Journal of Thermal Analysis, Vol. 37 (1991) 2259-2266

ANALYSIS OF THERMOGRAVIMETRIC DATA FOR SOME COORDINATION POLYMERS OF ZINC(II) AND CADMIUM(II)

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(Received November 26, 1990)

A detaliled thermal study on some new Zn(II) and Cd(II) coordination polymers with substituted biurat such as sebacyl bis-biurat (SBBU), adipyl bis-biurat (ABBU) and fumaryl bis-biurat (FBBU) is being reported. Freeman-Carroll and Sharp-Wentworth methods have been used to calculate activation energy and thermal stability of these polymers. Kinetic parameters have been calculated using the data of Freeman Carroll method. The results obtained have been suitably discussed.

Introduction

A large amount of work has been reported from these laboratories on the synthesis, characterisation, structure and thermal studies of several coordination polymers [1–3]. The present paper describes a detailed study of thermal degradation of polymeric chelates of Zn(II) and Cd(II) formed with sebacyl, adipyl and fumaryl bis-biurat, abbreviated as SBBU, ABBU and FBBU respectively.

The Freeman-Carroll [4] and Sharp-Wentworth [5] methods have been used to evaluate various kinetic parameters for these chelate polymers. The method for estimating kinetic parameters from dynamic TG studies suffers from the difficulty that the two parameters, temperature and time can not be continuously changed. This problem is eliminated in Freeman-Carroll method where the parameters of temperature and time can be varied. Methods for estimating kinetic parameters from dynamic TG studies [6–9] are mostly based on the assumptions that the Arrhenius equation is valid and that the thermal and diffusion barriers are negligible.

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Theoretical consideration

Freeman-Carroll method

The following expression is used to evaluate various kinetic parameters by this method:

$$\frac{\Delta\log(\mathrm{d}w/\mathrm{d}t)}{\Delta\log(W_r)} = \frac{(-E_a)}{2.303R}\,\frac{\Delta 1/T}{\Delta\log W_r} + n$$

This shows that a plot of $\Delta\log(\mathrm{d}w/\mathrm{d}t)/\log W_r$ against $\Delta(1/T)/\log W_r$ will give an intercept of the Y-axis at $x = 0$ which is equal to the values of n (the order of reaction) and a slope $m = -E_a/2.303$ R.
In expression above, $W_r = W_c - W$, W_c is the weight loss at the completion of the reaction or at a definite time; W is the total weight loss upto time t; $\mathrm{d}w/\mathrm{d}t$ is the weight loss with time t and T is the temperature.

Sharp-Wentworth method

The following expression is used to evaluate the activation energy using this method:

$$\frac{\log(\mathrm{d}c/\mathrm{d}t)}{(1-c)} = \log(A/\beta)\,\frac{-E_a}{2.303}\,1/T$$

where $\mathrm{d}c/\mathrm{d}t$ is the fraction of mass loss with time t, T is the temperature and $\beta = \mathrm{d}T/\mathrm{d}t$.

Experimental

Chemicals

All chemicals used were of Anal R grade.

Instruments used

The non-isothermal measurements were carried out using a T.G.S.– 2 Thermogravimetric analyser alongwith TADS computer system at Regional Sophisticated Instrumentation Centre, Nagpur University, Nagpur. The thermocouple used was Pt-Pt-Rh with a temperature range of 20°–1000°C. Sample masses ranged from 10 mg to 12 mg and furnace heating rate of 8 deg·min^{-1} was employed.

Preparation of ligand

The ligands, sebacyl, adipyl, fumaryl bis-biurat were synthesized by condensation with their respective acid dichlorides. Acid dichlorides were prepared by reacting respective acids with thionyl chloride or phosphorus pentachloride and then renoving excess of unreacted acid. The stepwise reaction are shown below.

