Journal of Thermal Analysis, Vol. 37 (1991) 803-811

THERMAL DECOMPOSITION KINETICS OF POLYMERIC COMPLEXES OF COPPER(II) AND MERCURY(II) WITH N,N'-BIS(DITHIOCARBOXY)PIPERAZINE

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(Received January 20, 1991)

The thermal decomposition behaviour of polymeric complexes of Cu(II) and Hg(II) with N,N'–bis(dithiocarboxy)piperazine is investigated in air by thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) techniques. The kinetic parameters (non-isothermal method) for their decomposition have been evaluated by graphical as well as by least-squares methods. The equations of Coats-Redfern, Freeman-Carroll and Horowitz-Metzger have been applied. The results indicate that the values of E, A and ΔS obtained by these three different methods agree well. It was also found that the decomposition of these metal chelates follow first-order kinetics.

The thermal decomposition of metal dithiocarbamate complexes have been attracting considerable interest [1–3] due to the wide range applications of these compounds and their oxidation products [4–6]. Preliminary thermogravimetric analyses were made to establish the optimum drying temperature ranges of these complexes [7] and to ascertain their thermal stabilities. These studies gave some interesting observations and a reference to literature showed that no work has been done on the thermal decomposition of polymeric metal chelates of dithiocarbamates of this type which may exhibit unusual dielectric, thermal and conductance behaviour. In this paper we present our investigations on the thermal behaviour and kinetics of thermal decomposition of polymeric complexes of Cu(II) and Hg(II) with N,N'–bis(dithiocarboxy)piperazine, $(C_4H_8N_2)(CS_2)_2$.

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Experimental

The ligand was synthesized as its disodium salt by the reported procedure [8]. The metal complexes were prepared by adding an aqueous solution of the disodium salt of the ligand dropwise with constant stirring to an aqueous solution of the respective metal chloride until the metal to ligand ratio reached 1:1. The solid complex that separated was filtered, washed several times with water and then with methanol and dried in vacuum over P_4O_{10}. The purity of the complexes were ascertained by elemental analyses using standard procedures [9] and they were found to be of the formulae $Cu(L)\cdot H_2O$ and Hg(L), where L = N,N'–bis(dithiocarboxy)piperazine. They were further characterized by spectral and magnetic studies [7].

Apparatus

The thermoanalytical measurements (TG and DTA) were carried out on a DuPont 990 thermal analyser system, in conjunction with 951 thermogravimetric analyser and 1200-901 modular DTA cell system. The operational characteristics are as given below: heating rate, 10 deg min^{-1}; sample size, 2 to 6 mg; atmosphere, static air; crucible, platinum. The numerical analyses of the thermogravimetric data were realized using a program written in Microsoft BASIC for an IBM computer using DOS 4.00.

The mass loss data obtained from TG were compared with those obtained from independent pyrolysis experiments, in which the samples were heated for 2 h in silica crucibles upto $\approx$675 K.

Treatment of data

The instrumental TG, DTG and DTA traces are shown in Figs 1 and 2. The TG curves were studied in greater detail. The instrumental TG curves were redrawn as the fraction decomposed (α) against temperature (T) curves to obtain the primary α–T data. The non-isothermal kinetics of the decomposition reactions of the two metal chelates have been studied and the order of the reaction (n) and the kinetic parameters such as apparent activation energy (E), the entropy of activation (ΔS) and the preexponential factor (A) were evaluated.

Determination of the order of reaction

The order of the decomposition reaction was determined by computing correlation coefficient (r) by least-squares method (LSM) for the equations suggested by Coats and Redfern [10], by differential method using the Freeman–Carroll equation [11] and by the method suggested by Horowitz and Metzger [12], for which a master curve was constructed as reported in earlier work [13].

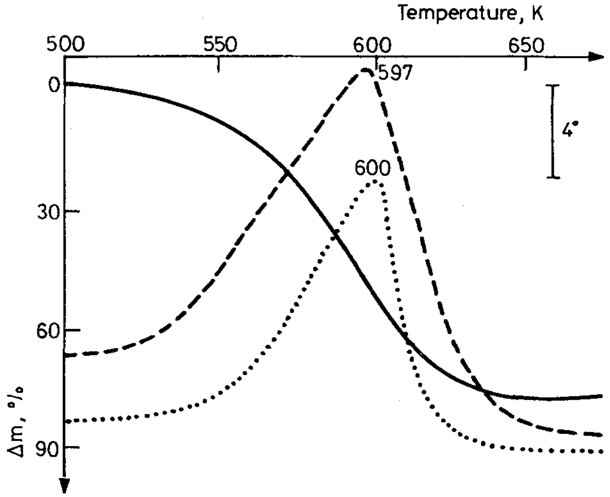

Fig. 1 TG (——), DTG (— — —) and DTA (· · ·) curves of Cu(L)·H_2O

Evaluation of kinetic parameters

Coats-Redfern equation [10]

