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ENTHALPIMETRIC MEASUREMENTS IN SOLID—SOLID REACTIONS. VII. A STUDY OF THE URANYL ACETATE—PHENYLUREA SYSTEM

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ABSTRACT

The solid—solid interaction reactions between uranylacetate and phenylurea have been investigated by DSC. The associated ΔH values, apparent activation energy and apparent reaction order have been evaluated. The kinetic parameters suggest that the solid—solid interaction can be considered to be a chemically-controlled process.

INTRODUCTION

The acetate ion, like the nitrate, is a potentially bidentate ligand toward uranyl and a close similarity between these two ligands is reasonable. In the structure of $UO_2Ac_2 \cdot 2\ H_2O$ [1], six oxygen atoms are present in the nearly planar equatorial coordination system: four oxygens of the two bidentate acetates and two of the water molecules, both *trans* to each other; the structure of the anhydrous UO_2Ac_2 is not available, as the compound seems to exist in different allotropic forms [2].

Several acetate complexes of the uranyl ion have been prepared [3—7] and the possible structure has been discussed; the usual equatorial coordination number of these complexes is six and the presence of binding acetate groups in polymeric structures has also been proposed [7].

Considering the above mentioned close similarity between the nitrate and acetate ligands, in this work, as a continuation of studies on solid—solid interactions, we consider the reactions of $UO_2Ac_2 \cdot 2\ H_2O$ and phenylurea in the solid state, according to the reaction

$$UAc_2 \cdot 2\ H_2O + n\ Ph \rightarrow UAc_2Ph_n + 2\ H_2O$$

where $n = 2$—6, $U = UO_2$ and Ph = phenylurea.

Owing to the possibility of obtaining anhydrous UAc_2 (thermally stable up to 295°C) the following reactions are also attempted

$$UAc_2 + n\ Ph \rightarrow UAc_2Ph_n$$

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where n = 2—6. The value of n was chosen in the range 2—6 to obtain the equatorial CN 6 around the uranium atom.

The enthalpic values associated with these reactions are calculated and compared with those obtained using the nitrate ligand. The kinetics and mechanism of the thermal synthesis and decomposition of the UAc_2Ph_n complexes were considered for this purpose to determine whether the overall synthesis, like the decomposition rate, is controlled by a chemical or physical process [8-10].

EXPERIMENTAL

Materials

Uranylacetate dihydrate (J.T. Baker) and phenylurea (C. Erba RP) were used without any further purification.

Differential scanning calorimetric measurements

The DSC curves were obtained with a Perkin-Elmer model 1B DSC, in an aluminium covered vessel in a dynamic nitrogen atmosphere (5 l h^{-1}) and at a heating rate of 4°C min^{-1}. The total weight of the system under study was about 5—6 mg. A closed empty vessel was used as reference. The solid—solid interaction reactions were performed by introducing finely powdered stoichiometric mixtures of the reactants into the vessel, and heating successively.

The ΔH values are referred to the melting ΔH value of indium (6.79 cal g^{-1}). All the obtained values are expressed in kcal $mole^{-1}$. The molecular weights of the synthesized complexes are calculated assuming that the solid—solid interaction is complete.

Thermal decomposition

The simultaneous TG, DTG and DTA were performed with a Mettler thermoanalyzer in static air, dynamic air and dynamic nitrogen atmospheres (5 l h^{-1}). The sample weight amounted to about 20 mg and the heating rates were 2 and 4°C min^{-1}. A Mettler model T-TD3 crucible holder, 0.1 ml aluminium microcrucibles and Al_2O_3 as the thermally inactive reference material were used. The activation energy, E_a^*, and the apparent order of the reaction, n, were determined by the methods described in the literature [11—13].

RESULTS

$UAc_2 \cdot 2\,H_2O$

The DSC curve of this compound exhibits an endothermic process due to dehydration, in one step, in the temperature range 87—127°C; the associated ΔH_d value is 19.7 kcal mole^{-1}. The anhydrous salt is thermally stable up to 295°C. Thermal analysis confirms the DSC results. The first step of the thermal decomposition, as indicated by TG and DTG curves, corresponds to the stoichiometry

$$UAc_2 \cdot 2\,H_2O_{(s)} \rightarrow UAc_{2(s)} + 2\,H_2O_{(v)}$$

At 295°C the uranylacetate decomposes exhibiting only one irregular endothermic DTA peak and giving rise to U_3O_8 and unidentified gaseous products. The thermal behaviour is reported in Fig. 1.

Phenylurea.

The thermal behaviour has previously been reported [14].

