Thermochimica Acta, 136 (1988) 153–161
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL BEHAVIOUR OF URANIUM(VI) COMPLEXES. URANYL ACETATE DIHYDRATE-*N*,*N*′-DIMETHYLTHIOUREA SYSTEM: SYNTHESIS AND DECOMPOSITION

L. ABATE, A. CHISARI and R. MAGGIORE

Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania (Italy)

G. SIRACUSA

Istituto Chimico della Facoltà di Ingegneria, Università di Catania, Viale A. Doria 6, 95125 Catania (Italy)

(Received 22 January 1988)

ABSTRACT

Reactions in the solid state between uranyl acetate dihydrate and *N*,*N*′-dimethylthiourea were attempted by heating the solid reactants directly in a DSC and in a TA apparatus. The results suggest that *N*,*N*′-dimethylthiourea melts at 60–62 °C and that the liquid compound reacts with uranyl acetate dihydrate simultaneously to the dehydration of the salt at 90–130 °C. Reaction is not complete in excess of *N*,*N*′-dimethylthiourea.

DSC, TG and IR results agree and suggest formation of a 1 : 1 adduct independently from molar ratios of reactant mixtures.

INTRODUCTION

The complexes of uranyl salts with oxygen or nitrogen donor ligands have been widely studied [1–6]. In previous papers we reported the results of our studies in which the ability of the uranyl ion to coordinate, in the solid state, with ligand molecules having sulphur as donor ligand atom was investigated. We showed that uranyl acetate dihydrate reacts with thiourea [7], *N*-phenylthiourea [8] and *N*,*N*′-diphenylthiourea [9] and that, in every case, 1 : 1 adducts are obtained independently from reactants molar ratios. Mass effects were also observed in the formation of *N*-phenylthiourea and *N*,*N*′-diphenylthiourea complexes.

In this paper we report on studies of interactions between uranyl acetate dihydrate ($UO_2Ac_2 \cdot 2H_2O$) and *N*,*N*′-dimethylthiourea (DMT), in order to investigate whether the presence of methyl groups in the thiourea molecule influences donor properties of the ligand.

The syntheses were attempted using solid reactants

$$UO_2Ac_2 \cdot 2H_2O + n\text{DMT} \rightarrow UO_2Ac_2 \cdot (\text{DMT})_n + 2H_2O \quad (n = 1\text{–}6)$$

Uranyl acetate dihydrate was used because of the inability of the anhydrous salt to react.

EXPERIMENTAL

Materials

Uranyl acetate dihydrate (J.T. Baker) and *N,N′*-dimethylthiourea (Schuchardt) were used without further purification.

DSC measurements

DSC measurements were performed using a Mettler 20 DSC calorimeter, in closed aluminium pans and in a dynamic nitrogen atmosphere (5 l h^{-1}). The reference was an empty closed aluminium pan.

Syntheses were performed by introducing into the pan a finely powdered stoichiometric mixture of reactants, the total weight being 5–15 mg, and heating successively. The ΔH values associated with the reactions were evaluated using the ΔH_{melt} value of indium (6.79 cal g^{-1}) as standard.

TG and DTG measurements

The TG and DTG measurements were performed by a Mettler TA model 50 thermoanalyser, in a dynamic nitrogen atmosphere (3.6 l h^{-1}), utilizing open alumina crucibles and a heating rate of 10 °C min^{-1}. The sample weights were about 5–15 mg. The solid–solid interactions were performed similarly to the method used for the DSC measurements.

IR spectra

The IR spectra were obtained from KBr pellets, using a Perkin-Elmer 457 spectrophotometer (4000–250 cm^{-1}). Pellets were obtained as follows: reactants (in several stoichiometric molar ratios) were intimately mixed with anhydrous KBr; mixtures obtained were put in an oven at 60 or 110 °C for 1 h and then cooled to room temperature. Products obtained as described before were finely powdered before forming pellets.

RESULTS AND DISCUSSION

DSC measurements

The reactions using solid reactants were performed in DSC equipment, and the curves obtained were compared with those of the reactants.

