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SOLID PHASE DECOMPOSITION OF AMMONIUM URANATE

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ABSTRACT

The thermal decomposition of ammonium uranate in air has been studied using TG, DTG, surface area measurements, chemical and X-ray analyses. The effect of washing and calcination at different temperatures is discussed. The optimum conditions for preparing β-UO_3 are chosen to be via ammonium uranate washed by distilled water and calcined at 500°C.

The kinetics of the thermal decomposition are studied using Kissinger's shape index method. The thermal decomposition includes dehydration reaction, complicated reactions to form UO_3 and thermal decomposition of UO_3 to U_3O_8. The order of reaction is calculated for each stage.

INTRODUCTION

Uranium dioxide powder from which either nuclear fuel pellets or uranium tetrafluoride are produced, is usually prepared via ammonium uranate (AU). The properties of the final products depend upon the nature of the precursor and its thermal treatment [1–4]. Therefore, in the production of nuclear fuel, an important step in the process is the thermal decomposition of ammonium uranate (AU) to intermediate uranium oxides.

Addition of ammonia to a solution of uranyl nitrate causes formation of a precipitate which was originally believed to be ammonium diuranate [5,6]. Cordefunke [7] found that four distinct compounds can be formed at different pH conditions with NH_3: U ratios 0.00, 0.33, 0.50 and 0.67. In contrast, Stuart and Whateley [8] claimed that the ammonium uranate system is single phase and that the NH_3 : U ratio can be varied continuously but Cordefunke [9] disputed this. Price and Stuart [10] concluded that the compounds observed by Cordefunke were in fact metastable, chemically non-uniform products formed under non-equilibrium conditions. Finally, according to Stuart [11], ammonium uranate can be represented by $UO_2\,(OH)_{2-x}(ONH_4)_x \cdot yH_2O$.

The composition of the compounds formed during the decomposition of AU in air or an inert gas had been studied by various authors using DTA, TG, IR,

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chemical and X-ray analyses [10–19]. The results did not give a clear picture of the compounds formed due to a variety of experimental conditions and materials used in obtaining such data. Despite the variations in composition and structure, it has been stated that the decomposition of AU occurs in some stages, the final one being conversion of β-UO_3 to U_3O_8.

The aim of the present investigation was to study the thermal decomposition of AU and some kinetic parameters using chemical, thermal and X-ray analyses and surface area measurements.

EXPERIMENTAL

Preparation of samples

Nuclear pure uranyl nitrate solution containing 70 g U l^{-1} was heated to 80°C. Air diluted ammonia gas was bubbled through the solution for 20 min while stirring the solution vigorously. The pH was adjusted to 8.0. Gaseous ammonia was chosen initially because it appeared to offer advantages in controlling the precipitation process [20] and was reported to produce a uniform particle size [20,21].

A sample layer was placed on a stainless steel tray and ignited in a muffle furnace at temperatures ranging from 100 to 800°C for 18 h to ensure complete compositional equilibration. Classification of samples is shown in Table 1.

Chemical analysis

Total ammonia content of a sample was estimated by distilling to dryness into standardized HCl solution. The total uranium was determined by dissolving a

TABLE 1

Classification of samples

Sample	Mode of preparation
a	AU washed using 2×100 ml distilled water, then dried at 50°C for 48 h (NH_4^+/U = 0.529).
b	Sample a dried at 100°C for 18 h.
c	Sample a dried at 200°C for 18 h.
d	Sample a calcined at 300°C for 18 h.
e	Sample a calcined at 350°C for 18 h.
f	Sample a calcined at 500°C for 18 h.
g	Sample a shaken with methanol for 3 h and the supernatant decanted. Shaking and filtration were repeated four times. The precipitate slurry was collected on a Buchner funnel, washed with methanol and dried at 50°C for 48 h (NH_4^+/U = 0.489).
h	AU without washing, dried by air suction.

sample in nitric acid followed by precipitation, washing, filtration and ignition to U_3O_8 as described elsewhere [19].

