relevant dissociation pressures. The present system presents an added complication in the fact that VH_2 decomposes in two stages instead of one, like UH_3. One needs to know the relative isotopic stabilities at each stage. We have no data on VH *vs.* VD, but an exchange experiment which was run with VH gave about the same separation factor as those run with VH_2. The isotopic pressure ratios were therefore taken as the same for the lower and higher hydride. Additional assumptions are that the isotope effect is independent of the $(H + D)/M$ ratio and of the (H/D) ratio in the solid.

A more extensive and much more reliable series of exchange measurements was made with tritium. In all the runs except those with Mg_2NiH_4 the gas was pumped continuously through the solid hydride, which greatly reduced the time necessary to attain equilibrium. Table II summarizes the results. The relation between T–H and D–H separation factors in the vanadium system is consistent with Bigeleisen's formula, $\ln \alpha_{T-H} = 1.4 \ln \alpha_{D-H}$.[45] Applying this to the 28° α_{T-H} value, 1.74, one predicts 1.48 for α_{D-H}, which agrees within its experimental error with the value found. For the rare earth alloys, whose hydriding properties were recently discovered by van Vucht, *et al.*,[46] the effect is in the same direction but smaller; a vanadium–chromium alloy resembles vanadium; zirconium–nickel hydride shows a very small effect in the same direction; while with Mg_2NiH_4, which is a relatively stable hydride, the heavy isotope becomes concentrated in the gas phase. There is no evidence for a dependence of separation factor on pressure. The temperature dependence is marked, however. Taking averages for all runs on VH_2 of similar origin at the same temperatures, one gets the following separation factors: 0°, 1.89; 28°, 1.74; and 45° (one run), 1.61.

TABLE III

DEUTERIUM–TRITIUM SEPARATION FACTORS IN THE VANADIUM DIHYDRIDE–HYDROGEN SYSTEM

	0°	28.2°	28.6°	42.8°
$\alpha \equiv (T/D)_{solid}/(T/D)_{gas}$	1.07_8	1.04_4	1.03_6	1.00_9
Tritium material balance	96.8	101.3	101.9	100.7

Tritium–deuterium exchange was the subject of four runs. In these, the dideuteride, VD_2, of zone-refined vanadium was equilibrated in the forced-circulation loop with deuterium gas to which tritium tracer had been added. Table III gives the results. As before, a marked temperature dependence was found. However, the 28° value of the separation factor, 1.04, falls considerably short of the 1.17 figure which would be predicted from α_{T-H}.

The kinetics of the isotope exchange reactions do not appear to follow any simple rate law, although the exchange is rapid as shown in Figure 5. These curves have a shape very like that found by Bigeleisen and Kant[34] in a similar exchange experiment involving U as the metal substrate. Their conclusion that diffusion within the solid was rate determining very probably applies here.

Acknowledgment.—The authors wish to express their thanks to Messrs. J. Hughes and A. Holtz for their expert assistance in the laboratory. This work was performed under the auspices of the U. S. Atomic Energy Commission.

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[46] J. H. N. van Vucht, F. A. Kuijpers, and H. C. A. M. Bruning, *Philips Res. Rep.*, **25**, 133 (1970).

CONTRIBUTION FROM SHELL DEVELOPMENT COMPANY, A DIVISION OF SHELL OIL COMPANY,
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Preparation and Properties of Perfluoroammonium Tetrafluoroborate, $NF_4^+BF_4^-$, and Possible Synthesis of Nitrogen Pentafluoride[1]

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A new crystalline compound, $NF_4^-BF_4^-$, has been prepared by exposing the heterogeneous ternary system NF_3–BF_3–F_2 to 3-MeV bremsstrahlung at 77°K. The *G* value for the reaction (molecules isolated per 100 eV absorbed) is about unity. The compound is stable at room temperature in dry air; it decomposes above 250° to the reactants. It reacts rapidly with moisture and with organic substances. The indicated ionic structure is confirmed by infrared and Raman spectroscopy. The X-ray powder pattern can be indexed on the basis of a tetragonal unit cell with $a = 7.01$ and $c = 5.22$ Å. Irradiation of mixtures of nitrogen trifluoride and excess fluorine at 77°K has led to isolation in low yields of a white solid. It decomposes below 143°K to liberate nitrogen trifluoride and reacts with boron trifluoride at low temperature to form NF_4BF_4. Its most likely identity is perfluoroammonium fluoride.

Introduction

Synthesis of two salts of the previously unknown tetrafluoronitrogen(V) cation, NF_4^+ (perfluoroammonium), was recently reported by two groups of investigators.[2,3] Tolberg[2] and his colleagues prepared $NF_4^+AsF_6^-$ and $NF_4^+SbF_6^-$ by a thermal reaction of NF_3 and F_2 with AsF_5 or SbF_5 at high pressures and moderately elevated temperatures. The perfluoroarsenate salt was also obtained by Christe, Guertin, and Pav-

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[1] This work was supported in large part by the Advanced Research Projects Agency under a contract administered by the U. S. Army Research Office.

