Thermochimica Acta, 42 (1980) 177—183
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

ENTHALPIMETRIC MEASUREMENTS IN SOLID—SOLID REACTIONS. PART V. STUDY OF THE MIXED COMPLEXES OF URANYL NITRATE WITH UREA AND THIOUREA

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(Received 19 May 1980)

ABSTRACT

The enthalpy values associated with solid—solid interactions of uranyl nitrate with both urea and thiourea to form mixed complexes are studied. The tendency of the urea to substitute the thiourea molecules bonded with the uranyl ion was observed. A greater facility of the ligand (hard or soft) to coordinate with the UO_2^{2+} ion in those complexes in which a greater number of ligand molecules are present was found.

INTRODUCTION

Solid—solid interactions involving the uranyl cation and neutral ligands containing oxygen or sulphur donor atoms have been reported previously [1—4]. The enthalpy values associated with these reactions indicated a lower reactivity of soft donors with respect to those having a hard character.

In this work, we report the solid state formation of mixed complexes of UO_2^{2+} (U) both with urea (L) and thiourea (Th). The aim of this investigation is to point out the reactivity of a hard ligand with a complex containing soft ligands, and vice versa.

The systems studied were

(a) $UL_{n(s)} + m\mathrm{Th}_{(s)} \rightarrow UL_n\mathrm{Th}_{m(s)}$

where $n = 2, 3, 4, 5$; $m = 1, 2, 3, 4$; $n + m = 3, 4, 5, 6$ and

(b) $U\mathrm{Th}_{2(s)} + nL_{(s)} \rightarrow U\mathrm{Th}_2L_{n(s)}$

where $n = 1, 2, 3, 4$.

The interactions of $U\mathrm{Th}_n + mL$ with $n \neq 2$ have not been considered owing to the impossibility of preparing such complexes.

EXPERIMENTAL

Materials

Uranyl nitrate hexahydrate (Fluka), urea (C. Erba RP) and thiourea (C. Erba RP) were used without any further purification. UL_n and $U\mathrm{Th}_2$ complexes were prepared following the procedure previously described [2,4]. The mixed complexes were prepared by intimately mixing stoichiometric amounts of reactants directly in the DSC apparatus.

DSC measurements

The ΔH measurements were performed with a Perkin-Elmer model 1B DSC calorimeter in covered aluminium pans. The heating rate was 4°C min^{-1} and the systems were kept in a dynamic nitrogen atmosphere (5 l h^{-1}). The total weight of the reactant mixture was about 5—6 mg. An empty closed vessel was used as reference.

The ΔH values have been evaluated using the ΔH melting value of indium as calibration standard (6.79 cal g^{-1}) and expressed in kcal mole^{-1}, assuming that the solid—solid interaction reaction is complete.

RESULTS AND DISCUSSION

The thermal behaviour of the unmixed reactants has been reported previously [2,4].

UL_2 + nTh system (n = 1, 2, 3, 4)

On heating stoichiometric mixtures of UL_2 and Th in the DSC apparatus, at all molar ratios considered, no thermal process occurs up to 118°C. In the temperature range 118—130°C, two unresolvable endothermic effects, followed by an exothermic one, were observed (Fig. 1). The endothermic effects vary on varying *n* and the corresponding total values are reported in

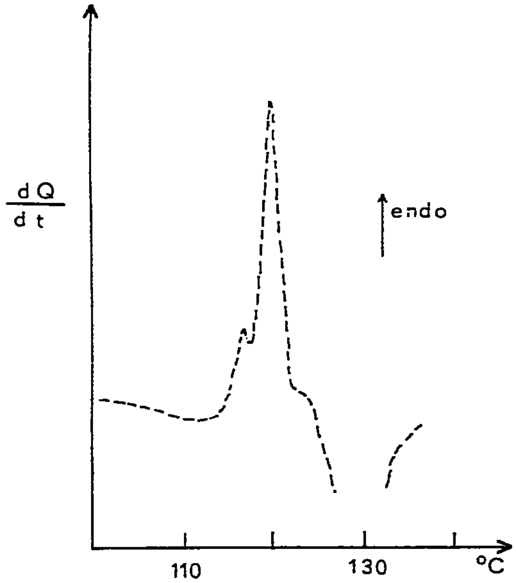


Fig. 1. Thermal behaviour of the UL_2 + 2Th system.

