In this computer version extrapolation is carried out only once and thus an accumulation of errors due to consecutive extrapolations is avoided.

It is interesting to mention here the authors' attempt to calculate the acid dissociation constants of dibasic acids with the aid of this new computer method. The undissociated acid form was considered as a complex of the ligand anion and a proton. In this way the stability constants for the itaconate-proton complexes (and the corresponding dissociation constants of the itaconic acid) were calculated. Good agreement was found with the values obtained by the classical graphical and algebraic methods.(5) This method seems also promising for the calculation of acid dissociation constants of polybasic acids, which are now being investigated.

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(5) H. SCHURMANS, Unpublished results.

J. inorg. nucl. Chem., 1967, Vol. 29, pp. 2112 to 2117. Pergamon Press Ltd. Printed in Northern Ireland

The thermal decomposition of hydrazinium (+1)- and hydroxylammonium pentafluorouranates(IV)*

(*Received* 1 *March* 1967)

THE SYNTHESIS, thermal decomposition and some other properties of hydrazinium (+1)- and hydroxylammonium pentafluorides(IV) were reported by LUKYANICHEV and co-workers.(1) Unfortunately, the authors do not describe the details of the thermal decomposition of these materials. Their quoted overall weight loss of 11·08 and 9·70 per cent for the thermal decomposition of hydrazinium (+1)- and hydroxylammonium fluorouranates(IV), respectively, is in disagreement with the expected values of 14·22 and 14·44 per cent for the decomposition to uranium tetrafluoride. The reported decomposition of uranium tetrafluoride upon further heating to temperatures above 400°C is rather astonishing.

The thermal decomposition of both materials was reinvestigated in order to elucidate these processes. That hydrazinium (+1)- and hydroxylammonium pentafluorouranates (IV) appear to be intermediate products in the thermal decomposition of hydrazinium (+2)- and hydroxylammonium hexafluorouranates(V)(2) adds to the interest in the nature of these decompositions.

EXPERIMENTAL

The hydrazinium (+1)-and hydroxylammonium pentafluorouranates(IV) were prepared following LUKYANICHEV(1) and the composition of the products was checked by chemical analysis. Anal. calcd. for $N_2H_5UF_5$; N_2H_4, 8·75; U, 65·0; F, 25·9. Found: N_2H_4, 8·80; U, 65·13; F, 25·1. Calcd. for $(NH_3OH)UF_5$: NH_2OH, 8·99; U, 64·8; F, 25·88. Found: NH_2OH, 8·84; U, 64·62; F, 23·3.

Infrared spectra of the solids were run using Nujol mulls with polyethylene and silver chloride windows and a Beckman IR-12 spectrometer.

The thermal decomposition studies were performed with a Mettler Recording Vacuum Thermoanalyzer. Conditions used in a typical run were as follows: High temperature furnace; macrostick

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(1) YU. A. LUKYANICHEV, N. S. NIKOLAEV and YU. N. MIHAILOV, *Zh. neorg. Khim.* **8**, 1617 (1963).

(2) B. FRLEC and H. H. HYMAN. To be published.

with alumina cups; heating rate: 2°/min; sample weights: ~100 mg; reference: alumina 60 mesh; argon atmosphere with 6 l/hr flow rate.

Both thermogravimetric and differential thermal analyses are performed simultaneously. An increase of a heating rate from 2°/min to 4°/min shifted characteristic temperatures as much as 20° in the 300°C region. Lower heating rates begin to smear out DTA records. Attempts to use the microstick arrangements with alumina inserts to avoid contact of the material with the standard platinium cups were unsatisfactory, presumably due to poor thermal contact. The obtained weight losses were corrected for the buoyancy by subtracting the weight of the empty container at the particular temperatures obtained in a calibration run.

