barrier is substantially higher than that encountered for most fast electron-transfer processes. Desai and Milburn have shown that large positive entropies of formation are largely responsible for the stability of iron(III)–phenolate complexes; $\Delta H_f°$ values in this system are negligibly small compared with $-T\Delta S_f°$.[25] For example, $\Delta H_f°$ and $\Delta S_f°$ values for the $C_6H_5O^-$–Fe(III) reaction in aqueous solution ($\mu = 0.1$ M) are −0.5 kcal/mol and +33 cal/(mol deg), respectively.[25] Release of water molecules bound by the phenolate anion evidently provides much of the driving force for the formation of this type of complex. It seems likely, therefore, that changes in substrate–solvent interactions accompanying formation of the activated complex in the HQ^-–$Cu(dmp)_2^{2+}$ reaction are primarily responsible for the $\Delta S^‡$ value of +18 cal/(mol deg). The data do not by any means prove the existence of an inner-sphere intermediate complex between HQ^- and $Cu(dmp)_2^{2+}$, however, as disordering of water molecules of hydration would be expected even for the formation of an outer-sphere complex between oppositely charged species. The reasonable adherence to the Marcus relationship exhibited by the $(HQ\text{-}X)^-$–$Cu(dmp)_2^{2+}$ system provides good support for the conclusion that these reactions involve outer-sphere electron transfer.

Our kinetic results for reactions of substituted hydroquinones with $Cu(dmp)_2^{2+}$ demonstrate that the poor correlation between rate and thermodynamic driving force observed for electron transfer from these substrates to laccase type 1 Cu(II) is the exception rather than the rule for Cu(II) oxidants. The laccase and $Cu(dmp)_2^{2+}$ systems also differ in that exceptionally high enzyme-substrate complex formation constants are found in the enzyme's reactions with many hydroquinones having substituents possessing at least one lone pair of electrons.[7] These substituents evidently stabilize the precursor complex by functioning as ligands toward either the type 2 or type 3 copper site. By contrast, substituents provide no special stabilization of the precursor complex in the $Cu(dmp)_2^{2+}$–H_2Q-X system, as the rate saturation expected with the formation of a strong intermediate complex was not observed for any of the substituted hydroquinones. Experiments are now under way to determine the importance of hydroquinone substituents as ligands and bridging groups in reactions with other transition-metal ion oxidants.

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Registry No. $Cu(dmp)_2^{2+}$, 14875-91-3; H_2Q, 123-31-9; H_2Q-F, 55660-73-6; H_2Q-Cl, 615-67-8; H_2Q-Br, 583-69-7; H_2Q-I, 23030-43-5; H_2Q-OH, 533-73-3; H_2Q-OCH_3, 824-46-4; H_2Q-COO^-, 490-80-2; H_2Q-$COOCH_3$, 2150-46-1; H_2Q-CH_3, 95-71-6; H_2Q-CF_3, 577-10-6; H_2Q-n-C_4H_9, 4197-69-7; H_2Q-$C(CH_3)_3$, 1948-33-0; H_2Q-CN, 4640-29-3; H_2Q-NO_2, 16090-33-8; H_2Q-SO_3^-, 68864-98-2.

Supplementary Material Available: Tables I and II, listing observed rate constants for the reduction of $Cu(dmp)_2^{2+}$ by substituted hydroquinones (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).
(2) E. Mentasti and E. Pelizzetti, *Int. J. Chem. Kinet.*, **9**, 215 (1977).
(3) E. Pelizzetti, E. Mentasti, and C. Baiocchi, *J. Phys. Chem.*, **80**, 2979 (1976).
(4) K. Reinschmiedt, J. C. Sullivan, and M. Woods, *Inorg. Chem.*, **12**, 1639 (1973).
(5) E. Pelizzetti, E. Mentasti, and E. Pramauro, *Inorg. Chem.*, **17**, 1688 (1978).
(6) Z. Amjad, J.-C. Brodovitch, and A. McAuley, *Can. J. Chem.*, **55**, 3581 (1977).
(7) J. D. Clemmer, B. L. Gilliland, R. A. Bartsch, and R. A. Holwerda, *Biochim. Biophys. Acta*, **568**, 307 (1979).
(8) A. E. Feiring and W. A. Sheppard, *J. Org. Chem.*, **40**, 2543 (1975).
(9) M. F. Hawthorne and M. Reintjes, *J. Am. Chem. Soc.*, **86**, 951 (1964).
(10) D. E. Kvalnes, *J. Am. Chem. Soc.*, **56**, 667 (1934).
(11) K. Wallenfels, D. Hofmann, and R. Kern, *Tetrahedron*, **21**, 2213 (1965).
(12) N. H. Beaugeard and J. Mattis, *Bull. Soc. Chim. Fr.*, 1612 (1956).
(13) F. Kehrmann, M. Sandoz, and R. Monnier, *Helv. Chim. Acta*, **4**, 941 (1921).
(14) J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, **49**, 1140 (1953).
(15) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5237 (1962).
(16) Supplementary material.
(17) G. Davies, R. Higgins, and D. J. Loose, *Inorg. Chem.*, **15**, 700 (1976).
(18) G. R. Williams, *Can. J. Biochem. Physiol.*, **41**, 231 (1963).
(19) R. A. Holwerda and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 6008 (1974).
(20) P. M. Wood, *Biochim. Biophys. Acta*, **357**, 370 (1974).
(21) G. S. Patterson and R. H. Holm, *Bioinorg. Chem.*, **4**, 257 (1975).
(22) M. A. Augustin and J. K. Yandell, *J. Chem. Soc., Chem. Commun.*, 370 (1978).
(23) J. R. Hall, N. K. Marchant, and R. A. Plowman, *Aust. J. Chem.*, **16**, 34 (1963).
(24) J. H. Baxendale, H. R. Hardy, and C. H. Sutcliffe, *Trans. Faraday Soc.*, **47**, 963 (1951).
(25) A. G. Desai and R. M. Milburn, *J. Am. Chem. Soc.*, **91**, 1958 (1969).