Thermal and X-ray analyses and surface area measurements

The derivatograph was used for thermal analysis. It measures simultaneously the temperature of the sample (T), the temperature difference between the sample and the thermally inert material (DTA), the change in mass of the sample (TG) and the rate of change in mass (DTG) of the sample. The sample weight was 0.2000 g and the heating rate was 6°C min^{-1} up to 900°C with α-Al_2O_3 as reference material.

The X-ray diffraction analysis techniques have been described previously [22]. Surface area measurements were carried out using the continuous flow-BET method as described previously [22].

Calculation of some kinetic parameters

The orders of reactions were calculated from DTA curves using Kissinger's shape index method [23]. According to Kissinger, the order of reaction, n, is given by the relation

$$n = 1.26\,(a/b)^{1/2} \tag{1}$$

The activation energy for decomposition was obtained by the method of Fuoss et al. [24]. According to them, for first order reactions the activation energy, E, is given by the relation

$$E = RT_i^2/W_i \cdot (dW/dT)_i \tag{2}$$

and the frequency factor, z, is expressed in terms of the activation energy by the relation

$$Z = a/W_i(dW/dT)\exp E/RT_i \tag{3}$$

where a = heating rate, T_i = temperature of inflection, i.e. the temperature at which the rate of weight loss dW/dT with respect to temperature is maximum, W_i = weight loss from the point of inflection on the thermogravimetric curve up to the end of reaction, and $(dW/dT)_i$ = rate of weight loss at the point of inflection.

RESULTS AND DISCUSSION

Thermal decomposition of AU

Figures 1 and 2 show typical data for the decomposition of AU in air to U_3O_8. The results show four stages of decomposition, each involving a loss in weight. The four stages are listed in Table 2 together with peak temperature and chemical analysis.

