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THERMOCHEMISTRY OF NF_4^+ SALTS

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SUMMARY

The decomposition, solid phase change, and the formation enthalpies were determined for NF_4BF_4, NF_4PF_6, NF_4AsF_6, NF_4SbF_6, NF_4GeF_5 and $(NF_4)_2GeF_6$ by differential scanning calorimetry. It is shown that $(NF_4)_2GeF_6$ is an intermediate in the decomposition of NF_4GeF_5. The enthalpies of reaction in water of NF_4BF_4, NF_4PF_6, NF_4AsF_6 and NF_4SbF_6 were measured and used to obtain an alternate set of formation enthalpies for these compounds. Recommended values for $H_f^o(NF_4XF)_{(s)}$ are: NF_4BF_4 = -1410±5, NF_4SbF_6 = -1669±12, NF_4AsF_6 = -1538±11, NF_4PF_6 = -1841±7, NF_4GeF_5 = -1473±1, and $(NF_4)_2GeF_6$ = -1606±5 kJ mol^{-1}. The formation enthalpies of the NF_4^+ salts were used to estimate the F^+ ion affinity of NF_3 and the enthalpy of formation of gaseous NF_4^+. The reaction enthalpy of the process $NF_3(g) + F_{2(g)} \rightarrow NF_4^+F^-_{(s)}$ was estimated.

INTRODUCTION

Although NF_4^+ salts have now been known for a number of years [1,2], thermodynamic data on these compounds are few. Thus, until very recently, the only available experimental data were in an unpublished report on the enthalpy of formation of NF_4BF_4 from its calorimetrically determined enthalpy of decomposition [3], and overall activation energies obtained from kinetic measurements on the thermal decomposition of NF_4BF_4 and NF_4AsF_6 [4]. Since NF_4^+ salts have considerable potential as principal ingredients in solid-propellant gas generators [5-7] and as high detonation pressure explosives [8], reliable thermochemical data are clearly needed for the computation of parameters such as theoretical performance and flame temperatures. In addition, from the enthalpies of formation of NF_4^+ salts it is possible to obtain the enthalpy of formation of gaseous NF_4^+ ion and hence the F^+ ion affinity of NF_3; knowledge of these quantities allows, for example, conclusions to be reached about the possible existence of NF_5 in the ionic form $NF_4^+F^-$. The existence of NF_5 has previously been claimed [9], however experiments carried out at Rocketdyne using UV-photolysis of NF_3 - F_2 mixtures at 77K [10] have failed to confirm this.

The major problem in the thermochemistry of NF_4^+ salts is the scarcity of suitable quantitative reactions leading to well defined products. In the present work two very different approaches have been used, viz. differential scanning calorimetry at 150-350°C [11], and solution calorimetry at 25°C [12, 13]. Under ideal conditions, the results from both methods should agree closely; the actual discrepancies are some measure of the experimental difficulties in preventing side reactions and, in some cases, of the lack of reliable auxiliary data. Very recent work by two of us [11] on NF_4SbF_6 is also referred to in the present communication.

EXPERIMENTAL AND RESULTS

Materials. The compounds NF_4BF_4, NF_4PF_6, NF_4AsF_6, NF_4SbF_6, NF_4GeF_5 and $(NF_4)_2GeF_6$ were prepared by literature methods [10,14,15], and, except for the last named compound, did not show impurities detectable by analytical or spectroscopic techniques [16]. The amount of impurities in $(NF_4)_2GeF_6$, mainly NF_4BF_4, and NF_4GeF_5, was only a few percent and was too low to significantly disturb the measurement of the thermal effects.

