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The Interaction of Some Nitrogen–Fluorine Compounds with Lewis Acids

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The interactions of NF_3, N_2F_4, HNF_2, $ClNF_2$, CF_3NF_2, $C_2H_5NF_2$, CH_3NF_2, and CD_3NF_2 with BF_3, BCl_3, PF_5, and SO_2 were studied. The thermal decomposition of complexes formed between the difluoramines and the Lewis acids was studied from −134 to 0°. The relative base strengths of the difluoramines decrease in the order $C_2H_5NF_2 > CH_3NF_2 \sim CD_3NF_2 > HNF_2 > ClNF_2 > N_2F_4 \sim CF_3NF_2 \sim NF_3$. The infrared spectra of the pure difluoramines, the pure Lewis acids, and addition compounds of the difluoramines were obtained at −196°. The spectra show that where complex formation occurs, the intermolecular bonding is through donation of the nitrogen lone-pair electrons to the Lewis acid. No evidence was found for ion formation, fluorine bridging, or appreciable hydrogen bonding in the solid addition compounds or solid difluoramines.

Introduction

Nitrogen–fluorine chemistry has been studied more intensively during recent years than previously and has been the subject of three review articles.[1–3] Compounds containing the NF_2 group are commonly referred to as difluoramines, but, intuitively, the nitrogen in these compounds is assumed to have little basic character. The lone pair of electrons of the nitrogen is more probably displaced toward the vicinity of the two fluorines than localized on the nitrogen. This speculation can be put forth simply on the basis of the inductive effect the two fluorines will have on this pair of electrons. The inductive effect of fluorine attached to other light elements such as boron, aluminum, or silicon is offset somewhat by pπ–pπ (or pπ–dπ in the case of silicon) bonding. However, there are no orbitals available on the nitrogen of energy low enough for significant π-bonding with the unshared electrons on the fluorine atoms.[4] The electron density on the nitrogen and the fluorines in XNF_2 compounds should thus be a direct function of the X group. The purpose of the investigation described here was to determine the electronic effect of the X group where X = F, NF_2, CF_3, CH_3, C_2H_5, Cl, or H. Steric effects have been assumed to be negligible. In particular, the interaction of these XNF_2 compounds with BF_3, BCl_3, PF_5, and SO_2 was studied by low-temperature infrared spectroscopy and by observing the thermal decomposition of low-temperature stable addition compounds of the difluoramines with the Lewis acids.

Results and Discussion

In a series of nitrogen compounds such as that described here, the relative Lewis base strengths, based on inductive effects, should decrease in the order $C_2H_5NF_2 > CH_3NF_2 > HNF_2 > ClNF_2 > NF_2NF_2 \sim CF_3NF_2 \sim FNF_2$. The electronegativity of the NF_2 group is about 3.3.[5] This order is based on the assumption that bonding of these compounds with Lewis acids will occur through coordination of the lone pair of electrons on the nitrogen with the acid. The observations of the thermal decompositions of XNF_2 adducts from −130 to 0° are roughly in agreement with this order of base strength. The decompositions were mostly irreversible or association was so weak that only a few true equilibrium expressions could be obtained. Thus, the total enthalpy of dissociation for the process

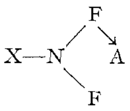
$$XNF_2 \cdot A(s) \rightleftharpoons XNF_2(g) + A(g)$$

was calculated only for $HNF_2 \cdot BF_3$, $HNF_2 \cdot SO_2$, and $CH_3NF_2 \cdot SO_2$ (ΔH = 20.97, 12.50, and 11.80 kcal. mole^{-1}, respectively). The data from the thermal decomposition experiments serve only as a rough guide to the degree of interaction between the XNF_2 compounds and the acids. The results of the thermal decompositions are presented in the Experimental section.

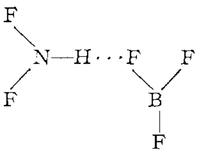
The more important considerations are the mechanism through which association occurs and the subsequent effects on the N–F and N–X bonds. In addition to structures of type I (A = electron acceptor), association in the solid phase could occur through fluorine bridging (II), hydrogen bonding (in some cases) (III), or ion formation (IV). Structure I is best supported by the data reported here. The physical method which appears to lend itself most readily to the determination of the nature of the bonding in these species is infrared spectroscopy. Since all of the adducts decompose well below room temperature, two low-temperature infrared cells were constructed which allowed the spectra of the solid adducts to be recorded at temperatures down to −196°. Reference spectra of the pure XNF_2 compounds and of the pure Lewis acids in the solid state were also obtained.

