KrF^+, can also oxidize NF_3, though the yield and purity of the NF_4^+ fluoroplatinate formed as a dark red solid were low. The pure salt was prepared for purposes of comparison by the thermal reaction at 125°C between NF_3, F_2, and PtF_6. The reaction between NF_3 and the hexafluoride was carried out either in HF solution at 25°C or under ultraviolet irradiation in the gas phase, also at ambient temperature. In each case the vibrational spectrum of the product showed the presence of a tetrafluoroammonium salt, but the product was a mixture of fluoroplatinate and polyfluoroplatinate which could not be purified by extraction with liquid HF.

Christe and his co-workers discussed the probable mechanism of these reactions, pointing out that the oxidizer strength of the three reagents used for preparing NF_4^+ salts should increase in the order F_2–Lewis acid $< PtF_6 < KrF^+$. This is in keeping with the observation that KrF^+ is able to oxidize NF_3, ClF_5, and BrF_5 to NF_4^+, ClF_6^+, and BrF_6^+; that PtF_6 will fluorinate NF_3 and ClF_5; and that a Lewis acid and F_2 mixture, which is the weakest oxidizer, is able only to oxidize. NF_3. The oxidation potentials of the fluoro cations increase in the order $NF_4^+ < ClF_6^+ < BrF_6^+$.

Christe considers the three mechanisms set out below to be the most probable for the formation of NF_4^+ salts.

Lewis acid and F_2 system

$$\begin{aligned} F_2 &\xrightarrow{\Delta E} 2F\cdot \\ F\cdot + AsF_5 &\longrightarrow \cdot AsF_6 \\ \cdot AsF_6 + NF_3 &\longrightarrow NF_3^+AsF_6^- \\ NF_3^+AsF_6^- + F\cdot\ (\text{or}\ \cdot AsF_6) &\longrightarrow NF_4AsF_6 \end{aligned}$$

PtF_6 system

$$\begin{aligned} NF_3 + PtF_6 &\longrightarrow NF_3^+PtF_6^- \\ NF_3^+PtF_6^- + PtF_6 &\longrightarrow NF_4^+PtF_6^-\cdot PtF_5 \end{aligned}$$

KrF^+ system

$$NF_3 + KrF^+SbF_6^- \longrightarrow [KrF\cdots NF_3]^+SbF_6^-$$
$$[KrF\cdots NF_3]^+SbF_6^- \longrightarrow NF_4^+SbF_6^- + Kr$$

The ionic oxidant (KrF^+) gives an ionic mechanism, whereas the Lewis acid in association with F_2 or PtF_6, which are radical oxidants, results in a radical mechanism. In all the systems the one-electron (Lewis acid–F_2 or PtF_6) or two-electron (KrF^+) oxidizer reacts with the substrate (NF_3). This leads to an electron transfer to the oxidant. Either simultaneously (for KrF^+) or subsequently (for Lewis acid–F_2 or PtF_6), the intermediate radical cation (NF_3^+) is fluorinated to give NF_4^+.

V. Metathetical Reactions

This type of reaction has been used to prepare several new tetrafluoroammonium salts from the hexafluoroantimonate NF_4SbF_6, which is readily produced in the thermal reaction between NF_3, F_2, and SbF_5 at an elevated temperature (see Section III). This salt is allowed to react with the cesium salt of another anion, usually in AHF solution but occasionally in BrF_5. This may be illustrated by the preparation of NF_4BF_4, shown in the following equation (*51*):

$$NF_4SbF_6 + CsBF_4 \xrightarrow[-78^\circ C]{AHF} CsSbF_6 + NF_4BF_4$$

The hexafluoroantimonate is chosen for this type of reaction because $CsSbF_6$ is sparingly soluble in AHF (1.8 mg/g of HF at −78°C) and can be filtered off at the reaction temperature in a specially designed apparatus (*61*). The tetrafluoroammonium salt isolated by evaporating the filtrate can then be further purified by recrystallization from HF or BrF_5.

The acid fluoride NH_4HF_2 may be prepared similarly from $CsHF_2$ in place of $CsBF_4$ (*66*).

$$NF_4SbF_6 + CsHF_2 \xrightarrow[-78^\circ C]{AHF} CsSbF_6 + NF_4HF_2$$

The product contains about 3% of $CsSbF_6$. In the preparation the reactants are stirred for some time in AHF solution at room temperature and cooled to −78°C before filtration. When the solvent is subsequently pumped off from the filtrate at $<0°C$, the solid with the composition $NF_4F \cdot HF \cdot nHF$ remains ($n = 2-60$). This decomposes at room temperature to NF_3, F_2, and HF, and pure NF_4HF_2 cannot be isolated. Its AHF solution is, however, stable at room temperature and may be used in preparing other tetrafluoroammonium salts, as described later.

Salts of several bivalent fluoro anions have been prepared by this simple type of metathetical reaction. Thus $(NF_4)_2TiF_6$ is formed from NF_4SbF_6 and Cs_2TiF_6 in AHF (*48*), and the hexafluoronickelate (*39*) and hexafluoromanganate (*63*) have been obtained similarly.

$$2NF_4SbF_6 + Cs_2NiF_6 \xrightarrow[-78°C]{AHF} (NF_4)_2NiF_6 + 2CsSbF_6\downarrow$$

$$2NF_4SbF_6 + Cs_2MnF_6 \xrightarrow[-78°C]{AHF} (NF_4)_2MnF_6 + 2CsSbF_6\downarrow$$

A further example is the preparation of $(NF_4)_2SnF_6$ (*52*). Such reactions of these salts as are known are described later.

The fluorosulfate NF_4SO_3F is obtained from NF_4SbF_6 and $CsSO_3F$ in AHF solution at room temperature. It is stable in solution at room temperature, but the solid salt decomposes quantitatively under these conditions, as shown below (*58*).

$$NF_4SO_3F \longrightarrow FOSO_2F + NF_3$$

Attempts to prepare the sulfate, $(NF_4)_2SO_4$, and fluorophosphate, $NF_4PO_2F_2$, from the cesium salts of these acids failed because they were solvolyzed by AHF. In the first case the major product was $CsSO_3F$, while the fluorophosphate gave a quantitative yield of $CsPF_6$.

Tetrafluoroammonium perchlorate was obtained from NF_4SbF_6 and $CsClO_4$ in AHF at $-78°C$ and was isolated as a white crystalline solid which decomposed slowly at 0°C and rapidly at 25°C with quantitative formation of NF_3 and $FOClO_3$ (*66*). When the reaction was repeated with $CsBrO_4$ in place of $CsClO_4$, reaction occurred and the presence of a tetrafluoroammonium salt in the AHF solution was shown by the ^{19}F NMR and Raman spectra, but there was slow decomposition at room temperature and the solid perbromate was not isolated. The decomposition products were NF_3, together with $FBrO_2$ and O_2, rather than $FOBrO_3$, which would be expected by analogy with the behavior of the perchlorate. Attempts to isolate solid NF_4BrO_4 resulted in explosions.

$$NF_4BrO_4 \longrightarrow NF_3 + [FOBrO_3] \longrightarrow FBrO_2 + O_2$$

The periodate could not be obtained since the IO_4^- ion solvolyzed in AHF with formation of IF_4O_2, and solvolysis also took place with $CsNO_3$.

$$NO_3^- + 4HF \longrightarrow NO_2^+ + H_2O + 2HF_2^-$$

More recently NF_4BrF_4 and NF_4BrF_4O have been prepared from low-temperature metathetical reactions in BrF_5 solution (*59*).

$$NF_4SbF_6 + CsBrF_4 \xrightarrow[-35°C]{BrF_5} CsSbF_6 + NF_4BrF_4$$

$$NF_4SbF_6 + CsBrF_4O \xrightarrow[-35°C]{BrF_5} CsSbF_6 + NF_4BrF_4O$$

Both are white solids, unstable at room temperature. Thermal decomposition of the two solids follows a different route:

$$NF_4BrF_4 \longrightarrow NF_3 + BrF_5$$

$$NF_4BrF_4O \longrightarrow NF_3 + F_2 + BrF_3O$$

Ionic formulation of both the compounds has been supported from their low-temperature vibrational spectra.

Attempts to prepare $(NF_4)_2SiF_6$ from NF_4SbF_6 and Cs_2SiF_6 also failed because HF displaces SiF_4 from the cesium salt. Negative results were also obtained in experiments on the low-temperature photolysis of an NF_3–F_2–SiF_4 mixture and on the direct thermal reaction between NF_3, F_2, and SiF_4 (*50, 51, 61*). The solvolysis of Cs_2SiF_6 by AHF is due to the fact that SiF_4 is a weaker Lewis acid than AHF. Wilson and Christe showed, however, that the solvolytic reaction is reversible (*296*).

$$Cs_2SiF_6 + 2HF \rightleftharpoons 2CsHF_2 + SiF_4$$

The equilibrium can be shifted completely to the left by using a large excess of SiF_4 and removing the HF evolved. On the basis of this observation the silicofluoride was obtained by first preparing a solution of NF_4HF_2 in AHF by reaction of NF_4SbF_6 and CsF in AHF at −78°C, as already described, and then removing as much AHF as possible without decomposing the NF_4HF_2. The residual material was then repeatedly pressurized with SiF_4, the displaced AHF being pumped off each time with the excess SiF_4.

$$2NF_4HF_2 \cdot nHF + SiF_4 \rightleftharpoons (NF_4)_2SiF_6 + 2(n+1)HF$$

Excess of NF_4HF_2 was allowed to decompose to NF_3 and HF. The purity of the $(NF_4)_2SiF_6$ finally obtained was 95.5 mol%.

The same principle was used in preparing the compounds NF_4UF_7 and NF_4WF_7 from the hexafluorides UF_6 and WF_6, both of which are weak Lewis acids with only a moderate tendency to form the MF_7^- ion. It is for this reason that the two tetrafluoroammonium salts cannot be made by direct synthesis from NF_3, F_2, and the Lewis acid, or indirectly by a metathetical reaction in AHF solution. Repeated treatment of NH_4HF_2 with the hexafluoride, accompanied by removal of the AHF set free, as in the synthesis of $(NF_4)_2SiF_6$, did, however, give the required compounds (*297*) (where X = U, W):

$$NF_4HF_2 \cdot nHF + XF_6 \rightleftharpoons NF_4XF_7 + (n + 1)HF$$

It is also possible to displace the anion from a weak Lewis acid in a tetrafluoroammonium salt by the anion from a stronger acid. Thus, chromium pentafluoride is a strong acid and the stable salt NF_4CrF_6 is produced when excess of a solution of NF_4HF_2 in AHF at 25°C is treated with CrF_5. The yield is quantitative (*25*). The reaction between NF_4BF_4 and SnF_4 is similar, the tin compound being the stronger acid (*52*).

$$NF_4BF_4 + SnF_4 \xrightarrow[-78^\circ C]{AHF} NF_4SnF_5 + BF_3$$

With GeF_4 in place of SnF_4 under the same conditions, a mixture of NF_4GeF_5 and $(NF_4)_2GeF_6$ results (*50*). There is an equilibrium in AHF solution between the penta- and hexafluorogermanates which can be shifted in favor of the latter by treating NF_4GeF_5 with AHF and removing the volatile GeF_4.

Other salts which have been prepared in this way are NF_4PF_6 (from NF_4BF_4 and PF_5) (*50*) and NF_4BiF_6 (from NF_4BF_4 and α-BiF_5) (*57*). The second of these preparations may be carried out either in AHF at 20°C or without a solvent at 180°C. In the previously mentioned direct thermal reaction between NF_3, F_2, and BiF_5, the product is the polybismuthate $NF_4BiF_6 \cdot nBiF_5$, which loses BiF_5 on heating in a dynamic vacuum at 280°C, giving NF_4BiF_6. There is also a displacement reaction between NF_4BF_4 and TiF_4 to form $NF_4Ti_2F_9$ and $NF_4Ti_3F_{13}$, which may be brought about either in AHF solution or by heating the solids together at 170°C (*48*).

The two fluorides AlF_3 and BeF_2 are involatile and polymeric and, therefore, are unsuitable for the direct synthesis of NF_4AlF_4 or a fluoroberyllate by direct reaction with NF_3 and F_2. Attempts to prepare such salts by a metathetical reaction such as that shown below also failed (*62*).

$$Cs_3AlF_6 + 3NF_4SbF_6 \xrightarrow{\text{solvent}} (NF_4)_3AlF_6 + 3CsSbF_6$$

The solvents examined were AHF at −78°C and BrF_5 at 25°C. The reaction of the cesium salt with molten NF_4SbF_6 was also studied. The salts were finally prepared by digesting AlF_3 or BeF_2 at 25°C with a concentrated solution of NF_4HF_2 in AHF, prepared as already described, until a clear solution was obtained. Excess of unreacted NF_4HF_2 was then decomposed to NF_3, F_2, and HF by raising the temperature to 55°C. After removing all volatile material the residue was found to be NF_4AlF_4 or $NF_4Be_2F_5$, together with a little NF_4SbF_6 and $CsSbF_6$. Attempts to purify this material by recrystallization were unsuccessful.

The same type of reaction was used earlier in preparing NF_4WOF_5 from WOF_4 (*298*) and NF_4UOF_5 from UOF_4 (*40*). Both of the oxyfluorides are involatile and polymeric, and their reaction with a concentrated NF_4HF_2 solution proceeds very smoothly. The salt NF_4WOF_5 is a white solid stable up to 60°C. Controlled vacuum pyrolysis at 180°C yielded $NF_4W_2O_2F_9$ together with NF_3, OF_2, and WF_6. The uranium compound NF_4UOF_5 is a yellow crystalline solid which is stable up to about 80°C. The main volatile decomposition products are NF_3, UF_6, and OF_2, and the solid residue contains UOF_4 and UO_2F_2.

