A Study of the Chemistry of Difluoramines

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INTRODUCTION

Compounds containing the NF_2 group are commonly referred to as difluoramines. The chemistry of these compounds has been studied more intensively during recent years than previously and has been the subject of three review articles (1,2,3). The aims of our work, part of which we describe here, are to get a picture of the relative electron distributions in X-NF_2 compounds, to gain an understanding of the nature of the N-F and N-X bonds, and to determine the existence and stabilities of N-F radicals and ions. We have concentrated on X-NF_2 compounds, where X = F, Cl, H, NF_2, CH_3, C_2H_5, and CF_3. The radical and ionic species which have held our attention are ·NF, ·NF_2, NF^+, NF^-, NF_2^+, NF_2^-, NF_3^+, and $H_2NF_2^+$. This paper emphasizes the chemistry of difluoramine, HNF_2, and the existence of NF_2-containing ions to illustrate our investigations in NF_2 chemistry.

RESULTS AND DISCUSSION

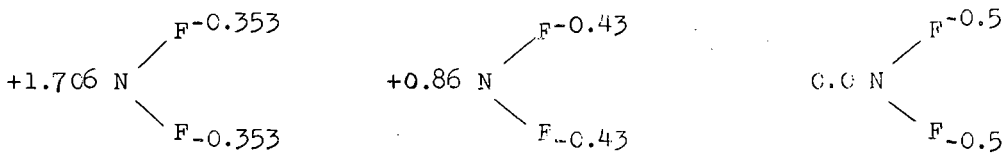
Theoretical Considerations

One of the approaches which we have taken is the calculation of molecular parameters of various N-F species by employing molecular orbital treatments (4,5). Of particular relevance to NF_2 chemistry are the π-bond orders and atomic charges calculated for NF_2 moieties (Table I).

TABLE I
CALCULATED CHARGES AND BOND ORDERS OF NF_2 SPECIES

	ATOMIC CHARGES Q_N	Q_F	π-Bond Orders
NF_2^+	+1.706	-0.353	0.3
NF_2	+0.86	-0.43	0.35
NF_2^-	0	-0.5	0

Kaufman and coworkers have made similar calculations and have shown that, in covalent NF_2 compounds, there are no orbitals available on the nitrogen of energy low enough for significant π-bonding with the unshared electrons on the fluorine atoms (6,7). In a series of X-NF_2 compounds, the relative electron distributions are thus a function of the inductive effects of the X group. The various situations are envisioned as follows:



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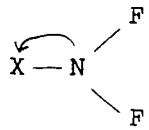

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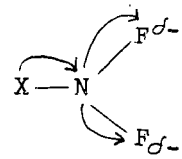


V

The relatively high negative charge on fluorines causes many NF_2 species to decompose readily by loss of a fluoride ion. This work indicates that the NF_2-containing ions which have the greatest probability of long term existence are the cations, because, of any of the NF_2 species, NF_2^+ has the lowest negative atomic charge on the fluorines. In all of the difluoramine derivatives studied, the non-bonding L-shell electrons of the nitrogen are more displaced toward the fluorines than strictly localized on the nitrogen. As a result, the nitrogen in many NF_2 species carries a relatively high positive charge. Any cationic NF_2 species would be expected to have a high electron affinity, probably higher than that of NO_2^+. Considerations in isolating an NF_2 cation are to stabilize it with a large anion of low charge density so that polarization can occur, or to select a hypothetical NF_2 salt in which the lattice stabilization energy is very high. Candidates for the latter are moderate-sized divalent anions. No NF_2-containing ions of any type have been observed, except for NF_2^+ which has been observed in the mass spectrometer (8).

Experimental Observations

The nearest we have come to demonstrating the existence of N-F ions is in the electrochemical oxidation-reduction reactions of HNF_2. The oxidation has been carried out in water and in various polar organic solvents under acid condition (9). The first step of this reaction has been shown to be formation of the $\cdot NF_2$ radical. The $\cdot NF_2$ radical undergoes combination processes on the surface of the electrode rather than diffusing into the body of the solution before being involved in further reactions. The combination process on the electrode surface has been used to prepare a variety of NF_2 compounds by simultaneously generating other radical species, e.g.,

$$HNF_2 \longrightarrow H^+ + e^- + \cdot NF_2$$
$$CH_3COOH \longrightarrow \cdot CH_3 + H^+ + CO_2 + e^-$$
$$\cdot NF_2 + \cdot CH_3 \longrightarrow CH_3NF_2$$