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Formation and Decomposition Mechanism of NF_4^+ Salts

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The thermal decompositions of NF_4BF_4 and NF_4AsF_6 were studied in a sapphire reactor at different temperatures by total-pressure measurements. It was found that the rates, previously reported by Solomon and co-workers for NF_4AsF_6, significantly differ from those of the present investigation, although both studies result in a $^3/_2$ reaction order. From the temperature dependence of the observed decomposition rates, the following values were obtained for the global activation energies: $E_{NF_4BF_4} = 36.6 \pm 0.8$ kcal mol^{-1} and $E_{NF_4AsF_6} = 44.7 \pm 4.2$ kcal mol^{-1}. The suppression of the decomposition rates by NF_3, F_2, and BF_3 or AsF_5 was measured. A critical evaluation of all experimental data available on the NF_4^+ salt formation and decomposition suggests the following reversible reaction mechanism: $F_2 \rightleftarrows 2\dot{F}$; $\dot{F} + NF_3 \rightleftarrows \dot{N}F_4$; $\dot{N}F_4 + AsF_5 \rightleftarrows \dot{N}F_3^+AsF_6^-$; $\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$. A Born–Haber cycle calculated for NF_4BF_4 shows that the global decomposition activation energy and the heat of the formation reaction are identical within experimental errors and that the second step of the above mechanism is approximately thermochemically neutral. The rate of the thermal formation of NF_4SbF_6 at 250 °C was also studied.

Introduction

The formation and decomposition reactions of NF_4^+ salts are of significant theoretical and practical interest. From a theoretical point of view, the question arises as to whether $\dot{N}F_4$ or NF_5 is produced as an unstable intermediate. This would be highly unusual because second-row elements generally do not form hypervalent molecules. From a practical point of view, a better knowledge of the formation and the decom-

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position mechanism is necessary in order to improve on existing synthetic methods.

Several mechanisms have previously been postulated for the formation of NF_4^+ salts. In 1966, Christe and co-workers suggested in their original reports[1,2] on the synthesis of NF_4AsF_6 by low-temperature glow discharge that either NF_3^+ or F^+ (or F_2^+) is generated in the discharge. These radical cations could then react with either F_2 or NF_3 to yield NF_4^+. In 1972, Solomon and co-workers reported[3] the results from a kinetic study of the thermal decomposition of NF_4AsF_6 in Monel. Based on total pressure measurements, their conclusion was that the decomposition involved the equilibrium dissociation step

$$NF_4AsF_6 \rightleftarrows NF_5 + AsF_5$$

followed by irreversible decomposition of the unstable NF_5

$$NF_5 \rightarrow NF_3 + F_2$$

The latter step was taken to be a $^3/_2$-order reaction. From the temperature dependence of the kinetic constants, a value of 41 kcal mol^{-1} was obtained for the sum of the overall heat of sublimation and the activation energy for the decomposition of NF_5. In 1973, Christe and co-workers proposed[4] an alternate mechanism for the formation of NF_4^+ salts. This mechanism accounted for the fact that NF_4^+ salts can be synthesized by UV photolysis. It involved the steps

$$F_2 \rightleftarrows 2\dot{F}$$

$$\dot{F} + AsF_5 \rightleftarrows \dot{A}sF_6$$

$$\dot{A}sF_6 + NF_3 \rightleftarrows \dot{N}F_3^+AsF_6^-$$

$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$$

Part of this mechanism was later experimentally confirmed by ESR studies[5-7] which showed that the $\dot{N}F_3^+$ radical cation is indeed formed as an intermediate in both the low-temperature UV photosynthesis and the γ-irradiation-induced decomposition of NF_4^+ salts.

Since the observation of $\dot{N}F_3^+$ as an intermediate[5-7] is incompatible with the mechanism proposed[3] by Solomon and since at elevated temperatures metal reactors rapidly absorb F_2–Lewis acid mixtures, a reinvestigation of the thermal decomposition of NF_4AsF_6 in an inert sapphire reactor was undertaken. In particular, a more detailed investigation of the suppression effects of NF_3, F_2, and AsF_5 was expected to yield valuable information. Furthermore, no quantitative data had previously been available on the decomposition rates of NF_4BF_4 and the formation rates of NF_4SbF_6.