[2] (a) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Nucl. Chem. Lett.*, **2**, 79 (1966); (b) *Inorg. Chem.*, **6**, 1156 (1967).

[3] K. O. Christe, J. P. Guertin, and A. E. Pavlath, *Inorg. Nucl. Chem. Lett.*, **2**, 83 (1966).

lath[3,4] by passing an electric discharge through a mixture of NF_3, F_2, and AsF_5. The latter technique, despite repeated attempts, did not yield detectable amounts of NF_4BF_4 from the system NF_3–F_2–BF_3,[5] though $N_2F^+BF_4^-$ was formed. An earlier estimate by one of us[6] indicated that $NF_4^+BF_4^-$ was likely to be thermodynamically unstable at room temperature and atmospheric pressure but might be stable at low temperature. We now report the successful synthesis of this compound *via* a radiation-induced reaction in the heterogeneous system NF_3–F_2–BF_3 at liquid nitrogen temperature. Contrary to previous expectation,[6] the compound, when free of dioxygenyl tetrafluoroborate, is stable against thermal decomposition well above room temperature. The same compound has been made by Tolberg, Rewick, Stringham, and Hill[7] in a parallel effort to ours. Their preferred procedure involved metatheses between stable salts of the cation NF_4^+ and the anion BF_4^- in anhydrous hydrogen fluoride.

Experimental Section

(a) **General Data.**—The stainless steel vacuum system used to handle reactants and products, the van de Graaf source of high intensity 3-MeV bremsstrahlung, and the methods used for irradiation, dosimetry, and temperature control have been described elsewhere.[8,9] A transparent sapphire reaction vessel[9,10] was used for visual observation of reaction mixtures and products; it consisted of a short test tube (24 mm × 8 mm i.d.) made of optical grade sapphire, silver soldered to a stainless steel tube, and fitted with a bellows-type stainless steel valve, Hoke No. 4112-G-4Y, and a Gyroloc connector. Its usable capacity was about 1 ml. Preliminary experiments in this vessel showed that the reaction mixtures of NF_3–F_2–BF_3 were heterogeneous but dispersible. In order to prepare larger amounts of product, a stainless steel reactor of 10–15 ml capacity that could be stirred by means of a solenoid-actuated plunger was designed by V. A. Campanile. To maintain adequate stirring and to achieve reproducible yields, it was found necessary to use an asymmetric canted flange on the plunger to avoid channeling and to scrape the walls of the reactor.

(b) **Materials.**—The nitrogen trifluoride (Air Products Co., Research Grade) and the boron trifluoride (98%, Matheson Co.) were purified by several low-temperature trap-to-trap vacuum distillations.

The fluorine (98%, Matheson) was freed of residual hydrogen fluoride by distillation through a stainless steel canister containing about 140 ml of powdered sodium fluoride "activated" by thermal cycling as recommended.[11] For all of the preparations described in this paper, except where otherwise noted, the fluorine was also given the following treatment[12] to remove the oxygen impurity and part of the nitrogen. Condensed at 77°K, it was exposed to about 10^8 rads of 3-MeV bremsstrahlung to convert the oxygen to fluorine oxides[9] and part of the nitrogen to NF compounds. It was then separated from these less volatile compounds by trap-to-trap distillation. This procedure was repeated at least twice to ensure complete removal of oxygen, as demonstrated by the absence of color after irradiation.

(c) **Preparation of NF_4BF_4.**—Reaction mixtures were prepared for irradiation by first condensing nitrogen trifluoride at 77°K into a preevacuated reaction vessel. This was followed by boron trifluoride which condensed as a dispersion of solid particles in the liquid NF_3. Finally the fluorine was added; it was only partially miscible with the nitrogen trifluoride and formed a second liquid phase. Any boron trifluoride that was trapped on the cold walls above the liquid was transferred to the liquid phase by lowering the liquid nitrogen bath temporarily and allowing the upper walls of the vessel to warm. This was done several times. It was found that the three-phase system prepared in this way could be dispersed fairly well by shaking, provided the volume ratio of liquid fluorine to other components was high enough. The loaded reaction vessel was then closed and transferred to a specially designed stainless steel Dewar vessel[9] containing liquid nitrogen. A closure with appropriate inlets and outlets was designed to limit access of air to the liquid nitrogen during extended irradiations; ozone formed by irradiation of oxygen-containing nitrogen is believed to be responsible for some explosions experienced in preliminary experiments. Liquid nitrogen which boiled off from the dewar during irradiation was automatically replenished.[8]

After irradiation the reaction vessel, still at −196°, was transferred to the vacuum system. Unreacted fluorine was measured volumetrically. Visual observation at this stage revealed a brownish red suspension of solid product. The unreacted fluorine was pumped away at −196° and the reaction vessel was warmed to −78°. During the warming process the reddish color faded and disappeared at about −100°. Unreacted nitrogen trifluoride and boron trifluoride were then measured volumetrically at −78°, identified by mass spectrometry, and pumped away. A white powder, later identified as NF_4BF_4, remained; it was transferred at room temperature to a Kel-F vial in a glove box filled with nitrogen at slightly greater than atmospheric pressure, dried by passage through a liquid nitrogen trap.

