

THE THERMAL DECOMPOSITION OF OXALATES. PART 20. THE DECOMPOSITION KINETICS OF ACID BARIUM OXALATES

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ABSTRACT

The thermal decomposition of barium oxalate is followed using isothermal and rising temperature techniques. The results obtained from the two methods are in good agreement for both loss of oxalic acid and carbon monoxide. The values of the activation energies for the loss of oxalic acid and carbon monoxide are: isothermally, 109 and 162 kJ mol⁻¹; and by the rising temperature method, 114 and 186 kJ mol⁻¹. The result also indicate that the loss of oxalic acid from the salt follows an Avrami–Erofeev type expression and the loss of carbon monoxide follows a contracting-sphere model.

INTRODUCTION

The background to the kinetics of decompositions of oxysalts has been extensively described by Dollimore and Griffiths [1]. They have also reported that the barium oxalate monohydrate was stable up to 76 °C when loss of water occurred and the anhydrous salt decomposed at 340 °C [2].

The thermal decomposition of barium oxalate heptahydrate has been reported by Strizhkov et al. [3]. Walter-Levy and Laniepce [4] and Mutin and Watelle-Marion [5] reported the decomposition of various hydrates and also studied the acid oxalates of barium. Here the decomposition kinetics of acid barium oxalates are reported.

EXPERIMENTAL

Sample preparation

The samples used were derived from a set of experiments previously described [6]. The sample abbreviations, together with their method of

TABLE 1

The concentration of the starting materials, and the abbreviation for each sample

Conc. of starting materials (mol)	Abbreviation	Conc. of starting materials (mol)	Abbreviation
0.2	BaOX1	1.0	BaOX7
0.4	BaOX2	1.1	BaOX8
0.5	BaOX3	1.2	BaOX9
0.6	BaOX4	1.3	BaOX10
0.7	BaOX5	1.4	BaOX11
0.8	BaOX6	1.6	BaOX12

preparation, are repeated here for clarification (Table 1).

Differential thermal analysis (DTA) experiments were performed using the Netzch unit and thermogravimetric analyses (TGA) were carried out on the Stanton-Redcroft TG 750 unit.

Isothermal experiments were carried out on samples BaOX₄ and BaOX₉ to enable the activation energy for the loss of an oxalic acid molecule and a carbon monoxide molecule to be calculated. A series of experiments were carried out over the temperature range 190–270 °C to determine which kinetic expression was obeyed for the loss of oxalic acid. A second series of experiments was carried out over the temperature range 400–570 °C to

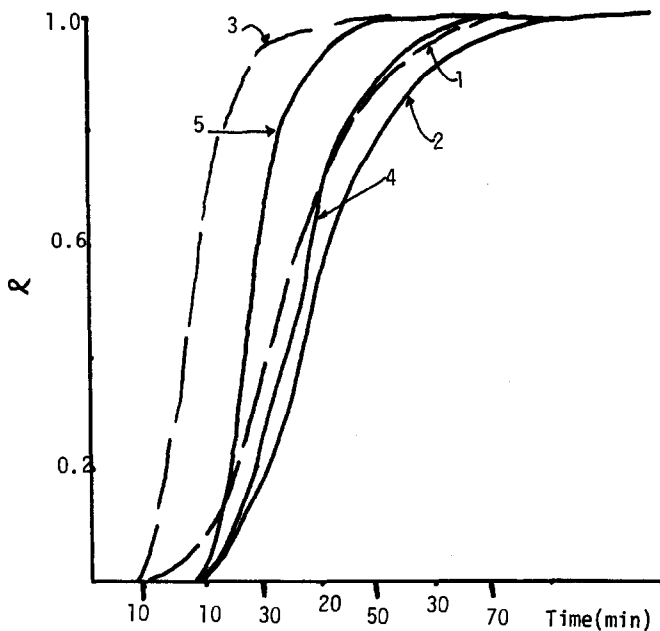


Fig. 1. Plot of α vs. t for sample BaOX₄.

