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The Reaction of Tetrafluorohydrazine with Arsenic Pentafluoride. Evidence for the Existence of $N_2F_3^+$ Salts

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The preparation of a stable adduct of tetrafluorohydrazine and antimony pentafluoride, $N_2F_4 \cdot 2SbF_5$, has recently been reported by Ruff.[1] Ruff suggests the possibility that tetrafluorohydrazine acts as a fluoride ion donor in forming this adduct and, in support of this, cites the presence of an absorption at 666 cm^{-1} in the infrared spectrum of the adduct which can be attributed to the hexafluoroantimonate ion. We have prepared a similar adduct of tetrafluorohydrazine with arsenic pentafluoride. The results of our studies of this material provide additional evidence that tetrafluorohydrazine acts as a fluoride ion donor.

Experimental Section

Materials.—Tetrafluorohydrazine (95%) was obtained from Air Products Inc. The principal impurities are CF_4 and C_2F_6. Arsenic pentafluoride (>95%) was obtained from Peninsular ChemResearch (impurities are BF_3 and SiF_4). These two reagents were used without further purification. Anhydrous hydrogen fluoride was obtained from the Matheson Co. and treated with the tetrafluorohydrazine adduct prior to its use as a solvent.

Preparation of Adduct.—Two methods of adduct preparation were employed. The principal one was the direct combination of N_2F_4 with liquid AsF_5 at −78°. Quantities of reagents used and recovered in specific runs are presented in Table I. In a typical run, N_2F_4 and AsF_5 were successively expanded from storage tanks to an evacuated Monel flask of calibrated volume to the desired pressure and then condensed into a 95-ml Pyrex pressure reactor (obtained from Fischer and Porter Co., Warminster, Pa.) at −196°. The reactor was fitted with a pressure gauge and could be isolated from the gas-measuring system by a Monel valve. The valve was closed and the reactor warmed to −78° and maintained there for 18–24 hr. The valve was then opened to admit the residual gases to the gas-measuring system. These gases (volatile at −78°) were collected in a Kel-F U trap at −196°. After closing the reactor valve, the material in the U trap was measured by allowing it to expand into a calibrated volume at ambient temperature and recording the pressure. It was identified by infrared spectroscopy. The reactor was then allowed to warm to room temperature where additional volatile material was released. This was measured and then identified by infrared spectroscopy. The residual solid adduct was pumped for 1–2 hr and then removed from the Pyrex reactor in a dry nitrogen atmosphere and stored in a Kel-F sample vial. (Storage for periods of 1–2 days in Pyrex at room temperature resulted in the conversion of the solid to $NOAsF_6$ and the liberation of decomposition gases containing *trans*-N_2F_2 and NF_3.) In a typical run (no. 4, Table I) 9.6 mmoles of N_2F_4 produced 2.67 g of adduct (calculated for $N_2F_4 \cdot AsF_5$, 2.63 g). Samples of the solid adduct prepared in this manner were examined by infrared, X-ray, and F^{19} nmr (HF solution). An elemental analysis, performed on a composite sample from several runs, gave the composition $N_2F_4 \cdot 1.33AsF_5$.

Table I

Reaction of N_2F_4 with AsF_5

Run no.	Initial, mmoles N_2F_4	Initial, mmoles AsF_5	Recovered at −78°, mmoles N_2F_4	Recovered at −78°, mmoles AsF_5	AsF_5/N_2F_4 consumed at −78°	Recovered at ambient temp, mmoles N_2F_4	Recovered at ambient temp, mmoles AsF_5	AsF_5/N_2F_4 consumed at ambient temp
1	12.0	4.8	9.6	0.0	2.0	...	...	...
2	6.5	13.1	1.5	0.0	2.6	...	...	...
3	11.0	11.0	5.4	0.0	2.0	0.0	5.1	1.1
4	10.5	21.0	0.9	0.0	2.2	0.0	6.9	1.5
5	13.8	27.6	2.9	0.0	2.5	0.0	10.6	1.6
6	5.9	23.6	0.0	10.4	2.3	0.0	7.8	0.92
7	1.4	5.6	0.0	2.4	2.3	0.0	1.6	1.14
					Av 2.3 ± 0.2			Av 1.3 ± 0.2

Anal. Calcd for $N_2F_4 \cdot 1.33AsF_5$: N, 8.37; F, 61.31; As, 30.22. Found: N, 8.39; F, 62.15; As, 30.56.