In experiments with the sapphire reactor, the maximum yield of product (15 mg from 28 mmol of reactant mixture) was obtained at a radiation dose of 100 Mrads with a well-dispersed suspension whose composition (molar ratios) was $NF_3:BF_3:F_2 = 1:1:6$. With the stirred reaction and the same composition, the yield was 100 mg/hr at 100 Mrads/hr. With a recently cleaned and passivated system and freshly purified reagents, it was possible to recycle unreacted reagents without significant loss in yield.

The yield was found, however, to be sensitive to the presence of unidentified inhibitors. For instance, after the vacuum system had been used to study another reaction involving nitric oxide, subsequent attempts to synthesize NF_4BF_4 by this procedure resulted in zero yield with either the sapphire or the stirred reactor. Yields were restored by thorough cleaning of both the reactor and the vacuum system with steam, drying them, and passivating with fluorine after reassembly and evacuation. It was necessary also to repurify any reagents that had been exposed to the contaminated system. In addition, with the stirred reactor there was a tendency for a yellow film to form on the stirrer during its exposure to the atmosphere of the glove box while the product was being collected. As the film increased in amount during a series of preparations, the yield declined in a systematic way but could be restored by cleaning the reactor and redistilling the reagents.

(d) **Instrumental Analytical Techniques.**—Mass spectra of gases were obtained with a quadrupole mass spectrometer.[13] In this instrument as received, gas samples were introduced through a hole in the end plate of a 5 in. × 10 in. vacuum chamber which houses the "naked" ionization chamber, quadrupole analyzer, and electron multiplier detector. Entering gas samples diffused freely toward the ionizer and had ample opportunity to collide with the metal walls before ionization. As a consequence, the sensitivity for reactive gases such as fluorine was very low, and small concentrations were undetectable. Subsequent to this work the sensitivity to reactive gases was substantially improved by modifying the inlet system so that incoming gases entered through a stainless steel tube, 0.25-in. i.d., which was aimed directly at the open ionization assembly and terminated a short distance from it. The interior of the mass spectrometer could not be passivated since the dynode surfaces of the electron multiplier are irreversibly damaged by exposure to appreciable pres-

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(12) C. T. Goetschel and V. A. Campanile (assigned to Shell Oil Co.), U. S. Patent 3,530,052 (1970).

(13) Quad 200 Mass Spectrometer, Electronic Associates, Inc., Palo Alto, Calif.

sures of reactive fluorine compounds. The vacuum jacket of the spectrometer was wound with heating tapes for bake-out purposes and to enable the jacket to be kept warm during operation. These tapes were disconnected during operation with reactive fluorine compounds since operation with a warm jacket (100°) accelerated the formation of insulating deposits on the surfaces of the quadrupole electrode rods. Formation of such deposits resulted in erratic performance and a drastic decline in resolution and sensitivity.

Infrared spectra (Beckman IR 4) were obtained with a cell that has been described elsewhere.[14] Solids were examined as thin layers of powder confined between silver chloride plates which were mounted within a vacuum chamber with cesium iodide or sodium chloride windows. The sample chamber could be cooled with liquid nitrogen to near −196°, but the minimum temperature maintainable during loading operations in the glove box was higher by 20° or more.

Raman spectra were obtained with a helium–argon laser (6328 A) as the source of excitation and a Jarrel-Ash scanning double monochromator. The exciting radiation was focused into a capillary tube containing the sample, and the light scattered at right angles from incident was focused on the entrance slit of the spectrometer.

X-Ray diffraction powder patterns of NF_4BF_4 were obtained with filtered Co Kα radiation and a cylindrical camera (Philips) of about 11-cm diameter; the precision in measurement of the scattering angle 2θ is estimated to be 0.05°. Four photographs covering a range of exposure times up to 30 hr were made with samples prepared from oxygen-free fluorine; each film was microphotometered twice. The powder samples were loaded in a drybox into thoroughly dried quartz capillaries whose ends were then plugged with fluorocarbon grease; the plugged capillaries were removed from the drybox for heat-sealing. Thorough drying of the capillaries is important; a trace of residual moisture causes attack on the walls of glass or even quartz capillaries with concomitant decomposition of the sample. In some instances with an incompletely dry capillary the gases evolved generated enough pressure to rupture the tube within a few hours.