The DTG curves shown in Fig. 1 were plotted for samples a–f. The analysis of the

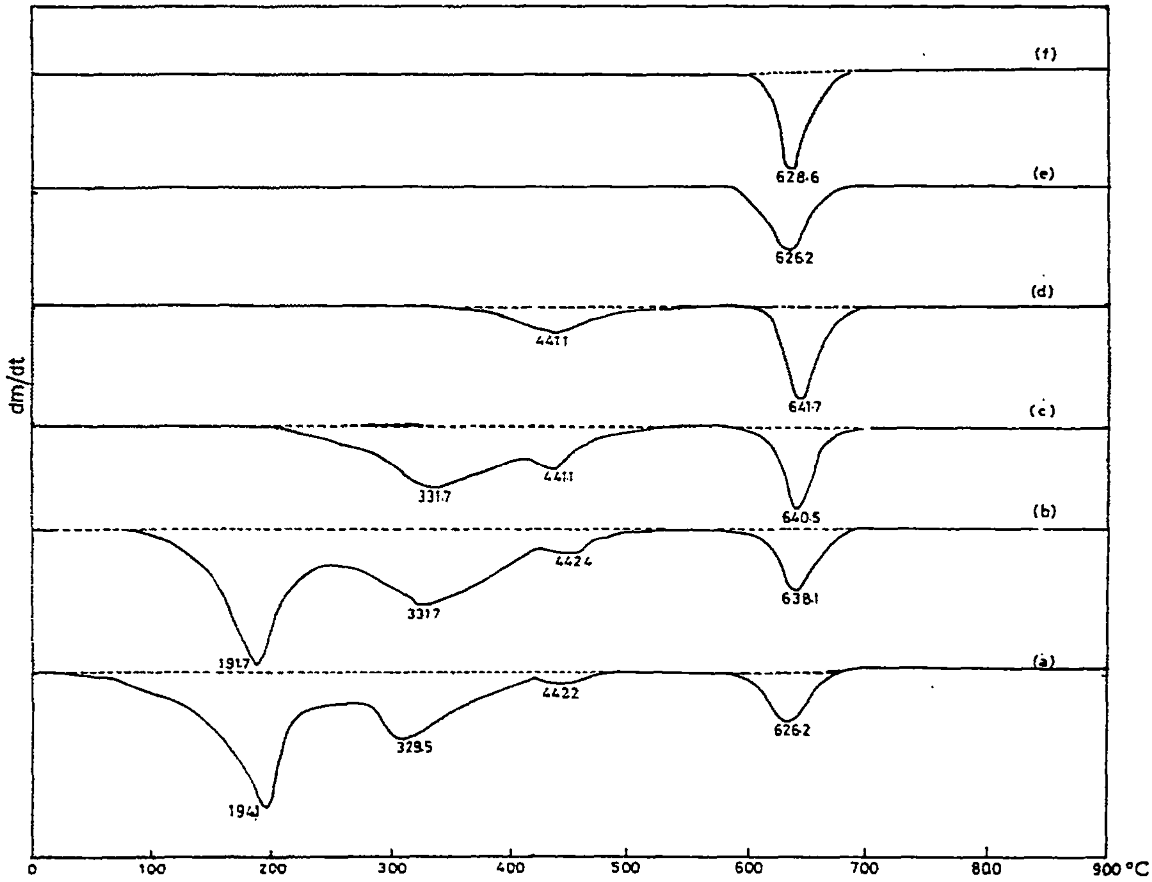

Fig. 1. Differential thermogravimetric curves for the thermal decomposition of ammonium uranate and uranium trioxide.

DTG curves for samples a–c indicates that the water loss for samples a and b starts at 50 and 100°C, respectively, i.e. at the temperatures at which the samples were prepared before thermal analysis. Below these temperatures no weight changes are obtained. The peak temperature appearing at 193 ± 1°C for these two samples corresponds to the removal of coordinated H_2O molecules. This peak disappears for sample c, indicating that the water is completely removed during drying to 200°C.

TABLE 2

Decomposition stages

Stage	Peak temp. (°C)	Type of deflection	NH_4^+/U
I	193 ± 1	Endothermic	0.363
II	327 ± 4	Exothermic	0.031
III	441 ± 1	Exothermic	0.015
IV	636 ± 10	Endothermic	

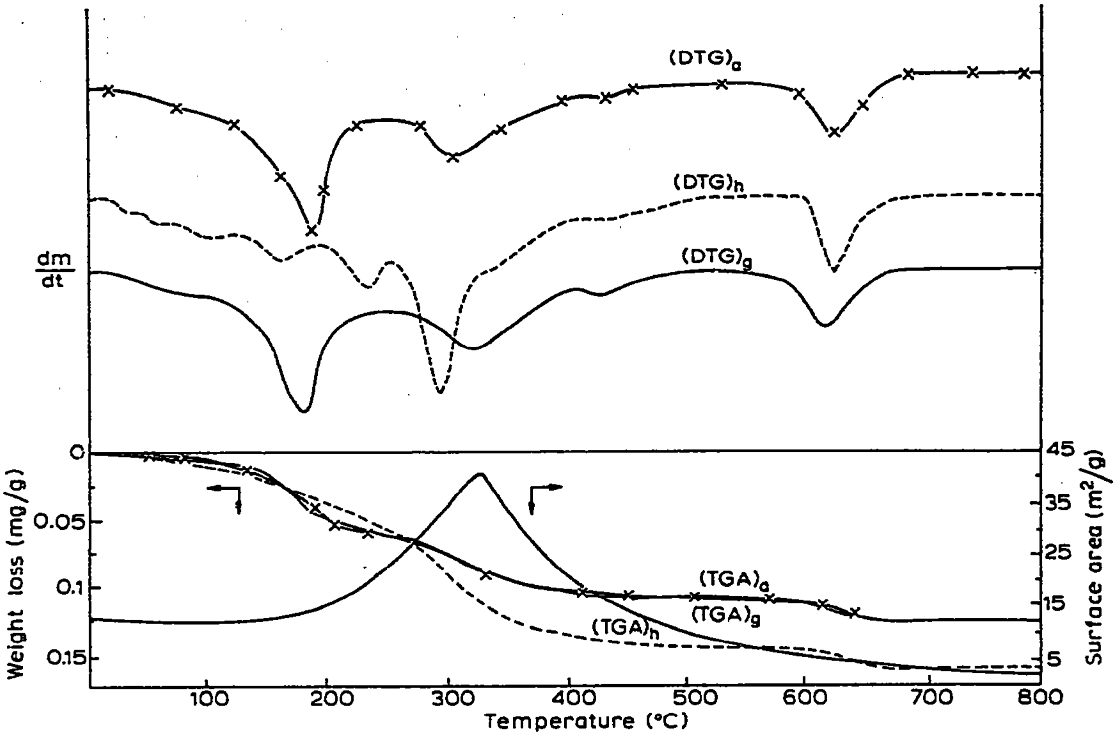

Fig. 2. Thermal decomposition of x–x, sample a; ————, sample g; and — — —, sample h. The lower part of the figure also shows the variation of surface area with calcination temperature for sample g.

