Thermochimica Acta, 36 (1980) 207—215
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

ENTHALPIMETRIC MEASUREMENTS IN SOLID—SOLID REACTIONS. PART II. STUDY OF THE URANYL NITRATE—UREA SYSTEM BY DSC

G. SIRACUSA and L. ABATE

Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università di Catania, Viale A. Doria 8, 95125 Catania (Italy)

(Received 6 August 1979)

ABSTRACT

The enthalpy values associated with solid—solid interactions of uranyl nitrate—urea in closed reaction vessels are studied by DSC. Results are compared with those obtained previously by DTA with open reaction vessels and a dynamic atmosphere of nitrogen. It is found that the different experimental conditions affect the results both qualitatively and quantitatively to a very marked extent.

INTRODUCTION

It is well known that thermodynamic parameters of reactions in solution are solvent-dependent, hence parameters obtained must be interpreted according to the nature and polarity of the solvent. Solid—solid interactions, however, have to date only been utilized for preparative purposes, not with the intention of obtaining thermodynamic parameters [1—5].

In previous papers [6,7] we have observed that, in several cases, enthalpy values can be obtained from solid—solid interactions by calorimetric analytical techniques such as DTA or DSC; it must be emphasized, however, that at present it is impossible to get confirmation of these values because of the limited number of systems studied.

In order to verify the limits of applicability of DTA and DSC we have compared the results previously obtained by DTA (in open vessels and in a dynamic atmosphere of nitrogen) with those now obtained by DSC from closed vessels.

The system studied is $UO_2(NO_3)_2 \cdot 6\ H_2O$: urea in the molar ratios previously reported [6].

EXPERIMENTAL

Materials

Reagent grade uranyl nitrate hexahydrate and urea were used without further purification.

Differential scanning calorimetric measurements

The dH/dt vs. temperature curves were obtained with a Perkin-Elmer model 1B DSC calorimeter, from closed aluminium vessels, at a heating rate of 4°C min^{-1}. The total weight of the reaction system was about 6 mg. An empty closed vessel was used as reference.

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

RESULTS

In order to explain the enthalpic effects of the system studied, we have initially taken the DSC curves of the reactants into account. The ΔH values are reported in Table 1.

Urea (denoted L) is thermally stable up to 130°C, then undergoes an endothermic melting process, analogous to DTA, and finally decomposes.

$UO_2(NO_3)_2 \cdot 6\ H_2O$ shows a very sharp endothermic peak (T_m = 58°C, ΔH = 5.7 kcal mole^{-1}) superimposed on a broad endothermic peak from dehydration at 25—130°C (Fig. 1). The sharp peak, not previously reported in the literature and not exhibited by DTA, might be due to an $\alpha \rightarrow \beta$ transition of the salt. Owing to the simultaneous dehydration process which occurs in one of the steps, it is impossible to attribute this transition to a particular species.

TABLE 1

Temperature (°C), thermal effects and ΔH values (kcal mole^{-1}) of the reactants

Reactant	DTA		DSC		
	Temp.	Thermal effect	Temp.	Thermal effect	ΔH
Urea	130	Melting with decomposition	130	Melting with decomposition	—
$UO_2(NO_3)_2 \cdot 6H_2O$	25—130	Dehydration	25—130	Dehydration	1.8
UL_2	—	—	118	$\alpha \rightarrow \beta$	13.5
	202	Melting	196	Melting	—
UL_3	—	—	80	$\alpha \rightarrow \beta$	0.5
	114	Melting	106	Melting	1.5
UL_4	—	—	40—60	$\alpha \rightarrow \beta$ of UL_5	—
	110	Melting	96	$\alpha \rightarrow \beta$ of UL_3 $\beta \rightarrow \gamma$ of UL_5 Melting	—
UL_5	—	—	50	$\alpha \rightarrow \beta$	—
	118	Melting	80—95 *	$\beta \rightarrow \gamma$ Melting	—

* Double inseparable peak.

