nmr study suggests that the high-field doublet represents the B_4 and B_6 atoms.

The 1:1 ratio of the high- and low-field doublets at +30.9 and −0.7 ppm, respectively, in the spectrum of the $BrB_{10}H_{11}CH^-$ ion leads us to suggest that halogenation of I also occurs initially at the B_4 atom (numbering is the same as Figure 5). Deamination of "labeled" $BrB_{10}H_{11}CN(CH_3)_3$ with sodium in ethereal solvents is much more sluggish than with $B_{10}H_{12}CN(CH_3)_3$. Thus far, a "labeled" $BrB_{10}H_{11}CH^-$ ion has not been obtained. Dihalogenation of both I and $B_{10}H_{12}CN(CH_3)_2C_3H_7$ yields ^{11}B nmr spectra in which the high-field doublet originally at +31.3 and +35 ppm, respectively, is completely absent. The stereochemistry of thse products is therefore probably 4,6-$Br_2B_{10}H_{10}CH^-$ and 4,6-$Cl_2B_{10}H_{10}CN(CH_3)_2C_3H_7$.

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Hydrazinium(+2) and Hydroxylammonium Hexafluorouranates(V)[1,2]

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In the reaction between uranium hexafluoride and hydrazinium(+2) fluoride in liquid hydrogen fluoride at room temperature, with excess uranium hexafluoride, the product is hydrazinium(+2) bishexafluorouranate(V), $N_2H_6(UF_6)_2$, and, with excess hydrazinium(+2) fluoride, the product is hydrazinium(+2) heptafluorouranate(V), $N_2H_6UF_7$. The analogous reaction with hydroxylammonium fluoride produces mixtures of hydroxylammonium and nitrosyl hexafluorouranates(V). X-Ray powder patterns, infrared spectra, and magnetic susceptibilities of the solids are given. In the Raman spectra of the hydrogen fluoride solutions of these materials, the 628-cm^{-1} band was assigned to the principal symmetric vibration of UF_6^- ion. The thermal decompositions in argon are discussed in terms of the schemes

$$N_2H_6(UF_6)_2 \xrightarrow{120^\circ} N_2H_5UF_5 + UF_4\cdot nHF \xrightarrow{250^\circ} NH_4F\cdot 3UF_4 \xrightarrow{300^\circ} 3UF_4\cdot HF \xrightarrow{380^\circ} UF_4$$

$$(NH_3OH)UF_6 + NOUF_6 \xrightarrow{110^\circ} (NH_3OH)UF_5 + NOUF_6 \xrightarrow{170^\circ} \text{unknown} \xrightarrow{350^\circ} UF_4$$

Hydrazinium(+2) fluoride solubility in hydrogen fluoride at 0° was found to be 15 g of $N_2H_6F_2$/100 g of HF. $N_2H_6^{2+}$ is the only important cationic species in such solutions.

Introduction

The complex fluorides of uranium(V) have been the subject of research in several laboratories in the past few years. Such compounds were prepared by allowing uranium pentafluoride to react with ammonium and alkali fluorides at elevated temperatures under anhydrous conditions.[4] The silver and thallium complexes were prepared in the same way.[5] Uranium pentafluoride also reacts with soluble binary fluorides in hydrogen fluoride at room temperature forming complex fluorouranates (V).[6]

Fluorination of a complex fluorouranate(IV) with elemental fluorine at carefully controlled temperatures[7] and fluorination of uranium tetrafluoride in the presence of alkali fluorides in hydrogen fluoride at room temperature[8] have been reported as alternate approaches to these compounds. Reduction of uranium hexafluoride is, however, a logical counterpart of oxidation methods. Under certain conditions uranium hexafluoride is reduced by ammonia to give ammonium hexafluorouranate(V)[9] and by nitrogen monoxide[10] or nitrosyl chloride[10] to give nitrosyl hexafluorouranate(V).

It was shown also that hyrazinium(+2) fluoride can be used to reduce uranium hexafluoride at 0° in hydrogen fluoride or carbon tetrachloride to give hydrazinium(+2) heptafluorouranate(V).[11] This study has been continued in this laboratory and hydroxylammonium fluoride has been introduced as another reducing and complex-forming agent.

The properties of the reacting solutions were studied previously. It was shown[12] that uranium hexafluoride

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Paper presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

(3) On leave from the Nuclear Institute, "Jozef Stefan," Ljubljana, Yugoslavia.

(4) R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *Inorg. Chem.*, **3**, 126 (1964).

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does not ionize appreciably in anhydrous hydrogen fluoride and that the only important cationic species in hydroxylammonium fluoride solutions in the same solvent is the NH_3OH^+ ion. In this work, the Raman studies of hydrazinium(+2) fluoride solutions in hydrogen fluoride are described and its solubility is reported.

The reactions between hydrazinium(+2) and hydroxylammonium fluorides with uranium hexafluoride in hydrogen fluoride were investigated under various conditions and the reaction products were characterized.