$$R(COOH)_2 + 2SOCl_2 \rightarrow R(COCl)_2 + 2SO_2 + 2HCl$$

$$R\text{-}(COCl)_2 + 2NH_2CONHCONH_2 \rightarrow$$

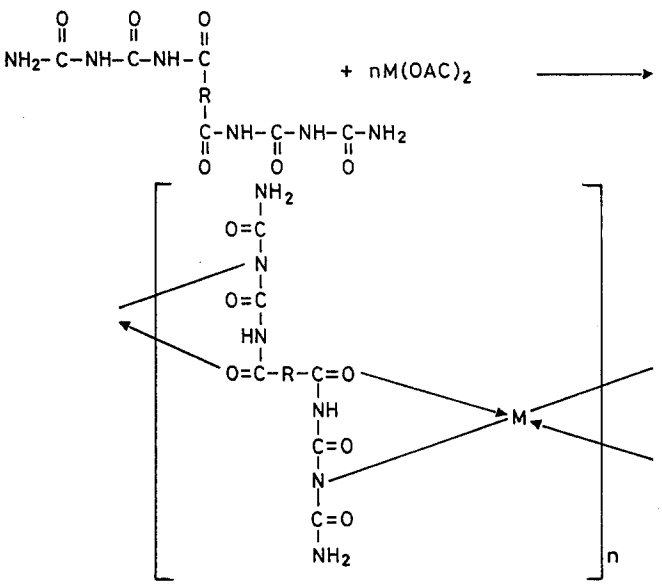
$$\rightarrow H_2N\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}CO\text{-}R\text{-}CO\text{-}NH\text{-}CO\text{-}NH\text{-}CO\text{-}NH_2.$$

The ligand thus formed was recrystallised, dried and characterised.

Preparation of coordination polymers

The coordination polymers were prepared by mixing the solution of ligand and metal acetates in the stoichiometric ratio in the minimum volume of DMF and refluxed for 4–5 hours.

The reaction is:



The polymer was then filtered, washed with DMF and alcohol, dried and characterised.

Results and discussion

The composition of the polymeric unit was assigned on the basis of detailed study of the elemental analysis of the polymers and ir spectral studies. The presence of water of crystallisation was ascertained on the basis of TG and DTA studies. The composition of the polymeric unit is of the following type:

$$\{[M(II)L]\cdot 2H_2O\}_n \text{ where}$$

M = Zn(II) or Cd(II)
L = SBBU or ABBU or FBBU

TG of Zn(II) polymers

TG curves of these polymers show water loss in one step between 120° to 160°C in SBBU, ABBU and FBBU polymers with Zn(II). There is then a rapid loss upto 220°C and then from 240°C a gradual loss takes place upto 520°C which represents the degradation of coordination polymers. In between 520° to 600°C, the formation of a stable metal oxide species, ZnO is evidenced after which no further mass loss is observed. To economise space only a representative TG plot of $\{[Zn(II)(FBBU)]\cdot 2H_2O\}_n$ is given in Fig. 1.

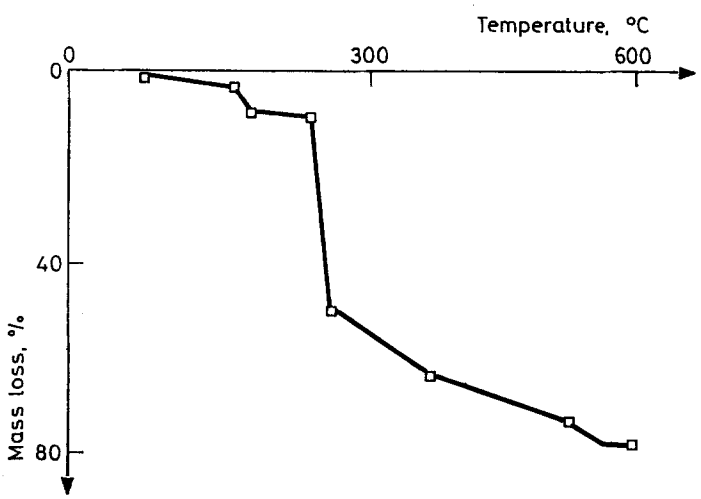


Fig. 1

TG of Cd(II) polymers

The mass loss curve of these polymers shows loss of two water molecules in one step between 100° and 150°C. There is then a gradual loss till 400°C which becomes rapid between 400° to 420°C corresponding to thermal degradation of the polymers and then consequently formation of stable metal oxide, viz. CdO upto 540°C after which there is no further mass loss.

