Thermochimica Acta, 70 (1983) 143–148
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF PENTACOORDINATE URANIUM(VI) COMPLEXES

L. ABATE, A. CHISARI, G. ROMEO

Istituto Dipartimentale di Chimica e Chimica Industriale, Facoltà di Scienze, Università di Catania, 95125 Catania (Italy)

R. MAGGIORE and G. SIRACUSA

Facoltà di Ingegneria, Università di Catania, 95125 Catania (Italy)

(Received 5 May 1983)

ABSTRACT

The thermal decomposition of some mixed uranyl complexes with Schiff bases and DMSO, EtOH or $(Ph)_3PO$ as neutral ligand, were investigated and the corresponding activation energy, E_a^*, and enthalpy of dissociation, ΔH_d, values were calculated.

The results obtained indicate that for the same neutral ligand, the thermal stability of the uranyl complexes is influenced by the Schiff base used; for the same Schiff base, the presence of $(Ph)_3PO$ results in a greater thermal stability of the mixed complexes than when the other two neutral ligands are present.

INTRODUCTION

The possibility of a correlation between the parameters evaluated by means of thermoanalytical techniques and the thermodynamic quantities or strength of the metal–ligand bond has been the subject of much discussion.

Excepting the uncertainties in the choice of thermochemical parameters, it was pointed out that an appropriate comparison can be made if the reaction rate of a thermal decomposition in the solid state is a chemically controlled process [1–4]. In this case it is possible to interpret the energy or enthalpic values in a chemical context.

Considering the strong complexing ability of Schiff bases towards the uranyl ion [5–9], in this work some mixed complexes of uranium(VI) with Schiff bases and EtOH, DMSO and $(Ph)_3PO$ were examined.

Since X-ray structural investigations pointed out the isomorphism of these complexes with an equatorial pentacoordination [10–13], we have studied to what extent the mechanism of the reactions, during the thermal decomposition, is influenced by the electronic effects of the substituent.

The complexes studied were: $[UO_2salen]EtOH$, $[UO_2salen]DMSO$, $[UO_2$-

0040-6031/83/$03.00

salen](Ph)$_3$PO, [UO$_2$salprop]EtOH, [UO$_2$salprop]DMSO, [UO$_2$salprop](Ph)$_3$PO, [UO$_2$salofd]EtOH, [UO$_2$salofd]DMSO, [UO$_2$salofd](Ph)$_3$PO, [UO$_2$glyox]EtOH, [UO$_2$glyox]DMSO and [UO$_2$glyox](Ph)$_3$PO, where: salen is *N*,*N*′-ethylenebis(salicylideneiminato); salprop is *N*,*N*′-propylenebis(salicylideneiminato); salofd is *N*,*N*′-*o*-propylenebis(salicylideneiminato); glyox is glyoxalbis(2-hydroxyanil); EtOH is C_2H_5OH; DMSO is $(CH_3)_2SO$; and (Ph)$_3$PO is $(C_6H_5)_3PO$.

EXPERIMENTAL

The preparation of the adducts was performed according to the procedure described in the literature [12].

The simultaneous TG, DTG and DTA were performed using a Mettler thermoanalyzer, in a dynamic nitrogen atmosphere (10 l h^{-1}) and at heating rates varying from 0.5 to 4°C min^{-1}. The sample weight was about 20 mg. A Mettler model T-TD$_3$ crucible holder, 0.3 ml platinum microcrucibles and thermically inactive Al_2O_3, as reference material, were used.

The activation energy, E_a^*, of a thermal decomposition process was calculated graphically after introducing the appropriate order of reaction as reported in literature [14]. Enthalpic values, ΔH_d, relative to the dissociation processes, were calculated by the method of Stepin et al. [15]. In this way, E_a^* and ΔH_d values were evaluated from the same TG curve.

RESULTS AND DISCUSSION

In a dynamic nitrogen atmosphere, the TG curves of the complexes MLEtOH and MLDMSO ($M = UO_2$; L = Schiff base) show a decomposition step in the temperature range 150–200 and 200–250°C, respectively. The decomposition processes are described by the reactions

$$\mathrm{MLEtOH_{(s)}} \rightarrow \mathrm{ML_{(s)}} + \mathrm{EtOH_{(v)}}$$

$$\mathrm{MLDMSO_{(s)}} \rightarrow \mathrm{ML_{(s)}} + \mathrm{DMSO_{(v)}}$$

The simultaneous DTA curve shows a large endothermic peak in the temperature range over which continuous weight loss is observed. When L = salen, a sharp exothermic peak follows the first one, due to loss of the ligand (Fig. 1). The simple UO_2L complexes have a large and well-defined range of thermal stability. An exothermic process takes place immediately before the thermal decomposition, which occurs exothermically in two consecutive thermogravimetric non-stoichiometric steps. For the same Schiff base, the decomposition process occurs in the same way, independent of the neutral ligand released before. The residual product of the decomposition process is U_3O_8. The experimental data are reported in Table 1.