Experimental Section

Materials.—Oak Ridge National Laboratory tank quality uranium hexafluoride was additionally purified by repeated removal of the volatiles at $-78°$.[13] Low-conductivity anhydrous hydrogen fluoride (10^{-5}–10^{-6} ohm^{-1} cm^{-1} at 0°) was prepared by fractional distillation as described elsewhere.[14]

Hydrazinium(+2) fluoride was prepared by neutralization of hydrofluoric acid with hydrazine hydrate.[15] Hydroxylammonium fluoride was prepared *in situ* by solvolysis of the chloride salt in hydrogen fluoride. Details of the preparation and properties of this compound will be described elsewhere.[16]

Apparatus and Methods.—Reactions were carried out in 30-ml reaction tubes fabricated from 0.75-in. o.d. Kel-F (polychlorotrifluoroethylene from Minnesota Mining and Manufacturing Co.) extruded tubing. The tubes were hot pinched together at one end and at the other end flare connected to the adaptor equipped with an all-Kel-F valve.[17] The tubes were connected *via* 0.25-in. o.d. Kel-F tubing and fittings designed to provide an all-plastic system in contact with the reagents. The assembly of several tubes was connected to a nickel vacuum manifold.

In a typical preparation, the hexafluoride solution in hydrogen fluoride was distilled onto solid reducing fluoride (*e.g.*, $N_2H_6F_2$) and the two were mixed at the lowest possible temperature. Several times during the experiment, the mixture was frozen down in liquid nitrogen, the evolved gas was expanded into a calibrated vacuum manifold, and the pressure was measured. The unknown volume in the reaction tube over a frozen mixture was calibrated separately by measuring the pressure after a second expansion of the reaction gases into the calibrated reevacuated manifold.

After several days, all volatile compounds were removed. The solids remaining were thoroughly dried under vacuum to constant weight. The reaction products were in general very sensitive to the moist air and were handled in a drybox.

The course of the reaction was followed by gas evolution. In addition to that, an extensive weight control of reactants and reaction products was carried out. It was found that an accurate material balance can sometimes be of great help, especially when other determinations are for some reason confusing.

Raman spectra of the concentrated solutions were obtained using a 7-ml sapphire cell[12] with a Cary Model 81 Raman spectrometer. For the more dilute solutions a 70-ml Kel-F cell was used. The cell is fabricated from the thin-walled 0.75-in. Kel-F tubing and fitted with a sapphire end window. The other end is equipped with an all-Kel-F valve. Both cell materials give rise to some Raman bands which have to be taken into account in the evaluation of the spectra.

Nujol mulls were prepared in a drybox and infrared spectra of the compounds were run using silver chloride windows with a Beckman IR-12 spectrometer. For near-infrared spectra sapphire windows were used with the Cary Model 14 spectrometer.

Magnetic susceptibility measurements were performed using Faraday's method. The samples were packed into thin-walled screw-capped Kel-F containers (4.8-mm o.d., 18-mm height). The apparatus and the measuring technique used has been described by Gruen.[18]

X-Ray powder diffraction patterns were photographed using a Phillips 114.56-mm diameter camera and Cu Kα radiation. The line intensities were estimated visually.

For the solubility determination of solids in anhydrous hydrogen fluoride an all-Kel-F filtering device was constructed. A porous Kel-F disk hot pressed in the Kel-F tube separates two demountable compartments. A solid was placed in the first one, the device, turned upside down, was evacuated, and a proper amount of hydrogen fluoride was distilled in. The mixture was equilibrated at the desired temperature and the saturated solution was filtered by turning the device into the normal position and pressurizing the upper compartment with an inert gas if necessary. The filtrate was collected into a preweighed tube, the connecting tube evacuated, and the solution weighed. Hydrogen fluoride was then distilled off and the weight of the solid material was determined. The composition of the solid residue was checked by chemical analysis.

The Mettler Recording Vacuum Thermoanalyzer was used for the thermal decomposition studies. Conditions of a typical run were as follows: sample weight, ~100 mg; reference, 100 mg of 60 mesh Al_2O_3; high-temperature furnace, heating rate 2°/min; macro dta–tga stick with alumina cups; argon atmosphere with a 6 l./hr flow rate.

In the isothermal decomposition studies, the sample was heated up to a particular temperature with the heating rate of 2°/min and kept at that temperature until a constant weight was observed. The weight losses as measured were corrected for buoyancy by subtracting the weight of the empty container at the particular temperatures obtained in a calibration run.

Infrared spectra of these solid intermediate products were run. It should be mentioned here that no X-ray diffraction patterns could be obtained from these samples.

