

CONTRIBUTION FROM THE NUCLEAR
INSTITUTE "JOŽEF STEFAN," LJUBLJANA, YUGOSLAVIA**Hydrazinium Heptafluorouranate(V). Preparation, Properties, and Thermal Decomposition^{1a}**By B. FRLEC,^{1b} B. S. BRČIĆ, AND J. SLIVNIK

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The new compound, hydrazinium heptafluorouranate(V), was prepared at 0° by the reaction of hydrazinium difluoride and uranium hexafluoride both in anhydrous hydrogen fluoride and in carbon tetrachloride. The magnetic moment of the yellowish compound at 0° is 1.66 BM. X-Ray powder diffraction data are given. The thermal decomposition of the compound in an inert atmosphere proceeds as follows:
$$\begin{array}{c} \text{N}_2\text{H}_5\text{UF}_7 \xrightarrow{70^\circ} \text{N}_2\text{H}_5\text{UF}_6 + \text{UF}_4 \xrightarrow{180-200^\circ} \text{N}_2\text{H}_5\text{UF}_6 + \text{UF}_4 \xrightarrow{310^\circ} 3\text{UF}_4\text{HF} \\ \xrightarrow{380^\circ} \text{UF}_4 \end{array}$$
 A detailed discussion of this thermal decomposition is given.

Introduction

Little is known about hydrazinium fluorouranates. Only a few compounds have been reported: hydrazinium (+1) pentafluorouranate(IV)² and hydrazine uranyl fluoride complexes of different compositions.³ Analogous to the ammonium fluorouranates, several hydrazine complex compounds resembling the ammonia derivatives could be expected. Since hydrazine is a powerful reducing agent and is less alkaline than ammonia, a reduction of uranium(VI) to lower valence states during the reaction could occur. However, the existence of two stable nitrates of hydrazine⁴ makes it plausible that, under favorable conditions, reduction of uranium(VI) to uranium(IV) in the presence of hydrazine salt will not take place. On the other hand, the thermal decomposition of hydrazinium uranates with uranium(VI) or -(V) should be of special interest because of the presence of a reducing agent in the compound itself. Uranium tetrafluoride should be expected as the final product.

The reactions of anhydrous hydrazine with uranium hexafluoride at 70° in the vapor phase⁵ and the sorption of uranium hexafluoride vapor on solid hydrazinium difluoride resulting in products containing quadrivalent uranium led to the effort to work at a lower temperature and concentration in a neutral solvent. However, the possible solvent choices are rather limited. Considering the presence of the hydrazinium salt, only anhydrous hydrogen fluoride, completely fluorinated hydrocarbons, and halogenated hydrocarbons are suitable for dissolving uranium hexafluoride without reaction.^{6,7} It is well known that the reaction mecha-

nism can be influenced by the solvent used as the reaction medium. Therefore, two substantially different solvents were chosen: anhydrous hydrogen fluoride and carbon tetrachloride. However, from a preparative standpoint, the relatively low solubilities of the reactants present severe limitations. Anhydrous hydrogen fluoride dissolves 7.95 g of UF₆⁷ and approximately 5 g of N₂H₅F₂ per 100 g of HF⁸ at 0°. In carbon tetrachloride, uranium hexafluoride is more soluble (38 g/100 g of CCl₄ at 0°⁹), but hydrazinium difluoride is practically insoluble and floats on the surface of the solvent.

Experimental Section

Materials and Methods.—Hydrazinium difluoride was prepared by neutralization of hydrofluoric acid with hydrazine hydrate.¹⁰ Uranium hexafluoride was prepared by fluorination of U₃O₈ with elemental fluorine¹¹ and purified by repeated sublimation under vacuum. Anhydrous hydrogen fluoride was prepared by pretreating the distilled technical product with uranium hexafluoride as described later. Carbon tetrachloride was dried over calcium chloride. The dried solvent was distilled over phosphorus pentoxide¹² and purified by subsequent distillation in a glass vacuum line.

