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THERMAL BEHAVIOUR OF URANIUM(VI) COMPLEXES. URANYL ACETATE DIHYDRATE–THIOUREA SYSTEM: SYNTHESIS AND DECOMPOSITION*

*L. Abate, A. Chisari, R. Maggiore*** and *G. Siracusa***

ISTITUTO DIPARTIMENTALE DI CHIMICA E CHIMICA INDUSTRIALE,
**FACOLTÀ DI INGEGNERIA, UNIVERSITÀ DI CATANIA, VIALE A. DORIA 6,
95125 CATANIA, ITALY

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The solid-state syntheses of uranyl acetate adducts with thiourea were attempted directly in a DSC apparatus according to the scheme: $UO_2Ac_2 \cdot 2\,H_2O_{(s)} + n$ thiourea$_{(s)} \rightarrow$ $\rightarrow UO_2Ac_2 \cdot$ thiourea$_{n(s)} + 2\,H_2O_{(v)}$ ($n = 1-6$), and the corresponding ΔH values were evaluated. At all stoichiometric ratios the same $UO_2Ac_2 \cdot$ thiourea product was obtained, to which a pentagonal bipyramidal structure was attributed. Thermoanalytical (TG and DTG) and infrared spectra measurements were also performed and agree with the DSC results.

In previous papers we have studied thermodynamically the solid-solid interactions of uranyl nitrate with several O and S-donor ligands, but the instability of uranyl nitrate at temperatures higher than 155° permits no decisive conclusions about the possibility that UO_2^{2+} ions coordinate with more than one S-donor ligand molecule [1].

Since it was shown that, similarly to the nitrate group, the acetate group acts as a bidentate chelating ligand for the uranyl group, and since uranyl acetate is thermally more stable than the nitrato salt, the following solid-solid interactions were attempted:

$$UO_2Ac_2 \cdot 2\,H_2O_{(s)} + n\,Th_{(s)} \longrightarrow UO_2Ac_2Th_{n(s)} + 2\,H_2O_{(v)}$$

$$(\mathrm{Th} = \text{thiourea},\ \mathrm{Ac} = CH_3COO,\ n = 1-6)$$

Uranyl acetate dihydrate has been used because of the inability of the anhydrous salt to react [2, 3]. Since the preparation of two species, $UO_2Ac_2 \cdot Th$ and $UO_2Ac_2 \cdot Th_4$, both from absolute ethanol, has been reported [4], it was possible to compare the behaviour of these complexes when prepared in solution or by solid-solid interactions.

Furthermore, in order to find evidence of possible differences in bonding between the two water molecules and between the two acetate ions, particular attention has been devoted to the thermal behaviour (DSC and TG) of uranyl acetate dihydrate.

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The structure of uranyl acetate dihydrate has been reported [5–7] to be a hexagonal bipyramid having a pair of trans water molecules and a pair of trans chelated acetates in the equatorial plane. The structure of the related dihydrate salt was shown by X-ray measurements to be a pentagonal bipyramid in which only one of the two water molecules is bonded directly to the uranium, while half of the acetate ions links adjacent bipyramids to form chains and the remaining acetate ions are chelated to individual uranium atoms [8].

Experimental

Materials

Uranyl acetate dihydrate (J. T. Baker) and thiourea (C. Erba RP) were used without any further purification.

DSC measurements

The DSC measurements were performed using a Mettler 20 DSC, in aluminium covered pans and in a dynamic nitrogen atmosphere (5 l h^{-1}). The heating rate was 4° min^{-1}. A closed covered pan was used as reference. The total weight of the studied systems was about 4–16 mg. The solid-solid interactions were performed by introducing finely powdered stoichiometric mixtures of the reactants into the pan, and heating successively. The corresponding ΔH values were calculated using the ΔH of melting of indium (6.79 cal g^{-1}) as calibration standard, and are reported in kJ mol^{-1}.

Other measurements

The compounds utilized for the thermal decompositions and IR measurements were prepared as follows: stoichiometric molar amounts of uranyl acetate dihydrate and thiourea (from 1:1 to 1:6), finely powdered, were well mixed and then put in an oven at 100° for few minutes.

