

Kinetics of the thermal decomposition of dicarboxylic acids

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Abstract

The kinetics of the thermal decomposition of dicarboxylic acids $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ in flowing Ar, CO_2 and air atmospheres have been studied using a microcomputer program. The activation energy E_a and the frequency factor A of the decomposition were evaluated. The results of the analysis of the TG curves showed that the best fit of the data to various kinetic equations is obtained with the random nucleation (A2 function) model for all the acids in the initial decomposition reaction. However, the experimental data in the main decomposition reaction fitted the three-dimensional diffusion (D3 function) mechanism from oxalic acid to adipic acid ($n = 0, 1-4$) and the A2 mechanism from pimelic acid to sebacic acid ($n = 5-8$). The relation between the activation energy and the number of CH_2 groups in the acids, except for malonic acid, was found to follow zig-zag lines for the initial and main decomposition reactions. Moreover, an approximate compensation effect between E_a and $\log A$ was observed for both the initial and main reactions in Ar atmosphere.

INTRODUCTION

There has been considerable discussion in the literature concerning the validity of the kinetic data obtained by thermal analysis under non-isothermal conditions [1]. It is known to be much more difficult to interpret the kinetic parameters, such as the reaction order n , the activation energy and the frequency factor, for the kinetics of reactions involving the participation of solid substances than for those of homogeneous reactions. The non-isothermal (TG) method also has a certain advantage [2], i.e. one weight loss–time curve is equivalent to a larger number of isothermal weight loss curves and a large amount of information is gained without sample-to-sample error, because the same sample is used throughout [3, 4]. Furthermore, there are advantages to using TG which provides the fraction decomposed

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α and the corresponding sample temperature throughout the thermal decomposition, and the TG curve commonly follows a characteristic path over a wide range of the decomposition. The shape of the curve is determined by the kinetic parameters of the decomposition. However, in these methods, the data to be analyzed are obtained from a TG curve on a recorder chart and are processed by complicated and tedious calculations. This necessitates computer programming for the acquisition of a large amount of accurate TG data. Computer systems, then, can be helpful in such methods. There is no information in the literature on the kinetics of decomposition of a series of dicarboxylic acids.

This paper deals with the microcomputer-aided treatment of TG data to analyze the thermal decomposition of dicarboxylic acids.

EXPERIMENTAL

Details regarding the purification of commercial dicarboxylic acids and the instruments used were described in a previous paper [5]. All the acids prepared were anhydrides. The TG curves were obtained with a Seiko TG/DTA 30 apparatus at a heating rate of $10^{\circ}\text{C min}^{-1}$ in various atmospheres at 200 ml min^{-1} . About 30 mg of powdered sample was placed in a Pt pan and was used in each measurement.

Kinetic treatment

Kinetic analysis of the TG data was carried out to find the kinetic model which gives the best description of the decomposition and allows calculation of meaningful kinetic parameters.

In the thermal decomposition of solid state materials, the rate of change of the decomposition fraction α with respect to time is often expressed as

$$f(\alpha) = kt \quad (1)$$

where $f(\alpha)$ is a function of α at time t . The kinetic model function depends on the reaction mechanism. The value of the rate constant k at different temperatures for the same reaction is generally assumed to be governed by the Arrhenius equation

$$k = A \exp(E_a/RT) \quad (2)$$

where R is the gas constant. The kinetics of solid state reactions can generally be written as

$$d\alpha/dt = f(\alpha)A \exp(-E_a/RT) \quad (3)$$

Table 1 shows the $f(\alpha)$ and $g(\alpha)$ functions commonly used for solid reactions [4]; $f(\alpha)$ is the reciprocal of the differentiation of $g(\alpha)$ with respect to α . The kinetic equations in Table 1 are used to describe the reaction

