Thermochimica Acta, 221 (1993) 1-12
Elsevier Science Publishers B.V., Amsterdam

The effect of the reaction heat on kinetic analysis by TG under a rising temperature program.
Part 3

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(Received 6 October 1992)

Abstract

In Parts 1 and 2 of this study (Thermochimica Acta 215 (1993) 83 and 97), the effect of the reaction heat changes on the rising temperature program was accounted for by using a relationship between the sample's temperature T and time t as a function of the degree of conversion α. The computer simulation and kinetic analysis in those publications dealt with two extreme situations. In the present study, the more common case is considered, in which the temperature recorded by the thermocouple has a value between those of the sample and the furnace. As before, a simulation of TG, DTG and T–t curves has been made, and a kinetic analysis has been achieved for the calculation of the Arrhenius parameters and the determination of the reaction mechanisms using the integral or differential methods. The results obtained show that either the kinetic parameters or the reaction mechanism changes as a result of the reaction heat. To obtain the correct mechanism and an accurate value of the kinetic parameters, it was found advantageous to use the initial decomposition data, rather than data for the whole decomposition period. The use of the initial decomposition data, however, makes it difficult to distinguish the mechanism but this can be overcome by using both single and multiple heating-rate kinetic analysis.

INTRODUCTION

The expression generally adopted for the rising temperature program is

$$T = T_0 + \beta t \tag{1}$$

where T is the temperature of the furnace at time t, T_0 is the starting temperature, and β is the constant heating rate.

Equation (1) is obeyed only if no reaction heat is evolved or absorbed. In part 1 of this study [1], when considering the reaction heat, a relation between the sample temperature T and the time t was established

$$T = T_0 + \beta t + C \ln(a/(a - \alpha)) \tag{2}$$

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where

$$C = \mu Q / C_p \tag{3}$$

$$a = W_0/(W_0 - W_f) \tag{4}$$

and

$$\alpha = (W_0 - W)/(W_0 - W_f) \tag{5}$$

where C_p is the specific heat of the sample, W is the weight at time t, μ is a fraction factor representing the amount of the reaction heat that is used to heat or cool the sample, Q is the reaction heat (J g^{-1}), W_0 is the sample weight at time = 0, W_f is the sample weight at the end of the reaction, α is the degree of conversion of the sample, a is a constant related to the initial mass and final residue ($a > 1$ always), and C is a constant representing the degree of self heating or self cooling of the sample.

In Parts 1 [1] and 2 [2], two extreme conditions were considered, and the effect of reaction heat on the kinetic analysis was discussed. In this paper, we consider the much more common case where the temperature recorded by the thermocouple lies between those of the sample and the furnace which infers that the thermocouple is neither too far from nor too near to the sample; therefore, the temperature recorded is influenced by the temperatures of both the sample and furnace.

SIMULATION RESULTS AND DISCUSSIONS

In general, solid state decomposition obeys the equations

$$\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha) \tag{6}$$

$$k = A \exp(-E/RT) \tag{7}$$

In a particular case, for a given set of Arrhenius parameters and a stated mechanism, the TG, DTG and T–t curves can be obtained by using a numerical method, solving either a) the case where the endothermic or exothermic character of the reaction affects the sample temperature, applying eqns. (1), (2), (6) and (7), or b) the ideal case where the sample temperature is not affected by the endothermic or exothermic character of the reaction applying eqns. (1), (6) and (7).

As in Part 1, calculation of the α value at each selected time t was made by using the approximation

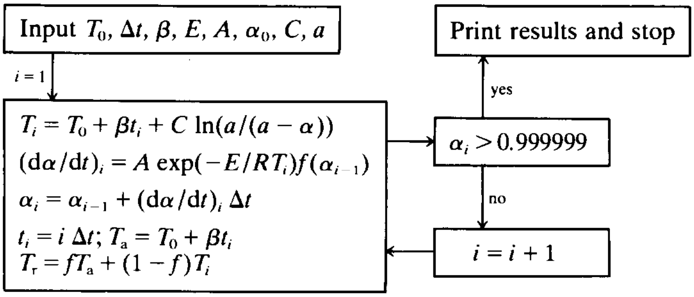
$$\alpha(t + \Delta t) = \alpha(t) + (\mathrm{d}\alpha/\mathrm{d}t)\,\Delta t \tag{8}$$

where Δt is a small time interval compared to the time taken for the reaction to complete. The smaller the Δt, the better the approximation.