TG and DTG measurements

The thermogravimetric curves and the corresponding kinetic parameters were obtained with a Mettler TA 3000 thermoanalyzer, utilizing alumina open crucibles, in a dynamic nitrogen atmosphere (3.6 l h^{-1}). The sample weight was about 3–15 mg.

The activation energy, E_a^*, of the thermal decomposition processes was also calculated graphically after introducing the appropriate reaction order as reported in the literature [9–12].

IR measurements

The IR spectra were obtained on KBr pellets, using a Perkin–Elmer 457 spectrophotometer (4000–250 cm^{-1}).

Results and discussion

DSC measurements

The DSC curves of both $UO_2Ac_2 \cdot 2\,H_2O$ and thiourea (Th) were preliminarly obtained in order to compare their thermal behaviour with those of the stoichiometric mixtures.

$UO_2Ac_2 \cdot 2\,H_2O$ shows a broad endothermic peak in the temperature range 90–130°, due to dehydration; at higher temperatures no thermal effect is evidenced up to 260°, when the anhydrous salt decomposes ($T_{max} = 360°$). The DSC curve is reported in Fig. 1 and the dehydration ΔH values is listed in Table 1.

The thiourea DSC curve (Fig. 2) shows an endothermic effect at 170–180° due to melting, followed by an endothermic, not evaluable vaporization process at 190°. The ΔH of melting is reported in Table 1.

At all molar ratios investigated, the DSC curves of the stoichiometric mixtures show three endothermic effects, at 90–130°, 170–180° and 190°. After this temperature a decomposition process is observed at 360° (Fig. 3).

In order to investigate if the endothermic effect at 90–130° in the DSC curves associated with the syntheses is due only to dehydration of the uranyl salt, the corresponding ΔH values were evaluated; the same value was obtained, independently of the stoichiometric ratio of the reactant mixture (Table 1), but different from the

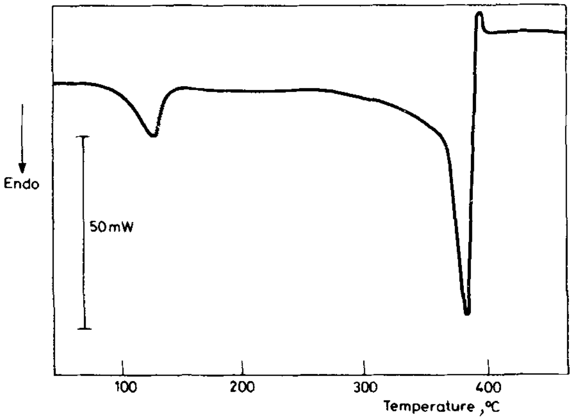

Fig. 1 DSC curve of $UO_2Ac_2 \cdot 2\,H_2O$ (11. 115 mg)

Table 1 Thermodynamic parameters associated with the solid-solid interactions. ΔH_d = enthalpic effect of the dehydration process; ΔH_{T_1} = total enthalpic effect at T_1; $\Delta H_{r_1} = \Delta H_{T_1} - \Delta H_d$; ΔH_m = enthalpic effect of the melt; ΔHT_2 = total enthalpic effect at T_2; $\Delta H_{r_2} = \Delta H_{T_2} - \Delta H_m$

	1st peak				2nd peak			
System	T_1, °C	ΔH_d	ΔH_{T_1} kJ/mol	ΔH_{r_1}	T_2, °C	ΔH_m	ΔH_{T_2} kJ/mol	ΔH_{r_2}
Thiourea					170–180	14.7		
$UO_2Ac_2 \cdot 2\,H_2O$	90–130	121.7						
$UO_2Ac_2 \cdot 2\,H_2O$:1 Th	90–130		113.2	−8.5	170–180		24.1	9.4
$UO_2Ac_2 \cdot 2\,H_2O$:2 Th	90–130		112.9	−8.8	170–180		23.8	9.1
$UO_2Ac_2 \cdot 2\,H_2O$:3 Th	90–130		111.5	−10.2	170–180		23.1	8.4
$UO_2Ac_2 \cdot 2\,H_2O$:4 Th	90–130		112.5	−9.2	170–180		23.7	9.0
$UO_2Ac_2 \cdot 2\,H_2O$:5 Th	90–130		113.2	−8.5	170–180		24.1	9.4
$UO_2Ac_2 \cdot 2\,H_2O$:6 Th	90–130		113.7	−8.0	170–180		24.5	9.8
Average		121.7	112.8	−8.9		14.7	23.9	9.2