RESULTS AND DISCUSSION

Infrared absorption maxima of hydrazinium (+1)- and hydroxylammonium pentafluorouranates(IV) are listed in Table 1. No structural studies on these two materials are available as yet. Therefore, only a tentative assignment of the observed i.r. absorption bands of the solids can be made. The spectra were compared with the spectra of solid hydrazinium (+1) chloride,(3) perchlorate(4) and of solid hydroxylammonium fluoride.(5)

TABLE 1.—INFRARED SPECTRA OF HYDRAZINIUM (+1)- AND HYDROXYLAMMONIUM PENTAFLUOROURANATES(IV)

$N_2H_5UF_5$			$(NH_3OH)UF_5$		
ν[cm^{-1}]	Intensity, shape	Tentative assignment	ν[cm^{-1}]	Intensity, shape	Tentative assignment
245	m	(U–F)$_s$	260	m, sh	(U–F)$_s$
355 380	vs, b		375	vs	
			585?	vb, sho	(O–H)$_{twist}$
955	s, sh	(N–N)$_s$	940	vw	(U–O)
			975	w, sh	
1086	s, sh	(NH$_3^+$)$_b$	1020	s, vsh	(N–O)$_s$
1118	m		1030	sho	
			1180	m, sh	(NH$_3^+$)$_b$
1218	m	(H–N–N)$_b$	1221	s, sh	(O–H)$_b$
1450?					
1540	s	(H–N–H)$_d$	1505	w	(NH$_3^+$)$_d$
1590	s		1529	m	
			1545	sho	
			1600	sho	
1632 1648	m	(H–N–H)$_d$	1618	s	
			1630	sho	
2630	w				
3090	w, b	(N–H)$_s$	2730	w	(N–H)$_s$
3150	w		3170	m, b	(O–H)$_s$
3240	w				
3300	w, sh				
3350	m, sh				

Intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.
Shape: b = broad, sh = sharp, sho = shoulder.
Assignment: *s* = stretch, *b* = bend *d* = deformation.

The observed frequencies agree with what should be expected for $N_2H_5^+$ and $(NH_3OH)^+$ ions. However, the NH deformation and rocking modes in the hydrazinium compound are shifted markedly towards lower frequencies while the NH stretching bands are shifted towards higher frequencies as

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(3) J. C. DECIUS and D. P. PEARSON, *J. Am. chem. Soc.* **75**, 2436 (1953).

(4) P. W. M. JACOBS and A. RUSSELL-JONES, *Can. J. Chem.* **44**, 2435 (1966).

(5) D. L. FRASCO and E. L. WAGNER, *J. chem. Phys.* **30**, 1124 (1959).

compared with the chloride salt. Therefore, very little if any hydrogen bonding is involved in this compound. This conclusion is confirmed by a free rotation observed in NMR spectra of the solid.(6) The sample of hydroxylammonium pentafluorouranate(IV) shows a small impurity of uranyl fluoride.

Several thermogravimetric curves of hydrazinium (+1) pentafluorouranate(IV) are presented in Fig. 1. The material starts to decompose at 220°C and the decomposition proceeds in several steps. The first step seems to be complete at 320°. However, the composition of the intermediate product was not reproducible. An ammonium fluoride–uranium tetrafluoride complex (probably $NH_4F{\cdot}3UF_4$ according to the weight loss) was observed in two of the four runs, while in the other two virtually all of the nitrogen was gone at 320° and only an $UF_4{\cdot}x HF$ complex remained. On continued decomposition, the ammonium complex lost volatile material more readily, but the end product at 420°C was uranium tetrafluoride in each instance, as shown by the X-ray powder pattern. The first decomposition step is accompanied by an endothermic DTA peak at 309 + 2°C. Another endothermic DTA peak was observed at 420°C.

In Fig. 2, the very reproducible thermogravimetric curve of hydroxylammonium pentafluorouranate(IV) is presented. This thermal decomposition proceeds in three steps, the first of which ends distinctly at 230° with a weight loss of 7·9 per cent. The associated DTA peak at 219°C is exothermic. The next two decomposition steps obviously overlap each other. Uranium tetrafluoride is formed at 370° according to X-ray powder pattern of the material and the overall weight loss. An endothermic DTA peak was observed at 364°C.