Results

From three determinations it was found that 15.00 ± 0.16 g of $N_2H_6F_2$ dissolves in 100 g of hydrogen fluoride at 0°. The composition of the solute obtained after prolonged drying under vacuum at room temperature was checked by chemical analysis and found to be $N_2H_4 \cdot nHF$ where $n = 3.3$–3.7. This is in agreement with Bock's observation.[19]

The Raman spectra of hydrazinium(+2) fluoride in hydrogen fluoride and of the equivalent chloride salt in acidified water solution are compared in Table I. Two bands at 968 and 1110 cm^{-1} are observed in the Raman spectrum of hydrazinium(+2) chloride in dilute hydrochloric acid and attributed to the $N_2H_5^+$ ion by Edsall.[20] The band observed at 1036 cm^{-1} is attributed to the $N_2H_6^{2+}$ ion and the intensities of this band compared with those at 968 and 1110 cm^{-1} show that both the $N_2H_5^+$ and $N_2H_6^{2+}$ ions are present in significant amounts, although the $N_2H_6^{2+}$ ion predominates in strongly acid aqueous solutions. $N_2H_6^{2+}$ is known to be a strong acid; the dissociation constant $k = (H^+)(N_2H_5^+)/(N_2H_6^{2+})$ as estimated by Schwarzenbach[21] is about 7.6.

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[20] J. T. Edsall, *J. Chem. Phys.*, **5**, 225 (1937).

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TABLE I

RAMAN BANDS, $\Delta\nu$ (CM^{-1}), OF HYDRAZINIUM(+2) FLUORIDE IN ANHYDROUS HYDROGEN FLUORIDE COMPARED WITH THE BANDS FOUND FOR HYDRAZINIUM CHLORIDES IN AQUEOUS HYDROCHLORIC ACID[a]

$N_2H_6Cl_2$[20] and N_2H_5Cl	$N_2H_6F_2$	Assignment[20]
968 m, b	. . .	$N^+–N$
1036 vs, sh	1048 vvs, sh	$N^+–N^+$
1110 w, vb	. . .	$-NH_2$ def

[a] Solution concentrations: 22% $N_2H_6Cl_2$ in 1 *N* HCl; 2.1 *m* $N_2H_6F_2$ solution in anhydrous HF. Intensities: vs, very strong; m, medium; w, weak. Shape: sh, sharp; b, broad; vb, very broad.

In a strongly acidic solvent, such as hydrogen fluoride, complete protonation of hydrazine to $N_2H_6^{2+}$ is, however, to be expected. Indeed, no $N_2H_5^+$ ions were detected in a hydrogen fluoride solution of hydrazinium(+2) fluoride. Only a single Raman band at 1048 cm^{-1} is observed, representing a small shift of the $N^+–N^+$ stretching frequency toward higher frequencies in hydrogen fluoride as compared with this band in aqueous acid.

In Table II, the results of several reductions of uranium hexafluoride with hydrazinium(+2) fluoride in hydrogen fluoride are summarized. Different reaction products were obtained depending on the reaction conditions. Any gas evolved during the reaction was shown by a mass spectrometric analysis to be rather pure nitrogen (N_2).

TABLE II

THE CONDITIONS AND THE PRODUCTS OF THE REACTION $N_2H_6F_2$–UF_6 IN HYDROGEN FLUORIDE

Starting mole ratio $N_2H_6F_2$:UF_6:HF; reaction conditions	Material balance: Product wt/mmole of $N_2H_6F_2$(g)	Material balance: Gas evolution: Moles of N_2/mole of $N_2H_6F_2$	Material balance: Gas evolution: Moles of N_2/mole of UF_6	Compn of product[a]
1.00:4.16:228; 0° 16 hr	0.328			$N_2H_6UF_7$
1.00:1.66:56; 0° 6 days	0.341			$N_2H_6UF_7$
Extensive unknown excess of UF_6; 25° 6 days	0.524	0.370		$N_2H_6(UF_6)_2$
1.00:1.32:74; 25° 12 days	0.462	0.338	0.255	$N_2H_6(UF_6)_2$ mainly $N_2H_6UF_7$ some
1.00:0.66:66; 25°	0.284	0.172	0.258	$N_2H_6UF_7$ $N_2H_6F_2 \cdot x$HF
1.00:0.66:*n* (calcd for $N_2H_6UF_6$)	0.286	0.333	0.500	
1.00:0.80:*n* (calcd for $N_2H_6UF_7$)	0.324	0.200	0.250	
1.00:1.33:*n* (calcd for $N_2H_6(UF_6)_2$	0.492	0.333	0.250	

[a] On the basis of observations other than chemical analysis.

A new compound hydrazinium(+2) bishexafluorouranate(V) was isolated as a greenish blue material when reaction was carried out at room temperature and with a large excess of uranium hexafluoride over the stoichiometric ratio. *Anal.* Calcd for $N_2H_6(UF_6)_2$: N_2H_4, 4.34; U, 64.50; F, 30.89. Found: N_2H_4, 4.38; U, 63.56; F, 28.2.