Differential Scanning Calorimetric Measurements. Thermograms (i.e. thermal effect vs time) of samples loaded in an evacuable prefluorinated Monel cell were obtained using an Arion M.C.B. microcalorimeter. The heat effect calibration was achieved by Joule effect generation of a known heat, the heat changes involved during the phenomena were evaluated by comparison of experimental and calibration peaks, the areas of which were measured with a planimeter. The principle of the microcalorimeter based upon differential calorimetric analysis has been described previously [17], and the method has already been shown to be successful in the thermal decomposition of other NF_4^+ salts [11]. For all runs the completion of decomposition was confirmed by weighing. The resulting data for NF_4BF_4, NF_4PF_6, NF_4AsF_6, NF_4GeF_5 and $(NF_4)_2GeF_6$ are given in Table 1 and are based on the average of five runs for each compound. The necessary ancillary data are listed in Table 2 together with those required for the thermochemical measurements. The previously observed [9,10] phase transitions were confirmed for NF_4BF_4, NF_4PF_6, NF_4AsF_6 and NF_4SbF_6. For the latter two compounds, x-ray powder patterns of the high temperature phases were also recorded. For NF_4AsF_6, a cubic phase with $a=9.13\pm0.03$Å was observed at 166°C. For NF_4SbF_6 a cubic phase with $a=5.66\pm0.08$Å, which was observed at ambient temperature in one of the sample preparations, might be due to the "frozen" high temperature form. For NF_4GeF_5, a three step decomposition was observed. The first two steps were shown by vibrational spectroscopy to mainly involve the chemical transformation of NF_4GeF_5 to $(NF_4)_2GeF_6$,

$$2NF_4GeF_5 \rightarrow (NF_4)_2GeF_6 + GeF_4 \qquad (1)$$

whereas the third step is mainly due to the thermal decomposition of $(NF_4)_2GeF_6$

$$(NF_4)_2GeF_6 \rightarrow 2NF_3 + 2F_2 + GeF_4 \qquad (2)$$

The latter step was also confirmed by comparison with the decomposition curve of an authenthic sample of $(NF_4)_2GeF_6$. From these data, the enthalpy change for reaction (1) was found to be 148kJ mol^{-1}.

The enthalpies of formation of the NF_4^+ salts (see Table 1) were calculated assuming the decomposition mode

$$NF_4^+XF^- \xrightarrow{T} NF_3 + F_2 + X \qquad (3)$$

well established [4,9,10] for closed containers. The validity of this assumption for the dynamic vacuum conditions of this study was confirmed by collection and identification of the decomposition products and by the excellent agreement between the results of this study for NF_4BF_4 and those previously carried out in a closed container [3]. The enthalpies of formation of the solid NF_4^+ salts are given by

$$\Delta H_f^\circ(NF_4XF)_{(s)} = \Delta H_f^\circ(NF_3)_{(g)} + \Delta H_f^\circ(X)_{(g)} - \Delta H^T_{decomp}(NF_4XF)_{(s)} +$$
$$+ [H^T-H^\circ](NF_3)_{(g)} + [H^T-H^\circ(F_2)_{(g)} + [H^T-H^\circ](X)_{(g)} - [H^T-H^\circ](NF_4XF)_{(s)}$$

TABLE 1

Results[a] of the DSC Study of NF_4^+ Salts

	Phase Change				Decomposition			Total ΔHdec (RT form)	ΔH_f298 (NF_4 salt)[b]
	T_{onset}	T_{max}	ΔH	ΔS	T_{onset}	T_{max}	ΔH		
NF_4BF_4	224±2	237±3	7.58±0.5	15.27±1.05	162±7	257±11	134.3±4.2	141.9±5.8	-1409±6
NF_4PF_6	131±2	142±0.5	5.90±0.37	14.50±0.95	173±3	260±3	126.5±6.8	132.4±7.0	-1841±7
NF_4AsF_6	145±1	155±2	4.62±0.38	10.96±0.86	245±7	323±5	164.7±10.6	169.3±10.9	-1538±11
NF_4SbF_6[c]					305±4	382±7	245.6±12	245.6±12	-1674±12
NF_4GeF_5[d]					101±6[d]	202±5[d]	149.6±1.2[d]	149.6±1.2	-1473±1
$(NF_4)_2GeF_6$[e]					167±0.7	208±1.6	151.3±5.3	151.3±5.3	-1606±5

[a] Units: T, °C; H, kJ mol^{-1}; S, JK^{-1}mol^{-1}. [b] The given standard deviations (1σ) are based on the uncertainties of H decomp. and do not include uncertainties in the heats of formation of the decomposition products.