TABLE 1

Equations commonly used in kinetic analyses for solid state reactions

Rate-controlling process	Symbol	$f(\alpha)$	$g(\alpha)$
Diffusion			
(a) One-dimensional diffusion, parabolic law	D1	α^{-1}	α^2
(b) Two-dimensional diffusion, cylindrical sym.	D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha) + \alpha$
(c) Three-dimensional diffusion, spherical sym., Jander eqn.	D3	$(1-\alpha)^{1/3}[(1-\alpha)^{-1/2} - 1]^{-1}$	$[1 - (1-\alpha)^{1/3}]^2$
(d) Three-dimensional diffusion, spherical sym.; Ginstling–Brounshtein eqn.	D4	$[(1-\alpha)^{-1/3} - 1]^{-1}$	$(1-2\alpha/3) - (1-\alpha)^{2/3}$
Nucleation and nuclei growth, based on order with respect to α			
(a) Random nucleation; Mampel eqn.	F1	$1-\alpha$	$-\ln(1-\alpha)$
(b) Two-dimensional nuclei growth	F2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$-[\ln(1-\alpha)]^{1/2}$
(c) Three-dimensional nuclei growth	F3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$-[\ln(1-\alpha)]^{1/3}$
Phase boundary reaction, based on geometric models			
(a) One-dimensional, zero order mechanism	R1	Constant	α
(b) Two-dimensional, cylindrical sym.	R2	$(1-\alpha)^{1/2}$	$1 - (1-\alpha)^{1/2}$
(c) Three-dimensional, spherical sym.	R3	$(1-\alpha)^{2/3}$	$1 - (1-\alpha)^{1/3}$
Random nucleation and the growth of nuclei			
(a) Avrami eqn.	A2	$(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
(b) Erofeev eqn.	A3	$(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$

Key: α , degree of reaction; sym., symmetry; eqn., equation.

under various conditions and to find the most appropriate reaction model. Their derivations can be found in the literature [6]. If the temperature increases linearly with time, the heating rate ϕ can be expressed

$$\phi = dT/dt \quad (4)$$

or

$$d\alpha/dt = d\alpha/dT \phi \quad (5)$$

and substitution into eqn. (3) gives

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} e^{-E_a/RT} dT \quad (6)$$

Owing to the difficulty in obtaining accurate differential data from TG charts, integration of the left-hand side of eqn. (3) is used instead

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\phi} e^{-E_a/RT} dT = \frac{AE_a}{\phi R} p(x) = g(\alpha) \quad (7)$$

where $g(\alpha)$ is the integrated form of $f(\alpha)$. The function $p(x)$ is defined as

$$p(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-u}}{u} du = \left(\frac{1!}{x^2} - \frac{2!}{x^3} \right) e^{-x} \quad (8)$$

where $u = E_a/RT$ and x is the corresponding value of u at which a fraction α of the material has decomposed. The $p(x)$ function depends on both temperature and E_a [7], and has been given by several authors [8].

Equation (7) is rewritten

$$\log \frac{AE_a}{\phi R} = \log g(\alpha) - \log p(x) = B \quad (9)$$

The correct E_a value is determined as the one calculated for the mechanism which has the lowest standard deviation δ . The maximum constancy of B gives the optimum E_a value and is quantitatively characterized by the δ of individual B_i values obtained from their arithmetic mean of \bar{B} . The most appropriate reaction mechanism is obtained by comparison of the minimum δ values calculated to each kinetic equation $g(\alpha)$.

Thus, the corresponding frequency factor A will be found from the equation

$$\log A = \log R\phi - \log E_a + \bar{B} \quad (10)$$

Equation (7), after taking logarithms and regrouping terms, can be written as

$$\log \frac{AE_a}{\phi R} - \frac{E_a}{2.3RT} = \log \frac{g(\alpha)}{T^2} \quad (11)$$

When the function $g(\alpha)$ has been properly selected, a plot of the right-hand side of eqn. (11) against $1/T$ ought to be a straight line from whose slope the activation energy E_a can be calculated. The frequency factor is calculated from the intercept. The numerical value of this slope depends on the function $g(\alpha)$.

