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Correlation between the shape of a TG/DTG curve and the form of the kinetic mechanism which is applying

D. Dollimore, T.A. Evans, Y.F. Lee and F.W. Wilburn

Department of Chemistry, University of Toledo, Toledo, OH 43606 (USA)

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Abstract

A method of identifying the reaction mechanism in non-isothermal kinetics is presented based on the symmetry, width and height of the DTG curve. Using a computer program, which allows the calculation of a thermogravimetric curve from selected Arrhenius parameters, heating rate and reaction mechanism, it has been possible to study how these variables alter the shape of the DTG curves. It is shown that the value of α (fraction decomposed) at which the maximum rate is obtained is characteristic for any specific mechanism, and is altered only slightly by the magnitude of the Arrhenius parameters and the heating rate. As such, with complementary information based on the width of the DTG peaks, it is usually possible to identify the mathematical expression which describes the reaction.

INTRODUCTION

Non-isothermal determination of solid-state kinetic parameters has a number of advantages over conventional isothermal methods. However, the major drawback with this procedure is that there is no recognized technique of evaluating the reaction mechanism $f(\alpha)$.

The rate of reaction of a thermal decomposition can be described using the general equation

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp(-E/RT)\cdot f(\alpha) \tag{1}$$

where β is the heating rate (dT/dt), and A and E are the pre-exponential factor and the activation energy, respectively. It is desirable to convert eqn. (1) into integral form

$$\int_{\alpha=0}^{\alpha=1} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta}\int_{T=0}^{T=T} \exp(-E/RT)\ dT \tag{2}$$

Correspondence to: D. Dollimore, Department of Chemistry, University of Toledo, Toledo, OH 43606, USA.

however, the right-hand side of the equation cannot be integrated in closed form.

To overcome this difficulty, the exponential integral has been solved using approximation methods [1], series expansion methods [2] and numerical solution methods [3].

Hence, once the mathematical form of $f(\alpha)$ is known the Arrhenius parameters can be evaluated.

For conventional isothermal analysis a number of methods are available to identify the reaction mechanism, the most common being the log–log method [4], the reduced time method [5] and the $\alpha_{\text{experimental}}$ vs. $\alpha_{\text{theoretical}}$ plot [6]. It is usually assumed, therefore, that the isothermal mechanism also holds in non-isothermal experiments for a particular system. This eliminates the greatest advantage of the non-isothermal method in that, although the Arrhenius parameters can be obtained from a single rising-temperature curve, the isothermal experiments must still be performed beforehand to identify the reaction mechanism. Furthermore, it may be envisaged that, due to the different conditions under which the nucleation process occurs during the two methods, the assumption of a fixed mechanism for a particular system may not be correct.

It is known [7] that in isothermal experiments the calculated Arrhenius parameters depend only slightly on the form of $f(\alpha)$ chosen; however, in the case of non-isothermal methods, the dependence is far more drastic. Therefore, without a method for precise determination of the reaction mechanism, the results produced are somewhat ambiguous.

Various methods of computational analysis have been proposed in the literature for attempted identification of the decomposition mechanism [8–11]. It would, however, be desirable to have a more effortless method of mechanism recognition.

In a previous investigation [12] we demonstrated how a thermogravimetric (TG) recreation computer program could be used to gain information concerning thermal stability. The program calculates the TG rising temperature (α–T) data once supplied with the activation energy, pre-exponential factor and the mathematical form of $f(\alpha)$. This process may be considered as the reverse of rising-temperature kinetics in which the Arrhenius parameters are calculated from α vs. temperature plots and the mechanism.

Here we report on how this program has been used to study the effect the mechanism has on the decomposition curve, and how this leads to a quick and easy method of identifying $f(\alpha)$.

EXPERIMENTAL

All TG experiments were performed on a Du Pont 1090 work station coupled to a TG 951 furnace. The theoretical TG curves were obtained using a computer program [13] written in BASIC.