$UO_2(NO_3)_2urea_2$ (denoted UL_2) undergoes an endothermic process owing to the known $\alpha \rightarrow \beta$ transition [1] at 118°C ($\Delta H = 1.8$ kcal mole^{-1}). This transition is slowly reversible and the exothermic peak is observed neither on cooling nor on re-heating.

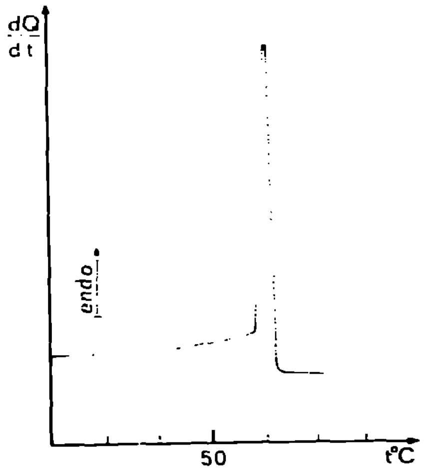
The UL_2 complex melts at 196°C ($\Delta H = 13.5$ kcal mole^{-1}) and subsequently decomposes.

$UO_2(NO_3)_2urea_3$ (denoted UL_3) undergoes a very small endothermic effect owing to the previously unreported and reversible $\alpha - \beta$ transition which was observed at 80°C ($\Delta H = 0.5$ kcal mole^{-1}). Subsequent melting occurs at 106°C ($\Delta H = 1.5$ kcal mole^{-1}) (Fig. 2). No modification was observed on re-heating at 25—130°C.

$UO_2(NO_3)_2urea_4$ (denoted UL_4) shows two endothermic peaks on the DSC curve at 25—130°C, specifically at 60°C and 96°C. On re-heating several times at 25—130°C it was observed that the second peak consists of two inseparable thermal effects and the DSC curve shows the thermal behaviour typical of UL_5 (Fig. 3).

A synthetically prepared mixture of UL_3 and UL_5 (1 : 1 mole ratio) shows exactly the same behaviour. Therefore we consider that the peak at 60°C is due to an $\alpha - \beta$ transition of UL_5 (see below), while the second effect is the sum of the $\alpha \rightarrow \beta$ transition of UL_3 with the $\beta - \gamma$ transition of UL_5 and melting of the mixture.

$UO_2(NO_3)_2urea_5$ (denoted UL_5) shows an irregular endothermic peak at 50°C. In the range 75—105°C a double unresolvable endothermic peak (Fig. 4a) at T_m 80°C and 95°C was observed. On cooling to 25°C the UL_5 com-



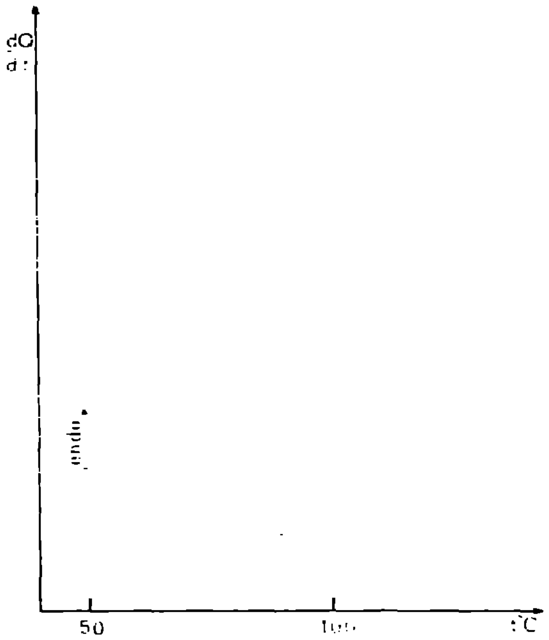


Fig. 1. The $\alpha \rightarrow \beta$ transition of $UO_2(NO_3)_2 \cdot 6\ H_2O$.

Fig. 2. Thermal behaviour of UL_3.