In the second method of preparation, anhydrous HF was used as a solvent for the reaction. Arsenic pentafluoride (12.5 mmoles) was condensed at −196° into a 75-ml Kel-F tube through a Teflon valve. Anhydrous liquid HF (25 ml) was distilled into the tube, a valve was closed, and the tube was warmed to −78° in order to form a homogeneous solution of arsenic pentafluoride in the HF. The solution was then frozen and cooled to −196°, and 9.6 mmoles of N_2F_4 was condensed into the reaction tube. The valve was again closed and the reactor was warmed to −78° (slightly below the boiling point of N_2F_4), where it was maintained for 20 hr. The valve was opened and unreacted N_2F_4 was removed by pumping the volatiles in the reaction tube at −78° into a series of three Kel-F traps at −196°. In this manner, 1.3 mmoles of N_2F_4 was recovered from the solution at −78°. The Dry Ice bath was removed from the reaction tube, and the HF was distilled into a Kel-F storage trap, leaving a white, solid residue. The latter was pumped for 30 hr at room temperature, and 1.7 g was recovered from the reactor in a dry nitrogen box. The X-ray pattern and infrared spectrum of this solid were identical with those of products obtained by the reaction of N_2F_4 with AsF_5 in the absence of HF.

Stoichiometry.—*PVT* measurements were made on initial reagents and volatile materials recovered at −78° and at ambient temperatures after approximately 20-hr reaction time. These enabled us to estimate the compositions of adducts stable at low temperatures (−78 to −45°) and at ambient temperatures, respectively. These data are presented in Table I. They indicate compositions approaching $N_2F_4 \cdot 2AsF_5$ at −78° and $N_2F_4 \cdot AsF_5$ at ambient temperatures. The over-all reaction may be approximately represented by eq 1. It should be noted (runs 6 and 7, Table I) that the tetrafluorohydrazine was completely com-

$$N_2F_4 + 2AsF_5 \xrightarrow{-78^\circ} N_2F_4 \cdot 2AsF_5 \xrightarrow{\text{ambient}} N_2F_4 \cdot AsF_5 + AsF_5 \quad (1)$$

plexed at −78° only in those runs in which arsenic pentafluoride was in large excess (at least 4:1). Complete elemental analysis on a sample of the adduct stable at ambient temperatures gave the composition $N_2F_4 \cdot 1.33AsF_5$. Since the only effort made to

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(1) J. K. Ruff, *J. Am. Chem. Soc.*, **87**, 1140 (1965).

purify adduct samples consisted of pumping for 1–2 hr, it is probable that varying amounts of excess AsF_5 were absorbed on the solid surfaces.

Infrared Spectrum.—Infrared spectra were obtained by pressing powder samples between AgCl optical plates. The samples were examined from 2 to 20 μ with a Perkin-Elmer Model 521 grating spectrometer. The infrared spectrum shows a very strong, broad absorption centered at 695 cm^{-1}, which suggests the presence of hexafluoroarsenate ion.[2] In addition, there are three strong peaks at 922, 1100, and 1295 cm^{-1} which are comparable to absorptions reported by Ruff[1] for the adduct of tetrafluorohydrazine with antimony pentafluoride. There is also a sharp peak of medium intensity at 1500 cm^{-1}.

