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THERMAL DECOMPOSITION OF AMMONIUM URANATES

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The thermal decomposition of ammonium uranates precipitated from uranyl nitrate solution on the addition of aqueous ammonium hydroxide and hexamine under various conditions has been studied by means of thermogravimetry, differential thermal analysis, infrared spectroscopy and X-ray diffraction. Although all precipitates show the composition corresponding to $UO_3 \cdot NH_3 \cdot H_2O$, the precipitates with hexamine give X-ray diffraction patterns designed as types I and II, in which type I is similar to the precipitates with ammonia. As a result, it is concluded that ammonium uranates thermally decompose to amorphous UO_3 at about 400°, and transform to U_3O_8 via β-UO_3 and/or α-UO_3, latter being formed in the case of type II only.

It has been reported that ammonium diuranate, $(NH_4)_2U_2O_7$, and ammonium uranate, $(NH_4)_2UO_4 \cdot H_2O$, are precipitated on the addition of aqeous solutions of ammonium hydroxide and hexamine, respectively, to aqueous uranyl nitrate solution [1]. A number of investigations have recently been carried out on the compounds in the NH_3–UO_3–H_2O system, but information on their compositions is limited [2–7]. The thermal decompositions of the hydrates of uranium peroxide, uranyl chloride and uranyl sulphate have been investigated previously [8–10]. The present study extends the work to the thermal decomposition of ammonium uranates.

Experimental

Ammonium uranates were prepared by the following procedures: Aqueous solutions of ammonium hydroxide or hexamine (hexamethylenetetramine) were added dropwise (5 cm^3 min^{-1}) or rapidly to 100 cm^3 of 0.1 mol dm^{-3} uranyl nitrate containing nitric acid with agitation, at 20–90°; the resulting precipitates were aged in the mother liquor for 1 h at the same temperature, centrifuged, washed with distilled water until as free as possible from nitrate ion and ammonium ion or hexamine, and then dried in air at room temperature or in vacuo at 25°. The uranium concentration of the aqueous solution was determined by titration with EDTA, using xylenol orange as indicator [11].

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The thermal decomposition products were prepared by heating the specimens in air at the stated temperature for 2 h after heating up to that temperature at a rate of 5 deg/min.

The materials so obtained were examined by mean of thermogravimetry (TG), differential thermal analysis (DTA), X-ray diffraction study and infrared spectroscopy, as described previously [12]. TG and DTA were carried out on the automatic recording thermobalance and DTA apparatus made by Agne Research Center, with platinum-platinum/rhodium thermocouples. For the measurement of differential thermal electromotive force, α-alumina was used as reference material. The specimen of 200–400 mg was heated at 5 deg/min under atmospheric pressure.

Results and discussion

For the precipitates from aqueous uranyl nitrate solution on the addition of ammonium or hexamine, the conditions of precipitation and the decomposition tempera-

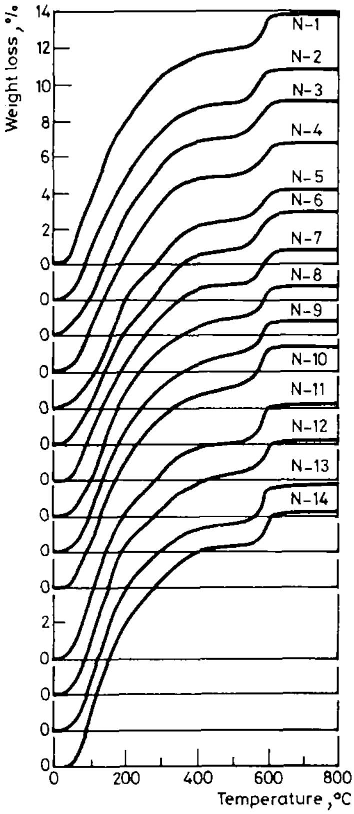

Fig. 1 TG curves of ammonium uranates precipitated with ammonia (numbers on curves are the specimen number in Table 1)

Table 1 Precipitates from aqueous uranyl nitrate solutions on addition of ammonia