Experimental Section

Thermal Decomposition Studies. The samples of NF_4BF_4[8] and NF_4AsF_6[8,9] were prepared as previously described and showed no detectable impurities. All decomposition experiments were carried out in a sapphire reactor (Tyco Co.). The reactor was connected by a Swagelok compression fitting, containing a Teflon front ferrule, to a stainless steel valve and a pressure transducer (Validyne, Model DP7, 0–1000 mm ± 0.5%), the output of which was recorded on a strip chart. The reactor had a volume of 38.7 mL and was heated by immersion into a constant-temperature (±0.05 °C) circulating oil bath. The reactor was passivated at 250 °C with F_2–BF_3 or F_2–AsF_5 mixtures until the pressure remained constant over a period of several days, and weighed amounts of NF_4^+ salts were added in the dry nitrogen atmosphere of a glovebox. After immersion of the reactor into the hot oil bath, the reactor was evacuated, and the pressure change was monitored as a function of time. Control experiments were carried out at the beginning and end of each series of measurements to ascertain that the rates had not significantly changed during each series. The composition of the gaseous decomposition products was shown by chemical analysis, infrared spectroscopy, and gas chromatography to be 1:1:1 mixtures of NF_3, F_2, and the corresponding Lewis acid. For the curve fitting of the kinetic data the method of linear least squares was used with the listed uncertainties being 2σ of the calculated slope.

Formation of NF_4SbF_6. Because of the high corrosivity of high-pressure NF_3–F_2–SbF_5 mixtures at elevated temperatures, the NF_3–F_2–SbF_5 reaction system could not be monitored directly with a pressure transducer or gage. Consequently, nine identical passivated 95-mL Monel cylinders were each loaded with 50 mmol of SbF_5, and a twofold excess of NF_3 and F_2 was added. The cylinders were simultaneously placed into an oven preheated to 250 °C and were removed separately from the oven after certain time intervals. After the cylinders were cooled, all material volatile at 25 °C was pumped off, and the amount of NF_4^+ salt formed was determined by the observed weight increase and spectroscopic analyses.

Results and Discussion

Thermal Decomposition of NF_4BF_4 and NF_4AsF_6. The thermal decomposition of NF_4BF_4 and NF_4AsF_6 in a constant-volume reactor was studied by total-pressure measurements over a temperature range of about 35 °C for each compound. Since screening experiments had shown that even well-passivated nickel or Monel reactors rapidly reacted with mixtures of hot F_2 and BF_3 or AsF_5, a sapphire reactor was used. This reactor was found to be completely inert toward these gas mixtures over extended time periods. Furthermore, it was found that the decomposition rates increased with increasing sample size. However, the rates did not increase linearly with the sample size because the increased pressure enhances the suppression of the rates (see below). In order to minimize the effect of changes in the sample size during a given series of experiments, we used the largest feasible samples and the smallest available reactor volume. In this manner, only a small percentage of the sample was decomposed in a given series of experiments. The first and the last experiment of each series were carried out under identical conditions and showed that the change in rate due to the small, but inevitable, sample-size change was indeed negligible.

The results of our measurements on NF_4BF_4 and NF_4AsF_6 are summarized in Tables I and II. In agreement with the previous report[3] on the thermal decomposition of NF_4AsF_6, smooth decomposition curves were obtained. The decomposition rates steadily decreased with increasing pressure in the reactor and the initial rates were restored upon evacuation of the reactor, indicating that the decomposition products suppress the decomposition rates. This was confirmed by studying the influence of different gases on the decomposition rates of NF_4BF_4 and of NF_4AsF_6. The addition of He did not noticeably influence the rates, whereas F_2 and NF_3 resulted in a weak suppression. However, the addition of BF_3 to NF_4BF_4 or of AsF_5 to NF_4AsF_6 resulted in strong rate suppressions (see Tables I and II).

For all decomposition experiments, plots of $P^{3/2}$ vs. time resulted in straight lines (see Figures 1 and 2) indicating a $^3/_2$ reaction order. The resulting global kinetic constants are given in Table III. Arrhenius plots of these constants resulted in straight lines (see Figure 3) and in the global decomposition activation energies $E_{NF_4BF_4} = 36.6 \pm 0.8$ kcal mol^{-1} and $E_{NF_4AsF_6} = 44.7 \pm 4.2$ kcal mol^{-1}, the latter value being in good agreement with that of 41 kcal mol^{-1} previously reported.[3]

The fact that the small mole fraction ranges of sample decomposition studied in these experiments were truly representative for the overall decomposition rates was established by following the decomposition of small samples at somewhat higher temperatures over almost the entire mole fraction (α) range. A typical decomposition curve obtained for NF_4BF_4 at 253 °C (see Figure 4) does not exhibit any sigmoid character, and the $P^{3/2}$ vs. time plot is linear for about the first 25% of α.

Although the results previously reported[3] for the decomposition of NF_4AsF_6 in Monel resulted in a linear $P^{3/2}$ vs. time plot, the reported rates were higher than ours by a factor of

Table I. Thermal Decomposition of NF_4BF_4[a] in a Sapphire Reactor[b]

	pressure change, mmHg										
				190.8 °C							
time, h	182.2 °C	188.9 °C	190.8 °C	He (500)[c]	F_2 (500)[c]	NF_3 (500)[c]	BF_3 (500)[c]	197.4 °C	204 °C	213.3 °C	215 °C
0	0	0	0	0	0	0	0	0	0	0	0
1	28	40	45	44	38	38	5	64	91	160	180
2	42	66	74	73	64	64	11	103	142	261	285
3	55	86	97	98	84	87	16	134	191	341	367
4	66.5	102	116	117	102	105	21	161	228	409	440
5	77	117	135	136	122	122	26	186	266	468	509
6	86.5	132	152	153	139	138	31	208	300	522	572
7	96	146	168	169	155	152	35	230	336	579	633
8	104	159	183		169	166	39	250		628	689
9	112	171	197		182	180	43	269		675	741
10	120.5	182	210		195	192	47	288		721	791
12	135	204	236		218	217	56	324		806	891
14	149	225	260		238	239	65	355		895	980
16	162	247	280		258	263	73	390			
18		267	300		277		82				
20					295		91				

[a] Sample size 2.65 g. [b] Reactor volume 38.7 mL. [c] The values given in parentheses indicate the pressure (in mmHg) of the added gas at the beginning of each experiment.

