

## DISSOCIATION MECHANISM FOR AMMONIUM URANATE

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### ABSTRACT

DTA, TG and DTG curves obtained in various atmospheres using different heating rates, as well as X-ray examination were used to study the dissociation mechanism of ammonium uranate. The activation energies for the initial stages of decomposition were determined.

### INTRODUCTION

Ammonium uranates are used as starting materials for the production of uranium dioxide, which is utilized as a nuclear fuel, and exist over a wide composition range depending on the preparation conditions. They can be represented by the formula  $\text{UO}_2 \cdot (\text{OH})_{2-x} \cdot (\text{ONH}_4)_x \cdot y\text{H}_2\text{O}$  where  $x$  ranges between 0 and 0.7 [1].

Woolfrey [2] summarized the previous work on thermal analysis, which will be discussed later in view of the present results.

### EXPERIMENTAL TECHNIQUE

A reaction-vessel containing 2 l of pure uranyl nitrate solution (with 70 g uranium/l in 0.02–0.04 M  $\text{HNO}_3$ ) was placed in a thermostat adjusted at 65°C. Ammonia solution was added while vigorously stirring; the final pH was adjusted to 8. After adding ammonia, the solution was stirred for a further 15 min, after which the pH was again readjusted. The precipitate was separated by filtration and was washed with distilled water, alcohol and then acetone before drying at 45°C for 24 h.

X-Ray examination of the powder obtained gave a pattern identical to  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , which is an end member in the solid solution range mentioned above.

Preliminary investigations on the effect of the thickness of the uranate layer and the type of crucible were carried out using the derivatograph. The effect of the type of the crucible is shown in Fig. 1.

To determine the intermediate phases present, X-ray examination was carried out, and to confirm the reactions deduced, thermal analysis was performed under various atmospheres.

Thermogravimetric curves obtained at different heating rates were utilized to calculate the activation energy using the technique recommended by Carroll and Manche [3]. This technique was selected since thermogravimetric curves give more reliable results than DTA curves and, in deducing this method, the reaction rate was not considered to be proportional to the  $n$ th power of the undecomposed solid as in the case of homogeneous reactions. The latter assumption was adopted by various authors and the equations developed can have theoretical significance only in the cases where the value of  $n$  is 0,  $1/2$ ,  $2/3$  or 1 [4-6].

In this method,  $-dw/dt = k f(w)$  where  $w$  is the weight of the reactive portion of the sample, and  $k$  is the rate constant related to temperature by the Arrhenius equation,  $k = Z \exp(-E/RT)$ . If the heating rate  $\phi = dT/dt$ ,

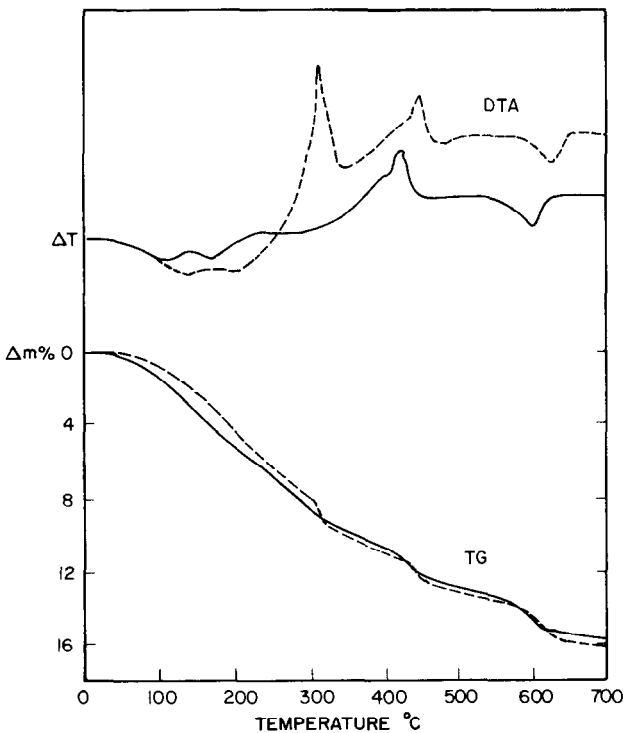


Fig. 1. Effect of the type of crucible on the decomposition of ammonium uranate. —,  $\text{Al}_2\text{O}_3$  crucible; - - - - - , Pt crucible.

