

THERMAL DEGRADATION OF SOME NEW COORDINATION POLYMERS

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ABSTRACT

A thermal study of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) coordination polymers with 4,4'-dihydroxy-3,3'-diacetylphenyl-dithiooxamide (DDBDO) has been carried out. Thermal decomposition curves are discussed with careful attention to minute details. The Freeman–Carroll and Sharp–Wentworth methods have been used to calculate activation energy and thermal stability. Thermal activation energies (E_a) calculated with the help of these methods are in agreement with each other. Thermodynamic parameters such as free energy change (ΔF), entropy change (ΔS), apparent entropy change (S^*), and frequency factor (Z) are also determined on the basis of the TG curve and by using data of the Freeman–Carroll method.

INTRODUCTION

The thermal degradation study of coordination polymers has become a subject of recent interest. Study of the thermal behaviour of polymers in air at different temperatures provides information about the nature of the species produced at various temperatures due to degradation. In this laboratory, extensive work on the thermal degradation of simple and polymeric chelates has been undertaken [1–3]. In a recent publication [4], Bhave and Iyer evaluated the kinetic parameters of some polymeric chelates of pseudothiohydantoin with Ni(II), Co(II) and Cu(II) with the help of isothermal and non-isothermal TG curves. This communication describes the thermal study of coordination polymers of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with 4,4'-dihydroxy-3,3'-diacetylphenyl-dithiooxamide (DDBDO) polymer. The decomposition temperatures of the polymeric chelates decrease in the order Ni > Fe > Co > Mn > Cu, while the thermal activation energy follows the order Mn > Co > Cu > Ni > Fe. Thermodynamic parameters calculated in the present course of study are also used to correlate the thermal behaviour of the polychelates.

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EXPERIMENTAL DETAILS

Chemicals

All chemicals used were of AnalaR grade.

Synthesis of ligand

The ligand 4,4'-dihydroxy-3,3'-diacetylphenyl-dithiooxamide (DDBDO) was prepared by condensing the dihydroxyketone with dithiooxamide at 1 : 2 stoichiometry in ethanol.

Synthesis of coordination polymers

An equimolar mixture of ligand and metal acetate was dissolved in the minimum volume of DMF. The resulting mixture was refluxed for 4–6 h. The insoluble polymer formed was filtered off and washed thoroughly several times with DMF and absolute alcohol to remove unreacted ligand and metal acetate. The polymer thus obtained was vacuum-dried. The polychelates were all air-stable coloured powders insoluble in water and in almost all organic solvents. The stereochemistry of the polychelates in the present investigation has been studied with the aid of diffuse reflectance spectra, IR spectra, magnetic moments and elemental analysis data [5].

Thermogravimetry

The non-isothermal measurements were carried out using a TGS-2 thermogravimetric analyser along with a TADS computer system at the 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 to 12 mg; a furnace heating rate of 10 °C min⁻¹ was employed.

Several methods for estimating the kinetic parameters from dynamic TG studies have been proposed [6–9]. These methods are based on two assumptions: (i) thermal and diffusion barriers are negligible, and (ii) the Arrhenius equation is valid.

The main difficulty in such methods is that the two parameters of temperature and time cannot be continuously changed. In the present study, Freeman–Carroll [10] and Sharp–Wentworth [11] methods have been used to determine the kinetic parameters of the coordination polymers with the help of the dynamic TG curve. The beauty of the Freeman–Carroll method is that the parameters of temperature and time can be varied and, at the same time, the order of reaction and energy of activation can be obtained in a single experiment.

In the Freeman–Carroll method, to determine various parameters, expression (1) is used

$$\frac{\log(dw/dt)}{\log w_r} = \left(\frac{-E_a}{2.303R} \right) \frac{(1/T)}{\log w_r} + n \quad (1)$$

Hence a plot of $\log(dw/dt)/\log w_r$ vs. $(1/T)/\log w_r$ should give an intercept on the y axis at $x=0$ equal to the value of n (the order of reaction), and a slope $m = -E_a/2.303R$. In expression (1), $w_r = w_c - w$, w_c is the weight loss at the completion of the reaction or at a definite time, w is the total weight loss up to time t , dw/dt is the weight loss with time t , and T is the temperature.

When using the Sharp–Wentworth method, expression (2) is used to evaluate the activation energy

$$\log \frac{(dc/dt)}{1-c} = \log(A/\beta) - \frac{E_a}{2.303} \frac{1}{T} \quad (2)$$

where dc/dt is the fraction of mass loss with time t , T is the temperature, and $\beta = dI/dt$.

RESULTS

Thermal degradation curves for the DDBDO polychelates are shown in Figs. 1 and 2 (the latter is a representative example).