[c] For NF_4SbF_6, the phase transition was observed as a shoulder on the decomposition peak and therefore could not accurately be measured. T_{onset} is estimated to be 325°C. [d] The decomposition of NF_4GeF_5 involves three steps (see text); T_{onset} (temp. of beginning decomp.) refers to step 1 and T_{max} (temp. of maximum heat effect) to step 3; step 1 and 2 = 45.0 kJ mol^{-1}, step 3 = 104.6 kJ mol^{-1}. [e] Due to the rapid decomposition rate of $(NF_4)_2GeF_6$, a slower heating rate (1°C min^{-1}) and smaller sample sizes had to be used to avoid solids to be blown out of the reactor.

TABLE 2

Ancillary Thermochemical Data (kJ mol^{-1})

ΔH_f^o	$NF_{3(g)}$	= -131.4	[18]	ΔH_f^o	$F^-_{(g)}$	= -249	[23]
ΔH_f^o	$BF_{3(g)}$	= -1136.0	[18]	E.A.	F	= -328	[23]
ΔH_f^o	$PF_{5(g)}$	= -1577.6	[18]	ΔH^o diss	$F_{2(g)}$	= +159	[23,24]
ΔH_f^o	$AsF_{5(g)}$	= -1236.8	[19]	ΔH_f^o	$F^+_{(g)}$	= +1760	[23,24]
ΔH_f^o	$SbF_{5(\ell)}$	= -1328	[20]	ΔH_f^o	$K^+_{(g)}$	= +514.9	[22]
ΔH_f^o	$GeF_{4(g)}$	= -1191.9	[19]	ΔH_f^o	$K^+_{(aq)}$	= -251	[22]
ΔH_{vap}^{418K}	$SbF_{5(\ell)}$	= 43.4[a]	[21]	ΔH_{sol}	$K^+_{(g)}$	= -766	[22]
ΔH_f^o	$SbF_{5(g.monomer)}$	= -1297.1[b]					
ΔH_f^o	$H_2O_{(\ell)}$	= -286	[22]				
ΔH_f^o	$HF_{(aq)}$	= -332	[22]				
ΔH_f^o	$F^-_{(aq)}$	= -335	[22]				

[a] Refers to an approximately trimeric vapor (see text).

[b] See text

Since the temperature dependence of the enthalpy of the solid NF_4XF salts is unknown, and since the $[H^T-H^o]$ terms of the solid starting material and of the gaseous decomposition products might cancel each other to a large extent, all $[H^T-H^o]$ terms were ignored in our calculations of $\Delta H_f^o(NF_4XF)_{(s)}$. In the case of NF_4SbF_6, ΔH_f^o was recalculated in the same manner using the previously given [11] experimental data and $\Delta H_f^o(SbF_5)_{(g,monomer)}$ = -1297.1 kJ mol^{-1} (see below) to conform with the other values listed in Table 1.

TABLE 3

Enthalpies of Solution Reactions (kJ mol^{-1}) of NF_4XF Salts

	NF_4BF_4 [d]	NF_4PF_6	NF_4AsF_6	NF_4SbF_6
H_2O	(-244±18)	(-269±10)	-330±10	(-269±10)
H_2O/Pt	-298±30	-309±20	-329±16	-304±20
0.1MKI [a]	(-472±15)	(-471±17)	(-505±17)	(-504±18)
0.1MKI [b]	-300±15	-299±17	-333±17	(-332±18)
1MKOH	(-345±20)	(-390±20)	(-429±20)	(-748±40)
1MKOH/Pt				(-872±30)
1MHClO$_4$		(-220±9)		
1M/3MHCl	-327±27	-293±9		-310±10
1MHBr	(-390±20)			
Average value [c]	308±26	300±16	330±13	307±15

[a] Experimental values based on equation (5)

[b] Recalculated values corresponding to equation (6)

[c] Average of the unbracketed values

[d] Bracketed values refer to non-stoichiometric reactions

Solution Calorimetry Measurements. These were made in a LKB calorimeter with ancillary apparatus as described previously [12]; the performance of the calorimeter was monitored from time to time via determination of the enthalpy of solution of potassium chloride in water [25]. Samples of betwee 10 and 40 mg were used, with 30 or 100 cm^3 of water or other aqueous hydrolyzing medium.