Specimen no.	Conditions of precipitation[a]					Temp. at DTA peak[c], °C					
	Temp., °C	Concn. of HNO_3, mol dm^{-3}	Concn. and amount of ammonia added, mol dm^{-3};	cm^3	Rate of addition of ammonia cm^3 min^{-1}	I	II	III	IV	V	VI
N − 1	20	0	5 ;	10	5	135	210	340	370	410	590
N − 2	20	0.1	5 ;	10	5	130	210	350	—	425	565
N − 3	20	0.1	5 ;	10	R[b]	(130)[d]	205	350	—	420	575
N − 4	20	0.1	1 ;	50	5	(135)	210	345	—	430	555
N − 5	90	0.1	5 ;	10	5	(135)	210	335	—	415	585
N − 6	90	0.1	5 ;	10	R	(130)	210	335	—	415	575
N − 7	20	1	5 ;	30	5	(130)	210	337	—	425	570
N − 8	50	0.1	5 ;	10	5	(125)	190	340	—	405	610
N − 9	70	0.1	5 ;	10	5	(135)	200	340	—	—	600
N − 10	20	0.1	5 ;	10	5	140	215	335	370	420	570
N − 11	90	0.1	5 ;	10	5	140	210	335	—	405	600
N − 12	30	0.1	5 ;	10	5	120	180	340	—	400	610
N − 13	40	0.1	5 ;	10	5	125	185	335	—	390	605
N − 14	50	0.1	5 ;	10	5	135	210	330	—	410	590

[a] Precipitates were aged at the stated temperature for 1 hr. Specimen N − 1 to N − 9 and N − 10 to N − 14 were dried in vacuo at 25 °C and air at room temperature, respectively. [b] R means that ammonia is added rapidly into aqueous solutions. [c] I, II and VI indicate the temperatures in endothermic reactions, and III, IV and V in the exothermic ones. [d] Parenthesis indicates a shoulder.

Table 2 Precipitates from aqueous uranyl nitrate solutions on addition of hexamine

Specimen no.	Conditions of precipitation[a]				Temp. at DTA peak[c], °C							
	Temp., °C	Concn. of HNO_3, mol dm^{-3}	Concn. of hexamine added[b], mol dm^{-3}	Rate of addition of hexamine, cm^3 min^{-1}	I	II	III	IV	V	VI	VII	VIII
H – 1	20	0.1	2	R	(130)[d]	185	300	–	–	410	495	580
H – 2	20	0.1	2	5	(125)	190	305	–	–	415	500	595
H – 3	30	0.1	2	5	(130)	175	–	–	355		520	585
H – 4	40	0.1	2	5	(125)	188	–	–	360	405	525	590
H – 5	50	0.1	2	5	130	183	–	310	–	405	512	585
H – 6	20	0	2	5	(135)	178	–	–	363		525	592, 615
H – 7	70	0.1	2	5	130	183	–	310	–	400	515	580
H – 8	20	0.1	0.5	5	(130)	180	–	–	360		525	590, 608
H – 9	90	0.1	2	5	130	185	–	310	–	405	520	580
H – 10	90	0.1	2	5	130	175	–	310	–	400	525	580

[a] Precipitates were aged at the stated temperature for 1 hr. Specimen H – 1 to H – 9 and H – 10 were dried in air at room temperature and vacuo at 25 °C, respectively. [b] The amount of hexamine added is excess (1.3 times) to uranyl concn. in aqueous solutions. [c] I, II, IV, V and VIII indicate the temperatures in endothermic reactions, and III, VI and VII in the exothermic ones. [d] Parenthesis indicates a shoulder.

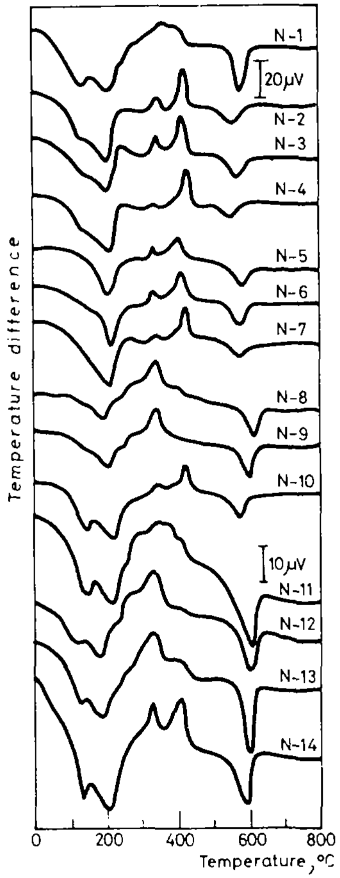

Fig. 2 DTA curves of ammonium uranates precipitated with ammonia (numbers on curves are the specimen number in Table 1)