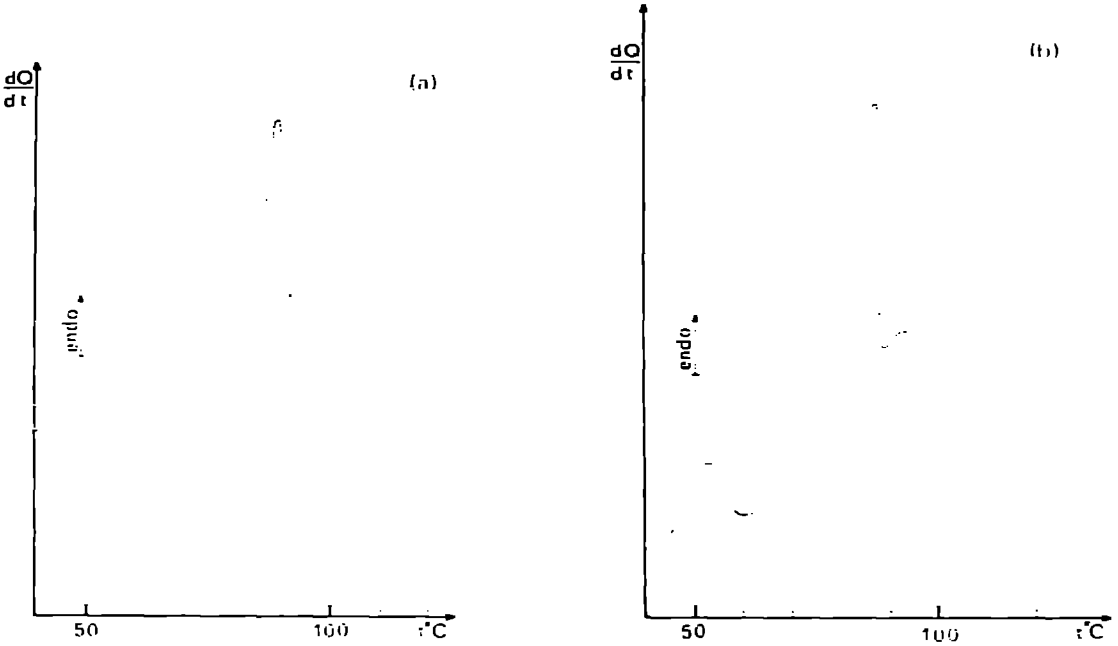


Fig. 3. Thermal behaviour of (a) UL_4, (b) UL_4 after several thermal cycles.

plex remains molten (Fig. 4b), whereas on cooling with solid CO_2 the product solidifies and the DSC curve behaves similarly to that in Fig. 4a.

The thermal effect at 50° C can be attributed to the previously unreported, reversible $\alpha \rightarrow \beta$ transition of UL_5. The subsequent double peak is explained by postulating the existence of a polymorphous form of UL_5 and a second $\beta \rightarrow \gamma$ transition immediately followed by melting.