NF_4XeF_7, a yellow solid, was prepared from XeF_6 and NF_4HF_2 and was converted to $(NF_4)_2XeF_8$ by selective laser photolysis. Raman spectra of both the compounds confirm the presence of NF_4^+ as well as XeF_7^- and XeF_8^- ions (*60*).

VI. Properties of Tetrafluoroammonium Salts

The tetrafluoroammonium salts are usually colorless crystalline compounds, except for the red compounds $(NF_4)_2NiF_6$, $(NF_4)_2CrF_6$, and NF_4PtF_6, and the yellow compounds $(NF_4)_2MnF_6$, NF_4XeF_7, NF_4UF_7, and NF_4UOF_5. These salts are soluble to different degrees in AHF. BrF_5 is another suitable solvent for some of them. They are extremely hygroscopic but stable at ambient temperature. Hydrolysis of NF_4^+ salts occurs quantitatively according to the following equation (*283*):

$$NF_4^+ + H_2O \longrightarrow NF_3 + H_2F^+ + \tfrac{1}{2}O_2$$

This hydrolysis reaction provides a convenient way to analyze NF_4^+ salts, because NF_3 does not hydrolyze in water. Subsequent studies (*57*) have shown that NF_3 evolution is always quantitative. The amount of oxygen evolved was consistently less than expected for the above equation. It is observed that the balance of oxygen was present at H_2O_2, the formation of which has been explained by initial formation of HOF as an unstable intermediate [$NF_4^+ + OH^- \rightarrow NF_3 + HOF$]. HOF either decomposes [$2HOF \rightarrow 2HF + O_2$] or reacts in a competing reaction with water to give H_2O_2 [$HOF + H_2O \rightarrow H_2O_2 + HF$].

These salts have a thermal stability which depends markedly on the nature of the anions. Salts having oxygen-containing anions decompose at temperature below 100°C, whereas the salts with fluoro-complex anions are much more stable (*24*). Decomposition on heating gives NF_3, F_2, and the Lewis acid. However, the thermal decomposition of NF_4^+ salts containing oxyanions is a useful synthetic route to hypofluorites (*53, 66*). Thermal decomposition of NF_4UF_5O gives UF_6, NF_3, and a small amount of OF_2 as condensable products, whereas the pale yellow residue obtained as a result of photolysis contained UF_4O and UO_2F_2.

The NF_4^+ cation has T_d symmetry. The four normal modes of vibration are classified as A_1, E, and $2F_2$. While all four modes are Raman active, only the $^2F_2$ modes are IR active. Consequently, the two IR bands around 1160 and 610 cm^{-1} are assigned to the triply degenerate antisymmetric stretch and triply degenerate antisymmetric deformation vibrations, $\nu_3(F_2)$ and $\nu_4(F_2)$, respectively. Of the remaining Raman bands, the one with the highest intensity around 810–850 cm^{-1} is assigned to symmetric stretching vibrations, $\nu_1(A_1)$. A Raman band around 440–460 cm^{-1} has been assigned to symmetric deformation vibrations, $\nu_2(E)$. A detailed study of the vibrational spectrum of NF_4AsF_6 and its comparison with $^{15}NF_4AsF_6$ gave for the normal vibrations of $^{14}NF_4^+$ the values $\nu_1 = 848.2$, $\nu_2 = 443.3$, $\nu_3 = 1158.95$, and $\nu_4 = 6.11.15\ cm^{-1}$. For $^{15}NF_4^+$ the same vibrations appear at 848.2, 443.3, 1129.7, and 609.35 cm^{-1} (*41*). The force constant of the N–F stretches of the NF_4^+ ion (6.15 mdyne A^{-1}) is much greater than the force constant 2.15 mdyne A^{-1} for FNO or 4.31 mdyne A^{-1} for NF_3, indicating that the strength of the NF bond in the NF_4^+ ion is unusually high for the nitrogen fluorides. The estimated interatomic distance N–F in NF_4^+ is 124 pm (151.2 pm for FNO and 136.5 pm for NF_3). The anions of the salts have practically no influence on the vibrational spectra of NF_4^+ ion. Additional bands observed in the vibrational spectra of NF_4^+ salts are of low intensity. Their frequencies are too high and intensities are too low for fundamental vibrations. These have been assigned as overtones or combination bands. The splitting observed in some of the degenerate modes and violation of some of the selection rules indicate that the

TABLE I

CRYSTALLOGRAPHIC DATA FOR NF_4^+ SALTS

Compound	Tetragonal unit cell dimensions (pm) a	b	Density (g/cm³)	Reference
NF_4AsF_6	770.0	573.0	2.72	*46*
NF_4SbF_6	790.3	580.6	2.98	*57*
NF_4PF_6	757.7	565.3	2.41	*50*
NF_4BiF_6	800.6	582.1	3.68	*57*
NF_4BF_4	999.4	522.9	2.27	*50*
$(NF_4)_2GeF_6$	692.0	925.0	2.75	*67*
$(NF_4)_2SnF_6$	705.0	941.0	2.93	*67*
$(NF_4)_2TiF_6$	699.0	928.0	2.54	*67*
$(NF_4)_2MnF_6$	690.0	923.0	2.64	*67*
$(NF_4)_2NiF_6$	683.0	927.0	2.71	*37*

actual site symmetry of NF_4^+ in the crystal is actually lower than T_d.

The ^{19}F NMR spectrum of NF_4^+ salts consists of a triplet centered around 210–228 ppm downfield from $CFCl_3$, with $J_{NF} \approx 230$ Hz. The bandwidth at half-height does not exceed 10 Hz, indicating that there is no N–F quadrupole coupling. The existence of this triplet and no other resonance attributable to NF structure shows that all fluorine atoms in NF_4^+ are equivalent and that the structure of the ion is tetrahedral.

X-Ray powder diffraction data of a large number of NF_4^+ salts are described by various workers. The data (Table I) indicate these salts have a tetragonal lattice. Single crystals of 98.9% pure $(NF_4)_2NiF_6$ showed that the compound has a body-centered tetragonal cell, space group $I\,4/m$ (*37*). The salt is made up of octahedral NiF_6^{2-} ions and tetrahedral NF_4^+ cations and has the antifluorite structure. The interatomic N–F distance in the NF_4^+ tetrahedron is 130–140 pm and the F---F distance is ~220 pm.

VII. Trifluoroamine Oxide, NF_3O

There are three oxyfluorides of nitrogen, two of which, NOF and NO_2F, are well known and will not be dealt with here. The third, trifluoroamine oxide, is less familiar and was isolated comparatively recently at roughly the same time by three independent groups. Fox and his co-workers made the compound in 10–15% yield by passing an NF_3–O_2 mixture at a pressure of 10–15 mm through an electrical discharge in a tube cooled to −196°C (*111, 112*). The discharge-tube method was also used in a synthesis reported in the patent literature by Maya (*208*), the reaction mixture being made up of fluorine with either air or an oxide of nitrogen. The products were condensed on a cold surface as before and were separated subsequently by vacuum fractionation. A later preparation (*219*) made use of an N_2O-F_2 mixture.

The other method that led to the synthesis of this compound was entirely different. It was found as a minor product in the course of a study of the reaction of NOF with PtF_6, the main product being $NOPtF_6$. A small yield was also obtained with OsF_6, the main product in this case being $NOOsF_7$. Iridium hexafluoride and NOF, on the other hand, gave a high yield of NF_3O, and it was also obtained, together with an approximately equal amount of NOF, in the pyrolysis of $(NO)_2NiF_6$ (*10–12*).

$$3NOF + 2IrF_6 \xrightarrow{20^\circ C} 2NOIrF_6 + NF_3O$$

$$(NO)_2NiF_6 \xrightarrow{350^\circ C} NF_3O + NOF + NiF_2$$

Observations on the properties of the compound made by these early authors are referred to later.

Several other preparative methods have been published more recently. A good yield of NF_3O is obtained in the reaction between NOF and F_2 in ultraviolet light (*113, 114*). A 1:1 mixture of the two gases was irradiated at ambient temperature and 1 atm pressure in a Monel metal infrared cell with fluorite windows. This was pretreated with the reaction mixture to passivate its surface. The progress of the reaction during irradiation could be monitored by comparing the infrared spectrum of the mixture with that of pure NOF at known pressures. The method is simple to operate and gives yields in the range 20–50%.

The quantum yield on this reaction was shown later to be less than unity (*27*). A low yield of NF_3O has also been obtained from the reaction of a 3:1:1 $F_2-N_2-O_2$ mixture in a microwave discharge (*13*). Other methods for preparing the compound have also been claimed in the patent literature. For example, difluoroamine, HNF_2, will react with ClF_3 and oxygenated halogen compounds such as ClO_2, $FClO_2$, and $FClO_3$ in the presence of an alkali metal fluoride, which acts as a complexing agent with HNF_2, and NF_3O is among the products (*181*). At room temperature and 1 atm pressure difluoroamine will also react with ClF_3O to give a 2:2:1 mixture of NF_3O, $ClNF_2$, and N_2F_4 (*264*). High yields are also claimed from NOF and F_2 in a Monel reactor at 350°C/330 atm (*206*). A further example from the patent literature is the synthesis of NF_3O by the reaction of NF_3 with OF_2, with He as a diluent gas (*110*). Yields of 20–40% NF_3O were obtained by discharging $NF_3 \cdot OF_2$–Ar mixtures (1:1:2) at −183°C (*268*). Low yields of NF_3O have also been obtained in the reaction of F_2NCOF and ClF_3O or UV irradiation of an N_2F_4–ClF_3O mixture (*263*).

PROPERTIES OF TRIFLUOROAMINE OXIDE

The compound is a colorless and highly toxic gas, the boiling point being −87.6°C and the melting point −160°C. Although it is formally the analog of the amine oxides, e.g., $N(CH_3)_3O$, these oxides are formed only by strongly basic amines, whereas NF_3 is almost devoid of basic properties. The amine oxides are also saltlike in character and have high melting points, $N(CH_3)_3O$, for example, melting at 208°C, whereas the low boiling point of NF_3O is a clear indication of covalent bonding in the molecule. The vibrational spectra (*2, 12, 44, 111, 112, 239*) show the molecule to be nearly tetrahedral with C_{3v} symmetry, and this is also consistent with its microwave spectrum (*173*). The ^{19}F NMR spectrum of liquid NF_3O shows a sharp 1:1:1 triplet at $\delta_{CCl_3F} = -363 \pm 2$ ppm with $J_{NF} = 136$ Hz. This shows that the three fluorine atoms are equivalent and in a highly symmetrical environment, as would be expected for an amine oxidelike structure. These spectroscopic properties also exclude the possibility that the compound could be the hypofluorite F_2NOF. *Ab initio* (*221*), electron diffraction (*239*), and photoelectron spectroscopy (*166*) studies on NF_3O indicate substantial delocalization of the oxygen lone pair to form a multiple NO bond.

Trifluoroamine oxide absorbs light in the ultraviolet at $\lambda < 2200$ Å and, when it is irradiated with light of shorter wavelength in an argon matrix, the $\cdot NF_2O$ radical is produced and can be identified by its nine-line ESR spectrum (*285*).

Trifluoroamine oxide begins to decompose at about 300°C when heated in a nickel or Monel reactor, prolonged heating above this temperature giving NOF, NO_2F, NO_2, and NO. It behaves as a strong oxidizing agent toward both organic and inorganic substances. Much of the current interest in the compound arises from its potential use as a liquid oxidizer in a propellant mixture, an example taken from the patent literature being the use of a 12–24% solution of NOF_3 in ClF_5 in conjunction with a variety of common fuels (*1*). It has also been suggested as a freezing-point depressant for NO_2 oxidizers. There is, however, no indication that these are actual rather than potential applications.

As in the case of NF_3 oxidation reactions, it is necessary to provide activation energy to initiate the oxidizing reactions of NF_3O. They do not occur spontaneously at room temperature, even though they are favored thermodynamically. In many instances reaction results in fluorination rather than oxygenation. This is in keeping with the greater strength of the N–O bond, as shown by spectroscopic evidence. The point is illustrated by the following inorganic reactions *(115)*:

$$NF_3O + Cl_2 \xrightarrow{400^\circ C} 2ClF + NOF$$

$$NF_3O + N_2F_4 \xrightarrow{h\nu} 2NF_3 + NOF$$

$$NF_3O + N_2O_4 \xrightarrow{0^\circ C} 2NO_2F + NOF$$

$$NF_3O + SF_4 \xrightarrow{h\nu} SF_6 + NOF$$

NF_3O reacts with nitric oxide, $NF_3O + 2NO \rightarrow 3NOF$. This reaction proceeds essentially quantitatively and is useful for the *in situ* generation of NOF in the preparation of fluorinated nitroso compounds *(171)*.

Other reactions, however, are more complicated. Thus, when a mixture of NF_3O and SO_2 is irradiated with ultraviolet light, the products are SO_2F_2, SOF_4, N_2O, NO, and $NOSO_3F$, together with SiF_4 and $(NO)_2SiF_6$ arising from attack on the glass reaction vessel. Under the same condition CO gave COF_2, CO_2, CF_4, NO_2, SiF_4, and $(NO)_2SiF_6$. Trifluoroamine oxide does not react with water and is decomposed only slowly by strong aqueous alkali at 90°C.