Elemental analyses of NF_4BF_4 were obtained as follows. Fluorine and nitrogen were determined by neutron activation analysis.[15] Boron was determined by flame emission photometry from a solution in glycol–chloroform. Some gas was evolved during the dissolution process and it is possible that some boron was lost.

A 5-g sample of pure NF_4BF_4 was prepared by means of repeated runs in the stirred reactor for a more thorough study[16] of the thermochemistry of this compound.

(e) **Reaction of Nitrogen Trifluoride and Fluorine.**—A suspension of 4 mmol of nitrogen trifluoride in 24 mmol of fluorine at 77°K was irradiated to a dose of 100 Mrads in the sapphire reaction tube. The excess fluorine was removed by venting and pumping at 77°K, and the temperature was raised to 113°K where the unreacted NF_3 was pumped away. A small amount of white solid residue was visible in the tube; such a residue was not observed after irradiation of either reactant alone. When the temperature was raised to 143°K the white solid disappeared and about 0.04 mmol of gas was evolved. Mass spectrometric examination of the gas showed nitrogen trifluoride as the major and only identifiable component; elementary fluorine was not detected but would not have been had it been present at the same concentration as the NF_3.

This experiment was repeated several times with essentially the same result though the yield was somewhat variable. Earlier preliminary experiments at lower molar ratios of fluorine to nitrogen trifluoride gave the same qualitative result, but there appears to be a systematic trend toward lower yields with decreasing values of this mole ratio. An unsuccessful attempt was made to obtain the infrared absorption spectrum of the white solid, but the amount was too small for handling by our techniques and it was difficult to avoid decomposition.

When boron trifluoride was added to these reaction mixtures at 77°K after irradiation but before complete removal of excess fluorine, a reddish brown suspension was formed whose appearance was similar to that observed after irradiation of mixtures of NF_3, BF_3, and F_2. The color changes previously described were observed as the system was warmed and pumped to remove excess reagents. After removal of volatile components, a small residue of white solid remained that was stable at room temperature and at 100° but decomposed above 200° to liberate a gas whose mass spectrum indicated the presence of equimolar quantities of NF_3 and BF_3; again fluorine was not detected. These observations are consistent with the formation of NF_4BF_4 *via* $NF_4^+F^- + BF_3 = NF_4^+BF_4^-$.

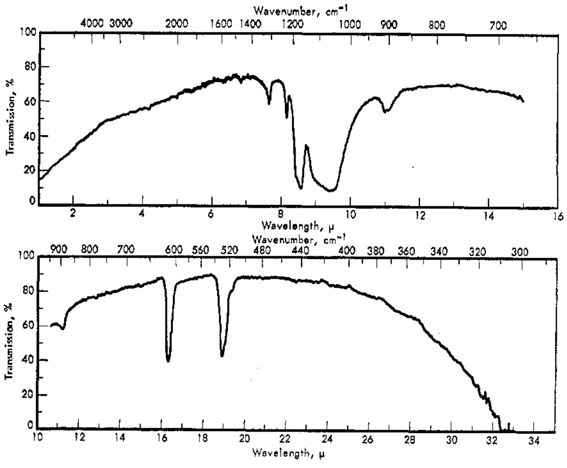

Figure 1.—Infrared spectrum of solid.

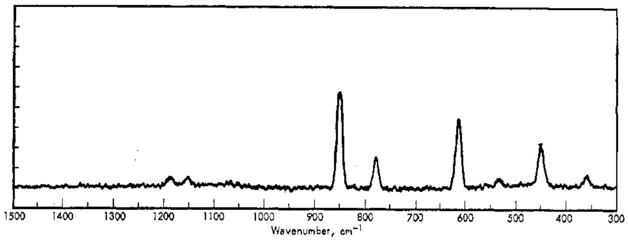

Figure 2.—Raman spectrum of solid.

Results. Properties of NF_4BF_4

(a) **Vibrational Spectrum.**—Conclusive evidence that the compound described as NF_4BF_4 is in fact $NF_4^+BF_4^-$ comes from its vibrational infrared and Raman spectra (Figures 1 and 2), which allow the identification of all fundamental vibrations of the NF_4^+ and BF_4^- ions.

The infrared spectrum was first obtained and analyzed for us through the courtesy of Dr. K. O. Christe;[17] its prominent features have since been confirmed by our own measurements on more recent preparations. The results are summarized in Table I.

Christe and coworkers have obtained and discussed the vibrational spectrum of $NF_4^+AsF_6^-$.[18] Our results are in good agreement with their assignments for the fundamental modes of the NF_4^+ cation, the improved quality of our Raman spectrum establishing them on a firmer basis. Of particular interest in the Raman spectrum is the much greater intensity of the NF_4^+ ν_1 stretching mode at 849 cm^{-1} as compared to the comparable band of BF_4^- at 778 cm^{-1}. The comparison is particularly significant since the two species are iso-

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[14] K. R. Loos, V. A. Campanile, and C. T. Goetschel, *Spectrochim. Acta, Part A*, **26**, 365 (1970).

