

The importance of the pre-history of a sample on its thermal behavior.

Part 1

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(Received 10 June 1992)

Abstract

In solid samples where the dominant effect of pre-history is the initial loss of material before the thermal decomposition commences, the effect of the pre-history is shown theoretically to lower the peak temperatures and the peak heights of the derivative thermogravimetric (DTG) curves. The thermogravimetric and DTG curves shift to a lower temperature range without changing the character of the reaction function.

The results of using the single-heating-rate methods show that the correct activation energy can be obtained for the reaction function in the form of $(1 - \alpha)^n$ (differential form) where α is the extent of the reaction and n an exponent. The frequency factor can be calculated by substitution back into the Arrhenius equation. However, for other forms of reaction mechanism such a direct calculation is not possible.

The results of the use of the multi-heating-rate methods show that they present a method by which the correct activation energy can be obtained which is not affected by the pre-history of the samples.

INTRODUCTION

The activity of the solid state is conditioned by its pre-history. Here, one limited part of the pre-history is the initial loss of material before the thermal decomposition commences. In research on solid phase materials in geology, pharmacy etc., the pre-history of the sample is very important. Differences in the pre-history of samples can be shown both in their physical and chemical properties and in their thermal properties.

In this paper, the influence of the pre-treatment of the sample on its thermal kinetics properties has been studied from a theoretical angle. The

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programs are published in another paper [1]; other programs for creating the data are discussed briefly in the experimental section. The process and the methods used to evaluate the kinetic analysis are discussed in the following section (Theory).

THEORY

In thermal analysis, the expression indicating the extent of reaction as a function of temperature is

$$d\alpha/dt = f(\alpha)k(T) \quad (1)$$

where α is the extent of the reaction and $f(\alpha)$ is the function of α which represents the reaction mechanism; Table 1 shows a list of the most commonly used equations. $k(T)$ is the rate constant at temperature T and

TABLE 1

The common forms of $f(\alpha)$ and $G(\alpha)$

Mechanism	$G(\alpha)$	$f(\alpha)$	
<i>Acceleratory α-t curve</i>			
P1	Power law		
		$\alpha^{1/4}$	$4\alpha^{3/4}$
		$\alpha^{1/3}$	$3\alpha^{2/3}$
		$\alpha^{1/2}$	$2\alpha^{1/2}$
		α	1
E1	Exponential law	$\alpha^{3/2}$	$2/3\alpha^{-1/2}$
		$\ln \alpha$	α
<i>S-Shaped α-t curve</i>			
A1.5	Avrami-Erofeev	$[-\ln(1-\alpha)]^{2/3}$	$1.5(1-\alpha)[- \ln(1-\alpha)]^{1/3}$
A2	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$
A3	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$
A4	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$
B1	Prout-Tompkins	$\ln[\alpha/(1-\alpha)]$	$\alpha(1-\alpha)$
		$[-\ln(1-\alpha)]^2$	$0.5(1-\alpha)[- \ln(1-\alpha)]^{-1}$
		$[-\ln(1-\alpha)]^3$	$(1/3)(1-\alpha)[- \ln(1-\alpha)]^{-2}$
		$[-\ln(1-\alpha)]^4$	$(1/4)(1-\alpha)[- \ln(1-\alpha)]^{-3}$
<i>Deceleratory α-t curve</i>			
R2	Contracting surface	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
R3	Contracting volume	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
D1	1-D Diffusion	α^2	$1/2\alpha$
D2	2-D Diffusion	$(1-\alpha)\ln(1-\alpha)+\alpha$	$-[\ln(1-\alpha)]^{-1}$
D3	3-D Diffusion	$[1-(1-\alpha)^{1/3}]^2$	$1.5[1-(1-\alpha)^{1/3}]^{-1}(1-\alpha)^{2/3}$
D4	Ginstling-Brouns	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$1.5[1-(1-\alpha)^{1/3}]^{-1}$
F1	First order	$-\ln(1-\alpha)$	$1-\alpha$
F2	Second order	$1/(1-\alpha)$	$(1-\alpha)^2$
F3	Third order	$[1/(1-\alpha)]^2$	$0.5(1-\alpha)^3$

it generally takes the Arrhenius equation form

$$k(T) = A \exp(-E/RT) \quad (2)$$

where A is the pre-exponential factor or frequency factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