The presence of the exothermic effects after the release of the neutral

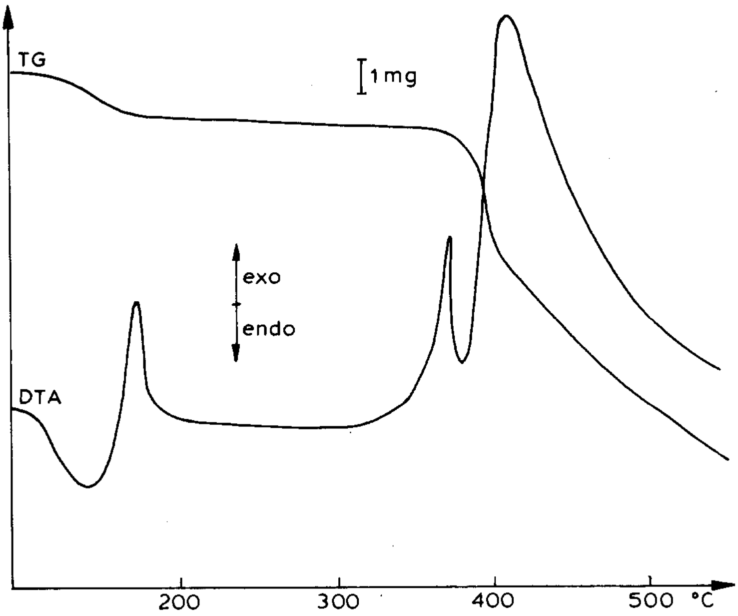

Fig. 1. Thermal behaviour of [UO_2salen]EtOH.

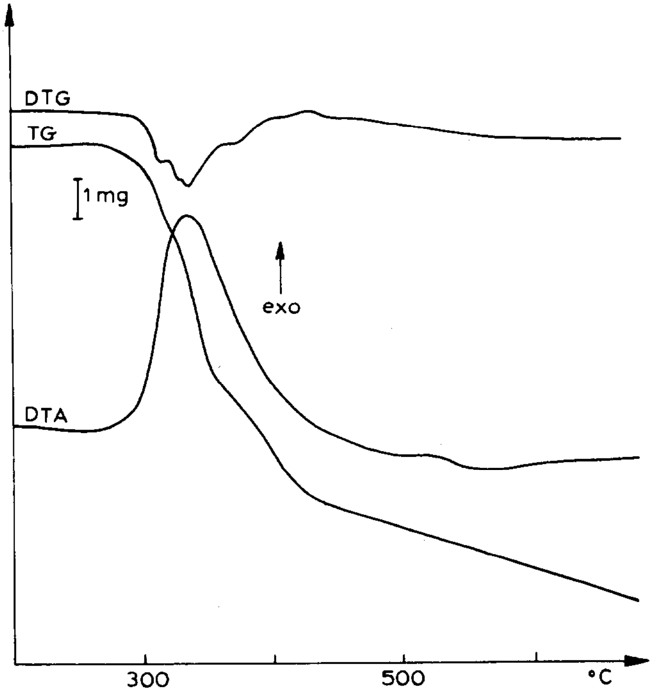

Fig. 2. Thermal behaviour of [UO_2salprop]$(Ph)_3$PO.

TABLE 1

Experimental data relative to thermal behaviour in a nitrogen atmosphere

Complex	Temperature range (°C)	Loss of [a]	Thermal effect
[UO_2salen]EtOH	150– 180	EtOH	Endo/exo
	370– 380		Exo
	380– 400	dcpn	Exo
	400–1000		
[UO_2salen]DMSO	198– 237	DMSO	Endo/exo
	370– 380		Exo
	380– 400	dcpn	Exo
	400–1000		
[UO_2salen](Ph)$_3$PO	278– 450	dcpn	Exo
	400–1000		
[UO_2salprop]EtOH	155– 198	EtOH	Endo
	360– 370		Exo
	370– 382	dcpn	Exo
	382–1000		
[UO_2salprop]DMSO	207– 252	DMSO	Endo
	360– 370		Exo
	370– 382	dcpn	Exo
	382–1000		
[UO_2salprop](Ph)$_3$PO	278– 450	dcpn	Exo
	450–1000		
[UO_2salofd]EtOH	176– 227	EtOH	Endo
	325– 338		Exo
	338– 352	dcpn	Exo
	352–1000		
[UO_2salofd]DMSO	232– 282	DMSO	Endo
	325– 338		Exo
	338– 352	dcpn	Exo
	352–1000		
[UO_2salofd](Ph)$_3$PO	278– 450	dcpn	Exo
	450–1000		
[UO_2glyox]EtOH	167– 175	EtOH	Endo
	350– 365		Exo
	365– 410	dcpn	Exo
	410–1000		
[UO_2glyox]DMSO	197– 240	DMSO	Endo
	350– 365		Exo
	365– 410	dcpn	Exo
	410–1000		
[UO_2glyox](Ph)$_3$PO	278– 450	dcpn	Exo
	450–1000		

[a] dcpn = decomposition.

ligand allows us to assert that, for the [UO_2salen]EtOH and [UO_2salen] DMSO complexes, a polymeric process involving formation of the species [UO_2salen]$_n$ must immediately follow the loss of the neutral equatorial ligand from the mixed complex. The absence of this exothermic effect in the

DTA curve of all other complexes cannot exclude that a similar polymeric structure can be achieved simultaneously with the loss of the neutral ligand. A possible explanation of the exothermic peak observed before the thermal decomposition of the simple UO_2L complexes is that the two aromatic rings of the Schiff bases, which are each in the *cis* position with respect to the equatorial plane at room temperature [12], become unstable up to the temperature of decomposition of the simple complexes and on attempting to reach a greater stability (as the *trans* form), decomposition occurs.