In agreement with previous reports [10,16], it was found that the hydrolysis of NF_4^+ salts resulted in rapid and quantitative NF_3 evolution, but that quantitative O_2 evolution was more difficult to achieve. Hence, different reaction conditions were studied. Of the various reactions listed in Table 3, those in water, 1M- or 3M-HCl and in 0.1M-KI are the most significant since in these cases quantitative or almost quantitative results were most likely achieved. Ideally, all the compounds studied should react with water according to the general equation,

$$NF_4XF_{(s)} + H_2O_{(\ell)} \xrightarrow{h_1} NF_{3(g)} + H^+_{(aq)} + HF_{(aq)} + XF^-_{(aq)} + \tfrac{1}{2}O_{2(g)} \qquad (5)$$

but O_2 evolution is not quantitative (except, apparently, for NF_4AsF_6), unless sufficient Pt black is present to decompose intermediates such as H_2O_2 [10]. If H_2O_2 were to be formed quantitatively as a hydrolysis product, then the measured enthalpy should be about 95 kJ mol^{-1} less exothermic than if the final product is oxygen; a situation that was approximated for NF_4PF_6 in 1M-$HClO_4$. Freshly prepared solutions of NF_4PF_6 in water showed considerable oxidizing power and decolorized permanganate, which indicates the presence of H_2O_2. Another significant side reaction is the formation of ozone. A recent study at Rocketdyne has shown that several mol percent of ozone are always formed in the hydrolyses of NF_4^+ salts in water,even under very carefully controlled reactions. If O_3 were to be formed quantitatively, then the measured enthalpy should be about 48 kJ per mol of NF_4^+ less exothermic than if the final product is oxygen. The results with alkali show that non-quantitative reactions were taking place which involved the hydrolysis of the anion as well as that the cation; as expected, this phenomenon is most apparent for SbF_6^-. Although the alkali metal salts (except Li^+) of PF_6^- and AsF_6^- are kinetically nearly inert towards dilute alkali at 298K, it should be noted that with the highly exothermic NF_4^+ salt hydrolyses there is always the possibility of anion involvement even under carefully controlled reaction conditions. The large uncertainties in many of the hydrolysis values are probably the results of such factors and perhaps of others, such as incomplete decomposition of H_2O_2 or O_3 formation which would act in the opposite sense. Assuming the followoing reaction with KI

$$NF_4XF_{(s)} + 3I^-_{(aq)} \longrightarrow NF_{3(g)} + XF^-_{(aq)} + F^-_{(aq)} + I^-_{3(aq)} \qquad (6)$$

and recalculating the measured values according to equation (5) excellent agreement with the H_2O-Pt black values is obtained (Table 3), except for NF_4SbF_6, where the redox reaction between Sb(V) and excess of I^- is important.

In choosing final values for the hydrolyses of NF_4XF salts according to equation (5) (Table 4), we have taken the average of the unbracketed values of Table 3 which, in our opinion, are least affected by side reactions.

From the data of Table 3, together with measured enthalpies of solution of KBF_4, KPF_6, and $KSbF_6$ and their known enthalpies of formation, the enthalpies of formation of the corresponding NF_4^+ salts may be determined (Table 4), using equations (5), (7), and (8)

TABLE 4

Thermochemical Data (kJ mol^{-1}) for NF_4XF Salts at 298.2K

Anion	BF_4^-	PF_6^-	AsF_6^-	SbF_6^-
$\Delta H_{sol}(NF_4^+$ salt)	-308 ± 26^a	-300 ± 16^a	-330 ± 13^a	-307 ± 15^a
$\Delta H_{sol}(K^+$ salt)	$+35.0^a$	$+38.1^a$	$+42.8^a$	$+38.5^a$
$\Delta H_f^o(K^+$ salt)	-1884[26-28]	-2312[29]	-	-2083[29]
$\Delta H_f(NF_4^+$ salt)	-1467	-1900		-1663

[a] This work

$$KXF_{(s)} \xrightarrow[H_2O]{h_2} K^+_{(aq)} + XF^-_{(aq)} \qquad (7)$$

$$\Delta H_f^o(NF_4XF)_{(s)} = h_2 - h_1 + \Delta H_f^o(NF_3)_{(g)} + \Delta H_f^o(H^+)_{(aq)} + \Delta H_f^o(HF)_{(aq)} - \Delta H_f^o(K^+)_{(aq)} - \Delta H_f^o(H_2O)_{(\ell)} + \Delta H_f^o(KXF)_{(s)} \qquad (8)$$