The Coats–Redfern equation, a typical integral method, can have the following two forms,

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = M/T + B \quad \text{for } n \neq 1 \tag{1}$$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = M/T + B \quad \text{for } n = 1 \tag{2}$$

where $M = \frac{-E}{R}$, $B = \ln\left[\frac{AR}{qE}\right]$, R is the universal gas constant and q represents the rate of heating.

It is evident from the above equations that a plot of the left-hand side against $1/T$ would be linear for correct mechanism of decomposition. In

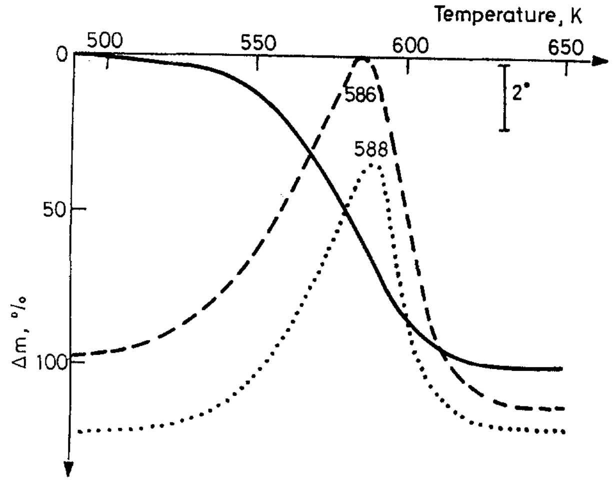

Fig. 2 TG (——), DTG (– – –) and DTA (· · ·) curves of Hg(L)

other words the function describing the correct mechanism of decomposition will give a maximum value of correlation coefficient ($r \approx 1$) for the least-squares fit. In the present study, Eqs (1) and (2) were applied to our data using the linear LSM. The best correlation was obtained with Eq. (2) for both complexes and therefore, the order of the reaction is 1. Accordingly the values of E and A were calculated from the slope and intercept, respectively, obtained from the least-squares plot of Eq. (2). The entropy of activation, ΔS was calculated from the equation,

$$A = \frac{KT_s}{h} \exp(\Delta S/R) \tag{3}$$

where k is the Boltzmann constant, h is the Planck constant and T_S is the DTG peak temperature. The kinetic parameters were also evaluated by graphical method using Eq. (2) (Fig. 3).

Freeman-Carroll equation [11] (Differential method)

The Freeman-Carroll was used in the following form,

$$\frac{\Delta \ln(dW/dt)}{\Delta \ln W_r} = \frac{-E/R\,\Delta(1/T)}{\Delta \ln W_r} + n \tag{4}$$

where $W_r = W_C - W$, W_C is the mass loss at the completion of the reaction and W is the total loss in mass upto time t. The temperature slopes, dW/dT were converted into time slopes, dW/dt by using the relation,

$$dW/dt = (dW/dT)\cdot(dT/dt) = (dW/dT)\,q \tag{5}$$

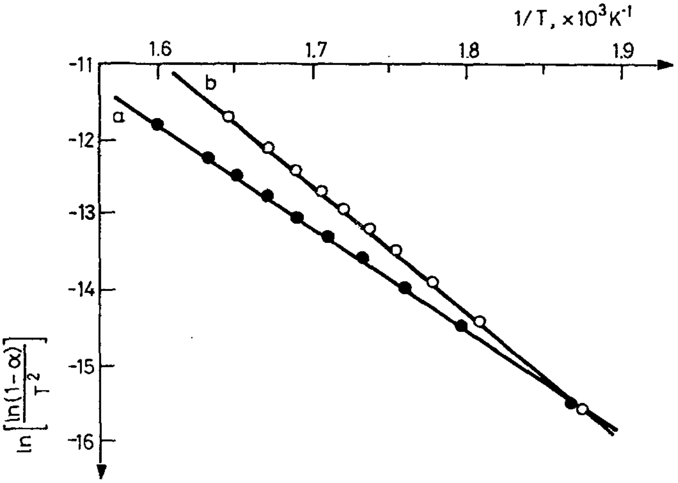

Fig. 3 Coats–Redfern plot for $a = Cu(L)\cdot H_2O$, $b = Hg(L)$

It is evident from Eq. (4) that a plot of $\frac{\Delta(1/T)}{\Delta \ln W_r}$ *vs.* $\frac{\Delta \ln(dW/dt)}{\Delta \ln W_r}$ would be linear, whose intercept would be equal to the order of the reaction and it was found to be almost unity for both complexes. By combining the usual first order rate equation with Arrhenius equation, we obtain,