X-Ray Diffraction Pattern.—Powder diffraction patterns of adduct samples sealed under nitrogen in Pyrex capillaries were photographed using Cu Kα radiation from an Ni filter. The diffraction lines were indexed on a cubic unit cell, a_0 = 10.8 A. The principal diffraction lines at 5.37, 4.45, and 3.39 A distinguish the adduct from N_2FAsF_6,[3] another possible reaction product of N_2F_4 with arsenic pentafluoride. Similarly, the pattern clearly shows no indication of the presence of oxygen-containing impurities such as NO_2AsF_6[3] and $NOAsF_6$.[4]

F^{19} Nmr Spectrum.—The F^{19} nmr spectrum of the adduct was obtained on a Varian HR-60 spectrometer at ambient temperature using 25–30% solutions in anhydrous HF. Kel-F tubes were used as sample holders. The chemical shifts of the NF fluorines were observed relative to the HF fluorine and then referred to $CFCl_3$ by a substitution technique. The spectrum shows three very broad (approximately 1000 c) absorptions at ϕ −122, −146, and −180, respectively. The areas under the peaks are virtually identical (1.09:1.09:1.04). As in the case of N_2FAsF_6, no fluorine on arsenic signal was observed because of solvent exchange with the As–F species.[3]

Discussion

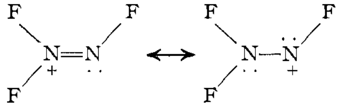
Probable Constitution of NF Species in the Adduct.—The presence of a strong absorption at 695 cm^{-1} in the infrared spectrum of the adduct suggests that the adduct may be ionic, since this absorption has the shape and frequency characteristic of the ν_3 fundamental of the octahedral AsF_6^- ion. There are three possible NF cations obtainable from N_2F_2 or NF_2 by a single fluoride ion transfer to AsF_5 or $H_2F^+AsF_6^-$ (in the case of preparation of the adduct in HF), namely, $N_2F_3^+$, $\dot{N}F^+$, and NF_2^+ (eq 2, 3, and 4). Of these, only an $N_2F_3^+$ cation is consistent with the observed F^1 nmr and infrared spectra, both of which suggest the presence of a nitrogen-to-nitrogen linkage.

$$2HF + N_2F_3^+ \xleftarrow{H_2F^+} N_2F_4 \xrightarrow{AsF_5} N_2F_3^+ + AsF_6^- \qquad (2)$$

$$HF + HNF_2 + NF_2^+ \xleftarrow{H_2F^+} N_2F_4 \xrightarrow{AsF_5} NF_2^+ + AsF_6^- + {}^1/_2N_2F_2 \qquad (3)$$

$$2HF + \dot{N}F^+ \xleftarrow{H_2F^+} \dot{N}F_2 \xrightarrow{AsF_5} \dot{N}F^+ + AsF_6^- \qquad (4)$$

The F^{19} nmr spectrum shows three nonequivalent N–F fluorines, as one would predict for an $N_2F_3^+$ species, in which one of the "NF_2" fluorines is *cis* and the other is *trans* with respect to the "NF" fluorine (structure I). The observed broadness of the peaks may be due to *cis*-, *trans*-, and *gem*-fluorine–fluorine couplings, on which the effect of fluorine–nitrogen coupling is superimposed, thus giving three sets of lines which are unresolvable at 60 Mc.


I

The infrared spectrum of the solid is readily interpreted in terms of structure I. The three strong, sharp absorptions at 922, 1100, and 1295 cm^{-1}, respectively, may reasonably be assigned to NF stretching vibrations of an $N_2F_3^+$ cation. (The recently reported ONF_2^+ ion[5] has NF stretching vibrations at 895 and 1150 cm^{-1}.) Furthermore, the presence of a medium-intensity peak at 1500 cm^{-1} is not inconsistent with the postulated structure (I), since this is just below (~20 cm^{-1}) the range of observed N=N stretching frequencies.[6,7]

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Correspondence

Stereochemically Nonrigid Organometallic Compounds. IV. Some Observations on π-Allylic Complexes

Sir:

Allyl Grignard reagents give rise to an A_4X nmr spectrum at room temperature owing to an interconversion which is rapid on the nmr time scale.[1] A_4X spectra in π-allyl transition metal complexes[2,3] and comparable spectra of some crotyl complexes consistent with rapid interconversion have been considered diagnostic for a so-called dynamic allyl. Upon sufficient cooling, a spectrum of a static, rigidly bound π-allyl is often observed. Much speculation and discussion have arisen concerning the interconversions which are responsible for the coalescence of the static π-allyl resonances to the more simple spectrum of a dynamic

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