ture, i.e. the peaks in the DTA curve are shown in Tables 1–2. The TG and DTA curves are illustrated in Figs 1–4. Further, the values of the molar ratio $[UO_3]/[H_2O]/[NH_3]$ for the precipitates from aqueous uranyl nitrate solutions on the addition of ammonia or hexamine, determined from the weight losses in the TG curves, are shown in Tables 3–4. Figures 5–10 and Tables 5–6 give the infrared and X-ray results for the ammonium uranate specimens and their products of thermal decomposition, but only representative X-ray diffraction diagrams and infrared spectra for the materials derived from a few specimens heated at various temperatures are indicated in these Figures.

The results of the thermal analyses (Tables 1–2 and Figs 1–4) suggest that the precipitates with ammonia behave in the same way on thermal decomposition, whereas the precipitates with hexamine behave in two ways. Further, the precipitates with ammonia yield almost the same X-ray diffraction pattern, while the patterns for the precipitates with hexamine fall into two types, depending on the temperature of

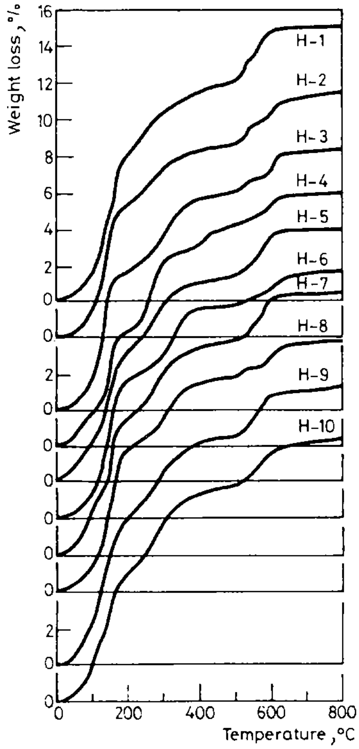

Fig. 3 TG curves of ammonium uranates precipitated with hexamine (numbers on curves are the specimen numbers in Table 2)

precipitation (Table 5). Accordingly, the precipitates with hexamine at above 50° specimens H — 5, 7, 9 and 10 and below 40° (specimens H — 1, 2, 3, 4, 6 and 8) are designated as types I and II, respectively. The diffraction pattern of type I is similar to that of the precipitate with ammonia, but that of type II is slightly different. For all precipitates, however, the TG curves show the weight loss corresponding to the value calculated for $UO_3 \cdot NH_3 \cdot H_2O$ (Tables 3–4). Further, it is inferred that the compositions of the precipitates are independent of the drying method in air or in vacuo. The DTA curves of the precipitates with ammonia give endothermic reactions at about 130, 210 and 590° and exothermic ones at about 340–420°. Endotherms at about 130, 185 and 590° and endotherms at about 510° are observed in the DTA curves of the precipitates with hexamine, and exotherms and/or endotherms also appear at 300–400°. The reactions in the DTA curve occur at points near the change in shape of the TG curves. However, since a change in shape of the DTA curve is observed in ammonium uranate left in air for a period of time, it is expected that the bonding between the ammonium group and the water molecule and the uranyl group may undergo change during storage: e.g. when the DTA curve of specimen N — 1 is measured in three months after preparation, the endothermic peak

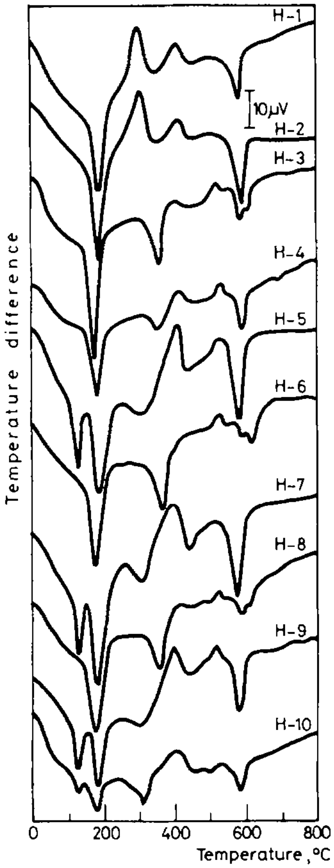

Fig. 4 DTA curves of ammonium uranates precipitated with hexamine (number on curves are the specimen numbers in Table 2)

at 135° and the exothermic one at 370° are decreased. In this work, therefore, the compounds ammonium uranate and ammonium diuranate are referred to together as ammonium uranate.

