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THERMAL DECOMPOSITION OF AMMONIUM URANATES PRECIPITATED FROM URANYL NITRATE SOLUTION WITH AMMONIUM HYDROXIDE

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ABSTRACT

Thermal decomposition of ammonium uranates precipitated from uranyl nitrate solutions on addition of aqueous ammonium hydroxide under various conditions has been examined by thermogravimetry (TG), differential thermal analysis (DTA), infrared spectroscopy and X-ray diffraction study. The TG curves of all precipitates show the weight-loss corresponding to the calculated value as $UO_3 \cdot NH_3 \cdot H_2O$. The DTA curves of the precipitates give the endotherms at about 130, 210 and 590 °C and the exotherms at 340-420 °C. As a result, it is found that ammonium uranates thermally decompose to amorphous UO_3 at about 400 °C, and transform to U_3O_8 via β-UO_3.

INTRODUCTION

So far 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 addition of aqueous solutions of ammonium hydroxide and hexamine, respectively, to aqueous uranyl nitrate solution (ref.1). Recently a number of investigations have been carried out on the compounds in the NH_3 - UO_3 - H_2O systems, but the information on their compositions is limited (refs.2-7). The thermal decomposition of the hydrates of uranium peroxide, uranyl chloride and uranyl sulphate has been investigated in previous papers (refs.8-10). In connection with these results, the present study extends the work to the thermal decomposition of ammonium uranates precipitated from uranyl nitrate solution with ammonium hydroxide.

EXPERIMENTAL

Ammonium uranates were prepared by the following procedures: Aqueous solutions of ammonium hydroxide added dropwise (5 cm^3 min^{-1}) or rapidly to 100 cm^3 of 0.1 mol dm^{-3} uranyl nitrate containing nitric acid by agitation at temperatures 20-90 °C; the resulting precipitates were aged in mother liquors for 1 hr at the same temperatures, centrifuged, washed with distilled water until as free as possible from nitrate and ammonium ions, and then dried in air at room temperature or vacuo at 25 °C. The uranium concentration in aqueous solution was de-

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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	$[HNO_3]$ (mol/dm^3)	Ammonia added			I	II	III	IV	V	VI
			$[NH_4OH]$ (mol/dm^3)	Amount (cm^3)	Addition rate (cm^3/min)						
1	20	0	5	10	5	135	210	340	370	410	590
2	20	0.1	5	10	5	130	210	350	–	425	565
3	20	0.1	5	10	R[b]	(130)[d]	205	350	–	420	575
4	20	0.1	1	50	5	(135)	210	345	–	430	555
5	90	0.1	5	10	5	(135)	210	335	–	415	585
6	90	0.1	5	10	R	(130)	210	335	–	415	575
7	20	1	5	30	5	(130)	210	337	–	425	570
8	50	0.1	5	10	5	(125)	190	340	–	405	610
9	70	0.1	5	10	5	(135)	200	340	–	–	600
10	20	0.1	5	10	5	140	215	335	370	420	570
11	90	0.1	5	10	5	140	210	335	–	405	600
12	30	0.1	5	10	5	120	180	340	–	400	610
13	40	0.1	5	10	5	125	185	335	–	390	605
14	50	0.1	5	10	5	135	210	330	–	410	590

[a] Precipitates were aged at the stated temperature for 1 hr. Specimens No.1 to No.9 and No.10 to No.14 were dried in vacuo at 25 °C and in 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
Composition of the precipitates from aqueous uranyl nitrate solutions on addition of ammonia [a]

