EVALUATION OF KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITION OF PIPERONALDEHYDE THIOSEMICARBAZONE COMPLEXES OF COBALT(II) AND ZINC(II) HALIDES

K.K. ARAVINDAKSHAN * and K. MURALEEDHARAN

Department of Chemistry, University of Calicut, Kerala, 673 635 (India)

(Received 1 November 1988)

ABSTRACT

The thermal decomposition of piperonaldehyde (3,4-methylenedioxybenzaldehyde) thiosemicarbazone complexes of Co(II) and Zn(II) halides has been studied thermogravimetrically in air (non-isothermal method). Reaction order n, apparent activation energy $E^{\star}$, the pre-exponential factor A and entropy of activation $\Delta S^{\star}$ were computed by the weighted least squares method using the Coats–Redfern and Horowitz–Metzger equations. The values of $E^{\star}$, A and $\Delta S^{\star}$ obtained by the two different methods agree well. The mechanism for the decomposition follows the Mampel model equation, i.e. $-\ln(1-\alpha)$ for g(α), and the rate-controlling process is random nucleation with the formation of a nucleus on every particle.

INTRODUCTION

As part of our investigations of the thermal behaviour of metal complexes with sulphur ligands [1–4], we report here on the thermogravimetric analysis and kinetics of the thermal decomposition of Co(II) and Zn(II) halide complexes of piperonaldehyde thiosemicarbazone ($C_9H_9N_3O_2S$). In view of the widespread applications of thiosemicarbazones as analytical reagents, the thermal decomposition of their metal complexes merits detailed study.

There has been considerable discussion in the literature concerning the validity of kinetic data obtained by thermal analysis under non-isothermal conditions [5,6]. However, the method does have certain advantages [7]. We have studied the thermal decomposition reactions of the chloride, bromide and iodide complexes of Co(II) and Zn(II) using non-isothermal kinetic methods, and evaluated the overall order of reaction n and kinetic parameters such as apparent activation energy $E^{\star}$, entropy of activation $\Delta S^{\star}$ and the pre-exponential factor A.

---

* Author to whom correspondence should be addressed.

EXPERIMENTAL

Materials

Piperonaldehyde thiosemicarbazone (LH) was synthesized by refluxing recrystallized samples of piperonaldehyde and thiosemicarbazide (1 : 1 ratio) in ethanol for 2 h and recrystallizing the product from ethanol. The metal complexes were prepared by adding a hot methanolic solution of the metal halide (10 mmol) to a refluxing solution of the ligand (20 mmol) in methanol. The reaction mixture was maintained at refluxing temperature for 3 h. The resulting solution was concentrated to obtain a pasty mass. The Zn(II) halide complexes separated as pale yellow solids on subsequent cooling of this pasty mass. With the Co(II) halide complexes, however, the pasty mass produced powdered samples on washing with benzene several times. The complexes were filtered off, washed with small quantities of methanol and dried over P_4O_{10}. The complexes, of general formulae $[Co(LH)_2]X_2$ and $[Zn(LH)_2X_2]$ (where X = Cl, Br or I), were characterized [8] by elemental analyses using standard procedures [9], molar conductance and magnetic measurements, and by spectral studies.

Thermogravimetric studies

The thermogravimetric (TG) measurements were carried out using a DuPont 990 thermal analyser system with the following operational characteristics: heating rate, 10 K min^{-1}; sample size, 2–6 mg; atmosphere, static air; crucible, platinum.

Computation

The numerical analyses of the TG data were performed using a program written in BASIC for a microcomputer (HCL system 4 lS) with 512K RAM.

RESULTS

TG traces

The instrumental TG traces were redrawn as curves of fraction decomposed α vs. temperature T (TG), and also as curves of the derivative mass loss (dW/dT) vs. temperature (differential thermogravimetric, DTG). The TG and DTG traces are given in Figs. 1 and 2.