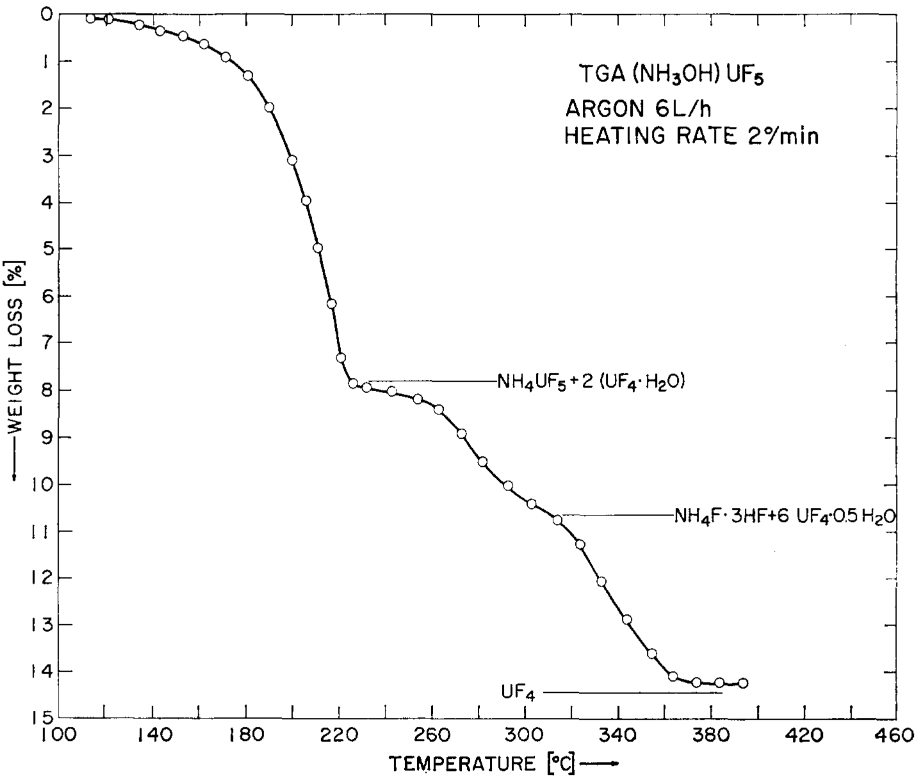

FIG. 1.—Thermogravimetric curve of hydrazinium (+1) pentafluorouranate(IV). Argon atmosphere 6 l/hr, heating rate 2°/min. Sample weights m_0: ○, 102·9 mg; ●, 142·6 mg; □, 99·4 mg; △, 87·3 mg.

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(6) M. PINTAR and B. FRLEC. Unpublished observation.

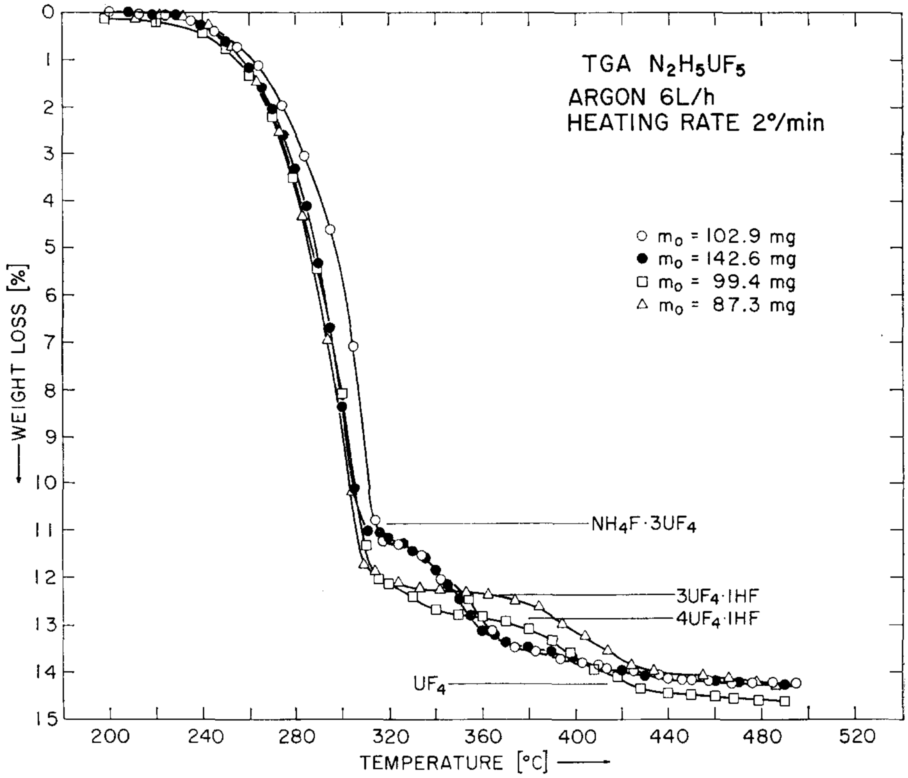

Fig. 2.—Thermogravimetric curve of hydroxylammonium pentafluorouranate(IV). Argon atmosphere 6 l/hr, heating rate 2°/min.