The formation of ionic compounds in the reactions of NF_3O with strong Lewis acids was reported in the initial publications on the compound and studied in greater detail subsequently *(47, 288)*. Loss of a fluoride ion occurs as shown below, as in the reactions of NOF and NO_2F with Lewis acids.

$$NF_3O + MF_n \longrightarrow NF_2O^+[MF_{n+1}]^-$$

The 1:1 compound $NF_2O^+AsF_6^-$ forms readily with AsF_5 at below room temperature, but, under these conditions, SbF_5 yields polyfluoroantimonates. However, with the same reactants in AHF solution at −95°C, the hexafluoroantimonate can be obtained. Two adducts with BF_3 have been isolated. At −126°C in AHF the product is $NF_2O^+B_2F_7^-$, and this loses BF_3 at −95°C to give $NF_2O^+BF_4^-$. In each case the Raman and infrared spectra provide evidence for the ionic structures. The NF_2O^+ cation has a planar trigonal structure like that of CF_2O, with which it is isoelectronic. The dissociation pressure of $NF_2O^+SbF_6^-$ cannot be detected at 25°C, whereas $NF_2O^+AsF_6^-$ has a dissociation pressure of 4 mm at 25°C and zero at 0°C. For $NF_2O^+B_2F_7^-$ at 94.5°C, the value is 180 mm and the extrapolated value for $NF_2O^+BF_4^-$ is 1 atm at −36.6°C. The stability order follows that of acid strengths in the usual way.

Attempts to obtain NF_2O^+ salts with other anions by metathetical reactions have all been unsuccessful. The three salts, $NF_2O^+SbF_6^-$, $NF_2O^+AsF_6^-$, and $NF_2O^+BF_4^-$, were allowed to react with an alkali metal perchlorate, chlorate, or fluorosulfate with AHF, BrF_5, or IF_5 as solvent. The products identified in the first case were ClO_3F and NOF, while with ClO_3^- and SO_3F^- as anions the respective products were ClO_2F and SO_2F_2, together with, in each case, NO_2F. It was also found that, when a solution of $NF_2O^+BF_4^-$ in AHF at −60°C was mixed with KHF_2, 85% of the BF_4^- ion was precipitated as KBF_4. It did not, however, prove possible to isolate $NF_2O^+HF_2^-$. nor was this compound produced in the direct reaction of NF_3O with AHF. Attempts to obtain $NF_2O^+NO_3^-$, which would be a highly energetic solid oxidizer, were also unsuccessful. Very little has been published on the general chemistry of the salts apart from the fact that all react very readily with water, e.g.,

$$NF_2O^+AsF_6^- + H_2O \longrightarrow NO_2^+AsF_6^- + 2HF$$

Trifluoroamine oxide has been found to undergo either an addition or fluorination reactions with certain olefins. It is unreactive toward olefins such as C_2H_4 or C_2F_4 at ambient temperature, and reaction is also not induced by irradiation. With C_2F_4 and C_2F_3Cl at 150°C, however, the main reaction is fluorination rather than addition (*294*). Lewis acids are found to catalyze the addition reactions with olefins C_2F_3X ($X = OC_2F_5$, $OCF_2CF(CF_3)OC_3F_7$, Cl, or Br). There is solely an anti-Markovnikov-type addition to give $F_2NOCF_2CF_2X$. The latter two compounds were formed either in the presence of $NF_2O^+BF_4^-$ at low temperature (−196 to −78°C) or with $NF_2O^+AsF_6^-$ at 55°C, while the ethers have only been reported using AsF_5 (*172*). However, in the case of totally fluorinated allyl-1-olefins, such as C_3F_6 and C_7F_{14}, or with other trifluorovinyl olefins, such as trifluorovinylsulfur pentafluoride and trifluoroacryloyl fluoride, only Markovnikov-type addition is observed to give, e.g., $(CF_3)_2CFONF_2$ with NF_3O in the presence of AsF_5 at 55°C. The orientation of addition can be explained by electrophilic attack of NF_2O^+ on the double bonds: pentafluoroalkenes gave Markovnikov products while perfluorovinyl ethers or halotrifluorovinyl compounds yielded products with the opposite orientation due to the reverse polarity of the double bond.

The yield decreases as the substituent group on the olefin changes from F to Br, with the competing fluorination reaction becoming more significant. When X = I, this is the only reaction.

With $CF_3C{\equiv}CCF_3$ or olefins with an internal double bond such as *cis*- or *trans*-F-2-pentene, F-cyclobutene, or 1,2-dichloro-1,2-difluoroethylene, or with a geminally disubstituted olefin such as 1,1-dichloro-2,2-difluoroethylene, only fully fluorinated products were obtained, likely through a nucleophilic fluorination mechanism. This fact, plus the necessity for a Lewis acid catalyst for addition to proceed, is evidence for an electrophilic addition mechanism. Others have suggested polar addition of BF_3 to the olefin with R_fBF_2 as a reactive intermediate (*294*).

VIII. Salts of Cations of the Type $(NF_xH_{4-x})^+$

The simplest cation of this type would be $(NFH_3)^+$, which should result from the protonation of NFH_2. The latter is, however, unknown, but several salts of the cation have been obtained indirectly by the reaction of an alkyl *N*-fluorocarbamate with a strong acid (*142, 143*).

$$NHFCO_2R + 2HX \longrightarrow NH_3F^+X^- + CO_2 + RX$$

where R = C_2H_5 and i-C_3H_7 and X = SO_4^{2-}, ClO_4^-, $CH_3SO_3^-$ (*143*), and $CF_3SO_3^-$ (*142*), or SO_3Cl^- and SO_3F^- (*210*). Here NH_3F^+ is isoelectronic with CH_3F; both belong to the point group C_{3v}. *Ab initio* MO calculations have been done (*169*). A 1:1 doublet in the ^1H NMR spectrum and a 1:3:3:1 quartet in the ^{19}F spectrum observed in protic acid solutions (*142, 143*) are consistent with the presence of a single F atom with three equivalent H atoms. The ^{14}N shift has also been reported (*205*). IR spectra of the solid salts have been measured (*210*).

The stability of the NH_3F^+ salts is influenced by the acidity of the protic acid and increases in the order $SO_3Cl^- < ClO_4^- < CH_3SO_3^- < SO_3F^- < CF_3SO_3^-$ (*210*). On exposure to a moist atmosphere, the salts undergo hydrolysis (*143, 210*). The NH_3F^+ salts of H_2SO_4 and $HClO_4$ etch glass. Reactions of a sulfuric acid solution of NH_3FHSO_4 with cyclohexanone or *n*-butyraldehyde gave ε-caprolactum or *n*-butyronitrile, respectively, giving additional evidence for the fluorammonium ion structure (*143*).

The perchlorate and methylsulfonate were likewise unstable, decomposing in a few months at room temperature. They were also very sensitive to atmospheric moisture. Both salts melted, with decomposition at 104–105°C. The trifluoromethylsulfonate was more stable, in keeping with the greater strength of the acid, and melted with partial decomposition at 164–165°C. It was sufficiently insensitive to moisture to be handled without the use of a dry box (*142*). It is of interest in this connection that fluorodimethylamine $(CH_3)_2NF$, which is formed with a small amount of CH_3NF_2 in the direct fluorination of unsymmetrical dimethylsulfamide in unbuffered solution at 30°C and is also unstable at ambient temperatures, but forms the salt $(CH_3)_2NFH^+Cl^-$ (mp 64–65°C) with dry HCl (*291*).

A salt of the $(NH_2F_2)^+$ cation is formed when HNF_2 is added at −140°C to AsF_5 and at −196°C to AHF and the mixture is warmed to −78°C. A white solid results which dissolves completely in AHF at 20°C. In the solid state at room temperature decomposition occurs to AsF_5, HF, and N_2, together with some NF_3 and *trans*-N_2F_2 (*42*). There is a similar reaction with SbF_5. The presence of the $(NF_2H_2)^+$ ion in these compounds has been established through their ^1H and ^{19}F NMR and vibrational spectra (*42*). There is no evidence for the existence of $(NF_3H)^+$ salts. Attempts to prepare them by protonation of NF_3 in $HF\text{–}SbF_5$ at −78°C (*42*) or in $HSO_3F\text{–}SbF_5\text{–}SO_3$ at 20°C (*127*), or by direct fluorination of NH_4AsF_6 by F_2 in AHF between −78 and 25°C (*42*), were unsuccessful. However, formation of $NHF_3{}^+$ was observed by ion cyclotron resonance spectroscopy in binary mixtures of NF_3 with CH_4 (*156*). Difluoroamine, HNF_2, gives 1:1 adducts with BF_3, BCl_3, PF_5, or SO_2 at −196°C, all of which decompose well below room temperature. Their infrared spectra provide no evidence for ion formation (*77*).

IX. Difluoroamine, HNF_2

Difluoroamine was reported in 1931 as a minor product in the preparation of NF_3 by the electrolysis of molten $NH_4F\cdot HF$ (*260*), but later work by Kennedy and Colburn (*170*), in which they prepared HNF_2 in low yield by reaction of water-vapor-saturated NF_3 with arsenic at 250°C, gave a product with a boiling point of −23°C, compared with −60°C reported earlier. This casts some doubt on the nature of the material reported initially. Several better preparative methods are now available. A moderate yield results from the reaction of N_2F_4 with AsH_3, which involves hydrogen abstraction from the hydride by the NF_2 radical (see Section XVII,A). There is a 74% yield in the reaction of N_2F_4 with C_6H_5SH, where hydrogen abstraction again occurs (*123*). A similar reaction takes place with aldehydes, e.g., $CH_3C(O)H$ (*234*).

$$2C_6H_5SH + N_2F_4 \xrightarrow{50^\circ C} 2HNF_2 + (C_6H_5)_2S_2$$

$$CH_3C(O)H + N_2F_4 \xrightarrow{150^\circ C} HNF_2 + CH_3C(O)NF_2$$

The reaction between N_2F_4 and alkanes, which occurs at higher temperatures and does not give difluoroamine, is referred to later (see Section XVII,A).

A particularly valuable synthesis of HNF_2 involves the acid hydrolysis of *N,N*-difluorourea, A 2:1 N_2/F_2 mixture is passed into an aqueous urea solution at 0–5°C until the theoretical amount of fluorine has been absorbed. The product is then hydrolyzed by adding concentrated H_2SO_4 and heating to 90°C, the yield of HNF_2 being quantitative (*9, 230*).

$$H_2NCONH_2 \xrightarrow[H_2O]{F_2/N_2} F_2NCONH_2 \xrightarrow[90^\circ C]{H_2SO_4} HNF_2$$

Essentially pure HNF_2 is produced by hydrolyzing (with 1 *N* H_3PO_4 or 1 *N* H_2SO_4) or by heating an aqueous solution of *N,N*-difluorosulfamid (*251*).

$$F_2NSO_2NH_2 + H_2O \xrightarrow{H^+} HNF_2 + HOSO_2NH_2$$

The acid hydrolysis of trityldifluoroamine with H_2SO_4 is also an excellent method (*141*).

$$(C_6H_5)_3CNF_2 + H^+ \longrightarrow (C_6H_5)_3C^+ + HNF_2$$

A. PROPERTIES OF DIFLUOROAMINE

Difluoroamine has a melting point of −116°C and a boiling point of −23.6°C, the high boiling point compared with that of NF_3 (−129°C) being due to hydrogen bonding in the liquid. The structure has been determined from the microwave spectrum (*187*) and also by electron diffraction (*153*). The molecule, like that of NF_3, is pyramidal with $\angle FNF = 102.9^\circ \pm 0.2^\circ$, $\angle HNF = 99.8^\circ \pm 0.02^\circ$, $N{-}H = 102.6 \pm 2$ pm, and $N{-}F = 140 \pm 2$ pm, the dipole moment being 1.93 ± 0.02 *D*. The heat of formation is -67.36 kJ mol^{-1} (*183*). The ^1H NMR spectrum consists of a triplet arising from proton spin–spin coupling with the two equivalent F atoms while the ^{19}F NMR spectrum shows two broad bands associated with spin–spin coupling of the two fluorine nuclei with the single proton (*170*). HNF_2 has C_s symmetry, having six fundamental vibrations. The following fundamental frequencies (in cm^{-1}) and assignments were given (*76*): 3193 (NH St.), 1307 (NH bend), 972 (NF St. sym), 500 (NF_2, def), 1424 (NH bend, asym), and 888 (NF St. asym).

B. REACTIONS OF DIFLUOROAMINE

Difluoroamine is an unstable compound which must be handle with great care since it often explodes spontaneously, especially on freezing or melting. The nature of the explosive decomposition reaction has not been investigated but probably involves the intramolecular elimination of HF. Much of the recent chemistry of the compound relates to its use in the syntheses of organic compounds containing the NF_2 or $=NF$ group and is reviewed briefly later, relatively little being known about the inorganic reactions. It is amphoteric, though the complexes with Lewis acids and bases are not particularly stable and their formation is sometimes irreversible. Craig (*77*) studied the reaction of a number of fluorine-containing nitrogen bases with the Lewis acids BF_3, BCl_3, PF_5, and SO_2 and found the basic strengths to decrease in the order $C_2H_5NF_2 > CH_3NF_2 > CD_3NF_2 > HNF_2 > ClNF_2 > N_2F_4 > CF_3NF_2 > NF_3$. The 1:1 adduct of HNF_2 with BF_3 dissociates reversibly in the range -56–24°C, while the corresponding BCl_3 adduct decomposes at room temperature, $ClNF_2$ being among the products (see Section X) (*232*).