Determination of the order of reaction

The Freeman–Carroll equation [10] was used to determine the overall order of reaction, but its applicability was found to be extremely poor, as
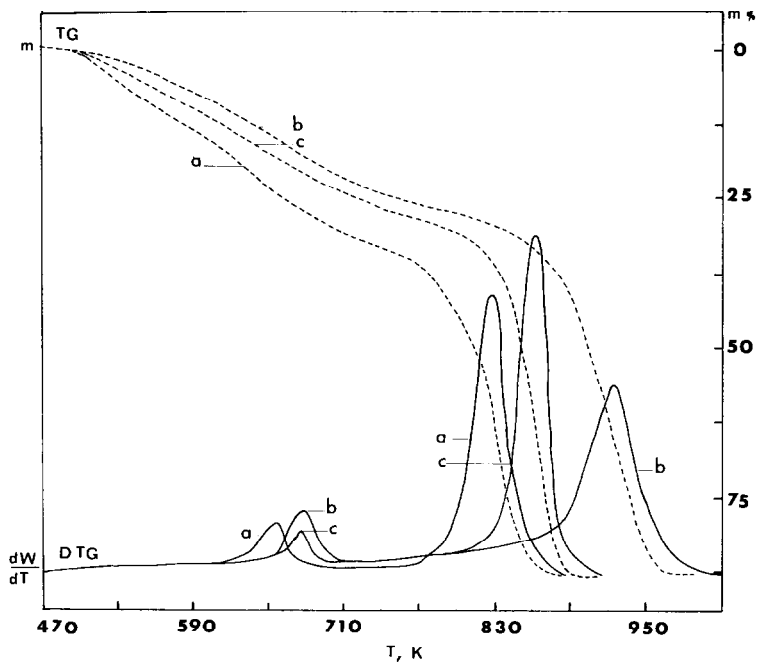
Fig. 1. TG and DTG traces of (a) $[Co(LH)_2]Cl_2$, (b) $[Co(LH)_2]Br_2$ and (c) $[Co(LH)_2]I_2$.
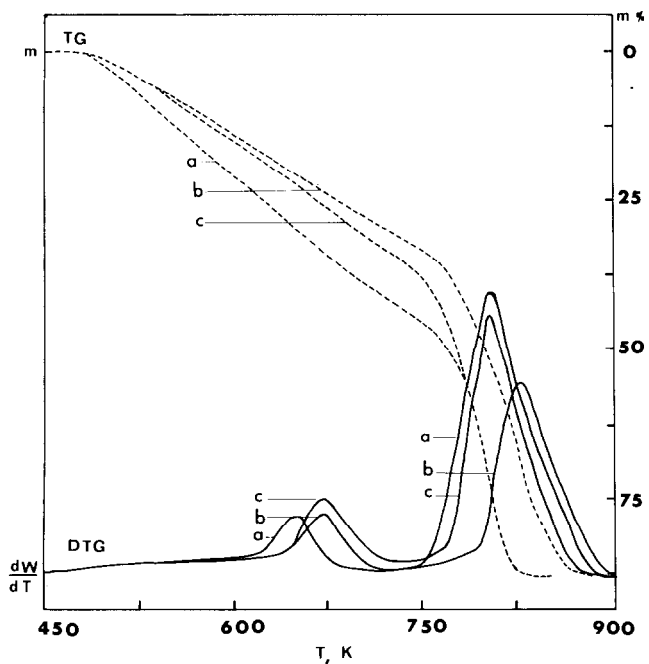
Fig. 2. TG and DTG traces of (a) $[Zn(LH)_2Cl_2]$, (b) $[Zn(LH)_2Br_2]$ and (c) $[Zn(LH)_2I_2]$.

the plot was scattered. Several authors [1,11,12] have made similar observations. Therefore, attempts were made to apply the method of Horowitz and Metzger [13] to determine the reaction order. Horowitz and Metzger related n and the concentration of substance C_s present at the maximum rate of decomposition (i.e. at T_s, the DTG peak temperature) as follows

$$C_s = n^{(1/1-n)} \tag{1}$$

Determination of n directly from C_s is complicated, so a 'master curve' between C_s and n was constructed [14]. The value of n corresponding to C_s was then read off from the master curve. It was found that the overall orders for both stages of decomposition of all the complexes are close to unity. We also computed the value of the correlation coefficient r using the weighted least squares method (weighted LSM) for the equations suggested by Coats and Redfern [15] (with $n = 0, 1/2, 2/3$ and 1) and obtained maximum value for the equation with $n = 1$. This value for the reaction order was then used in evaluating the kinetic parameters.

