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ENTHALPIMETRIC MEASUREMENTS IN SOLID—SOLID REACTIONS. VIII. STUDY OF THE URANYL ACETATE—UREA SYSTEM

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ABSTRACT

Solid complexes of uranyl acetate and urea were obtained by reaction in the closed vessel of a DSC apparatus. The ΔH values associated with the syntheses were evaluated The results suggest that these complexes have monomeric structure, different to the analogous complexes of phenylurea.

INTRODUCTION

On considering the theoretical and practical importance of the UO_2^{2+} ion, notable attention has always been directed toward the study of its complexes [1—4]; in particular, in order to obtain solid uranyl complexes, solid—solid interactions have often been studied [5—7].

In previous papers we have studied the formation of the uranyl nitrate complexes with several "soft" and "hard" ligands in order to correlate the thermodynamic parameters with the grasp and coordination power of the chelating ligands [8—12].

The uranyl acetate complexes have also been widely investigated [13,14]; in a previous study concerning the formation of uranyl acetate—phenylurea complexes, we observed that the enthalpy values associated with the solid—solid interactions are endothermic or exothermic, according to the even or odd number of ligand molecules, and that this is probably due to the existence of different stable structures depending on the number of ligand molecules [15].

The aim of this work is to ascertain if this behaviour is always observed or if it is characteristic of the phenylurea complexes. Therefore, we have investigated the formation of complexes of uranyl acetate with another "hard" ligand, urea, having greater electronic density, with respect to the phenylurea, on the oxygen donor atom according to the following reaction

$$UO_2Ac_2 \cdot 2\ H_2O + n\ \text{Urea} \rightarrow UO_2Ac_2\text{Urea}_n + 2\ H_2O\ (n = 2\text{—}6)$$

Owing to the possibility of obtaining the anhydrous UO_2Ac_2 (thermally stable up to 295°C), the following reactions were also attempted

$$UO_2Ac_2 + n\ \text{Urea} \rightarrow UO_2Ac_2\text{Urea}_n\ (n = 2\text{—}6)$$

Furthermore, we have utilized anhydrous reactants, according to the scheme

$UO_2Ac_2Urea_m + n\ Urea \rightarrow UO_2Ac_2Urea_{m+n}\ (m = 2\text{—}5; n = 1\text{—}4; m + n = 3\text{—}6)$

$n = 2\text{—}6$ was chosen to obtain the equatorial coordination number 6 around the uranium atom.

EXPERIMENTAL

Materials

Uranyl acetate dihydrate (J.T. Baker) and urea (C. Erba RP) were used without any further purification. The $UO_2Ac_2Urea_2$ complex was prepared by mixing stoichiometric 1 : 2 amounts of uranyl acetate dihydrate and urea; the obtained mixture, finely powdered, was put in an oven at 90°C for 1 day. The resultant anhydrous yellow product was analyzed and its composition was in agreement with the theoretical composition. The UO_2Ac_2-$Urea_m$ ($m = 3, 4, 5, 6$) complexes were prepared as follows: stoichiometric molar amounts of uranyl acetate—$urea_2$ and urea, finely powdered, were thoroughly mixed in a glass mortar and then put in an oven at 120°C for 2 h. The composition of the obtained yellow products was in agreement with the theoretical composition.

DSC measurements

The DSC measurements were performed with a Perkin-Elmer model 1 B DSC calorimeter, in aluminium covered pans, in a dynamic nitrogen atmosphere ($5\ l\ h^{-1}$), at a heating rate of $4°C\ min^{-1}$, and using an empty pan as reference. The ΔH values were evaluated using the $\Delta H_{melting}$ of indium as calibration standard ($6.79\ cal\ g^{-1}$) and are reported in $kcal\ mole^{-1}$.

Solid—solid interactions

The solid—solid reactions were performed by introducing finely powdered stoichiometric mixtures of the reactants into the DSC pan and successively heating. The total weight of the system was about 5—6 mg. The associated enthalpic values were calculated as mentioned above and by considering the reactions to be complete.