Fluorine content in samples was determined by a modified Willard–Winter distillation¹³ and thorium nitrate titration of the distillate.¹⁴ In the distillation residue, uranium was determined volumetrically using potassium dichromate,¹⁴ and hydrazine was determined potentiometrically by potassium iodide titration.¹⁵ X-Ray powder diffraction patterns were obtained using Cu Kα or Fe Kα radiation in a 57-mm diameter camera. The intensities of lines were estimated visually.

Magnetic susceptibility measurements were performed using Gouy's technique with an accuracy of ±6%. The apparatus used was similar to one described by Volavšek.¹⁶ Thermogravimetric analysis was performed on a quartz helix balance in argon atmosphere at a heating rate 2.5°/min. The same heating rate was used for the differential thermal analysis, which

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was carried out on a "Gebrüder Netzsch" type of apparatus with the Linseis measuring heads in a stream of argon. The reproducibility of transition temperatures was $\pm 3^\circ$.

Procedures.—In the preparation procedures to be described the solvent (hydrogen fluoride or carbon tetrachloride) first was treated with uranium hexafluoride, then the reaction products were removed, and finally the mixture of solvent and uranium hexafluoride was transferred to a reactor containing dry hydrazinium difluoride.

The reactions were carried out in Fluorothene¹⁷ tubes sealed at one end and attached at the other end through flare connection to an all-stainless-steel valve. The volume of the reaction vessels was limited (30 ml) by the diameter of the available Fluorothene tubing. Because of this and the relatively low solubilities of the reactants, it was necessary to work with a saturated solution with some undissolved material at the bottom in order to get enough product for all necessary examinations.

(A) **Preparation in Anhydrous Hydrogen Fluoride.**—Uranium hexafluoride was sublimed onto the hydrogen fluoride in one of the reaction vessels, and the mixture was then condensed on hydrazinium difluoride in a second, dry reaction tube attached to the first one and to a glass vacuum system by a tee. The reaction was carried out at 0° in a water-ice bath. To avoid pressure build-up, the gas evolved was expanded from time to time into the glass part of the vacuum system, and the reaction mixture was shaken several times. After 6–10 hr unreacted uranium hexafluoride and hydrogen fluoride were pumped off, and a yellowish reaction product was dried under vacuum. The reaction tube was filled with dried argon, and the product was poured into small glass apparatus in a stream of argon. The sample tube for magnetic measurements, capillary for X-ray examination, and bulbs for chemical analysis were filled and sealed under vacuum.

(B) **Preparation in Carbon Tetrachloride.**—Dried carbon tetrachloride was poured on the phosphorus pentoxide in the first bulb of the two-bulb glass apparatus connected to the reaction tube and to the glass part of the vacuum system. The first vessel was sealed. After several hours the contents of the vessel were frozen with liquid nitrogen and the apparatus was evacuated to approximately 10^{-3} torr. A part of the carbon tetrachloride was distilled into the second vessel, and the first one was sealed off. Carbon tetrachloride was then distilled to the reaction tube cooled by liquid nitrogen, and the proper amount of uranium hexafluoride was added by sublimation. The vessel was then warmed up to room temperature. At most, 1% of the uranium hexafluoride was reduced; evolved gases were pumped off, and a mixture of uranium hexafluoride and carbon tetrachloride was distilled finally to the other reaction tube with hydrazinium difluoride. Subsequent procedure was analogous to the one described previously.

(C) **Thermal Decomposition of Samples.**—The thermal decompositions of samples placed in copper boats inside a glass tube were carried out in a stream of carefully dried argon. The samples were heated at constant temperature until constant weight was obtained. The boat with the sample was transferred and weighed in an argon atmosphere.

The bulbs for chemical analysis, the tube for magnetic measurements, and the capillary for X-ray investigation were filled and sealed under vacuum. The decomposition tube was heated with an electric furnace made of glass, enabling us to watch the changes in the sample during the heating. Before heating, the apparatus was evacuated and thoroughly swept with dried argon.

Results

The results of the chemical analysis together with mole ratios of the reactants prior to reaction are presented in Table I. The precision of analytical data is given in absolute percentage.