If eqn. (2) is combined with eqn. (1) and rearranged, then

$$d\alpha/f(\alpha) = A \exp(-E/RT) dT/\beta \quad (3)$$

where β is the linear heating rate (dT/dt). Integration of the right-hand side of eqn. (3) is impossible and many approximations [2–4] to this integration have been made. The one used here is that proposed by Madhusudanan [4], i.e.

$$\ln[G(\alpha)/T^{1.921503}] = \ln(AE/\beta R) + 3.7720501 - 1.921503 \ln E - E/RT \quad (4)$$

where $G(\alpha)$ is the integral form of the reaction function. Various forms of $G(\alpha)$ are shown in Table 1.

Differential method

There are two differential kinetic methods used in this paper and both originate from the combination of eqns. (1) and (2) to give

$$d\alpha/dt = Af(\alpha) \exp(-E/RT) \quad (5)$$

In the first method, termed the single-heating-rate differential (SHRD) method, taking the logarithm form of eqn. (5) gives

$$\ln[(d\alpha/dt)/f(\alpha)] = \ln A - E/RT$$

By feeding the experimental data from a single heating-rate curve, a plot of $\ln[(d\alpha/dt)/f(\alpha)]$ vs. $1/T$ is obtained by testing all the functions $f(\alpha)$ in Table 1. The linear regression is calculated and then the activation energy E and the frequency factor A can be calculated from the slope and intercept of the regression line.

The second method was proposed by Friedman [5] and takes the form

$$\ln(d\alpha/dt)_i = \ln Af(\alpha_i) - E/RT_i$$

where the subscript i refers to the value of the variable at a degree of

conversion α_i , from at least two experiments under different heating rates. A plot of $\ln(d\alpha/dt)_i$ vs. $1/T_i$ is made by taking the experimental data directly from different heating-rate curves at the same α_i value. In the computer program the α_i values are taken from 0.05 to 0.95 in steps of 0.05. A linear regression is then made for each α_i value and from the slope the activation energy E can be calculated. In this paper, this method is called the Friedman method.

Integral method

From eqn. (4), a plot of $\ln[G(\alpha)/T^{1.921503}]$ vs. $1/T$ can be made from a single experimental heating-rate curve and all the integral forms of the function $G(\alpha)$ in Table 1 can be tested. The activation energy E and the frequency factor A are obtained from the slope and intercept of the linear best-fit line. This is the first integral method used in this study and is called the single-heating-rate integral (SHRI) method.

The second method in this paper is that proposed by Ozawa [6] and takes the form (after approximation as noted below)

$$-\log_{10} \beta_i - 0.4567E/RT_i = \text{constant}$$

where β_i and T_i are the heating rate and the absolute temperature for that heating rate with the same conversion value α_i . Therefore, at least two experiments with different heating rates must be performed. The α_i values in this paper are taken from 0.05 to 0.95 in steps of 0.05. By plotting $\log_{10} \beta_i$ vs. $1/T_i$, the activation energy E can be obtained from the slope of the best fitting line. In this paper, this method is called the Ozawa method.

EXPERIMENTAL

All the methods discussed in the methodology section are used and the flow charts of the programs for the methods have been published [1]. The data files for this paper have been created by using a computer program which can create the data file for the calculation and the file for the peak information at the same time. To study the effect of pre-history in terms of the initial loss of material before thermal decomposition commences (α_0), designated values of α_0 (given values of 0, 0.05, 0.1, 0.15 and 0.2) for a reaction commencing at an initial temperature T_0 (300 K) are used. The activation energy, the frequency factor, the heating rates (5, 10, 20 and $40^\circ\text{C min}^{-1}$), the interval of sampling Δt (0.01 second per point), together with a reaction mechanism, constitute the other information entered into the program. Then eqn. (3) with $T = T_0 + \beta t$ (t is the time of heating) and

$\alpha = \alpha_0 + (d\alpha/dt) \Delta t$ are used to obtain the $d\alpha/dt$, T and α values for the calculation. In order to be consistent with the data transmitted from the Du Pont thermal analyzer 1090 unit, $d\alpha/dt$ is calculated in units of $\% \text{ min}^{-1}$ by multiplying the theoretical $d\alpha/dt$ by $100 \times 60 \times (1 - \alpha)$. The α is also transferred to the weight percentage.

