JOURNAL OF MATERIALS SCIENCE 8 (1973) 606–610

Thermal decomposition of uranyl acetate

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The thermal decomposition of uranyl acetate has been studied. By means of thermogravimetric, differential thermal analysis, X-ray and infra-red analysis the intermediate and final products of the decomposition are identified. After dehydration uranyl acetate decomposes to UO_2 which is partially oxidized to UO_3. The final product, U_3O_8, is obtained from the interaction of UO_2 with UO_3 in solid state.

1. Introduction

Only a few papers have been published on thermal decomposition of metal acetates. In spite of the wide investigations on uranium oxides, the number of the published reviews concerning thermal decomposition of uranyl acetate is small. Duval [1] has studied the thermal stability of analytic standards including uranyl acetate. According to Duval, uranyl acetate is stable up to 100° C. The water of crystallization is released up to 159°C. Anhydrous salt is stable enough within the temperature interval between 159 and 247° C. It decomposes slowly at 247° C, rapidly at 380°C, and explosively at 412°C.

Kobayashi [2] has studied the decomposition of uranyl acetate in air. His results, however, do not agree with those of Duval. According to Kobayashi, the uranyl acetate dihydrate releases the water of crystallization between 60 and 120°C; no monohydrate was found and the anhydrous salt was reported to be stable up to 200°C, when slow decomposition occurred. At 297°C decomposition was complete. The slight weight increase observed between 300 and 320°C was supposed to be due to oxidation of UO_2. The solid residue was U_3O_8. Not long ago, Clough *et al* [3] published a detailed and systematized study of thermal decomposition of uranyl acetate in nitrogen and air. The changes in the specific surface area and density during decomposition were stated. Some residues of decomposition were identified, and the kinetics and mechanism of decomposition were suggested.

In a former paper of ours [4] we have done a derivatographic study of the mixture of semiconductive borate oxide glass. A high exothermal peak was observed at 400°C on the DTA curve of a mixture containing uranyl acetate. We assumed that this peak was due to the thermal decomposition of uranyl acetate. The purpose of the present paper is to study the thermal decomposition of uranyl acetate, to identify the intermediate and final products and to suggest a mechanism of decomposition.

2. Experimental

2.1. Materials

The experiments announced in that paper have been carried out on the commercially available hydrated uranyl acetate (UO_2 $(CH_3COO)_2$ $2H_2O$). The analysis of the latter, carried out according to [4], gave a purity of 99.5% of the theoretical uranium concentration.

2.2. Thermogravimetric and differential thermal analysis

The thermal and thermogravimetric analyses were carried out using a derivatograph Paulik-Paulik-Erdey (OD-102 model) [5]. The sample, a concentration of 0.4 g, was heated from ambient temperature up to 1000°C. The reference thermocouple was surrounded by an equivalent amount of Al_2O_3, previously heated at 1200°C. The heating-rate was maintained within 5°C min^{-1}, and the ambient atmosphere was air. The simultaneous plotting of TG, DTA and DTG curves, made possible by that method, secures separate evaluation even of an overlapping process and a more accurate picture of the thermal decomposition.

In order to give a more precise characteristic of the initial and reaction products and of the process of thermal decomposition of uranyl acetate as a whole, we used X-ray diffraction and infra-red spectroscopy of samples of uranyl acetate dihydrate roasted in the coarse of 3 h at a corresponding temperature.

2.3. X-ray diffraction

The X-ray diffraction analysis based on diffraction of X-ray was carried out by using the powder method [6]. The diffraction picture was obtained by a diffractometer URS-50IM with RKD camera and filtered CuK_α radiation, wave length $\lambda = 1.54$ Å. For absorbing the K_β radiation, a Ni foil, 20 µm thick was used as a filter. The ionizing record of the diffracted X-rays was done at a speed of the counter 1 ° min^{-1}, and diagram tape speed – 600 mmh^{-1}. Identification of the phases was effected according to the standard tables of Sidorenko [7], which contain information on the inter-plane space and the relative intensity of the lines of uranium minerals diffractograms.

2.4. Infra-red spectroscopy

The absorption infra-red spectrum in the interval between 400 and 2000 cm^{-1}, was recorded on a "Zeiss-Jena" spectrometer, UR-10 type. The samples were prepared following the technique of pelletizing 2 to 4 mg of the substance with 200 mg KBr. Pellets of KBr were taken as standards.

