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Enthalpimetric measurements in solid–solid reactions Part 9. The interactions of α- and β-$UO_2(NO_3)_2urea_2$ and $UO_2(NO_3)_2urea_3$ with n(urea)

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Abstract

The enthalpy values associated with solid–solid interactions of dinitratobis(urea)dioxouranium(VI) (UL_2) and dinitratotris(urea)dioxouranium(VI) (UL_3) with n(urea) (nL) were studied. The results were compared with those previously obtained under different experimental conditions, and it was found that UL_2 and UL_3 can react in both the α and β form and Hess's cycle is correctly followed for each system.

INTRODUCTION

In previous work we have investigated interactions in the solid state between uranyl salts and hard or soft donor ligands [1–7]. The ability of the uranyl ion to coordinate with one or more neutral ligand molecules has also been considered [8–13].

The syntheses were performed directly in a DSC or DTA apparatus, heating linearly a finely powdered stoichiometric mixture of reactants, in order to evaluate the enthalpic values associated with the reactions. The syntheses were attempted according to the following scheme:

$$UO_2(NO_3)_2L_n(s) + mL(s) \rightarrow UO_2(NO_3)_2L_{n+m}(s)$$

where L = urea, phenylurea, *sym*-diphenylurea or thiourea; $n = 2$–5; $m = 1$–4; $n + m = 3$–6.

In general, the ΔH values found for each system considered were well correlated with each other. However, in the case of the urea complexes alone (these complexes were studied first), we obtained different results, depending on the experimental method used (DTA or DSC) and, contrary to all expectations, the ΔH values obtained from DSC curves did not follow

TABLE 1

Temperature and ΔH values obtained from DSC curves [1]

Interaction	Product	Temp. (°C)	ΔH
UL_2+L	UL_3	70	1.1
UL_2+2L	UL_4	70	4.1
UL_2+3L	UL_5	70	4.1
UL_2+4L	UL_6	70	8.5
UL_3+L	UL_4	70	1.2
UL_3+2L	UL_5	70	0.8
UL_3+3L	UL_6	70	5.1

Hess's law. These differences were attributed to a different reaction mechanism under the different experimental conditions.

In this paper, we use several different systems of uranyl complexes to reconsider those results in order to explain the observed differences.

DISCUSSION

In Table 1 we report the previously found ΔH values [1] associated with the solid–solid interaction between $UO_2(NO_3)_2urea_n$ (denoted UL_n) and m(urea) (denoted L_m) to form $UO_2(NO_3)_2urea_{n+m}$ (denoted UL_{n+m}). On testing Hess's law for such a system, i.e.

$$
\begin{array}{lll}
UL_2 + L & \rightarrow UL_3 & \Delta H_1 = 1.1 \text{ kcal mol}^{-1} \\
UL_3 + 3L & \rightarrow UL_4 & \Delta H_2 = 5.1 \text{ kcal mol}^{-1} \\
\hline
UL_2 + 4L & \rightarrow UL_6 & \Delta H_3 = 8.5 \text{ kcal mol}^{-1}
\end{array}
$$

from DSC data, we observe that $\Delta H_3 > \Delta H_1 + \Delta H_2$.

For a rationalization of these results it is necessary to consider the following points.

(i) Both UL_2 and UL_3 complexes exist in two different structural forms, denoted $UL_2(\alpha)$, $UL_2(\beta)$, $UL_3(\alpha)$ and $UL_3(\beta)$.

(ii) The α–β transitions are observed to be endothermic by DSC.

(iii) The ΔH values associated with the transitions are 1.8 kcal mol^{-1} for the UL_2 complex ($T = 118$°C) and 0.5 kcal mol^{-1} for the UL_3 complex ($T = 80$°C). (iv) The α–β transitions are very slow reversible reactions and no peaks are observed on cooling and reheating the complex. The β form reverts to the α form after some weeks at room temperature.

It is thus of interest to throw some light on the following point: when an interaction involving a UL_2 or UL_3 molecule as reactant or product occurs, what structure is pertinent to the synthesis?