If the reaction is carried out at 0° and the other conditions remain unchanged, the reaction product is yellow hydrazinium(+2) heptafluorouranate(V). In the presence of a large excess of hydrazinium(+2) fluoride only the formation of hydrazinium(+2) heptafluorouranate(V) was observed. Thus, we did not observe the reported[11] reduction of hexafluoride to the hydrazinium(+2) hexafluorouranate(IV) even when the reaction was carried out as suggested at room temperature in little solvent with excess of hydrazinium(+2) fluoride present.

At the hydrolysis of hydrazinium(+2) bishexafluorouranate(V) a green precipitate, probably $N_2H_5UF_5$,[22] and a yellow solution (UO_2^{2+}) are formed. Such behavior is characteristic of uranium(V) compounds.

The reaction of hydroxylammonium fluoride with a large excess of uranium hexafluoride in hydrogen fluoride at room temperature yields a blue, crystalline material, reasonably soluble in the solvent. No gas evolution was observed. The weight relations suggest 1:1 stoichiometry for the reaction. *Anal.* Calcd for $(NH_3OH)UF_6$: NH_2OH, 8.55; U, 61.66; F, 29.53. Found: NH_2OH, 9.78; U, 61.96; F, 29.41.

Hydrolysis of this material is characteristic for uranium(V) compounds yielding a yellow solution (UO_2^{2+}) and a green precipitate, probably $(NH_3OH)UF_5$.[22] Nitrogen oxides are evolved in the hydrolysis.

Powder diffraction data were obtained for the hydrazinium(+2) and hydroxylammonium hexafluorouranates.[23] The patterns are very complicated and indexing of them was not attempted. The lines of nitrosyl hexafluorouranate(V) are fully represented in the powder pattern of the uranium hexafluoride–hydroxylammonium fluoride reaction product.[24] The many lines not belonging to the nitrosyl compound could readily be attributed to that of an hydroxylammonium complex. Regarding the number and positions of the lines, it is quite obvious that the symmetry of both hydrazinium(+2) and hydroxylammonium hexafluorouranates(V) is low. It should be mentioned here that crystals lose their habits when the last traces of the solvent are removed. Therefore, single-crystal studies were not attempted on these materials.

In Table III infrared absorption frequencies of the

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(22) Yu. A. Lukyanichev, N. S. Nikolaev, and Yu. N. Mihailov, *Zh. Neorgan. Khim.*, **8**, 1617 (1963).

(23) A table summarizing the diffraction data is available from the Chemistry Division, Argonne National Laboratory, Argonne, Ill. 60439

(24) F. J. Musil, P. R. Ogle, and K. E. Beu, GAT-T-553 or ASTM X-ray Powder Data File, Card 11-246.

TABLE III

INFRARED ABSORPTION SPECTRA OF SOME FLUOROURANATES(V)

$N_2H_6UF_7$		$N_2H_6(UF_6)_2$		$(NH_3OH)UF_6$	
ν, cm^{-1} Intens	Tentative assignment	ν, cm^{-1} Intens	Tentative assignment	ν, cm^{-1} Intens	Tentative assignment
435 vvs, vb	U–F str				
		526 vs, vb	U–F str	526 vs, vb	U–F str
590 w					
800 w		890 vw		895 vw	
		945 vw, br	U–O	950 w, b	U–O
		970 m, b	N–N str		
1050 shoulder				1016 vs, vsh	N–O str
1098 vs, vsh	NH_3^+ rock				
		1123 vs, sh	NH_3^+ rock		
1155 vs, sh				1168 vs, vsh	NH_3^+ rock
1285 m				1195 s,	O–H bend
1540 m	H–N–H def	1530 s, sh	H–N–H def	1495 s	NH_3^+ sym def
1580 m		1580 s		1529 s	NH_3^+ deg ds
				1580 s	
1620 shoulder		1608 shoulder		1600 shoulder	
		1940 vw, vb			
1990 w, vb					
				2335 m, vsh	NO^+
		2415 w, sh			
		2700 m, sh		2720 w	NH_3^+ comb.
3000 vb,	N–H str				
3100 shoulder		3100 b,	N–H str		
		3150 shoulder		3220 m, b	N–H str
				3300 sh	O–H str

reaction products are listed and their tentative assignments are given. U–O vibrations observed are due to small uranyl fluoride impurities formed during the sample handling. The samples of hydroxylammonium hexafluorouranate(V) definitely show also the NO^+ characteristic sharp absorption peak at 2335 cm^{-1}.

Both newly isolated materials show absorptions characteristic of uranium(V) in the region 1.0–1.6 μ (Figure 1). The difference in absorption spectra of both hydrazinium complexes makes these spectra very convenient for rapid identification of mixtures and pure compounds throughout the preparative work.