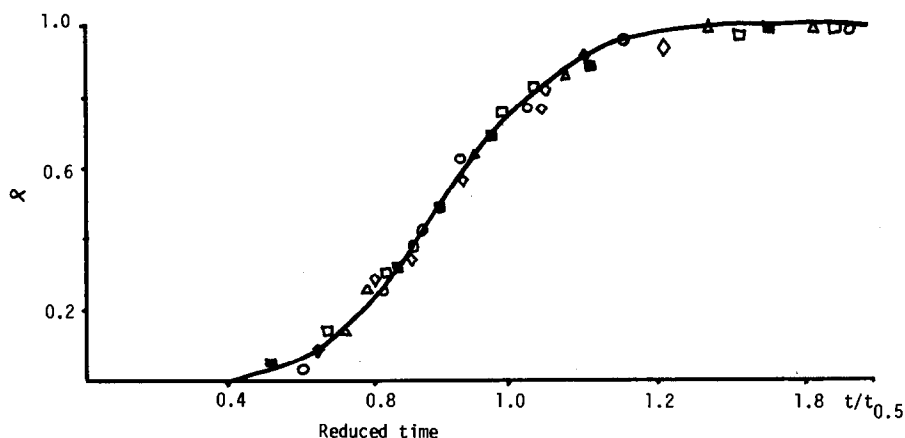


Fig. 2. Reduced time plots for loss of oxalic acid for sample BaOX₄. (Δ) 225 °C; (\square) 233 °C; (\blacksquare) 247 °C; (\circ) 255 °C; (\diamond) 268 °C.

determine which kinetic expression was obeyed for the loss of carbon monoxide. The α - t plots and the reduced time plot for sample BaOX₄ are shown in Figs. 1 and 2, respectively. The reduced time plots for the loss of oxalic acid for samples BaOX₄ and BaOX₉, when compared with the standard plots, showed that the mechanism most closely obeyed was best described by the Avrami-Erofeev equation [7]. Data obtained by plotting $\ln t$ vs. $\ln[-\ln(1-\alpha)]$ permitted the calculation of n from the gradient, the data were also plotted as time (min) vs. $n[-\ln(1-\alpha)]$. These plots are shown in Figs. 3 and 4. Figure 5 shows the plot of $\log K$ vs. $1/T$. The gradient of this graph has the value $-E/RT$ which allows the calculation of the activation energy. In these figures the solid is heat treated at: (1) 225 °C; (2) 233 °C; (3) 247 °C; (4) 255 °C; (5) 268 °C. The reduced time plots for the loss of carbon monoxide for samples BaOX₄ and BaOX₉, when compared with the master plots, showed that the decomposition followed a kinetic path which obeyed the Mempel intermediate expression [8].

The activation energy, E , was calculated from the gradient of the plot of $\log K$ vs. $1/T$ and the pre-exponential factor, A , from the intercept on the y axis. The following results were obtained.

Sample	Loss of oxalic acid		Loss of carbon monoxide	
	Activation energy, E (kJ mol ⁻¹)	Pre-exponential factor, A (s ⁻¹)	Activation energy, E (kJ mol ⁻¹)	Pre-exponential factor, A (s ⁻¹)
BaOX ₄	-106.2	4.8×10^8	-190.0	4.5×10^9
BaOX ₉	-109.0	9.33×10^8	-162.7	1.1×10^{10}

Kinetic data from rising temperature experiments

The calculation of activation energies and other kinetic parameters from rising temperature experiments is a much more convenient process than

