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Note

ENTHALPIMETRIC MEASUREMENTS IN SOLID—SOLID REACTIONS. PART VI. THE STUDY OF THE URANYL NITRATE—*SYM*-DIPHENYLUREA SYSTEM

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Considering the possibility of obtaining thermodynamic parameters from solid—solid interactions by DSC, in previous papers we have studied the reactions, in the solid state, between the uranyl UO_2^{2+} cation and some soft or hard ligands: urea [1], thiourea [2], phenylurea [3]. The formation of mixed complexes containing soft and hard ligands has also been studied [4]. The thermal behaviour of these systems indicates that the ligands are able to coordinate with UO_2^{2+} more easily in those complexes in which a greater number of ligand molecules of the same kind are present and the ΔH values associated with solid—solid interactions are greatly influenced by the kind of donor atom and the substituent present in the ligand molecule. In particular, the enthalpy values associated with the reactions from uranyl nitrate and phenylurea, at several stoichiometric ratios, suggested that the presence of the phenyl group in the urea molecule makes the reaction more favourable from an enthalpy point of view.

In this work we study, by DSC, the solid—solid interactions between uranyl nitrate (U) and *sym*-diphenylurea (DPh) according to the scheme

$$\mathrm{UDPh}_m + n\ \mathrm{DPh} \rightarrow \mathrm{UDPh}_{m+n}$$

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

EXPERIMENTAL

Materials

Uranyl nitrate hexahydrate (FLUKA) and *sym*-diphenylurea (C. ERBA RP) were used without any further purification.

$UDPh_2$ complex. Stoichiometric (1 : 2) molar finely powdered amounts of uranyl nitrate hexahydrate and *sym*-diphenylurea were intimately mixed and heated at 60°C for 1 day.

$UDPh_m$ complexes ($m = 3, 4, 5, 6$). These were prepared by mixing finely powdered $UDPh_2$ and DPh, at the appropriate molar ratios and successively heating at 60°C for 1 day.

All the products formed were characterized by elemental analysis. The results agreed with the theoretical compositions.

Differential scanning calorimetric measurements

The DSC curves were obtained with a Perkin-Elmer model 1B DSC using aluminium covered vessels in a dynamic nitrogen atmosphere (5 l h^{-1}) and a heating rate of 4°C min^{-1}. The total weight of the studied system was about 5—6 mg. An empty closed 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.

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

Thermal microscopy

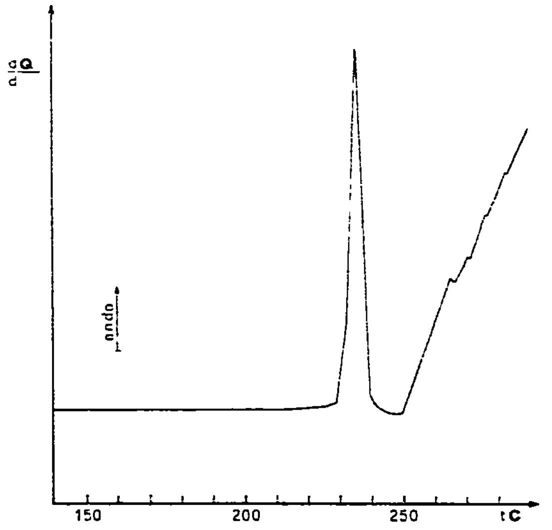
A Galileo polarizing microscope with a 20 × —0.22 objective and a Mettler FP 52 microfurnace for sample temperature control were used. The finely powdered mixtures were mounted on a glass slide and covered with a glass slip.

RESULTS AND DISCUSSION

The DSC curves of the reactants were investigated before those associated with the solid—solid interaction reactions.

U · 6 H_2O. The thermal behaviour of the U · 6 H_2O product has been previously reported [1].

DPh. This product is thermally stable up to 237°C. At this temperature it



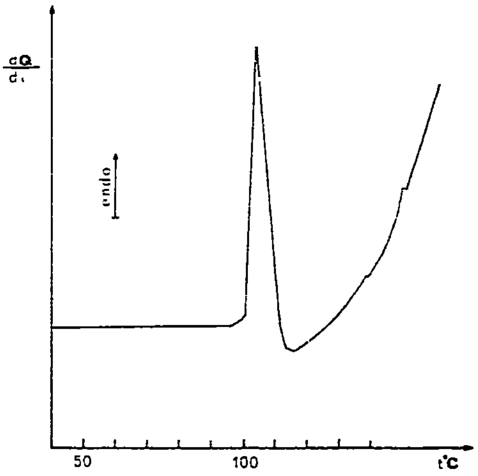


Fig. 1. Thermal behaviour of *sym*-diphenylurea.