Upon reaction of uranium hexafluoride with hy-

TABLE I
REACTION CONDITIONS AND ANALYSES OF
HYDRAZINIUM HEPTAFLUOROURANATES(V)

Mole ratio, $N_2H_6F_2:UF_6$: solvent, before reaction	Analyses			Mole ratio, $N_2H_4:U:F$, in product	Reaction medium
	% N_2H_4 ± 0.1	% U ± 0.3	% F ± 0.4		
1:5.5:104	7.4	57.7	34.2	0.95:1.00:7.42	HF
1:6.4:104	6.7	59.5	33.6	0.84:1.00:7.07	HF
1:3.4:71	7.8	57.5	32.5	1.01:1.00:7.08	HF
1:3.9:55	7.8	58.5	32.8	0.99:1.00:7.02	HF
1:2.7:10.8	7.6	58.4	32.1	0.97:1.00:6.88	CCl_4
1:1.5:4.2	7.8	59.2	32.4	0.98:1.00:6.85	CCl_4

drazinium difluoride, a yellowish product is formed with a composition corresponding to the stoichiometric formula $N_2H_6UF_7$. The course of the reaction strongly depends on the temperature and on the quantity of the solvent used. At room temperature or higher, and if little solvent is used, the yellow color of the reaction mixture turns to green, indicating reduction of uranium to a four-valent state. This is accompanied by the evolution of a greater quantity of gas as expected and in most cases by rupture of the reaction vessel.

Hydrazinium difluoride is insoluble in and less dense than carbon tetrachloride. However, the reaction product is more dense than the solvent; consequently, the course of the reaction could be observed easily. Particles of the hydrazinium fluoride react on the surface of the solvent, then sink down, and from the material on the bottom of the reaction vessel nitrogen is evolved. After the reaction was finished, all of the volatile components were condensed back into the first reaction vessel. At room temperature two layers were formed: one of carbon tetrachloride and another of hydrogen fluoride, which is obviously a reaction product. The amount of hydrogen fluoride was roughly estimated from the volume. It was found that approximately 1 mole of hydrogen fluoride per mole of hydrazinium difluoride was formed by the reaction.

As follows from Table I, all of the samples listed were prepared with an excess of uranium hexafluoride. Also, a synthesis of compounds with mole ratios of $N_2H_4:U = 2:1$ and $3:1$ in carbon tetrachloride was attempted. In neither case was liberation of hydrogen fluoride observed. Yellowish reaction products, extremely unstable at room temperature in glass, were obtained. Consequently, they could not be characterized.

X-Ray powder diffraction patterns of all samples obtained at 0° were found to be identical, independent of reaction medium or initial mole ratio used. They differ markedly from diffraction patterns of starting materials. The d values and visually estimated intensities of lines of a compound with composition corresponding to the stoichiometric formula $N_2H_6UF_7$ are presented in Table II.

Results of the magnetic susceptibility measurements are presented in Table III. The temperature dependence of the magnetic susceptibility follows the Curie-Weiss law over the temperature interval 160 – $280^\circ K$.

(17) Hosataflon C2, Farbwerke Hoechst A.G., Frankfurt/Main, Germany.

TABLE II
X-RAY POWDER DIFFRACTION DATA FOR
HYDRAZINIUM HEPTAFLUOROURANATE(V)

<i>d</i> , Å	<i>I</i> _{estd}	<i>d</i> , Å	<i>I</i> _{estd}	<i>d</i> , Å	<i>I</i> _{estd}	<i>d</i> , Å	<i>I</i> _{estd}	<i>d</i> , Å	<i>I</i> _{estd}
9.0	4	2.93	10	1.977	6	1.490	4	1.138	4
6.7	8	2.88	6	1.953	6	1.446	4	1.126	4
6.2	4	2.82	6	1.918	4	1.423	6	1.114	4
5.9	4	2.79	6	1.895	4	1.406	4	1.038	5
4.97	8	2.72	4	1.873	4	1.388	6	1.033	4
4.62	8	2.67	4	1.840	6	1.368	4	1.025	6
4.41	6	2.60	4	1.791	6	1.347	6	1.018	4
3.99	6	2.53	4	1.761	6	1.320	6	1.013	6
3.91	6	2.43	4	1.712	4	1.308	6	1.011	6
3.76	4	2.41	4	1.676	4	1.223	2	1.006	4
3.48	6	2.34	8	1.651	4	1.218	4	1.003	4
3.44	6	2.27	6	1.581	4	1.206	4	0.998	4
3.32	4	2.23	6	1.561	4	1.194	4	0.993	4
3.17	4	2.20	6	1.544	6	1.181	4	0.987	4
3.08	4	2.17	6	1.518	4	1.174	4	0.985	4
3.01	4	2.12	8	1.504	4	1.164	4	0.983	4