Substituting the appropriate ancillary data from Table 2, equation (8) becomes

$$\Delta H_f^o(NF_4XF)_{(s)} = h_2 - h_1 + \Delta H_f^o(KXF)_{(s)} + 74\text{kJ mol}^{-1} \qquad (9)$$

The solubility of NF_3 in water is small[30,31] so $\Delta H_{sol}(NF_3)_{(g)}$ has been neglected. Assuming that the uncertainties in the values of h_1 are most significant, the uncertainties in the $\Delta H_f(NF_4XF)_{(s)}$ values of Table 4 are probably ±30 kJ mol^{-1} or less, depending on the nature of the anion.

DISCUSSION

The data for enthalpies of formation of NF_4BF_4, NF_4PF_6, NF_4AsF_6, NF_4SbF_6, NF_4GeF_5 and $(NF_4)_2GeF_6$ are brought together in Table 5, which

TABLE 5

Enthalpies of Formation and Dissociation of Some NF_4^+ Salts (kJ mol^{-1})

Anion	BF_4^-	PF_6^-	AsF_6^-	SbF_6^-	GeF_5^-	GeF_6^{2-}
$\Delta H_f^o(NF_4XF)_{(s)}$						
DSC	-1409±6	-1841±7	-1538±11	-1674±12	-1473±1	-1606±5
Sol. Cal.	-1467	-1900		-1663		
TDC[a]	-1412±5					
$\Delta H\ (NF_4XF_{(s)} \rightarrow NF_{3(g)} + F_{2(g)} + X_{(g)})$						
DSC	142	132	169	246	150	151
Sol. Cal	200	191		232		
TDC[a]	145					

[a] Unpublished results from [3] determined by thermal decomposition calorimetry.

indicates clearly the agreement for NF_4SbF_6 and the divergences for NF_4BF_4 and NF_4PF_6 using the two very different approaches. The results for NF_4SbF_6 are based upon $\Delta H_f(SbF_5)_{(\ell)} = -1328$ kJ mol^{-1} rather than the previously used [11] value of -1336 kJ mol^{-1}, and it has been necessary to assume the equilibrium $\frac{1}{4}(SbF_5)_{4(g)} \rightleftarrows SbF_{5(g)}$ with a relative molecular mass corresponding to trimers at the b.p. [32] and to monomers at the decomposition temperature of NF_4SbF_6. The enthalpy of dissociation of $\frac{1}{4}(SbF_5)_4$ has recently been estimated to be 18.5 kJ mol^{-1} from vapor density measurements, assuming a mixture of two tetrameric and one monomeric SbF_5 corresponding to an average trimeric molecular weight [32]. Although gaseous SbF_5 has recently been shown by electron diffraction to consist at ambient temperature principally of the trimer [33], the above value, combined with the enthalpy of vaporaization of liquid SbF_5 to the gaseous trimer [21], can be used to estimate $\Delta H(SbF_{5(\ell)} \rightarrow SbF_{5(g)}$ (monomer)) $= 8/9\ \Delta H_{diss} + 1/3\ \Delta H_{vap} = 30.9$ kJ mol^{-1}, based on the following equations:

$$2(SbF_5)_4 + SbF_5 \rightleftharpoons 3(SbF_5)_3 \quad , \quad (SbF_5)_{3(\ell)} \xrightarrow{\Delta Hvap} (SbF_5)_{3(g)}$$

$$\tfrac{1}{4}(SbF_5)_{4(g)} \xrightarrow{\Delta Hdiss} SbF_5(g) .$$

A comparison of the data of Table 5 shows that for NF_4BF_4 the DSC and the previously found [3] thermal decomposition calorimetry value are in excellent agreement. Both values were obtained with relatively small uncertainties by direct methods and support a value of -1410±5 kJ mol^{-1} for $\Delta H_f^o(NF_4BF_4)_{(s)}$. For NF_4SbF_6, the DSC and the solution calorimetry value are in good agreement and support a value of -1669±12 kJ mol^{-1} for $\Delta H_f^o(NF_4SbF_6)_{(s)}$. For NF_4AsF_6, NF_4GeF_5 and $(NF_4)_2GeF_6$ only a DSC value is available, and for NF_4PF_6 the DSC and the solution calorimetry value differ by 59 kJ mol^{-1}. For the latter compound, we prefer the DSC value because it was obtained by a direct method with a relatively small uncertainty, and because two of the other DSC values have been confirmed by independent methods. It should be kept in mind, however, that all these values still need correction for the $[H^T-H^o]$ terms, when these become available.