The mass loss curve of this polychelate is shown in Fig. 1 as curve A. Dehydration of the polychelate takes place between 140°C and 240°C, corresponding to the loss of two water molecules (9.6% found, 8.1% theoretical). After dehydration, the polychelate loses mass in two steps. Rapid mass loss occurs up to 310°C, which may be a result of the degradation of the non-coordinated part of the ligand as shown in the representative example (Fig. 2). Subsequently, there is an increase in weight around 395–420°C, and finally the mass attains a constant level up to 480°C. This increase in weight may be a result of the formation of metal sulphide and sulphate. After 480°C a gradual mass loss up to 530°C is observed and then the mass stays constant, which may be a result of the formation of Mn_3O_4 (20.5% found, 18.0% theoretical).



The TG curve of this polymer is given as curve B in Fig. 1. The mass loss curve clearly indicates that thermal decomposition of the polymer takes

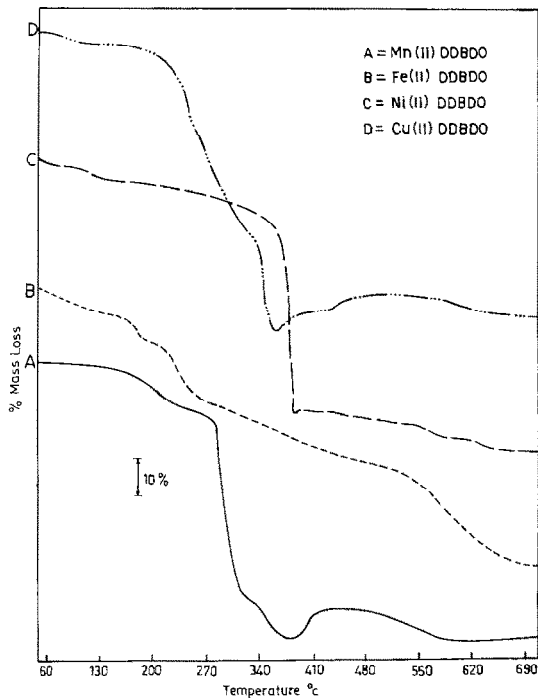


Fig. 1. Thermogravimetric analysis.

place between 140°C and 180°C , corresponding to loss of two molecules of water (10.2% found, 8.3% theoretical). Further slow degradation occurs up to 520°C , which may be indicative of the decomposition of the free part of

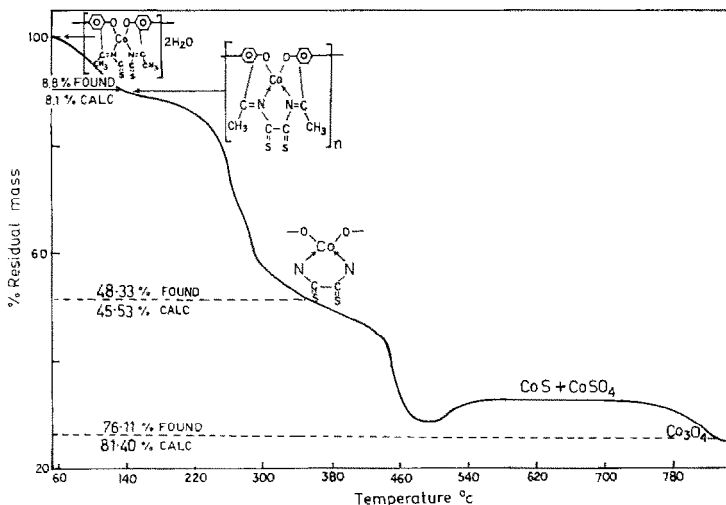
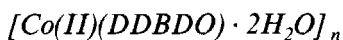


Fig. 2. Decomposition curve of representative polymer. Cumulative percentage mass losses (found and calculated) are also given.

the chelated ligand as shown in Fig. 2. There is then an inflection at 540 °C, and gradual mass loss again occurs up to 580 °C, which can be attributed to the oxidation–reduction reaction. The TG curve attains a constant level after 580 °C, which may be a result of the formation of Fe₂O₃ (23.0% found, 18.8% theoretical).



The thermogram of this metal chelate polymer is shown as the representative curve of Fig. 2. The polychelate loses its water molecules in one step between 100 and 140 °C (8.8% found, 8.1% theoretical). There is then no mass loss up to 220 °C, indicating the formation of an intermediate stable species [Co(II)(DDBDO)]. Next, rapid mass loss is observed up to 300 °C, indicating the decomposition of the free part of the chelated ligand. There is subsequent gradual mass loss up to 460 °C, which can be attributed to the oxidation–reduction reaction. It may also be seen that there is an increase in weight around 480–520 °C. This increase in weight suggests the formation of CoS and CoSO₄. The TG curve attains a constant level up to 780 °C, followed by the formation of an oxide, which may be Co₃O₄ (23.8% found, 18.0% theoretical).