Ippolitova et al. [12] found that the dehydration of AU starts at 20°C and proceeds up to 200°C. Szabo [25] observed it to proceed up to 220°C. Stuart [11] found that the rate of water release plotted as a function of temperature showed three maxima at 80, 160 and 275°C during decomposition in inert gas.

Figure 1 (samples a and b) and Table 2 indicate that the removal of nitrate impurities and ammonia starts before the termination of the removal of water. The peak temperature appearing at 327 ± 4°C for samples a–c corresponds mainly to the removal of nitrate impurities with some ammonia. Notz et al. [13] stated that the deflections in the region 250–350°C correspond mainly to nitrate loss with a small amount of ammonia. However, Ippolitova et al. [12] stated that the deflection in this region is associated with detachment of an NH_4^+ ion which takes place in two stages.

Chemical analysis (Table 2) indicates that ammonia is not completely removed at this stage and a portion is retained by the solid. The peak temperature appearing at 441 ± 1°C for samples a–c corresponds to the removal of this retained ammonia. According to the results of other investigators [12,13,26], the deflection in the region 350–450°C is mainly associated with the evolution of the remaining ammonia during decomposition to form UO_3. According to Fig. 1 and Table 2, the removal of water, nitrate impurity and ammonia for the three samples a–c is completed slightly before 500°C in three overlapping stages of decomposition.

For sample d, the DTG peak at 327.6 ± 4°C, noticed for samples a–c, disappears, indicating that the impurity is removed during calcination at 300°C for 18 h. The fourth deflection starts at 595 ± 5°C and terminates at 695 ± 5°C. The peak temperature appearing at 636 ± 10°C for all samples corresponds to the conversion of β-UO_3 to U_3O_8. This stage is associated with the loss of oxygen in the reaction

$$3\ UO_3 = U_3O_8 + 0.5\ O_2 + \text{anion vacancy} \tag{4}$$

The removal of oxide ions from the UO_3 lattice must produce anion vacancies, a result which agrees favourably with that of Ball et al. [18]. This was also proved by Khilla et al. [27] by measuring the electrical conductivity of seven samples calcined at different temperatures. The conductivity increased as a result of these anion vacancies.

Price [28] described this stage as a process of self-reduction within the solid and stated that it is not reduction of UO_3 by evolved NH_3 gas as proposed by Notz et al. [13]. Price and Stuart [10,11] identified this stage as a decomposition of the ammoniate $UO_3 \cdot x\ NH_3$ formally represented by

$$3(UO_3 \cdot 0.22\ NH_3) = U_3O_8 + 0.33\ N_2 + H_2O \tag{5}$$

It was suggested that the amount of NH_3 retained by the solid prior to this stage is generally too small to account for stoichiometry of this reaction. Price and Stuart also stated that the gas analysis and IR data gave no direct evidence to support this view, but thermoanalytical data indicate that weights of completely self-reduced residues exceed the estimated weight of U_3O_8 by about 0.5–1.0%. Excess material is driven off slowly by further heating above 650°C to give N_2 with some O_2.

The DTG curves for samples d–f and chemical analysis (Table 2) indicate that calcination of AU at 300°C for 18 h is not sufficient to produce UO_3 free of ammonia while calcination at 350°C (sample e) yields UO_3 which is more active than that prepared by calcination at 500°C (sample f).

Effect of washing on the thermal decomposition of AU

Difficulties are encountered in the preparation of UO_3 by ignition of AU because of the closeness of the limits of temperature required to completely remove the nitrogen without decomposing the UO_3 to U_3O_8. Therefore the AU was washed with methanol until free of nitrate [8].

