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KINETICS OF NON-ISOTHERMAL DECOMPOSITION OF POLYMERIC COMPLEXES OF *N,N'*-BIS(DITHIOCARBOXY)PIPERAZINE WITH IRON(III) AND COBALT(III)

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ABSTRACT

Thermogravimetry, in conjunction with differential thermogravimetry and differential thermal analysis, has been used to investigate the kinetics of thermal decomposition of polymeric complexes of *N,N'*-bis(dithiocarboxy)piperazine with Fe^{III} and Co^{III} in air. The results indicate that the values of kinetic parameters obtained using the Coats–Redfern, Freeman–Carroll and Horowitz–Metzger equations are reasonable and in good agreement. It has also been found that the decomposition processes of both the complexes follow first order kinetics.

INTRODUCTION

The thermal properties of dithiocarbamate complexes have been extensively investigated, because of the striking structural features presented by this class of compounds and also because of the diverse applications of the compounds themselves and of their decomposition products. A perusal of the literature reveals, however, that most of the work that has been done on the thermal properties of these compounds is superficial in nature, describing their modes of decomposition, thermal stability range, etc., and that there is great scope for further interesting and valuable investigation of the kinetics and mechanisms of their thermal decomposition. As a part of our investigations of the thermal behaviour and kinetics of decomposition of metal complexes with sulphur ligands [1–3], we report here on the kinetics of non-isothermal decomposition of polymeric complexes of *N,N'*-bis(dithiocarboxy)piperazine $[(C_4H_8N_2)(CS_2)_2]$ with two typical transition metal ions of higher oxidation state, Fe^{III} and Co^{III}.

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EXPERIMENTAL

The ligand, *N,N′*-bis(dithiocarboxy)piperazine (L), was synthesized as its disodium salt according to the procedure reported in a previous work [4]. The complexes were prepared by adding aqueous solution of the sodium salt of the ligand dropwise with constant stirring to an aqueous solution of iron(III) chloride or cobalt(II) chloride until the metal to ligand ratio reached 2 : 3. The iron(III) complex separated immediately as a black precipitate and was filtered. In the case of the cobalt complex, a stream of air was passed through the mixture for about 24 h to effect the complete conversion of Co^{II} to Co^{III}. A dark green complex separated, and this was filtered. Both the complexes were then washed several times, first with water and then with methanol, and dried in vacuum over P_4O_{10}. The purity of the complexes was ascertained by elemental analysis using standard procedures [5], and they were found to be of the general formula $M_2L_3 \cdot 4H_2O$, where $M \equiv Fe^{III}$ or Co^{III}. They were further characterized by magnetic and spectral studies [4].

The thermoanalytical measurements were performed using a DuPont 990 thermal analyser system, in conjunction with a 951 thermogravimetric (TG) analyser and a 1200-901 modular differential thermal analysis (DTA) cell system. About 4–6 mg of the powdered sample was placed in a platinum crucible in an atmosphere of static air and subjected to a linear heating rate of 10 K min^{-1}. The TG data obtained were processed using a program written in BASIC for an HCL system 4 1S with 512K RAM.

THEORETICAL

In recent years there has been increasing interest in determining the rate-dependent parameters of solid state non-isothermal decomposition reactions by analysis of TG curves. Several equations [6–13] have been proposed as means of analysing a TG curve and obtaining values for kinetic parameters. Many authors [6–10] have discussed the advantages of this method over the conventional isothermal method. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion [7], using

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{1}$$

where the function $k(T)$ is temperature-dependent, and $f(\alpha)$ is the conversion function dependent on the mechanism of the reaction. It has been established [14] that the temperature-dependent function $k(T)$ is of the Arrhenius type and can be written as the rate constant k

$$k = A\,\mathrm{e}^{-E/RT} \tag{2}$$

where A is the pre-exponential factor, E is the activation energy and R is the gas constant. Combining eqns. (1) and (2), we obtain

$$d\alpha/dT = (A/q)\ e^{-E/RT} f(\alpha) \tag{3}$$

where $q = dT/dt$, the linear heating rate. On integration and approximation, eqn. (3) becomes

$$\ln g(\alpha) = (-E/RT) + \ln(AR/qE) \tag{4}$$

The above representation is similar to the $y = ax + b$ model of the least-squares method (LSM). Least-squares analysis is based on the observation that, often, random experimental errors closely follow a Gaussian distribution. In the above equation the errors in $g(\alpha)$ are likely to follow a Gaussian distribution, but those in $\ln g(\alpha)$ definitely will not, since taking a logarithm tends to compress the high values while expanding the low values. This defect can be remedied by using a weighted LSM. Several authors [1,15] have reported that the best fit between their experimental and calculated data was obtained using a weighted LSM. The weights used in the present work, and other details, were as reported elsewhere [1]. The linearity of an appropriate plot was assessed by means of the correlation coefficient r obtained by the weighted LSM.