Solid—solid interaction

Considering the large thermal stability of anhydrous UAc_2, the solid—solid interactions between UAc_2 and Ph, in the stoichiometric ratios $1:n$ (n =

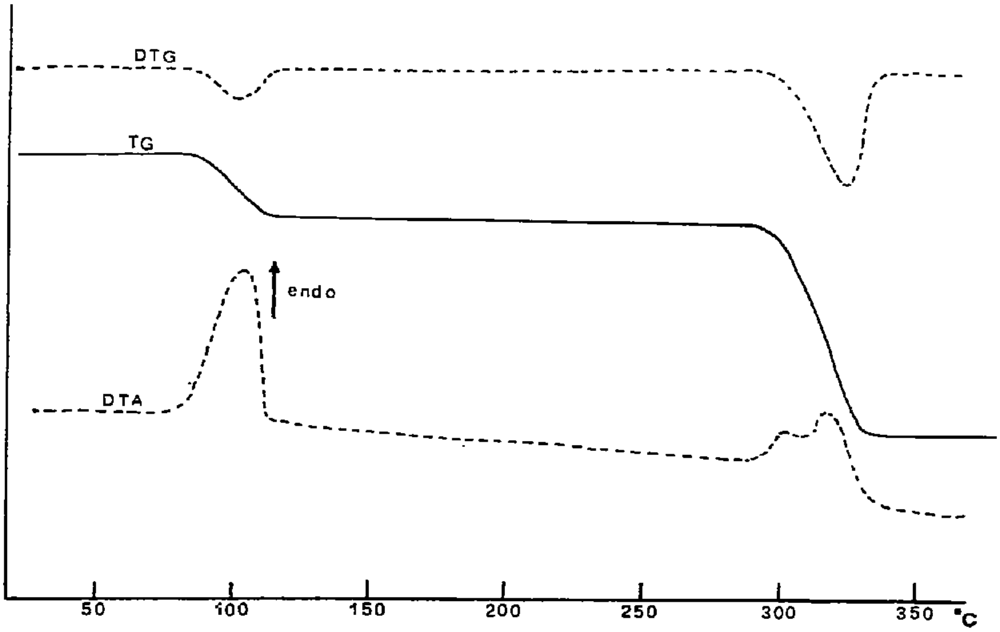

Fig. 1. The thermal behaviour of $UAc_2 \cdot 2\,H_2O$ in a dynamic nitrogen atmosphere at ϕ = 2°C min^{-1}.

TABLE 1

ΔH values (kcal mole^{-1}), apparent activation energy, E_a^* (kcal mole^{-1}), and apparent order, n, of the dehydration and associative reactions

	ΔH_d	ΔH_t	ΔH_r	E_a^*	n
$UAc_2 \cdot 2\,H_2O$	19.7	19.7		29	0.64
$UAc_2 \cdot 2\,H_2O + 2\,Ph$	19.7	15.2	−4.5	43	0.71
$UAc_2 \cdot 2\,H_2O + 3\,Ph$	19.7	27.9	+8.2	40	0.68
$UAc_2 \cdot 2\,H_2O + 4\,Ph$	19.7	11.2	−8.5	38	0.70
$UAc_2 \cdot 2\,H_2O + 5\,Ph$	19.7	22.3	+2.6	27	0.66
$UAc_2 \cdot 2\,H_2O + 6\,Ph$	19.7	26.45	+6.7	26	0.68

ΔH_d = Enthalpimetric value of the dehydration process.
ΔH_t = Enthalpimetric value of the overall process.
ΔH_r = Enthalpimetric value of the solid—solid interaction.

2, 3, 4, 5, 6), were investigated. In all the considered reactant systems the DSC curves exhibit an endothermic process only at $T = 149°C$. The ΔH value (6.1 kcal mole^{-1}) associated with this process, and coinciding with ΔH_m of the melting of phenylurea [14], clearly indicates that no interaction occurs between the reactants.

Different behaviour was observed using the dihydrated uranylacetate salt as reactant. Qualitatively the thermal behaviour in the range 25—160°C is similar to that of the hydrated salt alone, but different values of ΔH asso-