With regard to the proposed test, the only possible system to be considered, in terms of Hess's cycle, is the following.

$$\begin{array}{lll}
UL_2(\alpha) & \rightarrow UL_2(\beta) & \Delta H = 1.8\ \text{kcal mol}^{-1\ \text{a}} \\
UL_2(\beta) + L & \rightarrow UL_3(\alpha) & \Delta H = 1.1\ \text{kcal mol}^{-1\ \text{b}} \\
UL_3(\alpha) & \rightarrow UL_3(\beta) & \Delta H = 0.5\ \text{kcal mol}^{-1\ \text{a}} \\
UL_3(\beta) + 3L & \rightarrow UL_6 & \Delta H = 5.1\ \text{kcal mol}^{-1\ \text{b}} \\
\hline
UL_2(\alpha) + 4L & \rightarrow UL_6 & \Delta H = 8.5\ \text{kcal mol}^{-1\ \text{b}}
\end{array}$$

where the ΔH values marked with superscripts a and b refer to the assumed and experimental values respectively. In fact, of all the other combinations, none would be correct.

On observing these results it is possible to note that UL_2 reacts in the β form with L as well as reacting in the α form with 4L. On testing other systems we found that Hess's law is obeyed with regard to these reaction schemes:

$$\begin{array}{lll}
UL_2(\alpha) & \rightarrow UL_2(\beta) & \Delta H = 1.8\ \text{kcal mol}^{-1\ \text{a}} \\
UL_2(\beta) + L & \rightarrow UL_3(\alpha) & \Delta H = 1.1\ \text{kcal mol}^{-1\ \text{b}} \\
UL_3(\alpha) & \rightarrow UL_3(\beta) & \Delta H = 0.5\ \text{kcal mol}^{-1\ \text{a}} \\
UL_3(\beta) + 2L & \rightarrow UL_5 & \Delta H = 0.8\ \text{kcal mol}^{-1\ \text{b}} \\
\hline
UL_2(\alpha) + 3L & \rightarrow UL_5 & \Delta H = 4.2\ \text{kcal mol}^{-1\ \text{b}}
\end{array}$$

and

$$\begin{array}{lll}
UL_2(\alpha) & \rightarrow UL_2(\beta) & \Delta H = 1.8\ \text{kcal mol}^{-1\ \text{a}} \\
UL_2(\beta) + L & \rightarrow UL_3(\alpha) & \Delta H = 1.1\ \text{kcal mol}^{-1\ \text{b}} \\
UL_3(\alpha) + L & \rightarrow UL_4 & \Delta H = 1.2\ \text{kcal mol}^{-1\ \text{b}} \\
\hline
UL_2(\alpha) + 2L & \rightarrow UL_4 & \Delta H = 4.1\ \text{kcal mol}^{-1\ \text{b}}
\end{array}$$

where the superscripts a and b have the same meaning as before.

Using this hypothesis it is also possible to confirm the ΔH value for the interaction $UL_4 + L = UL_5$ (experimental 0.15 kcal mol^{-1}; theoretical 0.10 kcal mol^{-1}) and to assume theoretical values for the interactions

$$\begin{array}{lll}
UL_4 + 2L & \rightarrow UL_6 & \Delta H = 4.4\ \text{kcal mol}^{-1} \\
UL_5 + L & \rightarrow UL_6 & \Delta H = 4.1\ \text{kcal mol}^{-1}
\end{array}$$

The correct interpretation in terms of Hess's law of the experimental and theoretical data points to the following interactions:

$UL_2(\beta) + L \rightarrow UL_3(\alpha)$
$UL_2(\alpha) + 2L \rightarrow UL_4$
$UL_2(\alpha) + 3L \rightarrow UL_5$
$UL_2(\alpha) + 4L \rightarrow UL_6$

and

$UL_3(\alpha) + L \rightarrow UL_4$
$UL_3(\beta) + 2L \rightarrow UL_5$
$UL_3(\beta) + 3L \rightarrow UL_6$

In order to explain why UL_2 and UL_3 react in the α or β form, we must consider the method of preparation of UL_2 and UL_3: they were obtained by intimately mixing and grinding stoichiometric quantities of the appropriate powdered reactants ($UO_2(NO_3)_2 \cdot 6H_2O + n$(urea)) and heating the mixture in an oven at 120 °C. It is thus reasonable to assume that, under these experimental conditions the β form of both UL_2 and UL_3 was obtained. When we performed solid–solid interactions it was possible to consider the interaction of the β form when UL_2 or UL_3 was used immediately after preparation, or the interaction of the α form if the material was used after a longer time.