RESULTS AND DISCUSSION

In isothermal reaction kinetics the first consideration in selecting the mechanism is to characterize the decomposition curve as acceleratory, deceleratory or sigmoidal, based on the position of the maximum rate $(\mathrm{d}\alpha/\mathrm{d}t)_{\max}$. Considering the results obtained previously [12], it appeared that the maximum rate in rising temperature experiments $(\mathrm{d}\alpha/\mathrm{d}T)_{\max}$ may also be of use in mechanism identification.

The computer program was used to produce the curves using the activation energy, the pre-exponential factor, the heating rate and the mechanism as variables. Our observations agree with those of previous studies [14], in that increasing the activation energy while holding all variables constant resulted in the decomposition temperature being raised. Similarly, increasing the pre-exponential factor while holding everything else constant lowered the decomposition temperature, as did using slower heating rates.

However, in each recreation trial, it was noted that the value of α at which the maximum rate ($\alpha_{\max}$) was obtained remained virtually constant for any specific reaction mechanism, regardless of the Arrhenius parameters or heating rate employed. The difference between the respective mechanisms can be seen more clearly by considering the derivative of the thermogravimetric (DTG) curves (Fig. 1).

Considering the DTG curves allows the width of the peaks to be measured at a point which corresponds to half the height. This parameter has been termed the "half-width" and acts as an additional variable for describing the shape of the curves. Characteristic ranges of $\alpha_{\max}$ for each of the reaction mechanisms are given in Table 1 along with reasonable limits for the half-width.

However, in the above theoretical treatment the Arrhenius parameters and heating rates in the analysis of a particular mechanism are selected randomly. For a more comprehensive look at how the Arrhenius parameters affect the shape of a DTG curve for any particular mechanism a more organized approach is required.

In calculating the activation energy and pre-exponential factor from the Arrhenius plot, it is inevitable that the data will not produce an exact straight line. Therefore, it is possible to draw a series of straight lines through the points on the graph for various ranges of α, and subsequently to obtain E and A values for each region.

Carrying out the dehydration of calcium oxalate monohydrate under a dynamic flowing atmosphere of air, and using a heating rate of 10°C min^{-1} gave $\alpha_{\max}$ equal to 0.76 and a half-width of 46°C. Referring to Table 1, the data show two possible mechanisms having an $\alpha_{\max}$ range comparable to this experimentally determined value. Thus the R2 and D4 equations are both possibilities, with the magnitude of the half-width making the Ginstling–Brounshtein diffusion mechanism the most probable.

