Thermochimica Acta, 144 (1989) 109–116
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION KINETICS OF BARIUM ZIRCONYL OXALATE

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(Received 26 July 1988)

ABSTRACT

Thermal decomposition studies of barium zirconyl oxalate were carried out in air using TG, DTG and DTA techniques. The kinetic parameters (non-isothermal method) for each step of decomposition were evaluated by means of the Coats–Redfern, modified Horowitz–Metzger and Freeman–Carroll equations, using the weighted least-squares method. The results indicate that the initial oxalate decomposition is the rate-determining step.

INTRODUCTION

The zirconates of bivalent metals, especially those of alkaline earth metals and lead, are technologically important because of their electrical and magnetic properties. As high temperature preparatory methods yield only non-stoichiometric zirconates, low temperature chemical methods have had to be developed for the preparation of materials of high purity. It is therefore interesting to look at the zirconyl oxalates as possible precursors of the metazirconates. Several authors [1–3] have described methods of preparation and reported on the thermal behaviour of zirconyl oxalates of bivalent metals. However, the literature on their thermal decomposition kinetics is rather scanty. In this paper we describe the thermogravimetric analysis and kinetics of the various stages of decomposition of barium zirconyl oxalate.

Although there has been considerable discussion in the literature concerning the validity of kinetic data obtained by thermal analysis under non-isothermal conditions [4,5] Wendlandt [6] has pointed out several advantages of this method. Therefore, in the present investigation the non-isothermal method was employed for the evaluation of kinetic parameters.

EXPERIMENTAL

All reagents used were either BDH AnalaR or Merck "Proanalyse" grade chemicals. The acid $H_2ZrO(C_2O_4) \cdot 3H_2O$ was prepared according to a previously reported procedure [7,8]. Barium zirconyl oxalate heptahydrate (BZO) was prepared from $H_2ZrO(C_2O_4)_2 \cdot 3H_2O$, as has also been described previously [1]. The air dried sample was found by chemical analysis to correspond to the composition $BaZrO(C_2O_4)_2 \cdot 7H_2O$.

Instrumental methods

Thermogravimetric (TG) analysis in air was carried out on a manual thermobalance which employed a sensitive quartz spring. The experimental set-up was similar to that of Hooley [9], with the following characteristics: heating rate, 5 K min^{-1}; sample mass, 150 mg; crucible, platinum. Differential thermal analysis (DTA) in air was carried out in a unit similar to one described previously [10], with a heating rate of 12 K min^{-1} and a sample mass of 400 mg. The TG data were analysed using a program written in BASIC for an HCL microcomputer.

Treatment of data

The TG curves were studied in greater detail. TG, differential thermogravimetric (DTG) and DTA traces of BZO are given in Fig. 1. The three steps of decomposition (i.e. initial oxalate decomposition, main oxalate decomposition, and final carbonate decomposition) of BZO were subjected to non-isothermal kinetic investigations. The order of reaction n and kinetic parameters such as the apparent activation energy E^*, the entropy of

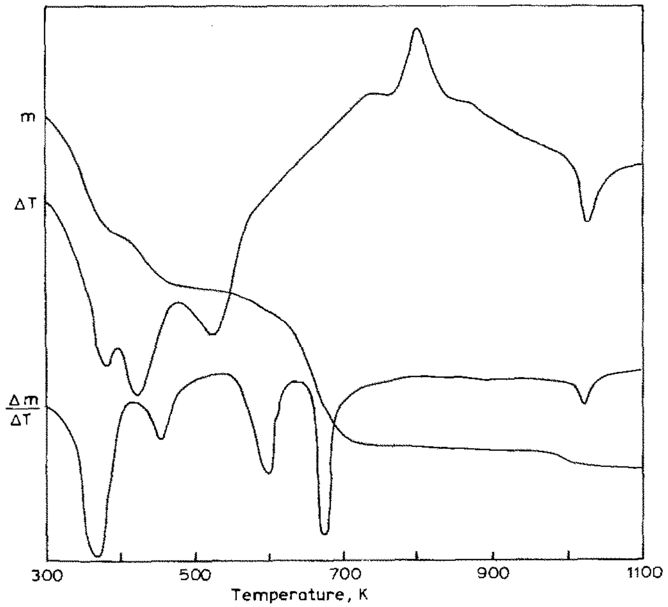

Fig. 1. TG, DTG and DTA curves of BZO.

activation ΔS^* and the pre-exponential factor A were evaluated for each step of decomposition, using the Coats–Redfern, modified Horowitz–Metzger and Freeman–Carroll equations.