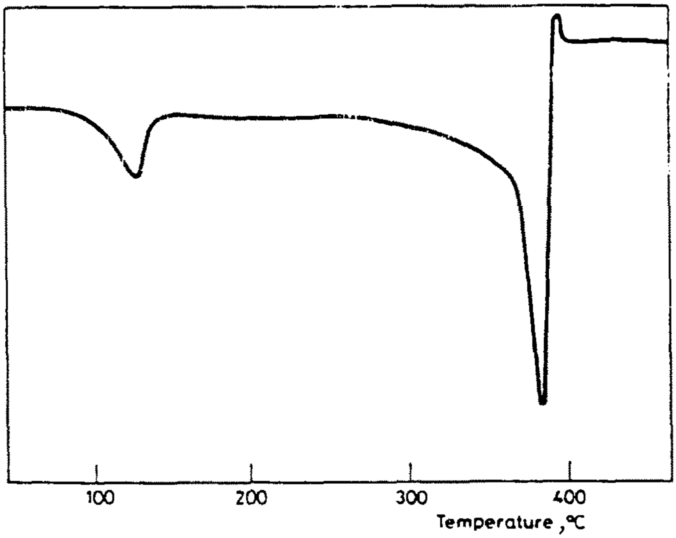

Fig. 1. DSC curve of uranyl acetate dihydrate.

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

The DSC curve of N,N'-dimethylthiourea shows an endothermic effect at 60–62 ° C due to melting: above this temperature only an unresolvable double thermal effect in the temperature range 180–290 ° C is seen, probably due to superimposition of boiling and decomposition processes (Fig. 2).

TABLE 1

Temperatures (° C) and ΔH values (kJ mol^{-1}) associated with the DSC peaks. ΔH_{T_1} = enthalpic effect at temperature T_1; ΔH_{T_2} = enthalpic effect at temperature T_2; ΔH_r = enthalpic effect associated with formation of the adduct. ΔH_{T_1} values refer to 1 mole of DMT; ΔH_{T_2} and ΔH_r values refer to 1 mole of uranyl acetate dihydrate

System	T_1	ΔH_{T_1}	T_2	ΔH_{T_2}	ΔH_r
DMT	60–62	12.8	–	–	–
$UO_2Ac_2 \cdot 2H_2O$	–	–	90–130	121.7	–
$UO_2Ac_2 \cdot 2H_2O$ + 1DMT	60–62	12.8	90–130	66.1	−55.6
$UO_2Ac_2 \cdot 2H_2O$ + 2DMT	60–62	12.8	90–130	61.9	−59.8
$UO_2Ac_2 \cdot 2H_2O$ + 3DMT	60–62	12.8	90–130	40.0	−81.7
$UO_2Ac_2 \cdot 2H_2O$ + 4DMT	60–62	12.8	90–130	25.0	−96.7
$UO_2Ac_2 \cdot 2H_2O$ + 5DMT	60–62	12.8	90–130	21.3	−100.44
$UO_2Ac_2 \cdot 2H_2O$ + 6DMT	60–62	12.8	90–130	20.0	−101.7

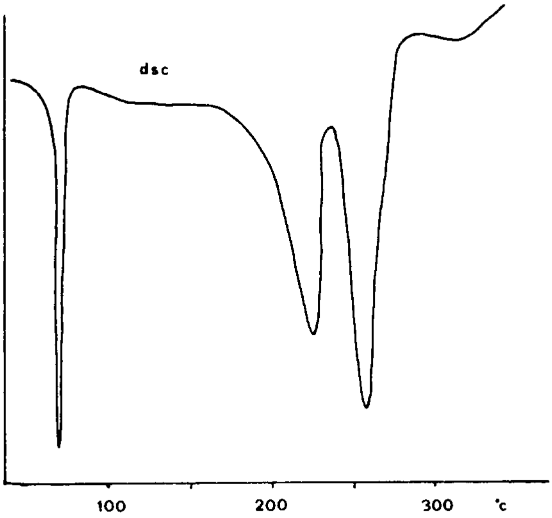

Fig. 2. DSC curve of *N*,*N*′-dimethylthiourea.