Hydrogen-bonded adducts of the type $M^+F^-HNF_2$ are formed with alkali metal fluorides (M = K, Rb, or Cs), which behave as bases (*92*). Small amounts of difluoroamide complex, $M^+FH \cdot NF_2^-$, may also be present. The potassium and rubidium complexes at room temperature react further to form *cis*- and *trans*-difluorodiazine, $2MF \cdot HNF_2 \rightarrow N_2F_2 + 2MHF_2$. The cesium fluoride adduct explodes before reaching room temperature. The $KF \cdot HNF_2$ complex is also useful as follows (*83*): $R_fC(O)F + KF \cdot HNF_2 \rightarrow R_fC(O)NF_2 + KHF_2$ ($R_f = CF_3$, C_2F_5, C_3F_7, $FC(O)C_3F_6$, F, or CH_3). Perfluoroalkyl hypofluorites react with HNF_2 in the presence of alkali metal fluorides to produce the corresponding $—ONF_2$-substituted perfluoroalkanes (*209*).

Difluoroamine reacts with ClF at low temperature (*238*) according to the equation $HNF_2 + ClF \rightarrow ClNF_2 + HF$. A small amount of N_2F_4 is also formed. Chlorine trifluoride and ClF_5 also react in a similar fashion. Difluoroamine with ClO_3F gives an equimolar mixture of ClO_2F and Cl_2 with a trace of ClF_3 and three compounds containing N–F: NF_3O, $ClNF_2$, and N_2F_4 (*263*).

Reactions of HNF_2 with Organic Compounds

Difluoroamine is one of the most suitable agents for the synthesis of organic difluoroamino and geminal bis(difluoroamino) derivatives of different classes of compounds (*106, 109, 121*).

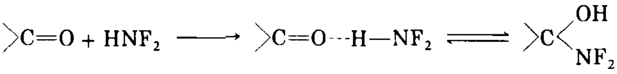
In the presence of protonating agents such as H_2SO_4 or HSO_3F, HNF_2 reacts with alkynes and alkenes to give geminal bis(difluoroamino) and difluoroaminoalkanes, respectively. The addition of HNF_2 occurs according to Markovnikov's rule. The reaction mechanism includes the formation of intermediate carbonium ions which alkylate HNF_2 (*15*).

$$R'C{\equiv}CR'' \xrightarrow{H^+} R'CH{=}C^+R'' \xrightarrow[-H^+]{HNF_2} R'CH{=}C(NF_2)R'' \xrightarrow{H^+}$$

$$R'CH_2{-}C^+(NF_2)R'' \xrightarrow[-H^+]{HNF_2} R'CH_2C(NF_2)_2R''$$

The addition of HNF_2 to olefinic compounds has also been described in the presence of the $BF_3{\cdot}H_3PO_4$ complex (*16*).

In the absence of catalysts, HNF_2 adds reversibly to cyclic and noncyclic aliphatic aldehydes and ketones to produce α-difluoroaminoalcohols: $R'COR'' + HNF_2 \rightleftharpoons R'C(OH)NF_2R''$. These alcohols are prepared by mixing the components at room temperature or below (*122*) in the presence or absence of solvents (*78*). The formation of α-difluoroaminoalcohols follows that of the complex formed by hydrogen bonding.

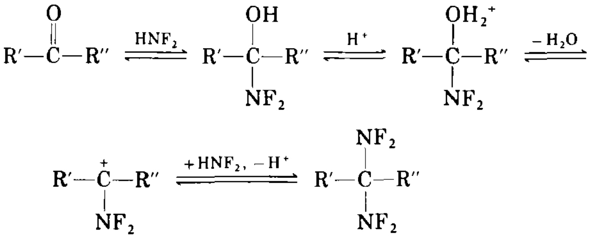


$$>C{=}O + HNF_2 \longrightarrow >C{=}O{\cdots}H{-}NF_2 \rightleftharpoons >C\begin{smallmatrix}OH\\NF_2\end{smallmatrix}$$

In the presence of concentrated or fuming sulfuric acid, cyclic and noncyclic aliphatic ketones react at room temperature with HNF_2 to form *gem*-bis(difluoroamino) derivatives in 60–85% yield (*108, 109*).

$$R'R''C{=}O + HNF_2 \xrightarrow{H^+} R'R''C(NF_2)_2 + H_2O$$

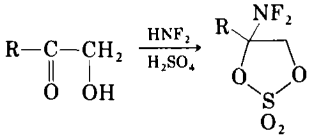
The formation of *gem*-bis(difluoroamino) compounds is considered to be a two-step process whose first step leads to the difluoroaminoalcohol:



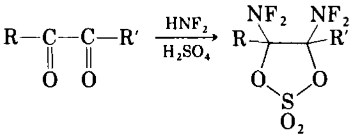
$$R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'' \xrightleftharpoons{HNF_2} R'{-}\underset{\underset{\displaystyle NF_2}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}R'' \xrightleftharpoons{H^+} R'{-}\underset{\underset{\displaystyle NF_2}{|}}{\overset{\overset{\displaystyle OH_2^+}{|}}{C}}{-}R'' \xrightleftharpoons{-H_2O}$$

$$R'{-}\underset{\underset{\displaystyle NF_2}{|}}{\overset{+}{C}}{-}R'' \xrightleftharpoons{+HNF_2,\ -H^+} R'{-}\underset{\underset{\displaystyle NF_2}{|}}{\overset{\overset{\displaystyle NF_2}{|}}{C}}{-}R''$$

The overall reversibility of the process was shown by the recovery of 2-octanone when 2,2-bis(difluoroamino)octane was shaken with H_2SO_4 at room temperature for 1 hr (*17*). In the presence of strong acids, aldehydes (RCHO) react to give bis(α-difluoroaminoalkyl)ethers [$RCH(NF_2)OCH(NF_2)R$, 50–60% yield], and *gem*-bis(difluoroamino)alkanes [$RCH(NF_2)_2$, 20–40% yield] (*108, 109*). The reactions of HNF_2 with α-hydroxyketones and α-β-diketones in fuming sulfuric acid lead to difluoroamino-1,3-dioxa-2-thiolane-2,2-dioxides (*215*).



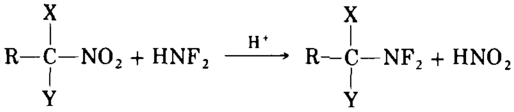
$R = CH_2CH_2C(NO_2)_2CH_3$,
$CH_2CH_2C(NO_2)_3$



$R,R' = CH_3$
$R = C_6H_5$
$R' = CH_3$

HNF_2 reacts with saturated and unsaturated mono- and diacetals at ambient temperature to 100°C (*250*) and also smoothly in the presence of a sulfonic acid ion-exchange resin (Amberlyst-15) (*140, 276*) to give α-difluoroamino ethers (*140*). These compounds react with a second molecule of HNF_2 in the presence of sulfuric acid to give bis(difluoroamino) derivatives (*140*).

Difluoroamine reacts as a weak Lewis acid with ethers to give 1:1 addition compounds, which are thought to be held together by hydrogen bonding (*184*). Their use as rocket propellants has been proposed (180). The 1:1 difluoroamine–diethyl ether adduct formation at −40°C has been proved by ^1H NMR analysis (*107*). HNF_2 reacts with 1,1-dihalo-1-nitroalkanes and 20% fuming sulfuric acid at the reflux temperature of HNF_2 or at ambient temperature for short periods of time to give 1,1-dihalo-1-(difluoroamino)alkanes in 30–60% yields (*18*). Transient blue–purple colorations in the solutions are indicative of nitrosyl difluoroamine formed by the nitrosation of HNF_2.

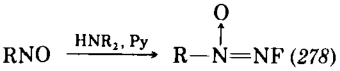


$$R-\underset{Y}{\overset{X}{C}}-NO_2 + HNF_2 \xrightarrow{H^+} R-\underset{Y}{\overset{X}{C}}-NF_2 + HNO_2$$

$R = C_3H_7, X = Y = Cl$ or Br
$= C_2H_5, X = Br, Y = F$
$= C_6H_5, X = Y = Br$

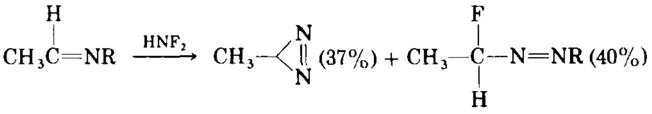
$$HNF_2 + HNO_2 \xrightarrow{-H_2O} F_2NNO \longrightarrow N_2F_4 + NO$$

Reaction of HNF_2 diluted with nitrogen with a nitroso compound in pyridine–dichloromethane solution gives *N*-substituted *N*′-fluorodiimide *N*-oxides (*278*):



$$\mathrm{RNO} \xrightarrow{\mathrm{HNR_2,\,Py}} \mathrm{R{-}\overset{\overset{O}{\uparrow}}{N}{=}NF}\ (278)$$

Difluoroamine reacts with primary and secondary amines to give alkanes (*32*). With imines, a variety of products are obtained depending on the structure of the imine. The three types of compounds obtained are diazirines (I), α-haloazo compounds (II), and α-fluoroalkylidinehydrazines (III) (*138*, *139*). The reaction of HNF_2 with formaldehyde imines or negatively substituted aromatic imines yields diazirines in fair yield as the principal product, whereas with imines derived from aliphatic aldehydes the reaction gives a mixture of the corresponding diazirine derivative and α-fluoroazo compound.



I II

When HNF_2 reacts with imines derived from conjugated aliphatic and aromatic aldehydes, the corresponding α-fluoroalkylidenehydrazines are obtained.

$$C_6H_5CH{=}NR \xrightarrow{HNF_2} C_6H_5CF{=}NNHR\ (62\%) \qquad R = (CH_3)_3CCH_2C(CH_3)_2$$

III

In the presence of pyridine or KF at −40°C, HNF_2 reacts with benzenediazonium fluoroborate to give *o*-fluorophenylazide, *p*-fluorophenylazide, and benzene (*19*).

With azoxybenzene in CH_2Cl_2 in the presence of HSO_3F, HNF_2 reacts at 0°C to give 4-(fluorosulfato)azobenzene (18–55%), 4-amino-4′-(fluorosulfato)azobenzene (16–45%), and 4,4′-diaminoazobenzene (3–10%). Excess of HNF_2 is used in these reactions and a considerable portion of it is oxidized to N_2F_4. The reaction of 3,3′-dichloroazoxybenzene gives analogous results (*277*). Anodic oxidation of HNF_2 produces intermediate NF_2 radicals which react with simultaneously generated alkyl radicals. Electrolysis of HNF_2 in glacial acetic acid gave as the main gaseous product CH_3NF_2. The method was also used to prepare $CH_3CH_2NF_2$ from propionic acid (*289*).

Primary amines on treatment with HNF_2 undergo reductive deamination, resulting in the formation of alkanes (*30, 32*). Optically active 2-phenyl-2-butylamine reacts with HNF_2 to give 2-phenylbutane with 56% net retention of configuration (*29*).

X. Chlorodifluoroamine, $ClNF_2$

Chlorodifluoroamine was first isolated from the products of the thermal decomposition of the 1:1 adduct formed by BCl_3 with HNF_2 at low temperatures (*232, 234*).

$$\begin{tikzcd}
HNF_2 + BCl_3 \arrow[r, "-130^\circ C"] & HNF_2\cdot BCl_3 \arrow[d, "-80 \text{ to } 25^\circ C"] \\
& ClNF_2 + HCl + Cl_2 + BF_3 + BCl_3
\end{tikzcd}$$

The yield is of the order of 50%. Various alternative routes are now available. Difluoroamine, HNF_2, may be chlorinated with gaseous Cl_2 in CCl_4 solution at room temperature (*234*), and there is an 80% yield in the reaction of HNF_2 with aqueous NaClO at 0°C and pH 6.0–6.5. At pH 12 the major product is N_2F_4 while at pH 6–12 both $ClNF_2$ and N_2F_4 result (*185*). A 100% yield of $ClNF_2$ is obtained in the reaction of HClO with HNF_2 in presence of HgO. A good yield also results from the reaction of aqueous HClO with difluorosulfamide, the latter being prepared by passing fluorine into aqueous $S(O)_2(NH_2)_2$ (*182, 192*). It has also been reported that KF or RbF will catalyze the formation of $ClNF_2$ from HNF_2 and Cl_2 (*104*).

Tetrafluorohydrazine can also be converted to $ClNF_2$ by chlorine by ultraviolet irradiation, though the reaction is reversible and a photostationary state is set up. The chlorination can also be effected by irradiation of HNF_2 with $SOCl_2$ (*306*). Difluoroamine is also converted to $ClNF_2$ by reaction with $COCl_2$, HCl (*184*), ClF_3, or ClF (*238*). In the reactions with the two chlorine fluorides very little NF_3 is produced. Chlorodifluoroamine is also a product in the reaction of ClF_3 with NH_4F (*124*) or of the reaction at −50 to −60°C of fluorine diluted with N_2 with a mixture of NaN_3 and NaCl (*7*). Chlorine azide is a likely intermediate in the second of these reactions as F_2 has been shown to react with ClN_3 to give $ClNF_2$. By far the best route to $ClNF_2$ in quantitative yield is the reaction of NF_2OSO_2F with NaCl in dry CH_3CN

(*252, 305*). Quantitative synthesis of $ClNF_2$ has also been achieved by the reaction of HNF_2 with *t*-butyl hypochlorite (*43*).