RESULTS

The TG curves were studied in greater detail. The instrumental TG curves were redrawn as curves of the fraction decomposed α vs. temperature T, to obtain primary α–T data. The TG, differential thermogravimetry (DTG)

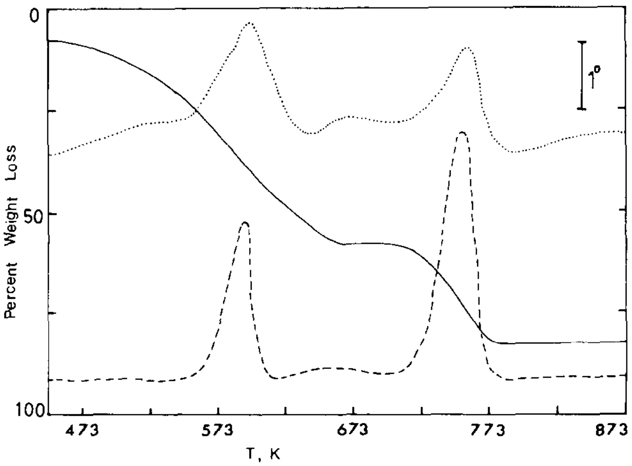

Fig. 1. TG (———), DTG (— — —) and DTA (· · · · · ·) curves for $Fe_2L_3 \cdot 4H_2O$.

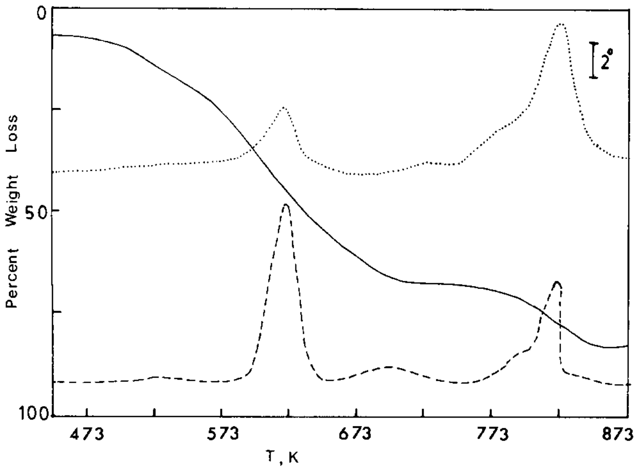

Fig. 2. TG (———), DTG (— — —) and DTA (· · · · · ·) curves for $Fe_2L_3{\cdot}4H_2O$.

and DTA curves obtained are shown in Figs. 1 and 2. Both the complexes decompose in three stages, the first stage being dehydration. The decomposition reactions were subjected to non-isothermal kinetic investigations. Kinetic parameters such as E, A, the activation entropy ΔS and the order parameter n were evaluated using the weighted LSM.

The Freeman–Carroll equation [6] has been used for determination of the order of reaction, but its applicability to the present case was found to be extremely poor, inasmuch as the resulting plots were very scattered. Several authors [1,16,17] have made similar observations. Therefore, the Horowitz–Metzger method [11] was applied, and the order was determined by constructing a ‘master curve’, by the method reported in an earlier work [18]. Values of r were also computed, using the weighted LSM, for the equations suggested by Coats and Redfern [8] (with $n = 0$, 1/2, 2/3 and 1), and a maximum value for the equation was obtained with $n = 1$. Using this value of n, the kinetic parameters were evaluated separately using the following three non-mechanistic equations.

Coats–Redfern equation

$$\ln[-\ln(1-\alpha)/T^2] = (-E/RT) + \ln\{(AR/qE)[1-(2RT/E)]\} \tag{5}$$

Freeman–Carroll equation

$$\ln[(\mathrm{d}W/\mathrm{d}t)/W_r] = (-E/RT) + \ln A \tag{6}$$

where W is the total loss in weight up to time t, $W_r = W_f - W$ and W_f is the weight loss at the completion of the reaction.