Fig. 2. Thermal behaviour of $UDPh_m$ complexes and $UDPh_m + n$ DPh systems.

TABLE 1

Temperature (°C), ΔH_m (kcal mole^{-1}), apparent reaction order and apparent activation energy (kcal mole^{-1}) values of UDPh$_m$ complexes

Compound	T	ΔH_m	n	E_a
UDPh$_2$	100	9.0	1.2	157
UDPh$_3$	100	10.3	1.2	128
UDPh$_4$	100	14.4	1.2	119
UDPh$_5$	100	11.1	1.0	110
UDPh$_6$	100	9.5	1.2	140

melts and immediately decomposes (Fig. 1).

UDPh$_m$ (m = 2, 3, 4, 5, 6). All the studied UDPh$_m$ complexes undergo only an endothermic process at 100—110°C, due to melting, and then immediately decompose (Fig. 2). The enthalpy values are reported in Table 1.

UDPh$_m$ + n DPh systems. At all investigated molar ratios, the DSC curves show only an endothermic process at 100—110°C. After this temperature, exothermic decomposition is observed (Fig. 2). The ΔH values associated with the peak at 100—110°C are calculated and reported in Table 2.

The obtained results, reported in Tables 1 and 2, suggest that UDPh$_m$ compounds react with n DPh molecules to form UDPh$_{m+n}$ complexes. In fact, the ΔH values associated with the UDPh$_m$ + n DPh systems are different from those associated with the corresponding UDPh$_m$ reactant compounds. Apparently, the ΔH values do not seem to verify Hess's law and, consequently, it is impossible to state if the reaction occurs at solid state or in the melted phase.

In order to understand this anomalous behaviour, we utilized the DSC curves to obtain kinetic parameters. The Kissinger method [5] was used and the apparent reaction order, n, was obtained and is reported in Tables 1 and 2.

TABLE 2

Temperature (°C), ΔH_t (kcal mole^{-1}), apparent reaction order and apparent activation energy (kcal mole^{-1}) values associated with the solid—solid interactions

Mixture	T	ΔH_t	n	E_a
UDPh$_2$ + DPh	100	9.8	1.2	135
+ 2 DPh	100	13.3	1.2	120
+ 3 DPh	100	9.8	1 2	115
+ 4 DPh	100	7.0	1.2	111
UDPh$_3$ + DPh	100	10.0	1.2	100
+ 2 DPh	100	8.7	1.2	95
+ 3 DPh	100	4.5	1.0	56
UDPh$_4$ + DPh	100	3.1	1.1	85
+ 2 DPh	100	6.4	1.2	80
UDPh$_5$ + DPh	100	8.5	1.0	65

For all the systems considered, the n values differ largely from 0.7, so indicating that physical processes are also associated with the endothermic peaks at 100—110°C [6]. This has been confirmed by thermal microscopy measurements: at all molar ratios, the $UDPh_m$ and DPh compounds react at 100—110°C and the start of decomposition is simultaneously observed. From these results it is impossible to obtain useful information on the reactivity of the *sym*-diphenylurea with the $UDPh_m$ compounds.

From the DSC curves of the associative reactions, utilizing the Piloyan method [7], the apparent activation energies of the interactions, E_a, were evaluated and are reported in Table 2. The apparent activation energies, E_a, associated with the melting of the $UDPh_m$ compounds were also evaluated and are reported in Table 1. The trend of the E_a values, obtained for the syntheses, but bearing in mind the prevalence of the physical over the chemical process, seems to confirm, as previously found for other complexes of uranyl nitrate, that the greater the number of same ligand molecules bonded to the UO_2^{2+} ion, the higher is the facility of the DPh to coordinate with the uranyl ion.

It is interesting to observe that the $UDPh_{m+n}$ complexes synthesized in the DSC apparatus are largely unstable and decompose before formation is complete. This may be due to a smaller donor capacity of DPh with respect to the previously studied ligands [1—3]; a steric hindrance due to the two phenyl groups is also possible.

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