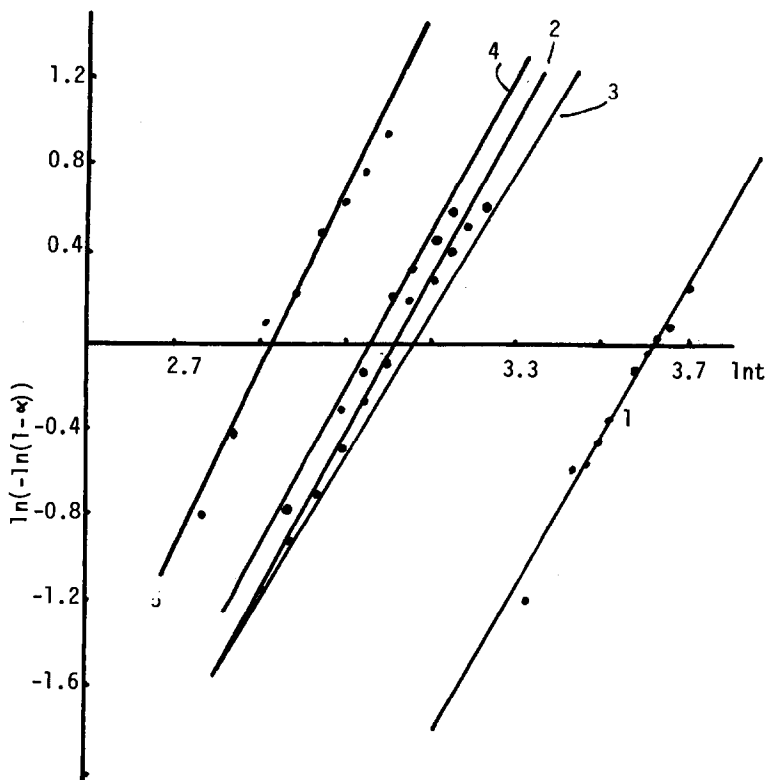


Fig. 3. Plot of $\ln[-\ln(1-\alpha)]$ vs. $\ln t$.

performing isothermal experiments at a series of temperatures. For the results to have any meaning other supporting data should ideally be available. It is also necessary that the region of the decomposition temperature produces isokinetic results. The most convenient starting equation is either

$$\frac{d\alpha}{dt} = K(1-\alpha)^n \quad (1)$$

or

$$\frac{d\alpha}{dt} = K^n \quad (2)$$

to describe the kinetics where α is the fraction decomposed, t is time, K and n are constants.

The type of data obtained from the TG traces is percentage weight loss vs. time which was then converted to show the data as $d(\text{percentage weight loss})$ vs. time. The calculations in rising temperature analysis involve the combination of three equations

$$\frac{d\alpha}{dt} = Kf(\alpha) \quad (3)$$

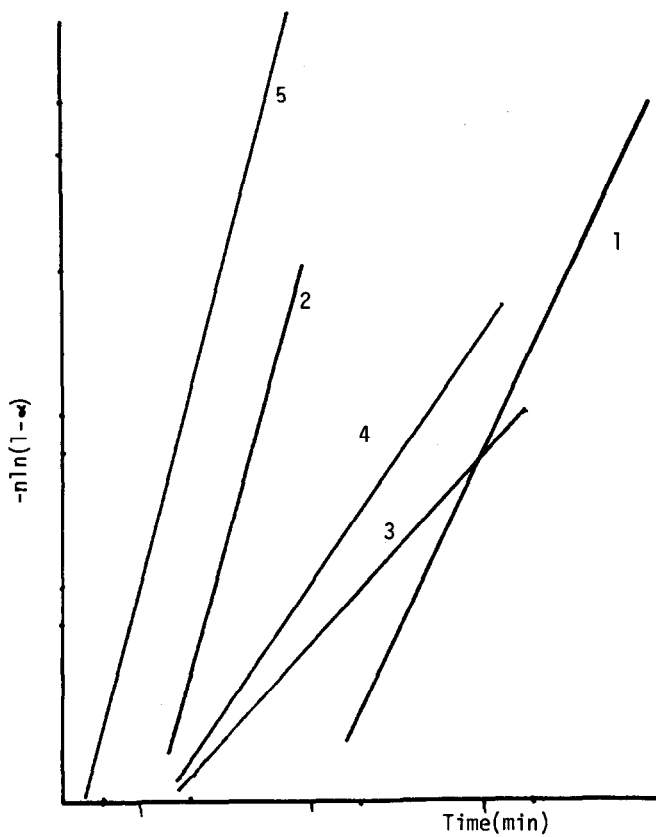


Fig. 4. Plot of $-n \ln(1 - \alpha)$ vs. time for sample BaOX4.