In Table IV, Raman spectra of the hydrogen fluoride solutions of different fluorouranates(V) are listed. Cesium hexafluorouranate(V) was prepared following Asprey and Penneman,[8] by fluorination of cesium fluoride–uranium tetrafluoride mixtures in hydrogen fluoride with elemental fluorine at room temperature. It should be mentioned here that such a preparation yields, besides the desired product, some higher cesium fluorouranates(V) (Cs_2UF_7) as shown by the near-infrared spectrum of the product mixture.

The molar magnetic susceptibilities for hydrazinium(+2) and hydroxylammonium hexafluorouranates(V) measured at different temperatures are listed in Table V. Corrections for diamagnetism were made using the magnetic susceptibility of uranium hexafluoride[25] as the most feasible correction for the diamagnetic core of UF_6^- ion, the measured value for the $N_2H_6^{2+}$ ion,[26] and the estimated value -13.10^{-6} cgs unit for the mixture $3NH_3OH^+ + NO^+$. Because of the relatively strong paramagnetism of the measured compounds, these corrections are not very significant.

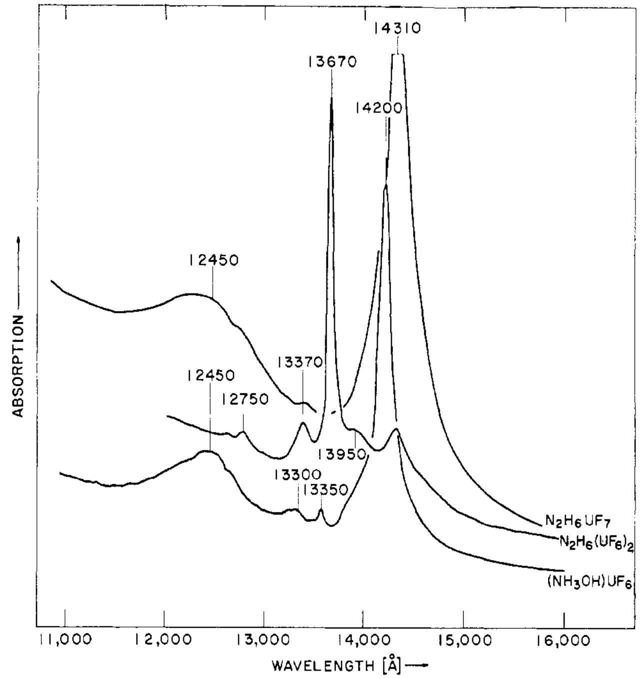

Figure 1.—Near-infrared absorption spectra of some fluorouranates(V).

The magnetic susceptibility of the hydrazinium(+2) complex follows the Curie–Weiss law from room temperature to 80°K. The Weiss constant θ obtained by the extrapolation of the linear portion of the curve χ^{-1} *vs.* T to zero reciprocal susceptibility is for this compound at 77°K. The corresponding effective magnetic moment calculated from the slope of the same curve ($\mu = 2.828[d(1/\chi)/dT]^{-1/2}$) is 1.61 BM. Below 80°K the susceptibility increases very rapidly.

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[25] V. P. Henkel and W. Klemm, *Z. Anorg. Allgem. Chem.*, **222**, 70 (1935).

[26] B. Frlec, unpublished observation.

TABLE IV

RAMAN BANDS, $\Delta\nu$ (CM^{-1}), OF SOME FLUOROURANATES(V) IN HYDROGEN FLUORIDE[a]

$N_2H_6UF_7$	$(NH_3OH)UF_6$	$CsUF_6$	Assignment
628	628	628	ν_1 UF_6^-
	1015		N–O str
1049			N–N str

[a] Solution concentrations: $N_2H_6UF_7$, 0.14 *m* in a Kel-F cell; $(NH_3OH)UF_6$, 0.64 *m* in a sapphire cell; $CsUF_6$, 0.81 *m* in a sapphire cell.

TABLE V

MOLAR MAGNETIC SUSCEPTIBILITIES OF HYDRAZINIUM(+2) AND HYDROXYLAMMONIUM FLUOROURANATES(V)

Temp, °K	$10^6\chi^M{}_{N_2H_6(UF_6)_2}$, cgs unit mole^{-1}	$10^6\chi^M{}_{(NH_3OH)UF_6}$, cgs unit mole^{-1}
4.2	3013.6	674
63.2	248.9	177.9
77.2	219.5	
145	141.1	118
195	128.2	111
243.4	109.8	105.9
298	96.8	99.8

The magnetic behavior of hydroxylammonium hexafluorouranate(V) is, on the other hand, quite different. Its susceptibility does not follow the Curie–Weiss law. However, the effective magnetic moment at 300° calculated using the expression $\mu_{\text{eff}} = 2.828(\chi_M'T)^{1/2}$ is 1.52 BM.