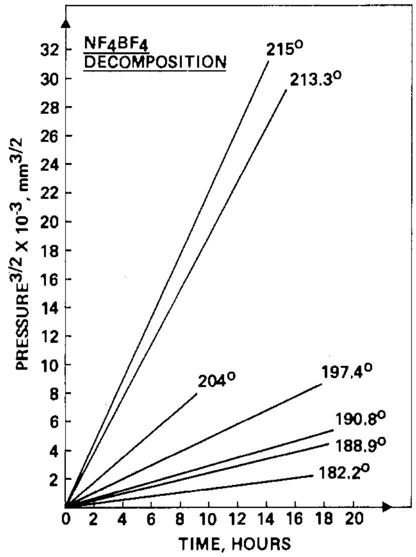


Figure 1. Total pressure ($P^{3/2}$) curves for the thermal decomposition of 2.65 g of NF_4BF_4 at different temperatures (°C).

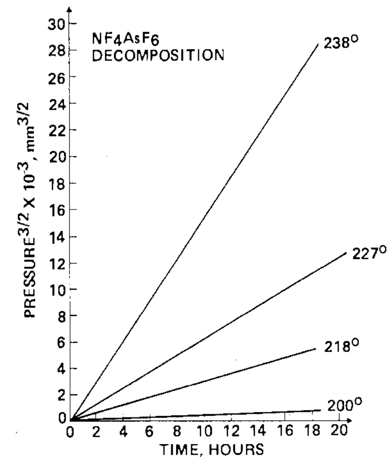


Figure 2. Total pressure ($P^{3/2}$) curves for the thermal decomposition of 1.86 g of NF_4AsF_6 at different temperatures (°C).

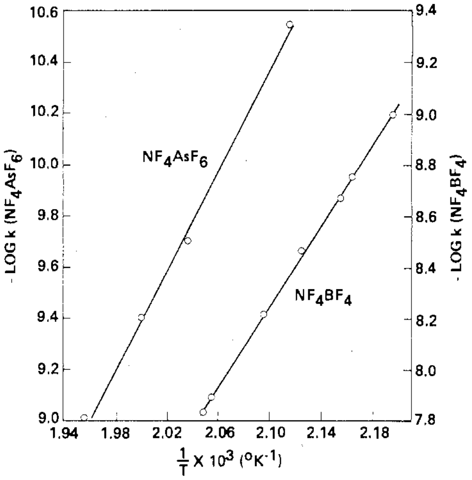


Figure 3. Arrhenius plots for NF_4BF_4 and NF_4AsF_6.

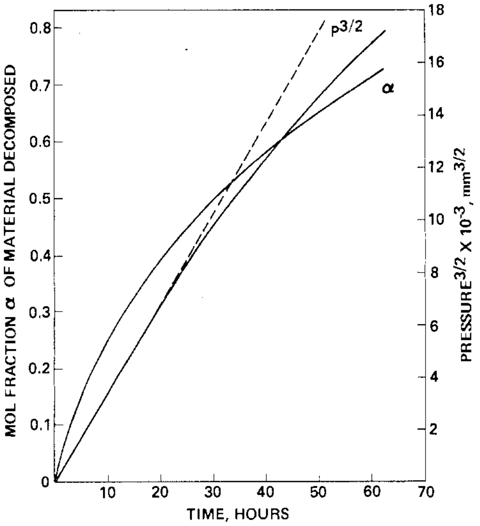


Figure 4. Decomposition curves for 75 mg of NF_4BF_4 at 253 °C. The solid lines are the observed data and the broken line represents the ideal straight line for the $P^{3/2}$ vs. t plot.

about 7. Unfortunately the sample size and the exact reactor volume used in ref 3 were not given. However, the estimated reactor volume (100-cm^3 Monel cylinder + Wallace-Tierman FA 145-780 gage) and the reported method of the NF_4AsF_6 synthesis suggest that the previously used sample weight to reactor volume ratios were almost certainly significantly