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

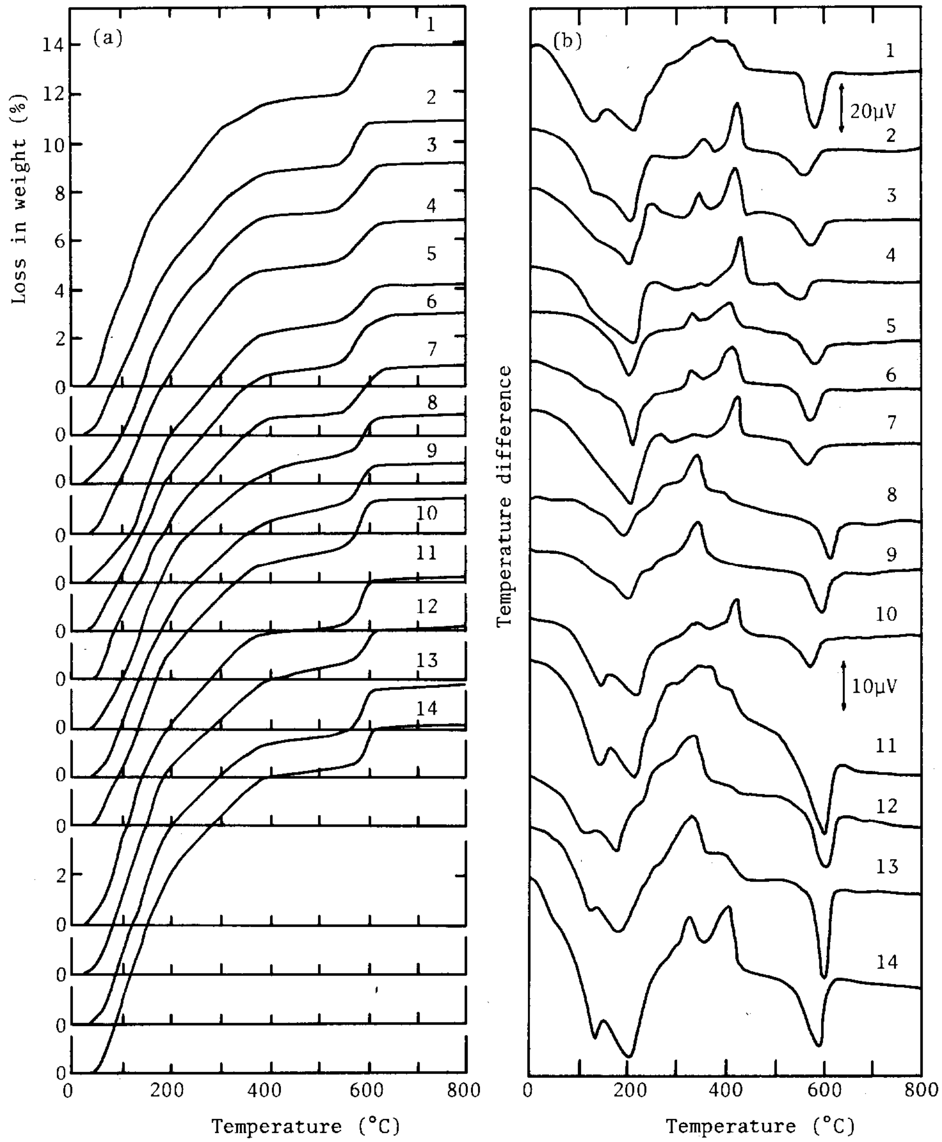

Fig. 1. TG(a) and DTA(b) curves for ammonium uranates precipitated with ammonia (numbers on curves are the specimen numbers in Table 1).

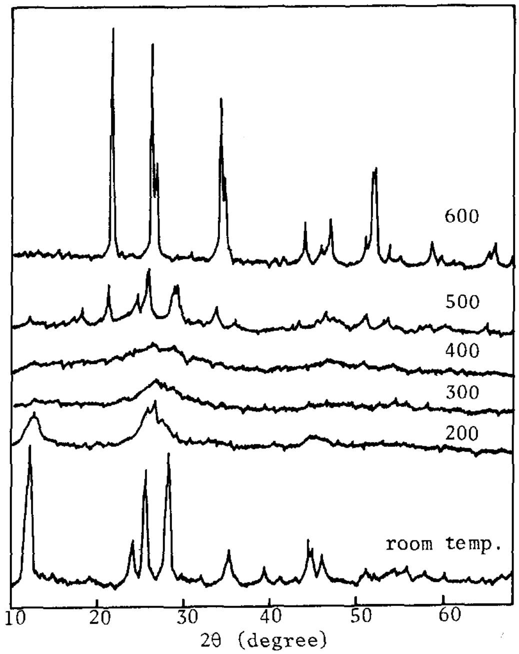

Fig. 2. X-ray diffraction diagrams for the materials derived from ammonium uranate heated at various temperatures (numbers on curves represent the heating temperatures, °C; from specimen No.10 in Table 1).

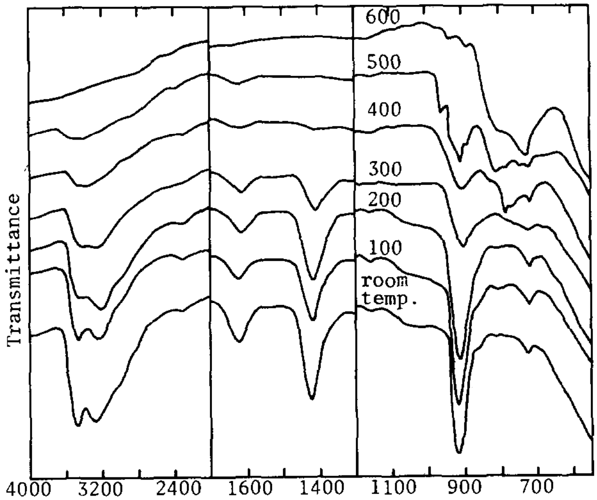

Fig. 3. Infrared spectra for the materials derived from ammonium uranate heated at various temperatures (numbers on curves represent the heating temperatures, °C; from specimen No.10 in Table 1).

termined by titration with EDTA using xylenol orange as indicator (ref.11).