TABLE 1

Temperature (°C) and ΔH (kcal mole^{-1}) values of $\alpha \rightarrow \beta$ transitions and the solid—solid reactions and decomposition temperature (°C) of the products obtained

Reactant	$T_{\alpha\rightarrow\beta}$	$\Delta H_{\alpha\rightarrow\beta}$	T_r	ΔH_r	T_d
UL_2 + 1 Th	118 *	1.8 *	125 *	5.2 *	130
+ 2 Th	118	1.8	125	12.1	130
+ 3 Th	118	1.8	125	13.5	130
+ 4 Th	118	1.8	125	14.8	130
UL_3 + 1 Th	80	0.5	80	7.5	130
+ 2 Th	80	0.5	80	13.8	130
+ 3 Th	80	0.5	80	15.2	130
UL_4 + *n* Th	Not calculable				
UL_5 + 1 Th	No reaction				

* Assumed values.

Table 1. The impossibility of separating the endo—exothermic effects makes it impossible to carry out thermal cycles.

UL_3 + nTh system (n = 1, 2, 3)

The DSC curves of mixtures of UL_3 and Th, at all molar ratios considered, show a sharp endothermic peak at 80°C, which disappears on reheating several times after cooling (Fig. 2). At 120°C the exothermic decomposition is observed. Table 1 shows the ΔH values obtained relative to the endothermic process.

UL_4 + nTh system (n = 1, 2)

On heating stoichiometric mixtures of UL_4 and Th at all molar ratios considered, three endothermic effects, at 60, 80 and 95°C, are observed. At

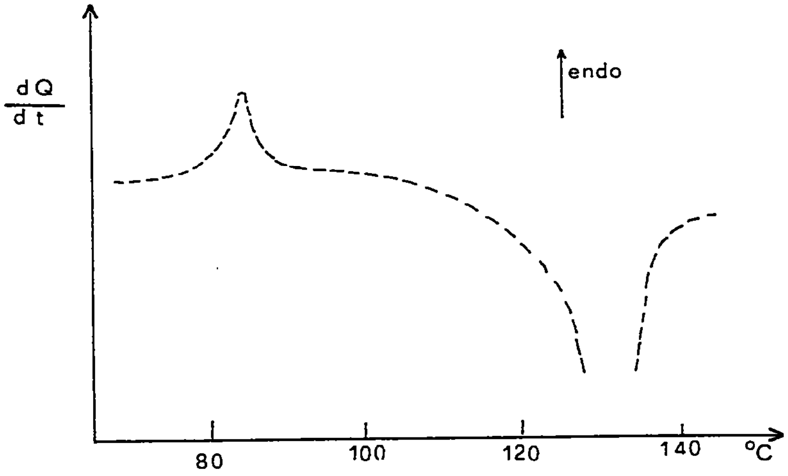
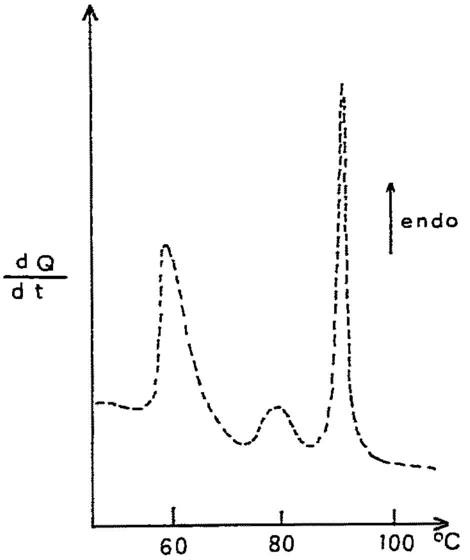


Fig. 2. Thermal behaviour of the UL_3 + Th system.