Evaluation of kinetic parameters

It has been shown [1,16,17] that the best fit of experimental and calculated data is obtained using the weighted LSM. Hence this method was used for the evaluation of slope and intercept in all cases. The weights used and other details are reported elsewhere [1]. All the weighted least squares plots were made by discarding the first few points (up to $\alpha = 0.15$), since these did not fall on the line and their inclusion would have resulted in poor correlations. This is to be expected, since several authors have reported [18,19] the decomposition of solids failing to obey first-order kinetics in the initial stages.

The present work applies the Coats–Redfern [15] and Horowitz–Metzger [13] methods, which use TG curves obtained under the conditions of non-isothermal decomposition, for the evaluation of the kinetic parameters. The methods of calculation based on the two equations are summarized below.

The Coats–Redfern method
This method considers that for a reaction of the type

$$a\text{A (s)} \rightarrow b\text{B (s)} + c\text{C (g)} \tag{2}$$

the rate of disappearance of A may be expressed by

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \tag{3}$$

where α is the fraction of A decomposed at time t ($\alpha = W/W_f$, where W is

the mass loss at time t and W_f the total mass loss) and k is the rate constant, which is given by

$$k = A e^{-E^*/RT} \tag{4}$$

R is the gas constant.

Consider a reaction carried out under non-isothermal conditions, by varying the temperature of the system at a constant heating rate given by,

$$q = dT/dt \tag{5}$$

By combining eqns. (3), (4) and (5), rearranging and integrating, these authors derived two different equations depending on the value of n, namely

$$\ln\left[\frac{1 - (1 - \alpha)^{(1-n)}}{(1 - n)T^2}\right] = M/T + B \text{ for } n \neq 1 \tag{6}$$

$$\ln\left[\frac{-\ln(1 - \alpha)}{T^2}\right] = M/T + B \text{ for } n = 1 \tag{7}$$

where $M = -E^*/R$ and $B = \ln(AR/qE^*)$. Equation (7) can be used for first order reactions. The slope M and intercept B of eqn. (7) were obtained from a weighted least squares plot of $\ln[-\ln(1 - \alpha)/T^2]$ vs. $1/T$. Values of E^* and A were calculated from the slope and intercept, respectively. The entropy of activation ΔS^* was calculated using the relation

$$A = \frac{kT_s}{h} e^{\Delta S^*/R} \tag{8}$$

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

The Horowitz–Metzger method

For first order reactions the Horowitz–Metzger equation can be written as

$$\ln[-\ln(1 - \alpha)] = \frac{E^* \theta}{RT_s^2} \tag{9}$$

where $\theta = T - T_s$. The weighted least squares plot of $\ln[-\ln(1 - \alpha)]$ vs. θ yielded a good straight line with a satisfactory value of r, from the slope of which the apparent energy of activation was calculated. The value of A was calculated using the equation

$$\frac{E^*}{RT_s^2} = \frac{A}{q} e^{-E^*/RT_s} \tag{10}$$

The entropy of activation was calculated using eqn. (8).

DISCUSSION

The TG and DTG results are summarized in Table 1. All the complexes under investigation decompose in two stages. The Co(II) halide complexes are stable up to 500 K. Their first decomposition steps, which take place between 500 and 830 K, are represented by DTG peaks in the range 650–680 K. The final decomposition of these complexes takes place between 790 and 965 K and is represented by DTG peaks in the range 836–925 K. The Zn(II) halide complexes are stable up to 490 K. The DTG peaks in the range 647–668 K represent initial decomposition which takes place between 490 and 770 K. The final decomposition takes place in the range 760–870 K. The corresponding DTG peaks are observed between 800 and 826 K.