PROPERTIES OF CHLORODIFLUOROAMINE

Chlorodifluoroamine boils at $-65.9°C$ and melts at $< -190.5°C$. An electron diffraction study (*286*) shows a general resemblance to both HNF_2 and NF_3. The ^{19}F NMR spectrum consists of a single peak at -140.6 ppm (*280*). Later workers found that the ^{19}F NMR spectrum consists of a broadened triplet at -141.5 ppm ($J_{N-F} = 122$ Hz) compared with $+145$ ppm ($J_{N-F} = 155$ Hz) for NF_3 and $+128$ ppm for Cl_2NF (*100, 280, 306*). The compound is thermally stable in Pyrex to 120°C (*26*). On irradiation with light of wavelength < 3000 Å, in which region absorption is continuous, a reversible photochemical decomposition to N_2F_4 and Cl_2 takes place.

The electronegativity of the difluoroamino group is 3.7, which is marginally greater than that of chlorine (3.3) (*157*) and, on this basis, $ClNF_2$ might be expected to behave as a positive halogen compound. There is no evidence, however, that this is so, and solutions in polar solvents do not conduct electricity. As a Lewis base, $ClNF_2$ is intermediate in strength between HNF_2 and NF_3 (*77*).

Very little is known about the inorganic reactions of $ClNF_2$, which is in striking contrast to the less reactive $ClN(CF_3)_2$, which has been very fully investigated (*3*). It is unattacked by 3 *N* aqueous HCl or NaOH. Reaction occurs with Hg to give N_2F_4. Attempts to prepare NF_2NH_2 by the reaction of $ClNF_2$ with NH_3 in alcoholic diglyme were unsuccessful. Addition reactions with unsaturated organic compounds and other organic reactions are referred to later (see Section XVII,B). $ClNF_2$ is easily decomposed to Cl_2 and N_2F_4. However, it reacts with bis(trifluoromethyl) hydroxylamine as

$$(CF_3)_2NOH + ClNF_2 \xrightarrow[CH_3CN]{25°C/10\ min} (CF_3)_2NONF_2$$

The product is thermally unstable at room temperature but is well characterized by low-temperature ^{19}F NMR (*192*). Under controlled conditions $ClNF_2$ forms a 1:1 adduct with AsF_5 at $-78°C$, which at slightly higher temperature decomposes, giving AsF_5, Cl_2, N_2, and NF_3 with smaller amounts of *trans*-N_2F_2, N_2F_4, $N_2F^+AsF_6^-$, and $N_2F_3^+AsF_6^-$ (*64*). Chlorodifluoroamine also reacts at low temperature in CH_2Cl_2 with $[M(CO)Cl(PEt_3)_2]$, where M = Ir or Rh, to give $[M(CO)Cl(PEt_3)_2]NF_2$. The resulting compounds have been characterized by ^{19}F and ^{31}P NMR spectroscopy (*68*).

XI. Other Mixed Halogen Compounds

The dichloro compound Cl_2NF, which is explosive in the liquid or solid state, was prepared by the following reaction (*280*):

$$ClF/N_2 + NaN_3 \xrightarrow{-10 \text{ to } 0^\circ C} Cl_2NF + NaF[+ClNF_2]$$

An alternative reaction is that of ClF with ClN_3 at 25°C or of ClF with NaN_3 in a perfluorinated ether at 25°C. The boiling point lies in the range −10 to 0°C. It is more reactive than Cl_2 and will react with either H_2O or dilute NaOH.

Bromodifluoroamine, $BrNF_2$, may be prepared by the reaction of aqueous bromine with HNF_2 in presence of HgO. It is a colorless liquid with a boiling point of −36°C and decomposes rapidly on warming.

XII. Difluorodiazene, N_2F_2

Difluorodiazenes were first isolated in 1942 by Haller (*148*) as one of the products of the thermal decomposition of fluorine azide, N_3F, which was obtained by reaction of F_2 with HN_3. It was subsequently shown to be produced in many other reactions, some of which are suitable for preparing the compound in quantity. There is a 10–15% yield in the electrolysis of molten acid ammonium fluoride at 125–145°C (*74*). It was in the course of this work that the cis and trans isomers were first isolated from the mixture produced in the electrolysis. The cis form was obtained with >97.5% purity by low-temperature distillation; the *trans* form was obtained by gas chromatography. Electrolysis of a solution of the ammonium salt in AHF yields only the trans isomer (*275*). Small amounts of HNF_2 are formed during the fused salt electrolysis and give rise to an explosion risk during subsequent handling. The difluoroamine may be removed by passing the mixed gases over MnO_2.

Nitrogen trifluoride reacts with mercury vapor in an electrical discharge to give a 15% yield of N_2F_2 (*118*). It is also produced in the reaction at room temperature of an F_2–N_2 mixture with NaN_3 (*246*) or when undiluted F_2 is passed over a mixture of NaN_3 and CaF_2 at 35–45°C; the CaF_2 serves to moderate the reaction (*229*). These reactions probably involve the initial formation of N_3F followed by its decomposition, as in Haller's original experiments referred to previously. Trinitrogen fluoride has also been obtained from NaN_3 and F_2 in a Ni-lined autoclave and was shown to decompose to N_2F_2 and N_2 when heated on a Ni spiral at 75°C (*247*). Decomposition of a 1:1 mixture of

NCl_3 and N_3F on a Ni wire at 120°C has been reported to give the compound $ClN{=}NF$, but details of this work have not been published (*179*).

A convenient preparative route to N_2F_2 is by passing difluoroamine, HNF_2, which is readily prepared (see Section IX), over KF at room temperature, the latter acting as a dehydrofluorinating agent. At −80°C the 1:1 adduct can be isolated.

$$HNF_2 + KF \xrightarrow{-80^\circ C} KF\cdot HNF_2 \xrightarrow{20^\circ C} KHF_2 + N_2F_2$$

Similar 1:1 complexes are formed at low temperature with RbF and CsF but not with NaF, the order of stability being $CsF > RbF > KF > NaF$. The adduct with CsF decomposes explosively on warming to ambient temperature. The yield of N_2F_2 with KF is quantitative when the KF adduct is decomposed. A 75% yield of N_2F_2 is produced with HNF_2 is passed into a 25% aqueous solution of KF. Both isomers are obtained in these reactions (*182*).

When concentrated aqueous KOH is added to an aqueous solution of *N,N*-difluorourea at −10°C, a 40% yield of a 3:1 mixture of the trans and cis isomers is obtained (*162*). A further convenient preparative reaction is that between the *N,N*-difluorocarbamate (NF_2CO_2-*i*-C_3H_7) and potassium *t*-butoxide in a nonaqueous solvent ($C_2H_2Cl_4$). A 3:1 trans–cis mixture results (*174*).

$$F_2NCOO\text{-}i\text{-}C_3H_7 + 2KOC(CH_3)_3 \longrightarrow 2(CH_3)_3COCOOR + N_2F_2 + 2KF$$

Irradiation of a gaseous mixture of N_2F_4 and Br_2 with ultraviolet light gives a 70% yield of N_2F_2 (70% trans) (*305*), and there is a 40% yield of the same isomer when N_2F_4 at a pressure of 15–20 mm reacts with an excess of solid $AlCl_3$ at −80°C (*158*).

Reduction of the 1:2 adduct formed between N_2F_4 and SbF_5 (see below) by reaction with iodine in liquid SO_2 gives the trans isomer in 90% yield (*253*), whereas the pure cis isomer results from reaction of the adduct $N_2F_2\cdot AsF_5$ with NaF in HF (see below) (*214*) or from the decomposition of the adduct $N_2F_2\cdot 2SbF_5$ (see below) at 200°C (*254*). A novel synthesis involves the reaction of N_2F_4 with the first-stage intercalation compound formed by AsF_5 with graphite (*217*) to give a high yield of trans isomer. The authors explain the reaction by postulating initial formation of the salt $N_2F_3{}^+AsF_6{}^-$ (see the latter part of Section XII,C) from which fluorine is abstracted by the graphite.

$$C_{10}AsF_{5+x}\,(\text{blue}) + N_2F_4 \longrightarrow C_{10}AsF_{7+x} + N_2F_2$$

The second- and third-stage compounds, $C_{16}AsF_5$ and $C_{24}AsF_5$, do not react with N_2F_4.

A direct synthesis of N_2F_2 in low yield and admixed with other nitrogen fluorides has been reported from the irradiation of N_2–F_2 mixtures with n-γ-radiation from a nuclear reactor admixed with other high-energy radiation from uranium fission products (*85*). There is also a radiochemical synthesis of N_2F_2 (1.5%) and NF_3 (42%) when an N_2–F_2 mixture is irradiated with 30-MeV electrons in an electron linear accelerator (*86*). Reaction of fluorine diluted with N_2 and NH_3 also gives some N_2F_2 (*159, 213*).

A. PHYSICAL PROPERTIES OF N_2F_2

The spectroscopic and other physical properties of difluorodiazene are reviewed in detail in the "Gmelin Handbook of Inorganic Chemistry" (*132*). Some of the properties are shown in Table II.

Values for the heat of formation were based on calorimetric measurements for the reaction $N_2F_2(g) + \frac{8}{3}NH_3(g) \rightarrow 2NH_4F(s) + \frac{4}{3}N_2(g)$ using mixtures of the isomers in different proportions. The bond lengths and bond angles were determined by electron diffraction (*23*) and microwave spectroscopy (*176*).

B. REACTIONS OF N_2F_2

The existence of two isomeric forms of N_2F_2 was first suggested by Bauer in his early electron diffraction study of the gas (*14*), but, as already mentioned, the two forms were first separated and characterized by Colburn and his co-workers (*74*). The latter showed that there

TABLE II

PHYSICAL PROPERTIES OF DIFLUORODIAZENES

	trans-N_2F_2	*cis*-N_2F_2	Reference
Melting point	−172°C	< −195°C	*74, 265*
Boiling point	−111.4°C	−105.7°C	*74, 265*
Heat of formation	81.16 ± 5.0 kJ/mol	68.62 ± 5.0 kJ/mol	*4*
r(N–N)	123 ± 1 pm	121.3 ± 1.2 pm	*23*
r(N–F)	139.6 ± 0.8 pm	141.0 ± 0.9 pm	*23*
r(N–N)	—	121.4 ± 0.5 pm	*176*
r(N–F)	—	138.4 ± 1 pm	*176*
∠(FNN)	105.5 ± 0.7°	114.4 ± 1.0°	*23*
∠(FNN)	—	114.5 ± 0.5°	*176*

was a reversible equilibrium between the two forms. When mixtures with various initial compositions (2–90% trans) were heated to >225°C, an equilibrium mixture was found; at 285°C, for example, this contained 12.7–13.7% of *trans*-N_2F_2. Later studies gave variable results, but all show equilibrium to be established at much lower temperatures. Thus it is claimed that *trans*-N_2F_2 is essentially quantitatively converted to *cis*-N_2F_2 at below 100°C (*179*). It is likely, too, that the interconversion is influenced by the surface of the containing vessel. Values obtained for the heat of isomerization are also variable but appear to be low (in the range -4 to -12 kJ mol^{-1}), both forms being endothermic.

Decomposition of either form to N_2 and F_2 is appreciable at 100°C and above, *cis*-N_2F_2 decomposing more readily than the trans form, decomposition being rapid at 200°C (*228*). The cis form is also the more reactive form chemically. Colburn and his co-workers showed that *cis*-N_2F_2 reacts more readily with mercury than does *trans*-N_2F_2, and the same is true of the reaction with glass (*74*). Both isomers react with water at >60°C to form N_2, O_2, and HF (*265*). They are stable to nonreducing acids and bases. With a solution of Na in liquid ammonia, reduction to N_2 and NaF is quantitative. There is also a quantitative reaction with an acidic KI solution: $N_2F_2 + 2I^- \rightarrow N_2 + 2F^- + I_2$ (*265*). No addition reactions at the double bond could be observed.

In a number of its reactions, N_2F_2 behaves as a fluorinating or deoxygenating and fluorinating agent. Thus with SO_2 at 100–300°C and at 80–100 atm pressure, the main products are SO_2F_2, SOF_2, N_2O, and N_2 (*194*). The same products are formed under ultraviolet irradiation (*195*). With SF_4 at 100°C the products are SF_6, S_2F_{10}, and N_2, while PF_3 is converted to PF_5 on standing at room temperature, POF_3 giving a mixture of PF_5, N_2, O_2, and N_2O at 85°C. Thionyl fluoride at 100°C is converted by N_2F_2 to a mixture of SOF_4 and N_2.

Colburn and his co-workers found that N_2F_4 appears to catalyze the polymerization of some vinyl and related compounds (*74*), and this observation has been followed up to a certain extent in the patent literature. Difluorodiamine has also been shown to convert certain enamines to α-fluoroketone (*20*).

C. THE N_2F^+ ION

The most striking difference in reactivity of the two isomers is that only the cis form will react with AsF_5 to form a salt of the N_2F^+ cation (*214*).

$$cis\text{-}N_2F_2 + AsF_5 \xrightarrow{-190 \text{ to } 25^\circ C} N_2F^+AsF_6^-$$

This formulation of the product is supported by its ^{19}F NMR and IR spectra. A similar reaction has been shown to take place with SbF_5, BF_3, or PF_5, the last two reacting only under pressure and at a low temperature. The BF_3 adduct, which dissociates to its components at atmospheric pressure and ambient temperature, has been used for separating the cis isomer from the trans, which does not form an adduct. The adducts with BF_3, PF_5, and SbF_5 have also been claimed as solid rocket propellants (*261*). In each instance salt formation has been shown to occur by observation of the characteristic infrared spectrum of the anion (*227, 246*).