If α_0, β, A, Δt, C and a are known, then the set of data t_i, T_a, T_i, α_i, $(d\alpha/dt)_i$ can be calculated for the whole period of reaction, where T_r is the temperature recorded by the thermocouple at time t_i, T_i is the temperature of the sample at time t_i and T_a is the temperature of the furnace. In the case considered here, T_r is a combination of the temperatures of sample and furnace, represented as

$$T_r = fT_a + (1 - f)T_i \tag{9}$$

where f and $1 - f$ represent the magnitudes of the contributions of the furnace temperature and sample temperature respectively ($0 < f < 1$ always). When $f = 0$, this refers to one extreme condition where the temperature recorded is the sample temperature; $f = 1$ refers to the other extreme condition where the temperature recorded is that of the furnace. The value of f is a function of the location of the thermocouple; it increases to approach unity when the thermocouple is far away from the sample, and decreases to approach zero when the thermocouple is very near to the sample.



Scheme 1. The flow chart of the calculation.

The flow chart for the calculation is only slightly different to that given in parts 1 and 2. Tables 1a and 1b show the changes in the characteristics of the TG and DTG curves when $f = 0.5$. In the table, T_i is the initial reaction temperature, defined as the temperature at which the $d\alpha/dt$ is 0.1% of the maximum $d\alpha/dt$, and α is almost zero; t_i is the time required to reach T_i, $(d\alpha/dt)_{max}$ is the maximum reaction rate, and α_{max}, T_{max}, t_{max} are the conversion degree, temperature and time at which $(d\alpha/dt)_{max}$ occurs, respectively. T_f and t_f are the temperature and time at which the reaction is complete, defined as the temperature and time when $\alpha = 0.999999$. From Tables 1a and 1b, it can be seen that the effect of changing C from zero to a more negative value is to decrease $(d\alpha/dt)_{max}$, α_{max} and T_{max}, but to increase

TABLE 1a

Variations in the characteristics of the TG and DTG curves due to the reaction heat ($f = 0.5$)

β/ (°C min^{-1})	C	T_i/K	t_i/s	T_f/K	t_f/s	T_{max}/K	t_{max}/s	α_{max}	$(\mathrm{d}\alpha/\mathrm{d}t)_{max}$/ ($\mathrm{s}^{-1}$)
1	−10	511	3600	568.9	7465	546.2	5912	0.555	7.97E − 4
	0	511	3600	565.8	6945	547.9	5876	0.620	1.03E − 3
5	−10	529	839.8	590.1	1748	566.2	1422	0.560	3.77E − 3
	0	529	839.7	587.0	1644	568.0	1416	0.625	4.79E − 3
10	−10	538	529.1	599.7	931.3	575.1	764.9	0.561	7.37E − 3
	0	544	529.0	569.3	879.5	577.0	762.0	0.625	9.28E − 3
20	−10	544	290.7	609.6	495.4	584.4	410.3	0.560	1.44E − 2
	0	544	290.6	606.5	469.6	586.2	408.5	0.620	1.80E − 2
40	−10	555	157.1	619.9	263.2	593.9	219.5	0.560	2.80E − 2
	0	555	157.2	616.7	250.2	595.8	218.6	0.620	3.49E − 2

Key: T_i is the initial reaction temperature, defined as the temperature at which $\mathrm{d}\alpha/\mathrm{d}t$ is 0.1% of the maximum $\mathrm{d}\alpha/\mathrm{d}t$, and α is almost zero; t_i is the time required to reach T_i; $(\mathrm{d}\alpha/\mathrm{d}t)_{max}$ is the maximum reaction rate; α_{max}, T_{max}, t_{max} are the conversion degree, temperature and time at which $(\mathrm{d}\alpha/\mathrm{d}t)_{max}$ occurs, respectively; T_f and t_f are the temperature and time at which the reaction is complete, defined as the temperature and time when $\alpha > 0.99999$.