Table II. Thermal Decomposition of NF_4AsF_6[a] in a Sapphire Reactor[b]

	pressure change, mmHg								
					238 °C				
time, h	200 °C	218 °C	227 °C	238 °C	He (736)[c]	F_2 (197)[c]	NF_3 (567)[c]	AsF_5 (247)[c]	AsF_5 (724)[c]
0	0	0	0	0	0	0	0	0	0
1	2.6	9.9	16	27	28	25	21	5	4
2	4.0	16.0	25	44	45	42	34	8.5	7
3	5.2	20.8	33	58	59	55	44	12	9
4	6.2	25.3	40	71	73	68	54	16.5	11
5	7.2	29.4	46.5	83	85	79	63	20	12
6	8.3	32.2	52.5	93.5	95	90	72	24	13
7	9.2	36.6	57	103.5	105	101	81	28	14
8	10.0	40.0	62	113	115	110	90	32	15.5
9	10.8	43.0	67.5	123	124	120	98	35	17
10	11.6	46.0	72.5	132	133	129	106	38	18
12	13.2	51.4	82	149	151	145	122	45	21
14	14.7	56.6	91	165	166	161	140	52	23
16	16.1	61.4	99.5	181	181	176	160	59	25
18	17.4	66.2	107	197.5	196	190	176	65	
20			115.5	214	213	205	192	72	
25			134				226		
30							252		

[a] Sample size 1.86 g. [b] Reactor volume 38.7 mL. [c] The values given in parentheses indicate the pressure (mmHg) of the added gas at the beginning of each experiment.

Table III. Global Kinetic Constants[a] for the Thermal Decomposition of NF_4BF_4 and NF_4AsF_6

NF_4BF_4		NF_4AsF_6	
temp, °C	10^9k	temp, °C	$10^{10}k$
182.2	0.96 ± 0.01	200	0.284 ± 0.002
188.9	1.74 ± 0.02	218	1.99 ± 0.03
190.8	2.11 ± 0.04	227	4.00 ± 0.02
197.4	3.39 ± 0.05	238	9.69 ± 0.10
204	6.08 ± 0.08	238 (He (736))	9.62 ± 0.08
213.3	12.79 ± 0.22	238 (F_2 (197))	9.22 ± 0.05
215	$14.68 + 0.18$	238 (NF_3 (567))	8.60 ± 0.16
190.8 (He (500))	2.29 ± 0.03	238 (AsF_5 (247))	1.94 ± 0.12
190.8 (F_2 (500))	1.86 ± 0.04	238 (AsF_5 (724))	0.48 ± 0.08
190.8 (NF_3 (500))	1.92 ± 0.02		
190.8 (BF_3 (500))	0.314 ± 0.02		

[a] Units $mol^{3/2}\ L^{-3/2}\ s^{-1}$; error limits 2σ.

smaller than those of our experiments. This should have resulted in rates lower than ours. The only possible explanations for the previously reported[3] higher rates are absorption of the suppressing AsF_5 by Monel and/or inaccurate temperature control (heating of the cylinder in a tube furnace).

A large discrepancy of ~10^6 exists between the previously reported[3] results and our kinetic constants (see Table III). Most of this discrepancy (~10^5) appears to be computational.

Furthermore, the previously reported[3] data for the suppression by AsF_5 are inconsistent. Whereas the experimental data in Tables 6 and 7 of ref 3 show strong rate suppression by AsF_5, the kinetic constants given in Table 8 of ref 3 imply only mild suppression by AsF_5. The previously reported[3] strong rate suppression by NF_3 could not be confirmed by the present study. Our data (see Table III) show that NF_3 is only a weak suppressor, comparable to F_2, and that AsF_5 or BF_3 is the only strong suppressor. This is an important observation, because the alleged[3] strong suppression by NF_3 had caused us to propose in a previous publication[4] a mechanism for the formation of NF_4AsF_6 involving the incorrect (see below) steps $\dot{F} + AsF_5 \rightarrow \dot{A}sF_6$ and $\dot{A}sF_6 + NF_3 \rightarrow \dot{N}F_3^+AsF_6^-$.

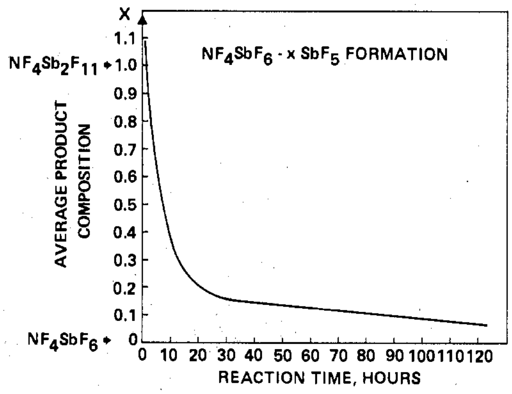


Figure 5. Formation rate of $NF_4SbF_6 \cdot xSbF_6$ from NF_3, F_2, and SbF_5 at 250 °C.

Table IV. Conversion of $NF_3 + F_2 + SbF_5$ to NF_4SbF_6 at 250 °C[a]

reacn time, h	prod compn, $NF_4^+SbF_6^- \cdot xSbF_5$ x	convrsn of SbF_5 to NF_4SbF_6, mol %
1	1.08	48.1
2	0.89	52.9
3	0.78	56.2
6	0.59	62.9
12	0.34	74.6
24	0.17	85.5
50	0.13	88.5
85	0.106	90.4
120	0.064	94.0

[a] Mole ratios of starting materials $NF_3:F_2:SbF_5 = 2:2:1$. Starting pressure 110 atm; residual pressure calculated for 100% conversion to NF_4SbF_6 44 atm. The Monel cylinders (95-mL volume) were placed horizontally in the oven, preheated to 250 °C. One hour was required until the cylinders reached 250 °C. This point was taken as zero reaction time.