Horowitz–Metzger equation

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

where $\theta = T - T_s$ and T_s is the DTG peak temperature.

The left-hand side of each of the above equations was plotted, using the weighted LSM, against reciprocal absolute temperature ($1/T$) for eqns. (5) and (6) and against θ for eqn. (7). E and A were calculated from the slope and intercept, respectively, for eqns. (5) and (6). In the case of eqn. (7), E was calculated from the slope and A was calculated using the equation

$$A = Eq\ \mathrm{e}^{E/RT_s}/RT_s^2 \tag{8}$$

In all cases, ΔS was calculated using the equation

$$\Delta S = R\ \ln(Ah/kT_s) \tag{9}$$

where k is the Boltzmann constant and h is the Planck constant.

DISCUSSION

The general thermal behaviours of the complexes, in terms of stability ranges, peak temperatures and values of kinetic parameters, are shown in Table 1. Both the complexes are stable up to about 360 K. The first step of the process is elimination of lattice-held water molecules, which is represented by DTG peaks at around 383 K and corresponding endothermic DTA peaks at around 388 K. The initial weight loss in TG for these complexes agrees well with the loss expected theoretically on the elimination of four molecules of water. After dehydration, both the complexes begin to decompose at around 455 K. The first stage of decomposition of the anhydrous complex of Fe^{III} is complete at around 675 K, while that of Co^{III} continues up to 720 K. These steps are respectively represented by DTG peaks at 593 and 620 K and corresponding exothermic DTA peaks at 595 and 618 K. The rate of the final stage of decomposition of the Fe^{III} complex is high, and is represented by DTG and exothermic DTA peaks at 752 and 755 K, respectively. The slow final decomposition of the Co^{III} complex is complete at around 860 K, and is represented by a DTG peak at 820 K and a corresponding exothermic DTA peak at 823 K. Analysis of the residues obtained on thermal decomposition of the Fe^{III} and Co^{III} complexes in air indicated that these were oxides of formulae Fe_2O_3 and Co_3O_4, respectively. There is close agreement among the weight loss values obtained, for the Fe^{III} and Co^{III} complexes, respectively, by TG (82.10 and 82.56%), by indepen-

TABLE 1

Thermal behaviour and kinetic parameters determined using the Coats–Redfern (CR), Freeman–Carroll (FC) and Horowitz–Metzger (HM) methods

Complex	Decomposition range (K)	T_s (K)	Method	E (kJ mol^{-1})	A (s^{-1})	ΔS (J K^{-1} mol^{-1})	r
$Fe_2L_3 \cdot 4H_2O$	455–675	593	CR	48.9	3.3×10^3	−183	0.9998
			FC	54.4	1.2×10^4	−173	0.9956
			HM	61.3	5.2×10^4	−160	0.9987
	693–788	752	CR	278.7	1.3×10^{19}	113	0.9994
			FC	285.9	9.4×10^{19}	130	0.9932
			HM	295.1	2.0×10^{20}	136	0.9995
$Co_2L_3 \cdot 4H_2O$	458–720	620	CR	46.9	1.3×10^3	−191	0.9996
			FC	51.5	7.6×10^3	−177	0.9943
			HM	59.5	1.9×10^4	−169	0.9978
	733–860	820	CR	216.7	2.4×10^{13}	3	0.9999
			FC	224.9	1.1×10^{14}	15	0.9971
			HM	234.6	3.7×10^{14}	25	0.9997

dent pyrolysis (82.05 and 82.60%) and by theoretical calculation (82.11 and 82.14%).

Analysis of the data obtained using the Horowitz–Metzger and Coats–Redfern equations indicated that both stages of the decomposition of these complexes follow first order kinetics. Accordingly, the kinetic parameters for both decomposition steps were evaluated using the above-mentioned three equations, by the weighted LSM (Table 1). The satisfactory values of r ($r \approx 1$) in all cases indicate good agreement with the experimental data. The values of the kinetic parameters obtained using the Coats–Redfern, Freeman–Carroll and Horowitz–Metzger methods show that the general agreement among these methods is good, within about 10%. The ΔS values obtained for both complexes for the first step of decomposition are negative, which indicates that the activated complex has a more ordered structure than the reactants, and that the reactions are slower than normal [19]. The ΔS values obtained for the final stages of decomposition of the complexes are positive.

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