The thermal decomposition of hydrazinium(+2) bishexafluorouranate(V) (Figure 2) starts in an argon atmosphere at 60° and proceeds in several decomposition steps which overlap each other until uranium tetrafluoride is formed at 380°. Three dta peaks were observed when a heating rate of 2°/min was used: an exothermic peak at 120°, an exothermic peak at 235°, and an endothermic peak at 350°. The first decomposition step involves an internal oxidation–reduction of the compound to yield a uranium(IV) complex as shown by a remarkable shift of the U–F stretching absorption frequency in the infrared spectrum of the intermediate product (415 cm^{-1} *vs.* 526 cm^{-1} in the starting material).

The thermal decomposition of the reaction product from the uranium hexafluoride–hydroxylammonium fluoride reaction starts in argon also at 60° (Figure 3). An exothermic dta peak at 111° is associated with the first decomposition step which ends at approximately 134° with a weight loss of about 10%. The infrared spectrum and X-ray powder diffraction pattern of the intermediate product obtained at the isothermal decomposition at 105° clearly indicate the presence of nitrosyl hexafluorouranate(V) and hydroxylammonium pentafluorouranate(IV). Further decomposition occurs immediately after that and ends at 220° with a weight loss of 17%. An endothermic dta peak at 175° accompanies this decomposition step. The material found in this intermediate stage is stable in the temperature region 240–300°. Its infrared spectrum reveals a complete reduction to a uranium(IV) compound and the presence of the NO$^+$ ionic species. However, the characteristic sharp absorption band at 2330 cm^{-1} observed in nitrosyl hexafluorouranate(V) is shifted in this case to 2230 cm^{-1}.

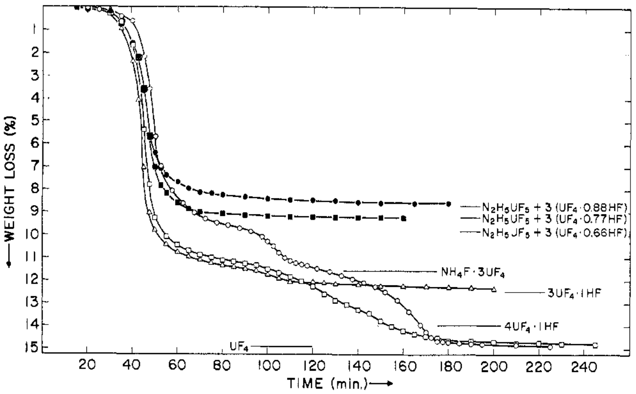

Figure 2.—Thermal decomposition of hydrazinium(+2) bishexafluorouranate(V) in argon (6 l./hr). Isothermal runs: ●, 110°; ■, 150°; △, 230°; □, 320°. Dynamic run: 2°/min heating rate.

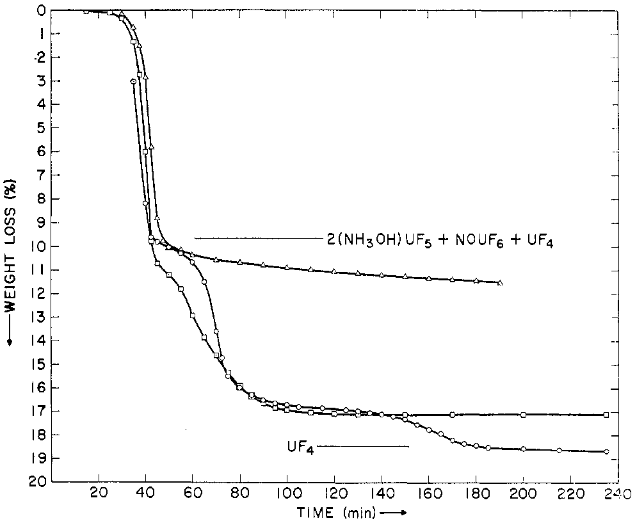

Figure 3.—Thermal decomposition of the hydroxylammonium fluoride–uranium hexafluoride reaction product in argon (6 l./hr). Isothermal runs: △, 105; □, 250°. Dynamic run: 2°/min heating rate.

At 400° uranium tetrafluoride is formed as the final decomposition step. The observed over-all weight loss of 18.45% indicates that the conversion of the starting material into uranium tetrafluoride is quantitative.

Discussion

The reaction of hydrazinium(+2) fluoride with an excess of uranium hexafluoride in hydrogen fluoride at room temperature proceeds according to the equation

$$3N_2H_6F_2 + 4UF_6 = 2N_2H_6(UF_6)_2 + N_2 + 6HF \qquad (1)$$

The greenish blue hydrazinium(+2) bishexafluorouranate(V) is not very soluble in hydrogen fluoride and yields a green solution.

If the reaction is carried out at 0°, a yield of hydrazinium(+2) heptafluorouranate has been reported previously.[11] The same compound is, however, formed also at room temperature if hydrazinium(+2) fluoride is present in an excess over uranium hexafluoride.