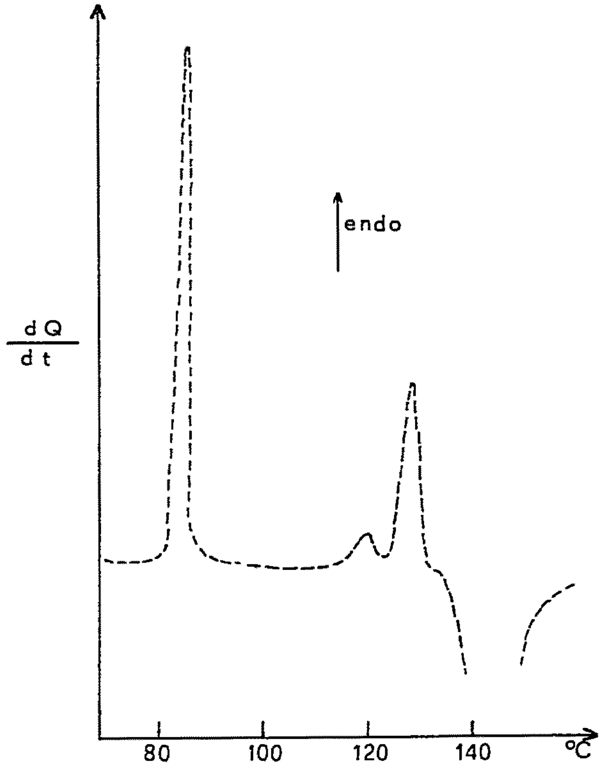


Fig. 3. Thermal behaviour of the UL_4 + Th system.

Fig. 4. Thermal behaviour of the UTh_2 + 2L system.

120°C, the mixture decomposes (Fig. 3). A synthetically prepared mixture of UL_3 and UL_5 (1 : 1 molar ratio) and nTh shows exactly the same behaviour. The ΔH values are reported in Table 1.

UL_5 + nTh system (n = 1)

This system does not seem to react and the thermal behaviour is indistinguishable from that described for UL_5 [2] and Th [4].

UTh_2 + nL system (n = 1, 2, 3, 4)

For $n = 1$, in the temperature range 25—130°C, the DSC curve exhibits two endothermic effects: at 80°C and at 115—130°C (double and unresolvable effect). An exothermic process, due to decomposition, is observed at 130°C. On reheating the reactant system several times before the decomposition in the temperature range 25—90°C, we observe the disappearance of the thermal effect at 80°C. Following the disappearance of this thermal effect, the ΔH value of the double unresolvable peak at 115—130°C is 3.3 kcal mole^{-1}.

For $n = 2$, the DSC curve exhibits three endothermic effects: at 85, 118 and 125°C. The exothermic process due to the decomposition is observed at 130°C (Fig. 4). It is worth noting that on reheating several times in the

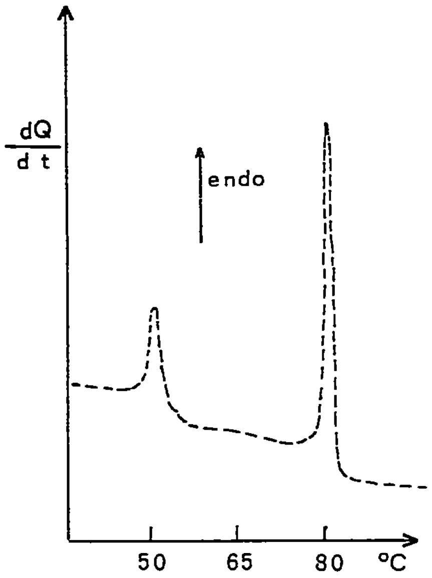


Fig. 5. Thermal behaviour of the UTh_2 + 3L system.

temperature range 25—90°C, the thermal effect at 85°C diminishes to zero. When this thermal effect disappears, the ΔH associated with the peak at 118°C is 1.8 kcal $mole^{-1}$ and that associated with the peak at 125°C is 12.5 kcal $mole^{-1}$.

For $n = 3$, the DSC curve shows two endothermic effects at 52 and 80°C. On reheating several times in this temperature range, both the endothermic peaks decrease and eventually disappear. At 130°C, the exothermic decomposition is observed (Fig. 5). The UTh_2 + 4L mixture shows a similar behaviour. The enthalpic values are listed in Table 2.

In order to correctly explain the results, it must be remembered [2,4] that: (i) the UL_2 complex shows the $\alpha \rightarrow \beta$ transition at 118°C ($\Delta H = 1.8$ kcal $mole^{-1}$) and the melting process at 196°C; (ii) the UL_3 complex undergoes an $\alpha \rightarrow \beta$ transition at 80°C (ΔH = 0.5 kcal $mole^{-1}$) and melts at 106°C; (iii) the UL_4 complex, which behaves as a stoichiometric mixture of UL_3 and UL_5, shows two endothermic peaks: one at 60°C, due to the $\alpha \rightarrow \beta$ transition of UL_5, and the other at 96°C, due to the sum of the $\alpha \rightarrow \beta$ transition of UL_3 and the $\beta \rightarrow \gamma$ transition of UL_5 and melting of the mixture; (iv) the

TABLE 2

Temperature (°C) and ΔH (kcal $mole^{-1}$) values of the solid—solid reactions and decomposition temperature (°C) of the products obtained

Reactant	T_r	ΔH_r	T_d
UTh_2 + 1 L	115 *	3.3	130
+ 2 L	125	12.5	130
+ 3 L	80	13.8	130
+ 4 L	80	14.9	130

* Assumed value.

presence of thiourea molecules as ligands in the uranyl nitrate complexes makes the products thermally unstable near 130°C.