The thermal decomposition of both materials may be interpreted under the supposition that free hydrazine or hydroxylamine are formed during early stages of the decompositions. Both bases thermally decompose further yielding nitrogen and ammonia or nitrogen, ammonia, and water, thus forming systems which allow several possible decomposition mechanisms. There is no actual evidence for the presence of free hydrazine or hydroxylamine and this hypothesis is not necessary. The end products, however, may well be similar and the above approach is a convenient way of constructing reasonable intermediate products.

Hydrazinium (+1) pentafluorouranate(IV) decomposes in the temperature region 220–310° according to the following equations:

$$N_2H_5UF_5 = UF_4 + N_2H_4 + HF. \quad (1)$$

Thermodynamically, the most favored reaction for the decomposition of gaseous hydrazine in the absence of hydrogen is:(7)

$$3N_2H_4 = 4NH_3 + N_2. \quad (2)$$

Such a decomposition has been observed experimentally at temperatures between 250 and 310°C on silica, the reaction being first order and heterogenous.(8,9)

The ammonia and hydrogen fluoride react in turn with the active uranium tetrafluoride to form

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(7) L. F. Audrieth and B. Ackerson-Ogg, *The Chemistry of Hydrazine*, p. 86. John Wiley, New York (1951).

(8) J. C. Elgin and H. S. Tayllr, *J. Am. chem. Soc.* **51**, 2059 (1929).

(9) P. J. Askey, *J. Am. chem. Soc.* **52**, 970 (1930).

ammonium pentafluorouranate(IV) which in this temperature region immediately decomposes further:

$$UF_4 + NH_3 + HF = NH_4UF_5 \quad (3)$$

$$3NH_4UF_5 = NH_4F{\cdot}3UF_4 + 2NH_4F. \quad (4)$$

The existence of $NH_4F{\cdot}3UF_4$ was well established by BENZ *et al.*(10)

The overall reaction for the first decomposition step is therefore:

$$3N_2H_5UF_5 = NH_4F{\cdot}3UF_4 + 2NH_4F + NH_3 + N_2. \quad (5)$$

The corresponding weight loss 10·84 per cent agrees with the observed value.

We believe that further decomposition depends on various factors. The heating rate, geometry and size of the sample seem to be important. These variables may also account for the disagreement between the published mechanisms of a thermal decomposition of ammonium pentafluorouranate (IV).(10–12)

The intermediate products are compounds of the general formula $xUF_4{\cdot}yHF$ observed or postulated previously.(11,13,14) These compounds are stable in the temperature region 310–420°C. The UF_4/HF ratio seems to grow with the increasing temperature. The two most probable compositions are $3UF_4{\cdot}HF$ formed by the decomposition of $NH_4F{\cdot}3UF_4$:

$$NH_4F{\cdot}3UF_4 = 3UF_4{\cdot}HF + NH_3, \quad (6)$$

and $4UF_4{\cdot}HF$ formed by a further decomposition of the first one. The corresponding weight losses 12·37 and 12·84 per cent respectively, were both observed (Fig. 1).

The following scheme for the thermal decomposition of hydroxylammonium pentafluorouranate (IV) fits the observed thermogravimetric pattern although it is not adequately established by analysis of intermediate products.

Hydroxylammonium pentafluorouranate(IV) decomposes in the temperature region 120–220° according to the following equations:

$$(NH_3OH)UF_5 = (NH_3OH)F + UF_4, \quad (7)$$

$(NH_3OH)Cl$ is known to decompose above 157°C as follows:(15)

$$3(NH_3OH)Cl = NH_4Cl + 2HCl + N_2 + 3H_2O. \quad (8)$$

The same type of decomposition is postulated for the fluoride salt. The resulting ammonium fluoride reacts with active uranium tetrafluoride forming ammonium pentafluorouranate(IV) which is stable in this temperature region,(10) and the remaining uranium tetrafluoride reacts with the water vapour(16) according to the following summary equation:

$$3(NH_3OH)UF_5 = NH_4UF_5 + 2UF_4{\cdot}H_2O + 2HF + N_2 + H_2O. \quad (9)$$

The corresponding weight loss 7·81 per cent is in a good agreement with the observed one.