Thermal Synthesis of NF_4SbF_6. Whereas the thermal synthesis of NF_4AsF_6 proceeds at too slow a rate for practical kinetic measurements, the rate of formation of NF_4SbF_6 is sufficiently fast. However, SbF_6^- tends to form polyantimonates such as $Sb_2F_{11}^-$ or $Sb_3F_{16}^-$ [5,9-11] with SbF_5, which makes a kinetic evaluation of any experimental data very difficult. In view of the importance of the thermal synthesis of NF_4SbF_6 (this compound serves as a starting material for the metathetical syntheses of most other NF_4^+ salts[11-15]) and because of the complete absence of data on its formation rate, nine reactions were carried at 250 °C and at a pressure of about 110 atm to determine its formation rate. The results are summarized in Table IV and Figure 5 and show that at this temperature the initial formation rate of NF_4^+ salts is surprisingly rapid. The subsequent slow-down of the reaction is probably caused by a lowering of the SbF_5 partial pressure in the system due to the formation of polyantimonate anions. Their thermal dissociation equilibria to SbF_6^- and SbF_5 will then control the SbF_5 pressure in the system and become the rate-limiting steps.

Reaction Mechanism. As pointed out in the Introduction, the formation and decomposition mechanism of NF_4^+ salts is of great interest because it appears to involve an unusual hypervalent species such as $\dot{N}F_4$, $\dot{N}F_5$, $\dot{A}sF_6$, or $\dot{B}F_4$. The following experimental data are known, and the correct mechanism must be compatible with all of these conditions.

(1) Certain NF_4^+ salts, such as NF_4SbF_6 and NF_4AsF_6, can, depending upon the system pressure, be either formed or decomposed at the same temperature.[5,9-11] This implies pressure-dependent equilibria and reversibility of the formation and decomposition reactions.

(2) ESR measurements have shown[5-7] that the $\dot{N}F_3^+$ radical cation is a crucial intermediate in both the low-temperature UV photolytic synthesis and γ-irradiation-induced decomposition of NF_4^+ salts. Furthermore, the fluorination of $\dot{N}F_3^+$ to NF_4^+ appears to require F atoms.

(3) In the thermal decomposition of either NF_4BF_4 or NF_4AsF_6, BF_3 or AsF_5 acts as a strong rate suppressor, whereas both NF_3 and F_2 suppress the decomposition rates only mildly (see above results).

(4) Filtered UV radiation[4,8] or heating[9] to 120 °C supply sufficient activation energy for the formation of NF_4^+ salts. This is a strong indication that the first step in the synthesis must be the dissociation of F_2 into two fluorine atoms ($D°(F_2) = 36.8$ kcal mol^{-1}).[16]

(5) The tendency to form NF_4^+ salts by thermal activation strongly decreases with decreasing Lewis acid strength, i.e., $SbF_5 > AsF_5 > PF_5 > BF_3$.[4,8,9] Since the corresponding NF_4^+ salts all possess sufficient thermal stability, a mechanism[3] involving the initial formation of NF_5, followed by its reaction with the corresponding Lewis acid, cannot explain the lack of thermal formation of salts such as NF_4PF_6 or NF_4BF_4. It can be explained, however, by the formation of intermediates of lower thermal stability such as $\dot{N}F_3^+$ salts. For SbF_6^- or AsF_6^-, these NF_3^+ salts were shown to still possess the lifetime required for their efficient conversion to NF_4^+ salts, whereas $NF_3^+BF_4^-$ was found to be of considerably lower thermal stability.[7]

(6) ESR flow-tube experiments[17] gave no indication of interaction between $\dot{F}$ atoms and AsF_5, as expected for the reaction step $AsF_5 + \dot{F} \rightarrow \dot{A}sF_6$.

(7) Infrared matrix isolation studies of the thermal decomposition products from either NF_4AsF_6[3] or $(NF_4)_2NiF_6$[18] gave no evidence for the formation of NF_5.

(8) Lewis acids such as BF_3, PF_5, AsF_5, or SbF_5 do not form stable adducts with NF_3, even at low temperatures.[18,19]

Since NF_3, F_2, and F have ionization potentials of 13.00,[20] 15.69,[21] and 17.44 eV,[22] respectively, any mechanism involving the initial formation of either NF_3^+, F_2^+, or F^+ can be ruled out, based on condition 4. This leaves us with Schemes I–IV as possibilities.