RESULTS AND DISCUSSION

The thermal syntheses were attempted using both anhydrous and hydrated uranyl acetate. The attempts using anhydrous UO_2Ac_2 were unsuccessful analogously to the $UO_2Ac_2Phenylurea_m$ complexes; this is probably due to the stable polymeric structure of the UO_2Ac_2. $UO_2Ac_2 \cdot 2\ H_2O$ reacts with urea to form complexes in the stoichiometric molar ratios 1 : *m*

TABLE 1

Temperature, thermal processes and ΔH values of the reactants

Compound	T (°C)	Thermal process	ΔH (kcal mole^{-1})
UL_2	118	$\alpha \rightarrow \beta$	0.3
UL_2	154	Melting	3.1
UL_3	110	Melting	3.3
UL_4	110	Melting	7.1
UL_5	110	Melting	7.3
UL_6	110	Melting	4.5

(m = 2, 3, 4, 5, 6), but dehydration of the uranyl acetate, simultaneous to the syntheses, makes this reaction unavailable for determining the reaction ΔH_r values. Therefore anhydrous reactants were utilized, according to the scheme

$$UO_2Ac_2Urea_m + n\ Urea \rightarrow UO_2Ac_2Urea_{m+n} \quad (m = 2\text{—}5;\ n = 1\text{—}4;\ m + n = 3\text{—}6)$$

The results obtained by DSC for the reactants and the syntheses are reported and discussed below.

$UO_2Ac_2 \cdot 2\,H_2O$ (denoted $U \cdot 2\,H_2O$) and Urea (denoted L)

The thermal behaviour of both compounds has been reported previously [8,15].

$UO_2Ac_2L_2$ (denoted UL_2)

The DSC curve of this compound shows two endothermic effects: the first at 118°C (ΔH= 0.3 kcal mole^{-1}), and the latter at 154°C (ΔH = 3.1 kcal mole^{-1}). On cooling and re-heating the sample in the temperature range 80—170°C, the thermal effect at 118°C disappears, while that at 154°C remains

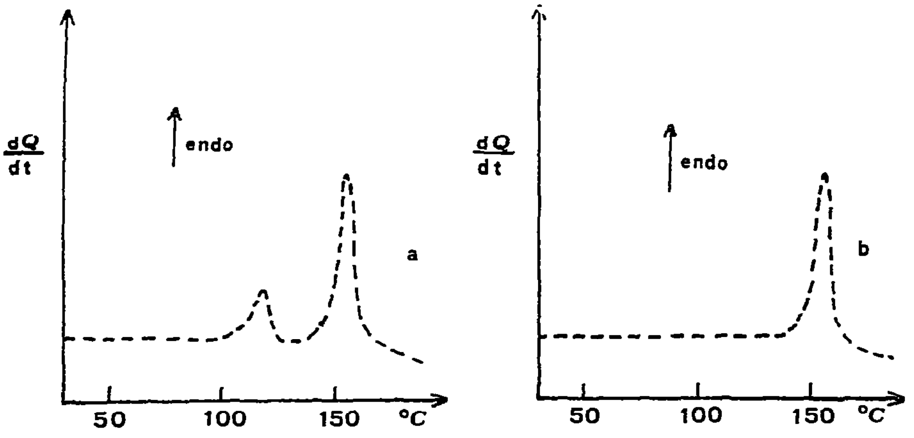

Fig. 1. Thermal behaviour of (a) UL_2 and (b) UL_2 re-heated after cooling.

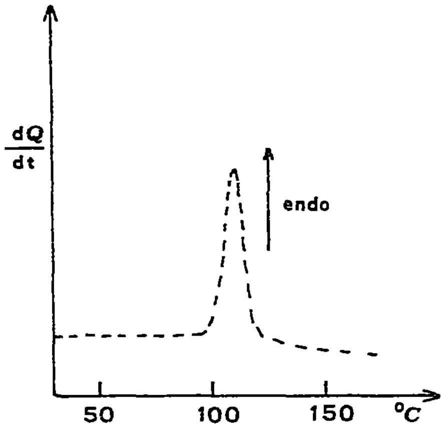

Fig. 2. Thermal behaviour of UL_m.

unchanged. The endothermic effect at 118°C seems to be due to a reversible $\alpha \rightarrow \beta$ transition; the β form reverts to the α form after 1 month, analogously to that previously found for the $UO_2(NO_3)_2Urea_2$ complex [8]. The ΔH values are reported in Table 1 and the DSC curves in Fig. 1.

$UO_2Ac_2Urea_m$ (denoted UL_m) (m -· *3, 4, 5, 6)*

The DSC curves of these compounds show only an endothermic effect at 110°C, due to the melting process, as confirmed by thermal microscopy analysis. The associated ΔH values (Table 1) are unchanged on cooling and re-heating in the temperature range 25—120°C. The thermal behaviour of the UL_m complexes is reported in Fig. 2

THERMAL SYNTHESES

UL_m + n L system (m = *2—5*, n = *1—4;* m + n = *3—6)*

At all considered molar ratios, the DSC curve shows only an endothermic effect at 110°C (Fig. 3a). On cooling and re-heating the mixtures in the temperature range 25—120°C, the enthalpic values associated with the peak decrease (Fig. 3b). It is worth noting that these latter ΔH values coincide with the melting ΔH_m of the UL_{m+n} complexes. The results are reported in Table 2.

