APPLICATION OF A NEW METHOD TO THE KINETIC STUDY OF THE THERMAL DECARBONYLATION OF SODIUM OXALATE

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ABSTRACT

The application of a new method for studying the kinetic parameters of the thermal decarbonylation of sodium oxalate in dinitrogen using differential scanning calorimetry is described.

The activation energy and the pre-exponential Arrhenius factor for the loss of carbon monoxide are calculated from the DSC curves and the reaction order and mechanism are also determined.

A comparison is made between the results obtained using the proposed method and those reported in the literature.

INTRODUCTION

The determination of kinetic parameters using non-isothermal methods offers advantages over conventional isothermal studies [1]; only a single sample and fewer data are required and the kinetics can be calculated over an entire temperature range in a continuous manner. In addition, if the sample undergoes considerable reaction when the temperature is raised to the optimum, the results obtained using isothermal methods are often questionable.

A disadvantage of the non-isothermal method, when compared with the isothermal technique, is that the reaction mechanism cannot usually be determined, and hence the meaning of the kinetic parameters is uncertain.

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However, the methods usually employed for kinetic analysis [2–14] lead to ambiguous results, especially if the reaction studied is diffusion controlled.

This paper reports a new non-isothermal method for studying the kinetic parameters of the thermal decarbonylation of sodium oxalate using differential scanning calorimetry. The mechanism of this reaction is determined using this method and the activation energy and the pre-exponential Arrhenius factor are calculated. A comparison is made between the results obtained in this study and those obtained previously by other workers [15].

EXPERIMENTAL

Products

The sodium oxalate used was a Merck commercial product of high grade purity.

Thermogravimetric analysis

Thermogravimetric analysis was performed on a Mettler HE-20 thermobalance. The constants were as follows: heating rate, $5\,^{\circ}C$ min^{-1}; TG range, 5 mV; chart speed, 20 cm h^{-1}; sample mass, 5 mg; reference, Al_2O_3; thermocouple, Pt/Pt–Rh 80%.

The analysis was carried out in a dynamic nitrogen atmosphere between 25 and $600\,^{\circ}C$. A platinum pan was used.

Differential scanning calorimetry

Differential scanning calorimetry was performed using a Mettler TA 3000 system with a Mettler DSC-20 differential scanning calorimeter.

The scanning rate used was $5\,^{\circ}C$ min^{-1} and samples of about 5 mg were employed, so as to render the temperature non-uniformity within the sample insignificant. An aluminium pan was used under a dynamic nitrogen atmosphere. The instrument calibration was checked periodically with standard samples of indium (purity, 99.99%). Several runs were carried out in all cases.

RESULTS AND DISCUSSION

The DSC curve of sodium oxalate shows an exothermic peak between 520 and $570\,^{\circ}C$; the mass loss which accompanies this exothermic transition corresponds to the loss of carbon monoxide on the TG curve; the residue was identified as Na_2CO_3 by IR spectroscopy and X-ray analysis.

TABLE 1

Kinetic equations

Mechanism (rate-controlling process)	$f(\alpha)$
D1 (one-dimensional diffusion)	$1/2\alpha$
D2 (two-dimensional diffusion)	$[-\ln(1-\alpha)]^{-1}$
D3 (three-dimensional diffusion: Jander equation)	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
D4 (three dimensional diffusion: Ginstling–Brounshtein equation)	$3/[2(1-\alpha)^{1/3}-1]$
F1 (random nucleation)	$1-\alpha$
R2 (phase-boundary reaction: cylindrical symmetry)	$2(1-\alpha)^{1/2}$
R3 (phase-boundary reaction: spherical symmetry	$3(1-\alpha)^{2/3}$

The rate of the thermal decomposition reaction of a solid can be expressed by the Arrhenius equation

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT}f(\alpha) \tag{1}$$

In eqn. (1), α is the fraction of material which has reacted at time t, E_a is the activation energy, $f(\alpha)$ is a function which depends on the actual reaction mechanism and A is the pre-exponential Arrhenius factor. The mathematical expressions of the functions $f(\alpha)$ corresponding to some of the mechanisms of thermal decomposition found in the literature [1] are collected in Table 1.