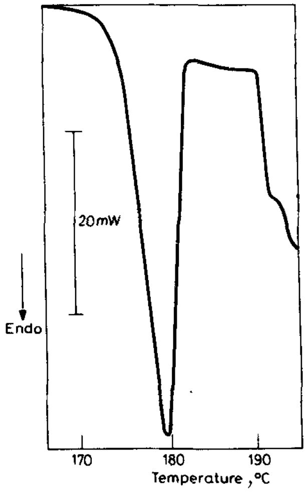

Fig. 2 DSC curve of thiourea (13.840 mg)

dehydration ΔH value of uranyl acetate. This result suggests that a solid-solid interaction occurs in the temperature range 90–130°, simultaneously with the dehydration process of the dihydrated salt, and that the same product, the 1:1 adduct, is formed in each case. The exothermic enthalpic effect due to the solid-solid interaction was also evaluated by difference between the two values and is reported in Table 1.

As concerns the second endothermic effect, at 170–180°, several hypotheses are possible: (i) the peak is due to the melting of unreacted Th molecules; (ii) the peak

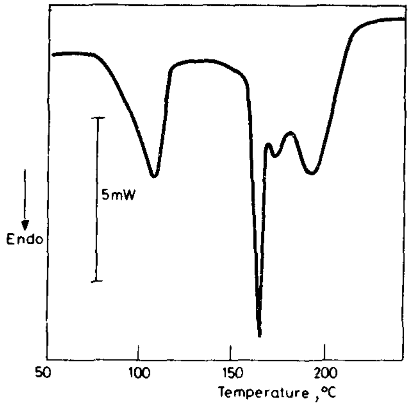

Fig. 3 DSC curve of $UO_2Ac_2 \cdot 2H_2O : 3Th$ system (6.010 mg)

is due to the release of Th from the adduct and to its simultaneous melting, together with that of unreacted Th molecules; (iii) the peak is due to an α → β transition of the $UO_2Ac_2 \cdot Th$ adduct formed. On the basis of the results described in the consideration of the dehydration process, it is possible to exclude that only the melting of unreacted thiourea occurs, as in this case no thermal effect at 170–180° could be evidenced for the 1:1 mixture. Further, the ΔH values of the 1:2, 1:3, 1:4, 1:5 and 1:6 mixtures, calculated according to hypothesis (i), are different from the ΔH of melting of Th, excluding this hypothesis.

It remains that the investigated endothermic peak is due to the release of Th from the 1:1 complex formed and to simultaneous melting of all the thiourea. This is supported by the enthalpic values calculated according to this second hypothesis: the same value as expected was obtained for all investigated mixtures, independently of the molar ratio (Table 1). This value is more endothermic than the ΔH of melting of thiourea and it is interesting to note that the endothermic difference is numerically equal to the exothermic formation ΔH value of the 1:1 adduct, calculated from the peak at 90–130°. This indicates in our opinion that this difference is due to the reaction:

$$UO_2Ac_2 \cdot Th \longrightarrow UO_2Ac_2 + Th$$

excluding the hypothesis of α → β transition of UO_2Ac_2 [13] or of the 1:1 adduct formed.

The enthalpic effects at 190°, due to the melted thiourea present in the mixtures, are not evaluable because of the irregular form.

