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THERMAL DECOMPOSITION KINETICS OF 2-FURALDEHYDE THIOSEMICARBAZONE COMPLEXES OF CADMIUM(II) AND MERCURY(II)

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ABSTRACT

Complexes of cadmium(II) and mercury(II) with 2-furaldehyde thiosemicarbazone have been subjected to non-isothermal kinetic investigation in air using TG, DTG and DTA techniques. The kinetic parameters for both stages of decomposition of these complexes were evaluated by the weighted least-squares approach, using the Coats–Redfern, Freeman–Carroll and Horowitz–Metzger methods. The values of kinetic parameters obtained by the three methods are in good agreement.

INTRODUCTION

In continuation of our investigations of the thermal behaviour of bivalent metal complexes of thiosemicarbazones [1–4], the present work describes the non-isothermal decomposition of complexes of Cd(II) and Hg(II) with 2-furaldehyde thiosemicarbazone $C_6H_7N_3OS$. These studies are particularly interesting in that thiosemicarbazones are potential gravimetric reagents for bivalent metal ions [5]. The decomposition processes of the two complexes were subjected to kinetic investigation, and the parameters overall order of reaction n, activation energy E, activation entropy ΔS and pre-exponential factor A were evaluated using the Coats–Redfern, Freeman–Carroll and Horowitz–Metzger equations.

EXPERIMENTAL

All the reagents used were BDH AnalaR grade. 2-Furaldehyde thiosemicarbazone (LH) was synthesized by refluxing equimolar solutions of 2-furaldehyde and thiosemicarbazide in ethanol for 2 h. The Cd(II) complex was

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prepared by slowly adding a hot aqueous solution of cadmium acetate to a refluxing methanolic solution of the ligand containing sodium acetate (≈ 1.0 g) until the metal to ligand ratio reached 1 : 2. The reaction mixture was kept at the refluxing temperature for about 1 h. The solid complex which separated was filtered after cooling of the reaction mixture, washed with water and then with methanol, and dried over P_4O_{10}. The complex of Hg(II) was prepared in a similar manner, but using an aqueous solution of mercuric chloride. The complexes, of general formula $M(L)_2$, where M = Cd(II) or Hg(II) and L = the monoanion of the ligand LH, were characterized [6] by elemental analyses and by other physico-chemical means.

TG and DTA analyses of the complexes were performed using a DuPont 990 thermal analyser system, in conjunction with a 951 thermogravimetric analyser and a 1200-901 modular DTA cell system, with a heating rate of 10 K $\min^{-1}$ and a sample size of 2–6 mg, in an atmosphere of static air, using a platinum crucible. Numerical analysis of the thermoanalytical data was performed using a program written in BASIC for an HCL system 4 1S with 512k RAM.

THEORETICAL

Non-isothermal methods have been widely used for the evaluation of kinetic parameters of decomposition reactions [7–11]. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion [8]

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

where α is the fraction decomposed at time t, $k(T)$ is the temperature-dependent function, and $f(\alpha)$ is the conversion function dependent on the mechanism of decomposition. It has been established [12] that the temperature-dependent function $k(T)$ is of the Arrhenius type and can be considered as the rate constant k

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

where R is the gas constant.

Substituting eqn. (2) into eqn. (1), we obtain

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

where q is the linear heating rate dT/dt.

On integration and approximation, this equation yields

$$\ln\ g(\alpha) = \frac{-E}{RT} + \ln\left[\frac{AR}{qE}\right] \tag{4}$$

where $g(\alpha)$ is a function of α dependent on the mechanism of the reaction.

This form of 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 $g(\alpha)$ are definitely not, because using the logarithmic function tends to compress the high values while expanding the low values. This defect can be remedied by using the weighted LSM. Several authors [13,14] have reported that the best fit of their experimental and calculated data is obtained using the weighted LSM. The weights used and other details were as reported elsewhere [14].