3. Results

3.1. Thermogravimetric and differential thermal analysis

When heated in air, dihydrate uranyl acetate loses its water of crystallization between 95 and 140° C. The anhydrous salt is stable up to 245° C, at which point it starts decomposing slowly. Decomposition can be noticed from 325 up to 400° C. Fig. 1 illustrates the slight weight increase which is observed within the temperature interval between 360 and 410° C.

The differential thermal analysis of air (Fig. 1) illustrates an endothermal peak between 95 and 140° C. At 325° C a very small endothermal peak is observed, followed by a great exothermal peak with maximum at about 400° C which tails off at 410° C. In that case the great exothermal peak completely overlaps the endothermal one which is due to the thermal decomposition of the anhydrous salt.

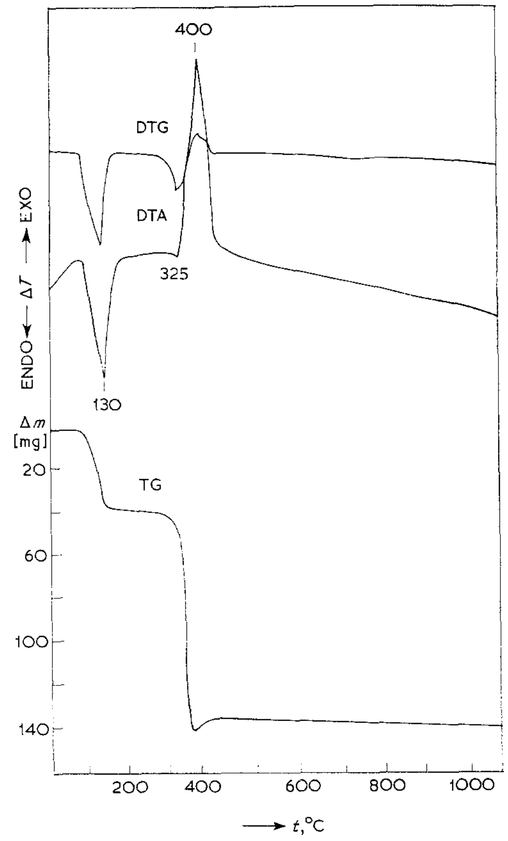


Figure 1 Thermal decomposition of uranyl acetate in air.

3.2. X-ray diffraction analysis

The samples of uranyl acetate dihydrate put in quartz boats were placed in a silite box furnace to undergo thermal decomposition at 150, 400, 1000, and 1600° C, in the course of 3 h. Fig. 2 illustrates the diffraction patterns of the initial acetate and of the products of its thermal decomposition at the above-mentioned temperatures.

The following data on the inter-plane space were obtained from the X-ray analysis of the initial uranyl acetate dihydrate: d (Å) = 1.43; 1.50; 1.70; 2.05; 2.40; 2.93; 3.91; 5.86; and 8.04. When uranyl acetate dihydrate is heated at 150° C, the X-ray responses which are due to anhydrous uranyl acetate, correspond to the inter-plane space d (Å) = 1.44; 1.56; 1.80; 2.25; 2.41; 2.74; 3.96; 4.62; and 6.32. The inter-plane space d (Å) at 400° C is: 1.42; 1.56; 1.76; 1.92; 2.07; 2.63; 3.40; and 4.15; with the rise of temperature up to 1000 and 1200° C, the change