Moreover, the DSC measurements suggest that when stoichiometric mixtures of uranyl acetate dihydrate and thiourea are heated, several processes occur, according to the scheme:

(a) $UO_2Ac_2 \cdot 2\,H_2O_{(s)} + n\,Th_{(s)} \xrightarrow{90-130^\circ} UO_2Ac_2 \cdot Th_{(s)} + 2\,H_2O_{(v)} +$
$+ (n-1)\,Th_{(s)}$

(b) $UO_2Ac_2 \cdot Th_{(s)} \xrightarrow{170-180^\circ} UO_2Ac_{2(s)} + Th_{(s)}$

$Th_{(s)} + (n-1)\,Th_{(s)} \xrightarrow{170-180^\circ} n\,Th_{(l)}$

(c) $n\,TH_{(l)} \xrightarrow{190^\circ}$ decomposition products

(d) $UO_2Ac_{2(s)} \xrightarrow{360^\circ}$ decomposition products

TG and DTG measurements

Thermal decomposition of $UO_2Ac_2 \cdot 2\,H_2O$

The dehydration process occurs in a single step at 90° and it is complete (heating 7.49 mg of salt) at 98°; the kinetic parameters relating to their reaction are: reaction order = 0.5; $E_a^* = 166$ kJ mol^{-1} and ln $K = 48.3$.

In an attempt to shift the loss of the two water molecules, the thermal decomposition was performed under isothermal conditions at 90°. It was possible to establish that under these conditions the reaction is complete after 20.9 minutes, as evidenced by the plot of the degree of conversion α *vs.* time (see Fig. 4). In this way, therefore no evidence of a different coordination environment of the two water molecules is exhibited and there is no possibility to obtain the monohydrate species.

Nevertheless, on examination of the thermal behaviour of the adducts described below, the isothermal synthesis at 90° of the system $UO_2Ac_2 \cdot 2\,H_2O:1$ Th (4.91 mg of stoichiometric mixture) shows quite clearly that the two water molecules are released one at a time. The plot of the degree of conversion α *vs.* time is linear, but a variation of slope at $\alpha = 0.5$ is clearly indicated (Fig. 5). Therefore, only the presence of a neutral ligand (in this case Th) able to occupy the internal coordination site of the water molecule allows an indirect distinction between the two water molecules.

The anhydrous acetate salt is thermally stable up to 250°. At this temperature it slowly decomposes in a single step. Isothermal kinetic studies on this reaction confirm the impossibility of demonstrating the different thermal behaviour of the acetate groups. The relative kinetic non-isothermal parameters of this decomposition are: reaction order = 0.1; $E_a^* = 226$ kJ mol^{-1} and ln $K = 38.6$. The residual product corresponds to non-stoichiometric UO_3, according to what was reported in [14].

Thermal decomposition of Th

The thermal decomposition of the thiourea occurs in accordance with the DSC measurement.

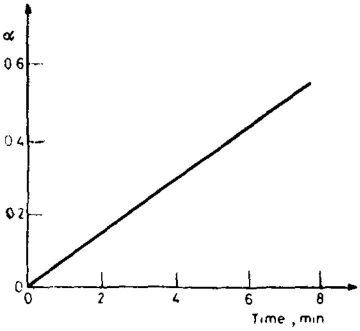

Fig. 4 Degree of conversion of $UO_2Ac_2 \cdot 2\ H_2O$ *vs.* time under isothermal conditions (at 90°)

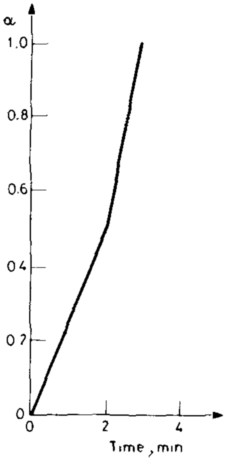

Fig. 5 Degree of conversion of $UO_2Ac_2 \cdot 2\ H_2O$:Th system *vs.* time under isothermal conditions (at 90°)

Thermogravimetric analysis of the system

The TG curves were obtained by heating both the mixtures and the products obtained in the oven, but no difference in thermoanalytical behaviour was observed, apart from the dehydration step.

The $UO_2Ac_2 \cdot 2\ H_2O : 1$ Th system, heated at $\phi = 1$ deg min^{-1}, first reacts in the temperature range 76–98°, according to the reaction:

$$\text{(a)}\quad UO_2Ac_2 \cdot 2\ H_2O_{(s)} + Th_{(s)} \xrightarrow{76^\circ} UO_2Ac_2 \cdot Th_{(s)} + 2\ H_2O_{(v)} \quad \text{(a)}$$

The kinetic parameters are: reaction order = 0.67; $E_a^* = 120$ kJ mol^{-1}.