The programs were run on QUICKBASIC software, which provides a much faster speed and is easy to edit. All the reaction cures were generated using the QUATTRO software from the data files created from the program discussed above.

In this paper, the A2 mechanism is studied fully and the R2 mechanism is also studied, in order to be sure that the results are not specific for a certain mechanism.

RESULTS AND DISCUSSION

The kinetic parameters used in the calculation for the A2 and R2 mechanisms are taken as: activation energy, 200 kJ mol^{-1} ; frequency factor, $1 \times 10^{10} \text{ s}^{-1}$.

The influence of the pre-history on the shape of the curves

Figures 1 and 2 show the theoretical patterns of the thermogravimetric (TG) and DTG curves for the A2 and R2 mechanisms respectively at heating rates of 10 and $40^\circ\text{C min}^{-1}$ without any initial pre-weight loss. From previous researches [7–9], the A2 mechanism has a sigmoid shaped curve and the R2 mechanism has a decelerated shaped curve.

When the pre-history of samples is taken into account, the corresponding patterns shown in Figs. 3 and 4 result for the A2 and R2 mechanisms

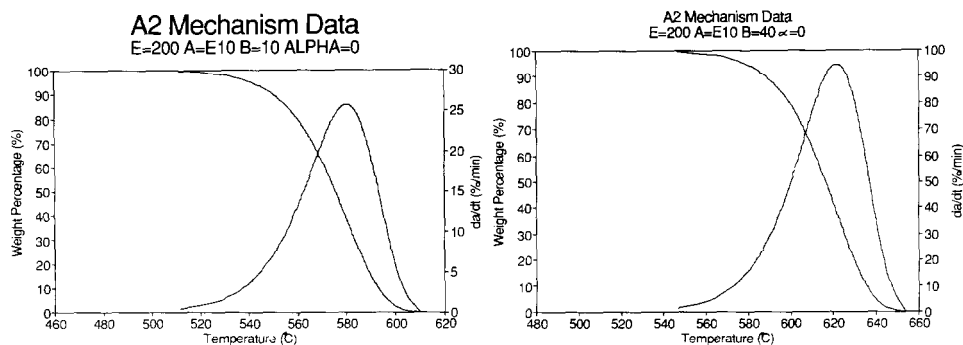


Fig. 1. The theoretical TG and DTG curves for the A2 mechanism without any pre-weight loss at heating rates of 10 and $40^\circ\text{C min}^{-1}$.

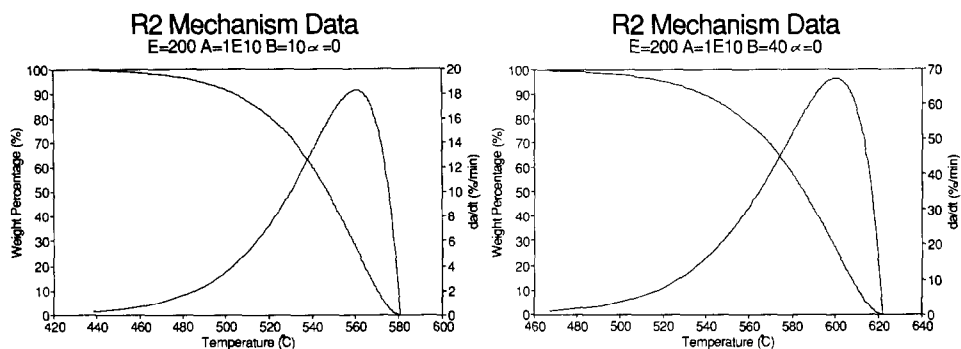


Fig. 2. The theoretical TG and DTG curves for the R2 mechanism without any pre-weight loss at heating rates of 10 and 40°C min⁻¹.

respectively. Although there are differences in the pre-history of the samples, they retain the same shape character, which is sigmoid for the A2 mechanism and decelerated for the R2 mechanism. There are, however, changes in the curves, such as in the peak temperatures, the peak heights, the final temperatures of the reactions and the initial values of $d\alpha/dt$, etc.