The final stable decomposition products were found to be oxides of the formulae Co_3O_4 and ZnO for the complexes of Co(II) and Zn(II) halides, respectively. The mass loss data obtained by TG were compared with data obtained from independent pyrolysis experiments in which the samples were heated for 2 h in silica crucibles up to ≈ 973 K. The sets of mass loss data from the TG analysis and the independent pyrolysis experiments both agree well with the theoretical values.

Analyses of the data using the Horowitz–Metzger and Coats–Redfern equations showed that the overall order of both stages of decomposition is unity. The kinetic parameters were evaluated accordingly, using the equations above for each stage of decomposition of the six complexes, by the weighted LSM. The results are listed in Table 2. Satisfactory values of r

TABLE 1

Thermal decomposition data

Complex	Stability range in TG from ambient to (K)	Decomposition temperature range in TG (K)	Peak temperature in DTG (K)	Total loss of mass %		
				From TG	Theoretical	From independent pyrolysis
$[Co(LH)_2]Cl_2$	500	500–790	654	86.77	86.07	86.90
		790–875	836			
$[Co(LH)_2]Br_2$	500	500–830	679	87.89	87.93	87.98
		830–965	925			
$[Co(LH)_2]I_2$	500	500–815	674	90.13	89.43	90.11
		815–885	864			
$[Zn(LH)_2Cl_2]$	490	490–760	646	86.14	86.03	86.00
		760–830	802			
$[Zn(LH)_2Br_2]$	490	490–770	667	87.44	87.88	87.60
		770–870	826			
$[Zn(LH)_2I_2]$	490	490–760	668	89.15	89.37	89.28
		760–830	800			

TABLE 2

Kinetic data

Equation	Complex	First stage				Second stage			
		$E^\star$ (kJ mol^{-1})	A (s^{-1})	$\Delta S^\star$ (J K^{-1} mol^{-1})	r	$E^\star$ (kJ mol^{-1})	A (s^{-1})	$\Delta S^\star$ (J K^{-1} mol^{-1})	r
Coats–Redfern	[Co(LH)$_2$]Cl$_2$	29.38	1.83×10^1	-227.30	0.9997	313.89	2.17×10^{19}	116.70	0.9984
	[Co(LH)$_2$]Br$_2$	35.19	4.59×10^1	-219.95	0.9973	273.86	1.12×10^{15}	33.75	0.9999
	[Co(LH)$_2$]I$_2$	26.76	0.83×10^1	-234.06	0.9976	408.66	3.33×10^{24}	215.70	0.9992
	[Zn(LH)$_2$Cl$_2$]	26.91	1.15×10^1	-231.06	0.9995	350.22	4.23×10^{22}	180.02	0.9992
	[Zn(LH)$_2$Br$_2$]	27.21	0.99×10^1	-232.59	0.9996	217.95	2.30×10^{13}	2.41	0.9994
	[Zn(LH)$_2$I$_2$]	29.67	1.67×10^1	-228.22	0.9997	290.16	5.27×10^{18}	105.29	0.9968
Horowitz–Metzger	[Co(LH)$_2$]Cl$_2$	42.37	2.88×10^2	-204.35	0.9953	331.24	2.83×10^{20}	138.04	0.9978
	[Co(LH)$_2$]Br$_2$	47.96	6.12×10^2	-198.41	0.9909	293.81	1.61×10^{16}	55.95	0.9995
	[Co(LH)$_2$]I$_2$	39.53	1.21×10^2	-211.81	0.9904	427.64	4.92×10^{25}	238.09	0.9994
	[Zn(LH)$_2$Cl$_2$]	39.55	1.80×10^2	-208.18	0.9943	367.84	6.23×10^{23}	202.39	0.9995
	[Zn(LH)$_2$Br$_2$]	40.33	1.57×10^2	-209.58	0.9947	235.52	3.25×10^{14}	24.43	0.9993
	[Zn(LH)$_2$I$_2$]	42.99	2.67×10^2	-205.18	0.9953	309.94	1.01×10^{20}	129.81	0.9982

$(r \approx 1)$ in all cases indicate good agreement with the experimental data. The values for the kinetic parameters obtained from the two different equations are comparable and in good agreement.