In the present work, the determination of the mechanism was calculated using a 16-bit microcomputer, the NEC PC-9801VM. The values of α ranging from 0.01 to 0.99 were selected from 150 data points with an interval of 0.01. BASIC is used in the operation, whose speed is compatible with the generation of data from digital TG. The program gives the best kinetic model, and a quantitative description and kinetic analysis of the decomposition process. These kinetic parameters were actually determined on the basis of the least-squares fitting of the solution of the kinetic equation to the experimental TG data.

Figure 1 shows a flow chart for the BASIC program used.

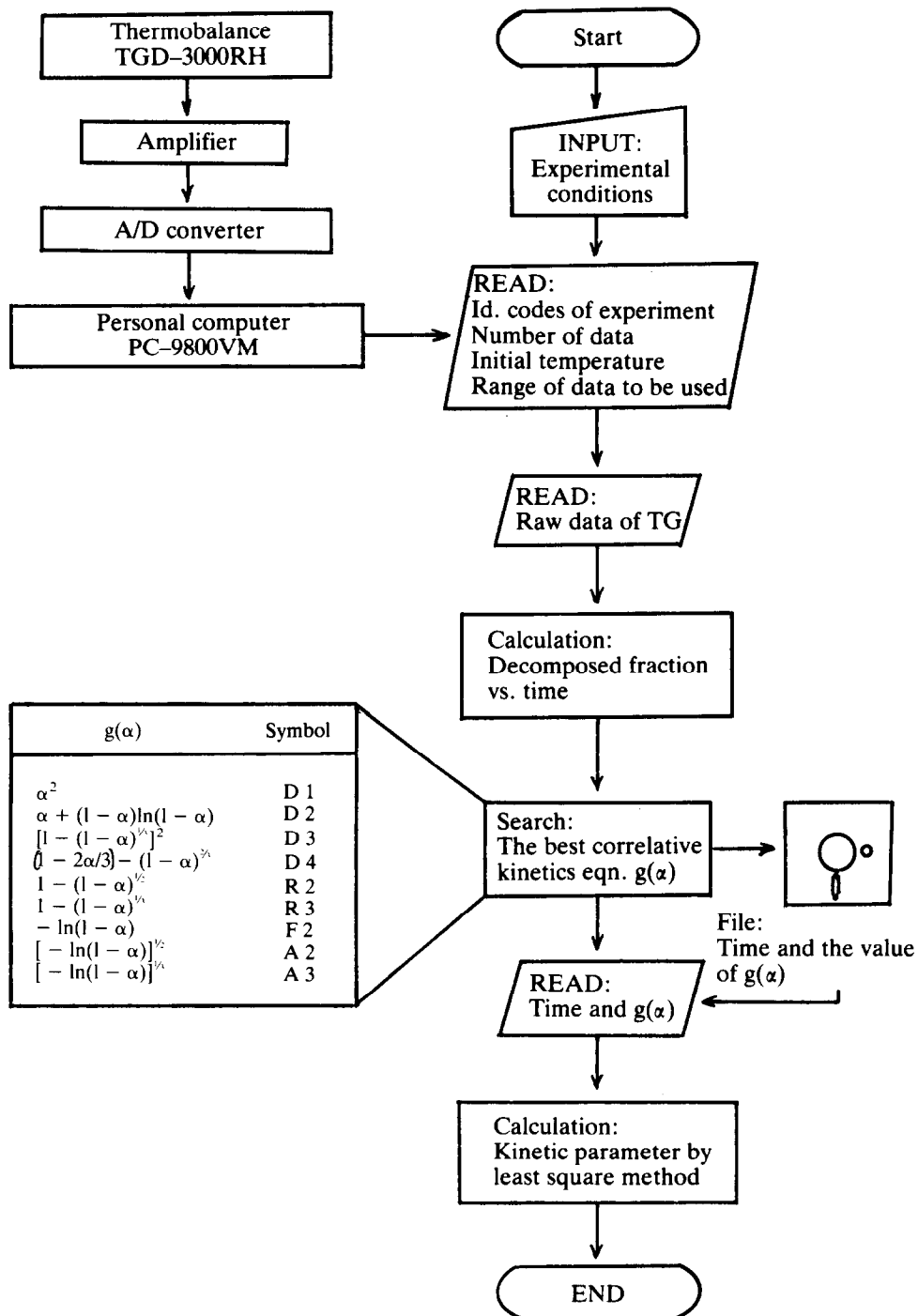


Fig. 1. Computer flow diagram for calculation of activation energy and frequency factor by a least-squares method.

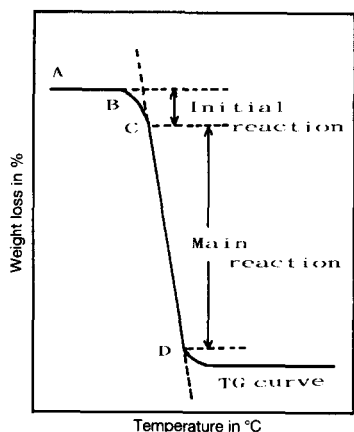


Fig. 2. Schematic TG curve: B–C, initial reaction; C–D, main reaction; B, initial decomposition temperature.

RESULTS AND DISCUSSION

An accurate evaluation of the relative stability of various systems using a computer program requires consideration of both the activation energy and the frequency factor, and of the reaction mechanism [9]. For the kinetic analysis, the initial and main reactions on the TG curves of the decomposition of dicarboxylic acids were quoted as shown in Fig. 2.

