Journal of Thermal Analysis, Vol. 37 (1991) 259-265

KINETICS AND THERMAL DECOMPOSITION OF Fe(III) AND UO_2(II) COMPLEXES WITH EMBELIN (2,5-DIHYDROXY-3-UNDECYL-P-BENZOQUINONE)

*M. L. Dhar** *and O. Singh*

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JAMMU, JAMMU-180 004, INDIA

(Received October 9, 1989; in revised form May 5, 1990)

The thermal decomposition of the complexes: $[Fe(C_{17}H_{24}O_4)_{1.5}\cdot 2H_2O]_n$ and $[UO_2(C_{17}H_{24}O_4\cdot 2H_2O]_n$, and evaluation of kinetic parameters (E, Z and ΔS^*) by making use of Piloyan-Novikova, Coats-Redfern and Horowitz-Metzger equations are reported. The complexes are found to decompose in three well defined steps involving random nucleation mechanism. The intermediates formed during decomposition usually undergo further decomposition without remaining stable over a considerable range of temperature.

Although the preparation of biologically active and analytically important complexes of embelin [1-4] have been reported earlier by us [3], there is no reference in literature regarding the differential thermal analysis and thermogravimetric studies. This communication deals with the thermogravimetric analysis and the kinetics of thermal decomposition of these complexes.

Experimental

The simultaneous DTA and TG curves of the complexes were obtained on Paulik-Paulik MOM derivatograph (Hungary). The samples were heated at the rate of 10 deg/min in a cylindrical heat resistant ceramic crucible [5]. α-alumina was used as the reference material.

---

* To whom all correspondence should be addressed

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

The kinetics of thermal decomposition steps were investigated by non-isothermal method. For obtaining the kinetic parameters and the reaction model, the thermogravimetric data was analyzed by making use of appropriate equations commonly used in non-isothermal kinetic studies of decomposition reactions. The model giving the best linear fit for different equations was considered.

The values obtained from Piloyan-Novikova and Coats-Redfern equations were plotted against $\frac{1}{T}$ while in the case of Horowitz-Metzger, values obtained were plotted against Θ ($\Theta = T - T_m$, where T_m = peak temperature).

Results and discussion

The thermal decomposition of the complexes occur in three distinct steps as obtained in the TG and the corresponding peaks of the DTA curves (Fig. 1).

The Fe(III) complex yields a horizontal line extending upto 333 K showing stability of the complex upto this temperature. The decomposition started at 333 K and continues upto 498 K. The weight remaining at this stage corresponds to $[Fe(C_{17}H_{24}O_4)_{1.5}]_n$ indication thereby loss of two coordinated water molecules. The second step of decomposition started at 498 K and extended upto 753 K corresponding to the loss of the side chain of the ligand. The weight remaining at this stage corresponded to $[Fe(C_6H_1O_4)_{1.5}]_n$. The third step of decomposition starts beyond 753 K and continues upto 1043 K corresponding to the loss of benzoquinone moiety. The ultimate decomposition product Fe_2O_3 is formed beyond 1043 K and no further loss in weight occurs on subsequent heating.

The UO_2(II) complex yields horizontal line extending upto 318 K showing stability of the complex upto this temperature. The decomposition of the complex starts beyond 318 K and continues upto 518 K. The weight remaining at this stage corresponds to $[UO_2(C_{17}H_{24}O_4)_1]_n$ which indicates the loss of two coordinated water molecules. A further regular decomposition starts beyond 518 K and extends upto 673 K corresponding to the loss of the side chain of the ligand. The decomposition starts further beyond 673 K and ends at 1003 K with the formation of the stable product U_3O_8. There is no further loss in weight on subsequent heating.

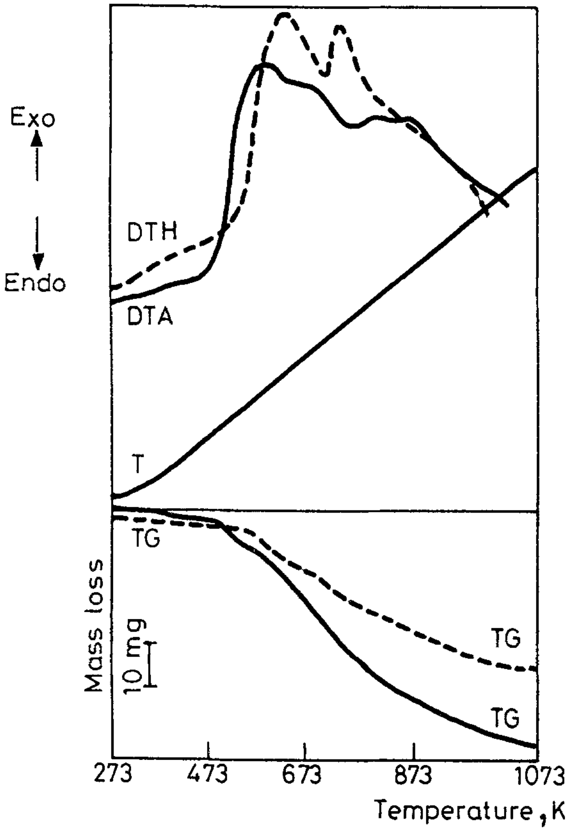

Fig. 1 Simultaneous DTA-TG curves of $[Fe(C_{17}H_{24}O_4)_{1.5}\cdot 2H_2O]_n$ (———) and $[UO_2(C_{17}H_{24}O_4)\cdot 2H_2O]_n$ (– – –)