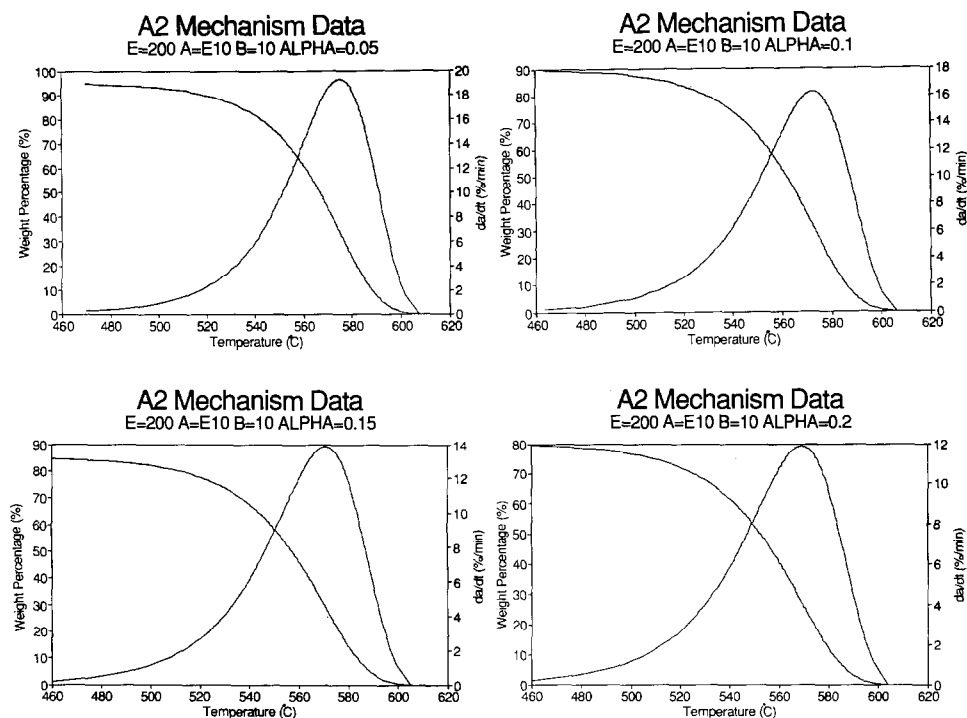


Fig. 3(a). The theoretical TG and DTG curves for the A2 mechanism with pre-history at a heating rate of 10°C min⁻¹: $\alpha_0 = 0.05$, $\alpha_0 = 0.1$, $\alpha_0 = 0.15$ and $\alpha_0 = 0.2$.

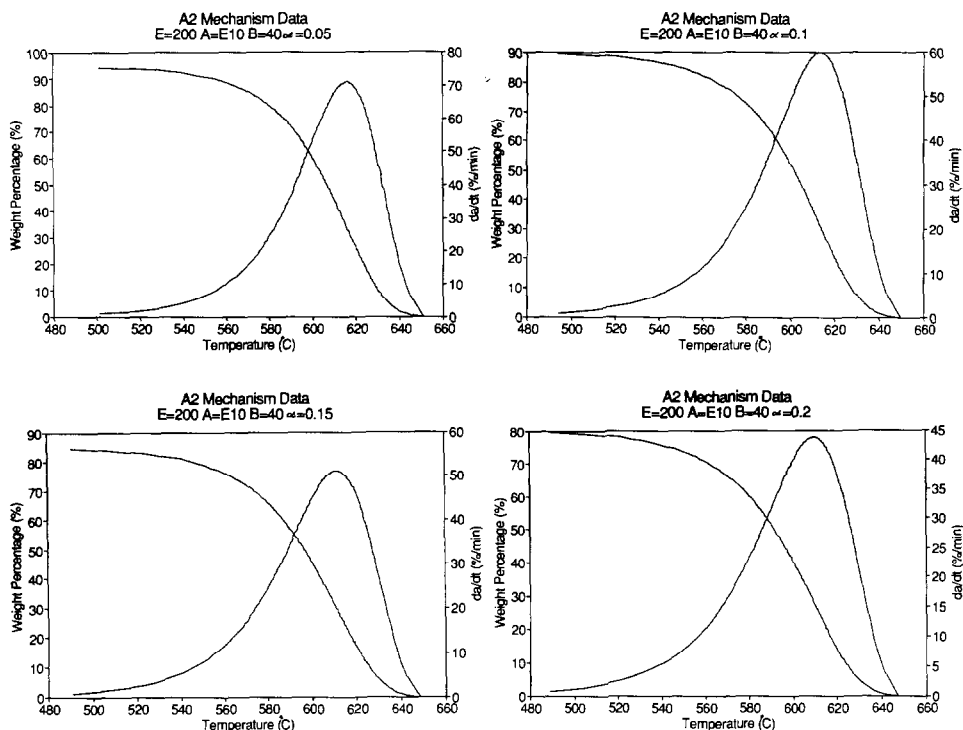


Fig. 3(b). The theoretical TG and DTG curves for the A2 mechanism with pre-history at a heating rate of 40°C min⁻¹: $\alpha_0 = 0.05$, $\alpha_0 = 0.1$, $\alpha_0 = 0.15$ and $\alpha_0 = 0.2$.