TABLE 1b

Variations in the characteristics of the TG and DTG curves due to the reaction heat ($f = 0.5$, $\beta = 10$°C min^{-1})

C	T_i/K	t_i/s	T_f/K	t_f/s	T_{max}/K	t_{max}/s	α_{max}	$(\mathrm{d}\alpha/\mathrm{d}t)_{max}$/($\mathrm{s}^{-1}$)
−20	538	528.8	603.6	987.8	573.6	766.1	0.500	6.06E − 3
−10	538	529.1	599.7	931.3	575.1	764.9	0.561	7.37E − 3
0	538	529.0	596.3	879.5	577.0	762.0	0.625	9.28E − 3
10	538	528.9	594.6	834.3	579.2	756.3	0.690	1.22E − 2
15	538	528.9	594.0	814.8	580.4	752.8	0.720	1.42E − 2
25	538	528.8	594.1	782.1	583.1	744.5	0.771	2.02E − 2

See the footnotes for Table 1a.

the values of t_{max}, t_f and T_f. The more positive the C, the larger the $(\mathrm{d}\alpha/\mathrm{d}t)_{max}$, α_{max} and T_{max}, but the smaller the t_{max} and t_f; T_f is almost constant (all these values for $f = 0.5$). For the same C value but at the different heating rate, the α_{max} values are almost the same.

Thus, the TG, DTG and T–t curves all change their shape because of the effect of the reaction heat.

Tables 2a, 2b and 3 show the probable mechanism and Arrhenius parameters calculated from the simulated T–t curves, TG and DTG curves using the differential [3] and integral [4] methods; the details of the

TABLE 2a

The probable mechanism and kinetic parameters calculated from the differential and integral methods ($f = 0.5$, $C = -10$)

$\beta/(°\mathrm{C\,min^{-1}})$	Mechanism	$E/(\mathrm{kJ\,mol^{-1}})$	$A/(\mathrm{s^{-1}})$	R	S_{xy}	S_b
Integral method						
1	A2	202.7	3.05E + 16	0.9993	3.84E − 2	1354
	A1.5	273.1	2.14E + 23	0.9994	3.44E − 2	1213
	F1	414.1	5.69E + 31	0.9994	5.44E − 2	1919
5	A2	202.7	2.99E + 16	0.9994	3.73E − 2	1318
	A1.5	273.3	1.24E + 23	0.9995	3.24E − 2	1144
	F1	414.4	2.84E + 32	0.9995	5.16E − 2	1820
10	A2	202.8	3.02E + 16	0.9995	3.68E − 2	1302
	A1.5	273.4	1.01E + 23	0.9995	3.14E − 2	1112
	F1	414.7	4.11E + 32	0.9995	5.02E − 2	1773
20	A2	202.8	3.00E + 16	0.9995	3.64E − 2	1287
	A1.5	273.5	8.03E + 22	0.9995	3.07E − 2	1084
	F1	414.9	4.10E + 32	0.9996	4.90E − 2	1733
40	A2	202.7	2.93E + 16	0.9995	3.61E − 2	1276
	A1.5	273.5	6.26E + 22	0.9996	3.00E − 2	1061
Differential method						
1	A2	161.3	2.58E + 12	0.9957	0.2762	9748
	A1.5	231.8	1.83E + 12	0.9977	7.02E − 2	2477
5	A2	163.8	5.96E + 12	0.9963	0.2723	9624
	A1.5	234.4	2.51E + 19	0.9980	6.80E − 2	2403
10	A2	165.1	9.02E + 12	0.9966	0.2728	9650
	F1	377.2	2.96E + 32	0.9991	6.71E − 2	2372
	D3	895.2	4.12E + 52	0.9991	0.1314	4648
20	A2	166.2	1.28E + 13	0.9969	0.2732	9673
	A1.5	237.0	3.47E + 19	0.9983	6.62E − 2	2343
40	A2	167.0	1.69E + 13	0.9970	0.2737	9694
	A1.5	237.8	3.64E + 19	0.9984	6.57E − 2	2327

Key: E is the activation energy; A is the frequency factor; R is the R-squared or regression factor; S_{xy} is the standard error of y estimate; S_b is the standard error of the x coefficient. The testing mechanism is A2, $f(\alpha) = 2(1-\alpha)(-\ln(1-\alpha))^{1/2}$; $E = 200\,\mathrm{kJ\,mol^{-1}}$, $A = 1.6\mathrm{E} + 16\,\mathrm{s^{-1}}$.

determination of the mechanism and the calculation of the Arrhenius parameters can be found in ref. 5.