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, DTG and DTA curves are given in Figs. 1 and 2. Both complexes were found to decompose in two stages.

The Freeman–Carroll equation [10] was used to determine the order of reaction, but its applicability was found to be extremely poor, as can be seen from the scattered plot. Several authors [14–16] have made similar observations. Therefore, the Horowitz–Metzger method [17] was applied and the order determined by constructing a 'master curve', as described in an earlier work [18]. We also computed the values of the correlation coefficient r using the weighted LSM for the equations suggested by Coats and Redfern [19] (with $n = 0$, 1/2, 2/3 and 1), and found a maximum value for the equation with $n = 1$. The kinetic parameters for both stages of decomposition were then evaluated accordingly, using the following three methods.

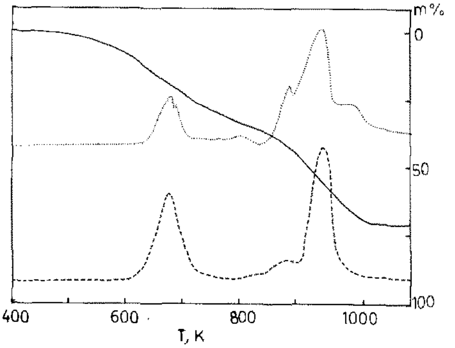

Fig. 1. TG (———), DTG (- - - - - -) and DTA (· · · · · ·) curves for $Cd(L)_2$.

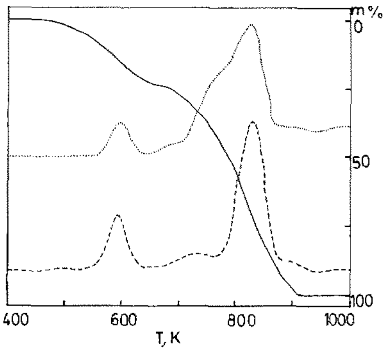

Fig. 2. TG (———), DTG (- - - - - -) and DTA (· · · · · ·) curves for $Hg(L)_2$.

Evaluation of kinetic parameters

The integral method of Coats and Redfern

For first order reactions, the Coats–Redfern equation can be written in the form [19]

$$\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right) = \frac{-E}{RT} + \ln\left(\frac{AR}{qE}\right) \tag{5}$$

The slope and intercept of the above equation were obtained from a weighted least-squares plot of $\ln(-\ln(1-\alpha)/T^2)$ vs. $1/T$. E was calculated from the slope and A from the intercept value. The entropy of activation ΔS was calculated using the equation

$$\Delta S = R \ln\left(\frac{Ah}{kT_s}\right) \tag{6}$$

where k is the Boltzmann constant, h is the Planck constant, and T_s is the DTG peak temperature.

The differential method of Freeman and Carroll

The Freeman–Carroll equation was used in the form [10]

$$\ln\left(\frac{\mathrm{d}W/\mathrm{d}t}{W_r}\right) = \frac{-E}{RT} + \ln A \tag{7}$$

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. A plot of $\ln[(\mathrm{d}W/\mathrm{d}t)/W_r]$ vs. $1/T$ was made using the weighted LSM, and E was calculated from the slope. A was calculated from the value of the intercept, and ΔS using eqn. (6).

The approximation method of Horowitz and Metzger

The equation suggested by Horowitz and Metzger for first order reactions is of the form [17]

$$\ln[-\ln(1-\alpha)] = \frac{E\theta}{RT_s^2} \tag{8}$$

where $\theta = T - T_s$. The weighted least-squares plot of $\ln[-\ln(1-\alpha)]$ vs. θ was found to be linear, and E was calculated from the slope. A was calculated using the equation

$$A = \frac{Eq}{RT_s^2}\exp(E/RT_s) \tag{9}$$

and ΔS was calculated using eqn. (6).