$XF_2N \rightarrow A$

I



II



III

$XNF^+ + AF^-$

IV

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[1] C. B. Colburn in "Advances in Fluorine Chemistry," Vol. 3, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworths, Washington, D. C., 1963, p. 92 ff.

[2] C. J. Hoffman and R. G. Neville, *Chem. Rev.*, **62**, 1 (1962).

[3] A. V. Pankratov, *Russ. Chem. Rev.*, **32**, 157 (1963).

[4] J. J. Kaufman, *J. Chem. Phys.*, **37**, 759 (1962).

[5] R. Ettinger, *J. Phys. Chem.*, **67**, 1558 (1963).

TABLE I

INFRARED ABSORPTION MAXIMA (CM.$^{-1}$) OF HNF_2 AND HNF_2 COMPLEXES[a]

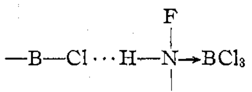
Assignment	$HNF_2(g)$[b]	HNF_2	BF_3[c]	BCl_3	$HNF_2 \cdot BF_3$	$HNF_2 \cdot BCl_3$	$HNF_2 \cdot SO_2$
N–H str.	3193	3110 s			3110 s	2950 s	3100 s
Combination bands		2840 w			2800 vvw	2750 w	2860 w
		2600 vw			2650 vvw	2650 w	2660 w
N–H bend.	1424	1450 s			1430 sh	1460 sh	1440 m
N–H bend.	1307	1350 s			1380 sh	1380 m	1330 sh
Combination band		1300 m			1340 m	1330 m	
$SO_2(s)$							1320 s
							1145 s
B–F antisym. str.			1465 sh		1260 to 1190 s		
			1406 s				
B–F sym. str.			632		Not obsd.		
			622				
B–Cl antisym. str.				985 s		855–810 s	
				950–925 s			
B–N str.					870 br	860 br	
N–F antisym. str.	888	880 s			990 s	985 s	860 s
N–F sym. str.	972	972 s			1065 s	1045 s	975 s

[a] All of these spectra are of the materials in the solid state at −196° except $HNF_2(g)$. [b] J. J. Comeford, D. E. Mann, T. J. Schoen, and D. R. Lide, Jr., *J. Chem. Phys.*, **38**, 461 (1963). [c] D. F. Hornig, *Discussions Faraday Soc.*, **9**, 115 (1950).

HNF_2 Complexes.—The major bands of the absorption spectra of HNF_2, $HNF_2 \cdot BF_3$, $HNF_2 \cdot BCl_3$, and $HNF_2 \cdot SO_2$ and their assignments are given in Table I. The spectrum of solid HNF_2 appears to be essentially the same as that for the gas phase except for a decrease in the N–H stretching frequency and increases in the N–H bending frequencies. These shifts are probably due to hydrogen bonding in the solid. The spectrum of $HNF_2 \cdot SO_2$ indicates that little or no change has occurred in the bonding in HNF_2. Very little, if any, hydrogen bonding appears to be involved, since there are only small changes in the N–H stretching and bending frequencies as compared with those in solid HNF_2. The spectral data and the vapor pressure study indicate that the weak association between HNF_2 and SO_2 involves only small van der Waals forces.

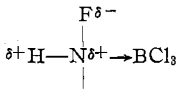
The B–F antisymmetric stretch has shifted from 1465 and 1406 cm.$^{-1}$ (two bands due to B^{10} and B^{11}) in BF_3 to a broad band at 1200 cm.$^{-1}$ in $HNF_2 \cdot BF_3$. This shift is consistent with the same relative shift in $CH_3CN \cdot BF_3$.[6] The B–Cl antisymmetric stretch in $HNF_2 \cdot BCl_3$ is assigned to an envelope centered at 830 cm.$^{-1}$. This type of envelope is diagnostic of the partially tetrahedral BCl_3 group in coordination complexes.[7] There is no indication of any BF_4^- or BCl_3F^- ions in these solids, since the general BF_4^- absorption is an envelope centered at approximately 1050 cm.$^{-1}$ and has been shown to be essentially independent of the cation.[8] The BCl_3F^- envelope would be expected to be in the same region as the envelope at 750 cm.$^{-1}$ of BCl_4^-.[9] The N–F stretching bands in both $HNF_2 \cdot BCl_3$ and $HNF_2 \cdot BF_3$ have been shifted to higher frequencies. This shift is probably caused by a shortening of the N–F bond length. The N–F bond should become shortened if the electron density on the nitrogen is decreased through coordination with the p-orbitals on the boron. The shift of the N–F stretches to higher frequencies indicates that fluorine bridging is not involved in these complexes. If fluorine bridging were involved the N–F bond would be weakened and the N–F stretches should occur at lower frequencies than in HNF_2.