The first stages of decomposition for all the complexes are slow and have approximately the same value of $E^\star$. The entropy of activation for this step varies from -198 to -236 J K^{-1} mol^{-1}. The negative values indicate that the activated complex has a more ordered structure than the reactants and that the reactions are slower than normal [20,21]. The second stages of decomposition for all the complexes are very fast and have higher values of $E^\star$, which vary from 218 to 428 kJ mol^{-1}. The $\Delta S^\star$ values are positive for this stage.

Mechanism of reaction from non-isothermal TG trace

Deduction of a reaction mechanism through the use of non-isothermal kinetic methods has been discussed by several authors [22–24]. The procedure is based on the assumption that one non-isothermal mass loss curve is equivalent to a large number of isothermal mass loss curves [23,25]. It has been established [24] that the instantaneous reaction rate of a non-isothermal reaction can be represented as

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{q} e^{-E^\star/RT} \, dT \tag{11}$$

where f(α) is a function of α dependent on the mechanism of the reaction. Integration of this equation yields [24]

$$g(\alpha) = \frac{A}{q} \int_0^T e^{-E^\star/RT} \, dT \tag{12}$$

Using $x = E^\star/RT$, eqn. (12) takes the form

$$g(\alpha) = \frac{AE^\star}{qR} \int_x^\infty (e^{-x}/x^2) \, dx = \frac{AE^\star}{qR} \, p(x) \tag{13}$$

where

$$p(x) = \int_x^\infty (e^{-x}/x^2) \, dx$$

Taking the logarithm, eqn. (13) becomes

$$\ln g(\alpha) = \ln\left(\frac{AE^\star}{qR}\right) + \ln p(x) \tag{14}$$

Having established that the function $\ln p(x)$ is, to a first approximation, a linear function of $1/T$, it is apparent from eqn. (14) that $\ln g(\alpha)$ must also be a linear function of $1/T$, since $AE^\star/qR$ is independent of temperature. That is, for the correct mechanism the plot of $\ln g(\alpha)$ vs. $1/T$ should be a straight line. For incorrect mechanisms this will not be the case. Although

TABLE 3

Mechanistic equations for solid state reactions

Function	Equation $[g(\alpha) = kt]$	Rate-controlling process
D_1	$\alpha^2 = kt$	One-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha) + \alpha = kt$	Two-dimensional diffusion, cylindrical symmetry
D_3	$[1-(1-\alpha)^{1/3}]^2 = kt$	Three-dimensional diffusion, spherical symmetry, Jander equation
D_4	$(1-2\alpha/3)-(1-\alpha)^{2/3} = kt$	Three-dimensional diffusion, spherical symmetry. Ginstling–Brounshtein equation
R_2	$1-(1-\alpha)^{1/2} = kt$	Phase boundary reaction, cylindrical symmetry
R_3	$1-(1-\alpha)^{1/3} = kt$	Phase boundary reaction, spherical symmetry
F_1	$-\ln(1-\alpha) = kt$	Random nucleation, one nucleus on each particle, Mampel equation
A_2, A_3 or A_4	$[-\ln(1-\alpha)]^{1/n} = kt$ $n = 2, 3$ or 4	Random nucleation, ingestion and overlap of growth nuclei; Avrami–Erofeyev equation

the sensitivity of this procedure for mechanism determination is not very high, it does yield very useful information.