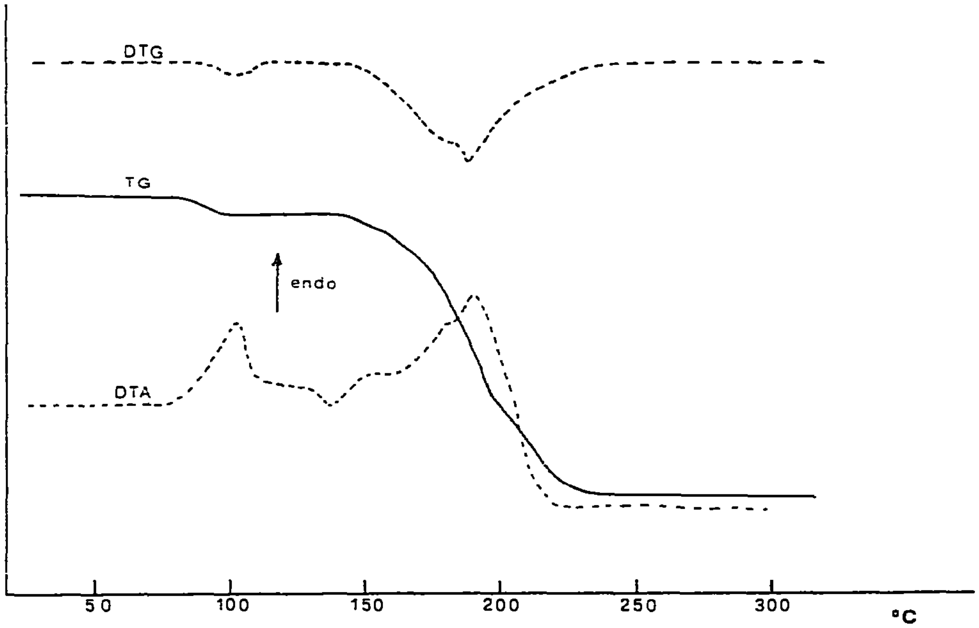

Fig. 2. The thermal behaviour of UAc_2Ph_5 complex in a dynamic nitrogen atmosphere at $\phi = 2°C\ min^{-1}$.

TABLE 2

Apparent order, n, apparent activation energy E_a^* (kcal mole^{-1}) and starting temperature of decomposition T_i(°C) of the dissociative reaction at $\phi = 2°\text{C min}^{-1}$

Complex	n	E_a^*	T_i
UAc_2Ph_2	1.8	53.5	146
UAc_2Ph_3	1.4	45.8	144
UAc_2Ph_4	1.8	29.8	152
UAc_2Ph_5	1.5	46.8	158
UAc_2Ph_6	1.5	28.6	156

ciated with the dehydration processes were observed depending on the ratios used. The chemical process, as indicated by the TG curve, is

$$UAc_2 \cdot 2\,H_2O_{(s)} + n\,Ph_{(s)} \rightarrow UAc_2Ph_{n\,(s)} + 2\,H_2O_{(v)}$$

Assuming that ΔH_t is the enthalpic content of the overall process (dehydration and simultaneous coordination of phenylurea), it is reasonable to evaluate ΔH_r of the interaction from

$$\Delta H_r = \Delta H_t - \Delta H_d$$

The values are reported in Table 1.

The activation energy, E_a^*, and the associated reaction order, n, were also calculated from DTA and TG curves and the relative values are also reported in Table 1.

Thermal decomposition

All the UAc_2Ph_n obtained complexes at $\phi = 2°\text{C min}^{-1}$ decompose in several steps, as indicated by the thermoanalytical TG, DTG and DTA curves (Fig. 2), according to the following scheme

$$UAc_2Ph_n \rightarrow UAc_2 + n\,Ph \qquad \text{(a)}$$

$$UAc_2 \rightarrow U_3O_8 + CO_2 + H_2O + \text{unidentified gaseous products} \qquad \text{(b)}$$

The E_a^* values and the apparent order of reaction, n, were determined for reaction (a) and the values are reported in Table 2.

CONCLUSIONS

As shown in Table 1, the 2/3 apparent order of reaction was found for all the considered systems, using $UAc_2 \cdot 2\,H_2O$ as reactant. Therefore, the crystal structure of the reactants allows the nucleation of the new species, and the solid—solid interaction can be considered to be a chemically-controlled process.

The impossibility of obtaining products by solid—solid interaction using anhydrous UAc_2 salts suggests that this salt can maintain CN = 6 in the solid state through the presence of bridging acetato groups in a stable polymeric structure.

It seems of interest to point out the differences between the ΔH_r values, endothermic and exothermic, reported in Table 1. In our opinion, this indicates the possibility of obtaining different stable structures depending on the number of Ph molecules. Considering the reaction

$$UAc_2 \cdot 2\,H_2O + n\,Ph \rightarrow UAc_2Ph_n + 2\,H_2O$$

the uranyl group, losing the water molecules, maintains CN = 6 in the solid state as a monomeric unit when $n = 2$ and 4. A different and polymeric form is obtained when $n = 3$, 5, 6. With acetato bridges and the uranyl groups CN = 5 is probably achieved. The activation energies of the two types of complexes are not very different.

In fact, monomeric complexes of the type UAc_2L_2 have been prepared, as well as dimeric complexes containing the same neutral ligand [5,6]. Structural data for the dimeric form of $[UAc_2(Ph_3PO)_2]_2$ indicate that the equatorial CN of each of the two uranium atoms is five and the dimeric unit is realized by two bridging acetato groups. The presence of bridging acetato groups in polymers has also been indicated by PMR [7] and luminescence spectra [15].

The apparent order of reaction (Table 2) obtained from TG and DTG curves of the thermal decomposition of the considered complexes indicates that the rate controlling step is not the U—Ph bond rupture, at variance with that found for the solid—solid interactions.

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