TABLE III
MAGNETIC SUSCEPTIBILITY AND MOMENT OF
HYDRAZINIUM HEPTAFLUOROURANATE(V)^a

$10^3 \chi_M'$	θ	μ_{eff}
0.86	104	1.62
0.95	104	1.70
0.89	110	1.66
0.94	122	1.73
0.91	114	1.66

^a $10^3 \chi_M'$ is the molar magnetic susceptibility corrected for diamagnetism in cgs units at 273°K. θ is the Weiss constant in °K. μ_{eff} is the effective magnetic moment in BM.

When exposed to moist air or to reaction with water, the yellow color of the samples turns rapidly to green. In water a green precipitate and a yellow solution were obtained. The analysis of the precipitate is as follows. *Anal.* Calcd for $\text{N}_2\text{H}_5\text{UF}_5$: N_2H_4 , 8.75; U, 65.0; F, 25.9. Found: N_2H_4 , 8.9; U, 64.6; F, 26.3.

In Figure 1 differential thermal analysis diagrams of hydrazinium fluorouranates are shown. Hydrazinium pentafluoro-^{2a} and hexafluorouranate⁵ were taken for comparison. The average values of the dta peak temperatures are collected in Table IV.

TABLE IV
DIFFERENTIAL THERMAL ANALYSES OF
HYDRAZINIUM FLUOROURANATES

Thermal effect	$\text{N}_2\text{H}_5\text{UF}_7$		$\text{N}_2\text{H}_5\text{UF}_6$		$\text{N}_2\text{H}_5\text{UF}_5$	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
Exothermic	70	141				
Endothermic		194				
Exothermic		214	130	200		
Endothermic	247	296	253	310	270	309
Endothermic	350	405	356	412	353	405

^a Average temperature of the beginning of a thermal effect.

^b Average temperature of a peak of a thermal effect.

The temperatures of the last two endothermic effects are nearly identical for all three compounds, and the temperature of the exothermic effect is almost the same for the first two compounds. Therefore, it might be concluded that this part of the decomposition scheme must be the same.

In Figure 2 the thermogravimetric decomposition curves of hydrazinium heptafluorouranate(V) are plotted. Weight losses observed at isothermal decompositions are presented in plot by points I. Several

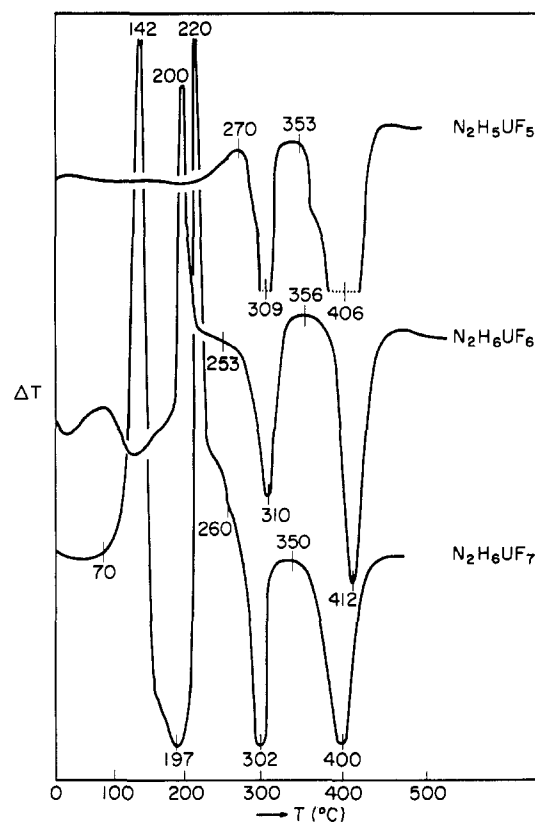


Figure 1.—The differential thermal analysis diagrams of hydrazinium fluorouranates.