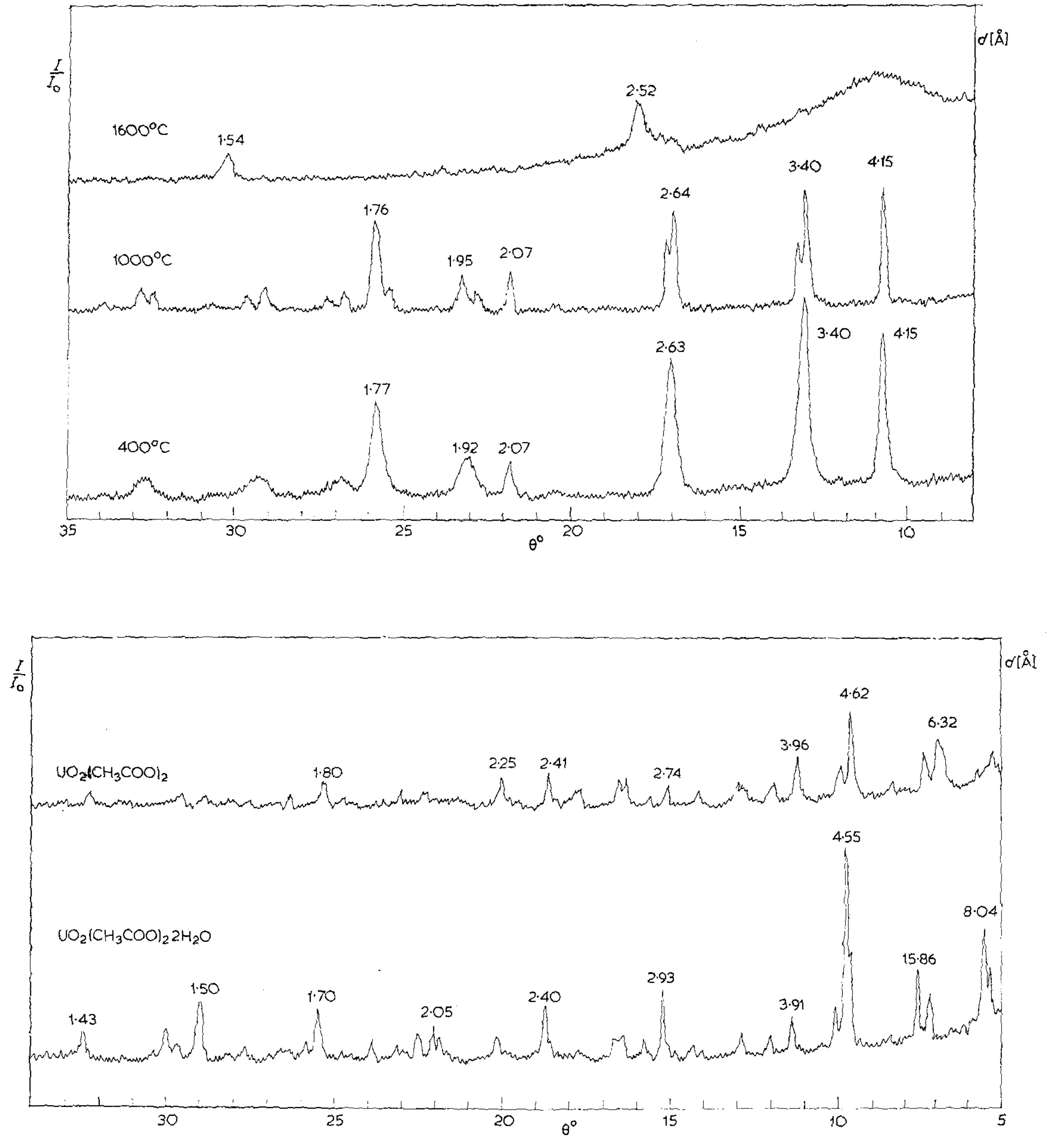


Figure 2 X-ray diffraction bands of hydrated, anhydrous uranyl acetate and the uranium oxides related with its thermal decomposition, at 400, 1000 and 1600° C.

is negligible: 1.42; 1.58; 1.77; 1.95; 2.07; 2.64; 3.42; and 4.15. Besides, at these temperatures, doubling of the X-ray lines is observed.

At a roasting temperature of 1600° C the diffraction pattern of the polycrystal substance disappears. Only two weak responses corresponding to inter-plane space *d* (Å) = 1.54 and 2.52 are observed and there appears a halo characteristic of the amorphous state.