Hydroxylammonium fluoride reacts with an excess or uranium hexafluoride in hydrogen fluoride according to the equations

$$4(NH_3OH)F + 3UF_6 = 3(NH_3OH)UF_6 + NO + 4HF \quad (2)$$

$$NO + UF_6 = NOUF_6 \quad (3)$$

or to summarize

$$4(NH_3OH)F + 4UF_6 = 3(NH_3OH)UF_6 + NOUF_6 + 4HF \quad (4)$$

The mixture of hydroxylammonium and nitrosyl hexafluorouranates(V) is therefore formed. It is evident that the weight of the reaction products is very close to the weight of the pure hydroxylammonium complex $(NH_3OH)UF_6$ because of the very similar molecular weights (386 for $(NH_3OH)UF_6$ *vs.* 382 for $NOUF_6$). The chemical analysis is also not very helpful in this case because of the reducing properties of both compounds. The near-infrared spectra of the two reaction products are characteristic of only the UF_6^- portion present in both molecules. The X-ray powder pattern and infrared spectrum of the solid, however, clearly point out the presence of nitrosyl hexafluorouranate(V).

The shape and the positions of the absorptions in the near-infrared region for hydrazinium(+2) bishexafluorouranate(V) resemble the spectra of lithium, sodium, and cesium hexafluorouranates(V).[4] The same similarity exists also between spectra of hydrazinium(+2) heptafluorouranate(V), hydroxylammonium hexafluorouranate(V), and potassium, ammonium, and rubidium hexafluorouranates(V).[4] The uranium(V) species must be therefore in a similar environment in these compounds. However, on comparing X-ray powder patterns such a resemblance cannot be established.

The very strong infrared absorption band in the metal–fluorine stretching region at 526 cm^{-1} observed with both of the isolated hexafluorouranates(V) may be attributed to the ν_3 frequency of a UF_6^- species. The observed frequency, however, does not agree with a previously reported value (550 cm^{-1} in $NOUF_6$)[10] which might be due to difference in the nature of the cations or to different structures. The presence of only one symmetrical peak in this region suggests an octahedral structure for the UF_6^- ion. On the other hand, the two absorptions observed with hydrazinium(+2) heptafluorouranate(V) indicate lower symmetry in the coordination sphere, not unreasonable for a UF_7^{2-} species in the solid. The existence of such an ionic species was recently confirmed by a synthesis of the corresponding barium compound.[27]

The measured magnetic properties of both compounds confirm the presence of pentavalent uranium. The effective magnetic moment for the hydrazinium(+2) complex is very close to the spin-only value for one single electron (1.73 BM) thus indicating that the orbital contribution to the magnetic moment is quenched to a significant extent but not completely in this material.

The strong band observed in Raman spectra of different fluorouranates(V) in hydrogen fluoride can be attributed to the symmetrical uranium–fluorine stretching mode of the UF_6^- species with ν_1 628 cm^{-1}. It is interesting that the same Raman band was observed also with the solution of hydrazinium(+2) heptafluorouranate(V). We believe, therefore, that this compound dissolved in hydrogen fluoride according to the equation

$$2N_2H_6UF_7 \xrightarrow{HF} N_2H_6(UF_6)_2 + N_2H_6F_2 \cdot nHF \quad (5)$$

It was observed that only hydrazinium(+2) bishexafluorouranate(V) and hydrazinium(+2) fluoride solvate can be isolated from the hydrogen fluoride solutions of pure hydrazinium(+2) heptafluorouranate(V). Evidently UF_7^{2-} ions as a less symmetrical species are unstable in hydrogen fluoride and undergo conversion to UF_6^-. They are apparently stable only in a solid material; however, attempts to obtain a Raman spectrum of a solid hydrazinium(+2) heptafluorouranate(V) have so far been unsuccessful.

The thermal decomposition of hydrazinium(+2) bishexafluorouranate after the internal reduction–oxidation in the first step should be very similar to the decomposition of hydrazinium(+1) pentafluorouranate(IV) which was discussed elsewhere.[28]

We believe that the internal oxidation–reduction occurs in this material according to the equation

$$2N_2H_6(UF_6)_2 = N_2H_5UF_5 + 3(UF_4 \cdot nHF) + N_2 + (7 - 3n)HF \quad (6)$$

where $1 > n > 0$. The weight losses accompanying such a decomposition may vary from 7.32% for $n = 1$ to 11.39% for $n = 0$. The two weight losses observed with the isothermic decompositions at 110 and 150° indicate that the composition of the intermediate product depends upon temperature. The infrared spectra of the two solids show identical absorption bands. The exothermic dta peak observed in the dynamic run at 120° is most probably associated with the internal reduction–oxidation of the material.