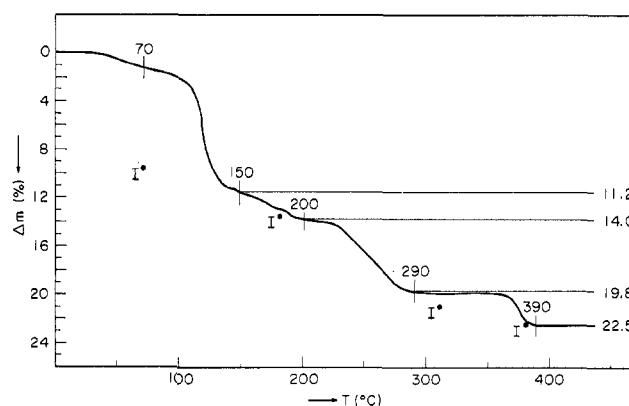


Figure 2.—The percentage weight losses of hydrazinium heptafluorouranate(V) observed both at the thermogravimetric analysis and at the isothermal decomposition (points I).

steps are shown. However, in the middle part of the diagram, there is a gradual transition.

The results of the chemical analysis and of the magnetic susceptibility measurements of the decomposition products obtained at the isothermal decomposition of hydrazinium heptafluorouranate(V) are collected in Table V.

The X-ray investigation shows that originally well-crystallized hydrazinium heptafluorouranate(V) decomposes at 70° to a product, from which no X-ray powder diffraction patterns could be obtained. First X-ray patterns were observed on the product obtained at 180°. In the patterns, lines of hydrazinium pentafluorouranate(IV) and lines of uranium tetrafluoride were

TABLE V
CHEMICAL ANALYSIS AND MAGNETIC DATA OF THE
DECOMPOSITION PRODUCTS

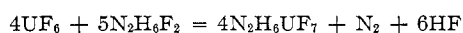
Temp, °C	Time, hr	Analyses			$10^3 \chi_M'$, cgsu	θ , °K	μ_{eff} , BM
		% N ₂ H ₄ ±0.1	% U ±0.3	% F ±0.4			
0	...	7.8	59.2	32.4	0.91	114	1.66
70	70	6.1	65.1	27.9	3.56	124	3.38
180	75	5.8	66.1	27.4	3.92	110	3.48
310	36	0.0	72.2	24.9	3.61	146	3.49
380	20	...	75.5	24.0	3.41	174	3.51

observed. Lines of hydrazinium pentafluorouranate (IV) became weaker, and the lines of uranium tetrafluoride became stronger as the temperature of the decomposition increased. X-Ray patterns show that pure uranium tetrafluoride was obtained at 380°.

Discussion

Hydrazinium heptafluorouranate(V) is formed by the reaction of uranium hexafluoride with hydrazinium difluoride both in saturated solution in anhydrous hydrogen fluoride in the presence of some undissolved material and also in carbon tetrachloride. It is interesting that hexavalent uranium is reduced to only a pentavalent state if the reaction is carried out at 0°. In more dilute solutions and at lower temperatures it might be possible to obtain a complex compound of hexavalent uranium.

According to Clifford,¹⁸ molybdenum and tungsten hexafluorides dissolved in anhydrous hydrogen fluoride exhibit definite but rather weak acidity and some oxidizing power. Since uranium could be regarded as an analog and hydrazinium difluoride is basic in hydrogen fluoride, the reaction between them might be considered as an acid-base reaction involving oxidation-reduction. The over-all reaction might be described by the equation