3.3. Infra-red spectroscopy

The absorption infra-red spectra of uranyl acetate and the products of the thermal decomposition studied in the interval of between 400 and 1200

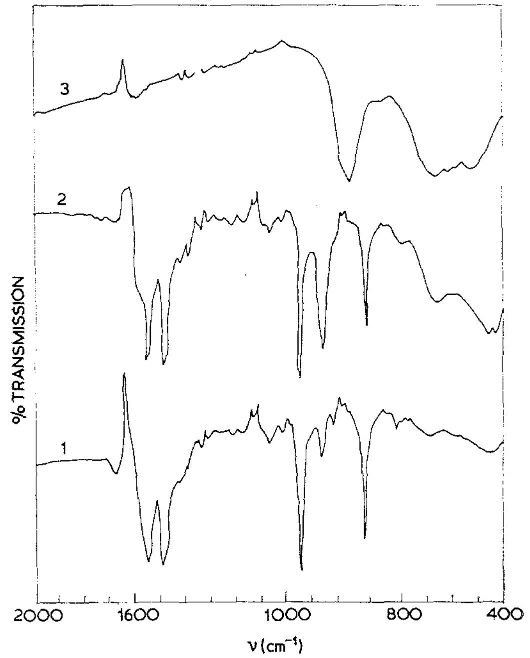


Figure 3 Infra-red spectra of hydrated, anhydrous uranyl acetate and uranium oxides related with its thermal decomposition, at 280 and 1000° C.

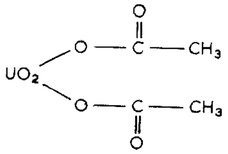
cm^{-1} are shown on Fig. 3. The absorption of the UO_2^{2+} group of the uranyl acetate dihydrate is mainly manifested at 740 and 940 cm^{-1} (curve 1). Uranyl acetate decomposed at 280° C is represented by curve 2. Apart from the response characteristic of the UO_2^{2+} group, an additional response at 850 cm^{-1} is also observed. According to the recent investigations [8] on the uranium-oxygen system $U_3O_8-UO_3$, that response is due to U–O bonds. It can be assumed that at 280° C an intermediate amorphous modification of UO_3 appears. The responses occurring at 1000° C are due to U_3O_8 and they agree with the above-mentioned investigations [8].

4. Discussion of results

Considering the experimental results shows that decomposition of uranyl acetate dihydrate starts with dehydration according to the equation

$$UO_2(CH_3COO)_2 2H_2O \rightarrow UO_2(CH_3COO)_2 + 2\,H_2O.$$

The initial stage of the thermal decomposition of the anhydrous uranyl acetate represents the breaking of the chemical bonds



denoted with the small endothermal peak at 325° C. The large exothermal peak on the differential thermogram at 400° C is due to the reaction

$$3UO_2 + O_2 \rightarrow U_3O_8$$

When uranyl acetate is heated slowly, however, at the point of 280° C presence of an intermediate phase, orange coloured, is observed. Identification of the latter by means of infra-red spectroscopy shows that it represents active UO_3. On account of that, oxidation of UO_2 to U_3O_8 may be represented by the next two intermediate processes: oxidation of UO_2 to UO_3

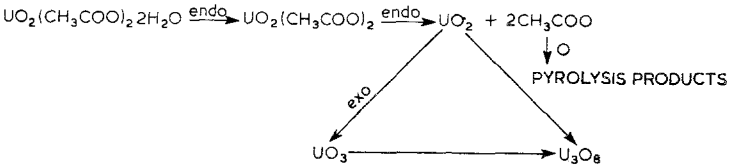
$$UO_2 + O_2 \rightarrow UO_3$$

and interaction in a solid phase of UO_2 and UO_3 according to the equation

$$UO_2 + 2UO_3 = U_3O_8$$

U_3O_8 thus obtained is identified by means of X-ray diffraction analysis, infra-red spectroscopy and oxy-red analysis. At a temperature of 1600° C, the latter is decomposed to $\alpha-U_4O_9$ [9].

The diagram of the thermal decomposition of uranyl acetate can be represented thus:



5. Conclusions

Thermal decomposition of uranyl acetate dihydrate is studied using thermal and thermogravimetric analysis.

Anhydrous uranyl acetate is obtained in the first phase of the multi-stage decomposition.

Decomposition of anhydrous uranyl acetate to UO_2 occurs in the second stage. At the same time, oxidation of UO_2 to UO_3 takes place; it is expressed by a large exothermal peak at 400°C on the differential thermogram. Simultaneously, a weight increase is observed on the thermogravimetric curve. It is due to the process of oxidation of UO_2 to UO_3. Formation of U_3O_8 is due ot the interaction of UO_2 and UO_3 in solid phase.

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Received 31 May and accepted 4 July 1972.