[15] We are indebted to Dr. R. A. Johnson for development and refinement of these methods.

[16] Dr. G. C. Sinke, Thermochemistry Laboratory, Dow Chemical Co., Midland, Mich., private communication, 1968. Results to be published.

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TABLE I

VIBRATIONAL SPECTRUM OF $NF_4{}^+BF_4{}^-$ (CM^{-1})

Raman		Infrared				
		$NF_4{}^+$		$BF_4{}^-$		
$NF_4{}^+$	$BF_4{}^-$	Christe (IR 9)	Present (IR 4)	Christe (IR 9)	Present (IR 4)	Assignment (Christe and Loos)
450 m	358 w	. . .	448 w	. . .	. . .	δ_{sym}, $\nu_2(E)$
613 s	535 w	613 s	611 s	527	529 s	δ_{asym}, $\nu_4(F_2)$
849 s	778 m	. . .	. . .	775 w	775 w	ν_{sym}, $\nu_1(A_1)$
1153 1185 w	1065 vw	1165 s	1162 s	1025 s, vb	1063 s, b	ν_{asym}, $\nu_3(F_2)$
			1063 s, b		904 911 m	$\nu_2 + \nu_4(F_1 + F_2) = 1062, 886$
		1225 m	1230 m		1063 s, b	$2\nu_4(A_1 + E + F_2) = 1223, 1056$
		1456 mw	1460 w	1302 m	1310 m	$\nu_1 + \nu_4(F_2) = 1462, 1313$
		1760 vw				$\nu_3 + \nu_4(A_1 + E + F_2) = 1776$
		2000 vw	2000 vw	1830 vsw		$\nu_1 + \nu_3(F_2) = 2011, 1835$
		2370 vw	2380 vw			$2\nu_3(A_1 + E + F_2) = 2330?$

TABLE II

X-RAY POWDER PATTERN OF NF_4BF_4 PREPARATIONS

	d, Å		I		d, Å		I
hkl	Calcd	Obsd	(rel)	hkl	Calcd	Obsd	(rel)
001	5.224	5.21	8.4	213	1.522	1.523	0.4
110	4.955	4.95	0.7	421	1.501	1.503	1.8
I[a]	. . .	4.62	0.7	402	1.455	1.455	0.6
101	4.188	4.19	8.0	223, 412	1.425	1.425	6.5
111	3.595	3.597	100				
200	3.504	3.520	58	303, 332	1.396	1.397	0.6
210?	3.134	3.126	1.0	I	. . .	1.383	0.3
201	2.910	2.907	2.5	313	1.369	1.370	0.3
I	. . .	2.743	0.8	501	1.354	1.357	0.6
211	2.688	2.683	1.8	422	1.344	1.347	0.3
002	2.612	2.607	6.7	511	1.329	1.331	2.4
102	2.448	2.439	8.4	004	1.306	1.307	0.6
I	. . .	2.409	3.6	114, 521	1.263	1.265	0.7
112	2.311	2.307	4.1	440	1.239		
221	2.239	2.238	1.3	502, 432	1.235	1.236	0.5
310?	2.216	2.181	3.3	413, 512	1.216	1.217	0.8
301	2.132	2.135	30.3	441	1.205		
202	2.094	2.090	0.3	214	1.206	1.206	1.8
311	2.040	2.050	1.1	333	1.198	1.198	1.2
212	2.006	2.006	16.9	I	. . .	1.191	0.5
I	. . .	1.892	1.7	522, 423	1.165	1.166	2.9
I	. . .	1.856	3.2	601, 304	1.140	1.141	0.3
231	1.822	1.821	11.3	314, 611	1.125	1.125	1.0
222	1.798	1.791	1.0	620	1.108	1.109	0.7
302, 003	1.741	1.741	4.1	532	1.092		
312, 103	1.690	1.689	0.8	504, 433	1.092	1.091	0.3
401	1.661	1.658	3.4	513	1.079	1.079	0.2
330	1.652			105	1.033	1.033	0.6
113	1.643	1.643	8.5	631, 334	1.024	1.023	0.8
411	1.616	1.616	0.6	115	1.022		
331	1.575	1.579	1.3	542	1.009	1.008	0.6
203, 322	1.559	1.558	0.4	551, 711	0.974	0.973	1.0
I	. . .	1.547	0.4	640	0.972		
213				305	0.954	0.953	0.5

[a] I = possible impurity.

electronic and, of necessity, present in equal concentrations in the sample. The Raman intensity has been shown[19] to be proportional to the square of the bond polarizability derivative $(\partial\bar{\alpha}/\partial\nu)^2$, which in turn is directly proportional to the covalent bond order. The observed relative intensities are consistent with a higher degree of covalency in the bonds of $NF_4{}^+$ than in those of $BF_4{}^-$; such a trend is consistent with the expected differences in electronegativity between the bonded atoms. The higher polarizability expected for N than for B may, however, also contribute.