The product of reaction (a), thermally stable up to 160°, decomposes in a single step, as also shown by the DTG curve, with loss of the neutral ligand:

$$\text{(b)}\quad UO_2Ac_2 \cdot Th_{(s)} \xrightarrow{160^\circ} UO_2Ac_{2(s)} + Th_{(v)} \qquad \text{(b)}$$

The kinetic parameters are: reaction order = 0.76; $E_a^* = 69.7$ kJ mol^{-1}. This decomposition is complete at 240° and the product is uranyl acetate, whose decomposition occurs in the temperature range 275–480°:

$$\text{(c)}\quad UO_2Ac_{2(s)} \xrightarrow{275^\circ} UO_{3(s)} + \text{gaseous products} \qquad \text{(c)}$$

This thermal behaviour is reported in Fig. 6.

The TG curves of the mixtures $UO_2Ac_2 \cdot 2\,H_2O{:}n\,Th$ ($n = 2$–6) indicate a dehydration step, analogously as obtained for the 1:1 system. The kinetic parameters associated with these reactions are the same for all considered stoichiometric ratios and coincide with those for the 1:1 system, independently of the number of thiourea molecules ($n > 1$). This confirms the DSC results indicating that the same kind of interaction occurs:

$$UO_2Ac_2 \cdot 2\,H_2O_{(s)} + n\,Th_{(s)} \xrightarrow{76^\circ} UO_2Ac_2 \cdot Th_{(s)} + 2\,H_2O_{(v)} + \\ + (n-1)\,Th_{(s)}$$

The presence of an unreacted thiourea excess is evidenced by the successive decomposition step that, differently from the reported reaction (b), occurs in two unresolved processes:

(i) loss of the bound thiourea;

(ii) loss of the unbound thiourea excess.

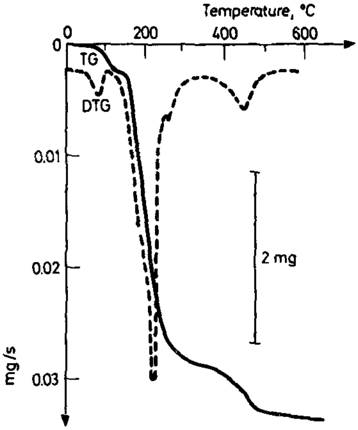

Fig. 6 Thermal behaviour of $UO_2Ac_2 \cdot 2\,H_2O{:}Th$ system (5.107 mg)

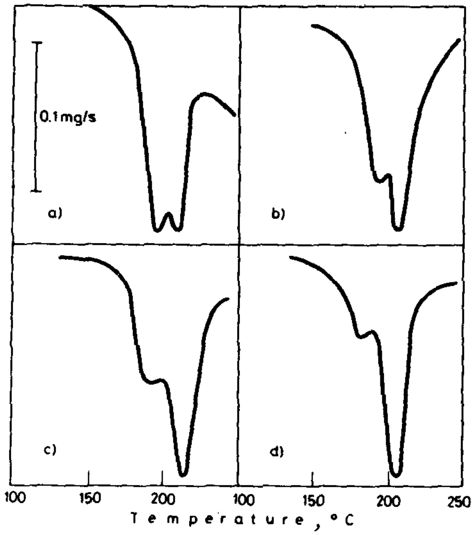

Fig. 7 DTG curves of a) $UO_2Ac_2 \cdot 2\,H_2O:2\,Th$ (5.976 mg); b) $UO_2Ac_2 \cdot 2\,H_2O:3\,Th$ (6.868 mg); c) $UO_2Ac_2 \cdot 2\,H_2O:4\,Th$ (5.549 mg); d) $UO_2Ac_2 \cdot 2\,H_2O:5\,Th$ (7.282 mg)

The sequence of the two processes is shown by the DTG curves. In fact (Fig. 7), if the amount of unreacted Th increases compared to the $UO_2Ac_2 \cdot Th$ complex formed, the shortening of the first DTG peak with respect to the second is observed. The reactions are:

$$\text{(i)}\quad UO_2Ac_2 \cdot Th_{(s)} + (n-1)\,Th_{(s)} \xrightarrow{160^\circ} UO_2Ac_{2(s)} + Th_{(v)} + (n-1)\,Th_{(s)}$$

$$\text{(ii)}\quad (n-1)\,Th_{(s)} \longrightarrow \text{gaseous products}$$

Process (ii) begins before reaction (i) is complete. Owing to the impossibility of resolving the two processes, the kinetic parameters have not been evaluated. The product UO_2Ac_2 successively decomposes at 275°, as previously described.