The X-ray diffraction diagrams for the materials derived from all the precipitates with ammonia or hexamine on heating at 300–400° indicate the amorphous form (Figs 5–7) [8]. On heating at 500°, the material precipitated with ammonia or with hexamine at above 50° (type II) forms a mixture of crystalline β-UO_3 [12] and U_3O_8 [13], while the material precipitated with hexamine at below 40° (type I) gives the pattern of U_3O_8 accompanied by α-UO_3 [14].

The infrared spectra (Figs 5–7) for ammonium uranate specimens show the following absorptions: for the precipitate with ammonia (specimen N – 10) OH stretching and bending absorptions at 3500 and 1630 cm^{-1}, respectively, NH_4^+ stretching and bending bands at 3300 and 1420 cm^{-1}, respectively, and the

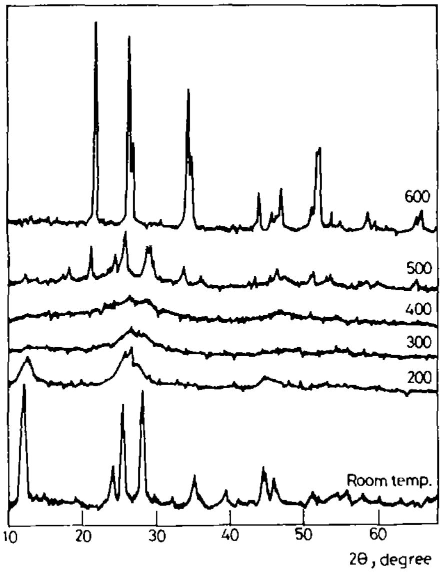

Fig. 5 X-ray diffraction diagrams of the material derived from ammonium uranate heated at various temperatures (numbers on curves represent the heating temperatures, °C; from specimen N – 10 in Table 1)

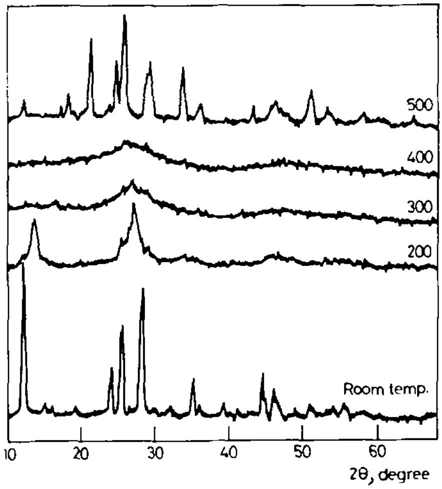

Fig. 6 X-ray diffraction diagrams of the material derived from ammonium uranate heated at various temperatures (numbers on curves represent the heating temperatures, °C; from specimen H – 2 in Table 2)

asymmetric vibration of the uranyl group at 920 cm^{-1}; for the type I precipitate with hexamine (specimen H – 9), OH stretching and bending absorptions at 3460 and 1625 cm^{-1}, respectively, NH_4^+ stretching and bending bands at 3250 and

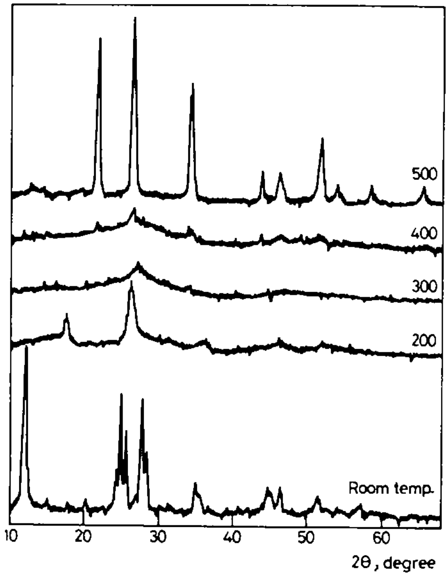

Fig. 7 X-ray diffraction diagrams of the material derived from ammonium uranate heated at various temperatures (numbers on curves represent the heating temperatures, °C; from specimen H – 9 in Table 2)