Therefore, regarding the $UL_2 + n\mathrm{Th}$ system ($n = 1, 2, 3, 4$), we think that the peak observed at 118—130°C before the decomposition can be attributed to two simultaneous effects: $\alpha \rightarrow \beta$ transition of UL_2 and its reaction with $n\mathrm{Th}$ molecules to form UL_2Th_n complexes. This product immediately decomposes exothermically.

For the $UL_3 + n\mathrm{Th}$ system ($n = 1, 2, 3$), the higher ΔH values of the thermal effect at 80°C with respect to the ΔH of the $\alpha \rightarrow \beta$ transition of UL_3 (and the absence of the melting process of UL_3) indicates the solid—solid interaction between the reactants to form the mixed complexes which decompose at 130°C.

Since the UL_4 complex behaves as a stoichiometric 1 : 1 mixture of UL_3 and UL_5, and considering that UL_5 and Th do not react, we suppose that the thermal effects exhibited by the $UL_4 + n\mathrm{Th}$ system are due to the overlapping of the DSC curves of UL_5 and the $UL_3 + n\mathrm{Th}$ reaction.

The results obtained for the $UTh_2 + 2L$ mixture indicate that the system reacts at 85°C according to the scheme

$$UTh_2 + 2L \rightarrow UL_{2(\alpha)} + 2Th$$

This reaction is complete after reheating several times in the temperature range 25—90°C. The formation of $UL_{2(\alpha)}$ is supported by the presence of the successive endothermic effect at 118°C ($\Delta H = 1.8$ kcal mole^{-1}), characteristic of the $\alpha \rightarrow \beta$ transition of UL_2. The β form reacts endothermically with 2Th at 125°C to form the UL_2Th_2 mixed complex.

A similar behaviour can only be supposed for the $UTh_2 + L$ system, owing to the impossibility of resolving the double thermal effect at 118—130°C.

For the $UTh_2 + nL$ systems ($n = 3, 4$), the disappearance, on reheating several times, of both thermal effects suggests that, at 52°C UTh_2 slowly reacts with nL molecules, giving the interchange reaction $UTh_2 + nL \rightarrow UL_n + 2Th$ and at 80°C the formation of the mixed UL_nTh_2 complex occurs.

Therefore, the mechanism of the studied solid—solid interactions can be summarized schematically as follows.

For $n = 1, 2$

$$UTh_2 + nL \rightarrow UL_{n(\alpha)} + 2\ Th \tag{1}$$

$$UL_{n(\alpha)} \rightarrow UL_{n(\beta)} \qquad \text{(for } n = 1\text{, assumed)} \tag{2}$$

$$UL_{n(\beta)} + 2\ Th \rightarrow UL_nTh_2 \tag{3}$$

$$UL_nTh_2 \rightarrow \text{decomposition} \tag{4}$$

and for $n = 3, 4$

$$UTh_2 + nL \rightarrow UL_n + 2\ Th \tag{5}$$

$$UL_n + 2\ Th \rightarrow UL_nTh_2 \tag{6}$$

$$UL_nTh_2 \rightarrow \text{decomposition} \tag{7}$$

It is interesting to observe the tendency of the urea to substitute the thiourea molecules bonded with the uranyl ion [reactions (1) and (5)], while the opposite behaviour was not observed [reactions (3) and (6)].

The ΔH values reported in Tables 1 and 2 show that the same UTh_2L_n complex can be formed by interactions of either $UTh_2 + nL$ or $UL_n + 2Th$. The trend of the reaction ΔH_r values confirms what was observed for the simple complexes UL_n [2] and UTh_n [4]. A greater facility of the ligand (hard or soft) to coordinate with UO_2^{2+} ion in those complexes in which a greater number of ligand molecules are present was found.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. U. Filia and Mr. L. Cappelletti of Centro Ricerche Dipe Montedison, Priolo, for helpful discussions, and to Montedison S.p.A. for providing the equipment.

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