Scheme I

$$NF_3 + AsF_5 \rightleftarrows NF_2^+AsF_6^-$$

$$F_2 \rightleftarrows 2\dot{F}$$

$$NF_2^+AsF_6^- + \dot{F} \rightleftarrows \dot{N}F_3^+AsF_6^-$$

$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$$

Scheme II

$$F_2 \rightleftarrows 2\dot{F}$$

$$\dot{F} + AsF_5 \rightleftarrows \dot{A}sF_6$$

$$\dot{A}sF_6 + NF_3 \rightleftarrows \dot{N}F_3^+AsF_6^-$$

$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$$

Scheme III

$$F_2 \rightleftarrows 2\dot{F}$$

$$\dot{F} + NF_3 \rightleftarrows \dot{N}F_4$$

$$\dot{N}F_4 + \dot{F} \rightleftarrows NF_5$$

$$NF_5 + AsF_5 \rightleftarrows NF_4^+AsF_6^-$$

Scheme IV

$$F_2 \rightleftarrows 2\dot{F}$$

$$\dot{F} + NF_3 \rightleftarrows \dot{N}F_4$$

$$\dot{N}F_4 + AsF_5 \rightleftarrows \dot{N}F_3^+AsF_6^-$$

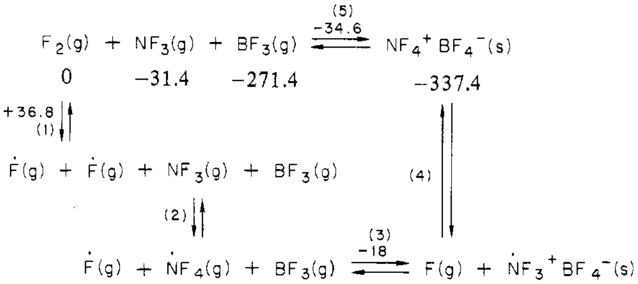
$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$$

Scheme I can be ruled out because it does not comply with conditions 8 and 3. In Scheme I, NF_3 would be expected to suppress as strongly as AsF_5. Scheme II can be eliminated because of the fact that it violates condition 3 (i.e., NF_3 should be a stronger suppressor than AsF_5) and because of condition 6. Scheme III is unacceptable because it does not comply with conditions 2 and 5. Scheme IV is the only mechanism which agrees with all experimental data and therefore is our preferred mechanism. This mechanism differs from all the mechanisms previously proposed. It appears to be generally applicable to NF_4^+ salts, except for certain decomposition reactions in which NF_4^+ oxidatively fluorinates the anion.[18]

In view of the rather complex mechanism of Scheme IV and the observed fractional reaction order for the decomposition process, a mathematical analysis of the kinetic data was too complex and beyond the scope of the present study.

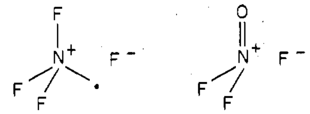
Born–Haber Cycle for NF_4BF_4. It was of interest to examine the thermodynamic soundness of Scheme IV. NF_4BF_4 was chosen for this purpose because it is the only NF_4^+ salt for which the heat of formation has experimentally been determined.[23] The Born–Haber cycle is shown in Scheme V, where all heats of formation or reaction are given in kcal mol^{-1}. From the known heats of reaction of NF_3,[24] BF_3,[24] and NF_4BF_4,[23] the heat of reaction 5 is known to be −34.6 kcal mol^{-1}. Furthermore, the heat of dissociation of F_2, reaction 1, is known[16] to be 36.8 kcal mol^{-1}. A reasonably close estimate for step 3, the heat of formation of solid $NF_3^+BF_4^-$ from NF_4 and BF_3, can be made from the known heat of dissociation of $NF_2O^+BF_4^-$. Since NF_3O and $\dot{N}F_4$ are expected to be quite similar (see below), it is reasonable to assume that step 3 has a heat of reaction similar to that of $NF_3O + BF_3 \rightarrow NF_2O^+BF_4^-$, i.e., −18 kcal mol^{-1}. Consequently, the sum of steps 2 and 4 should be about −53 kcal mol^{-1}. Whereas the heat of reaction of step 2 is difficult to estimate, the heat of

Scheme V

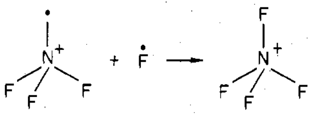


reaction of (4) is easier to estimate because it represents the dissociation energy of the fourth N–F bond in NF_4^+. In NF_3, the heat of dissociation of the third N–F bond is 58 kcal mol^{-1},[26,27] and it seems reasonable to assume that the dissociation energy of the fourth N–F bond in NF_4^+ is similar to or slightly less than this value. Consequently, step 2 should be approximately thermochemically neutral.

The proposition that steps 2 and 4 should so markedly differ in their heats of reaction, although both involve the formation of one additional N–F bond, is not unreasonable. In step 2 a hypervalent $\dot{N}F_4$ radical is formed which would possess nine valence electrons on the central nitrogen atom. By analogy with the known NF_3O molecule,[28] this energetically unfavorable structure can be circumvented by assuming strong contributions from resonance structures such as



These resonance structures result in a strong polarization, i.e., weakening of all N–F bonds, when compared to those in NF_3. This is demonstrated by the bond lengths of 1.371 and 1.43 Å observed for NF_3[29] and NF_3O,[28] respectively. Thus the energy gained by the formation of a fourth N–F bond in the NF_4 radical is largely compensated by a significant weakening of the remaining N–F bonds. In contrast, the reaction of the $\dot{N}F_3^+$ radical cation with a fluorine atom, i.e.



does not significantly change the nature of the existing N–F bonds and, therefore, is expected to result in a heat of reaction close to the energy of this bond.

An alternate, attractively simple, and preferable explanation for the above bond weakening effect in NF_4 can be offered if one assumes that, due to the large energy difference between the 2p and 3s nitrogen orbitals, the ninth nitrogen valence electron occupies an antibonding orbital. Experimental evidence for such a model has recently been reported[30] by Nishikida and Williams for the $\dot{N}F_3O^-$ radical anion which is isoelectronic with $\dot{N}F_4$. On the basis of the observed ESR data, $\dot{N}F_3O^-$ possesses a spin density of 0.27 in the nitrogen 2s orbital suggesting that the unpaired electron indeed occupies an antibonding orbital.