Basic theory

The integral form of a non-isothermal kinetic equation is as follows

$$\ln g(\alpha) = M/T + B \tag{1}$$

where α is the fraction decomposed at temperature T, $g(\alpha)$ is a function of α dependent on the mechanism of decomposition, $M = -E^*/R$, $B = \ln[AR/qE^*]$, R is the gas constant, and q is the constant rate of heating.

The above form is similar to the $y = ax + b$ model of the least-squares method (LSM). The 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 high values while expanding low values. This defect can be remedied by using the weighted LSM. Several authors [11,12] have reported that the best fit of their experimental and calculated data was obtained using the weighted LSM. In the present investigation, the weighted LSM was used to evaluate kinetic parameters. The weights used and other details are reported elsewhere [12].

Evaluation of kinetic parameters

The order of reaction of each step of decomposition was determined using the method of Horowitz and Metzger [13], for which a ‘master curve’ was constructed [14], and was found to be near unity. We also computed the values of correlation coefficients r using the weighted LSM, for the equations suggested by Coats and Redfern [15] (with $n = 0$, $1/2$, $2/3$ and 1), and obtained a maximum value for the equation with $n = 1$. Accordingly, the kinetic parameters for each step of the decomposition reaction were evaluated according to the following three methods, using the weighted LSM. For all weighted least squares plots the first few points (up to $\alpha = 0.15$) were discarded, since they do not fall on the line. This is to be expected, since it is known that the decomposition of solids does not obey first order kinetics in the initial stages [16,17].

The Coats–Redfern method [15]

For first order reactions the widely accepted Coats–Redfern equation [15] can be written in the form

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

The slope M and intercept B were obtained from a weighted least-squares plot of $\ln[-\ln(1-\alpha)/T^2]$ vs. T^{-1}. E^* and A were calculated from M and B respectively. ΔS^* was calculated using the relation

$$A = \frac{kT_s}{h} e^{(\Delta S^*/R)} \tag{3}$$

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

The Horowitz–Metzger method [13,18]

The present data were analysed using the Horowitz–Metzger equation [13] as modified by Dharwadkar and Karkhanavala [18] in the form

$$\ln[-\ln(1-\alpha)] = \frac{E^*}{RT_i^2} \frac{100}{(T_f - T_i)} \theta + C \tag{4}$$

where T_i is the temperature of inception of reaction, T_f is the temperature of completion of reaction, and $\theta = T - T_s$.

A weighted least-squares plot of $\ln[-\ln(1-\alpha)]$ vs. θ was found to be linear as required by the theory, and E^* was calculated from the slope. A and ΔS^* were calculated according to a previously reported method [19].

The Freeman–Carroll method [20]

The usual first order rate expression can be represented as

$$\mathrm{d}W/\mathrm{d}t = kW_r \tag{5}$$

where $W_r = W_f - W$, W_f is the weight loss at the completion of the reaction, W is the total loss in weight up to time t, and k is the rate constant. Combining eqn. (5) with the Arrhenius equation

$$k = A\ \mathrm{e}^{-E^*/RT} \tag{6}$$

we get

$$\ln\left[\frac{\mathrm{d}W/\mathrm{d}t}{W_r}\right] = \frac{-E^*}{RT} + \ln A \tag{7}$$

where $\mathrm{d}W/\mathrm{d}t = (\mathrm{d}W/\mathrm{d}T)q$.

The weight–temperature gradient $\mathrm{d}W/\mathrm{d}T$ could be obtained from the TG trace by employing Stirling's central difference formula for six points [21], or by drawing tangents.

A weighted least-squares plot of the left-hand side of eqn. (7) vs. T^{-1} was linear, as required. E^* and A were calculated from the slope and the intercept, respectively. ΔS^* was calcuated using eqn. (3).

Evaluation of enthalpy (ΔH) terms

It has been stated [22] that the DTG peak temperature T_S may be identified with the thermodynamic decomposition temperature. On this basis, since the free energy change ΔG at this equilibrium temperature can be equated to zero, the Gibbs–Helmholtz equation becomes

$$\Delta H = T_s \Delta S \tag{8}$$

The enthalpy terms were calculated using the above equation and are listed in Table 2.

RESULTS AND DISCUSSION

The general thermal behaviour of BZO (the temperature range of each step of decomposition, DTG peak temperatures, and mass loss data) is described in Table 1. Values of kinetic parameters, enthalpy terms and correlation coefficients for the various decomposition steps are given in Table 2.

Thermal behaviour

There are three principal steps in the decomposition of BZO, the likely reactions being (i) dehydration, (ii) decomposition of the oxalate to an intermediate carbonate, and (iii) decomposition of the carbonate to barium zirconate.