IR spectra

The IR spectra of the products obtained in the oven as described in the experimental section were measured and compared with those of the reactants. The IR spectral assignments for the principal peaks of the reactants were made in accordance with literature data [4]; for the product obtained from the 1:1 mixture, red shifts of the O—U—O ν_3 antisymmetric stretching frequency from 942 cm^{-1} to 900 cm^{-1} and of the $\nu_{(C-S)}$ band of the thiourea from 636 cm^{-1} to 575 cm^{-1} are observed, thereby indicating metal-sulfur bonding in the 1:1 adduct. In the IR spectra of the products obtained in the oven from 1:n mixtures ($n \neq 1$), the ν_3 band of uranyl group shifts from 942 cm^{-1} to 900 cm^{-1}, whereas the bands at 636 cm^{-1} and 575 cm^{-1}, due respectively to the unbound and bound thiourea, are both present; this confirms that the products obtained in the oven are mixtures of 1:1 adduct with a thiourea excess.

Conclusions

All the performed DSC, TG and IR measurements agree with one another and clearly indicate that only the 1:1 adduct is formed by solid-solid interaction between uranyl acetate and thiourea. The small differences observed between the DSC and TG temperatures of the thermal processes can be explained by considering that the DSC measurements were performed in aluminium closed pans, whereas the TG measurements were performed in alumina open crucibles. No evidence of formation of 1:n adducts ($n \neq 1$) has been obtained, though the formation of the 1:4 adduct from ethanolic solution has been reported [4].

The pentagonal bipyramidal structure of uranyl acetate dihydrate, the results of the IR measurements indicating a S–U bond in the 1:1 complex, and the results of the isothermal kinetic measurements on the $UO_2Ac_2 \cdot 2\,H_2O$:1 Th mixture (Fig. 5) suggesting that the Th molecule substitutes the internally bonded water molecule, lead us to consider that a similar pentagonal bipyramidal structure can be attributed to the 1:1 adduct.

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Zusammenfassung — In einer DSC-Apparatur wurde die Synthese von Uranylacetat-Thioharnstoff-Addukten in situ durch Festkörperreaktion entsprechend dem Schema

$$UO_2Ac_2 \cdot 2\,H_2O_{(s)} + n\,\text{Thioharnstoff}_{(s)} \rightarrow UO_2Ac_2 \cdot \text{Thioharnstoff}_{n(s)} + 2\,H_2O_{(v)}\ (n = 1\text{–}6)$$

ausgeführt. Die entsprechenden ΔH-Werte wurden berechnet. Für alle stöchiometrischen Verhältnisse wurde das gleiche $UO_2Ac_2 \cdot$ Thioharnstoff-Produkt erhalten, dem eine pentagonale bipyramidale Struktur zuzuordnen ist. Die Ergebnisse thermoanalytischer (TG und DTG) und infrarotspektrophotometrischer Messungen stimmen mit den DSC-Ergebnissen überein.

Резюме — Непосредственно в приборе ДСК был проведен твердотельный синтез аддуктов ацетата уранила с тиомочевиной по следующей схеме реакции:

$$UO_2Ac_2 \cdot 2\,H_2O_{(\text{тв.})} + n\ \text{тиомочевина}_{(\text{тв.})} \longrightarrow$$
$$\longrightarrow UO_2Ac_2 \cdot \text{тиомочевина}_{(\text{тв.})} + 2\,H_2O_{(\text{пары})},\quad \text{где}\ n = 1\text{–}6.$$

Определены значения ΔH. Несмотря на различные стехиометрические соотношения взятых исходных веществ, был получен один и тот же продукт $UO_2Ac_2 \cdot$ тиомочевина, которому была приписана структура пятиугольной бипирамиды.