For the correct mechanism, $\log g(\alpha)$ versus $1/T$ should plot as a straight line. The functional values of $\log g(\alpha)$ required for this purpose are taken from Table 1, and the E_a values are calculated by the method of Šesták [10]. The results showed that the best fit of the data for the thermal decomposition of dicarboxylic acids in Ar, CO_2 and air atmospheres was obtained with the three-dimensional diffusion (D3 function) and the random nucleation (A2 function) models. Although the D3 mechanism has been selected most often for solid state reactions, other mechanisms are also indicated [1c]. However, a somewhat poorer correlation coefficient was obtained for the D3 function for the initial reaction.

This means that the experimental data fit the A2 mechanism much better. Accordingly, we conclude that the initial thermal decomposition of the acids in various atmospheres follows the random nucleation A2 mechanism. However, the experimental data in the main decomposition reaction fitted the D3 mechanism from oxalic acid to adipic acid ($n = 0, 1-4$) and the A2 mechanism from pimelic acid to sebacic acid ($n = 5-8$).

In order to obtain precise E_a values, the data from the computational methods were subjected to the method of least squares. The higher values of the correction coefficient γ show a good linearity. The values of E_a obtained from the regression analysis agree well with those obtained directly from the slope of the straight line plot. The uncertainty is $\pm 0.5 \text{ kcal mol}^{-1}$. The

TABLE 2
Kinetic parameters of the initial and main thermal decomposition reactions of dicarboxylic acids [HOOC(CH₂)_nCOOH] calculated from TG curves in a flowing Ar atmosphere by assuming various reaction mechanisms