For the case where the temperature of the sample is increased at a constant rate, we can write

$$\frac{d\alpha}{dT} = \alpha' = \frac{A}{\beta}e^{-E_a/RT}f(\alpha) \tag{2}$$

where β is the heating rate dT/dt.

On integration, this gives

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^T e^{-E_a/RT}f(\alpha)\,dT \tag{3}$$

By differentiating the logarithmic form of eqn. (1) with respect to $d\ln(1-\alpha)$, we obtain

$$\frac{d\ln(d\alpha/dT)}{d\ln(1-\alpha)} = \frac{d\ln\alpha'}{d\ln(1-\alpha)} = -\frac{E_a}{R}\frac{d(1/T)}{d\ln(1-\alpha)} + \frac{d\ln f(\alpha)}{d\ln(1-\alpha)}$$

or

$$\frac{\Delta\ln\alpha'}{\Delta\ln(1-\alpha)} = -\frac{E_a}{R}\frac{\Delta(1/T)}{\Delta\ln(1-\alpha)} + \frac{\Delta\ln f(\alpha)}{\Delta\ln(1-\alpha)}$$
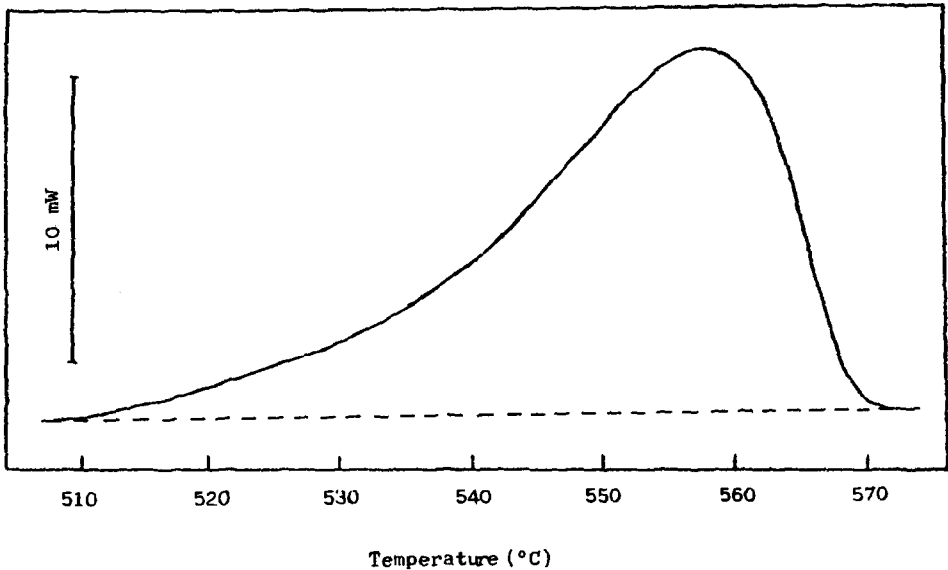
Fig. 1. DSC curve of sodium oxalate.

and

$$\frac{\Delta \ln \alpha' - \Delta \ln f(\alpha)}{\Delta \ln(1 - \alpha)} = -\frac{E_a}{R} \frac{\Delta(1/T)}{\Delta \ln(1 - \alpha)} \tag{4}$$

Thus the plots of $[\Delta \ln \alpha' - \Delta \ln f(\alpha)]/[\Delta \ln(1 - \alpha)]$ vs. $\Delta(1/T)/[\Delta \ln(1 - \alpha)]$ should be a straight line with a slope of $-E_a/R$, irrespective of the

TABLE 2

ΔH, α, T and α' obtained from the DSC curve

ΔH (mJ)	α	T (°C)	α' (K^{-1})
408.62	0.10776	534.0	0.00940
494.10	0.13031	536.0	0.01098
595.91	0.15716	538.0	0.01279
712.02	0.18778	540.0	0.01485
845.53	0.22299	542.0	0.01715
997.02	0.26294	544.0	0.01972
1169.80	0.30852	546.0	0.02252
1366.90	0.36048	548.0	0.02552
1588.80	0.41900	550.0	0.02864
1830.60	0.48277	552.0	0.03179
2095.10	0.55255	554.0	0.03476
2370.80	0.62524	556.0	0.03737
2667.50	0.70350	558.0	0.03902
2958.20	0.78015	560.0	0.03940
3247.90	0.85656	562.0	0.03730

f(α) value employed. However, we can select the f(α) value that best fits the actual mechanism of the reaction studied using the intercept value; this should be zero from eqn. (4).