The thermogram of the Ni(II) (DDBDO) polymer is shown in Fig.1 as curve C. From the thermogram it is observed that dehydration of the polymer takes place between 90° and 140 °C. There is then a small weight loss up to 340 °C, indicating the formation of an intermediate stable species [Ni(II)(DDBDO)]. Beyond 340 °C a rapid mass loss is observed up to 355 °C. A slight inflection at 388 °C of increase in weight indicates the formation of NiS and NiSO₄, followed by the formation of metal oxide, NiO, above 400 °C (22.5% found, 18.0% theoretical).



The mass loss curve of this polymer is shown as curve D in Fig. 1. Dehydration of the polychelate takes place up to 120 °C, and above this temperature a stable intermediate species is formed for a short time around 160 °C. Above 160 °C a gradual mass loss is observed up to 300 °C. This may be due to the decomposition of the free part of the ligand. From the thermogram it is seen that there is a increase in weight in the range 360–450 °C, which may be a result of the formation of CuS and CuSO₄. This is then followed by a gradual decomposition, leading to the formation of CuO (22.3% found, 20.0% theoretical; temp. 500 °C).

DISCUSSION

According to Nikolaev et al. [12] and Singh et al. [13], water eliminated below 140–150 °C can be considered as crystal water, and water eliminated above 150 °C may be that coordinated to the metal atom in chelates. In the present investigation, in the case of the Co(II), Ni(II) and Cu(II) polychelates, water and hydration is eliminated below 140 °C, while in the case of the Mn(II) and Fe(II) polychelates the water is presented as coordinated water; this is supported by IR studies.

In all the polychelates of DDBDO except Fe(II)(DDBDO), it is observed that there is a small increase in the weight of the residue due to the formation of metal sulphide and metal sulphate in the course of decomposition at certain temperatures. Results of this type have been obtained by Sceney et al. [14], D'Ascenzo and Wendlandt [15] and Bhave and Kharat [16] in their thermal study of some coordination compounds containing sulphur ligands. The increase may be a result of oxidation of Cu_2S to CuO and CuSO_4 , while in the case of Co(II) a mixture of Co_3O_4 and CoS is obtained; the latter oxidized to CoSO_4 and then dissociated to the oxide. In the present course of study, a result confirming this effect is well depicted in the representative Fig. 2.

By using the thermal degradation data, thermal activation energy and thermodynamic parameters for all the polychelates have been calculated. These values are given in Table 1.

The thermal decomposition can be explained tentatively by considering one unit of the polymer. The initial decomposition temperature is frequently used to define the relative thermal stability of complexes. However, the degree of decomposition is neglected. From the decomposition temperature data, it can be concluded that the thermal stability of the metal chelate polymers of DDBDO is in the order $\text{Ni} > \text{Fe} > \text{Co} > \text{Mn} > \text{Cu}$.

In some cases, decomposition of polychelates occurred at a fairly low temperature, which may be due to oxidation of the polymer by the catalytic action of metal ions present in the polychelate. Thermal activation energy values calculated by two methods are in agreements with each other, and the order of activation energies is $\text{Mn} > \text{Co} > \text{Cu} > \text{Ni} > \text{Fe}$. But the order predicted on the basis of electropositive character is not in perfect agreement.

From the data of Table 1 it can be observed that the values of the thermodynamic parameters are nearly the same for each polychelate. The similarity of the thermodynamic parameters indicates a common reaction mode. With regard to the abnormally low value of Z , it may be concluded that the reaction of decomposition of the polychelates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) can be classed as a 'slow' reaction, and no other plausible reason can be given.

Fairly good straight line plots are obtained using both methods. In the

TABLE I

Results of thermogravimetric analysis of polychelates of DDBDO

Polymer	Decomposition temperature (°C)	Activation energy ^a (kJ mol ⁻¹)		ΔS (J)	ΔF (kJ)	Z (s ⁻¹)	S* (kJ)	n
		FC	SW					
[Mn(II)(DDBDO)·2H ₂ O] _n	250	29.74	31.88	-312.71	127.65	82.40	-97.48	0.52
[Fe(II)(DDBDO)·2H ₂ O] _n	270	21.25	22.97	-315.30	119.95	38.25	-110.87	0.68
[Co(II)(DDBDO)·2H ₂ O] _n	260	23.30	22.30	-312.46	121.08	62.00	-108.57	0.67
[Ni(II)(DDBDO)·H ₂ O] _n	325	22.92	16.98	-307.98	119.36	82.91	-107.69	0.71
[Cu(II)(DDBDO)]·H ₂ O] _n	220	22.97	23.55	-319.65	123.00	239.00	-102.59	0.81

^a FC, Freeman-Carroll method; SW, Sharp-Wentworth method.

Freeman–Carroll method some abnormal points must be disregarded to get a clear picture. Similarly, in the Sharp–Wentworth method, the straight line plots have some points either at the beginning or at the end which do not fall on the straight line. This is to be expected, since the decomposition of polychelates is known not to obey first-order kinetics perfectly, as observed by Jacobs and Tompkins [17] and by Coats and Redfern [18].

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