The N–H stretching and bending frequencies are not appreciably changed in $HNF_2 \cdot BF_3$ from what they are in solid HNF_2. There is apparently no more hydrogen bonding in this complex than in solid HNF_2. The N–H stretch in $HNF_2 \cdot BCl_3$, however, has shifted 160 cm.$^{-1}$. This shift may represent hydrogen bonding (V) or simply a weakening of the N–H bond due to a decrease in the electron density on the nitrogen (VI).



$$—B—Cl\cdots H—\overset{F}{\underset{F}{N}}\rightarrow BCl_3$$

V



$$^{\delta+}H—\overset{F^{\delta-}}{\underset{F^{\delta-}}{N^{\delta+}}}\rightarrow BCl_3$$

VI

A greater change in the electron density on the nitrogen in $HNF_2 \cdot BCl_3$ as compared with $HNF_2 \cdot BF_3$ is expected, since BCl_3 is the stronger Lewis acid.[10] These changes are not reflected as much in the N–H bending frequencies. The weakening of the N–H bond is probably the initial step in the decomposition of $HNF_2 \cdot BCl_3$ to yield $ClNF_2$.[11] $HNF_2 \cdot BF_3$ dissociates reversibly.

$$HNF_2 \cdot BF_3 \rightleftharpoons HNF_2 + BF_3$$

The B–N stretching frequencies have tentatively been assigned to the 870 to 850 cm.$^{-1}$ region in both HNF_2 species. This is in agreement with similar assignments by Coerver and Curran for $(CH_3)_3N \cdot BX_3$ and $RCN \cdot BX_3$ complexes.[12] The assignment of the B–N stretch to this frequency range appears reasonable

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(6) S. Sujishi, paper presented at the New York Regional Meeting of the American Chemical Society, Jan. 27, 1964.

(7) W. Gerrard, H. R. Hudson, and E. F. Mooney, *J. Chem. Soc.*, 5168 (1960).

(8) D. W. A. Sharp, *ibid.*, 4804 (1957).

(9) W. Gerrard, E. F. Mooney, and H. A. Willis, *ibid.*, 4255 (1961).

(10) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

(11) R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

(12) H. J. Coerver and C. Curran, *ibid.*, **80**, 3522 (1958).

Table II

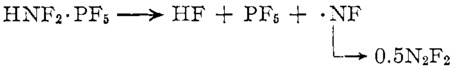
Infrared Absorption Maxima (cm.$^{-1}$) of Alkyldifluoramines

Assignment	$C_2H_5NF_2$(g)^a	$C_2H_5NF_2$(s)^{b,c}	CH_3NF_2(g)^a	CH_3NF_2(s)^b	CD_3NF_2(g)^a
CH_3 C–H asym. str.	3000 m		3030 w	3025 vw	2280 w
CH_3 C–H sym. str.	2950 sh		2950 w	2950 vw	2140 vw
CH_2 C–H str.	2900 sh				
CH_3 asym. def.	1460 wm		1445 m	1435 ms	1140 m
CH_3 sym. def.	1390 w		1410 sh	1390 m	1125 m
C–H bend.	1115 vw		1135 m	1125 m	990 s
C–N str.	1045 wm	1040	1030 s	1035 s	980 s
				1015 sh	970 sh
N–F sym. str.	973 s	960 s	840 br	852 s	785 s
			(850–810)		
			820 sh	840 sh	
N–F antisym. str.	870 s	853		805 s	775 s

^{a} Spectra recorded at 25°. ^{b} Spectra recorded at −196°. ^{c} No assignments were made for the C–H vibrations.

in light of the force constants reported by Goubeau.[13,14] The general force constants for $R_2N–BX_2$, $R_3N–BX_3$, and borazoles were given as 7, 2.5 to 3.1, and 5.7 to 6.3 mdynes/Å., respectively. The general B–N stretch in borazoles and $R_2N–BX_2$ is in the 1350 to 1550 cm.$^{-1}$ region.