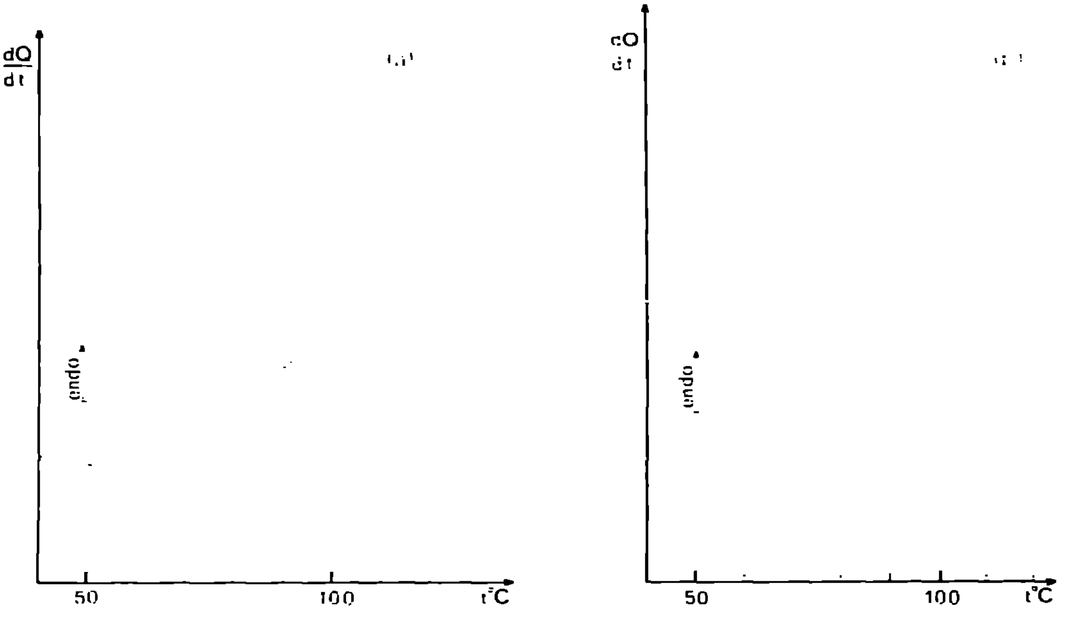


Fig. 4. Thermal behaviour of (a) UL_5, (b) UL_5 re-heated after cooling.

Results from the DSC curves of the reacting systems, obtained under the same experimental conditions of the products, and the ΔH values of the thermal processes associated with these reactions are reported in Table 2.

$UL_2 + nL$ system ($n = 1$—4)

At all molar ratios, the DSC curves show an endothermic peak at 70°C followed by a double endothermic effect at 100°C which is not easily separated. On re-heating the first thermal effect disappears while the second becomes a simple peak (Fig. 5). The enthalpy of the latter thermal effect stabilizes after re-heating several times in the temperature range 25—130°C.

$UL_3 + nL$ systems ($n = 1$—3)

TABLE 2

Temperature (°C) and ΔH values (kcal mole^{-1}) obtained from DTA and DSC curves for the solid—solid reactions

System	DTA		DSC			
	Temp.	ΔH	1° thermal cycle		Successive	
			Temp.	ΔH	Temp.	ΔH
UL_2 + L	74	1.2	70	1.1	—	—
	114		100 *	1.2	100	3
				1.6		
UL_2 + 2L	80	2.7	70	4.1		
	110		100 *	1.1	100	6.5
				1.7		
UL_2 + 3L	80	4.5	70	4.1		
	118		100 *	0.7	100	8.5
				0.4		
UL_2 + 4L	78	8.7	70	8.5		
	120		100 *	0.4	100	1.7
				0.4		
UL_3 + L	80	1.6	70	1.2		
	110		90		90	0.5
			105	3.6	105	1.6
UL_3 + L	80	3.4	70	0.8		
	118		90		90	0.3
			105	3.8	105	4.8
UL_3 + 3L	78	7.6	70	5.1		
	120		105	0.2	105	6
UL_4 + L	74	1.7	50	0.15		
	118		80		80	
UL_4 + 2L	76	6.1	50		50	
	120					
UL_5 + L	80	4.3				
	120					

* Double peak.