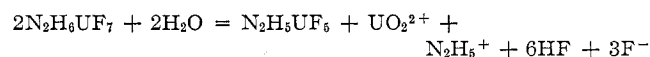


Taking for granted that the ion $\text{N}_2\text{H}_6^{2+}$ exists in hydrazinium heptafluorouranate(V) and that a maximum coordination number of 8 is observed for U^{5+} , only one hydrazinium fluorouranate(V) is possible, namely, $\text{N}_2\text{H}_6\text{UF}_7$. By X-ray evidence this compound is formed regardless of the starting mole ratios and reaction medium used. The X-ray powder diffraction patterns indicate a low symmetry for this compound. The yellowish products obtained with the starting mole ratios of $\text{UF}_6:\text{N}_2\text{H}_6\text{F}_2 = 1:2$ or $1:3$ were highly unstable in glass at room temperature. Probably, mixtures of hydrazinium heptafluorouranate(V), $\text{N}_2\text{H}_4 \cdot 4\text{HF}$, a compound reported by Bock,¹⁹ and unreacted hydrazinium difluoride were formed under these conditions.

Comparison of the measured and calculated magnetic data leads to the conclusion that uranium exists in the investigated compound with a stoichiometric formula $\text{N}_2\text{H}_6\text{UF}_7$ in a five-valent state. Measured values of the effective magnetic moment are very close to the spin

only value for a single electron (1.73 BM). However, the molar magnetic susceptibility and Weiss constant show that the orbital contribution is not completely quenched.

Hydrolysis of hydrazinium heptafluorouranate(V) might be described by the equation



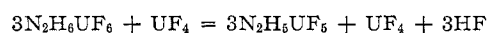
The green precipitate obtained from the hydrolysis is hydrazinium pentafluorouranate(IV).^{2a} The compound remaining in supernatant solution could be the hydrazine uranyl complex described by Sahoo and Sathapathy.³ Such a hydrolysis reaction is characteristic for a compound of five-valent uranium and is consistent with the magnetic evidence.

On the basis of experimental data and analogy to the thermal decomposition of ammonium fluorouranates,^{16, 20-23} the following decomposition scheme of hydrazinium heptafluorouranate(V) might be supposed.

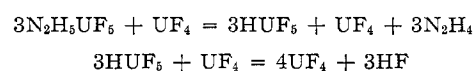
Up to 70° self-reduction of hydrazinium heptafluorouranate(V) occurs, and hydrazinium hexafluorouranate(IV) is formed by



In the next step of the thermal decomposition hydrazinium pentafluorouranate(IV) should be formed, which is stable according to Lukyanichev^{2a} up to 250°



By analogy with the thermal decomposition of ammonium pentafluorouranate(IV) the hydrazinium compound should decompose further in two steps. In the first step, the compounds HUF_5 or $\text{UF}_4 \cdot \text{HF}$ should be formed,²² which should decompose in the second step to uranium tetrafluoride according to



The comparison between mole ratios and percentage weight losses calculated on the basis of the proposed scheme of the decomposition and the ones observed at isothermal decomposition are given in Table VI. Also, the percentage weight losses for successive steps obtained by thermal gravimetric analysis are added.

In Table VII the calculated, obtained from mole ratio data of particular steps, and observed compositions of products are given.

The thermal decomposition of hydrazinium heptafluorouranate(V) might be, therefore, described as follows. Up to 70° self-reduction to hydrazinium hexafluorouranate(IV) takes place. The color of a sample turns to green, and the effective magnetic moment value rises from 1.66 to 3.38 BM, that is, to the value

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TABLE VI
COMPARISON BETWEEN CALCULATED AND OBSERVED DATA FOR
THE THERMAL DECOMPOSITION OF
HYDRAZINIUM HEPTAFLUOROURANATE(V)

Temp of de- compn, °C	Calcd		Obsd		Tga Weight loss, %
	Mole ratio N ₂ H ₄ :U:F	Weight loss, %	Isothermal decompn Mole ratio N ₂ H ₄ :U:F	Weight loss, ^a %	
0	1:1:7	...	0.98:1:6.85	...	...
70	0.75:1:5.5	9.14	0.70:1:5.37	9.68	11.2
180	0.75:1:4.75	3.75	0.65:1:5.26	4.17	2.8
310	0:1:4.75	5.93	0.00:1:4.32	7.13	5.8
380	0:1:4	3.71	0.00:1:3.98	1.63	2.7
	Σ	22.49		22.59	22.5

^a Weight loss for step obtained at isothermal decomposition is given relative to weight of the sample at the very beginning of decomposition.