Trans-N_2F_2 forms an adduct ($N_2F_2 \cdot 2SbF_5$) with SbF_5 which has been formulated as $N_2F^+Sb_2F_{11}^-$ (*254*). Bond lengths and ^{14}N and ^{19}F NMR and vibrational spectra of N_2F^+ have been reported (*205, 241, 269*).

Little is known about the chemical reactions of these salts. The hexafluoroarsenate decomposes without melting at 150°C, but $N_2F^+BF_4^-$ is 75% decomposed in 1 hr at ambient temperature. The N_2F^+ and NO_2^+ ions are isoelectronic and the X-ray patterns of N_2FAsF_6 and NO_2AsF_6 are very similar. Few reactions have been reported. The hexafluoroarsenate is decomposed by water to N_2O, HF, and $HAsF_6$. With O_2 at 2 atm, the reaction products are O_2AsF_6, N_2, and *cis*-N_2F_2. The cis isomer is also formed in the reaction with either NO or (NaF + HF).

$$N_2F^+AsF_6^- + NO \longrightarrow NO^+AsF_6^- + N_2 + cis\text{-}N_2F_2$$

$$N_2F^+AsF_6^- + NaF + HF \longrightarrow Na^+AsF_6^- + cis\text{-}N_2F_2$$

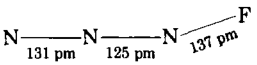
There is also a metathetical reaction with $AgClO_4$ or $NH_4^+SO_3F^-$, the products being unstable.

$$N_2F^+AsF_6^- + AgClO_4 \xrightarrow{HF} AgAsF_6 + [N_2F^+Cl_2O_7^-] \longrightarrow N_2O + ClO_3F$$

$$N_2F^+AsF_6^- + NH_4SO_3F \longrightarrow NH_4AsF_6 + [N_2F^+SO_3F^-] \longrightarrow N_2O + SO_2F_2$$

XIII. Fluorine Azide (Triazadienyl Fluoride), N_3F

Fluorine azide is a greenish-yellow gas (mp −139°C) with an odor resembling that of ClO_2. It is best prepared from dry hydrazoic acid and fluorine diluted with nitrogen in the gas phase at 25°C (*82, 125*). It has a planar structure with the following parameters (*131, 231*):



$\widehat{N{-}N{-}N} = 165.3^\circ$ $\widehat{F{-}N{-}N} = 113.5^\circ$

The IR spectrum of N_3F is consistent with C_s symmetry (*125*). Controlled thermal decomposition of N_3F in the diluted gas phase results in N_2F_2 according to the reaction

$$2N_3F \longrightarrow N_2F_2 + 2N_2$$

The decomposition probably proceeds by means of the biradical NF. It does not react with H_2O, O_2, XeF_2, OF_2, or Me_3SiN_3. With CO, NO, and COS the products formed have been interpreted as arising from the formation of NF as an intermediate (*125*). N_3F diluted with He reacts with excess of chlorine at 75°C to give $ClNF_2$ (*135*).

XIV. Tetrafluorohydrazine, N_2F_4

Tetrafluorohydrazine was first prepared in 1958 by Colburn and Kennedy (*75*). As would be expected from the weakness of the N–Cl bond relative to the N–F bond, which results in the instability of NCl_3, the chlorine analog N_2Cl_4 is unknown and unlikely to be prepared. The original preparation of N_2F_4 was by passing NF_3 through a reactor packed with copper turnings and heated to 375°C.

$$NF_3 + Cu \xrightarrow{375^\circ C} \cdot NF_2 + CuF$$

$$2\dot{N}F_2 \rightleftharpoons N_2F_4$$

The difluoroamine radical produced dimerizes to N_2F_4, the reversible equilibrium resembling that between NO_2 and N_2O_4. The reactivity of the copper, which acts as a defluorinating agent in this reaction, decreases as its surface becomes coated with the involatile fluoride. This difficulty was overcome when it was replaced by arsenic, antimony, or bismuth, the fluorides of which are volatile at the reaction temperature. Conversion of NF_3 to N_2F_4 in these reactions was of the order of 40–60%. There was a similar conversion when the trifluoride was passed over liquid mercury at 320–330°C (*91*). Alternatively, the trifluoride could be defluorinated by mercury vapor in an electrical discharge (*118*).

Tetrafluorohydrazine has proved to be a valuable synthetic agent for the preparation of organic compounds containing $—NF_2$ or $=NF$ groups, as described in the next section. This has led to the development of other methods of preparation, which are described below. Good yields have been reported from a process in which the trifluoride is passed through a fluidized bed of carbon at 440°C. Volatile fluorocarbons are produced in the reaction, one of which in particular

(C_2F_6) has much the same volatility as tetrafluorohydrazine (bp −73°C) and is difficult to separate completely by distillation (*136*).

The fluorination of ammonia has already been referred to as a method for preparing the trifluoride (see Section II) but, with ammonia in excess, this reaction also gives some tetrafluorohydrazine together with fluoroamine and difluorodiazene (*213*). Another method, which could be used in the large-scale production of tetrafluorohydrazine, involves the oxidation of difluoroamine by aqueous sodium hypochlorite at pH 12 (*180*). Difluoroamine is readily prepared by the acid hydrolysis of *N,N*-difluorourea, which is obtained in high yield in the reaction of fluorine with an aqueous solution of urea. The difluoroamine may also be oxidized by aqueous ferric chloride (*204*). Exposure of NF_3 to large doses of 3-MeV bremsstrahlung at 77 K gives N_2F_4 (*218*) besides *cis*- and *trans*-N_2F_2, N_2, and F_2. $ClNF_2$ reacts rapidly with mercury to form N_2F_4 and Hg_2Cl_2 (*232*). $ClNF_2$ is nearly quantitatively converted into N_2F_4 on reaction with dimethylamine in diethyl ether at −80°C. Lower yields of N_2F_4 are obtained in dimethyl ether or with sodium methoxide. In addition to other products, N_2F_4 is formed on reacting $ClNF_2$ with aqueous KI, NO, or LiH (*226*).

A. PHYSICAL PROPERTIES OF N_2F_4

The boiling point of N_2F_4 is −73°C and its melting point −164.5°C. The molecular structure has been determined by microwave spectroscopy (*188*), the bond lengths found being $N{-}N = 140.1 \pm 2$ pm, $N{-}F = 135.5$ pm with $\angle FNF = 106.9 \pm 1.6°$ and $\angle NNF = 102.8 \pm 2.8°$. The corresponding values from an electron diffraction study (*22, 153, 179*) are $N{-}N = 148.0 \pm 2$ pm, $N{-}F = 139.2 \pm 0.8$ pm, $\angle FNF = 103.0 \pm 0.1°$, and $\angle NNF = 102.5 \pm 1.5°$. The structure resembles that of hydrazine, and this is also consistent with observations on the ^{19}F NMR spectrum (*73, 302*) and the infrared spectrum (*95, 149, 150, 164*). These data were interpreted only in terms of the gauche form.

The first experimental evidence for the coexistence of both conformations, i.e., gauche-form symmetry C_2 and a trans-form symmetry C_{2h}, in approximately equal amounts came from the ^{19}F NMR spectrum of N_2F_4 in various nonpolar solvents between −130 and −180°C (*163*). The five-line spectrum could be reasonably assigned by allocating the sharp, intense line to the four equivalent F nuclei in *trans*-N_2F_4 and the remaining four lines, an AB quartet, to the *d,l* pair of gauche rotamers. Finally, the presence of two rotamers in all phases of N_2F_4 has been proved by electron diffraction (*34, 126*) and detailed Raman and IR studies (*94, 96, 175, 222, 267, 270*).

Other studies have been made on the $\cdot NF_2$ radical, including the mass spectrum (*71, 193*) and EPR spectrum (*70, 101, 103, 150, 168*). The group electronegativity of $\cdot NF_2$ has been estimated as 3.7 (*99*).

The dissociation equilibrium of tetrafluorohydrazine has been studied by four different methods, all of which have given heats of dissociation for the N–N bond in the range 80–91 kJ mol^{-1} (*69*). In the first, gaseous, N_2F_4 was heated to a series of temperatures in the range 100–150°C in a metal vessel, the inner surface of which had been passivated by treatment with fluorine. Measurements of the pressure at constant volume as a function of temperature gave the heat of dissociation as 83.05 ± 0.2 kJ mol^{-1} (*165*).

In the second method measurements were made of the variation with temperature (25–150°C) of the intensity of an ultraviolet absorption band centered at 2600 Å (*100, 237*). It was shown that this band is associated with the $\cdot NF_2$ radical and that the intensity is proportional to its concentration. The heat of dissociation found was 90.8 kJ mol^{-1}. In the third method the height of a peak due to the $\cdot NF_2$ radical in the electron paramagnetic resonance spectrum was measured over the temperature range 70–180°C. The heat of dissociation found was 89.9 ± 6.7 kJ mol^{-1} (*237*).

The last of the four methods used in studying this equilibrium involved measurement of the $N_2F_4^+/NF_2^+$ peak ratio in the mass spectrum of N_2F_4 over the temperature range 50–400°C. This gave a value for $D(NF_2\text{–}NF_2)$ of 89.95 ± 6.67 kJ mol^{-1} (*151, 152*). A mean value of 87.7 kJ mol^{-1} (*224, 290, 299*) is generally used. From this it can be calculated that the degree of dissociation is 0.004% at 25°C and 0.9% at 100°C, which lends weight to the statement which has often been made that the chemistry of tetrafluorohydrazine is, in the main, that of the radical. The weakness of the N–N bond in N_2F_4 is in sharp contrast to the position for $N_2(CF_3)_4$, where, in spite of the high electronegativity of the CF_3 group, the N–N bond is clearly much stronger because the compound is thermally stable to at least 325°C (*36*).

B. REACTIONS OF N_2F_4

Tetrafluorohydrazine is a powerful oxidizing and fluorinating agent. Its high reactivity is associated with the ready dissociation of the molecule to yield difluoroamino radicals, and much of the interest in the chemistry is associated with its use in the synthesis of organic compounds containing the $-NF_2$ or $=NF$ group. A brief account of this aspect of the subject is given in the next section. Reaction with organic compounds in general may be explosive; great care is necessary in all work with tetrafluorohydrazine. It has been proposed as a fuel in rocket and laser technology, but no details of such an application have been published. The rather limited range of inorganic reactions which it undergoes is dealt with in this section.

The simplest type of reaction involves the combination of $\cdot NF_2$ with another radical present in the reaction system or produced in it either thermally or photochemically. When N_2F_4 was first prepared (*75*), it was found to have a deep purple–blue color at low temperatures in the liquid or solid state; this color was traced to a compound, F_2NNO, formed by the $\cdot NF_2$ radical with NO present as an impurity. The compound was prepared in quantity by passing NO with N_2F_4 through a coil heated to 300°C and collecting the product, F_2NNO, on a cold finger (*72*). Dissociation to a 2:1 mixture of NO and N_2F_4 took place when the blue compound was allowed to vaporize.

NO_2 reacts with N_2F_4 vigorously at room temperature to give FNO (97%) along with FNO_2 and NF_3 (*88, 225*). A highly unstable white solid, F_2NNO_2, is formed in 50–70% yield by the reaction of N_2F_4 and NO_2 at 310°C with rapid quenching to −196°C (*268*).

Several other reactions of this type are known. Thus N_2F_4 and bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, react at ambient temperatures, forming F_2NOSO_2F, the second radical resulting from dissociation of the peroxy compound at the O–O bond (*198*). The thermally unstable compound PF_2I also reacts with N_2F_4 at room temperature to give F_2NPF_2, which is highly explosive (*274*). When a mixture of N_2F_4 and S_2F_{10} is heated to 140°C, a 70% yield of $F_2N{\cdot}SF_5$ is obtained following thermal cleavage of the S–S bond to form $\cdot SF_5$ radicals (*33*). CF_3SFO reacts with N_2F_4 on heating up to 300°C in a nickel vessel to give CF_3NF_2 (*242*).

The reaction of N_2F_4 with Cl_2 is initiated photochemically, as already mentioned (see Section X), and NF_2Cl is formed reversibly. Other examples of reactions initiated photochemically are those of N_2F_4 with SF_5OF (*147, 252*) and CF_3OF (*147, 272*). Both of the hypofluorites are cleaved in ultraviolet light at the O–F bond. In the first case there is a 40% yield of F_2NOSF_5, together with NF_3, NO, SF_4, SF_6, SO_2F_2, SOF_4, and NO_2 (*147*), while the products from CF_3OF are CF_3ONF_2 (40%), NF_3, CF_4, and COF_2 (*272*). Pentafluorosulfur chloride and N_2F_4 also react in ultraviolet light to form F_2NSF_5 and Cl_2; the first of these is also formed together with NF_3 and SF_6 in the photochemical reaction of SF_4 with N_2F_4 or, in very low yield, when sulfur is heated with N_2F_4 at 110–140°C (*191*). Some additional examples of photochemical reactions are tabulated in Table III. Other examples of reactions which are initiated photochemically are given later in describing the reactions with organic compounds.