In Tables 2 and 3 the peak maxima information for various pre-histories is shown and the data includes the peak maxima temperatures, the value of α at this temperature and the $d\alpha/dt$ values at the peak maxima. From Tables 2 and 3, it can be shown that as the α_0 values (the initial decomposition extent) increase, the peak maxima temperature is shifted to a lower value and that the same is true for the $d\alpha/dt$ values at peak maxima. From the above discussion and from Figs. 3(a), 3(b) and 4, it can be seen that overall the curves are moved to a lower temperature range. It can also be seen that the peak heights are lowered.

Results of the kinetic analysis

In kinetic analysis, the single-heating-rate methods and the multi-heating-rate methods are used. Owing to the difference in the results, they are discussed separately.

Results from the single-heating-rate methods

Tables 4 and 5 show the results from the SHRI and SHRD methods at a heating rate of 10°C min⁻¹ for the A2 and R2 mechanisms respectively.

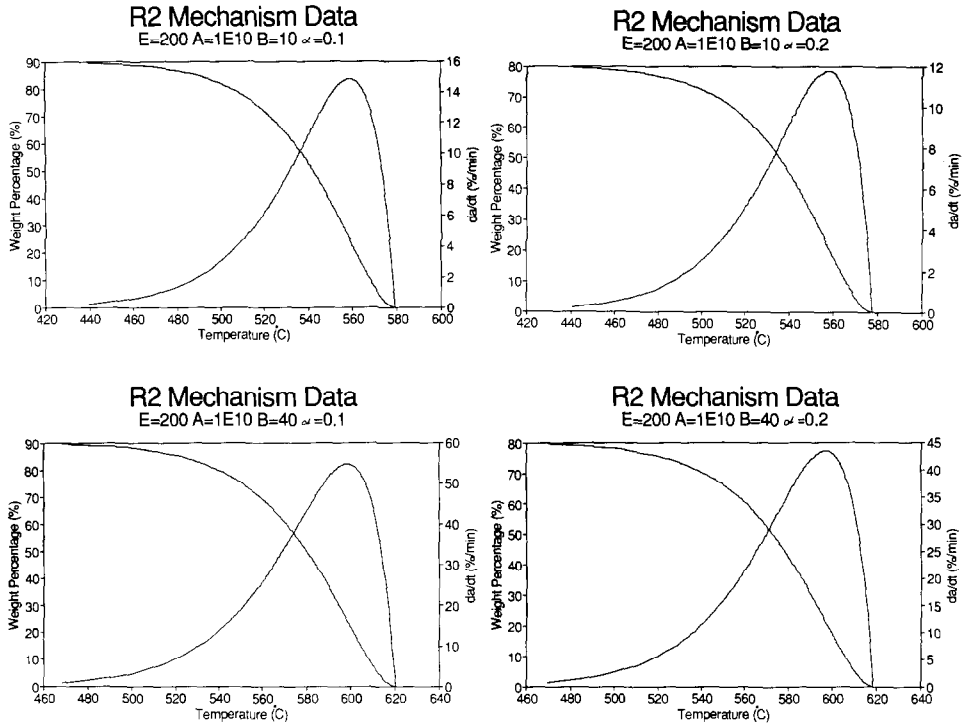


Fig. 4. The theoretical TG and DTG curves for the R2 mechanism with pre-history: $\alpha_0 = 0.1$ at a heating rate of $10^\circ\text{C min}^{-1}$; $\alpha_0 = 0.2$ at a heating rate of $10^\circ\text{C min}^{-1}$; $\alpha_0 = 0.1$ at a heating rate of $40^\circ\text{C min}^{-1}$ and $\alpha_0 = 0.2$ at a heating rate of $40^\circ\text{C min}^{-1}$.