TABLE VII
THE COMPOSITIONS OF PARTICULAR STEPS OF THE THERMAL
DECOMPOSITION OF HYDRAZINIUM HEPTAFLUOROURANATE(V)

Temp, °C	Calcd, %	Obsd, %
0	100 N ₂ H ₆ UF ₇	99 N ₂ H ₆ UF ₇ + 1 N ₂ H ₆ UF ₆
70	75 N ₂ H ₆ UF ₆ + 25 UF ₄	70 N ₂ H ₆ UF ₆ + 30 UF ₄
180	75 N ₂ H ₆ UF ₆ + 25 UF ₄	61 N ₂ H ₆ UF ₆ + 4 N ₂ H ₆ UF ₅ 35 UF ₄
310	75 HUF ₅ + 25 UF ₄	32 HUF ₅ + 68 UF ₄
380	100 UF ₄	100 UF ₄

characteristic for quadrivalent uranium compounds. The percentage weight loss is a little greater than the calculated one. Not only nitrogen and hydrogen fluoride but also some hydrazinium difluoride is lost. The product obtained at 70° shows no X-ray powder diffraction pattern resembling hydrazinium hexafluorouranate(IV) obtained in the gaseous phase.⁵ To this decomposition step the first exothermic dta peak might belong. The shift to higher temperatures might be due to the difference between dynamic and isothermic courses of the decomposition. It has been shown by X-ray evidence that this effect does not belong to an eventual crystallization process.

The first X-ray powder diffraction pattern was obtained from the product at 180°. It could be shown from the tga curve that this step of the decomposition is not very distinctive. Therefore, a disagreement between percentage weight loss or compositions found and calculated could be expected. From the composition of the sample at 180° (Tables VI, VII) a further loss of hydrazinium difluoride is shown. As shown by the high fluorine content in the sample at this temperature, the decomposition under isothermic conditions is not completed. The endothermic effect at 194° and the exothermic effect at 214° on the dta curve are probably related to the decomposition of hydrazinium hexafluorouranate(IV) and the crystallization of hydrazinium pentafluorouranate(IV), re-

spectively. An analogous effect is shown on the dta curve of hydrazinium hexafluorouranate(IV).

The percentage weight loss in the next step is again greater than expected. This might be due both to incomplete decomposition from the former step and to the decomposition of the products formed at this step. Up to 310° hydrazine is given off from hydrazinium pentafluorouranate(IV). In the cold trap droplets of a relatively nonvolatile liquid were observed. The composition of the product obtained at 310° shows no hydrazine content but some excess of fluorine. Therefore, it might be concluded that the thermal decomposition stops at the unconfirmed equilibrium composition, 2UF₄·HUF₅ or 3UF₄·HF. The compound HUF₅ proposed on the basis of Galkin's supposition seems to decompose immediately after formation to the above equilibrium composition. Accordingly, the proposed decomposition scheme should be corrected. Taking into account this correction, the unexpected rise in uranium tetrafluoride content in the decomposition products can be understood. This step is accompanied on the dta curve by an endothermic effect at 296° shown by all three of the hydrazinium fluorouranates investigated.

The final step of the thermal decomposition is finished at 380°. As could be expected, the percentage weight loss for this step is smaller than calculated.

The over-all percentage weight losses calculated and observed at isothermal and tga decompositions are 22.49, 22.59, and 22.5%, respectively, and agree within the limits of experimental error.

After the first remarkable increase associated with the self-reduction of the compound, the magnetic moment of the decomposition products rises to the order of magnitude of the magnetic moment for uranium(IV) compounds. The rise of the Weiss constant shows decreasing magnetic dilution of the system.

The thermal decomposition of hydrazinium heptafluorouranate(V) is much more complicated than the decomposition of ammonium hexafluorouranate(V) investigated by Nguyen-Nghi and co-workers.²⁰ In some respects it resembles the decomposition of ammonium pentafluorouranate(IV), where there are, in spite of its great technological importance, several inconsistencies in the reported data.²¹⁻²³ In both cases, hydrazinium or ammonium difluorouranate are lost steadily during the decomposition, and there are decomposition steps which proceed from one to another without clear distinction.

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