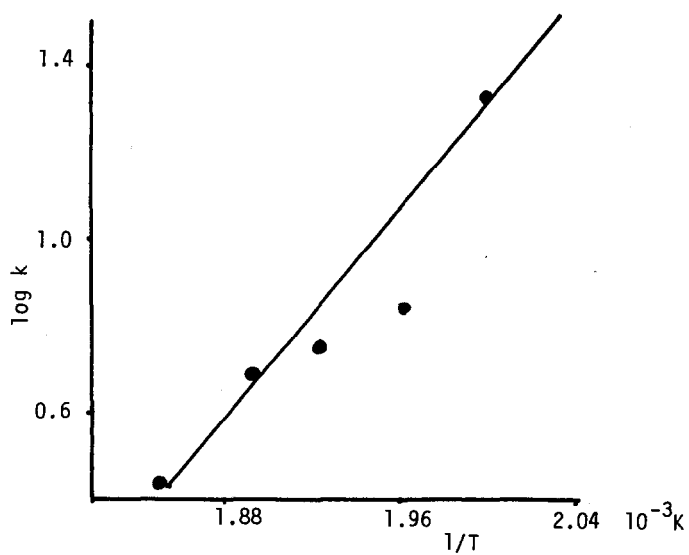


Fig. 5. Plot of $\log k$ vs. $1/T$ for sample BaOX4.

$$K = A \exp(-E/RT) \quad (4)$$

$$T = T_0 + bt \quad (5)$$

where K is the rate constant at temperature T ; A is the pre-exponential factor; E is the activation energy; R is the gas constant; b is the heating rate; α is the fraction decomposed.

From eqns. (4) and (5)

$$K = \frac{d\alpha}{dT} f(\alpha) = A \exp(-E/RT) \quad (6)$$

Taking natural logs gives

$$\ln K = \ln \frac{d\alpha}{dT} f(\alpha) = \ln A - E/RT \quad (7)$$

By plotting in $dt/f(\alpha)$ vs. $1/T$, the activation energy can be calculated from the slope and A from the intercept. The results from the TG were in the form percentage weight loss vs. temperature. The T and α values ascribed to the $d\alpha/dT$ term were calculated by taking the average of the α and T values used when determining this term. The values of $d\alpha/dT$ were found using eqn. (5) which gives

$$b = \frac{dT}{dt} \quad (8)$$

so

$$\frac{d\alpha}{dT} = b \frac{d\alpha}{dT} \quad (9)$$

combining eqns. (6) and (9) gives

$$K = b \frac{d\alpha}{dT} f(\alpha) = A \exp(-E/RT) \quad (10)$$

Taking natural logs gives

$$\ln b \frac{d\alpha}{dT} f(\alpha) = \ln K - E/RT \quad (11)$$

A plot of the left-hand side of eqn. (11) against $1/T$ should give a straight line if the correct $f(\alpha)$ was used, the slope (which is equal to $-E/R$) thus yields E and the intercept gives the value of $\ln A$. A simple expression for $f(\alpha)$ is $1 - \alpha$ which implies a first-order process. It would be difficult to justify the precise application of this expression when the kinetic expression found isothermally was of a different type. However, as an initial calculation and to a first approximation the calculation may be attempted using $f(\alpha) = 1 - \alpha$. This can be defended on the basis that, as an approximation to within 5–10%, it would describe the reaction and that the calculation of E and A is not critically dependent on the form of the isothermal kinetic law. There is also the possibility that the laws describing isothermal experimental behaviour may not apply to rising temperature conditions where the experi-

mental conditions are very different. The following activation energies and pre-exponential values were found for samples BaOX_4 and BaOX_9 .