The spectra of $HNF_2 \cdot PF_5$ obtained at −196° were of little value for interpretation in terms of bond characteristics. The regions of the spectra from 830 to 1100 and 2500 to 3100 cm.$^{-1}$ are very complex. Most of the observed bands in the 2500–3100 cm.$^{-1}$ region are probably overtone and combination bands. The interpretation of the spectra is further complicated by the fact that PF_5 is ionic in the solid state. Thus, the spectra are probably a mixture of those of $HNF_2 \cdot PF_5$, ionic PF_5, and possibly PF_5 trapped in covalent form. The absence of absorption in the 972 cm.$^{-1}$ region indicates some change in the bonding of HNF_2, but no assignments can be made. It is therefore not possible to say if HNF_2 is bound to PF_5 in $HNF_2 \cdot PF_5$ through fluorine bridging, hydrogen bonding, or donation of the nitrogen lone-pair electrons to the phosphorus. All of these bonding possibilities are compatible with the observed decomposition.



$$HNF_2 \cdot PF_5 \longrightarrow HF + PF_5 + \cdot NF \quad (\cdot NF \longrightarrow 0.5N_2F_2)$$

Alkyldifluoramine Complexes.—Interpretation of the spectra for the CH_3NF_2 complexes was a little more involved than for those of HNF_2. To date, no rigorous analysis of the vibrational spectrum of CH_3NF_2 has appeared in the literature. The high resolution infrared spectra of CH_3NF_2 and of CD_3NF_2 were obtained in the regions of 2–15 μ and 15–35 μ. Analysis of the spectra is in progress and will be presented elsewhere. Tentative assignments are given in this paper (Table II). Assignments have also been made for the spectrum of $C_2H_5NF_2$ for comparative purposes. The symmetric and antisymmetric N–F stretching frequencies of HNF_2 and $C_2H_5NF_2$ occur at about the same place: 972 and 888 cm.$^{-1}$ for HNF_2, and 973 and 870 cm.$^{-1}$ for $C_2H_5NF_2$ (gas phase spectra). The N–F stretching frequencies of CH_3NF_2 in the gas phase appear as a broad band centered at 840 cm.$^{-1}$ which could not be resolved into two distinct bands with a high resolution instrument. There is no absorption in the 970 cm.$^{-1}$ region. It is difficult to determine from the gas phase spectrum whether or not the broad band at 840 cm.$^{-1}$ is due to both N–F stretching frequencies. The spectrum of CH_3NF_2 was therefore obtained as a solid at −196°.

The effect of temperature on band width, band splitting, and intensity has been well described by Hornig[15] and Brown and Sheppard.[16] In general, narrowing of bands is observed on decreasing the temperature. Variations in the spectra may, of course, be due simply to phase changes which involve large alterations in intramolecular bonding. Methyl halides do not show such great shifts in absorption bands[17] nor did HNF_2 in going from the gaseous to the solid state. Little change was observed in the C–H and C–N modes in solid CH_3NF_2 as compared with gaseous CH_3NF_2. The broad band at 840 cm.$^{-1}$, however, is split into two separate and distinct bands: one at 852 cm.$^{-1}$ and one at 805 cm.$^{-1}$. Little alteration of the intramolecular bonding in CH_3NF_2 has appeared to occur in going from the gaseous to the solid state. The band at 852 cm.$^{-1}$ is tentatively assigned as the N–F symmetric stretch and the band at 805 cm.$^{-1}$ as the N–F antisymmetric stretch. The broad band in the gas phase spectra may then be explained as the result of overlapping of the N–F stretching frequencies.

The anomalous positioning of the N–F stretching frequencies is probably due primarily to coupling of these vibrations with the methyl group vibrations. This coupling effect is shown to an even greater extent in the spectrum of D_3CNF_2 where the N–F stretching frequencies appear at 785 and 775 cm.$^{-1}$. If the N–F vibrations were not significantly coupled with those of the methyl group, the isotopic substitution of the hydrogens should have little effect. Electronic effects cannot be completely ruled out, so that the appearance of the N–F stretches in CH_3NF_2 at lower

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(13) J. Goubeau in "Boron-Nitrogen Chemistry," R. F. Gould, Ed., Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p. 87 ff.

(14) See also R. C. Taylor, *ibid.*, p. 59 ff.