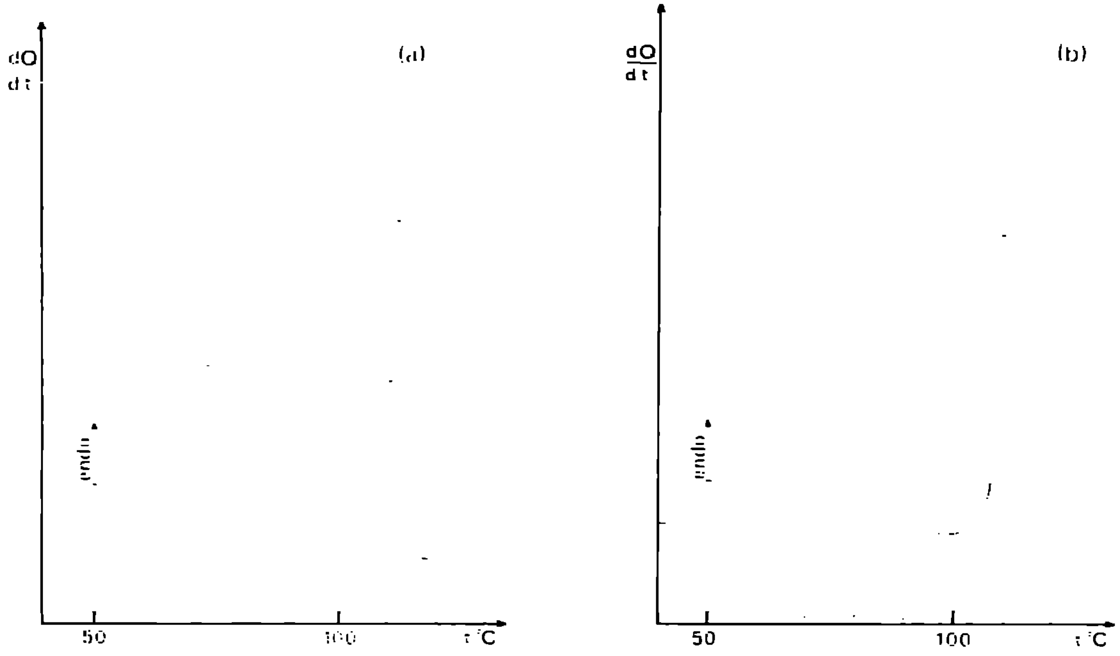


Fig. 5. Thermal behaviour of (a) the UL_2 + L system, (b) the UL_2 + L system after several thermal cycles.

For $n = 1$ or 2 the DSC curves show two sharp endothermic effects at 70°C and 105°C. A very small effect is also observed at 90°C (Fig. 6a). On re-heating, after cooling, the first effect disappears, while the peak at 90°C becomes very sharp and the ΔH value associated with the peak at 105°C alters (Fig. 6).

On re-heating several times in the range 25—130°C the ΔH value of the two effects stabilizes but at a lower ΔH value for the UL_3 + L system and a higher value for the UL_3 + 2 L system.

For $n = 3$ no peak appears at 90°C; on re-heating the peak at 70°C disappears and the ΔH value of the peak at 105°C increases.

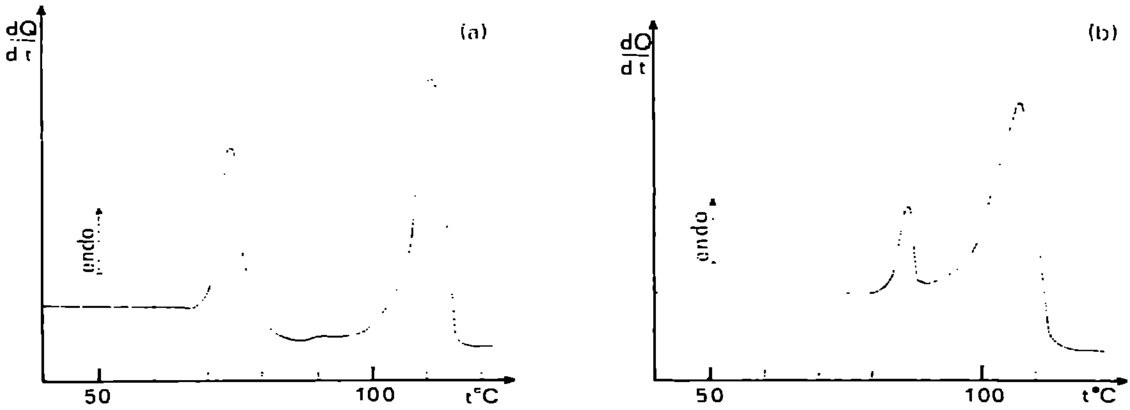


Fig. 6. Thermal behaviour of (a) the UL_3 + L system, (b) the UL_3 + L system after several thermal cycles.