Tables 6 and 7 show the results from the SHRD method at the heating rates of 5, 20 and $40^\circ\text{C min}^{-1}$ for the A2 and R2 mechanisms respectively; R in the tables is the regression factor.

From Table 4, the results show that as α_0 increases, so the calculated activation energy and frequency factor decrease. The standard deviation R also decreases. It can be seen that there are significant deviations in the Arrhenius parameters from theoretical values. This is especially true for the SHRI method. This may be due to the approximation in eqn. (4). The SHRD method has advantages in use over the SHRI method [10, 11]. Further calculations at different heating rates were performed using the SHRD method and the results are given in Tables 6 and 7.

In Table 6, the activation energy values for the same sample at various heating rates show very small differences. This is expected, because the same pre-history of the samples would be expected to have the same effect on the properties of the samples. The problem however is to calculate the correct reaction mechanism and the correct activation energy. Although, by using different heating rates on the samples the correct reaction mechanism can be found, the correct activation energy is very difficult to find from the pre-history. One further problem is to ascertain the reaction

TABLE 2

The peak maxima information for the A2 mechanism^a

β ($^{\circ}\text{C min}^{-1}$)	α_0	Temp. (K) at α_{\max}	α_{\max}	$(d\alpha/dt)_{\max}$ (10^{-3} s^{-1})
5	0	835.2	0.620	2.313
	0.05	830.3	0.649	1.827
	0.1	828.1	0.655	1.625
	0.15	826.3	0.658	1.470
	0.2	824.8	0.659	1.338
10	0	853.4	0.620	4.278
	0.05	848.3	0.666	3.379
	0.1	846.0	0.689	3.007
	0.15	844.2	0.658	2.720
	0.2	842.5	0.659	2.475
20	0	874.0	0.620	8.321
	0.05	868.7	0.648	6.574
	0.1	866.3	0.655	5.852
	0.15	864.3	0.657	5.293
	0.2	862.6	0.659	4.817
40	0	894.7	0.620	15.76
	0.05	889.1	0.648	12.45
	0.1	886.7	0.654	11.09
	0.15	884.6	0.657	10.03
	0.2	882.8	0.659	9.127

^a Theoretical parameters: $E = 200 \text{ kJ mol}^{-1}$ and $A = 1 \times 10^{10} \text{ s}^{-1}$.

TABLE 3

The peak maxima information for the R2 mechanism^a

β ($^{\circ}\text{C min}^{-1}$)	α_0	Temp. (K) at α_{\max}	α_{\max}	$(d\alpha/dt)_{\max}$ (10^{-3} s^{-1})
5	0	816.3	0.734	1.642
	0.1	814.9	0.734	1.483
	0.2	813.4	0.734	1.323
10	0	833.7	0.733	3.040
	0.1	832.3	0.733	2.745
	0.2	830.7	0.734	2.449
20	0	853.4	0.733	5.919
	0.1	851.9	0.733	5.345
	0.2	850.3	0.733	4.769
40	0	873.1	0.733	11.22
	0.1	871.6	0.733	10.13
	0.2	869.9	0.733	9.042

^a Theoretical parameters: $E = 200 \text{ kJ mol}^{-1}$ and $A = 1 \times 10^{10} \text{ s}^{-1}$.

TABLE 4

Results from the SHRD and SHRI methods for the A2 mechanism at a heating rate of $10^{\circ}\text{C min}^{-1}$ ^a

α_0	Method	E (kJ mol ⁻¹)	A (s ⁻¹)	R
0	SHRD	200.03	1.004×10^{10}	1.0000
	SHRI	199.93	9.968×10^9	1.0000
0.05	SHRD	171.52	1.712×10^8	0.9965
	SHRI	140.21	1.878×10^6	0.9954
0.1	SHRD	159.46	2.966×10^7	0.9948
	SHRI	129.23	3.911×10^5	0.9954
0.15	SHRD	151.60	9.262×10^6	0.9941
	SHRI	123.13	1.646×10^5	0.9958
0.2	SHRD	145.76	3.833×10^6	0.9938
	SHRI	119.01	9.219×10^4	0.9963

^a Theoretical parameters: $E = 200$ kJ mol⁻¹ and $A = 1 \times 10^{10}$ s⁻¹.

mechanism and the activation energy from the single-heating-rate data. This will be discussed in a following paper [12].