The relatively large discrepancies between the DSC and the solution calorimetry values for NF_4BF_4 and NF_4PF_6 are not surprising in view of the experimental difficulties encountered with finding and selecting suitable hydrolysis conditions, the relatively large uncertainties and variation in values as a function of the hydrolysis media, and perhaps most of all, the additional uncertainties in certain of the required ancillary data. Our present preference for the DSC values is also supported by the dissociation enthalpy values of Table 5, since the DSC values exhibit values and trends which are more in line with our expectations based on the strongly differing F^- affinities of the corresponding Lewis acids. To obtain the F^+ ion affinity, h_3, of NF_3 (equation 10), and the

$$NF_{3(g)} + F^+_{(g)} \xrightarrow{h_3} NF_4{}^+_{(g)} \qquad (10)$$

enthalpy of formation of gaseous $NF_4{}^+$, a knowledge of the lattice enthalpies of the $NF_4{}^+$ salt and of the corresponding K^+ salt of the same anion is required. The appropriate thermochemical cycle and equations are given by (10) to (12).

$$\begin{tikzcd}
H_2O_{(\ell)} + & NF_4XF_{(s)} \arrow[d, "-U(NF_4XF)"'] & - KXF_{(s)} \arrow[r, "h_1-h_2"] \arrow[d, "U(KXF)"] & NF_{3(g)} - & K^+_{(aq)} & + H^+_{(aq)} + HF_{(aq)} + \tfrac{1}{2}O_{2(g)} \\
H_2O_{(\ell)} + & NF_4{}^+_{(g)} + & XF^-_{(g)} - K^+_{(g)} - XF^-_{(g)} \arrow[r, "-h_3"] & NF_{3(g)} - & K^+_{(g)} \arrow[u, "\Delta H_{hydr}\, K^+_{(g)}"] & + H_2O_{(\ell)} + F^+_{(g)} \arrow[u, "h_4"']
\end{tikzcd} \qquad (11)$$

$$h_4 = \Delta H(H_2O_{(\ell)} + F^+_{(g)} \rightarrow H^+_{(aq)} + HF_{(aq)} + \tfrac{1}{2}O_{2(g)}) = -1806 \text{ kJ mol}^{-1} \qquad (12)$$

Substitution of the known thermochemical values given in Table 2 yields

$$h_3 = h_2 - h_1 + U_{KXF} - U_{NF_4XF} - 1040 \text{ kJ mol}^{-1} \qquad (13)$$

The lattice enthalpy of $KSbF_6$ is known (-585 kJ mol^{-1}) [29], and that of NF_4SbF_6 may be estimated, utilizing incomplete structural data [34]. NF_4SbF_6 has a tetragonal unit cell; the $NF_4{}^+$ ions have been placed in the structure with $r_{N-F} = 1.25$Å, but the $SbF_6{}^-$ ions are disordered. Using $q(Sb) = 1.7$, as in $KSbF_6$, we have estimated lattice enthalpies for NF_4SbF_6 from $q(N) = 0$ to $q(N) = 1.0$, using the real structural information, as far as it can be determined. In practice, the variation of lattice enthalpy with both q(N) and q(Sb) is small, and we estimate a value for U(NF_4SbF_6) (q(N)=1.0) of -435±10 kJ mol^{-1}. From (13), the F^+ affinity of NF_3 is -845 kJ mol^{-1} and the enthalpy of formation of gaseous NF_4^+ is +784 kJ mol^{-1}. In view of the various assumptions involved, it is difficult to gauge the error in these quantities, but it is likely to be of the order of ±30 kJ mol^{-1}. Our value of +784±30 kJ mol^{-1} for $\Delta H_f^o(NF_4^+)_{(g)}$ is in fair agreement with a previous estimate [9] of +854±40 kJ mol^{-1}, derived from the thermal calorimetric $\Delta H_f^o(NF_4BF_4)_{(s)}$ value [3], $\Delta H_f^o(BF_4^-)_{(g)}$ and an estimated lattice energy of -494 kJ mol^{-1} for NF_4BF_4.