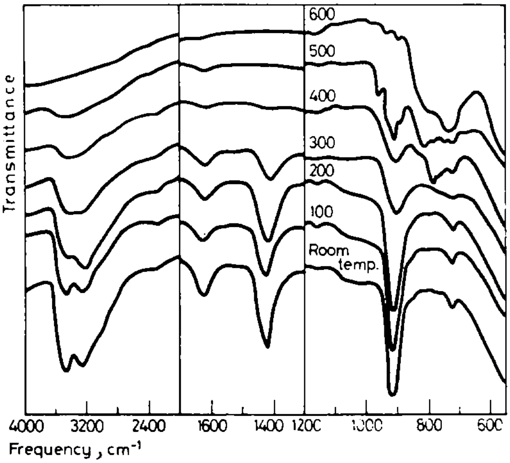

Fig. 8 Infrared spectra of the material derived from ammonium uranate heated at various temperatures (numbers on curves represent the heating temperatures, °C; from specimen N – 10 in Table 1)

1420 cm^{-1}, respectively, and the asymmetric vibration of the uranyl group at 915 cm^{-1}; for the type II hexamine precipitate (specimen H – 2). OH stretching and bending absorptions at 3560 and 1625 cm^{-1}, respectively, NH_4^+ stretching and bending bands at 3350 and 1420 cm^{-1}, respectively, and the asymmetric vibration

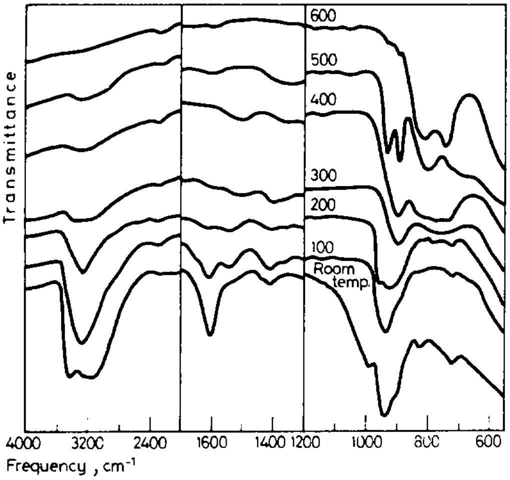

Fig. 9 Infrared spectra of the material derived from ammonium uranate heated at various temperatures (numbers on curves represent the heating temperatures, °C; from specimen H – 2 in Table 2)

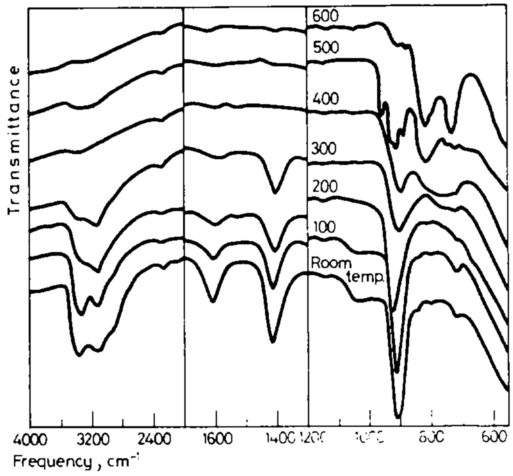

Fig. 10 Infrared spectra of the material derived from ammonium uranate heated at various temperatures (numbers on curves represent the heating temperatures, °C; from specimen H – 9 in Table 2)

of the uranyl group at 1015 and 945 cm^{-1}. For the precipitate with ammonia (Fig. 8), the OH and NH_4^+ absorption bands decrease in intensity with rising temperature, and disappear on heating at 400°; additionally, broad bands centred at around 905 and 720 cm^{-1} appear, considered to be due to the U–O stretching vibration of amorphous UO_x ($3 \leqslant x \leqslant 3.5$) [8]. At 500°, absorptions appear at 965, 915, 890, 815 and 750 cm^{-1} because of the formation of β-UO_3 [13]. On

Table 3 Composition of the precipitates from aqueous uranyl nitrate solutions on addition of ammonia[a]