The DSC curves corresponding to the reactions show, for all stoichiometric ratios, several endothermic effects, the first at 60–62 °C and the second one at 90–130 °C. Above this temperature only an irregular thermal effect is observed, owing to probable superimposition of the DMT thermal effect at 180–290 °C with thermal effects due to decomposition of anhydrous uranyl acetate and of the adduct formed. In Fig. 3 the DSC curve of the 1 : 3 stoichiometric mixture is illustrated as an example. All calculated ΔH values are reported in Table 1.

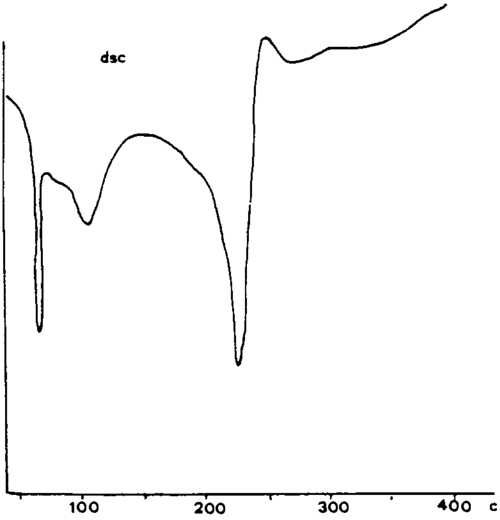

Fig. 3. DSC curve of $UO_2Ac_2 \cdot 2H_2O$: 3DMT system.

Quantitative analysis of the thermal effects observed during synthetic processes shows that the enthalpic values associated with the peaks at 60–62 °C are the same as those of melting of *N,N′*-dimethylthiourea; by contrast the ΔH values associated with the peaks at 90–130 °C are less endothermic than the ΔH value of uranyl salt dehydration. No quantitative information can be obtained from the thermal effects at 180–300 °C because of the irregular shape of the curves; this is due to several simultaneous processes.

Results obtained for reactant mixtures, compared with those of reactants, suggest that:

(i) *N,N′*-dimethylthiourea melts at 60–62 °C;
(ii) Uranyl salt dehydration occurs in the temperature range 90–130 °C and, simultaneously, the anhydrous salt partially reacts with melted *N,N′*-dimethylthiourea by an exothermic process. This was confirmed performing reactions in a Kofler apparatus: we observed the melting process at 60 °C and red colour formation at 90–110 °C, indicating formation of a new compound;
(iii) Above 130 °C *N,N′*-dimethylthiourea boils and decomposition processes of uranyl acetate and of adducts formed occur.

The ΔH values obtained seem to exclude formation of $1:n$ adducts having the same molar ratios as reactant mixtures. Considering that uranyl acetate reacts with thiourea, *N*-phenylthiourea and *N,N′*-diphenylthiourea with formation of 1 : 1 adducts, we suppose that, in this case also, a 1 : 1 adduct is formed. Inability of the anhydrous salt to react suggests the same mechanism of reaction as other thioureas investigated previously. Furthermore, the ΔH values obtained indicate incomplete formation of the adduct obtained; the percentage of unreacted uranyl acetate decreases with increasing n, that suggesting a mass effect, although the reaction is also not completed in a large ligand excess. Moreover, DSC measurements suggest that, when stoichiometric mixtures of uranyl acetate dihydrate and *N,N′*-dimethylthiourea (DMT) are heated, several processes occur

(a) $$\mathrm{DMT_{(s)}} \xrightarrow{60\text{–}62\,^\circ\mathrm{C}} \mathrm{DMT_{(l)}}$$

(b) $$\mathrm{UO_2Ac_2 \cdot 2H_2O_{(s)}} + n\mathrm{DMT_{(l)}} \xrightarrow{90\text{–}130\,^\circ\mathrm{C}} \mathrm{UO_2Ac_2 \cdot DMT + 2H_2O} + (n-1)\mathrm{DMT_{(l)}}$$

(c) $$\left.\begin{array}{ll} (n-1)\mathrm{DMT_{(l)}} & \rightarrow \text{boiling process} \\ \mathrm{UO_2Ac_2 \cdot DMT} & \rightarrow \mathrm{UO_2Ac_2 + DMT_{(l)}} \\ \mathrm{DMT_{(l)}} & \rightarrow \text{boiling} \\ \mathrm{UO_2Ac_2} & \rightarrow \text{decomposition} \end{array}\right\} \text{in the range } 180\text{–}300\,^\circ\mathrm{C}$$