For all the weighted least-squares plots, the first few points (up to $\alpha = 0.15$) were discarded, since they did not fall on the line and their inclusion would hence result in a poor correlation. (This was as expected, since it is known that solids decomposition does not obey first order kinetics in the initial stages [20,21].)

DISCUSSION

The thermal behaviour of the complexes, including stability ranges, peak temperatures and weight loss data, are presented in Table 1. Both the complexes decompose in two steps.

The Cd(II) complex, which is stable up to 470 K, registers the first stage of decomposition between 470 and 785 K. This is represented by a DTG peak at 675 K and a corresponding exothermic DTA peak at 680 K. The

TABLE 1

Thermal decomposition data

Complex	Stability range in TG (K)	Decomposition temperature range in TG (K)	Peak temperature (K)		Total loss of weight (%)		
			DTG	DTA	From TG	Theoretical	From independent pyrolysis
$Cd(L)_2$	Ambient–470	470–785	675	680	70.3	71.37	69.77
		785–1030	945	943			
$Hg(L)_2$	Ambient–460	460–670	593	595	100.00	100.00	100.00
		670–910	827	825			

TABLE 2

Kinetic data

Equation	Complex	Decomposition stage	E (kJ mol^{-1})	A (s^{-1})	ΔS (J K^{-1} mol^{-1})	r
Coats–Redfern	$Cd(L)_2$	First	38.1	8.7×10^1	−215	0.9997
		Second	108.4	1.4×10^5	−156	0.9997
	$Hg(L)_2$	First	51.7	6.3×10^3	−178	0.9999
		Second	89.9	7.4×10^4	−160	0.9997
Freeman–Carroll	$Cd(L)_2$	First	42.7	9.0×10^2	−195	0.9972
		Second	119.9	1.8×10^5	−154	0.9980
	$Hg(L)_2$	First	58.4	2.1×10^4	−168	0.9987
		Second	101.3	3.7×10^5	−147	0.9972
Horowitz–Metzger	$Cd(L)_2$	First	51.7	1.4×10^3	−192	0.9963
		Second	128.1	2.1×10^6	−134	0.9985
	$Hg(L)_2$	First	64.3	1.0×10^5	−155	0.9985
		Second	107.5	1.1×10^6	−136	0.9992

main decomposition, which takes place between 785 and 1030 K, is represented by a DTG peak at 945 K and an exothermic DTA peak at 943 K.

In the case of $Hg(L)_2$, which is stable up to 460 K, both the stages of decomposition take place at lower temperature ranges. The first step occurs between 460 and 670 K, and the final decomposition between 670 and 910 K. These steps are respectively represented by DTG peaks at 593 and 827 K, and corresponding exothermic DTA peaks at 595 and 825 K.

The weight loss observed in the TG studies of the cadmium complex corresponds to the formation of CdO, which is stable beyond 1030 K. This agrees with the weight loss obtained in independent pyrolysis experiments. The final decomposition product was analysed as being CdO. For the mercury complex, as expected, no residue was left on heating up to ~ 950 K.

Analysis of the data obtained using the Horowitz–Metzger and Coats–Redfern equations indicated that both stages of decomposition of the two complexes follow first order kinetics. Accordingly, the kinetic parameters were evaluated using the Coats–Redfern, Freeman–Carroll and Horowitz–Metzger equations, by the weighted LSM. The results are listed in Table 2. The satisfactory values of r in all cases ($r \approx 1$) indicate good agreement with the experimental data. The values of the kinetic parameters obtained from the various equations are reasonable and in good agreement. For both complexes, the first stage of decomposition is very slow. The entropy of activation values vary from − 215 to − 134 J K^{-1} mol^{-1}. The second decomposition steps are faster than the first steps but still have negative values of activation entropy, which indicates that, in both cases, the activated complex has a more ordered structure than the reactants and the reactions are slower than normal [22,23]. A close examination of the results reveals that both complexes show similar thermal behaviour, which is as expected given their similar structures [6].

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