Acid	n	Initial reaction			Main reaction				
		E_a /(kcal mol ⁻¹)	A /(v/s ⁻¹)	Correlation coefficient		E_a /(kcal mol ⁻¹)	A /(v/s ⁻¹)	Correlation coefficient	
				A2	D3			D3	A2
Oxalic	0	37.8	7.0×10^{15}	0.9999	0.9985	23.7	5.2×10^8	0.9992	0.9884
Malonic	1	43.5	8.2×10^{17}	0.9980	0.9961	27.0	3.1×10^{11}	0.9975	0.9993
Succinic	2	40.6	8.5×10^{16}	0.9928	0.9871	26.2	1.5×10^{11}	0.9944	0.9932
Glutaric	3	38.7	9.4×10^{15}	0.9979	0.9942	24.4	8.6×10^{10}	0.9963	0.9854
Adipic	4	41.1	6.5×10^{17}	0.9989	0.9960	26.8	1.7×10^{11}	0.9985	0.9966
Pimelic	5	39.6	3.5×10^{16}	0.9978	0.9936	25.0	9.8×10^{10}	0.9944	0.9972
Suberic	6	43.0	7.9×10^{17}	0.9979	0.9941	27.2	3.3×10^{11}	0.9916	0.9985
Azelaic	7	40.2	6.3×10^{16}	0.9975	0.9940	25.5	1.2×10^{10}	0.9877	0.9992
Sebacic	8	44.5	7.8×10^{17}	0.9985	0.9955	28.0	3.5×10^{11}	0.9904	0.9994

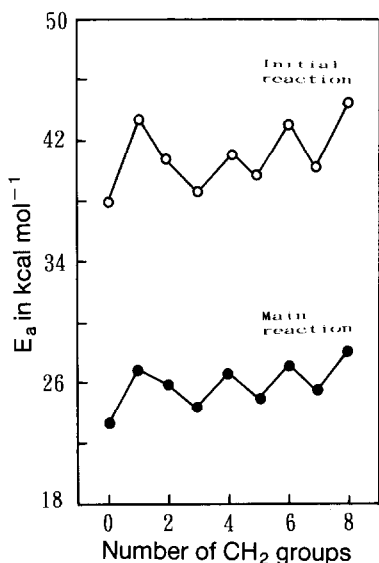


Fig. 3. Kinetic compensation effect in the thermal decomposition of dicarboxylic acids in a flowing Ar atmosphere. The numbers in the figure show the number of CH₂ groups n in the dicarboxylic acids.

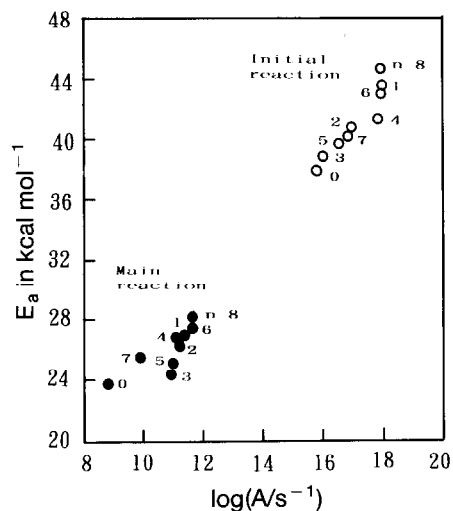


Fig. 4. Relation between activation energy E_a and number of CH₂ groups n in the decomposition of dicarboxylic acids in a flowing Ar atmosphere.

results of these evaluations are summarized in Table 2 and Fig. 3. The E_a values in the initial reaction are somewhat lower than those of the main reaction. On the whole, the E_a values for both the initial and the main decomposition reactions of dicarboxylic acids increase gradually with increase in n .

The E_a values of the even n members of the dicarboxylic acid series, except for malonic acid, were higher than those of the odd-membered ones. It can be assumed that this property, illustrated in Fig. 3, depends on whether an acid contains an even or odd number of carbon atoms because of the zig-zag structures in dicarboxylic acids [11]. The results described above follow the same trend for the decomposition in CO_2 and air atmospheres. The zig-zag correlation between the melting point and the n value in the acids is well known. The zig-zag correlation was also found by Takasuka et al. [12] between the percentage of the double cyclic intermolecular hydrogen-bonded molecules and the n value of the acids. The plot of E_a versus $\log A$ shows an approximate compensation effect for the initial and main reactions (Fig. 4).

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