The possibility of attributing this thermal effect to a polymerization process, on the other hand, is excluded by the presence of this exothermic peak also in the DTA curves of the $[UO_2salen]$ complex.

The TG curves of the mixed complexes, with general formula $ML(Ph)_3PO$, denote a different pathway. The release of the neutral ligand is simultaneous to the decomposition of the Schiff base and stoichiometric steps are not indicated. The total thermal effect is exothermic (Table 1 and Fig. 2).

CONCLUSION

The thermal behaviour of the complexes UO_2LDMSO and UO_2LEtOH point to a general reaction mechanism, involving the release of the neutral ligand followed by decomposition of the UO_2L complex.

This behaviour indicates that the ligand type does not play a determinant role in the reaction mechanism.

The absence of exothermic effects after the release of the neutral ligand, when the Schiff base is not salen, makes it difficult to evaluate the influence of the polymerization process upon the decomposition reaction. Therefore, comparison of the E_a^* or ΔH_d values obtained for different complexes is also difficult.

The kinetic data (Table 2) agree with the enthalpic data (Table 3); for the same neutral ligand, the thermal stability of the uranyl complexes is influenced by the Schiff base used, and the order found was: salprop > glyox > salen > salofd.

TABLE 2

Activation energy values under non-isothermal conditions ($\Phi = 4°C\ min^{-1}$) relative to the decomposition reaction
$UO_2LX_{(s)} \rightarrow UO_2L_{(s)} + X_{(v)}$

L	E_a^*(kcal $mole^{-1}$)	
	UO_2LEtOH	UO_2LDMSO
salen	22.3	23.2
salofd	14.2	20.8
salprop	19.8	27.4
glyox	20.9	26.5

TABLE 3

Enthalpy values under non-isothermal conditions ($\Phi = 4°C\ min^{-1}$) relative to the decomposition reaction
$UO_2LX_{(s)} \rightarrow UO_2L_{(s)} + X_{(v)}$

L	ΔH_d(kcal mole^{-1})	
	UO_2LEtOH	UO_2LDMSO
salen	18.6	20.0
salofd	10.8	19.8
salprop	15.7	23.1
glyox	16.0	22.8

For the same Schiff base, the presence of DMSO results in a greater thermal stability for the mixed complexes with respect to the presence of EtOH.

On considering the thermal behaviour of the $[UO_2L](Ph)_3PO$ complexes, we note the greater stability of the mixed complex, as shown by the initial temperature of decomposition, even if the presence of this neutral ligand does not allow the formation of a thermally stable simple complex. In this case, a different mechanism is shown for the thermal processes and kinetic or enthalpic evaluation has not been possible owing to the overlapping of several thermal effects.

REFERENCES

1 I. Proks, Chem. Zvesti, 20 (1966) 697.
2 E. Iona, V. Iesenak, T. Sramko and I. Gazo, J. Therm. Anal., 5 (1973) 57.
3 L. Abate, F. Castelli and G. Siracusa, Thermochim. Acta, 41 (1980) 87.
4 G. Siracusa, L. Abate and R. Maggiore, Thermochim. Acta, 56 (1982) 333.
5 S.K. Mandal and J. Das, J. Indian Chem. Soc., 55 (1978) 845.
6 G. Manecke, W.E. Wille and G. Kossmehl, Makromol. Chem., 160 (1972) 111.
7 B.S. Pannu, B.S. Sekhov and S.L. Chopra, Ann. Chim. (Rome), 2 (1977) 245.
8 L.F. Capitan-Vallvey, F. Salinas, C. Jimenez and L. Cuadros, Can. J. Chem., 60 (1982) 1076.
9 L.F. Capitan-Vallvey, F. Salinas, C. Jimenez and L. Cuadros, Can. J. Chem., 60 (1982) 1713.
10 U. Croatto, Acc. Peloritana Pericolanti, (1971) 99.
11 G. Bandoli, D.A. Clemente, U. Croatto, M. Vidali and P.A. Vigato, Inorg. Nucl. Chem. Lett., 8 (1972) 961.
12 G. Bandoli, L. Cattalini, D.A. Clemente, M. Vidali and P.A. Vigato, J. Chem. Soc. Chem. Commun., (1972) 344.
13 G. Bandoli, D.A. Clemente, U. Croatto, M. Vidali and P.A. Vigato, J. Chem. Soc. Chem. Commun., (1971) 1330.
14 B. Durairaj and K. Venkatarao, Thermochim. Acta, 43 (1981) 125.
15 B.D. Stepin, G.R. Allakhverdov and G.M. Serebrennikova, Russ. J. Phys. Chem., 43 (1969) 1377.