Sample	Activation energy, $E(\text{kJ mol}^{-1})$	Pre-exponential factor, $A (\text{s}^{-1})$
<i>Loss of oxalic acid</i>		
BaOX_4	100.6	9.33×10^9
BaOX_9	114.1	2.42×10^{10}
<i>Loss of carbon monoxide</i>		
BaOX_4	282	2.36×10^{19}
BaOX_9	186	4.2×10^{12}

Figure 6 shows the type of plot obtained from $\ln d\alpha/dt(1-\alpha)$ vs. $1/T$. The activation energies from the rising temperature experiments were in good agreement with those obtained from the isothermal experiments.

However, the kinetic expression found in the isothermal experiments indicated that for the loss of oxalic acid an Avrami–Erofeev expression was obeyed i.e.

$$Kt = -\ln(1-\alpha)^{1/n} \quad (12)$$

where n varies between 2.8 and 4.8. From rising temperature calculations of

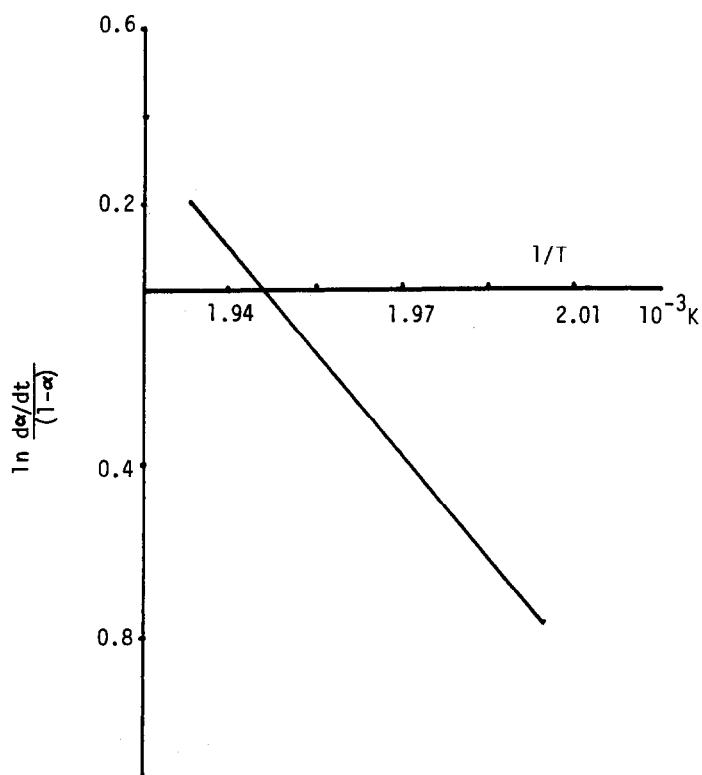


Fig. 6. Plot of $\ln d\alpha/dt(1-\alpha)$ vs. $1/T$ for loss of oxalic acid for sample BaOX_9 .

the kinetics it may be supposed that the loss of oxalic acid is governed by an Avrami-Erofeev equation with $n = 3$, where

$$\frac{d\alpha}{dt} = 3K - \ln(1 - \alpha)^{2/3}(1 - \alpha) \quad (13)$$

and

$$f(\alpha) = -\ln(1 - \alpha)^{2/3}(1 - \alpha) \quad (14)$$

The rising temperature data may then be calculated from the decomposition stage involving the loss of oxalic acid by using eqn. (12) with $n = 3$. However, the function $f(\alpha)$ varies from the previous set of data by the factor $-\ln(1 - \alpha)^{2/3}$. The function also varies in the limit that for $\alpha = 0$

$$f(\alpha)_0 = (1 - \alpha) = 1$$

but

$$f(\alpha)_0 = -\ln(1 - \alpha)^{2/3}(1 - \alpha) = 0$$

This is seen by plotting $(1 - \alpha)$ vs. α , $-\ln(1 - \alpha)^{2/3}$ vs. α , and $f(\alpha)$ vs. α over the range of α values from zero to unity. These plots are demonstrated in Fig. 7.