$$\ln\left[\frac{dW/dt}{W_r}\right] = \frac{-E}{RT} + \ln A \tag{6}$$

A plot of $\ln\left[\frac{dW/dt}{W_r}\right]$ *vs.* $1/T$ was found to be linear (given in Fig. 4). E was calculated from the slope, A was calculated from the intercept and ΔS was calculated from the Eq. (3) used earlier for this purpose. These kinetic parameters were also evaluated by the method of least–squares.

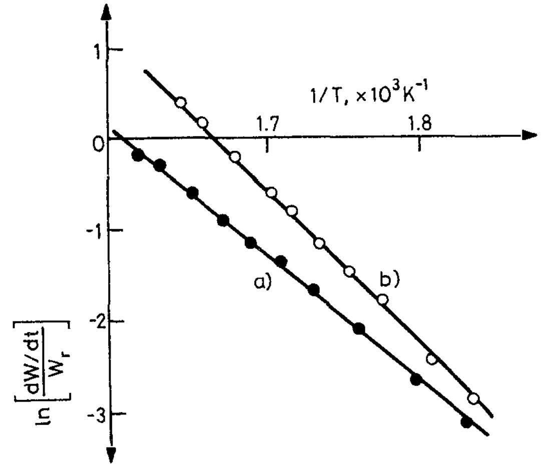

Fig. 4 Freeman–Carroll plot for $a = Cu(L) \cdot H_2O$, $b = Hg(L)$

Horowitz–Metzger equation [12]

An approximation method suggested by Horowitz and Metzger was also used for the evaluation of kinetic parameters. Here the equation for first-order kinetics is in the form,

$$\ln[-\ln(1-\alpha)] = \frac{E\Theta}{RT_s^2} \tag{7}$$

where $\theta = T - T_S$.

A plot of ln [–ln(l–α)] *vs*. θ was found to be linear (Fig. 5), from the slope of which E was calculated. A was calculated from the equation,

$$\frac{E}{RT_s^2} = \frac{a}{q\exp(E/RT_s)} \tag{8}$$

The entropy of activation, ΔS was calculated by using Eq. (3) mentioned earlier. The kinetic parameters were also evaluated from the values of slope and intercept obtained from the method of least–squares.

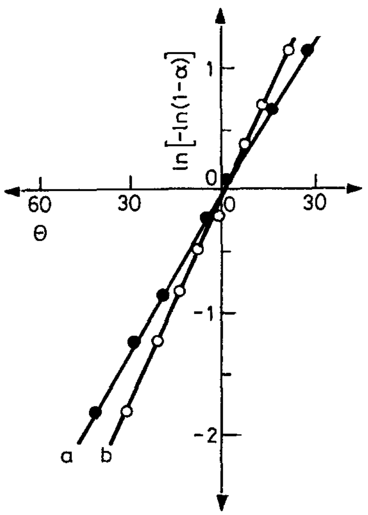

Fig. 5 Horowitz–Metzger plot for $a = Cu(L)\cdot H_2O$, $b = Hg(L)$

Results and discussion

The values of correlation coefficient, slope and intercept obtained by the method of least-squares for Coats–Redfern, Freeman-Carroll and Horowitz–Metzger equations are listed in Table 1. The values of kinetic parameters are given in Table 2.

Thermal behaviour

The thermal decomposition of $Cu(L)\cdot H_2O$ occurs in two distinct steps. It is stable upto ≈ 363 K. The elimination of water takes place in a single step, shown by the DTG peak at 380 K and corresponding endothermic DTA peak at 383 K. Further, the IR spectral study of this complex indicates that the water molecule is present as purely lattice–held one [7]. The initial mass loss in TG (5.45%) for this complex agrees well with the theoretically expected loss (5.66%) due to the elimination of one molecule of water. The second step of decomposition starts at 513 K and a regular loss in mass occurs upto 635 K. The DTG peak at 597 K and exothermic DTA peak at 600 K represent this stage. The mass loss (75.18%) in this step corresponds to the formation of CuO which is stable beyond 635 K. This agrees with the mass loss (75.25%) obtained in independent pyrolysis experiment. The final decomposition product was analysed to be CuO.