then

$$-\frac{dw}{dT} = \frac{Z}{\phi} \exp(E/RT) f(w)$$

$$\ln\left[\phi\left(-\frac{dw}{dT}\right)\right] = \ln[Z(f(w))] - \frac{E}{RT}$$

A plot of  $\ln[\phi(-dw/dT)]$  versus  $1/T$  for a given value of  $w$ , obtained at different heating rates, will lead to a value of  $E$ .

## RESULTS AND DISCUSSION

The DTA curve obtained using an alumina crucible (Fig. 1) is similar to those published earlier [2]. Dehydration occurred in the range 40–200°C and the appearance of two successive endothermic peaks here suggest dehydration, giving a solid phase and liquid water followed by evaporation of the water. Both peaks occurred at higher temperatures in the presence of humid air. The exothermic peak was attributed to the dissociation of nitrate impurities and detachment of  $\text{NH}_4^+$  [2,7]. It is evident from Fig. 1 that the alumina crucible shifted all the reactions towards lower temperatures and the presence of platinum caused a new exothermic peak to develop, suggesting that Pt acts as a catalyst for the removal of ammonia which occurred in two steps. The two exothermic peaks were retarded in the presence of humid air.

The existence of a shoulder in the second exothermic peak led some authors to suggest that the evolved ammonia reduced part of the  $\text{UO}_3$  formed to  $\text{U}_3\text{O}_8$  [7,8] or  $\text{UO}_{2.9}$  [8,9]. To examine this hypothesis, the uranate heated at 450°C was examined by X-rays. The presence of hexagonal  $\text{U}_3\text{O}_8$  (ASTM card 8-244) indicates partial autoreduction of  $\text{UO}_3$ . This reduction may be due to cracking of the evolved ammonia producing a reducing atmosphere. To support this idea a run was carried out in oxygen and it was found that the above exothermic peaks were shifted to higher temperatures due to the presence of a high oxygen partial pressure.

The last endothermic peak is due to reduction of  $\text{UO}_3$  to  $\text{U}_3\text{O}_8$ . In oxygen this peak was shifted to higher temperatures, as expected, and the X-ray powder pattern proved the existence of orthorhombic  $\text{U}_3\text{O}_8$  (ASTM card 2-0276). Above 650°C the slight continuous loss in weight can be attributed to the formation of non-stoichiometric oxygen-deficient  $\text{U}_3\text{O}_{8-x}$ .

From the thermogravimetric curves obtained in dry air, using heating rates of 5, 10, 15 and 20°  $\text{min}^{-1}$ , average values of activation energies were calculated using the method mentioned above. They were found to be 13  $\text{kcal mole}^{-1}$  for the dehydration reaction (first endothermic peak) and 6.7 and 20.5  $\text{kcal mole}^{-1}$  for the first and second exothermic peaks, respectively. The undetected change in the final endothermic peak, corresponding to the reduction of  $\text{UO}_3$  did not allow the authors to estimate the corresponding activation energy.

## CONCLUSIONS

Ammonium uranate dehydrates below 100°C in air giving liquid water which evaporates at higher temperatures. The activation energy for the dehydration is 13 kcal mole<sup>-1</sup>. At higher temperatures ammonia evolves exothermally on two steps. The cracked ammonia produces a reducing atmosphere causing partial reduction of UO<sub>3</sub> to hexagonal U<sub>3</sub>O<sub>8</sub>. The activation energy for the two steps are 6.7 and 20.5 kcal mole<sup>-1</sup>. Finally, UO<sub>3</sub> is reduced to oxygen-deficient U<sub>3</sub>O<sub>8</sub>.

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