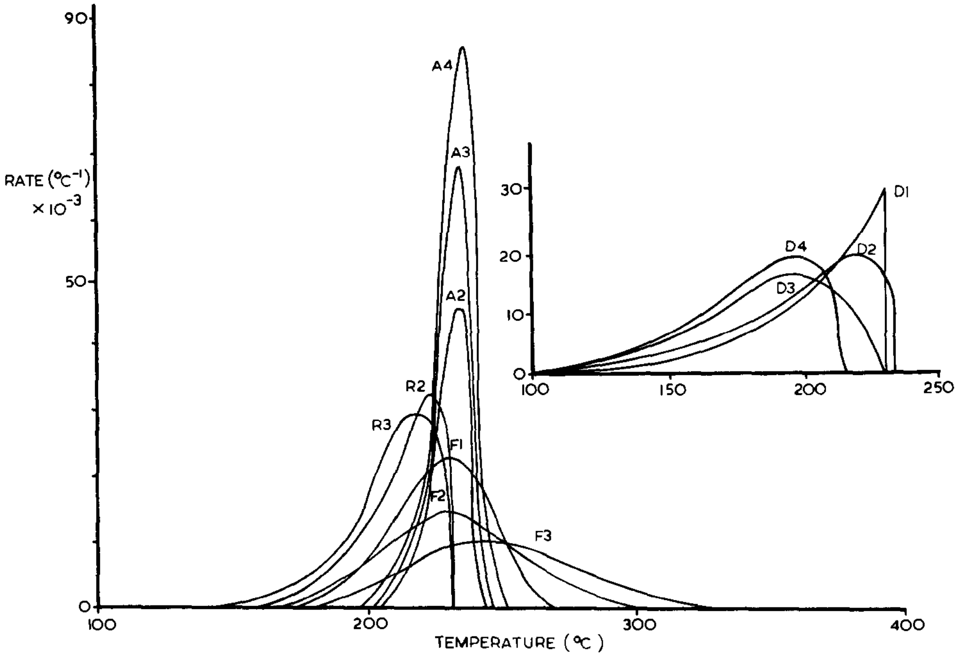

Fig. 1. Recreated DTG curves showing the effect of the reaction mechanism on the peak shape ($E = 124$ kJ mol^{-1}, $A = 6.23 \times 10^{10}$ s^{-1}).

Using the conventional rising-temperature differential kinetic equation

$$(\mathrm{d}\alpha/\mathrm{d}T)\beta/f(\alpha) = k = A\ \mathrm{e}^{-E/RT} \qquad (3)$$

in conjunction with the D4 mechanism produced the Arrhenius plot shown

TABLE 1

Reasonable limits for $\alpha_{\max}$ and the half-width for each reaction mechanism

Mechanism	$\alpha_{\max}$	Half-width (°C)
P1 Power law	1.000	12–4
A2 Avrami–Erofeev $n = 2$	0.610–0.625	34–12
A3 Avrami–Erofeev $n = 3$	0.623–0.630	24–10
A4 Avrami–Erofeev $n = 4$	0.630–0.638	10–4
B1 Prout–Tompkins	0.538–0.542	16–4
R2 Contracting area	0.725–0.735	40–18
R3 Contracting volume	0.680–0.700	42–24
D1 One-dimensional diffusion	1.000	50–18
D2 Two-dimensional diffusion	0.790–0.820	78–24
D3 Three-dimensional diffusion	0.663–0.689	80–38
D4 Ginstling–Brounstein	0.735–0.765	62–20
F1 First-order decay	0.600–0.625	60–20
F2 Second-order decay	0.450–0.490	94–20
F3 Third-order decay	≈ 0.389	–

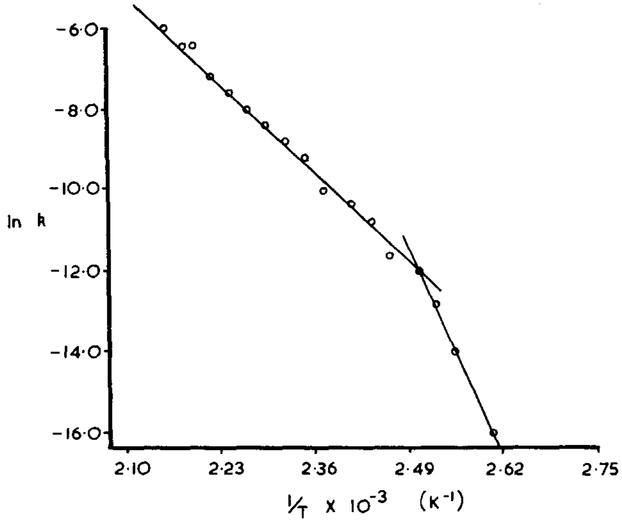

Fig. 2. Arrhenius plot for the dehydration of calcium oxalate monohydrate at 10°C min^{-1} under an atmosphere of air using the D4 mechanism.

in Fig. 2. The plot appears to consist of two linear regions which intersect around $\alpha = 0.05$. However, it is unclear where to draw the best fitting straight line or lines. It was calculated from the slope of the two regions in Fig. 2 that, below $\alpha = 0.05$, an activation energy of 281 kJ mol^{-1} was obtained, while above this point a value of 147 kJ mol^{-1} was seen. Meanwhile, drawing a single best fitting straight line through the points gave rise to an activation energy of 165 kJ mol^{-1}. Table 2 shows the E and A values obtained from lines drawn through various ranges of α in order to illustrate the disadvantage of extracting these parameters directly from the Arrhenius plot.