Specimen no.	Loss in weight[b], % ~ 190 °C	~ 400 °C	~ 600 °C	Molar ratio $[UO_3]/[NH_3]/[H_2O]$		
N – 1	7.2	11.6	13.8	1	0.84	1.30
N – 2	6.6	11.0	12.8	1	0.83	1.18
N – 3	6.6	11.1	13.1	1	0.85	1.18
N – 4	6.0	10.8	12.8	1	0.90	1.07
N – 5	5.3	10.2	12.2	1	0.92	0.94
N – 6	5.7	10.7	13.0	1	0.94	1.02
N – 7	6.6	10.7	12.8	1	0.77	1.18
N – 8	7.1	10.8	12.8	1	0.74	1.27
N – 9	6.6	10.9	12.8	1	0.81	1.18
N – 10	6.8	11.2	13.3	1	0.83	1.22
N – 11	7.4	12.2	14.2	1	0.92	1.34

[a] The values determined by the weight loss in the TG curve. [b] The following assumption is introduced to determine the composition: the weight loss at ~ 190 °C is due to the release of water, at ~ 400 °C the release of water and ammonia, and at ~ 600 °C the total one.

heating at 600°, the broad band at 740 cm^{-1} of U_3O_8 [13] appears, while the absorptions which arise from the presence of α-UO_3 decrease. On further heating, the absorption band of U_3O_8 becomes stronger. When the precipitates with hexamine (types I and II) are heated (Figs 9–10), the OH and NH_4^+ absorptions disappear at

Table 4 Composition of the precipitates from aqueous uranyl nitrate solutions on addition of hexamine[a]

Specimen no.	Loss in weight[b], % ~ 170 °C	~ 400 °C	~ 600 °C	Molar ratio $[UO_3]/[NH_3]/[H_2O]$		
N – 1	7.5	12.0	15.1	1	0.86	1.36
N – 2	6.8	10.4	13.2	1	0.85	1.23
N – 3	7.2	12.1	14.2	1	0.94	1.27
N – 4	6.0	11.8	14.0	1	1.10	1.08
N – 5	7.0	11.5	14.0	1	0.86	1.26
N – 6	7.3	11.4	13.7	1	0.78	1.31
N – 7	7.0	11.8	14.3	1	0.86	1.26
N – 8	7.5	11.6	13.8	1	0.89	1.35
N – 9	7.0	12.5	15.2	1	1.00	1.25
N – 10	6.5	11.8	14.4	1	1.01	1.17

[a] The values determined by the weight loss in the TG curve. [b] The following assumption is introduced to determine the composition: the weight loss at ~ 170 °C is due to the release of water, at ~ 400 °C the release of water and hexamine, and at ~ 600 °C the total one.

Table 5 X-ray diffraction data (interplanar spacings and intensities) for ammonium uranates

Specimen A – 10		Specimen H – 2		Specimen H – 9	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
7.62	100	7.37	100	7.56	100
6.65	11	4.69	6	6.10	5
6.15	11	3.67	33	5.71	6
4.72	9	3.59	90	4.74	4
3.78	34	3.50	54	3.78	28
3.54	83	3.23	85	3.56	51
3.22	94	3.15	46	3.54	55
3.05	9	2.96	8	3.22	75
2.83	9	2.90	8	3.21	82
2.69	6	2.85	8	3.03	5
2.59	26	2.74	6	2.85	5
2.52	11	2.57	23	2.58	24
2.31	11	2.55	15	2.51	5
2.21	9	2.45	8	2.37	7
2.06	31	2.15	6	2.21	5
2.03	23	2.08	6	2.06	28
1.99	23	2.07	8	1.98	19
1.98	23	2.04	15	1.80	9
1.97	17	2.01	15	1.77	4
1.80	11	1.96	23	1.74	4
1.78	9	1.78	15	1.72	5
1.77	9	1.74	6	1.69	4
1.69	9	1.61	8	1.67	8
1.66	11			1.55	2
1.60	9			1.41	4
1.55	6				
1.38	9				

200 and 400°, respectively, and simultaneously the broad band due to the formation of amorphous UO_x appears. At 500°, however, type I exhibits absorptions at 965, 930, 915, 895, 820 and 775 cm^{-1}, because of the formation of α-UO_3, while type II reveals absorption bands at 930, 890 and 805 cm^{-1}, assigned to β-UO_3. On heating at 600°, the strong bands of U_3O_8 are observed for the precipitates with hexamine (types I and II). From this it is seen that the absorptions of the thermal decomposition products of the precipitate with ammonia basically resemble those of the products derived from the precipitate with hexamine at above 50° (type I) on heating, and are slightly different from those of the products derived from the precipitate with hexamine at below 40° (type II), corresponding to the X-ray diffraction and thermal analysis results. The following possible interpretation is therefore proposed for the DTA curve of the precipitate with ammonia: the endotherms at ~ 180 and ~ 210° are due to the release of the water molecule; the exotherms at 340–420° arise from