The above comments refer to the A2 mechanism, but in Table 5, dealing with the R2 mechanism, the results show that changing the α_0 value has no effect on the calculated activation energy value. Although there is a difference between the frequency factor values, the regression factor values are perfect ($R = 1.0000$). This result is also shown in Table 7, for a method employing different heating rates.

This phenomenon may be explained as follows. Whether or not there is a pre-history of the sample, the extent of the reaction α' can be expressed as

$$\alpha' = (\alpha - \alpha_0)/(1 - \alpha_0) \quad (6)$$

where α is the reaction extent of the sample with no pre-weight loss

TABLE 5

Results from the SHRD and SHRI methods for the R2 mechanism at a heating rate of $10^{\circ}\text{C min}^{-1}$ ^a

α_0	Method	E (kJ mol ⁻¹)	A (s ⁻¹)	R
0	SHRD	200.01	1.001×10^{10}	1.0000
	SHRI	199.94	9.985×10^9	1.0000
0.1	SHRD	200.01	9.500×10^9	1.0000
	SHRI	199.94	1.053×10^{10}	1.0000
0.2	SHRD	200.01	8.957×10^9	1.0000
	SHRI	199.94	1.117×10^{10}	1.0000

^a Theoretical parameters: $E = 200$ kJ mol⁻¹ and $A = 1 \times 10^{10}$ s⁻¹.

TABLE 6

Results from the SHRD method for the A2 mechanism^a

β	α_0	E (kJ mol ⁻¹)	A (s ⁻¹)	R
5	0	200.02	1.002×10^{10}	1.0000
	0.05	171.54	1.575×10^8	0.9965
	0.1	159.51	2.635×10^7	0.9948
	0.15	151.66	8.044×10^6	0.9941
	0.2	145.82	3.273×10^6	0.9938
20	0	200.06	1.008×10^{10}	1.0000
	0.05	171.49	1.876×10^8	0.9964
	0.1	159.42	3.373×10^7	0.9948
	0.15	151.55	1.080×10^7	0.9940
	0.2	145.69	4.550×10^6	0.9937
40	0	200.11	1.016×10^{10}	1.0000
	0.05	171.48	2.052×10^8	0.9964
	0.1	159.39	3.823×10^7	0.9948
	0.15	151.50	1.253×10^7	0.9940
	0.2	145.64	5.373×10^6	0.9937

^a Theoretical parameters: $E = 200$ kJ mol⁻¹ and $A = 1 \times 10^{10}$ s⁻¹.

($\alpha_0 = 0$). When the form of the reaction function $f(\alpha)$ is taken into account,

$$f(\alpha) = 2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2} \quad (\text{A2 mechanism}) \quad (7)$$

and

$$f(\alpha) = 2[1 - \alpha]^{1/2} \quad (\text{R2 mechanism}) \quad (8)$$

TABLE 7

Results from the SHRD method for the R2 mechanism^a

β	α_0	E (kJ mol ⁻¹)	A (s ⁻¹)	R
5	0	200.00	1.001×10^{10}	1.0000
	0.1	200.00	9.494×10^9	1.0000
	0.2	200.00	8.951×10^9	1.0000
20	0	200.02	1.003×10^{10}	1.0000
	0.1	200.02	9.512×10^9	1.0000
	0.2	200.02	8.968×10^9	1.0000
40	0	200.03	1.005×10^{10}	1.0000
	0.1	200.03	9.533×10^9	1.0000
	0.2	200.03	8.988×10^9	1.0000

^a Theoretical parameters: $E = 200$ kJ mol⁻¹ and $A = 1 \times 10^{10}$ s⁻¹.

The α' values need to be substituted into $f(\alpha)$ because the new curve is taken as the calculation data. This gives

$$f(\alpha') = 2(1 - \alpha')[-\ln(1 - \alpha')]^{1/2} \quad (\text{A2 mechanism})$$

and

$$f(\alpha') = 2(1 - \alpha')^{1/2} \quad (\text{R2 mechanism})$$

Substituting into eqn. (6), the form of the reaction function is

$$f(\alpha') = 2(1 - \alpha)[-\ln(1 - \alpha) + \ln(1 - \alpha_0)]^{1/2}/(1 - \alpha_0) \quad (9)$$

for the A2 mechanism and

$$f(\alpha') = 2(1 - \alpha)^{1/2}/(1 - \alpha_0)^{1/2} \quad (10)$$

for the R2 mechanism. When the new forms of the reaction functions (eqns. (9) and (10) for the A2 and R2 mechanisms respectively) are compared with the original equations (eqns. (7) and (8)), the result shows that for the R2 mechanism the equations have the same form, except for a constant for certain α_0 values. This is the reason for the differences in the frequency factors but the lack of difference in the activation energies. However, for the A2 mechanism, eqns. (7) and (9) are totally different, which is the reason for the difference in the activation energies and the frequency factors.