TABLE III

REACTIONS OF TETRAFLUOROHYDRAZINE

Substrate	Product	Yield (%)	Reference
SF_4	SF_5NF_2	40	*117, 191*
$SF_4 + CF_3OF$	$CF_3OSF_4NF_2$	14	*93*
$R_fN{=}SF_2$ ($R_f = CF_3, C_2F_5, C_3F_7$)	SF_5NF_2	—	*89*
SO_3	FSO_3NF_2	55	*117, 197*
SO_2	FSO_2NF_2	89	*31, 196*
CO	F_2NCFO	10–15	*116*
$(CF_3)_3COF$	$(CF_3)_3COO(CF_3)_3$	—	*284*
$(ClCO)_2$	F_2NCClO	20–40	*35, 303*
$CSCl_2$	F_2NCl_2CSCl	22	*307*
$CSCl_2 + Cl_2$	F_2NCCl_3	16	*307*
SOF_2	SOF_4	20	*197*
POF_3	$NOPF_6$	50	*197*

In a number of instances oxidative fluorination occurs. Thus with $(C_6H_5)_3P$ and $(C_6H_5)_2PH$ the reactions shown below take place at room temperature in ether or chlorobenzene solution (*105*).

$$2(C_6H_5)_3P + N_2F_4 \longrightarrow 2(C_6H_5)_3PF_2 + N_2$$

$$(C_6H_5)_2PH + N_2F_4 \longrightarrow (C_6H_5)_2PF_3$$

The reaction shown below occurs in $POCl_3$ solution at 100°C (*167*)

$$PCl_3 + N_2F_4 \xrightarrow[POCl_3]{100^\circ C} P_2Cl_6NF \xrightarrow{SO_2} P_2Cl_4ONF$$

On the basis of IR and ^{31}P NMR spectral data, P_2Cl_4ONF has the structure $POCl_2PCl_2(:NF)$.

XV. Salts of the $N_2F_3^+$ Cation

Both N_2F_4 and N_2F_2 react with certain fluoride ion acceptors to form salts of the $N_2F_3^+$ or N_2F^+ cation, this being very similar to the behavior of NF_3O in forming salts of NF_2O^+ (see Section VII). Salts of $N_2F_3^+$ were first obtained in 1965 by Ruff (*255*) who found that, when a solution of SbF_5 in AsF_3 was treated with N_2F_4, either a 1:2 or a 1:3 adduct was produced, depending on the N_2F_4 pressure over the solution.

The 1:3 adduct was converted to the 1:2 adduct by reaction with SO_2 at −45°C.

$$N_2F_4\cdot 3SbF_5 + SO_2 \xrightarrow{-45^\circ C} N_2F_4\cdot 2SbF_5 + SO_2SbF_5$$

The complex $N_2F_4\cdot 2SbF_5$ was first shown to be the salt $N_2F_3^+Sb_2F_{11}^-$ by its infrared and ^{19}F spectra (*255*).

For the complex $N_2F_4\cdot 3SbF_5$ the formulation $N_2F_3^+Sb_3F_{16}^-$ has been given (*49*). If the reaction of SbF_5 with an excess of N_2F_4 (~1 atm) is carried out in AHF solution at room temperature, the salt $N_2F_3^+SbF_6^-$ is obtained (*49, 262*). The salt $N_2F_3^+AsF_6^-$ results from the reaction of AsF_5 with N_2F_4 without any solvent at −78°C (*178*) and at room temperature (*49*). The existence of $N_2F_3^+$ in the salt has been established by ^{19}F NMR and IR spectroscopy (*304*). The salt $N_2F_3^+SnF_5^-$ has been prepared by a metathetical reaction between $N_2F_3^+SbF_6^-$ and Cs_2SnF_6 at −78°C in AHF (*49*) according to:

$$2N_2F_3SbF_6 + Cs_2SnF_6 \longrightarrow 2CsSbF_6\downarrow + N_2F_3SnF_5 + N_2F_4$$

On the basis of IR and Raman spectroscopy (*49*) and ^{19}F NMR (*49, 255, 304*) and ^{14}N NMR (*205*), $N_2F_3^+$ possesses a planar structure having C_s symmetry.

XVI. Organic Reactions of N_2F_4

Tetrafluorohydrazine is a powerful oxidizing and fluorinating agent, but its importance in organic synthesis stems, as Colburn and Kennedy found, from the ready dissociation to difluoroamino radicals. These are highly reactive and can combine with other free radicals, initiate reactions by hydrogen abstraction, or add to unsaturated systems, so that it is often possible to tailor a specific reaction and avoid the breakdown and side reactions associated with earlier fluorination procedures. Two other related compounds, difluoroamine (HNF_2) and chlorodifluoroamine ($ClNF_2$), also yield difluoroamino radicals; their uses in the synthesis of organic nitrogen–fluorine compounds are discussed elsewhere in this paper. No attempt will be made, however, to cover fully the extensive literature, as is done in a reveiw by Freeman (*121*). Instead, examples will be given of the main types of reaction which can occur so as to provide a broad picture of the organic reactions of the difluoroamino radical to supplement the earlier review of its inorganic reactions.

XVII. Reactions of the Difluoroamino Radical with Other Radicals

Tetrafluorohydrazine is readily dissociated to $\cdot NF_2$ radicals which will combine with other free radicals generated in the reaction system either thermally or photochemically. An example of a reaction initiated thermally is that between N_2F_4 and $C_2(C_6H_5)_6$, the product being $F_2N\cdot C(C_6H_5)_3$ (*234*). A further example is the production of $(CH_3)_3CNF_2$ by heating N_2F_4 with either *tert*-BuI or azoisobutane (*137, 234*).

$$\begin{tikzcd}[row sep=small]
(CH_3)_3CI + N_2F_4 \arrow[dr, "\Delta"] & \\
& (CH_3)_3CNF_2 \\
(CH_3)_3CN{=}NC(CH_3)_3 + N_2F_4 \arrow[ur, "\Delta"'] &
\end{tikzcd}$$

When these radical–radical reactions are initiated photochemically, the products depend on the wavelength of the light used. Tetrafluorohydrazine absorbs at wavelengths less than 2600 Å to give an excited $\cdot NF_2$ radical which, in the absence of a second reactant, decomposes to NF and $\cdot F$, the final products being N_2F_2 and NF_3. If a suitable organic substrate is present, it will undergo fluorination. With wavelengths above 2600 Å this complication is avoided. When, for example, biacetyl is irradiated in Pyrex with light of wavelength 3000 Å in presence of N_2F_4, there is a high yield of *N*-difluoroacetamide, other diketones, e.g., benzil and glyoxal, behaving similarly (*234*).

$$[CH_3C(O)]_2 + N_2F_4 \xrightarrow{h\nu} 2CH_3C(O)NF_2$$

Photolysis of CH_3I, C_2H_5I, or CF_3I in presence of N_2F_4 gives the corresponding difluoroaminoalkanes (*119, 120*).

Bis(trifluoromethyl)disulfide can also be cleaved photochemically at the S–S bond and, in the presence of N_2F_4, CF_3SNF_2 is obtained (*279*). With CF_3SCl and N_2F_4, however, the products on irradiation are $ClNF_2$ and $(CF_3)_2S_2$ (*179*). The thermally initiated reaction between the trioxide CF_3OOOCF_3 and N_2F_4 has also been investigated (*155*). At a reaction temperature of 84°C the trioxide is believed to break down to $\cdot OCF_3$ and $\cdot OOCF_3$ radicals, evidence that the latter is an intermediate coming from the thermal reaction of the trioxide with SO_2, which gives $(CF_3O)_2SO_2$ and $(CF_3OO)SO_2(OCF_3)$. Reaction with CO also gives a product in which the $—OOCF_3$ group is intact:

$$CF_3OOOCF_3 + CO \longrightarrow (CF_3)_2O_2 + CF_3OC(O)(OOCF_3)$$

In the reaction with N_2F_4, however, the only products isolated were CF_3ONF_2, $(CF_3)_2O_2$, NF_3, and O_2.

A. HYDROGEN ABSTRACTION REACTIONS

The difluoroamino radical is able in some instances to abstract hydrogen from an organic substrate, producing a radical which can then itself react with $\cdot NF_2$. The best known examples of this type are the reactions of N_2F_4 with some aldehydes (*234*), the following reaction being typical:

$$CH_3CHO \xrightarrow[-HNF_2]{\cdot NF_2} CH_3CO\cdot \xrightarrow[150^\circ C]{\cdot NF_2} CH_3C(O)NF_2$$

With thiophenol at 50°C there is a 74% yield of HNF_2, the other product in this case being the disulfide $(C_6H_5)_2S_2$ rather than $C_6H_5SNF_2$ (*123*). Yields are not as high with aliphatic thiols, which have a greater tendency to reduce the tetrafluorohydrazine to molecular nitrogen.

The activation energy of the abstraction reaction has been estimated to be approximately 108.7 kJ mol^{-1} (*145*). This means that, except for highly reactive substrates such as the thiols and aldehydes, a moderately high temperature will be necessary for reaction to occur and the HNF_2 produced may then decompose. Thus, N_2F_4 and CH_4 or C_2H_6 react only at 250°C, the major product being CH_3NF_2 or $C_2H_5NF_2$, but HCN and HF are also produced due to thermal decomposition of HNF_2, which cannot be isolated (*165*). It is clear that the absence of HNF_2 in the products does not necessarily mean that hydrogen abstraction is not a step in the reaction mechanism.

In the reaction of higher aliphatic hydrocarbons with N_2F_4 a complicated mixture of products results, as, for example, in the case of isobutane:

$$\begin{aligned}(CH_3)_3CH + N_2F_4 \longrightarrow\ & (CH_3)_2(CH_2NF_2)CH + (CH_3)_3CNF_2 \\ & + (CH_3)_2CH_2NF_2CH_2NF_2 + CH_3CH(CHNF_2)_2\end{aligned}$$

A small amount of product containing C–F bonds is also found (*244*).

Mixtures are also formed in reactions with aliphatic ethers at 250°C:

$$CH_3OCH_3 + N_2F_4 \xrightarrow{250^\circ C} CH_3OCH_2NF_2 + FCH_2OCH_2NF_2 + (CH_2NF_2)_2O + HOCH_2NF_2$$

The presence of difluoroaminomethanol among the products can be accounted for by a reaction of difluoroamine formed in the abstraction reaction with formaldehyde. The latter could result from decomposition of the $\cdot CH_2OCH_3$ radical to CH_2O and $\cdot CH_3$ (*122*).

The difluoroamino radical may also react with a radical produced by a reaction with a third reactant in the system. Thus, for example, N_2F_4 will react with ethers when irradiated with light of wavelength 3000 Å in the presence of benzophenone (*80*). There is no reaction between N_2F_4 and benzophenone, and it is thought that the latter abstracts hydrogen from the ether and so initiates reactions.

B. Addition Reactions

The difluoroamino radical adds readily to unsaturated systems, addition of a single $—NF_2$ group being brought about by the use of chlorodifluoroamine, $ClNF_2$ (*233*). Reaction may be initiated either by heat or by irradiation. When heat is used, only chlorine addition will occur if the temperature is insufficiently high to provide the activation energy needed for $\cdot NF_2$ addition, which is about 58.57 kJ mol^{-1} (*84*). Thus in the reaction of $ClNF_2$ and C_2H_4 at 70°C only chlorination takes place and N_2F_4 is formed. At a somewhat higher temperature both Cl and NF_2 are added, as the following examples show.

Olefin	Reaction temperature (°C)	Products
Ethylene	130	$ClCH_2CH_2NF_2$, $NF_2CH_2CH_2NF_2$
Propylene	130	$CH_3CHClCH_2Cl$, $CH_3CHClCH_2NF_2$, $CH_3CHNF_2CH_2NF_2$
trans-Butene-2	120	$CH_3CHClCHClCH_3$ (*d,l* and meso) $CH_3CH(NF_2)CHClCH_3$ (erythro and threo) $CH_3CH(NF_2)CHNF_2CH_3$ (*d,l* and meso)

When the reactants are exposed to ultraviolet light, only chlorine addition takes place.

$$\begin{aligned} NF_2Cl &\overset{h\nu}{\rightleftharpoons} \cdot NF_2 + \cdot Cl \\ \cdot Cl + CH_2CH_2 &\longrightarrow ClCH_2CH_2^{\cdot} \\ ClCH_2CH_2^{\cdot} + ClNF_2 &\longrightarrow ClCH_2CH_2Cl + \cdot NF_2 \\ \cdot NF_2 + \cdot NF_2 &\rightleftharpoons N_2F_4 \end{aligned}$$

Two other reactions which would result in NF_2 substitution are $ClCH_2CH_2^{\cdot} + \cdot NF_2 \rightarrow ClCH_2CH_2NF_2$ and $ClCH_2CH_2^{\cdot} + N_2F_4 \rightarrow ClCH_2CH_2NF_2 + \cdot NF_2$, but both are thought to require too high an activation energy for them to occur at room temperature.

A reaction closely related to the above is that of *o*-difluoroamino fluorosulfate with fully fluorinated olefins (*28*, *199*), an example of which is shown below.

$$CF_3CF{=}CF_2 + F_2NOSO_2F \longrightarrow CF_3CF(NF_2)CF_2OSO_2F$$

o-Difluoroaminofluorosulfate reacts with perfluorocyclobutene to form 1-(difluoroamino)-2-(fluorosulfato)hexafluorocyclobutane, which undergoes a defluorosulfurylation reaction and concomitant ring expansion when reacted with KF to give heptafluoroazapentan-2-one. The ring is further expanded upon reaction with phosphine (*281*).