The mercury complex Hg(L) was found to be an anhydrous one by elemental analysis and IR spectral studies [7] and was confirmed by the thermogravimetric studies. It is stable upto 493 K and decomposes in a single step which is represented by the DTG peak at 586 K and corresponding exothermic DTA peak at 588 K. As expected, for the mercury complex, no residue was left on heating upto 675 K.

Table 1 Values of slope, intercept and correlation coefficient obtained from LSM

Equation	Complex	Slope	Intercept	Correlation coefficient
Coats–Redfern	Cu(L)·H_2O	–13500	9.823	–0.9999
	Hg(L)	–16864	16.047	–0.9999
Freeman–Carroll	Cu(L)·H_2O	–13999	24.400	–0.9858
	Hg(L)	–17245	29.018	–0.9876
Horowitz–Metzger	Cu(L)·H_2O	0.0436	0.001	0.9985
	Hg(L)	0.0552	–0.030	0.9993

Table 2 Kinetic data

Equation	Parameters	From graph		From LSM	
	+	Cu(L)·H_2O	Hg(L)	Cu(L)·H_2O	Hg(L)
Coats–Redfern	E	112.37	138.79	112.24	140.21
	A	$2.62\cdot10^{9}$	$1.87\cdot10^{12}$	$2.49\cdot10^{9}$	$1.57\cdot10^{12}$
	ΔS	–70.38	–15.60	–70.81	–17.05
Freeman–Carroll	E	115.48	141.39	116.39	143.38
	A	$2.17\cdot10^{10}$	$2.97\cdot10^{12}$	$3.95\cdot10^{10}$	$4.00\cdot10^{12}$
	ΔS	–52.80	–11.75	–47.82	–9.26
Horowitz–Metzger	E	125.89	156.55	129.20	158.50
	A	$4.39\cdot10^{10}$	$4.94\cdot10^{13}$	$8.78\cdot10^{10}$	$6.08\cdot10^{13}$
	ΔS	–46.95	11.62	–41.26	13.35

* Units: $E = \text{kJ}\cdot\text{mol}^{-1}$; $A = \text{s}^{-1}$; $\Delta S = \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Decomposition kinetics

The analyses of data using Coats–Redfern, Freeman–Carroll and Horowitz–Metzger methods showed that the order of the decomposition reaction is unity for both complexes. Based on this value of reaction order the kinetic parameters of decomposition reactions were evaluated by using the above mentioned three equations by graphical as well as by the method of least-squares and are listed in Table 2. The satisfactory values of correlation coefficients ($r \approx 1$) in all cases indicate good agreement with the experimental data. The negative values of ΔS for these complexes indicate that the activated complex has a more ordered structure than the reactants and the reactions are slower than normal [14, 15].

The Hg(II) complex began to decompose slowly at about 493 K with considerable induction period and was complete at about 615 K, while the slow decomposition of the Cu(II) complex started at a higher temperature of about 513 K and was complete at about 635 K. This indicates that the rate of nucleus formation is faster in Hg(II) complex than in Cu(II) complex, which may be due to the absence of residual solid phase in Hg(II) complex.

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The authors are thankful to Prof. C. G. R. Nair, Head of the Department of Chemistry, University of Kerala and Dr. M. P. Kannan, Department of Chemistry, University of Calicut for some helpful discussions.

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Zusammenfassung — Mittels TG, DTG und DTA wurde das thermische Zersetzungsverhalten von Polymerkomplexen aus Cu(II) bzw. Hg(II) mit N,N'-Bis(dithiocarboxy)piperazin an Luft untersucht. Für ihre Zersetzung (nichtisotherme Methode) wurden die kinetischen Parameter sowohl graphisch als auch durch Methoden mit den kleinsten Fehlerquadraten ermittelt. Dabei wurden die Gleichungen von Coats-Redfern, Freeman-Carroll und von Horowitz-Metzger angewendet. Alle drei Verfahren zeigen übereinstimmende Resultate für E, A und S. Es wurde weiterhin gefunden, daß diese Metallchelate einer Reaktion erster Ordnung unterliegen.