It is concluded that the Avrami-Erofeev expression is suspect under these conditions and is probably related to the fact that in the use of the function $f(\alpha) = 1 - \alpha$, one is dealing with a traditional order reaction for which the Arrhenius equation is applicable in that when $1 - \alpha \rightarrow 1$, $\alpha \rightarrow 0$ and $d\alpha/dt = K$. However, when dealing with the Avrami-Erofeev equation, the value of $d\alpha/dt = 0$ when $\alpha \rightarrow 0$, and the kinetic constant, K , although varying with temperature, does not obey the basic concept regarding the definition of the specific-reaction rate-constant used in the classical form of the Arrhenius equation.

It must be noted that the isothermal data based on the Avrami-Erofeev equation, when repeated at various temperatures, does provide data which compare well with the rising temperature data reported using the approximation $f(\alpha) = 1 - \alpha$.

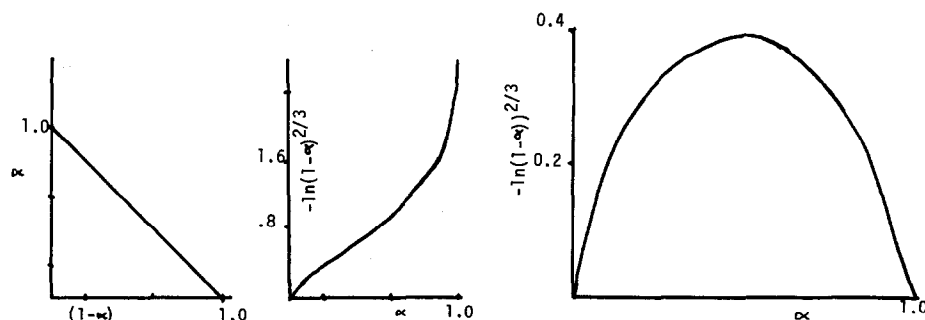


Fig. 7. Plots of $(1 - \alpha)$ vs. α , $(-\ln(1 - \alpha))^{2/3}$ vs. α , and $f(\alpha)$ vs. α .

The isothermal data for the loss of carbon monoxide indicated a contracting sphere model equation, i.e.

$$Kt = 1 - (1 - \alpha)^{1/3}$$

where

$$\frac{d\alpha}{dt} = 3K(1 - \alpha)^{2/3} \quad (15)$$

and

$$f(\alpha) = (1 - \alpha)^{2/3} \quad (16)$$

Here we have an order of reaction given by $n = 2/3$ and the traditional definition of an Arrhenius specific reaction rate constant is obeyed, namely, as

$$\alpha \rightarrow 0, 1 - \alpha \rightarrow 1, \text{ and } \frac{d\alpha}{dt} = K$$

As expected, use of this expression in the rising temperature method gives good straight lines (Fig. 8) from which the following values were deduced.

Sample	Activation energy, E (kJ mol ⁻¹)	Pre-exponential factor, A (s ⁻¹)
<i>Loss of carbon monoxide</i>		
BaOX ₄	140.0	1.901×10^9
BaOX ₉	190.5	7.356×10^{12}

Comparison of these values with the isothermal data and with the approximate method of rising temperature calculations shows that the values of the activation energy are very similar and justify the initial use of $f(\alpha) = 1 - \alpha$. The values of the pre-exponential terms would seem to be satisfactory as well.

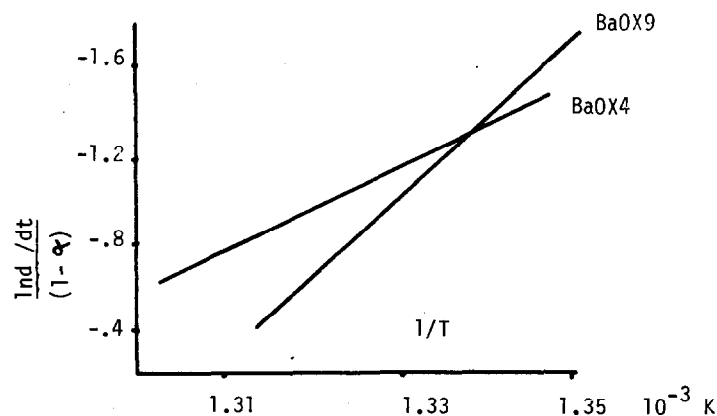


Fig. 8. The plot of $\ln d\alpha/dt/(1 - \alpha)$ vs. $1/T$ for loss of carbon monoxide for samples BaOX9 and BaOX4.