(15) D. F. Hornig, *Discussions Faraday Soc.*, **9**, 115 (1950).

(16) J. K. Brown and N. Sheppard, *ibid.*, **9**, 144 (1950).

(17) I. L. Mador and R. S. Quin, *J. Chem. Phys.*, **20**, 1837 (1952).

TABLE III

INFRARED ABSORPTION MAXIMA (CM.$^{-1}$) OF ALKYLDIFLUORAMINE COMPLEXES

Assignment	$C_2H_5NF_2\cdot BF_3$[a]	$C_2H_5NF_2\cdot BCl_3$[a]	$CH_3NF_2\cdot BF_3$	$CD_3NF_2\cdot BF_3$[a]	$CH_3NF_2\cdot BCl_4$	$CD_3NF_2\cdot BCl_3$[a]
C–H asym. str.			3025 vw		3000 w	
C–H sym. str.			2950 vw			
C–H asym. def.			1435 ms		1430 m	
C–H sym. def.			1390 w		1390 w	
C–H bend.			1120 w		1120 m	
C–N str.	1075 m	1070 m	1090 m	1035 s or 1020 s	1030 s 1015 sh	1035 s or 1020 s
N–F sym. str.	970 s	970 s	915 s	825 s	905 s	825 s
N–F antisym. str.	930 s	930 s	852 s,br	805 s	850 s,br	810 s
B–F antisym. str.	1250 s		1290 sh 1245 s	1285 sh 1245 s		
B–Cl antisym. str.		820 s,br			820–800 s	850–830 s,br
B–N str.	845 ms	845 s,br	850 s,br	850 vs 890 sh	840 s,br	875 sh 800 sh

[a] Assignments were not made for the C–H vibrations because of the complexity of the spectra in that region. All spectra recorded are of solids at −196°.

frequencies may also be partly due to a weaker N–F bond than those in $C_2H_5NF_2$ or HNF_2.

The spectra of the complexes of methyl- and ethyldifluoramine have been interpreted (Table III) in terms of the assignments given to solid CH_3NF_2 and $C_2H_5NF_2$. The spectra are quite analogous to those of the HNF_2 adducts. The spectrum of $CH_3NF_2\cdot SO_2$ did not show any significant changes in the various absorption bands. The intermolecular bonding in $CH_3NF_2\cdot SO_2$ is apparently as weak as it is in $HNF_2\cdot SO_2$. The same problems of complexity in the 800–1100 cm.$^{-1}$ region of the spectrum of $HNF_2\cdot PF_5$ were encountered in the spectrum of $CH_3NF_2\cdot PF_5$ and no good analysis could be made.

The spectra of $CH_3NF_2\cdot BF_3$, $CH_3NF_2\cdot BCl_3$, $C_2H_5NF_2\cdot BF_3$, $C_2H_5NF_2\cdot BCl_3$, $CD_3NF_2\cdot BF_3$, and $CD_3NF_2\cdot BCl_3$ all show a shift of the N–F stretches to frequencies higher than in the uncomplexed difluoramines. The B–X vibrations have all shifted to locations typical of $\rightarrow BX_3$ tetrahedral configurations and appear in about the same locations as in $HNF_2\cdot BX_3$. The B–X vibrations are similar in both cases and the N–F vibrations have shifted less in the alkyldifluoramines. These observations are consistent with a greater electron density on the nitrogens in the alkyldifluoramines than in HNF_2. The assignment of the B–N stretch in $CD_3NF_2\cdot BF_3$ and in $C_2H_5NF_2\cdot BF_3$ to 850 cm.$^{-1}$ is unambiguous in light of the spectra of the other complexes.

The weakness of the N–F bond and high electron density on the fluorines are probably the causes for the ready tendency of the alkyldifluoramines to undergo fluorine abstraction reactions. The general mechanism proposed for the reactions of difluoramines with Lewis acids may be exemplified by

$$CH_3NF_2 + BF_3 \rightleftharpoons CH_3NF_2\cdot BF_3 \qquad (1)$$

$$CH_3NF_2\cdot BF_3 \longrightarrow CH_2{=}NF + HF + BF_3 \qquad (2)$$

$$CH_2{=}NF + BF_3 \rightleftharpoons CH_2{=}NF\cdot BF_3 \qquad (3)$$

$$CH_2{=}NF\cdot BF_3 \longrightarrow HC{\equiv}N + BF_3 + HF \qquad (4)$$

The point of attack is most probably not the protons since CH_3NF_2 is relatively stable to attack by KOH as compared with attack by BF_3. CH_3NF_2 can be pumped across solid KOH in the vacuum system with little decomposition. HNF_2 is completely destroyed by such treatment. Reactions 3 and 4 appear to be much faster than 2 because even (with BCl_3 and PF_5 as well as BF_3) when some unreacted CH_3NF_2 was recovered, no $CH_2{=}NF$ was detected.