To go further with the R2 mechanism, the difference in the frequency factors from the SHRD and SHRI methods comes from eqns. (4) and (5). For the SHRF method (using eqn. (5)), $d\alpha'/dt$ may be converted to $(d\alpha/dt)/(1 - \alpha_0)$. Therefore, the equation

$$d\alpha'/dt = Af(\alpha') \exp(-E/RT)$$

is the same as

$$d\alpha/dt = Af(\alpha)(1 - \alpha_0)^{1/2} \exp(-E/RT)$$

The difference in the frequency factors is therefore due to the factor $(1 - \alpha_0)^{1/2}$. This can also be verified from the results shown in Tables 5 and 7.

For the SHRI method, $G(\alpha')$ is the same as $G(\alpha)(1 - \alpha_0)^{-1/2}$ which arises from the integration of the function $f(\alpha')$. This can also be verified from the results shown in Tables 5 and 7.

From the discussion in this sub-section, the use of the SHRD and SHRI methods to obtain the activation energy can be seen to be affected by the pre-history of the samples only for those reactions which have a reaction function not of the form $(1 - \alpha)^n$ (differential form). For reactions following the function $(1 - \alpha)^n$, only the calculated frequency factors are changed, but not the activation energies.

Results from the multi-heating-rate methods

The results calculated from the Friedman and Ozawa methods for the A2 and R2 mechanisms are listed in Tables 8 and 9 respectively.

From these results it can be seen that there is a very good fit of the results with the theoretical values. This means that there is no difference in or influence on the activation energies if the multi-heating-rate methods are used for the samples with pre-history. This enables a rising-temperature kinetic analysis to be made when a sample's pre-history is not known.

The reason for the above result can be seen from a consideration of eqn. (5). Thus, when the sample has a pre-history, calculations for the data at different heating rates are actually from the same initial condition. This will have the same effect on the data calculated at different heating rates. Therefore, the correct activation energy can still be calculated from the multi-heating-rate methods. Further, this is the reason for the very small differences in the activation energies of samples with the same pre-history at different heating rates in Tables 4, 5, 6 and 7.

Therefore, the use of multi-heating-rate methods can overcome the effect of the pre-history on the samples and can obtain the correct activation energy. There is still however the problem of determining the correct mechanism, which is the intrinsic disadvantage of the multi-heating-rate methods.

TABLE 8

Activation energies^a from the multi-heating-rate methods for the A2 mechanism

Method	α_0				
	0	0.05	0.1	0.15	0.2
Friedman	200.010	200.010	200.010	200.009	200.006
Ozawa	205.141	205.007	204.960	204.916	204.887

^a In kJ mol⁻¹; theoretical value 200 kJ mol⁻¹.

TABLE 9

Activation energies^a from the multi-heating-rate methods for the R2 mechanism

Method	α_0		
	0	0.1	0.2
Friedman	200.008	200.010	200.009
Ozawa	204.672	204.648	204.625

^a In kJ mol⁻¹; theoretical value 200 kJ mol⁻¹.

CONCLUSIONS

The pre-history of samples lowers the peak temperatures and the peak heights of the DTG curves. Further, the TG curves shift to a lower temperature range with the same character for each reaction function.

The use of single-heating-rate methods to obtain the activation energies for samples with pre-history has been discussed. The results show that the correct activation energy can be obtained for the reaction function in the form $(1 - \alpha)^n$ (differential form). Although the frequency factor can be calculated by a factor corresponding to the pre-existing reaction extent, the activation energies and the frequency factors for other reaction mechanisms cannot be obtained directly.

The multi-heating-rate methods are used to obtain the activation energies; the results show that they are one solution to the problem of obtaining the correct activation energy, and are not affected by the pre-history of the samples. The problem, however, is the difficulty of obtaining the correct reaction mechanism.

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