A third possible, although less likely, explanation would be the assumption of a trigonal-bipyramidal structure for NF_4, in which two axial fluorines and nitrogen form a semiionic three-center, four-electron bond while the three equatorial positions are occupied by two fluorine ligands and the unpaired electron. Although all three models are basically a formalism describing the same net result, i.e., an increase of the bond length and ionicity of the NF bonds, model III should result in significantly different bond angles and therefore be experimentally distinguishable from models I and II.

It should be pointed out that the global activation energy (36.6 ± 0.8 kcal mol^{-1}) of the decomposition of NF_4BF_4 to $NF_3 + F_2 + BF_3$ and the heat of formation of NF_4BF_4 from $NF_3 + F_2 + BF_3$ (–34.6 kcal mol^{-1}) are the same within experimental error. It is difficult to say whether this is coincidental or if it implies that the corresponding forward reactions, i.e., steps 2–4 of the Born–Haber cycle, occur without activation energy. Examples of the latter case are known for the endothermic dissociation of solids such as carbonates.[31] If for NF_4^+ salts the global decomposition activation energies should indeed be identical with the heats of formation from NF_3, F_2, and the corresponding Lewis acid, a value of about –372 kcal mol^{-1} can be predicted for $\Delta H_f{}^{\circ}{}_{NF_4AsF_6}$ on the basis of $E_{NF_4AsF_6} = 45$ kcal mol^{-1} and $\Delta H_f{}^{\circ}{}_{AsF_5} = 29.55$ kcal mol^{-1}.

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Registry No. NF_4BF_4, 15640-93-4; NF_4AsF_6, 16871-75-3; NF_4SbF_6, 16871-76-4; NF_3, 7783-54-2; F_2, 7782-41-4; SbF_5, 7783-70-2.

References and Notes

(1) K. O. Christe, J. P. Guertin, and A. E. Pavlath, *Inorg. Nucl. Chem. Lett.*, **2**, 83 (1966).
(2) J. P. Guertin, K. O. Christe, and A. E. Pavlath, *Inorg. Chem.*, **5**, 1921 (1966).
(3) I. J. Solomon, J. N. Keith, and A. Snelson, *J. Fluorine Chem.*, **2**, 129 (1972).
(4) K. O. Christe, R. D. Wilson, and A. E. Axworthy, *Inorg. Chem.*, **12**, 2478 (1973).
(5) S. P. Mishra, M. C. R. Symons, K. O. Christe, R. D. Wilson, and R. I. Wagner, *Inorg. Chem.*, **14**, 1103 (1975).
(6) K. O. Christe and I. B. Goldberg, *Inorg. Chem.*, **17**, 759 (1978).
(7) I. B. Goldberg, H. R. Crowe, and K. O. Christe, *Inorg. Chem.*, **17**, 3189 (1978).
(8) K. O. Christe, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, **15**, 1275 (1976).
(9) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Chem.*, **6**, 1156 (1967).
(10) K. O. Christe, R. D. Wilson, and C. J. Schack, *Inorg. Chem.*, **16**, 937 (1977).
(11) K. O. Christe, C. J. Schack, and R. D. Wilson, *J. Fluorine Chem.*, **8**, 541 (1976); U.S. Patent 4 107 275 (1978).
(12) K. O. Christe, W. W. Wilson, and C. J. Schack, *J. Fluorine Chem.*, **11**, 71 (1978).
(13) K. O. Christe, *Inorg. Chem.*, **16**, 2238 (1977), and U.S. Patent 4 108 965 (1978).
(14) K. O. Christe, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, **16**, 849 (1977).
(15) K. O. Christe and C. J. Schack, *Inorg. Chem.*, **16**, 353 (1977).
(16) J. Berkowitz and A. C. Wahl, *Adv. Fluorine Chem.*, **7**, 147 (1973).
(17) I. B. Goldberg, unpublished results.
(18) K. O. Christe, unpublished results.
(19) A. D. Craig, *Inorg. Chem.*, **3**, 1628 (1964).
(20) V. H. Dibeler and J. A. Walker, *Inorg. Chem.*, **8**, 1728 (1969).
(21) V. H. Dibeler, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.*, **51**, 4230 (1969).
(22) R. E. Huffman, J. C. Larrabee, and Y. Tanaka, *J. Chem. Phys.*, **47**, 856 (1967).
(23) G. C. Sinke, unpublished results.
(24) "JANAF Interim Thermochemical Tables", The Dow Chemical Co., Midland, Mich., 1965, and subsequent revisions.
(25) K. O. Christe and W. Maya, *Inorg. Chem.*, **8**, 1253 (1969).
(26) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schuman, *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **No. 270-3** (1969).
(27) E. W. Lawless and I. C. Smith, "Inorganic High-Energy Oxidizers", Marcel Dekker, New York, 1968, p 28.
(28) V. Plato, W. D. Hartford, and K. Hedberg, *J. Chem. Phys.*, **53**, 3488 (1970).
(29) J. Sheridan and W. Gordy, *Phys. Rev.*, **79**, 513 (1950).
(30) K. Nishikida and F. Williams, *J. Am. Chem. Soc.*, **97**, 7168 (1975).
(31) W. E. Garner, "Chemistry of the Solid State", Butterworths Scientific Publications, London, 1955, p 224.