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THE DECOMPOSITION OF NF_4AsF_6

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SUMMARY

NF_4AsF_6 decomposes smoothly at 175° and above, to the starting materials NF_3, F_2 and AsF_5. The decomposition has been followed by total pressure measurements and found to obey the equation

$$P^{3/2} = At + B$$

This has been interpreted in terms of an equilibrium dissociation step

$$NF_4AsF_6 \rightleftharpoons NF_5 + AsF_5$$

followed by irreversible decomposition of the unstable NF_5

$$NF_5 \rightarrow NF_3 + F_2$$

The latter step is taken to be a 3/2-order reaction:

$$\frac{dP}{dt} = k_1 P_n P_a^{1/2}$$

where P_n is the partial pressure of NF_5 and P_a that of AsF_5. Taking the equilibrium into account, the above equation is integrated to yield

$$P_a^{3/2} - (P_a^0)^{3/2} = 3k_1K_{eq}t/2$$

An attempt to identify NF_5 in the products by matrix isolation methods yielded, besides the expected NF_3 and AsF_5, an unknown minor product which appeared not to contain nitrogen.

INTRODUCTION

The stability of the recently reported tetrafluoroammonium salts[1,2] is quite remarkable in view of the low basicity of difluoramine[3,4] and the absence of detectable basic properties in nitrogen trifluoride[4]. The existence of such salts is particularly interesting since the conjugate base, nitrogen pentafluoride, is not known, and is expected to be extremely unstable. The case is analogous to that of the dioxygenyl salts, such as O_2BF_4, which have been shown[5] to be derived from the very unstable base O_2F:

$$O_2F + BF_3 \rightarrow O_2BF_4 \qquad (1)$$

We thus have stable salts of very unstable bases, which can be prepared only by the use of forcing conditions, such as glow discharge or high-pressure methods.

As in the case of the dioxygenyl salts, neither synthetic route is conducive to kinetic studies, but it is possible to obtain some kinetic information on the thermal decomposition by pressure measurements. As with O_2BF_4, the kinetic data indicated the existence of an equilibrium dissociation which controls the rate of decomposition.

Attempts were made to obtain infrared spectra of primary dissociation products by matrix isolation techniques, but it was not possible to draw definite conclusions.

EXPERIMENTAL

Materials and equipment

All synthetic work and the kinetic and isotopic exchange studies were performed in metal vacuum lines of the type used for reactive fluorine compounds. Transfers of solid NF_4AsF_6 were made in a nitrogen-filled dry box.

Nitrogen trifluoride was purchased from Air Products and Chemicals, Inc. and arsenic pentafluoride from Ozark–Mahoning Co. Fluorine (Matheson Co.) was passed through sodium fluoride prior to use. Isotopically enriched nitrogen (95% ^{15}N, Merck Sharpe and Dhome) was fluorinated in a glow discharge reaction[6] at −196° to form $^{15}NF_3$.

Preparation of NF_4AsF_6

NF_4AsF_6 was prepared in a glow-discharge reaction at −80° using a reactant ratio of $F_2:NF_3:AsF_5 = 1.5:1:1$. The Pyrex glow-discharge tube was evacuated and removed from the vacuum line by sealing the connecting tubing, and opened in a dry box to transfer the contents. Analysis of the thermal decomposition products indicated the presence of NF_3, F_2 and AsF_5 in equal amounts. Hydrolysis produced a 2:1 mixture of NF_3 and O_2.

Kinetic measurements

The thermal decomposition of NF_4AsF_6 was followed by measurement of the total pressure in a passivated 100 cc Monel cylinder by means of a Wallace–Tiernan FA145-780 vacuum gauge. The cylinder was heated with a 1650 W, 10 × 30 cm Lindberg Hevi-Duty tube furnace, using a copper–constantan control thermocouple. A record of the temperature of the sample (by means of a thermocouple taped directly to the cylinder) was kept on a Varian millivolt recorder.

Infrared spectra

The infrared spectra of the starting materials and of the decomposition products were recorded using a Perkin–Elmer Model 621 Grating Spectrophotometer. Conventional matrix isolation equipment was used consisting of a cesium iodide window mounted in a copper block attached to a cold finger which can be rotated to position the window. The Dewar was of metal construction, the outer jacket being filled with liquid nitrogen surrounding the liquid helium-filled cold finger. The furnace consisted of a 3 mm × 2.5 cm platinum tube heated by induction. The temperature was measured by means of a thermocouple.

RESULTS AND DISCUSSION

As in the similar case of O_2BF_4, the rate of decomposition of NF_4AsF_6 in a sealed container decreases steadily during the reaction the initial rate being restored upon removal of the decomposition products by evacuation. The data are well represented by the equation

$$P^{3/2} = At + B \tag{2}$$

and are presented in Tables 1–7.