According to Nikolaev *et al.* [10] and Singh *et al.* [11] water eliminated below 140°–150°C can be considered as crystal water and water eliminated above 150°–180°C may be that of coordination with the metal. In present investigation, water molecules are completely lost upto about 150°C which indicates that in these polymers, the water is present as water of crystallisation.

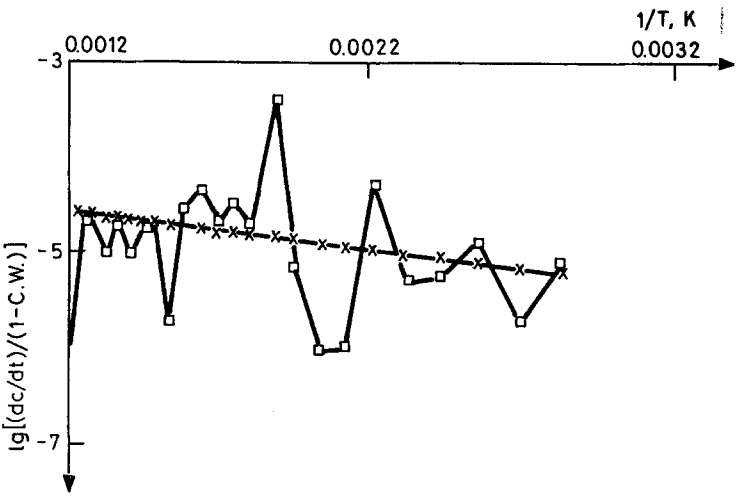


Fig. 2

By using thermal decomposition data and then applying the Sharp-Wentworth Method (a representative Sharp-Wentworth plot for the polychelates is shown in Fig. 2) activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll Method (Table 1). A representative thermal activation energy plot (Fig. 3) and Freeman-Carroll Plot (Fig. 4) for the polymer has been shown. Thermodynamic parameters have been calculated on the basis of thermal activation energy. These values are given in Tables 1 and 2.