From the DSC curve (Fig. 1) of sodium oxalate, we constructed Table 2.

Using the mechanisms listed in Table 1, we plotted [Δ ln α' − Δ ln f(α)]/[Δ ln(1 − α)] vs. $\Delta(1/T)$/[Δ ln(1 − α)] for the compound

TABLE 3

Results obtained using the seven mechanisms for the plot of [Δ ln α' − Δ ln f(α)]/[Δ ln(1 − α)] vs. $\Delta(1/T)$/[Δ ln(1 − α)]

Mechanism D1
   Correlation coefficient $r = -0.99970$
   Slope $m = -119114.1$
   Intercept value $i = 0.86391$
   Activation energy $E_a = 990.3621$ kJ mol^{-1}

Mechanism D2
   Correlation coefficient $r = -0.99981$
   Slope $m = -120020.6$
   Intercept value $i = 0.45511$
   Activation energy $E_a = 997.8991$ kJ mol^{-1}

Mechanism D3
   Correlation coefficient $r = -0.99980$
   Slope $m = -119916.8$
   Intercept value $i = -0.05526$
   Activation energy $E_a = 997.0364$ kJ mol^{-1}

Mechanism D4
   Correlation coefficient $r = -0.99980$
   Slope $m = -119916.8$
   Intercept value $i = 0.27807$
   Activation energy $E_a = 997.036$ kJ mol^{-1}

Mechanism F1
   Correlation coefficient $r = -1.00000$
   Slope $m = -55195.13$
   Intercept value $i = -0.50000$
   Activation energy $E_a = 458.9144$ kJ mol^{-1}

Mechanism R2
   Correlation coefficient $r = -1.00000$
   Slope $m = -55195.14$
   Intercept value $i = -0.00003$
   Activation energy $E_a = 458.9144$ kJ mol^{-1}

Mechanism R3
   Correlation coefficient $r = -1.00000$
   Slope $m = -55195.18$
   Intercept value $i = -0.16667$
   Activation energy $E_a = 458.9148$ kJ mol^{-1}

$$[\Delta \; (1/T) \; / \; \Delta \; \ln(1-\alpha)] \; . \; 10^{-5}$$
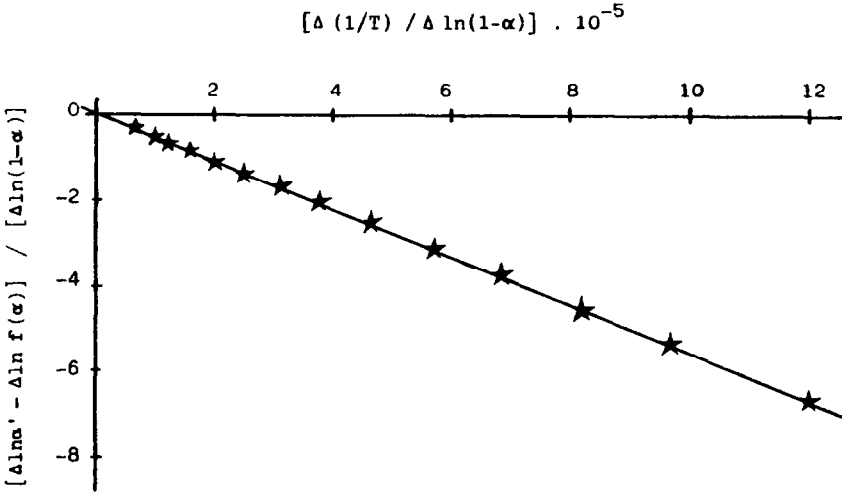

Fig. 2. Plot of $[\Delta \ln \alpha' - \Delta \ln f(\alpha)]/[\Delta \ln(1-\alpha)]$ vs. $\Delta(1/T)/[\Delta \ln(1-\alpha)]$ for mechanism R2.

studied. Table 3 shows the results for the correlation coefficient r, the slope m, the intercept value i and the activation energy E_a obtained for the seven mechanisms. Figure 2 shows the representation obtained for the mechanism R2.