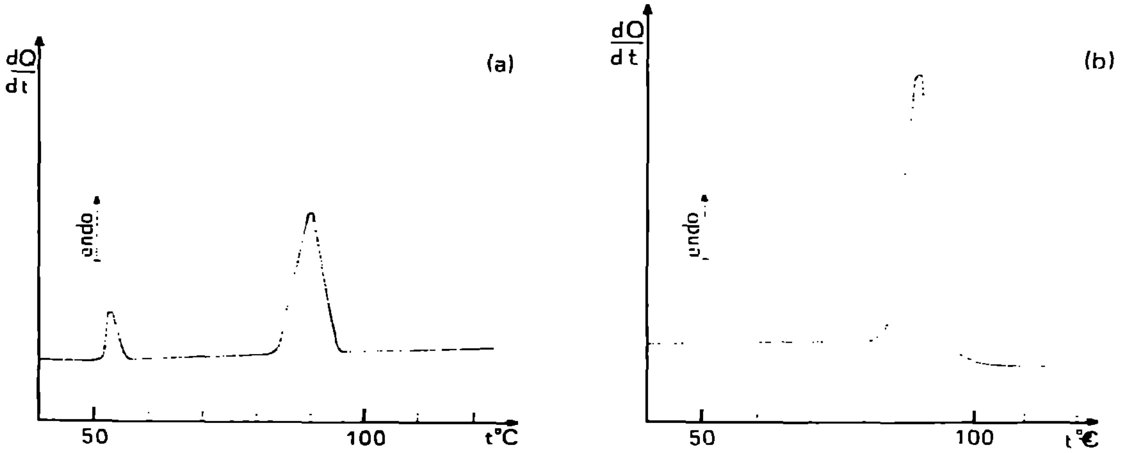


Fig. 7. Thermal behaviour of (a) the UL_4 + L system, (b) the UL_4 + L system after several thermal cycles.

UL_4 + nL system (n = 1, 2)

For $n = 1$ a small endothermic peak is apparent at 50°C ($\Delta H = 0.15$ kcal mole^{-1}) and a second endothermic effect appears at 80°C owing to melting of the UL_5 complex formed (Fig. 7a). On re-heating, the first effect disappears while the ΔH value of the second effect stabilizes (Fig. 7b).

Remembering that UL_4 can be considered as a 1 : 1 mole ratio mixture of UL_3 and UL_5, it is reasonable to suppose that the peak at 50°C is due to $\alpha \rightarrow \beta$ transition of UL_5; the thermal effect at 80°C can be explained as the sum of the $\alpha \rightarrow \beta$ transition of UL_3, the solid—solid interaction, the $\beta \rightarrow \gamma$ transition of UL_5 and melting of the UL_5 formed or present in UL_4.

For $n = 2$ the DSC curve shows only one small endothermic peak at 50°C. On re-heating, even this effect disappears and the system seems to be undergoing no reaction (Fig. 8).

UL_5 + L system

The thermal behaviour of this system is similar to that described above for the UL_4 + 2 L system.

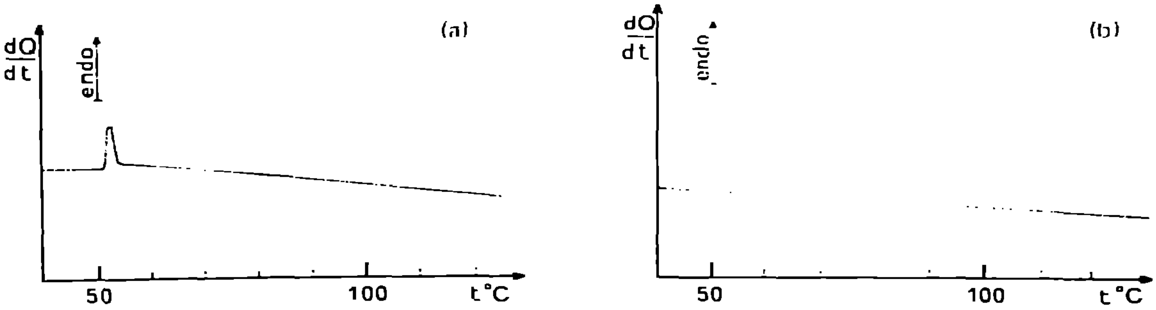


Fig. 8. Thermal behaviour of (a) the UL_4 + 2 L system, (b) the UL_4 + 2 L system re-heated after cooling.