The oxidation of HNF_2 involves the removal of an electron from the nitrogen in a solvated HNF_2 species rather than from NF_2^-. All of our work on the solution chemistry of HNF_2 shows that under conditions favoring the formation of NF_2^- (proton removal), this species loses a fluoride ion to form difluorodiazine.

$$NF_2^- \longrightarrow 1/2\ N_2F_2 + F^-$$

The reduction of HNF_2 in aqueous media is a four-electron process in which HNF_2 is reduced to ammonia (10). In nonaqueous solvents, the reduction is dependent on the availability of protons in the system and the reduction potential is strongly influenced by the degree and type of solvation (Table II). Nitrogen trifluoride is electrolytically reduced in aqueous solution at ~-1.40 v. vs. S.C.E.

Six electrons per molecule of NF_3 are involved in the reduction.

$$HNF_2 + 4e^- + 2H^+ \longrightarrow NH_3 + 2F^-$$
$$NF_3 + 6e^- + 3H^+ \longrightarrow NH_3 + 3F^-$$

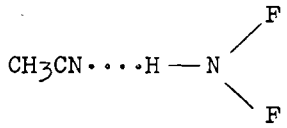
NF_3 could not be electrolytically oxidized in systems similar to those used for the reduction.

TABLE II
EFFECT OF SOLVENT ON THE POLAROGRAPHIC REDUCTION OF HNF_2

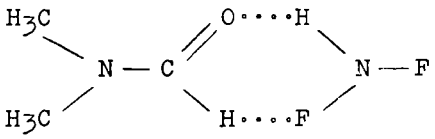
Solvent	$E^{1/2}$ HNF_2 (volts versus S.C.E.)
H_2O	1.22
C_2H_5OH	1.64
CH_3CN	1.42
Dimethyl Formamide	1.61
Dimethyl Sulfoxide	1.64

The solvation of HNF_2 in a variety of solvents was studied by conventional and low-temperature infrared techniques and by determining the dissociation pressure-temperature relationships of several HNF_2-solvent complexes (6,10). Total enthalpies of dissociation were determined where experimentally feasible. Shifts in the N-H and N-F stretching frequencies in the IR spectra of 1:1 complexes of HNF_2 with solvents and of one-molar solutions of HNF_2 were examined to determine the nature of the bonding in the solvated species (Table III). In general these data indicate the order $H_2O < CH_3OH < CH_3CN < HCONH_2 < HOCN(CH_3)_2 \sim (CH_3)_2SO$ for the strength of solvation of HNF_2. It was found that 1:2 complexes of HNF_2 with DMF and DMSO exert very little vapor pressure at room temperature. Equimolar complexes of HNF_2 with formamide, dimethyl formamide, and dimethyl sulfoxide exert relatively little vapor pressure at 0°. HNF_2 is by far least solvated by water.

In all of the solvents studied, the most important factor, determined from vibrational spectra, is the strength of the difluoramine hydrogen bond with the solvent. Thus, HNF_2 appears to be bonded to these solvents in structures of the type



However, in some systems the infrared spectra indicate moderate bonding of the fluorines with the solvent, e.g.,



Attempts were made to protonate HNF_2 and CH_3NF_2 to determine if ammonium-type ions such as $H_2NF_2^+$ and $CH_3NF_2H^+$ could be formed. Three approaches were employed. First, 1 M amounts of H_2O and $HClO_4$

were added to 1 M solutions of HNF_2 in acetonitrile or dimethyl formamide. Conventional infrared spectroscopic techniques indicated that no interaction with the HNF_2 occurred. Second, the strengths of association of CH_3NF_2 and HNF_2 with anhydrous HCl, anhydrous HBr, and water were measured. The techniques employed were similar to those described earlier (11). No association of the difluoramines with any of the acids was observed. Third, infrared spectra of the solid equimolar mixtures HNF_2-H_2O, HNF_2-HCl, HNF_2-HBr, CH_3NF_2-H_2O, CH_3NF_2-HCl, and CH_3NF_2-HBr showed no evidence of protonation. Spectra were obtained at -160°. Both HNF_2 and CH_3NF_2 were observed to oxidize HBr to bromine. No reaction was observed with HCl or H_2O.