Further treatment of these data allows the plotting of ln A against E to produce the compensation plot shown in Fig. 3. Although the general significance of such plots is still not understood, it is known that they are a

TABLE 2

Arrhenius data over various ranges of the overall fraction decomposed, for the dehydration of calcium oxalate monohydrate

α_{range}	E (kJ mol^{-1})	A (s^{-1})
0.00–1.00	165	1.29×10^{16}
0.00–0.50	177	4.46×10^{17}
0.50–1.00	125	2.46×10^{11}
0.00–0.05	281	3.06×10^{31}
0.05–1.00	147	8.54×10^{13}
0.10–0.60	153	5.628×10^{14}

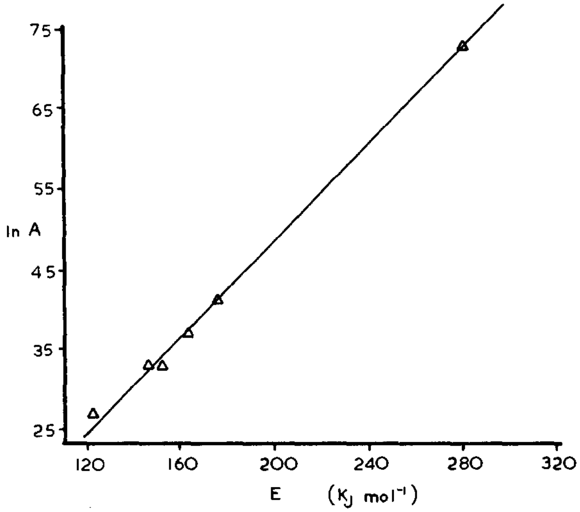

Fig. 3. Compensation plot obtained from the Arrhenius parameters given in Table 2.

consequence of a set of Arrhenius plots possessing a common isokinetic point. Therefore, drawing various straight lines through different places in a single Arrhenius plot appears to give rise to a "forced" compensation plot.

Thus a straight-line relationship exists between ln *A* and *E* allowing one parameter to be calculated if the other is known. This now allows the shape of the DTG curve to be observed as a function of kinetically related Arrhenius parameters rather than a random selection of values for *E* and *A*.

Table 3 shows the reconstructed α_{max} and half-width values as a function of the kinetically related Arrhenius parameters obtained for the dehydra-

TABLE 3

Variation of α_{max} and the half-width as a function of the Arrhenius parameters obtained for the dehydration of calcium oxalate monohydrate using the D4 mechanism

E (kJ mol^{-1})	A (s^{-1})	α_{max}	Half-width (°C)
100	9.411×10^{7}	0.739	62.0
110	1.883×10^{9}	0.742	54.0
120	3.767×10^{10}	0.746	50.0
130	7.535×10^{11}	0.748	44.0
140	1.507×10^{13}	0.750	40.0
150	3.016×10^{14}	0.753	36.0
160	6.033×10^{15}	0.754	34.0
170	1.207×10^{17}	0.755	32.0
200	9.663×10^{20}	0.759	26.0
250	3.096×10^{27}	0.763	20.0

tion of calcium oxalate monohydrate, using the D4 mechanism. It is seen that $\alpha_{\max}$ does change in a regular manner as a function of the Arrhenius parameters. However, the change is only slight with a 0.024 increase in $\alpha_{\max}$ being observed over a 150 kJ mol^{-1} span in activation energy. The half-width can be seen to alter more significantly, with increasing magnitudes of the Arrhenius parameters bringing about an exponential type decrease in the DTG breadth.

If it is assumed that reasonable values for the pre-exponential factor fall in the range 10^6–10^{30} s^{-1} then the D4 mechanism can be characterized by an $\alpha_{\max}$ value within the limits 0.735–0.765 and a half-width in the range 62–20°C.