TABLE 2

Values of the order of reaction, n , α for $d\alpha/dt_{\max}$ and $1 - \alpha$ for $d\alpha/dt_{\max}$

n	0	1/3	1/2	2/3	1	1.5	2	3	4	5	10
$1 - \alpha$	0	0.192	0.250	0.298	0.368	0.444	0.5	0.576	0.63	0.669	0.919
α	1	0.808	0.750	0.702	0.632	0.556	0.5	0.424	0.37	0.331	0.081

TABLE 3

The values of α for which $d\alpha/dt$ is a maximum for the loss of oxalic acid and carbon monoxide from samples BaOX4 and BaOX9

Sample	α	$d\alpha/dt_{\max}$ for loss of oxalic acid	α	$d\alpha/dt_{\max}$ for loss of CO
BaOX4	0.36	3.65×10^{-2}	0.28	5.6×10^{-2}
BaOX9	0.25	4.7×10^{-2}	0.29	6.7×10^{-2}

One further point, arising from the rising temperature data, is the possibility that the order of the reaction may be determined by the inspection of the plot of $d\alpha/dt$ vs. temperature or $d\alpha/dt$ from the TG plot. Sestak et al. give

$$1 - \alpha \frac{d\alpha}{dt}_{\max} = n(1/1 - n) \quad (17)$$

where $\alpha_{d\alpha/dt_{\max}}$ = value of α at maximum rate of decomposition and n = order of reaction (for all values of n except $n = -1$). Data in this form are given in Table 2.

Data taken from the experiments made in this study are shown in Table 3. It is also seen that the $d\alpha/dt_{\max}$ values occur at α values expected for a first-order equation but the curves do not permit a precise evaluation of $d\alpha/dt_{\max}$ at a specific value of α .

Kinetic data from isothermal and rising temperature studies

The results obtained from rising temperature and isothermal experiments were in good agreement for both loss of oxalic acid and carbon monoxide.

Sample BaOX ₉	Activation energy, E (kJ mol ⁻¹)	Pre-exponential factor, A (s ⁻¹)
<i>Loss of oxalic acid</i>		
Isothermal	109	9.33×10^8
Rising temperature	114.1	2.42×10^{10}
<i>Loss of carbon monoxide</i>		
Isothermal	162	1.1×10^{10}
Rising temperature	186	4.2×10^{12}

This work shows that the preparative conditions determine not only the

particle size but also the chemical formula of the barium oxalate samples produced. The presence of oxalic acid in concentrations of ≥ 0.2 mol results in the formation of the acid salt. The kinetic results indicated that the loss of oxalic acid from the acid salt followed an Avrami–Erofeev type expression and the loss of carbon monoxide followed a contracting sphere model.

REFERENCES

- 1 D. Dollimore and D.L. Griffiths, *J. Therm. Anal.*, 2 (1970) 229.
- 2 G. Brunhs, *Z. Anorg. Allg.*, (1916) 194; *Chem. Zentralbl.*, 11 (1916) 454.
- 3 B.V. Strizhkov, A.V. Lapistskii and L.G. Vlasov, *Russ. J. Inorg. Chem.*, 7 (1962) 1220.
- 4 L. Walter-Levy and J. Laniece, *C.R. Acad. Sci.*, 258 (1964) 217.
- 5 J.C. Mutin and G. Wattle-Marion, *C.R. Acad. Sci., Ser. C*, 266 (1968) 315.
- 6 A.S. Bhatti, D. Dollimore and A. Fletcher, *Thermochim. Acta*, 78 (1984) 63.
- 7 B.V. Erofeev, *C.R. (Dokl.) Acad. Sci., URSS*, 52 (1946) 511.
- 8 K.L. Mempel, *Z. Phys. Chem. (Leipzig)*, 187 (1940) 235.