Table 6 X-ray diffraction results of the products derived from ammonium uranate heated at various temperatures

Temperatures, °C	Phase detected N – 10[a]	 H – 2[a]	 H – 9[a]
100	$UO_3 \cdot NH_3 \cdot H_2O$	$UO_3 \cdot NH_3 \cdot H_2O$	$UO_3 \cdot NH_3 \cdot H_2O$
200	$UO_3 \cdot NH_3 \cdot H_2O$	$UO_3 \cdot NH_3$	$UO_3 \cdot NH_3$
300	$UO_3 \cdot NH_3$	$UO_3 \cdot NH_3$	$UO_3 \cdot NH_3$
400	$A - UO_x$[b]	$A - UO_x$	$A - UO_x$
500	β-$UO_3 + U_3O_8$	$U_3O_8 + \alpha$-UO_3	β-$UO_3 + U_3O_8$
600	U_3O_8	U_3O_8	U_3O_8
700	U_3O_8	U_3O_8	U_3O_8

[a] Refere to specimen no. In Table 1 or 2. [b] $A - UO_x$ represents amorphous UO_x ($3 \leqslant x < 3.5$).

the release of the ammonium group; and the endotherm at ~ 590° is ascribed to the transformation to U_3O_8. A similar explanation is given for the precipitates with hexamine: the endotherms at ~ 130 and ~ 185° are attributed to the release of the water molecule; the exotherms and/or endotherms at 300–400° result from the release of the ammonium group; the exotherm at ~ 515° is caused by the transformation of amorphous UO_x to crystalline UO_3; and the endotherm at ~ 590° is due to the conversion of crystalline UO_3 to U_3O_8.

Hence, it is concluded that the ammonium uranates can be classified into two types, I and II, on the basis of their thermal decomposition behaviour; they thermally decompose to amorphous UO_x at about 400°, and transform to U_3O_8 via β-UO_3 and/or α-UO_3, the latter being formed in the case of type II only:

For type I:

$$UO_3 \cdot NH_3 \cdot H_2O \rightarrow UO_3 \cdot NH_3 \rightarrow UO_x \rightarrow \beta\text{-}UO_3 \rightarrow U_3O_8$$

and for type II:

$$UO_3 \cdot NH_3 \cdot H_2O \rightarrow UO_3 \cdot NH_3 \rightarrow UO_x \rightarrow \alpha\text{-}UO_3 \rightarrow U_3O_8$$

where UO_x ($3 \leqslant x \leqslant 3.5$) is amorphous.

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Zusammenfassung — Die thermische Zersetzung von unter verschiedenen Bedingungen durch wässrige Lösungen von Ammoniumhydroxid und Hexamin aus Uranylnitrat-Lösung gefällten Ammoniumuranaten wurde mittels TG, DTA, IR-Spektroskopie und Röntgendiffraktometrie untersucht. Obwohl die Zusammensetzung aller Niederschläge der Formel $UO_3 \cdot NH_3 \cdot H_2O$ entspricht, geben die mit Hexamin gefällten Niederschläge die als Typ I und II bezeichneten Röntgendiffraktogramme, von denen das des Typs I ähnlich dem der mit Ammoniak gefällten Niederschlage ist. Es wird festgestellt, daß Ammoniumuranate bei 400° thermisch zu amorphen UO_3 zersetzt werden und sich über β-UO_3 und/oder α-UO_3 — wobei beim Typ II nur das letztere gebildet wird — in U_3O_8 umwandeln.

Резюме — Методами термогравиметрии, дифференциального термического анализа, инфракрасной спектроскопии и рентгенофазового анализа изучено термическое разложение уранатов аммония, полученных осаждением в различных условиях растворов нитрата уранила водным раствором гидроокиси аммония и гексамина. Хотя все осадки соответствовали составу $UO_3 \cdot NH_3 \cdot H_2O$, осадки с гексамином дали рентгенограммы, обозначенные как I и II. Первый тип рентгенограммы подобный таковой для осадка с аммиаком. Сделано заключение, что аммоний уранаты при температуре около 400° разлагаются до аморфной UO_3 и превращаются до U_3O_8 через стадию образования β-UO_3 или же α-UO_3. Последная форма наблюдалась только на рентгенограмме типа II.