At 300°C, the only stable compounds in the investigated system are $NH_4F{\cdot}3UF_4$ and $UF_4{\cdot}0{\cdot}5H_2O$. The weight loss corresponding to the overall reaction:

$$9(NH_3OH)UF_5 = NH_4F{\cdot}3UF_4 + 6UF_4{\cdot}0{\cdot}5H_2O + 8HF + 3N_2 + 6H_2O, \quad (10)$$

is 10·64 per cent and in a reasonable agreement with the observed value. In the last step pure uranium tetrafluoride is formed at 370°C.

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(10) R. BENZ, R. M. DOUGLASS, F. H. KRUSE and R. A. PENNEMAN, *Inorg. Chem.* **2**, 799 (1963).

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(15) W. H. ROSS, *Trans. Nova Scotia Inst.* **11**, 95 (1906).

(16) J. K. DAWSON, R. W. M. D'EYE and A. E. TRUSWELL, *J. chem. Soc.* 3922 (1954).

Note that the hydrates of uranium tetrafluoride $UF_4 \cdot H_2O$ and $UF_4 \cdot 0{\cdot}5H_2O$ may be more properly written as $U(OH)F_3 \cdot HF$ and $UF_4 \cdot U(OH)F_3 \cdot HF$.

Acknowledgement—The author is indebted to the International Atomic Energy Agency, Vienna, Austria, and to the Nuclear Institute, "Jozef Stefan", Ljubljana, Yugoslavia, who jointly granted one-year fellowship. The helpful discussions with Dr. H. H. HYMAN are gratefully acknowledged.

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J. inorg. nucl. Chem., 1967, Vol. 29, pp. 2117 to 2119. Pergamon Press Ltd. Printed in Northern Ireland

The (n, γ) absorption cross section of ^{146}Pm for reactor neutrons*

(*Received* 6 *March* 1967)

IN THE course of investigating the shielding requirements of 2·7-yr ^{147}Pm, ROBERTS *et al.*⁽¹⁾ noted the presence of 1600-day ^{146}Pm in fission-product ^{147}Pm and pointed out that the presence of even small amounts of ^{146}Pm in megacurie ^{147}Pm power sources may introduce severe shielding problems. Since ^{147}Pm in large quantities is available only from fission-product recovery processes, the ^{146}Pm is inherently present. Analyses of two different ^{147}Pm fission products show, for example:

690 mc of ^{146}Pm per 10^6 c ^{147}Pm (at reactor discharge⁽¹⁾)
300 mc of ^{146}Pm per 10^6 c ^{147}Pm (aged eight years⁽²⁾).

A possible explanation for the difference in the ^{146}Pm/^{147}Pm ratio is a difference in the irradiation time or in the flux, which would make a noticeable difference in the ^{146}Pm burnup. Shielding for the 0·460- and 0·740-MeV ^{146}Pm gamma rays⁽³⁾ could present a formidable problem, particularly in limited payload space vehicles. The 41-day ^{148m}Pm is not considered since it is presumed that aged fission products are involved. The long half-life of ^{146}Pm precludes allowing the ^{146}Pm to decay to negligible levels within a reasonable time.

Neutron irradiation of the ^{146}Pm–^{147}Pm product presents a possible means of reducing the ^{146}Pm content by burnup if the (n, γ) absorption cross section of ^{146}Pm is sufficiently large, i.e. large compared with the 230-barn (n, γ) cross section of ^{147}Pm. The present investigation deals only with the measurement of this ^{146}Pm absorption cross section.

Promethium-146, free of ^{147}Pm, may be produced in a cyclotron, purified, isolated, and subsequently irradiated in a reactor. The amount of ^{147}Pm produced in the course of the burnup of ^{146}Pm can not be readily nor accurately determined in the presence of ^{146}Pm since ^{147}Pm is a weak beta emitter with no associated gamma emission. Hence the most convenient method is to determine the loss of ^{146}Pm.

Promethium-146 was prepared by the ^{146}Nd(p, n)^{146}Pm reaction in the Oak Ridge National Laboratory 86-Inch Cyclotron.⁽⁴⁾ A 50-mg sample of isotopically enriched $^{146}Nd_2O_3$ was wrapped in nickel foil and irradiated for 8 hr in the internal beam of the cyclotron at a beam current of 80–100 μa. The enriched ^{146}Nd had the following isotopic analysis:

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* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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