TABLE 1

DECOMPOSITION OF NF_4AsF_6 AT 175°

T (min)	P (mmHg)
0.0	0.0
2.8	0.7
11.2	1.3
16.9	1.7
27.2	2.2
38.4	2.7
64.7	3.7
127.0	5.7

$A = 0.106$, $B = 0.290$, $r = 0.9995$*.

* A and B are the coefficients of equation (2), as determined by the treatment of the data by the method of least squares, using program number 09100-70803 for the Hewlett-Packard Model 9100B Electronic Calculator. The correlation coefficient, r, was determined using the same program.

TABLE 2

DECOMPOSITION OF NF_4AsF_6 AT 195°

T (min)	P (mmHg)
0.0	0.3
0.5	0.7
2.1	1.7
4.1	2.7
6.9	3.7
10.0	4.7
13.7	5.7
18.4	6.7
32.8	9.7
45.0	11.7
57.8	13.7
78.7	16.7
93.3	18.7
126.7	22.7

$A = 0.852$, $B = 1.18$, $r = 0.9999$.

TABLE 3

DECOMPOSITION OF NF_4AsF_6 AT 205°

T (min)	P (mmHg)
0.0	0.3
0.2	0.7
1.0	1.7
2.0	2.7
4.5	4.7
6.2	5.7
12.1	8.7
14.1	9.7
27.3	14.7
36.4	17.7
42.4	19.7
49.3	21.7
60.3	24.7
80.8	29.7
93.6	32.7
102.8	34.7
131.7	40.7

$A = 1.98$, $B = 1.57$, $r = 0.9999$.

TABLE 4

DECOMPOSITION OF NF_4AsF_6 AT 218.5°

T (min)	P (mmHg)
0.0	0.6
1.1	4.7
3.1	9.7
5.9	14.7
10.8	21.7
15.0	26.7
18.6	30.7
22.5	34.7
31.5	42.7
40.7	49.7
47.5	54.7
54.7	59.7
64.5	65.7
71.0	69.7
80.0	74.7
89.9	79.7
100.2	84.7

$A = 7.99$, $B = 10.55$, $r = 0.9988$.

TABLE 5

DECOMPOSITION OF NF_4AsF_6 AT 222°

T (min)	P (mmHg)
0.0	0.6
1.0	5.7
2.1	8.7
4.6	14.7
7.3	19.7
10.5	24.7
14.2	29.7
18.2	34.7
28.0	44.7
34.8	50.7
39.6	54.7
46.0	59.7
52.8	64.7
59.6	69.7
67.5	74.7
75.6	79.7

$A = 9.65$, $B = 11.96$, $r = 0.9987$.

TABLE 6

DECOMPOSITION OF NF_4AsF_6 AT 222°
IN THE PRESENCE OF AsF_5

T (min)	P (mmHg)
0.0	99.0
24.9	107.7
30.0	110.0
43.9	115.0
57.0	120.0
85.7	130.0
114.6	140.0
180.0	161.0
240.0	178.6

$A = 9.15$, $B = 5082$, $r = 0.9997$.

TABLE 7

DECOMPOSITION OF NF_4AsF_6 AT 222°
IN THE PRESENCE OF NF_3

T (min)	P (mmHg)
0.0	111.5
4.3	113.0
7.4	114.0
9.9	115.0
12.2	116.0
17.2	118.0
22.3	120.0
27.7	122.0
35.5	125.0
44.0	128.0
58.7	133.0
71.5	137.0
84.3	141.0
100.3	145.0
131.9	153.0

$A = 2.77$, $B = 43.7$, $r = 0.9997$.

It is evident that an equilibrium step is involved in the decomposition reaction, just as with the dioxygenyl salts *. It is extremely unlikely that the synthetic reaction

$$NF_3(g) + F_2(g) + AsF_5(g) = NF_4AsF_6(s) \tag{3}$$

is involved here, considering the rather extreme conditions required for this reaction. It is more likely that an equilibrium dissociation step is involved.

$$NF_4AsF_6(s) \rightleftharpoons NF_5(g) + AsF_5(g) \tag{4}$$

This is followed by decomposition of the unstable NF_5

$$NF_5 \xrightarrow{k_1} NF_3 + F_2 \tag{5}$$

The form of equation (2) indicated that this step must be considerably more complex than indicated by equation (5). A 3/2-order reaction will produce the correct results **:

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* In most of the experiments the first couple of points were lower than those calculated from the rate constants. This initial departure from linearity can probably be attributed to the fact that early in the experiment the deviation from equilibrium is greatest, and therefore the rate of the reaction is greater, since in this region it is less controlled by the dissociative equilibrium.

** The fractional order itself suggests the involvement of fluorine atoms in steps such as: $NF_5 + M \rightarrow NF_4 + F + M$, *etc.* Equations were derived from rate equations such as
$\mathrm{d}P/\mathrm{d}t = kP_{NF_5}P_{NF_3}{}^{1/2}$ and $\mathrm{d}P/\mathrm{d}t = k_{NF_5}P_{NF_2}{}^{1/2}$.