The splitting of the ν_4 $BF_4{}^-$ bands in the spectra of KBF_4[20] and O_2BF_4[14] has been previously attributed to isotope effects. Our observation of a single band at 529 cm^{-1} in the spectrum of $NF_4{}^+BF_4{}^-$ shows that the splitting is related instead to crystal field effects and that the local symmetry of the BF_4 is different in $NF_4{}^+$-$BF_4{}^-$ from that in $O_2{}^+BF_4{}^-$. It has been suggested to us[21] that the narrow band at 1225–1230 cm^{-1} could conceivably be due to the presence as an impurity of trace amounts of bifluoride ion, which also has an exceedingly strong and narrow absorption band in this region.[22] We did not observe other prominent features of the bifluoride spectrum, in particular the moderately strong band[22] at 1700 cm^{-1}, but these bands are relatively much weaker. This fact, the precautions taken to eliminate water and hydrogen fluoride from our reagents, and internal evidence from the spectrum lead us to believe that the band under discussion is in fact intrinsic to NF_4BF_4.

(b) X-Ray Powder Pattern and Probable Space Group.—The observed reflections and their assignments are listed in Table II. The indicated intensities are based on the maximum deflections of the microphotometer trace and have not been corrected for nonlinearity of the photographic process. The indexed reflections are referred to a tetragonal unit cell, a = 7.008, c = 5.224 Å, very similar in shape to those of tetramethylammonium permanganate and perchlorate.[23] The dimensions of the latter have been redetermined by McCullough[24] as 8.343 × 5.982 Å; he confirmed the space group previously[23] assigned as $D_4{}^7$-$P4/nmm$ and showed that the symmetry requirements of that space group were met only because the perchlorate ions are orientationally disordered.

The extinction rule for that space group is $hk0 = 0$ unless $h + k = 2n$. Our observations follow this rule with one exception; the very weak reflection at 3.126 Å can be indexed as (210) within experimental error. That reflection may be due to an impurity, however, since its relative intensity was 1.0 in one preparation and 2.0 in another. Similar variations in intensity were not observed for other indexable reflections. Of the other reflections that have been provisionally ascribed to impurities, the six with the largest interplanar spacings, d, were observed in three different preparations. A relatively short-exposure pattern was obtained from a small sample that had been dissolved in anhydrous hydrogen fluoride, decanted away from traces of insoluble matter, and recovered by evaporation of the solvent under vacuum. The 2.18- and

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(20) N. N. Greenwood, *J. Chem. Soc.*, 3811 (1965).

(21) R. T. Rewick, Stanford Research Institute, private communication, 1971.

(22) R. Newman and R. M. Badger, *J. Chem. Phys.*, **19**, 1207 (1951), and references cited therein.

(23) K. Hermann and W. Ilge, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **71**, 47 (1929).

(24) J. D. McCullough, *Acta Cryst.*, **17**, 1067 (1964).

1.86-Å "impurity" spacings were observed in this pattern; the 2.74-, 2.41-, and 1.89-Å spacings were not, though they should have been observable at the indicated intensities.

We have not identified the postulated impurities; likely candidates are corrosion products or other conceivable reaction products such as $N_2F_5^+BF_4^-$. The sum of the "impurity" intensities is 2.8% of the sum of those indexed; if, as seems likely, many of the impurities are corrosion products containing metallic elements, the corresponding weight per cent of impurity will be substantially lower.

(c) **Chemical and Thermal Properties.**—The powder is very hygroscopic; when a small sample is exposed to the atmosphere it hydrolyzes to form a clear colorless liquid within minutes. The products of hydrolysis were not analyzed. The powder also reacts rapidly at room temperature with organic substances such as acetone, isopropyl alcohol, and benzene; unlike the case of O_2BF_4, however, when a small amount of the powder is dropped into a few milliliters of one of these liquids, the mixture does not immediately enflame. The compound is extremely soluble in anhydrous hydrogen fluoride at about 0° from which it can be recovered by evaporation *in vacuo;* prolonged pumping was required to remove the last traces of solvent. On the basis of X-ray diffraction data, it was recovered unchanged. Differential thermal analysis of a small sample in an improvised apparatus showed a small endotherm at 236° which was accompanied by detectable gas evolution. This endotherm was subsequently identified by investigators at the Thermochemistry Laboratory of Dow Chemical Co.[16] as a solid-phase transition. Extensive thermal decomposition was observed calorimetrically by the same investigators to set in at about 285° at atmospheric pressure; on the basis of the measured heats of transition and decomposition, they estimate the standard enthalpy of formation[16] at 25° to be -337 kcal/mol. We have detected thermal decomposition manometrically *in vacuo* at much lower temperatures, slightly above 200°.