Other NF_2 Species.—The spectra of $NF_3\cdot BCl_3$, $NF_3\cdot BF_3$, $CF_3NF_2\cdot PF_5$, and $CF_3NF_2\cdot BF_3$ were also obtained at −196°. In all the spectra which were examined, there were no bands which could not be attributed to the parent covalent molecules. The spectra indicate that the weak association in these systems is through small van der Waals forces and does not involve any appreciable fluorine bridging, charge transfer, or electron donation. Many substances which are covalent in the gaseous state have been shown to be ionic in the solid state, *e.g.*, $PCl_5 \rightleftharpoons PCl_4^+ PCl_6^-$.[18] It may be possible that some NF_2 compounds exhibit ionic forms in the solid state at low temperatures, *e.g.*, NF_2^+ and NF_2^- in N_2F_4. The spectra of solid N_2F_4, NF_3, $ClNF_2$, and HNF_2 were obtained at −196°, but no absorption bands were observed which could be attributed to ionic species. These NF_2 compounds appear to be covalent in all three phases.

Conclusion

All of the complexes studied in this work are formed primarily by donation of the nitrogen lone-pair electrons to the Lewis acid. Very little evidence was found for hydrogen bonding and no evidence was found for fluorine bridging or ion formation in the solid state. The nitrogen in $X-NF_2$ is in a tetrahedral sp^3 configuration and most probably retains this configuration in the complex. The boron is in a planar sp^2 configuration in BX_3 and reorganizes to an sp^3 form in the complex. Donation of electrons reduces the amount of B–X $p\pi-p\pi$ bonding and probably causes a lengthening of the B–X bond as reported for amine–boron halide complexes.[19]

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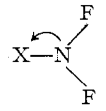
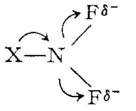
(18) G. L. Carlson, *Spectrochim. Acta*, **19**, 1291 (1963).

(19) J. L. Hoard, S. Geller, and T. B. Owen, *Acta Cryst.*, **4**, 405 (1951).

In general, the work reported here indicates that the inductive effect of the X group in XNF_2 has a significant effect on the availability of the lone pair of electrons on the nitrogen and on the character of the N–F bond. The data in Table IV show that as X becomes more electronegative (VII), the N–F stretches shift to higher frequencies, empirically indicating a shortening of the N–F bond. The spectra of the complexes of NF_2 compounds and the thermal decomposition of the complexes indicate a lowering of the availability of the lone pair of electrons on the nitrogen. If X becomes more of an electron donor (VIII), then the availability of electrons on the nitrogen increases, but the apparent electron density on the fluorines also increases. The increase in electron density on the fluorines causes NF_2 compounds such as the alkyldifluoramines to undergo ready fluoride abstraction. Compounds such as CF_3NF_2, where X is strongly electronegative, are much more resistant to decomposition by loss of a fluoride ion.



VII



VIII

TABLE IV

Compound	N–F sym. str., cm.$^{-1}$	N–F antisym. str., cm.$^{-1}$
CH_3NF_2[a]	852	805
$C_2H_5NF_2$	975	850
HNF_2	972	888
$ClNF_2$	925	855
NF_3	1032	910
FSO_2ONF_2[b]	1032	913
CF_3NF_2	1030	950

[a] The anomalous positioning of the N–F bands here is due to the mass effect described in the Results and Discussion. [b] M. Lustig and G. H. Cady, *Inorg. Chem.*, **2**, 388 (1963).

Experimental

Apparatus.—All work was carried out in a conventional glass high-vacuum system. Fluorocarbon grease was used to lubricate the stopcocks. Temperatures below 0° were measured by a standardized iron–constantan thermocouple. A glass spiral gauge was employed to make pressure readings when the compounds being studied might react with mercury.