The value of $\Delta H(NF_{3(g)} + F^+_{(g)} \rightarrow NF_4^+{}_{(g)}) = -845$ kJ mol^{-1} is close to the proton affinity of NH_3(-860.5± 2.0 kJ mol^{-1}) [35,36]. Although the average bond energy in NF_3(278 kJ mol^{-1}) is significantly lower than that in NH_3(391 kJ mol^{-1}) [37], the addition of a positively charged fourth ligand to NH_3 enhances the $\overset{\delta+\delta-}{\text{H-N}}$ polarity of the existing N-H bonds and thereby weakens them. In NF_3, the polarity of the bonds is reverse, i.e. $\overset{\delta-\delta+}{\text{F-N}}$, and the addition of F^+ results in more covalent and stronger N-F bonds. This opposite effect of X^+ addition to NH_3 and NF_3 is also reflected by their bond distances and stretching force constants [38-40] shown in the Table 6. The dramatic strengthening of the N-F bonds of NF_3 by addition of F^+ is further demonstrated by the large dissociation enthalpy of the first N-F bond in $NF_4^+{}_{(g)}$, $\Delta H(NF_4^+{}_{(g)} \rightarrow NF_3^+{}_{(g)} + F_{(g)}) = 419$ kJ mol^{-1}, obtained from the above $\Delta H_f^o(NF_4^+)_{(g)}$ value and the known $\Delta H_f^o(F)_{(g)} = 80$ kJ mol^{-1} [24] and $\Delta H_f^o(NF_3^+)_{(g)} = 1123$ kJ mol^{-1} values. The latter value was calculated from the enthalpy of formation [18] and the first ionization potential [41] of NF_3.

TABLE 6

Comparison of Bond Distances (Å) and Stretching Force Constants (mdyn/Å) in NX_3 and NX_4^+.

	r	f_r
NH_3	1.01	6.54[38]
NH_4^+	1.03	6.0[38]
NF_3	1.365	4.31[40]
NF_4^+	1.25-1.30[a]	6.15[39]

[a] Estimated from force constants [39] and incomplete structural data [34].

The Existence of NF_5. For the hypothetical NF_5 molecule, the ionic $NF_4^+F^-$ form should energetically be more favorable than a covalent NF_5[42]. The above derived value for the F^+ ion affinity of NF_3 may be utilized to derive a value for the enthalpy of formation of solid $NF_4^+F^-$ from NF_3 and F_2. In the following cycle

$$\begin{tikzcd}
NF_{3(g)} + F_{2(g)} \arrow[rr, "h_5"] \arrow[d, "+159"] & & NF_4^+F^-{(s)} \\
NF_{3(g)} + 2F_{(g)} \arrow[d, "+1352"] & & NF_4^+{(g)} + F^-{(g)} \arrow[u, "U(NF_4F)"'] \\
NF_{3(g)} + F^+{(g)} + F^-{(g)} \arrow[urr, "-845"'] & &
\end{tikzcd} \qquad (14)$$

all the quantities are known except for the lattice enthalpy of $NF_4^+F^-$. Using the configuration of NF_4^+ from the NF_4SbF_6 structure [34], it is possible to estimate $U(NF_4F)$, assuming a CsCl type of structure as in NH_4Cl, and suitable F-F distances. A cell dimension of $a_o = 4.51Å$ gives N-F - 1.25Å and F-F' = 2.66Å, which yields a lattice enthalpy for $q(N) = 1.0$ of -630 kJ mol^{-1}. This value is not sensitive to changes in $q(N)$ and is similar to a previous estimate [9] of -615 kJ mol^{-1}. Substitution in (14) yields $\Delta H(NF_{3(g)} + F_{2(g)} \rightarrow NF_4F_{(s)}) = +36(\pm 40)$ kJ mol^{-1}. The free energy change would, of course, be even less favorable and it is very unlikely that a covalent NF_5 would be more stable. These conclusions are in agreement with previous failures [10] to synthesize NF_4F at temperatures down to 77K from NF_3 + F_2 by uv-photolysis.

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