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ENTHALPIMETRIC MEASUREMENTS IN SOLID—SOLID REACTIONS. IV. THE STUDY OF THE URANYL NITRATE—THIOUREA SYSTEM BY DSC

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ABSTRACT

The solid—solid interactions of uranyl nitrate—thiourea in closed reaction vessels are studied by DSC. The thiourea (Th) appears able to coordinate with uranyl ion, in the absence of the solvent, to form complexes in which the Th molecules are more than two. The associated enthalpic values are evaluated from DSC curves and the results are briefly compared with those obtained using urea or phenylurea as neutral ligands.

INTRODUCTION

The typical "hard" character that the uranyl ion, UO_2^{2+}, shows by its ability to coordinate through O or N donor atoms has been the subject of several works [1]. Although the inability of thioethers to form S → UO_2^{2+} coordinative bonds has been affirmed, recent structural studies concerning some complexes with "soft" donor atoms show the possibility that under particular conditions, polydentate ligands containing S or Se donor atoms can coordinate because of the entropic contribution [2].

Considering the competitivity of the solvent with the neutral ligand, especially when its electronic capacity is very weak, we study in this work the solid—solid interactions between the uranyl nitrate and thiourea (Th) in several stoichiometric ratios to form solid $UO_2(NO_3)_2Th_n$ complexes, and the relative ΔH values are correlated with the previously obtained results using O as donor atom [3—5].

The DSC has been used to study the solid—solid reactions according to the scheme

$$UO_2(NO_3)_2Th_2 + n\ Th \rightarrow UO_2(NO_3)_2Th_{2+n}$$

(where n = 1—4).

The interactions

$$UO_2(NO_3)_2Th_n + m\ Th \rightarrow UO_2(NO_3)_2Th_{n+m}$$

(where n = 3—5; m = 1—3; $n + m$ = 4—6) were not considered owing to the impossibility of obtaining stable $UO_2(NO_3)_2Th_n$ complexes.

EXPERIMENTAL

Materials

Uranyl nitrate hexahydrate (Fluka) and thiourea (C. Erba RP) were used without any further purification.

$UO_2(NO_3)_2Thiourea_2$ (UTh_2)

Stoichiometric molar amounts (1 : 2) of uranyl nitrate hexahydrate and thiourea, finely powdered, were well mixed in a glass mortar and then put in an oven at 110°C for several hours. The resultant anhydrous orange product was analyzed. Analysis: calculated (%) for $UO_2(NO_3)_2Th_2$: U 43.58, O 23.43, N 15.38, C 4.40, H 1.47, S 11.74; found (%) U 43.79, O 23.34, N 15.20, C 4.43, H 1.47, S 11.77.

No reaction was observed on heating finely powdered amounts of $UO_2(NO_3)_2 \cdot 6\,H_2O$ and thiourea in stoichiometric ratios 1 : 3, 1 : 4, 1 : 5, 1 : 6 in a stove up to 120°C. At 130°C decomposition of the mixture was observed. Analogous behaviour was noted using mixtures of UTh_2—Th in the molar ratios 1 : 1, 1 : 2, 1 : 3, and 1 : 4.

DSC measurements

All measurements were performed in a dynamic nitrogen atmosphere (5 l h^{-1}) in aluminum covered pans using a Perkin-Elmer DSC model 1B calorimeter, at a heating rate of 4°C min^{-1}.

Solid—solid reactions

These were carried out by introducing finely powdered stoichiometric mixtures of the reactants into the pan of the DSC (the total weight of the system being about 5—6 mg). The empty pan was used as reference. ΔH of the reactions was evaluated using ΔH of melting of indium as calibration standard (6.79 cal g^{-1}). All ΔH values are reported in kcal $mole^{-1}$.

RESULTS AND DISCUSSION

DSC measurements were performed for all the unmixed reactants. It was observed that: (a) the thiourea is thermally stable up to 170°C and then sublimes (Fig. 1); (b) the UTh_2 complex only exhibits an exothermic process due to decomposition at 140°C (Fig. 2); (c) for the thermal behaviour of the $UO_2(NO_3)_2 \cdot 6\,H_2O$ see refs. 4 and 5.