Materials.—The purity of all of the starting materials was checked by their infrared spectra, mass spectra, and low-temperature gas chromatographic analyses. BF_3, BCl_3, PF_5, SO_2, N_2F_4, and NF_3 were obtained from commercial suppliers in research grade quality and further purified by low-temperature vacuum distillations. Difluoramine, HNF_2, was prepared by the reaction of concentrated H_2SO_4 with trityldifluoramine.[20] Trityldifluoramine, ethyldifluoramine, and some of the methyldifluoramine were obtained from Peninsular Chemresearch, Inc. Perfluoromethyldifluoramine was obtained from the Hynes Chemical Research Corp. Trideuteriomethyldifluoramine, D_3CNF_2, and most of the methyldifluoramine were prepared electrolytically by the method of Ward and Wright.[21] All of the alkyldifluoramines were purified immediately prior to their use. Other methods of preparation of alkyldifluoramines are included in a recent review of N–F chemistry by Colburn.[1]

Formation and Decomposition of Complexes.—Equimolar quantities of the difluoramine and the Lewis acid to be studied were measured separately in a calibrated bulb, allowed to mix momentarily in the gas phase at room temperature, and then immediately condensed together in a cold finger at −196°. Complexes which underwent reversible dissociation were further mixed by allowing them to warm to about −25° and recooling to −196°. Complexes which underwent irreversible decomposition were not mixed after initially being cooled to −196°. Preliminary experiments were carried out to determine the reversibility of decomposition of the various complexes before more exacting studies were made. The dissociation pressures of the complexes were measured as they were allowed to warm slowly from −134 to 0°. Three or four points were taken on cooling the mixtures back to −196° at the end of each experiment to determine if the dissociation was completely reversible. The total time elapsed during a typical experiment was about 10 hr. Temperatures were measured to ±0.1° and pressures to ±0.2 mm. Equations were obtained through simple regression analysis of the data on a Bendix G-15 computer. When the amount of association was small, no equilibrium expressions or degrees of association were derived. The fact that any association was involved is based on deviations of the observed vapor pressures from ideality. No association of any of these mixtures, where no chemical reaction took place, was observed in the gas phase. The absence of association in the gas phase was determined by gas density measurements. The boiling points of the compounds studied are: NF_3,[22] −129°; N_2F_4,[23] −73°; HNF_2,[24] −23.6°; $ClNF_2$,[11] −67°; CF_3NF_2,[25] −77°; CH_3NF_2,[26] −16.0°; $C_2H_5NF_2$,[26] +14.9°; BF_3,[27] −110.7°; BCl_3,[27] +12.7°; PF_6,[28] −75°; SO_2,[27] −10.0°.

The products of dissociation or decomposition of the complexes were separated by low-temperature vacuum distillations. The products were monitored by infrared spectra and analyzed by mass spectrometry.

$HNF_2 \cdot BF_3$.—This complex begins to exert a measurable dissociation pressure at −63°. The reversible dissociation over the range −56.5 to −23.1 is described by the equation: $\ln Kp = -10{,}566/T + 54.286$; $Kp = P^2/4$; $\Delta H = 20.97$ kcal. mole^{-1}.

t, °C.	−56.5	−53.8	−49.2	−48.1
P, mm.	32.0	42.5	70.5	77.0
t, °C.	−42.4	−40.7	−36.0	−30.7
P, mm.	139.0	171.0	248.0	424.5

$HNF_2 \cdot BCl_3$.—This complex exerts little or no measurable vapor pressure up to −80°, where it begins to decompose irreversibly to yield $ClNF_2$, as previously reported by Petry.[11] Other volatile products of the decomposition were found to be primarily BF_3, BCl_3, and HCl.

$HNF_2 \cdot SO_2$.—This adduct exerts a measurable vapor pressure above −80°. The reversible decomposition over the range −73.4 to −29.5° is described by the equation: $\ln Kp = -6291.2/T + 35.978$; $\Delta H = 12.50$ kcal. mole^{-1}.

t, °C.	−73.4	−65.9	−57.9	−49.9
P, mm.	17.5	34.0	58.0	100.5
t, °C.	−46.8	−40.6	−31.6	−29.5
P, mm.	125.0	166.8	274.0	321.0

$HNF_2 \cdot PF_5$.—This complex exerts only a small (about 10 mm.) vapor pressure up to −50°, where it undergoes irreversible decomposition to yield N_2F_2 (*cis* and *trans*), PF_5, and HF.

$ClNF_2 + BF_3$.—$ClNF_2$ was found to be weakly associated with BF_3 below −78°.