Kinetics of decomposition

Non-isothermal kinetics of the first two decomposition steps of the complexes were studied. The values of the degree of decomposition (α) at different temperatures were obtained from TG curves. From the values of α, corresponding $(1-\alpha)^n$ values were calculated where n depends upon the reaction model. The equations of Piloyan-Novikova [6], Coats-Redfern [7] and Horowitz-Metzger [8] were employed. For Piloyan-Novikova, plot of $\log\left(\frac{\alpha}{T^2}\right)$ *vs.* $\frac{1}{T}$; for Coats-Redfern, plot of $\log\left[-\ln\frac{1-\alpha}{T^2}\right]$ *vs.* $\frac{1}{T}$ and for

Horowitz-Metzger, plot of log [–ln (1–α)] *vs.* Θ have been found to be best fits. The model which corresponds to the linear fit has been used to give the probable mechanism of the decomposition.

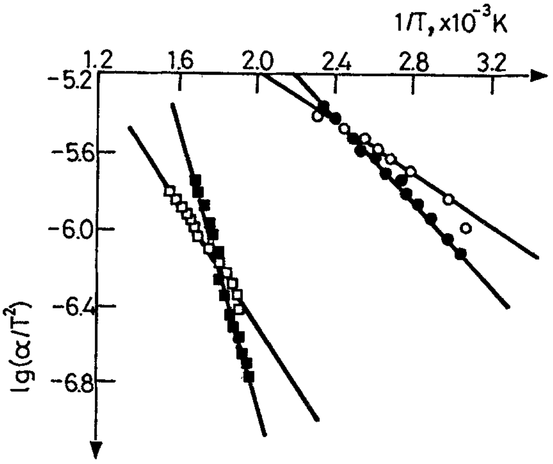

Fig. 2 Piloyan-Novikova plots; Fe(III) complex: 1st step (□), 2nd step (■); UC2(II) complex: 1st step (o), 2nd step (•)

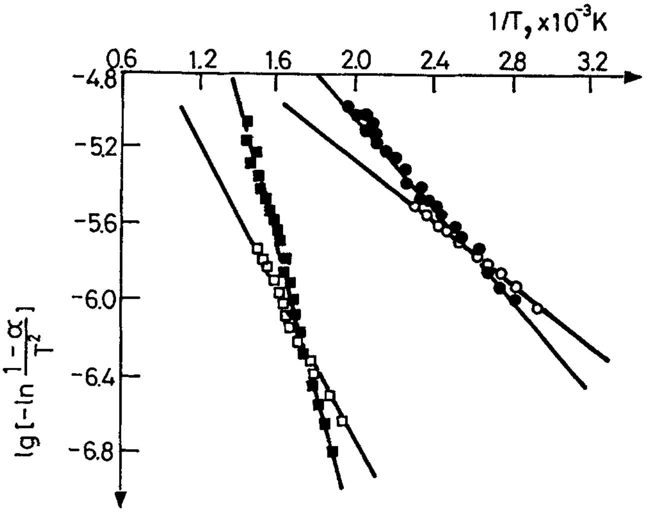

Fig. 3 Coats-Redfern plots; Fe(III) complex: 1st step (□), 2nd step (■); UC2(II) complex: 1st step (o), 2nd step (•)

Figures 2-4 were analysed for the values of slope, intercept and the energy of activation. From these values, the corresponding values of Z were obtained in case of Piloyan-Novikova and Coats-Redfern while the values of Z in case of Horowitz-Metzger were calculated by making use of the relation

$$Z = \frac{E}{RT_m} \beta \exp\left(\frac{E}{RT_m^2}\right)$$

and the entropies of activation (ΔS^*) were obtained from the relation

$$Z = \frac{KT_m}{h} \exp\left(\frac{\Delta S^*}{R}\right)$$

where, R represents molar gas constant, β the rate of heating (KS^{-1}), K the Boltzman constant and h the Planck's constant.