In all cases the correlation coefficients r are close to unity, consistent with the results of Criado et al. [16]. Nevertheless, the straight line passes through the origin only when the analysis is performed using mechanism R2.
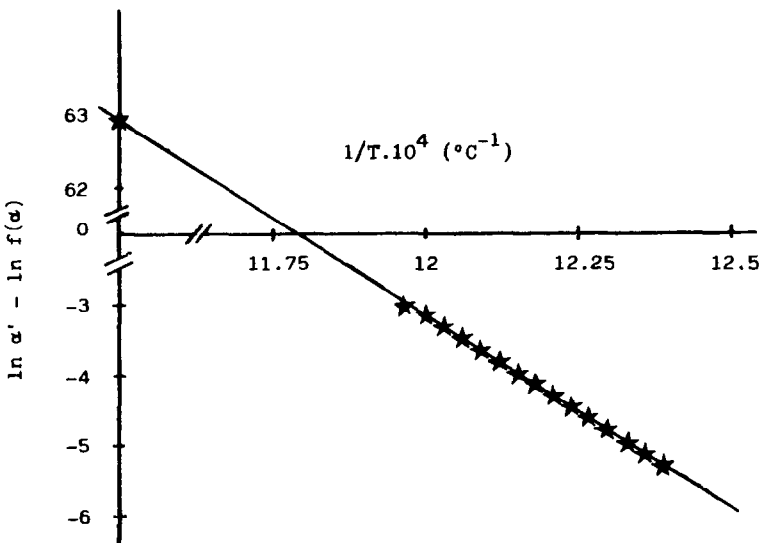

Fig. 3. Arrhenius plot of $\ln \alpha' - \ln f(\alpha)$ vs. $1/T$ for mechanism R2.

TABLE 4

Activation energy values obtained using the seven mechanisms

Mechanism	E_a [a] (kJ mol^{-1})	E_a [b] (kJ mol^{-1})	Difference (%)
D1	990.36	717.52	27.54
D2	997.89	854.74	14.34
D3	997.03	1015.99	−1.86
D4	997.03	910.13	8.71
F1	458.91	617.10	−34.47
R2	458.91	458.28	0.13
R3	458.91	511.23	−11.40

[a] Calculated from the representation of eqn. (4). [b] Calculated from the representation of eqn. (5).

Therefore, we conclude that the mechanism of the thermal decomposition of sodium oxalate with the loss of carbon monoxide is R2 (phase-boundary reaction (cylindrical symmetry)).

In order to test the validity of the above conclusion we substituted the seven forms of $f(\alpha)$ into the Arrhenius equation (eqn. (2)) in logarithmic form

$$\ln \alpha' = \ln(A/\beta) - E_a/RT + \ln f(\alpha)$$

or

$$\ln \alpha' - \ln f(\alpha) = \ln(A/\beta) - E_a/RT \tag{5}$$

The plot of $\ln \alpha' - \ln f(\alpha)$ vs. $1/T$ should be a straight line with a slope of $-E_a/R$ and an intercept of $\ln(A/\beta)$. If the proposed mechanism is correct, the activation energy value should be the same as that obtained previously.

Figure 3 shows this plot for the mechanism R2, and Table 4 shows the values of the activation energy for both analyses. It can be seen that only mechanism R2 shows very good agreement.

Therefore, the activation energy for the process of decarbonylation of sodium oxalate has a value of 458.91 kJ mol^{-1} (mechanism R2), and consequently the reaction order is 0.5. The pre-exponential Arrhenius factor obtained from the intercept value (plotting $\ln \alpha' - \ln f(\alpha)$ vs. $1/T$) is 1.882×10^{26} s^{-1}. These results are in agreement with those obtained previously be other workers using TG analysis [15].

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