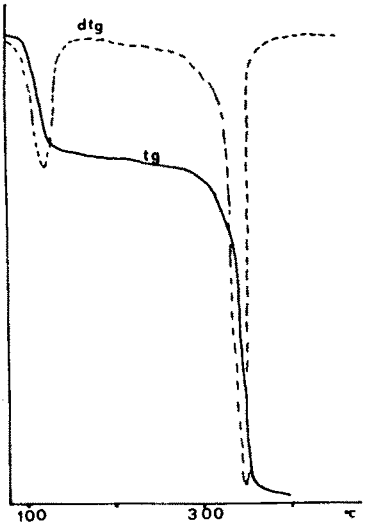

Fig. 4. Thermal behaviour of uranyl acetate dihydrate.

TG and DTG measurements

On heating uranyl acetate dihydrate in the thermoanalyser, two steps are observed, the first at 90–140 ° C, due to dehydration, and the other from 250 to 370 ° C, due to decomposition of anhydrous salt (Fig. 4); the residual product corresponds to a non-stoichiometric UO_3 compound.

TG and DTG curves of *N,N'*-dimethylthiourea show only a decomposition process in the range 160–240 ° C, the weight loss being 96.6% (Fig. 5).

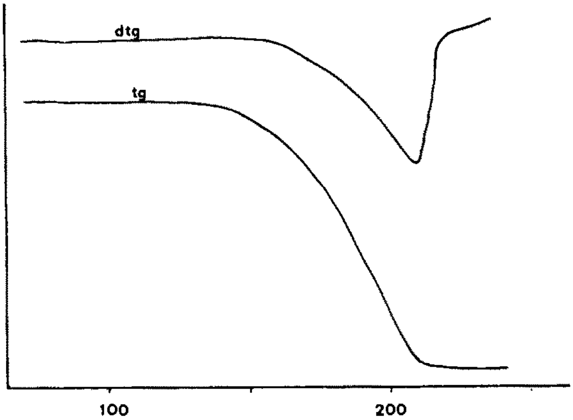

Fig. 5. Thermal behaviour of *N,N'*-dimethylthiourea.

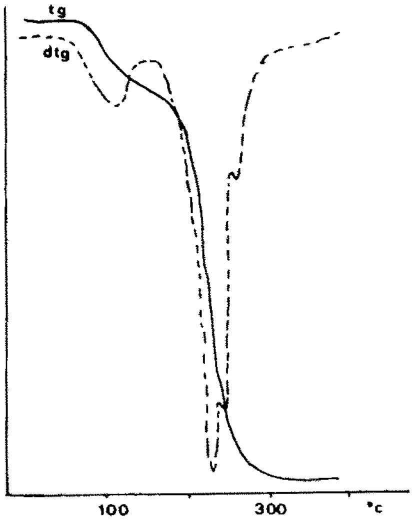

Fig. 6. Thermal behaviour of $UO_2Ac_2 \cdot 2H_2O:3DMT$ system.

TG curves of all mixtures investigated provide evidence of three processes: the first is observed in the temperature range 90–140 °C; above this temperature two unresolved processes occur in the temperature ranges 160–240 °C

TABLE 2

Temperatures (°C) and corresponding weight losses (%) of thermal processes

System	*T*	Weight loss
$UO_2Ac_2 \cdot 2H_2O + 1DMT$	90–140	8.30
	160–240 240–300	38.46
$UO_2Ac_2 \cdot 2H_2O + 2DMT$	90–140	7.49
	160–240 240–300	46.82
$UO_2Ac_2 \cdot 2H_2O + 3DMT$	90–140	5.97
	160–240 240–300	53.78
$UO_2Ac_2 \cdot 2H_2O + 4DMT$	90–140	5.31
	160–240 240–300	60.30
$UO_2Ac_2 \cdot 2H_2O + 5DMT$	90–140	5.19
	160–240 240–300	62.24
$UO_2Ac_2 \cdot 2H_2O + 6DMT$	90–140	5.12
	160–240 240–300	66.17

and 240–300 °C. In Fig. 6 TG and DTG curves of 1 : 3 stoichiometric mixture are reported as examples.