Neither of these equations gave straight lines with the data for the experiments with excess AsF_5 or NF_3. Equation (6), however, did produce a good fit with the data, indicating a half-order dependence on AsF_5. Heterogeneous reactions, however, also often follow fractional-order kinetics.

$$\frac{dP}{dt} = k_1 P_n P_a{}^{1/2} \tag{6}$$

where P_n = NF_5 pressure and P_a = AsF_5 pressure. Since P_n is controlled by the equilibrium, $P_n = K_{eq}/P_a$, and

$$\frac{dP}{dt} = k_1 K_{eq} P_a{}^{-1/2} \tag{7}$$

Taking $dP = dP_a$, and integrating

$$P_a{}^{3/2} - (P_a^0)^{3/2} = \frac{3}{2} k_1 K_{eq} t \tag{8}$$

In terms of the experimental quantities

$$\frac{\sqrt{3}}{9}(P_T + 2P_a^0)^{3/2} - (P_a^0)^{3/2} = \frac{3}{2} k_1 K_{eq} t \tag{9}$$

except for the experiment in which NF_3 was added:

$$\frac{\sqrt{3}}{9}(P_T - P_c)^{3/2} - (P_a^0)^{3/2} = \frac{3}{2} k_1 K_{eq} t \tag{10}$$

where P_c is the calculated partial pressure due to the NF_3 added at the beginning of the experiment and P_T is the total pressure.

The rate constant cannot be determined separately from the equilibrium constant. The products of the constants k_1K_{eq} presented in Table 8 can be computed from the slopes of $(P_T + 2P_a^0)^{3/2}$ or $(P_T - P_c)^{3/2}$ versus t. An Arrhenius plot of these products was linear and yields, for the sum of the overall heat of sublimation and the activation energy for the decomposition of NF_5, a value of 41 kcal mole^{-1}.

In an attempt to obtain support for the postulate that NF_5 is present as an intermediate, matrix isolation studies were performed with NF_4AsF_6.

TABLE 8

KINETIC CONSTANTS

Temperature	$10^6 k_1 K_{eq}$*
175	3.78
195	28.5
205	64.1
218.5	248
222	296
222 (AsF_5)	281
222 (NF_3)	85.1

* Mole$^{3/2}$liter$^{-3/2}$sec^{-1}.

Reference spectra of NF_3 and AsF_5 were obtained and compared with the literature[9,10]. The spectra were in satisfactory agreement and no evidence of significant impurities was seen. Several runs were made with NF_4AsF_6, decomposing at different temperatures. The results are shown in Table 9.

TABLE 9

INFRARED SPECTRA IN NEON MATRIX

Frequency (cm^{-1})				
$^{14}NF_4AsF_6$	$^{15}NF_4AsF_6$	$^{14}NF_3$	$^{15}NF_3$	AsF_5
1049	1043			
1027	1026	1027	1027	
	1003.5		1004	
899	898.5	899	899	
	878.5		878	
827	822.5			
809	808			809
782	782			782.5
		642	638	
489		490	489	
398	397.5			398
367	367			367
332	331			
309	307			

In the experiments which produced strong spectra, new peaks were observed at 1049, 827, 332 and 309 cm^{-1}, which did not appear to be due to overtones, matrix effects, *etc.* A search of the literature did not disclose a likely impurity to which these peaks could be attributed.

Examination of the spectra of the products from $^{15}NF_4AsF_6$, however, revealed the presence of the same new peaks with the same relative intensities. The fact that no isotopic shift is observed indicates that the source of these peaks is not a nitrogen compound derived from the NF_4AsF_6 but an impurity common to the two samples, or resulting from interaction of the decomposition products with the materials of the apparatus. We have not been able to identify this impurity nor has any evidence of NF_5 been found.

CONCLUSIONS

NF_4AsF_4 decomposes smoothly above 175° at a rate which decreases as the reaction proceeds, in a manner similar to that of O_2BF_4. The data can be correlated with a mechanism consisting of an equilibrium dissociation

$$NF_4AsF_6 \rightleftharpoons NF_5 + AsF_5 \tag{4}$$

followed by decomposition of NF_5

$$NF_5 \rightarrow NF_3 + F_2 \tag{5}$$

This process must be somewhat more complex than indicated above since the data indicate that the overall order is 3/2. A process which is first order in NF_5 and 1/2 order in AsF_5 will fit the data.

$$\frac{dP}{dt} = k_1 P_n P_a^{1/2} \tag{6}$$

The implication of this mechanism (that NF_5 exists as an intermediate in this process) was not supported by matrix isolation studies. It would be expected, however, to be very unstable and to have only transitory existence.

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