Attempts to prepare UTh_n complexes were unsuccessful: mixtures of $UTh_2 + n$ Th or U + nTh put in a stove at 120°C, either do not react at all or decompose when left for a long time. Samples of the systems, put in a stove for different times and analyzed by DSC, show no reproducible thermal behaviour. The existence of the $UO_2(NO_3)_2Th_3$, $UO_2(NO_3)_2Th_4$, $UO_2(NO_3)_2Th_5$ and $UO_2(NO_3)_2Th_6$ complexes is only supported by DSC curves obtained

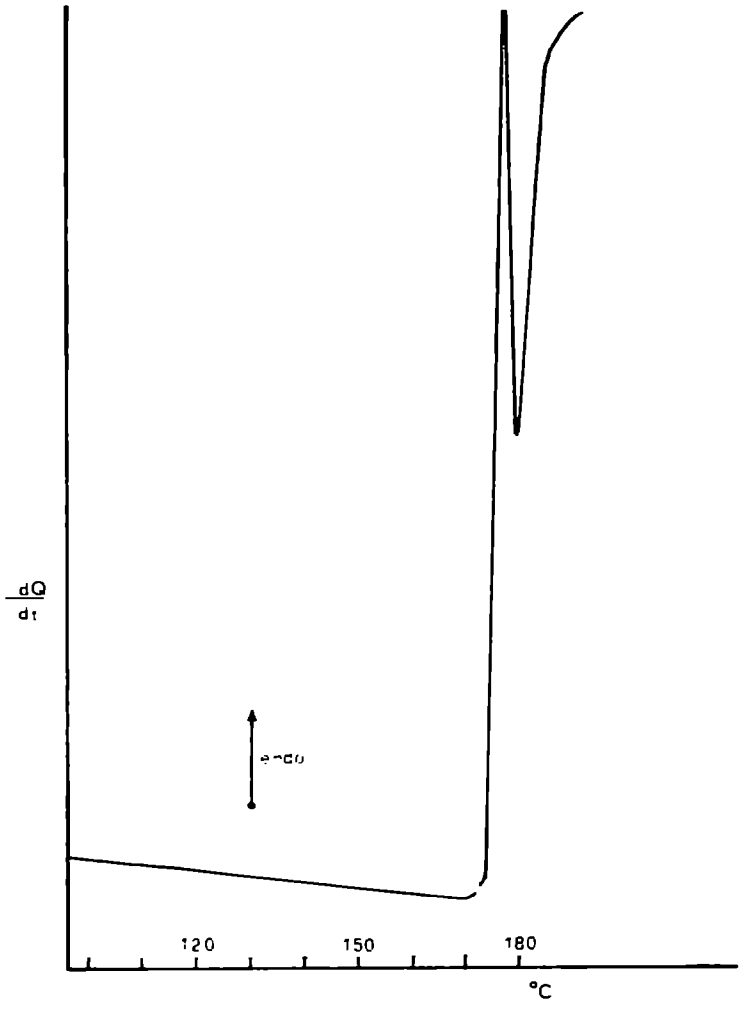

Fig. 1. Thermal behaviour of thiourea.

when the $UO_2(NO_3)_2Th_2$ reacts with Th in the calorimeter before the decomposition (see below).

Solid—solid interactions

UTh_2 + n Th system

The DSC exhibits the same thermal behaviour for all the *n* values (Fig. 3). It is evident that the existence of the endothermic process of the association reaction at 120° C, immediately followed by the exothermic effect at 130° C, is due to decomposition of the formed product. The enthalpic values associated with the endothermic process for each system are

	ΔH (kcal mole^{-1})
$UTh_2 + Th \rightarrow UTh_3$	+3.3
$UTh_2 + 2\,Th \rightarrow UTh_4$	+5.9
$UTh_2 + 3\,Th \rightarrow UTh_5$	+6.9
$UTh_2 + 4\,Th \rightarrow UTh_6$	+7.7