The addition of N_2F_4 to unsaturated systems was first studied in detail by Petry and Freeman (*235*). They found that in most cases vicinal bis(difluoroamines) resulted in good yield. Only with weakly nucleophilic olefins, such as tetracyanoethylene, was there no addition. The aliphatic olefins reacted smoothly at about 100°C, the electron-rich olefins reacting more readily than those which were electron-poor. Thus, perfluoropropylene required a temperature of 140°C, whereas α-methyl styrene absorbed N_2F_4 even at room temperature. Reactions were usually carried out under pressure and in a solvent such as chloroform or chlorobenzene.

Table IV below shows examples of vicinal bis(difluoroamino) compounds obtained in this way. There were usually no side reactions resulting from hydrogen abstraction as the temperature was insuffi-

TABLE IV

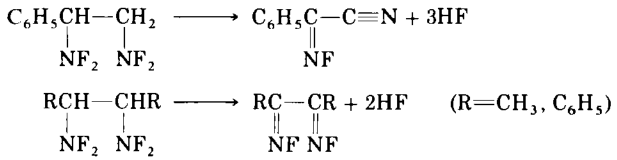
VICINAL BIS(DIFLUOROAMINO) COMPOUNDS[a]

Substrate	Compound	Yield (%)
$C_4H_9CH{=}CH_2$	$C_4H_9CH(NF_2)CH_2NF_2$	82
$CH_2{=}CH{-}CH{=}CH_2$	$F_2NCH_2CH{=}CHCH_2NF_2$	70
	$F_2NCH_2CH(NF_2)CH{=}CH_2$	24
$C_6H_5C(CH_3){=}CH_2$	$C_6H_5C(CH_3)(NF_2)CH_2NF_2$	73
$Cl_2C{=}CHCl$	$Cl_2C(NF_2)CHCl(NF_2)$	—
$CF_3{\cdot}CF{=}CF_2$	$CF_3CF(NF_2)CF_2(NF_2)$	95
$CH_2{=}C(CH_3)COCH_3$	$F_2NCH_2C(CH_3)COCH_3$	—
$CH_3OCH{=}CH_2$	$CH_3OCH(NF_2)CH_2NF_2$	83
$CH_2{=}CHCH_2CO_2H$	$F_2NCH_2CH(NF_2)CH_2CO_2H$	68

[a] From Ref. *122*.

ciently high for these to occur. Fluorination took place only in the temperature range 200–250°C (*235, 243*).

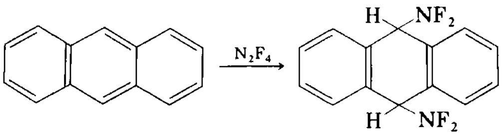
It will be seen that addition reactions can take place with olefinic compounds of various types. A number of adducts in which there is hydrogen in the α position in relation to the difluoroamino group tend to undergo dehydrofluorination, with formation of fluoroimines. The following examples show the production of fluoroimines:



$$\underset{NF_2}{C_6H_5CH}-\underset{NF_2}{CH_2} \longrightarrow \underset{NF}{C_6H_5\overset{}{C}}-C{\equiv}N + 3HF$$

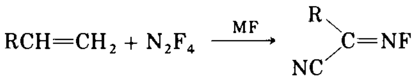
$$\underset{NF_2}{RCH}-\underset{NF_2}{CHR} \longrightarrow \underset{NF}{RC}-\underset{NF}{CR} + 2HF \qquad (R{=}CH_3, C_6H_5)$$

Addition reactions also occur at 50–100°C with polycyclic hydrocarbons and some of their substituted derivatives (*189*), anthracene and N_2F_4, for example, giving a mixture of the cis and trans isomers of 9,10-bis(difluoroamino)anthracene.



(cis and trans)

Certain olefins react with N_2F_4 in the presence of alkali metal fluorides giving (fluoroimino)acetonitriles (*97, 98, 190*).

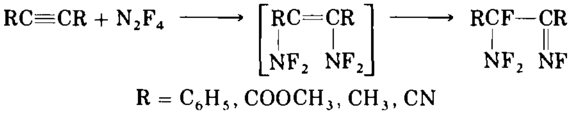


R = CN, F, CF_3, C_6H_5, CH_3, $COOCH_3$, SF_5, $CH_2OC(O)CH_3$
M = Na, K, Cs

Tetrafluorohydrazine reacts with $CF_2{=}CH_2$, $CFH{=}CH_2$, and CF_3-$CH{=}CH_2$ in the presence of KF to give, respectively (difluoroamino)-difluoroacetonitrile, F_2NCF_2CN; *syn*-fluoro(fluoroimino)acetonitrile, $FC({=}NF)CN$; and *syn*-3,3,3-trifluoro-2-(fluoroimino)propanenitrile, $CF_3C({=}NF)CN$ (*202*).

Addition Reactions with Acetylenes

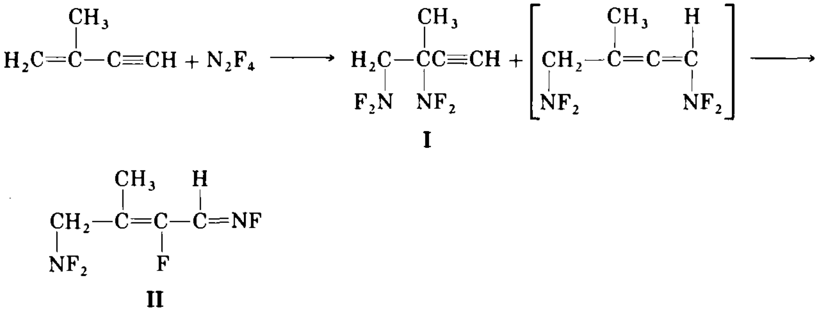
In theory it should be possible to prepare tetrakis(difluoroamines) by the addition of difluoroamino radicals to an acetylene. It is found, however, that the vinylbisdifluoroamine formed in the first addition normally rearranges with formation of a fluoroimino group, which precludes further addition (*236, 256*).



$$RC\equiv CR + N_2F_4 \longrightarrow \left[\underset{NF_2}{RC}=\underset{NF_2}{CR}\right] \longrightarrow \underset{NF_2}{RCF}-\underset{NF}{\overset{\|}{C}}R$$

$R = C_6H_5, COOCH_3, CH_3, CN$

With acetylene the reaction was more complicated and there was no clear indication of the process taking place. With diphenylacetylene and N_2F_4 in CH_2Cl_2 at 80°C, on the other hand, there appeared to be normal addition to give $C_6H_5C(NF_2){=}C(NF_2)C_6H_5$, but the ^{19}F NMR spectrum showed that a rearrangement had taken place, the product being $C_6H_5CF(NF_2)C({=}NF)C_6H_5$. A similar rearrangement was found in the product from the reaction of N_2F_4 with dimethylacetylene dicarboxylate at 120°C. Isopropenyl acetylene, as shown below, gave the olefin adduct (I), cis and trans, and isomers of a rearranged product (II), which stems from the 1:4 addition product.

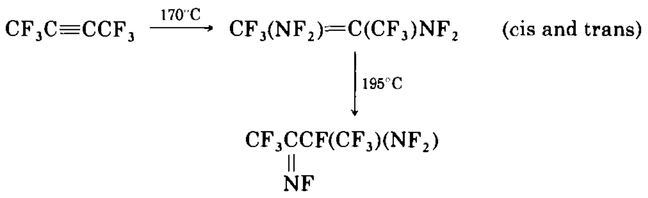


$$H_2C=\overset{CH_3}{C}-C\equiv CH + N_2F_4 \longrightarrow \underset{F_2N}{H_2C}-\underset{NF_2}{\overset{CH_3}{C}}C\equiv CH + \left[\underset{NF_2}{CH_2}-\overset{CH_3}{C}=C=\underset{NF_2}{\overset{H}{C}}\right] \longrightarrow \underset{NF_2}{CH_2}-\overset{CH_3}{C}=\underset{F}{C}-\overset{H}{C}=NF$$

I

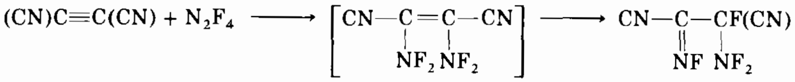
II

With acetylenes containing perfluoroalkyl groups (CF_3, C_4F_9) as substituents, cis and trans isomers of the bis(difluoroamino) compound could be isolated in good yield, but rearrangement took place at a higher temperature.



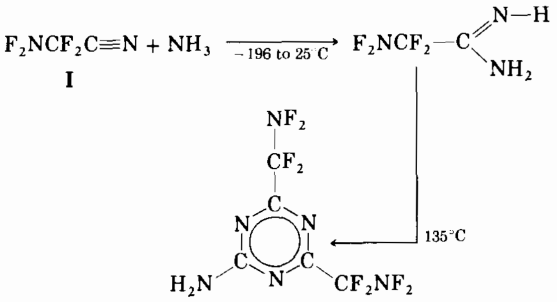
$$CF_3C\equiv CCF_3 \xrightarrow{170^\circ C} CF_3(NF_2){=}C(CF_3)NF_2 \quad \text{(cis and trans)} \xrightarrow{195^\circ C} CF_3\underset{NF}{\overset{}{\underset{\|}{C}}}CF(CF_3)(NF_2)$$

With dicyanoacetylene and N_2F_4 at 140°C the chief product was again the rearranged product.

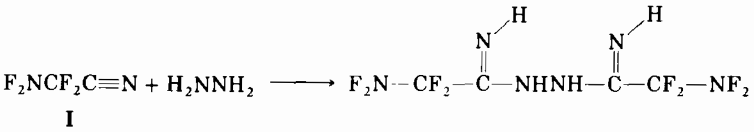


$$(CN)C{\equiv}C(CN) + N_2F_4 \longrightarrow \left[CN{-}\underset{NF_2}{\overset{}{C}}{=}\underset{NF_2}{\overset{}{C}}{-}CN\right] \longrightarrow CN{-}\underset{\overset{\|}{NF}}{C}{-}\underset{\overset{|}{NF_2}}{C}F(CN)$$

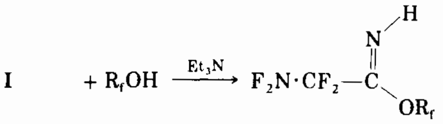
Some recent reactions of N_2F_4 being carried out by John and Shreeve (*160*) involve its reaction with $CF_2{:}CH_2$ in the presence of KF in CH_3CN solution to give $F_2N{\cdot}CF_2C{\equiv}N$, which further reacts with NH_3 at 135°C to give a cyclic compound:



Structure **I** undergoes the following reactions with various substrates.

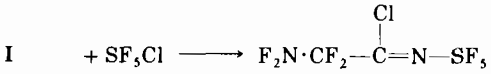


$$\underset{\mathrm{I}}{F_2NCF_2C{\equiv}N} + H_2NNH_2 \longrightarrow F_2N{-}CF_2{-}\overset{NH}{\overset{\|}{C}}{-}NHNH{-}\overset{NH}{\overset{\|}{C}}{-}CF_2{-}NF_2$$

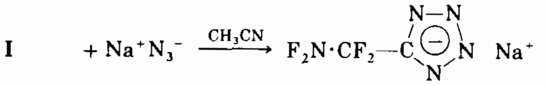


$$\mathrm{I} \quad + R_fOH \xrightarrow{Et_3N} F_2N{\cdot}CF_2{-}\overset{NH}{\overset{\|}{C}}{-}OR_f$$

$$\mathrm{I} \quad + SF_4 \xrightarrow[100°C,\ 12\ hr]{CsF} F_2N{\cdot}CF_2{\cdot}CF_2N{=}SF_2$$

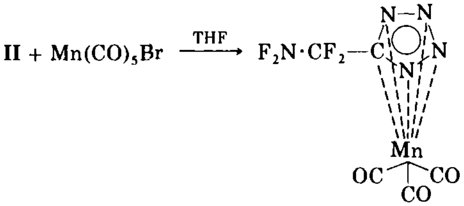


$$\mathrm{I} \quad + SF_5Cl \longrightarrow F_2N{\cdot}CF_2{-}\overset{Cl}{\overset{|}{C}}{=}N{-}SF_5$$

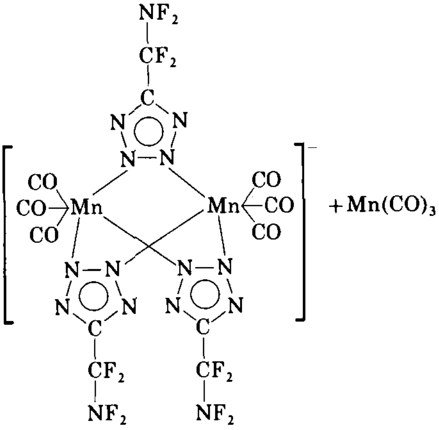


II

The tetrazole derivative, II, further reacts with $Mn(CO)_5Br$ in THF to give the following compounds.

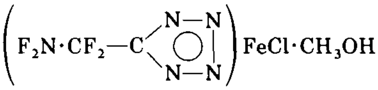


III

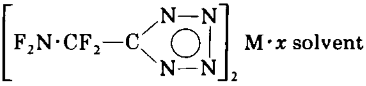


IV

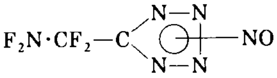
Structures **III** in THF solution and **IV** in the solid state have been proposed on the basis of IR, NMR, and X-ray crystallographic data. Structure **II** also reacts with anhydrous $FeCl_2$ in CH_3OH to give



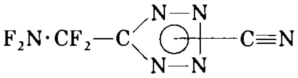
With MCl_2 (M = Fe, Cu, Ni) in CH_3OH/H_2O the following products are obtained:



Structure II with NOCl and ClCN in THF or CH_3CN gives, respectively,



and



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