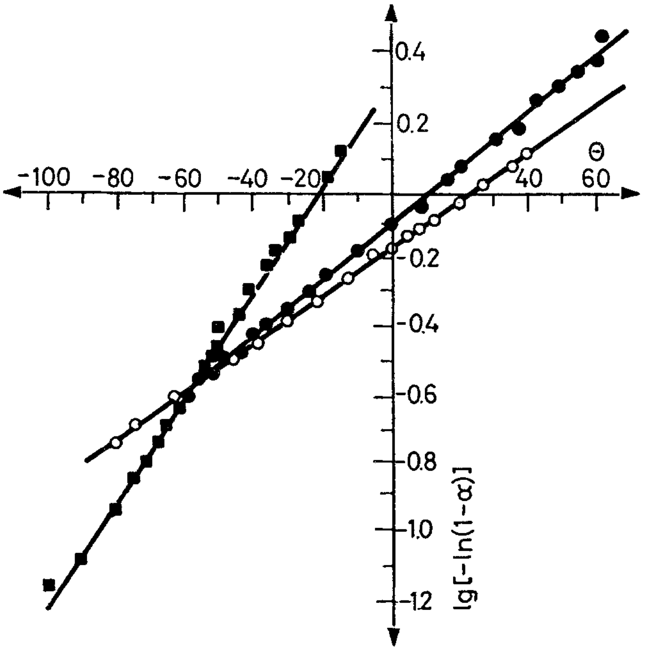

Fig. 4 Horowitz-Metzger plots; Fe(III) complex: 1st step (■); UC_2(II) complex: 1st step (o), 2nd step (•)

Table 1

Complex	Step	Equation	E, kJ·mol^{-1}	Z, s^{-1}	ΔS^*, J·K^{-1}·mol^{-1}	Model
$[Fe(C_{17}H_{24}O_4)_{1.5}\cdot H_2O)]_n$	First	Piloyan-Novikova	20.515	0.542	–109.941	-
	Second	Piloyan-Novikova	33.943	0.365	–112.514	-
$[UO_2(C_{17}H_{24}O_4)\cdot 2H_2O)]_n$	First	Piloyan-Novikova	25.530	0.154	–114.327	-
	Second	Piloyan-Novikova	76.591	9687.238	–456.071	-
$[Fe(C_{17}H_{24}O_4)_{1.5}\cdot H_2O)]_n$	First	Coats-Redfern	22.526	1.083	–107.441	R.N.
	Second	Coats-Redfern	38.295	1.531	–107.340	R.N.
$[UO_2(C_{17}H_{24}O_4)\cdot 2H_2O)]_n$	First	Coats-Redfern	16.155	0.1097	–115.566	R.N.
	Second	Coats-Redfern	79.782	19326.30	–453.577	R.N.
$[Fe(C_{17}H_{24}O_4)_{1.5}\cdot H_2O)]_n$	First	Horowitz-Metzger	30.192	$3.688\cdot 10^{-3}$	–127.789	R.N.
	Second	Horowitz-Metzger	47.931	$2.788\cdot 10^{-3}$	–130.118	R.N.
$[UO_2(C_{17}H_{24}O_4)\cdot 2H_2O)]_n$	First	Horowitz-Metzger	19.069	$2.255\cdot 10^{-3}$	–129.592	R.N.
	Second	Horowitz-Metzger	123.524	$6.728\cdot 10^{-3}$	–150.434	R.N.

R.N. = Random nucleation

The value of kinetic parameters and the mechanism of decomposition are recorded in Table 1.

It is concluded that both the polymeric complexes have uniform decomposition patterns. In both the complexes, dehydration being the first step, loss of the side chain being the second step and the loss of the ligand moiety completely being the third step with the ultimate products being the two oxides Fe_2O_3 and U_3O_8. The decompositions involve the random nucleation mechanism [9].

References

1 M. L. Dhar and Onkar Sing, Journal fiir Prakt. Chemie, 331 (1989).
2 Ch. Rao Bheemasankara and V. Venkteswarlu, Indian J. Pharm., 24 (1962) 263.
3 O. Singh, Ph. D. Thesis (1984), University of Jammu, India.
4 Ch. Rao Bheemasankara and V. Venkteswarlu, Z. Anal. Chem., 178 (1961) 227, 185 (1962) 216, 192(2) (1963) 183.
5 F. Paulik, J. Paulik and L. Erdey, Z. Anal. Chem., 160 (1958) 241.
6 G. O. Piloyan, I. D. Pyabohikov and I. S. Novikova, Nature (London), 212 (1966) 1229.
7 A. W. Coats and J. P. Redfern, Nature (London), 68 (1964) 101.
8 H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
9 K. L. Mampal, Z. Phys. Chem., 187 (1940) 43 and 235.

Zusammenfassung — Es wird über die thermische Zersetzung der Komplexe $[Fe(C_{17}H_{24}O_4)_{1.5}\cdot 2H_2O]_n$ und $[UO_2(C_{17}H_{24}O_4)\cdot 2H_2O]_n$ und über die Ermittlung der kinetischen Parameter durch Anwendung der Piloyan-Novikova, der Coats-Redfern und der Horowitz-Metzger-Gleichungen berichtet. Die Komplexe werden in drei gut definierten Stufen mit Random-Keimbildungsmechanismus zersetzt. Die während der Zersetzung gebildeten Zwischenprodukte unterliegen stets einer weiteren Zersetzung, ohne in einem erheblichen Temperaturbereich Stabilität zu zeigen.