The thermal decomposition products were prepared by heating the specimens in air at the stated temperature for 2 hr after heating up to that temperature at a rate of 5 °C min^{-1}.

The materials so obtained were examined by thermogravimetry (TG), differential thermal analysis (DTA), X-ray diffraction study and infrared spectrophotometry as described previously (ref.12). TG and DTA were carried out on the automatic recording thermobalance and DTA apparatus, made by Agne Research Center, by using platinum - platinum / rhodium thermocouples. For the measurement of differential thermal electromotive force, α - alumina was used as a reference material. The specimen of 200-400 mg was heated as a heating rate of 5 °C min^{-1} under atmospheric pressure.

RESULTS AND DISCUSSION

For the precipitates from aqueous uranyl nitrate solution on addition of ammonia, the condition of precipitation and the decomposition temperature, i.e., the peaks in DTA curves are shown in Table 1. The TG and DTA curves for each specimen are illustrated in Fig.1, respectively. Further the value of the molar ratio $[UO_3]/[H_2O]/[NH_3]$ for the precipitates with ammonia is determined by the weight-loss in TG curves, as shown in Table 2. Figs.2-3 give the X-ray and infrared results for ammonium uranate specimens and their thermally decomposed products, but only representative X-ray diffraction diagrams and infrared spectra for the materials derived from a few specimems heated at various temperatures are indicated in these figures.

The precipitates with ammonia indicate almost the same X-ray diffraction pattern. The results of their thermal analyses (Table 1 and Fig.1) suggest that the thermal decomposition behaviour occurs in a way. For all precipitates, the TG curves show the weight-loss corresponding to the calculated value as $UO_3 \cdot NH_3 \cdot H_2O$ (Table 2). The similar results are also obtained for precipitates from aqueous uranyl nitrate solution on addition of hexamine, and accordingly ammonium diuranate is expressed as ammonium uranate in this work. Further it is inferred that the composition of the precipitates are independent on the drying method in air or vacuo. The DTA curves give the endothermic reactions at about 130, 210 and 590 °C and the exothermic ones at about 340-420 °C. The reactions in the DTA curves occur at points near the change in shape of the TG curves. However, since the change in the shape of DTA curve is observed in the ammonium uranate left in air for a period of time, it is excepted that the bonding of ammonium group and water molecule with uranyl group may be replaced during storage: e.g., the DTA curve of specimen No.1 kept for three months after precipitation shows the decreases in the endothermic peak at 135 °C and the exothermic ones centerd around 370 °C.

The X-ray diffraction diagrams for the materials derived from all specimens of the precipitates with ammonia heated at 300-400 °C give the amorphous form (Fig.3) (ref.8). By heating their precipitates at 500 °C, the precipitates form a mixture of crystalline β-UO_3 (ref.12) and U_3O_8 (ref.13).

The infrared spectra (Fig.3) for ammonium uranate specimens show the following absorptions: for specimen No.10, the OH stretching and bending absorptions at 3500 and 1630 cm^{-1}, respectively, the NH_4^+ stretching and bending bands at 3300 and 1420 cm^{-1}, respectively, and the asymmetric vibration of uranyl group at 920 cm^{-1}. The OH and NH_4^+ absorption bands decrease in the intensities with rising temperature and disappear on heating at 400 °C, and in addition the broad band centered around 950 and 720 cm^{-1}, considered as being due to the U-O stretching vibration of amorphous UO_x ($3 \leq x \leq 3.5$) (ref.8), appears. At 500 °C, the absorptions at 965, 915, 890, 815 and 750 cm^{-1} appear because of the formation of β-UO_3 (ref.13). On heating at 600 °C the broad band at 740 cm^{-1} of U_3O_8 (ref.13) appears, while the absorptions which arise from the presence of β-UO_3 decrase. With further heating the absorption band of U_3O_8 becomes stronger owing to the disappearance of β-UO_3. Therefore the following possible interpretation is proposed for the DTA curve of the precipitate with ammonia: the endotherms at 180 and 210 °C are due to the release of water molecule; exotherms at 340-420 °C arise from the release of ammonium group; the endotherm at ~590 °C is ascribed to the transformation to U_3O_8.

Hence it is concluded that ammonium uranate thermally decomposes to amorphous UO_x at about 400 °C, and transforms to U_3O_8 via β-UO_3 at above 500 °C:

$$UO_3\cdot NH_3\cdot H_2O \rightarrow UO_3\cdot NH_3 \rightarrow \underset{(3 \leq x \leq 3.5)}{UO_x} \rightarrow \beta\text{-}UO_3 \rightarrow U_3O_8$$

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