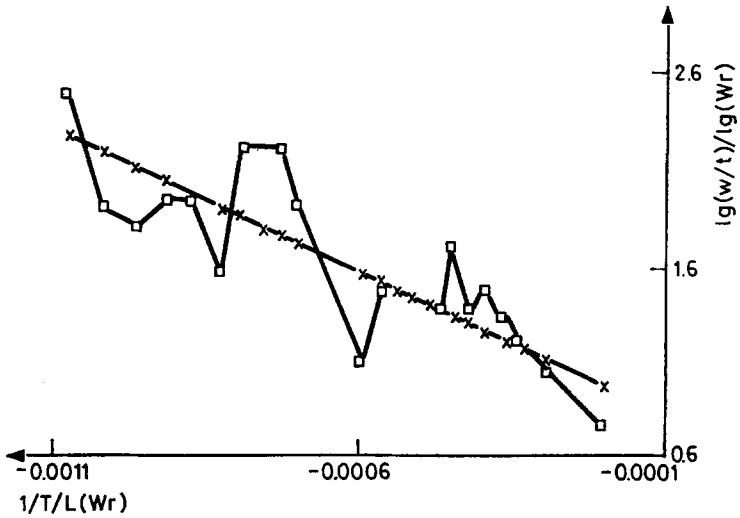


Fig. 3

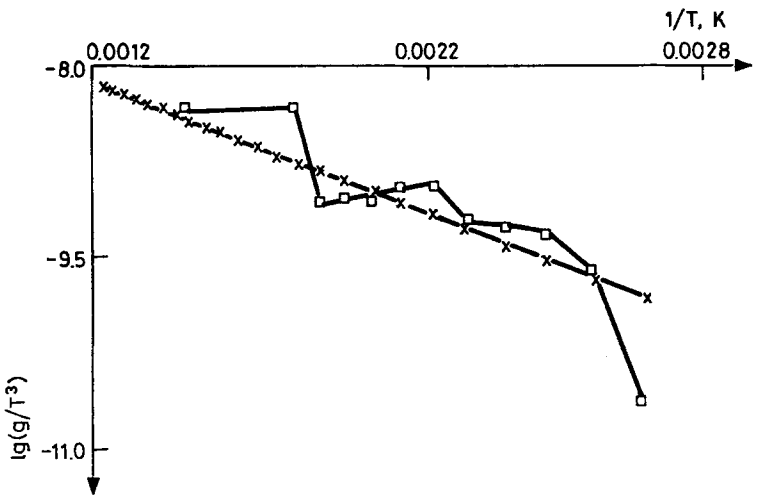


Fig. 4

These calculations were done after devising two computer programmes so as to reduce the personal errors. Secondly and more importantly due to calculated regression curve, the activation energy calculated is more accurate.

From the data given in Tables 1 and 2, it can be seen that the values of thermodynamic parameters are comparable. The similarity of the ther-

modynamic parameters indicates a common reaction mode. Due to the abnormally low values of Z (frequency factor), it may be concluded that the reaction of decomposition of polychelates can be classified as a slow reaction and no other plausible reason can be given.

Table 1 Activation energy and decomposition temperature of coordination polymers of SBBU, ABBU and FBBU

S.R.	Polymer	Decomposition Temp.(°C)	Activation Energy (kJ·mole^{-1})	
			FC	SW
1	{[Zn(II)(SBBU)]·2H$_2$O}$_n$	385	68.79	83.63
2	{[Cd(II)(SBBU)]·2H$_2$O}$_n$	420	68.79	83.63
3	{[Zn(II)(ABBU)]·2H$_2$O}$_n$	390	68.79	83.63
4	{[Cd(II)(ABBU)]·2H$_2$O}$_n$	410	43.24	16.61
5	{[Zn(II)(FBBU)]·2H$_2$O}$_n$	400	68.79	83.63
6	{[Cd(II)(FBBU)]·2H$_2$O}$_n$	410	65.90	16.61

FC ... Freeman-Carroll Method

SW ... Sharp-Wentworth Method

The decomposition of polychelates is known not to obey first order kinetics perfectly, as observed by Jacobs and Tompkins [12] and by Coats and Redfren [13]. These lower values found in almost all the cases are shown in Table 2.

Table 2 Kinetic parameters of coordination polymers of SBBU, ABBU and FBBU

Sl.No	Polymer	Entropy change	Free Energy change	Frequency factor	Apparent entropy change	Order of reaction
		ΔS(J)	ΔF(kJ)	Z(s^{-1})	S (kJ)	n
1	{[Zn(II)(SBBU)]·2H$_2$O}$_n$	9.38	43.46	25.78	– 71.02	0.66
2	{[Cd(II)(SBBU)]·2H$_2$O}$_n$	9.88	45.33	25.78	– 70.90	0.66
3	{[Zn(II)(ABBU)]·2H$_2$O}$_n$	9.38	54.71	26.57	– 71.39	0.66
4	{[Cd(II)(ABBU)]·2H$_2$O}$_n$	14.97	79.17	44.70	– 70.32	1.19
5	{[Zn(II)(FBBU)]·2H$_2$O}$_n$	9.41	33.22	25.63	– 70.27	0.66
6	{[Cd(II)(FBBU)]·2H$_2$O}$_n$	9.82	46.85	27.97	– 70.86	0.90

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Zusammenfassung — Es wird über eine ausführliche Untersuchung einiger neuer Zn(II)- und Cd(II)- Koordinationspolymere mit substituiertem Hydrogenurat, wie z.B. Sebacyl-bis-hydrogenurat (SBBU), Adipyl-bis-hydrogenurat (ABBU) und Fumaryl-bis-hydrogenurat (FBBU) berichtet. Zur Berechnung der Aktivierungsenergie und der thermischen Stabilität dieser Polymere wurde das Freeman-Carroll und das Sharp-Wentworth-Verfahren angewendet. Unter Anwendung der Daten des Freeman Carroll Verfahrens wurden kinetische Parameter berechnet. Die erhaltenen Ergebnisse wurden angemessen diskutiert.