EXPERIMENTAL

In order to confirm the above interpretation we prepared $UL_2(\alpha)$ (α-dinitratobis(urea)dioxouranium(VI)) and $UL_2(\beta)$ (β-dinitratobis(urea)dioxouranium(VI)) as reported in the literature both from solution and by solid–solid interaction [14]. The $UL_3(\alpha)$ (α-dinitratotri(urea)dioxouranium(VI)) was obtained by conversion from the β form after exposure to the atmosphere for 2 weeks, and $UL_3(\beta)$ (β-dinitratotris(urea)dioxouranium(VI)) by solid–solid interaction of UL_2 (α or β) with urea (molar ratio 1 : 1) in an oven at 90 °C.

The following solid–solid interactions were then considered:

$UL_2(\alpha) + nL \rightarrow UL_{2+n} \quad (n = 1\text{–}4)$
$UL_2(\beta) + nL \rightarrow UL_{2+n} \quad (n = 1\text{–}4)$
$UL_3(\alpha) + nL \rightarrow UL_{3+n} \quad (n = 1\text{–}3)$
$UL_3(\beta) + nL \rightarrow UL_{3+n} \quad (n = 1\text{–}3)$

The DSC measurements were performed with a Mettler 20 DSC instrument in a dynamic nitrogen atmosphere (5 l h^{-1}). Stoichiometric quantities

TABLE 2

Temperature and ΔH values obtained from DSC curves

Interaction	Product	Temperature (°C)	ΔH (kcal mol^{-1})
$UL_2(\alpha)$	$UL_2(\beta)$	118	1.8
$UL_2(\alpha)+L$	$UL_3(\alpha)$	70	2.9
$UL_2(\alpha)+2L$	UL_4	70	4.1
$UL_2(\alpha)+3L$	UL_5	70	4.1
$UL_2(\alpha)+4L$	UL_6	70	8.5
$UL_2(\beta)+L$	$UL_3(\alpha)$	70	1.1
$UL_2(\beta+2L$	UL_4	70	2.3
$UL_2(\beta)+3L$	UL_5	70	2.3
$UL_2(\beta)+4L$	UL_6	70	6.7
$UL_3(\alpha)$	$UL_3(\beta)$	80	0.5
$UL_3(\alpha)+L$	UL_4	70	1.2
$UL_3(\alpha)+2L$	UL_5	70	1.3
$UL_3(\alpha)+3L$	UL_6	70	5.6
$UL_3(\beta)+L$	UL_4	70	0.7
$UL_3(\beta)+2L$	UL_5	70	0.8
$UL_3(\beta)+3L$	UL_6	70	5.1

of the appropriate reactants, intimately mixed together, were put into covered aluminium pans, and an empty covered pan was used as reference.

The enthalpy values associated with the synthesis were evaluated by using the ΔH value of the melting of indium as the calibration standard.

RESULTS

In Table 2, values of temperature (°C) and ΔH (kcal mol^{-1}) associated with the considered interactions are reported. These results confirm the hypothesis considered above: UL_2 and UL_3 can be used as reactants with *n* urea molecules both in the α and β forms, and Hess's cycle is correctly followed for each respective system, but the products are always formed by interaction of the β form.

Moreover, it can be noted that the UL_3 obtained by interaction of $UL_2(\alpha)$ or $UL_2(\beta)$ with urea is in the α form: this is an expected result if we consider the temperature at which the interaction occurs (70 °C) and the temperature of the α–β transition of UL_3 (80 °C).

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