Hydrazinium(+1) pentafluorouranate(IV) decomposes above 200° yielding an ammonium fluoride–uranium tetrafluoride adduct. This decomposition involves the thermal dissociation of gaseous hydrazine on the surface of the uranium tetrafluoride into ammonia and nitrogen. Ammonia reacts in turn with uranium tetrafluoride–hydrogen fluoride adducts forming an ammonium fluoride–uranium tetrafluoride complex of the composition which is stable in this temperature region. The summary equation for this process is

$$3N_2H_5UF_5 + 9(UF_4 \cdot nHF) = 4(NH_4F \cdot 3UF_4) + N_2 + 9nHF \quad (7)$$

The weight loss accompanying the over-all decomposition

$$6N_2H_6(UF_6)_2 = 4(NH_4F \cdot 3UF_4) + 4N_2 + 20HF \quad (8)$$

is 11.56%. The exothermic dta peak observed at 235° is probably connected with the reaction shown in eq 7. The further decomposition proceeds obviously through

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(27) L. B. Asprey and R. A. Penneman, personal communication.

(28) B. Frlec and H. H. Hyman, *J. Inorg. Nucl. Chem.*, in press.

$3UF_4 \cdot HF$ with an over-all weight loss of 12.47% to uranium tetrafluoride

$$NH_4F \cdot 3UF_4 = 3UF_4 \cdot HF + NH_3 \qquad (9)$$

and

$$3UF_4 \cdot HF = 3UF_4 + HF \qquad (10)$$

The total weight loss for the thermal decomposition of hydrazinium(+2) bishexafluorouranate(V) to uranium tetrafluoride is 14.90%. The decomposition of $3UF_4 \cdot HF$ adduct is most probably associated with the endothermic dta peak at 350°.

The thermal decomposition of the hydroxylammonium and nitrosyl hexafluorouranates(V) is rather complicated. It has been reported[10] that nitrosyl hexafluorouranate(V) gradually decomposes above 200° with melting occurring at approximately 350°. The first decomposition step we observe appears to involve a reduction of the hydroxylammonium compound while the nitrosyl complex remains unchanged. This internal oxidation–reduction probably occurs according to the equation

$$3(NH_3OH)UF_6 + NOUF_6 = 2(NH_3OH)UF_5 + NOUF_6 + UF_4 + NO + 4HF \qquad (11)$$

The corresponding weight loss 9.65% was also observed. The slow weight loss of the intermediate product with time observed at the isothermal decomposition at 105° is most probably due to the slow decomposition of the hydroxylammonium pentafluorouranate(IV) which is known to occur at this temperature.

The nature of the next decomposition step remains uncertain. The shift of the NO^+ infrared absorption band toward lower frequencies mentioned above indicates that the formal charge on the ion was decreased. The reduction of nitrosyl hexafluorouranate(V) to a uranium(IV) compound might be caused by a secondary reaction product from the hydroxylammonium pentafluorouranate(IV) decomposition. It is also obvious from the relatively small weight loss in the last decomposition step that the product obtained at 250° contains very little thermally degradable material in addition to the bulk of uranium tetrafluoride.

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A Study of Dimolybdate and Dichromate Formation in Fused Equimolar Sodium Nitrate–Potassium Nitrate Solvent

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An electrochemical study of dimolybdate and dichromate formation from the orthooxy anions in an equimolar sodium nitrate–potassium nitrate solvent is reported. Selected values of the equilibrium constant for the reaction $2MO_4^{2-} = M_2O_7^{2-} + O^{2-}$, when M = Mo, at several temperatures are: 533°K, 2.5×10^{-8}; 583°K, 8.5×10^{-8}; 617°K, 2.1×10^{-7}. For M = Cr, selected equilibrium constants are: 544°K, 1.2×10^{-8}; 587°K, 2.4×10^{-8}; 615°K, 3.3×10^{-8}. The values of $\Delta H°$ for this reaction when M is Mo and Cr are, respectively, 17 and 10 kcal. The values of $\Delta S°$ for this reaction when M is Mo and Cr are, respectively, −4 and −17 eu. An explanation for the large difference in $\Delta S°$ is proposed which involves a mixed coordination number in the dimolybdate polymer.

Introduction

The acidic nature of the group VIb oxides CrO_3, MoO_3, and WO_3 in fused potassium nitrate has been demonstrated.[1] This acidity is easily explained in terms of the Lux–Flood acid–base theory if the polymeric nature of these oxides is considered. Generally, polymeric oxides will tend to be acidic, reacting with basic solvents and oxide ion and depolymerizing to smaller units, the ortho anion, MO_4^{2-}, representing the limit in the case of the group VIb oxides. The first step in the reverse process, the dimerization of the ortho anion, is illustrated by the occurrence of dichromate, and the formation of ditungstate, $W_2O_7^{2-}$, from orthotungstate has recently been shown.[2] Compared with orthochromate, orthotungstate is quite basic, the formation of ditungstate with the concurrent release of an oxide ion occurring rather readily. It becomes of interest, then, to know how orthomolybdate behaves in the same type of reaction. Also, the weak basic properties of orthochromate have been inferred from studies of rates of reaction of the acidic dichromate

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