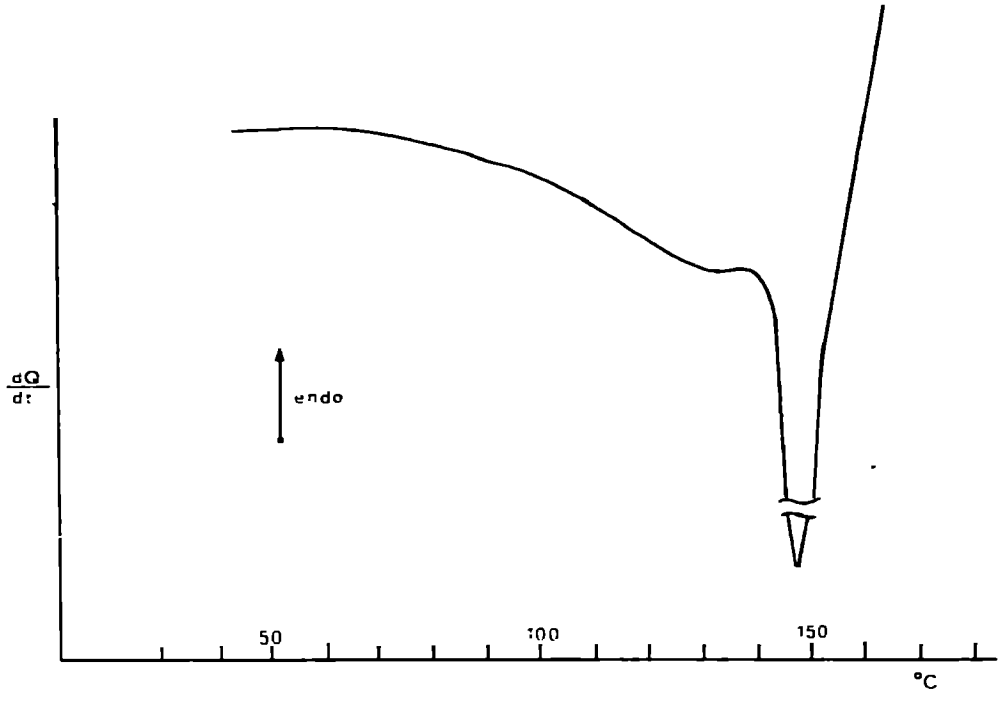

Fig. 2. Thermal behaviour of UTh_2 product.

Although the UTh_{2+n} complexes decompose in the temperature range of the interaction, it is nevertheless reasonable to assume from the obtained enthalpic values and from the thermal behaviour of the system considered, that the thiourea is able to coordinate with uranyl ion to form complexes in which the Th molecules are more than two. This hypothesis is supported by the reported thermal behaviour of both UTh_2 and Th.

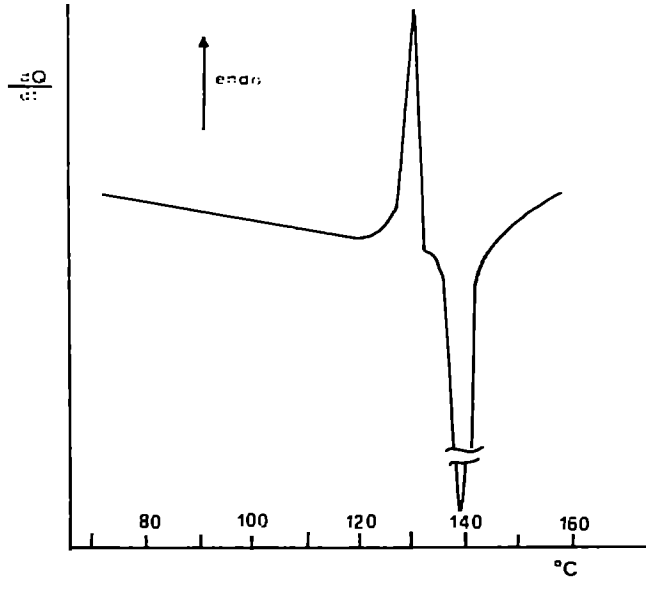

Fig. 3. Thermal behaviour of the UTh_2 + 4 Th system.

The differences of the associated ΔH values between the interactions of $UTh_2 + n$ Th and $UTh_2 + (n-1)$ Th decrease on increasing n. This trend indicates the important facility of the thiourea to coordinate with UO_2^{2+} ion in those complexes in which a greater number of ligand molecules of the same kind are present. A similar behaviour was observed for the ΔH of formation of the urea—uranyl nitrate and phenylurea—uranyl nitrate complexes.

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