TG results, compared with DSC results, show that at 90–140 °C the uranyl salt dehydration occurs and simultaneously anhydrous salt and melted DMT react; successively, at 160–300 °C, unreacted *N,N′*-dimethylthiourea decomposes together with the anhydrous uranyl salt. The results are reported in Table 2.

The reactions are:

$$\text{(a)}\quad UO_2Ac_2\cdot 2H_2O_{(s)} + n\text{DMT}_{(l)} \xrightarrow{90\text{–}140\,^\circ C} UO_2Ac_2\cdot \text{DMT} + 2H_2O + (n-1)\text{DMT}$$

$$\text{(b)}\quad (n-1)\text{DMT}_{(l)} \xrightarrow{160\text{–}240\,^\circ C} \text{gaseous products}$$

$$\text{(c)}\quad UO_2Ac_2\cdot \text{DMT} \xrightarrow{240\text{–}300\,^\circ C} UO_3 + \text{gaseous products}$$

IR spectra

IR spectra of products obtained at 60 °C as described in the experimental section were compared with IR spectra of unheated reactant mixtures; no difference was observed. Also, IR spectra of products obtained at 110 °C were compared with IR spectra of unheated reactant mixtures; in this case several differences were observed. A red shift of O–U–O ν_3 antisymmetric stretching frequency occurs from 942 to 920 cm^{-1}; furthermore, two bands due to the C=S bond of DMT at 643 cm^{-1} (unlinked DMT) and at 613 cm^{-1} (linked DMT) were observed. This behaviour shows incomplete metal–sulphur bond formation.

No difference was observed between products obtained from mixtures with different stoichiometric ratios.

CONCLUSIONS

All DSC, TG and IR measurements performed agree with each other and suggest that $UO_2Ac_2\cdot 2H_2O$ and *N,N′*-dimethylthiourea partially react in melted DMT. Small differences between DSC and TG temperatures are due to different experimental conditions.

No evidence of formation of 1 : *n* adducts ($n \neq 1$) was obtained; the IR measurements suggest a S–U bond in the 1 : 1 complex obtained. As DMT substitutes for a water molecule in the $UO_2Ac_2\cdot 2H_2O$ compound [7], we think that a pentagonal bipyramidal structure can be attributed to the 1 : 1 adduct, analogous to the structure of uranyl acetate dihydrate [6].

The decomposition temperature of the adduct is less than that of anhydrous uranyl acetate, suggesting a lower thermal stability for the complex obtained. Also, it suggests that the thermal stability of uranyl acetate decreases in the presence of DMT.

A mass effect was observed, but the reaction seems incomplete also in a large excess of DMT.

ACKNOWLEDGEMENT

This work was supported by Italian Ministero della Pubblica Istruzione (fondi 40%).

REFERENCES

1 A.D. Jones and G.R. Choppin, Actinides Rev., 1 (1969) 311.
2 M.J. Cleveland, Coord. Chem. Rev., 5 (1970) 101.
3 L. Cattalini, U. Croatto, S. Degetto and S. Tondello, Inorg. Chim. Acta Rev., 5 (1971) 19.
4 S.M. Eberle, Comprehensive Inorganic Chemistry, Vol. 5, Pergamon Press, Oxford, 1973.
5 J. Howatson, D.M. Grevand and B. Morosin, Inorg. Nucl. Chem., 37 (1975) 1933.
6 U. Casellato, P.A. Vigato and M. Vidali, Coord. Chem. Rev., 26 (1978) 85.
7 L. Abate, A. Chisari, R. Maggiore and G. Siracusa, J. Therm. Anal., 27 (1983) 139.
8 L. Abate, A. Chisari, G. Romeo, R. Maggiore and G. Siracusa, J. Therm. Anal., 28 (1983) 227.
9 L. Abate, A. Chisari, R. Maggiore and G. Siracusa, Thermochim. Acta, 90 (1985) 23.