CONCLUSION

Tables 1 and 2 compare the data obtained by DSC (in closed vessels) with those obtained by DTA (in open vessels and in a dynamic atmosphere of nitrogen). It is apparent that the experimental conditions modify the results significantly. In particular: (i) the thermal effects shown by DSC curves are generally qualitatively and quantitatively different from those obtained by DTA curves; (ii) the ΔH values obtained from DSC curves for the nL: $UO_2(NO_3)_2$ systems, compared to values obtained from DTA curves apparently do not follow Hess's law; (iii) the values of enthalpy of some of the thermal effects shown by DSC become constant only after re-heating several times in the temperature range 25—130°C.

Therefore the products obtained under the two experimental conditions are molecularly similar but structurally different, hence the reaction mechanism is different.

The DSC curves of the $UL_2 + n$L systems suggest that UL_2 interacts in the solid state with nL in the temperature range 70—80°C to form the product $UL_2 \cdot n$L, in which the nL molecules are in the external coordination sphere. The $UL_2 \cdot n$L product melts (the initial endothermic process being incorporated into the double DSC peak), and then nL molecules become located in the internal coordination sphere as the crystalline structure of UL_2 modifies and the complex UL_{2+n} is formed (the latter endothermic process being incorporated into the double DSC peak). In subsequent thermal cycles, the double DSC peak disappears and is replaced by melting of UL_{2+n}.

For $UL_3 + n$L systems: (i) UL_3 reacts at 70—80°C to form the adduct $UL_3 \cdot n$L; (ii) an $\alpha \rightarrow \beta$ transition of UL_3 into $UL_3 \cdot n$L occurs; (iii) this product melts at 110°C. Hence UL_4 or UL_5 was not produced but rather $UL_3 \cdot$ L and $UL_3 \cdot 2$ L. This is in agreement with the different ΔH values obtained for the melting of $UL_3 \cdot$ L and $UL_3 \cdot 2$ L, compared to UL_4 obtained from $UL_2 + 2$ L, and UL_5 from $UL_2 + 3$ L, respectively (see Table 2).

For the $UL_3 + 3$ L system, the peak at 80°C is not observed, and we consider that solid—solid interaction occurs at 70—80°C with formation of the adduct $UL_3 \cdot 3$ L. This product melts and, simultaneously, in the liquid phase, forms UL_6. The ΔH value associated with this latter thermal effect is the sum of the values for the melting process and transformation of $UL_3 \cdot 3$ L to UL_6. On re-heating, the value of ΔH becomes constant, indicating that formation of UL_6 is exothermic.

No conclusions will be made for $UL_4 + n$L systems because of the complexity of the reacting systems owing to the simultaneous presence of UL_3 and UL_5 in UL_4.

The UL_5 + L system seems to be almost completely unreactive.

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 provision of equipment.

REFERENCES

1 P.S. Gentile and L.S. Campisi, J. Inorg. Nucl. Chem., 27 (1965) 2291.
2 P.S. Gentile and T.L. Mao, J. Inorg. Nucl. Chem., 27 (1965) 867.
3 P.S. Gentile and L.H. Talley, J. Am. Chem. Soc., 79 (1957) 4296, 5889.
4 G. Cohn, Chem. Rev., 42 (1948) 527.
5 F. Feigl, L.I. Miranda and H.A. Suter, J. Chem. Educ., 21 (1944) 18.
6 G. Siracusa, A. Seminara, V. Cucinotta and S. Gurrieri, Thermochim. Acta, 23 (1978) 109.
7 L. Abate and G. Siracusa, Thermochim. Acta, 29 (1979) 157.