$NF_3 + BF_3$.—Weak association of NF_3 with BF_3 was observed below −125°. The heat of dissociation is so small that a true equilibrium expression was not obtainable.

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$NF_3 + BCl_3$.—Weak association of NF_3 with BCl_3 was observed below −100°. No chemical reaction took place on warming to room temperature.

$NF_3 + PF_5$.—No association or chemical reaction was observed down to −128°.

$NF_3 + SO_2$.—No association or chemical reaction was observed down to −130°.

$N_2F_4 + BF_3$.—Weak association was observed below −120°. A good equilibrium expression was not obtainable.

$N_2F_4 + BCl_3$.—Weak association was observed below −78°.

$N_2F_4 + SO_2$ and $N_2F_4 + PF_5$.—No association was observed down to −120°. No chemical reaction occurred on warming to room temperature.

$CH_3NF_2 \cdot BF_3$, $CH_3NF_2 \cdot BCl_3$, and $CH_3NF_2 \cdot PF_5$.—These complexes exerted no vapor pressure up to −50, −78, and −96°, respectively. All of these addition compounds decomposed irreversibly to give HCN, HF, and the Lewis acid. $CH_3NF_2 \cdot BCl_3$ yielded a small amount of BF_3 on decomposition.

$CH_3NF_2 \cdot SO_2$.—This complex began to exert a measurable vapor pressure above −97°. The reversible dissociation over the range −97.0 to −21.1° is described by the equation: $\ln Kp = -5937.9/T + 34.910$; $\Delta H = 11.80$ kcal. mole^{-1}.

t, °C.	−77.5	−66.0	−57.9	−52.7	−47.4	−32.5	−28.2	−21.1
P, mm.	20.0	44.5	75.5	105.7	150.5	338.0	414.5	575.8

$C_2H_5NF_2 \cdot BF_3$ and $C_2H_5NF_2 \cdot BCl_3$. These species were both stable up to about −100°, where they decomposed irreversibly to yield $CH_3CN \cdot BF_3$ and $CH_3CN \cdot BCl_3$, respectively, plus HF.

$CF_3NF_2 + BF_3$ and $CF_3NF_2 + BCl_3$.—Weak association was observed in these two systems below −121 and −91°, respectively. No chemical reaction took place on warming to room temperature.

Infrared Spectra.—Gas phase spectra were obtained using 10-cm. gas cells, 38 mm. in diameter, fitted with sodium chloride windows. Solid phase spectra were obtained using two cells similar to that described by Sharp.[29] One cell contained an inner window which was cooled by a copper block connected through a Kovar seal to a dewar flask. The other cell was constructed entirely of glass to eliminate possible contamination by metal fluorides. The internal window of this cell was cooled by liquid nitrogen, from the dewar flask, which flowed around the window in a glass ring. The copper block affords better heat transfer than the glass and usually does not cause contamination after being passivated. No sealant was used on the internal windows of either cell. All the windows used were sodium chloride. Since very low temperatures (usually −196°) were involved in all the experiments, there was seldom any interaction of the compounds with the windows.

Light coatings of single compounds on the internal cell window were obtained by rapidly condensing the compound from a gas at room temperature to a solid on the window at −196°. No phase transitions were observed once the compound was condensed onto the window. All of the spectra were reproducible. Therefore, unusual glass phases were not being observed. Spectra of all of the individual compounds studied were obtained as references for analysis of the spectra of the complexes. The spectra of the complexes and mixtures of compounds were obtained by allowing equimolar (*ca.* 0.1 mmole) amounts of the two compounds to mix for about 1 min. in the gas phase at room temperature and then condensing them onto the window at −196°. After the spectrum of the solid phase was obtained, the internal window was allowed to warm to room temperature and the gas phase spectrum was obtained. These gas phase spectra were very helpful in determining if any reaction had occurred on warming to room temperature. Most of the spectra were obtained with a Perkin-Elmer Model 137 spectrometer. Gas phase spectra of CH_3NF_2 and CD_3NF_2 were obtained with a Beckman IR-7 spectrometer. The choice of the lower resolution instrument for the solid phase spectra was made because of the explosive properties of most of the difluoramine compounds studied.

Caution: The reader is reminded that organodifluoramines are shock-sensitive explosives. N_2F_4 and HNF_2 form explosive mixtures with hydrocarbons. HNF_2 is known to detonate spontaneously in the solid state and in the liquid–solid transition. Suitable safety shielding should be employed when handling these compounds.

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