TABLE III
INFRARED ABSORPTION MAXIMA OF HNF_2 COMPLEXES

Material	N-H Stretch	N-H Asym. Bend	N-H Sym. Bend	N-F Sym. Stretch	N-F Asym. Stretch
$CH_3CN \cdot HNF_2$ (solid)[a]	2710	1424		960	860
1 M HNF_2 in CH_3OH (liquid)[b]	2725	*	1325*	955	855
$H_2O \cdot HNF_2$ (solid)[a]	2800 2975	1390	1320	973	875
$DMF \cdot HNF_2$ (solid)[a]	2725	*	*	952	850
1 M HNF_2 in DMSO (liquid)[b]	2740	*	*	*	855
HNF_2 (solid)[a]	3110	1450	1350	972	880

*Solvent interference
(a) At -160°
(b) At 25°

A measure of the relative distribution of electrons in a variety of NF_2 compounds was obtained by studying the interaction of the difluoramines with Lewis acids (11). The low-temperature infrared spectra of complexes of difluoramines showed that bonding occurs through donation of electrons on the nitrogen to the Lewis acid. In no cases was evidence found for fluorine bridging or complete charge transfer. The strength of the complexes formed was directly dependent on the electron-withdrawing or -donating power of the attached group. A strongly electron-withdrawing group such as CF_3 renders the X-NF_2 compound an essentially nonpolar species. An electron-donating group such as CH_3 increases the electron density on the nitrogen but also increases the apparent electron density on the fluorines so that compounds such as $CH_3CH_2NF_2$ or HNF_2 readily undergo fluoride abstraction reactions, e.g.,

$$CH_3CH_2NF_2 \longrightarrow CH_3CN + 2HF$$
$$HNF_2 \longrightarrow 1/2\ N_2F_2 + HF$$

Studies of the proton resonance of CH_3NF_2 and $C_2H_5NF_2$ showed that the effective electronegativity of the NF_2 group is about 3.3. Recently, the electronegativity was calculated to be between 3.6 and 3.7 (12). Thus, the NF_2 group is a strong electron-withdrawing moiety itself. The competition for nonbonded electrons may be pictured as in IV and V above. In V the N-F bond is weakened so that reactions of XNF_2 favor routes which involve loss of F^-. In IV the N-F bond is stronger so that XNF_2 reactions favor the

loss of $\cdot NF_2$. We examined the mass spectral cracking patterns of CH_3NF_2 and CF_3NF_2 at low ionization potentials (11 electron volts) and found that the most abundant ions (99%) were $CH_3NF_2^+$ and CF_3^+, respectively. These data indicate that the C-N bond in CF_3NF_2 is weaker than that of CH_3NF_2. This observation is also consistent with analysis of the ultraviolet spectra of these compounds (13). The N-F bond in CH_3NF_2, however, appears to be weaker than in CF_3NF_2. The thermal decompositions of these two difluoramines probably occur through different mechanisms. CF_3 will lose an NF_2 radical in the first step, whereas CH_3NF_2 will lose a fluorine:

$$CF_3NF_2 \longrightarrow \cdot CF_3 + \cdot NF_2$$
$$CH_3NF_2 \longrightarrow CH_3NF + \cdot F$$

The $\cdot NF_2$ and $\cdot F$ will probably then undergo further reactions with the parent molecules:

$$\cdot NF_2 + CF_3NF_2 \longrightarrow NF_3 + CF_3\dot{N}F$$
$$\cdot F + CH_3NF_2 \longrightarrow HF + \cdot CH_2NF_2, \text{ etc.}$$

The CF_3NF_2 does not easily lose a fluoride ion to Lewis acids such as BF_3 (9).

Conclusion

These studies tend to substantiate the prediction of the theoretical calculations that if N-F anions are formed, the electron density on the fluorines will be so high that loss of a fluoride ion would be almost impossible to prevent. Further, the electron affinity of NF_2^+ appears to be extremely high, so that addition of an electron to form $\cdot NF_2$ or addition of an anion to form a covalent NF_2 compound is highly favored. In general, the reaction routes of NF_2 compounds appear to be favored where the reaction intermediate is an $\cdot NF_2$ radical. The $\cdot NF_2$ radical is a relatively stable species with a π-bond order of 0.35. The electron distribution in this species is much more symmetrical than those of the anion or cation. Reaction routes which involve an NF_2 anion intermediate are not very favorable because of the ease of fluoride loss. The NF_2 cation is equally as unfavorable since its oxidizing power will probably prevent it from existing in most systems.

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