Therefore, similar treatment of data for the other remaining mechanisms also allows dinstinctive limits to be observed, and it is these limits which are given in Table 1.

The limitations of this identification technique involve precisely pinpointing the maximum rate, and distinguishing between those mechanisms with similar values of $\alpha_{\max}$. The power law and the one dimensional diffusion mechanism are both observed to be highly acceleratory in nature, each having an $\alpha_{\max}$ of 1.000. Considering the general expression for the power law

$$\mathrm{d}\alpha/\mathrm{d}t = kn\alpha^{(n-1)/n} \tag{4}$$

shows that using a value of $n = 0.5$ produces the expression for the D1 mechanism

$$\mathrm{d}\alpha/\mathrm{d}t = k/2\alpha \tag{5}$$

i.e. P0.5 is the same as D1.

Therefore it should not be considered unusual for the two mechanisms to have similar values of $\alpha_{\max}$. Nevertheless it is still possible to distinguish between these two mechanisms based on the half-width, as it is observed that the power law produces significantly narrower DTG peaks.

Similarly, differentiating between the various Avrami–Erofeev equations and the first-order expression also presents a problem. If the general expression is used in the integral form

$$\left[-\ln(1-\alpha)^{1/n}\right] = kt \tag{6}$$

it can be seen that Fl is also Al and, considering the data in Table 1 and Fig. 1, shows that increasing the value of n results in the DTG peak becoming taller and thinner. However, precisely distinguishing between these mechanisms is not as easy as in the above case, in that some overlap occurs between the half-width ranges of each particular mechanism. The value of the maximum rate may also be of some use in recognizing the mechanism as it is observed that higher values of n give rise to greater rates. Table 4 gives approximate ranges for the value of the maximum rate

TABLE 4

Typical values of the maximum rate for the various Avrami–Erofeev equations (heating rate = 10°C min^{-1})

	A1 (FI)	A2	A3	A4
Maximum rate of range (K^{-1})	$1.7–3.0\times10^{-2}$	$3.4–6.0\times10^{-2}$	$5.0–9.0\times10^{-2}$	6.4×10^{-2}–0.12

TABLE 5

The effect of heating rate on the maximum rate of a reaction

Heating rate (°C min^{-1})	Max. rate (K^{-1})	Heating rate (°C min^{-1})	Max. rate (K^{-1})
1	5.249×10^{-2}	10	4.545×10^{-2}
2	4.997×10^{-2}	15	4.433×10^{-2}
5	4.740×10^{-2}	20	4.355×10^{-2}

$E = 124$ kJ mol^{-1}, $A = 6.23\times10^{10}$ s^{-1}, mechanism A2.

$(d\alpha/dt)_{max}$ obtained for the various mechanisms by inputting various randomly obtained Arrhenius parameters into the regeneration program. It can be seen that, while faster rates are obtained for the mechanisms with higher values of n, again too much overlap is observed to make a precise selection. At best it may be possible to narrow down the mechanism to the best of two, based on the magnitude of the half-width and $(d\alpha/dt)_{max}$. In addition, the effect of the heating rate must also be considered. Table 5 shows the variation of the maximum rate with a change in heating rate.

CONCLUSIONS

It has been shown that the reaction mechanism in rising-temperature kinetics can be obtained by considering the value of α at which the maximum rate occurs. Each mechanism has a characteristic range of α_{max} which is found to be virtually constant over wide ranges of Arrhenius parameters and is also unaffected by the heating rate. As such, it is possible to identify $f(\alpha)$ by simply reading the maximum rate from a DTG curve and correlating this value with the rising temperature thermogravimetric curve. The procedure, however, fails to distinguish between the first-order mechanism and the various forms of the Avrami–Erofeev equations due to the close proximity and overlapping of the α_{max} and half-width ranges. It is observed that differentiating between these mechanisms may be obtained to a certain extent by the magnitude of the maximum rate; however, this practice is better suited to rejection of unacceptable mechanisms rather than the positive identification of a specific mathematical expression.

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