The compound is similar in this respect to O_2BF_4 which decomposes rapidly at around 40° at atmospheric pressure, is reasonably stable at room temperature in sealed vials, but decomposes at a measurable rate[25] *in vacuo* at 0°. The explanation proposed by Keith, *et al.*,[25] for the effect of pressure on decomposition rate involves rapid reversibility of the postulated initial reaction $O_2BF_4(c) = FO_2(g) + BF_3(g)$. In our case the lower temperature observed for the onset of thermal decomposition *in vacuo* may be attributed in part simply to the high sensitivity of pressure measurements under high vacuum and possibly also to inhibition of a postulated initial reaction, $NF_4BF_4(c) = NF_5(g) + BF_3(g)$, by gas-phase or adsorbed boron trifluoride.

The mass spectrum of the thermal decomposition products showed only fragments derived from NF_3, BF_3, and F_2. The molar ratio of NF_3/BF_3 in the decomposition products was unity as determined by calibration of the mass spectrometer; this is consistent with the proposed identification as NF_4BF_4. A quantitative determination of the fluorine by this method was not possible for reasons described earlier. Elemental analysis of the powder by neutron activation, however, showed 85.9 wt % as an average of three determinations with a standard deviation of 1.5% (calculated for NF_4BF_4, 86.0%). The analyses for nitrogen and boron (8.9 ± 2.0 and 5.8 ± 1.0%, respectively), though reasonable, were not sufficiently precise to be meaningful.

When fluorine containing small amounts of oxygen as an impurity was used in the synthesis, the product isolated as described above was less stable thermally, more reactive as an oxidizer (causing isopropyl alcohol to enflame), and also impact-sensitive. A few milligrams detonated sharply when the sample was laid on an anvil and struck with a hammer. A preparation from oxygen-free fluorine, however, did not detonate when it was struck repeatedly and vigorously in this manner in a drybox. The impurity in samples prepared from oxygen-contaminated fluorine appears to be O_2BF_4; that compound can be prepared by irradiation of mixtures of oxygen, fluorine, and BF_3 under similar conditions,[9] and we were able to detect O_2^+ in the mass spectrum of thermal decomposition products from the less pure preparations. Weak reflections attributed to O_2BF_4 also were detected in the X-ray powder pattern.

Discussion

From the standard enthalpy of formation of NF_4BF_4 as determined by Sinke, *et al.*,[16] the lattice energy of 118 kcal/mol as estimated by one of us,[6] and a value of -423 kcal/mol for the enthalpy of formation of $BF_4^-(g)$, we calculate the enthalpy of formation of $NF_4^+(g)$ to be $+204 \pm 10$ kcal/mol. This value for $\Delta H_f(BF_4^-(g))$ was determined from the calculations of Altschuller[26] and a more recent value[27] for $\Delta H_f(KBF_4(c))$ and is in fair agreement with our earlier independent estimate[6] of -426 kcal/mol.

From the enthalpy of formation[28,29] and ionization potential[30] of NF_3, we obtain 268.4 ± 0.6 kcal/mol at 25° for $\Delta H_f(NF_3^+(g))$. On this basis the energy of dissociation of a fluorine atom from $NF_4^+(g)$ is 83 ± 10 kcal/mol at 25° (the stated uncertainty is a rough estimate). This value lies between the estimate of 115 kcal/mol made by Price, Passmore, and Roessler[31] and our own subsequent independent estimate,[6] also based on isoelectronic analogies, of 55 kcal/mol. We have recently revised the latter estimate[32] using the same method as before but more recent data on the thermochemistry of the species CF_n[33] and NF_n^+,[30] with $0 \leq n \leq 4$; the revised estimate of the energy of dissociation of F from $NF_4^+(g)$ on this basis is 108 ± 14 kcal/mol.

In view of the value given above for $\Delta H_f(NF_4^+)$, it is surprising that our earlier attempt[6] to observe NF_4^+ mass spectrometrically *via* the ion–molecule reaction

$$NF_3^+ + NF_3 = NF_4^+ + NF_2$$

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(25) J. N. Keith, I. J. Solomon, I. Sheft, and H. H. Hyman, *Inorg. Chem.*, **7**, 230 (1968).

(26) A. P. Altschuller, *J. Amer. Chem. Soc.*, **77**, 6187 (1955).

(27) "JANAF Interim Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1965, and subsequent revisions.

(28) W. H. Evans, *Nat. Bur. Stand. (U. S.) Rept.*, No. 8504, 164 (1964).