Dehydration of BZO takes place in two steps. In the first step, five moles of water are lost in the temperature range 300–400 K. Anhydrous BZO is formed in the temperature range 400–470 K. The DTG peaks at 372 and 457 K represent these two steps. The observed weight loss (23.38%) is in

TABLE 1

Thermal decomposition data

Decomposition step	Temperature range (K)	Peak temperature in DTG (K)	Loss of mass (%)	
			Observed	Theoretical
Dehydration	300– 470	–	23.38	23.03
Initial oxalate decomposition	475– 635	600	2.70	3.83
Main oxalate decomposition	635– 725	678	18.92	18.48
Final carbonate decomposition	960–1070	1025	4.46	4.03

TABLE 2

Kinetic parameters calculated using the Coats–Redfern (CR), modified Horowitz–Metzger (M–HM) and Freeman–Carroll (FC) equations

Decomposition stage	Equation	E^* (kJ mol^{-1})	A (s^{-1})	ΔS^* (J K^{-1} mol^{-1})	ΔH (J mol^{-1})	r
Initial oxalate decomposition	CR	65.30	5.87×10^{4}	−159.4	-9.57×10^{4}	0.9994
	M–HM	70.42	1.59×10^{5}	−151.2	-9.07×10^{4}	0.9990
	FC	68.25	9.98×10^{4}	−155.0	-9.30×10^{4}	0.9992
Main oxalate decomposition	CR	200.01	6.82×10^{14}	32.23	2.19×10^{4}	0.9998
	M–HM	208.65	3.24×10^{15}	45.19	3.06×10^{4}	0.9996
	FC	205.92	1.99×10^{15}	41.14	2.79×10^{4}	0.9991
Final carbonate decomposition	CR	502.82	1.24×10^{25}	225.20	2.31×10^{5}	0.9999
	M–HM	523.74	1.47×10^{26}	245.78	2.52×10^{5}	0.9999
	FC	508.36	2.45×10^{25}	230.87	2.37×10^{5}	0.9995

agreement with the calculated value (23.03%) for the removal of $7H_2O$ mol^{-1}.

The decomposition of the oxalate is also a two-step process. The first endothermic reaction occurs in the temperature range 475–635 K, with a weight loss of 2.7%. This is represented by the DTG peak at around 600 K. Two possible explanations for the endothermic nature of this step may be suggested. Either the decomposition takes place virtually in an atmosphere of water vapour from the preceding dehydrating step; or, alternatively, the oxidation of carbon monoxide takes place at a higher temperature. The residue at the end of this stage appears to have the composition $Ba_2Zr_2O_2(C_2O_4)_{2.5}(CO_3)_{1.5}$, and could not be isolated as a stable intermediate [1]. The second stage of oxalate decomposition, which is exothermic in nature, occurs between 635 and 725 K and is represented by the DTG peak at around 678 K. The exothermic nature of this step may be due to masking of the endotherm by the highly exothermic oxidation of carbon monoxide. This second step of oxalate decomposition, which might be expected to be the principal event in the thermoanalytical experiments [23], is not prominent in the DTA curve.

The final decomposition of the carbonate, $Ba_2Zr_2O_5CO_3$, occurs between 960 and 1070 K. This is represented by the endothermic DTA peak around 1028 K, and the corresponding DTG peak at 1025 K. The observed weight loss is 4.46%, compared with a calculated loss of 4.03%. The end product is crystalline barium metazirconate [1].

Decomposition kinetics

Analyses of data using the Horowitz–Metzger and Coats–Redfern equations gave the order of reaction for each step of decomposition as unity.

Based on this value for the reaction order, the kinetic parameters for each step of decomposition were evaluated using the previously mentioned three methods by the weighted LSM (Table 2). The satisfactory values of r (≈ 1) in all cases indicate good agreement with the experimental data. The values of the kinetics parameters obtained by means of the Coats–Redfern, modified Horowitz–Metzger and Freeman–Carroll methods show that the general agreement between these methods is good, within about 10%. The ΔS^* values for the initial oxalate decomposition step are negative, which indicates that the activated complex has a more ordered structure than the reactants, and that the reactions are slower than normal [24]. Therefore, it may be concluded that the initial oxalate decomposition is the rate-determining step, and that the rate-controlling process is random nucleation with the formation of a nucleus on every particle [25,26].

ACKNOWLEDGEMENTS

T.G. thanks Dr. M. Subba Rao and Dr. T.R. Narayanankutty of the Indian Institute of Science, Bangalore, and K.M. thanks Dr. K.K. Aravindakshan of Calicut University for some helpful discussions.

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