To study the effect of washing, the TG and DTG for samples a, g and h are compared (Fig. 2). The TG for samples a and g proved to have an identical weight loss of 13% up to 800°C. Sample h showed a weight loss of 16.4%. The wide variation between a, g and h can be divided into three regions. Up to 350°C, the loss reached 11.9% for sample h instead of 9.4% for samples a and g. This is easily accepted as a result of washing either with water or methanol. In the second region, from 350 to 600°C, the three samples lost about 1.86% which corresponds to the $UO_3 \rightarrow U_3O_8$ conversion. After 650°C, the losses correspond to the decomposition of U_3O_8 to some lower oxygen content. The presence of impurities (nitrate radical and water) was clearly reflected in the DTG of these samples.

(i) The first endothermic peak at 193°C corresponds to removal of coordinated water molecules. This happened in more than one step in the case of sample h which gave in addition to loss of water two peaks at 170 and 220°C which may represent the melting point (169°C) and boiling point (210°C) of ammonium nitrate present.

(ii) The second exothermic peak at 328°C corresponds to the removal of nitrate impurity with some retained ammonia. This is much deeper and began at earlier temperature in the case of sample h. Here it is worth noting that this peak disappears completely in the case of samples d, e and f which are washed with distilled water and heated at 300, 350 and 500°C, respectively.

(iii) The third exothermic peak at 442°C corresponds to removal of retained ammonia and complete conversion to β-UO_3.

(iv) The fourth endothermic peak at 640°C corresponds to conversion of β-UO_3 to U_3O_8. The decomposition terminates at about 660°C. This temperature is in good agreement with that reported by Price and Stuart [10]. Dharwadkar and Karkhanavala [29] stated that the decomposition of β-UO_3 starts above 545°C and terminates at about 625°C. This variation can be attributed to the use of different sample weights during heating, i.e. this variation is due to the effect of thickness of sample on the holder. Thickness of sample was found to have a pronounced effect on the compounds formed during thermal decomposition [30–32]. Dharwadkar and Karkhanavala [29] mentioned that 3 g of sample were used on the holder.

The peak positions for sample h differ very much from those of sample g, meanwhile, the peak temperatures for sample g are quite similar to those for samples a–f. The exothermic peak at 328°C indicates that this mode of washing (with methanol) does not remove all nitrate impurity from AU powders and the residual nitrate is tightly bound to the surface or occluded within the solid, a result which agrees with that of Woolfrey [33]. Washing by this method only reduces NH_4^+ /U in all powders from 0.529 (sample a) to 0.489 (sample g). When shaking with methanol, and filtration were repeated 10 times, the NH_4^+ /U ratio was equal to 0.488. This is also confirmed by measuring the change in the surface area. The relation between weight loss, surface area and temperature for sample g is shown in Fig. 2. The surface area increase between 100 and 300°C is followed by a sharp increase at 330°C and again decreases below 2 m^2/g^{-1} at 800°C due to microsintering. Other investigators [30,34] also found that the surface area of calcined AU increased rapidly between 300 and 400°C. Figure 1 indicates that heating to 330°C produces a three-fold increase in surface area. This increase is associated with cracking and formation of pores as commonly supposed [35], and removal of nitrate impurities with some ammonia as shown in Table 2.

The results of chemical and thermal analyses indicate that each AU powder (prepared under fixed conditions) has a fixed composition (combined NH_3 content) and the excess ammonia is due to the presence of ammonium nitrate impurity.

The presence of nitrate impurities can be explained by the fact that AU precipitated from a uranyl nitrate solution contains residual nitrate as a major impurity. The majority of the nitrate impurity can be removed by washing with water [7]. Woolfrey [33] found that washing reduced the nitrate content of the solid to a level below which it was extremely difficult to remove further nitrate and it was stated that the residual nitrate is tightly bound to the surface or occluded within the solid. Thus one can conclude that the washing with methanol could not be applied in routine refinery practice, it is only motivated in order to remove as much nitrate as possible from AU precipitated from uranyl nitrate solution. Washing with water also removes ammonia [36], most of which is associated with nitrate removal and some of the combined ammonia in the AU structure by an exchange mechanism.