The types of mechanism most frequently encountered in solid state reactions are shown in Table 3. We have computed the values of $E^\star$ and r using the weighted LSM for all the functions listed in Table 3. The F_1 mechanism was found to give the maximum value of r in all cases. This

TABLE 4

Values of $E^\star$ and r calculated using mechanism-based equation

Complex	First stage		Second stage	
	$E^\star$ (kJ mol^{-1})	r	$E^\star$ (kJ mol^{-1})	r
$[Co(LH)_2]Cl_2$	39.84	0.9999	327.45	0.9978
$[Co(LH)_2]Br_2$	46.18	0.9988	288.96	0.9994
$[Co(LH)_2]I_2$	37.57	0.9994	423.06	0.9995
$[Zn(LH)_2Cl_2]$	37.24	0.9999	363.34	0.9990
$[Zn(LH)_2Br_2]$	37.87	0.9999	231.47	0.9991
$[Zn(LH)_2I_2]$	40.36	0.9999	303.17	0.9966

shows that the thermal decomposition of these complexes follows the Mampel model equation [26], i.e. $-\ln(1 - \alpha)$ for $g(\alpha)$, and that the rate-controlling process is random nucleation with the formation of a nucleus on every particle. The values of $E^{\star}$ and r obtained for the Mampel equation using the weighted LSM are given in Table 4. The good agreement of the values of $E^{\star}$ obtained using the mechanistic equation (Table 4) with those obtained using the non-mechanistic equations (Table 2) confirms the mechanism suggested above.

REFERENCES

1 K.K. Aravindakshan and K. Muraleedharan, Thermochim. Acta, 140 (1989) 325.
2 K.K. Aravindakshan and K. Muraleedharan, J. Therm. Anal., accepted.
3 K.K. Aravindakshan and K. Muraleedharan, J. Therm. Anal., communicated.
4 K.K. Aravindakshan and K. Muraleedharan, React. Kinet. Catal. Lett., accepted.
5 C.H. Bamford and C.F.H. Tipper, Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam, 1980.
6 P.M.D. Benoit, R.G. Ferrillo and A.H. Granzow, J. Therm. Anal., 30 (1985) 869.
7 W.W. Wendlandt, Thermal Methods of Analysis, Wiley, New York, 1974.
8 K.K. Aravindakshan, Indian J. Chem., 26A (1987) 241.
9 A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, ELBS and Longman, London, 1978.
10 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
11 R.L. Bohn, in H.G. McAdie (Ed.), Proceedings of the First Toronto Symposium on Thermal Analysis, Chemical Institute of Canada, Toronto, 1959.
12 R.L. Reed, L. Weber and B.S. Gottfried, Ind. Eng. Chem., Fundam., 4 (1965) 38.
13 H.H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
14 P.M. Madhusudanan, P.N.K. Nambissan and C.G.R. Nair, Thermochim. Acta, 9 (1974) 149.
15 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
16 C. Rozycki and M. Maciejewski, Thermochim. Acta, 96 (1985) 91.
17 R. de Levice, J. Chem. Educ., 63 (1986) 10.
18 A.W. Coats and J.P. Redfern, J. Polymer Sci., Part 3(B) (1965) 917.
19 P.W.M. Jacobs and Tompkins, in D.W.E. Garner (Ed.), Chemistry of the Solid State, Butterworths, London, 1955.
20 A.A. Frost and R.G. Pearson, Kinetics and Mechanism, Wiley, New York, 1961.
21 V. Indira and G. Parameswaran, J. Therm. Anal., 32 (1987) 1151.
22 J. Sestak and G. Berggren, Thermochim. Acta, 3 (1971) 1.

23 V. Satava, Thermochim. Acta, 3 (1971) 423.
24 M.P. Kannan, Chemistry Education, 4(2) (1987) 26.
25 C.D. Doyle, in P.E. Slade and L.T. Jenkins (Eds.), Techniques and Methods of Polymer Evaluation, Marcel Dekker, New York, 1966.
26 K.L. Mampel, Z. Phys. Chem. Abt. A, 187 (1940) 235.