This thermal behaviour suggests that the UL_m compounds react at near 110°C with n L molecules to form UL_{m+n} complexes. Moreover, for the UL_2 + n L system, the absence of the thermal process at 154°C due to the melting of UL_2 provides further evidence of the reaction.

In order to investigate if the UL_m + n L reactions are solid—solid interactions or occur in the melted phase, we have utilized Hess' law. The reaction ΔH_r evaluated by $\Delta H_r = \Delta H_T - \Delta H_m$ (i.e. on supposing that the mixtures react in the solid phase) follow Hess' law, indicating that the nucleation of the new species occurs in the solid state.

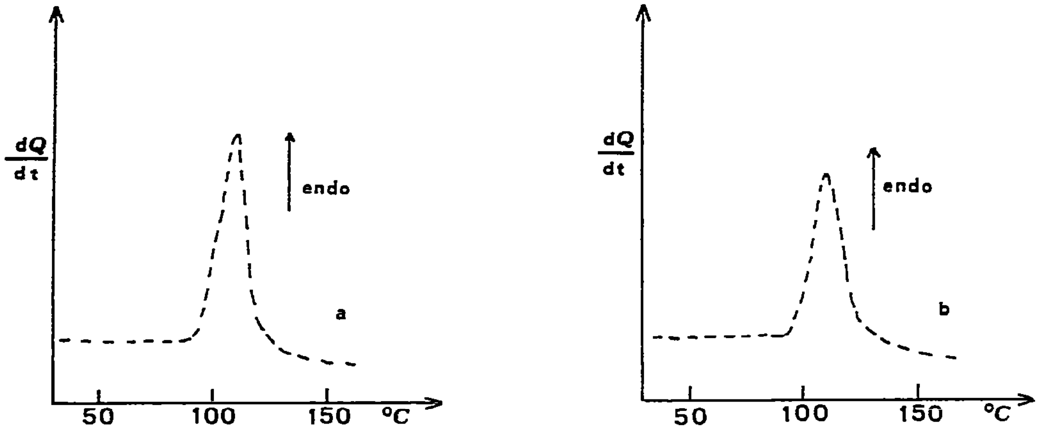

Fig 3. Thermal behaviour of (a) the $UL_m + n\,L$ system, and (b) the same mixture re-heated after cooling.

On comparing these results with those obtained for the corresponding syntheses of the uranyl nitrate complexes [8], we note that they are remarkably different. This may be due to a different reaction mechanism. In fact, the formation of the uranyl nitrate complexes seems to occur by formation of intermediate adducts in which the urea molecules are located in the external coordination sphere, whereas in the formation of the uranyl acetate complexes, the urea molecules enter directly into the internal coordination sphere, consistent with the presence of a single endothermic effect.

The differences of the associated ΔH_r values between the $UL_m + n\,L$ and $UL_m + (n-1)L$ interactions increase on increasing n. This trend indicates a smaller facility of the urea to coordinate with uranyl ion in those complexes in which a greater number of ligand molecules of the same kind are

TABLE 2

Temperature and ΔH values for the solid—solid reactions

System	1° Thermal cycle		Successive thermal cycles		
	T(°C)	ΔH_T (kcal mole^{-1})	T (°C)	ΔH_m (kcal mole^{-1})	ΔH_r (kcal mole^{-1})
$UL_2 + L$	110	4.9	110	3.3	1.6
$UL_2 + 2L$	110	9.8	110	7.1	2.7
$UL_2 + 3L$	110	13.7	110	7 3	6.4
$UL_2 + 4L$	110	18.8	110	4.5	14 3
$UL_3 + L$	110	8.2	110	7.1	1.1
$UL_3 + 2L$	110	12.3	110	7.3	5.0
$UL_3 + 3L$	110	15.9	110	4 5	11.4
$UL_4 + L$	110	11.3	110	7.3	4.0
$UL_4 + 2L$	110	15.2	110	4.5	10.7
$UL_5 + L$	110	12.1	110	4.5	7.6

present. This behaviour is different in respect to that of the uranyl nitrate complexes and in agreement with the more endothermic ΔH_r values obtained.

Also in contrast to the UAc$_2$Phenylurea$_m$ complexes, the ΔH_r values are all endothermic, indicating that a polymeric structure, by acetate bridges, similar to that supposed for the phenylurea complexes is not possible, and we believe that in all the considered complexes in the solid state, the uranyl group maintains the coordination number 6. Therefore, we believe that all these complexes have a hexagonal bipyramidal structure through the equatorial coordination of the ligand molecules and of the acetate groups in the plane perpendicular to the uranyl.

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