(29) Report No. AFRPL-TR-69-70, Dow Chemical Co., Midland, Mich., 1969.

(30) V. H. Dibeler and J. A. Walker, *Inorg. Chem.*, **8**, 1728 (1969).

(31) W. C. Price, T. R. Passmore, and D. M. Roessler, *Discuss. Faraday Soc.*, **35**, 201 (1963).

(32) J. N. Wilson, Shell Development Co., unpublished results.

(33) (a) T. C. Ehlert, *J. Phys. Chem.*, **73**, 949 (1969); (b) M. Farber, M. A. Frisch, and H. C. Ko, *Trans. Faraday Soc.*, 3202 (1969).

was unsuccessful. Based on present estimates, the reaction should be exothermic by about 20 kcal/mol. A further attempt to observe this reaction seems warranted.

From our previous estimate[6] of the lattice energy of $NF_4^+F^-$ as 147 kcal/mol and accessory data cited therewith and above, we estimate the enthalpy of formation of that substance to be -4 ± 10 kcal/mol. Decomposition to NF_3 and F_2 at 25° is therefore exothermic by 26 ± 10 kcal/mol. Nevertheless, the formation of $NF_4^+F^-$ at low temperatures is thermodynamically reasonable since NF_4^+ is stable with respect to its likely decomposition products, F^- is stable, and their union to form $NF_4^+F^-$ is favored by the lattice energy. The crystal is probably only kinetically stable, even at low temperatures, with respect to decomposition to nitrogen trifluoride and fluorine.

The formation of $NF_4^+F^-$ in the irradiation of mixtures of nitrogen trifluoride and fluorine at low temperatures therefore appears to be a reasonable possibility. The dependence of the yield on the mole ratio of fluorine to nitrogen trifluoride suggests that the rate of the reaction depends on the limited solubility of the latter substance in the former. The yield should be capable of enhancement by use of a stirred reactor. The alternative possibility for the product of this reaction,[34] $NF_4^+HF_2^-$ *via* a possible hydrogen fluoride impurity, seems unlikely for several reasons. (1) Precautions were taken to remove hydrogen fluoride and water from the reagents. (2) If the product had been $NF_4^+HF_2^-$, we are confident that we would have observed HF^+ in the mass spectrum of the decomposition products; we saw no trace of it. (3) The decomposition temperature of $NF_4^+HF_2^-$ is given by Tolberg, *et al.*,[35] as about 230°K, whereas our product decomposed below 143°K.

Further investigation of the radiation-induced reaction between nitrogen trifluoride and fluorine at low temperatures appears to be merited. Additional confirmation of NF_5 as a product could be obtained by improved mass spectrometry designed to detect fluorine in the decomposition products and by laser-Raman spectroscopy, which was not available to us when the experiments described herein were done.

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[34] We are grateful to a referee for pointing out to us this possibility.

[35] W. E. Tolberg, R. T. Rewick, G. R. Zeilenga, M. P. Dolder, and M. E. Hill, submitted for publication.

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Extraction of Some Anions from Molten Lithium Nitrate–Potassium Nitrate by Tetraoctylphosphonium Nitrate in Polyphenyl or 1-Nitronaphthalene Solvent

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Tetraoctylphosphonium nitrate (TOPN) in a polyphenyl or 1-nitronaphthalene solvent has been used to extract perrhenate, chloride, and $AgCl_2^-$ ions from a eutectic molten salt mixture of $LiNO_3$–KNO_3 at 150°. The distribution coefficients of perrhenate and of chloride with TOPN in polyphenyl are comparable to those obtained previously with tetraheptylammonium nitrate (THAN), while the distribution coefficient of $AgCl_2^-$ in TOPN is greater. Distribution coefficients using 1-nitronaphthalene as the organic solvent are somewhat higher for ReO_4^- both with the phosphonium salt and with the ammonium salt. The dependence of the perrhenate distribution on the temperature and solute concentration was also studied with both polyphenyl and 1-nitronaphthalene. As in the case with THAN, the distribution of the anions is interpreted in terms of a simple anion-exchange equilibrium followed by polymerization of some species in the organic phase. The equilibrium constants for the anion-exchange and the dimerization constants were derived from the distribution data. Both quaternary salts polymerized strongly even at low solute concentrations although polymerization in 1-nitronaphthalene is less than that in polyphenyl. Also, the polymerization of the ammonium salt is stronger than that of the phosphonium salt in either solvent.

Introduction

Tetraheptylammonium nitrate (THAN) has been used to extract simple and complex anions from a $LiNO_3$–KNO_3 eutectic melt.[2] The distribution of the anions between the melt and the extractant has been interpreted in terms of a simple anion-exchange equilibrium followed by polymerization of some species in the organic phase. It was of interest to extend these studies to other organic extractants having ion-exchange characteristics.

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