X-Ray diffraction analysis

From the aforementioned discussion, one can conclude that the β-UO_3 can be routinely and easily prepared from the AU as it is followed in the case of samples e

TABLE 3

X-Ray powder diffraction patterns of β-UO_3

Hockstra and Siegel [37]		Dharwadkar and Karkhanavala [29]		Debets [39]		Sample e		Sample f	
d (Å)	I/I_0	*d* (Å)	I/I_0	*d* (Å)	*hkl*	*d* (Å)	I/I_0	*d* (Å)	I/I_0
7.225	vw			7.158	020	7.10	8	7.200	5
5.096	vvw			5.106	200			5.096	13
4.796	vw			4.809	210	4.82	25	4.796	40
				4.330	130			4.31	8
				4.163	220	4.16	12	4.16	16
3.969	vvw			3.864	001			3.86	8
3.739	vw	3.708	16	3.726	011			3.70	20
3.590	s	3.576	67	3.583	040	3.57	56	3.58	62
				3.486	230				
3.440	w	3.433	20	3.437	101	3.420	84	3.42	70
3.401	wm	3.401	53	3.404	300				
3.099	vw	3.089	5	3.099	121				
3.074	wm	3.068	85	3.074	320	3.07	92	3.07	67
3.038	wm	3.032	100	3.029	221	3.04	100	3.04	100
		2.779	5	2.815	211			2.82	10
		2.637	5	2.627	041	2.637	10	2.63	11
2.508	vw	2.508	5	2.512	410			2.507	16
		2.495	24	2.497	250			2.496	29
2.468	vw	2.468	32	2.479	341	2.468	25		
				2.251	430			2.25	5
				2.191	427			2.202	7
				2.074	440			2.07	8
								1.98	6
1.957	w	1.957	5	1.956	161			1.95	32
1.945	vw	1.939		1.942	261	1.94	35		
1.916	vw	1.916	32	1.916	421	1.915	32	1.918	36
1.890	vw	1.895	27	1.904	450				
		1.884	21	1.885	122	1.876	23	1.887	16
				1.790	080	1.784	12	1.79	14

[a] s=strong, w=weak, wm=fairly weak, vw=very weak, vvw=extremely weak

and f. The X-ray diffraction data obtained for sample e (350°C) and sample f (500°C) are represented in Table 3. These data agree with similar data for β-UO_3 obtained by other investigators [29,37–39]. The recorded patterns differ in the following respects:

(i) change in the relative intensities of a number of lines, and

(ii) few lines are broadened which can be attributed to difference in crystallite size of UO_3 powders.

However, the coincidence of sample f with the data of Debets [39] is more pronounced than in the case of sample e.

Kinetics

The previous results indicate that the thermal decomposition of AU includes dehydration reaction, complicated reactions to form β-UO_3 and thermal decomposition of β-UO_3 to U_3O_8. The average value for the order of the dehydration reaction at 193°C for samples a and b is found to be 1.021 (approximately unity), i.e. first order reaction. The kinetics of the thermal decomposition of dehydrated AU to β-UO_3 has passed through two stages. The average value for the order of the chemical reaction in the first stage, at 327.6 ± 4°C for samples a–c is found to be 1.526. This may be due to the removal of some ammonia beside the nitrate impurity which may complicate the chemical reactions occurring. The average value for the order of the chemical reaction in the second stage at 441.5°C is found to be 0.961 (approximately unity), i.e. first order reaction, and this is due to removal of the retained ammonia.

The kinetics of the thermal decomposition of β-UO_3 to U_3O_8 at 636 ± 10°C are found to be typically that of a first order reaction (the average value for samples a–g = 1.075). This is in fair agreement with Dharwadkar and Karkhanavala [29], where the order of reaction calculated by this method was found to be 0.889, i.e. approximately unity.

The activation energy and frequency factor are computed from the method of Fuoss et al. [24]. The specific reaction rate constant, K_r, for the thermal decomposition of β-UO_3 to U_3O_8 is found to be

$$K_r(\mathrm{s}^{-1}) = 1.4323 \times 10^{18} \exp(-84798.16/RT)$$

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