From the tables, it can be seen that the results obtained by the integral method were slightly improved when $f = 0.5$; this is merely a chance occurrence. Overall, either the mechanism or the kinetic parameters have been changed. From Table 3, it can be seen that when f changes gradually from 0 to 1, the activation energy E changes from 246.0 to 170.7 kJ mol^{-1} using the integral method, and from 200.0 to 139.0 kJ mol^{-1} using the differential method for A2 mechanism, when the heating rate is 10°C min^{-1}

TABLE 2b

The probable mechanism and kinetic parameters calculated from the differential and integral methods ($f = 0.5$, $\beta = 10°\mathrm{C\,min}^{-1}$)

C	Mechanism	$E/(\mathrm{kJ\,mol}^{-1})$	$A/(\mathrm{s}^{-1})$	R	S_{xy}	S_b
Integral method						
−20	A2	199.2	1.40E + 16	0.9969	5.74E − 2	1998
	A1.5	268.6	3.66E + 22	0.9970	6.54E − 2	2276
−10	A2	202.8	3.02E + 16	0.9995	3.68E − 2	1302
	A1.5	273.4	1.01E + 23	0.9995	3.14E − 2	1112
0	A2	200.6	1.78E + 16	1.000	1.98E − 3	283
	A4	90.1	4.12E + 07	1.000	1.01E − 3	120
10	A2	191.8	2.56E + 15	0.9997	3.25E − 2	1087
	A1.5	258.6	3.83E + 21	0.9998	2.46E − 2	824
15	A2	186.1	7.50E + 14	0.9995	3.54E − 2	1154
	A4	88.5	5.68E + 05	0.9995	9.03E − 3	294
25	A2	173.1	4.34E + 13	0.9986	4.48E − 2	1362
	A1.5	233.9	1.73E + 19	0.9986	4.65E − 2	1413
Differential method						
−20	A2	129.6	4.37E + 09	0.9807	0.2657	9261
	D3	850.0	1.71E + 49	0.9999	8.07E − 2	2814
−10	A2	165.1	9.02E + 12	0.9966	0.2728	9650
	F1	377.2	2.96E + 32	0.9991	6.71E − 2	2372
	D3	895.2	4.12E + 52	0.9991	0.1314	4648
0	A2	199.9	1.58E + 16	1.000	2.99E − 2	1043
	A4	95.4	2.70E + 06	1.000	7.68E − 5	2.68
10	A2	233.6	2.16E + 19	0.9984	0.2688	9005
	F1	434.6	6.36E + 36	0.9996	5.55E − 2	1861
15	A2	248.6	5.40E + 20	0.9972	0.2621	8539
	F1	444.0	5.65E + 37	0.9993	6.45E − 2	2107
25	A2	275.1	1.56E + 23	0.9953	0.2510	7636
	F1	457.6	1.70E + 38	0.9990	7.73E − 2	2353

See the footnotes to Table 2a.

and $C = -10$. The reaction mechanism stays in the same group when using the integral method, but shift from A2 to F1, and then to D3, when using the differential method, when f changes in the same way. This means that only a slight difference in the location of the thermocouple leads to different kinetic results.

SOLUTIONS

From the above discussion, it is clear that the effect of the reaction heat can lead to difficulties in identifying the correct mechanism and obtaining accurate values of the kinetic parameters. Kinetic parameter values can be expected to fall in a wide range for the same substance; this explains the

TABLE 3

The probable mechanism and kinetic parameters calculated by the differential and integral methods with different values of f ($\beta = 10°\mathrm{C\,min}^{-1}$, $C = -10$)

f	Mechanism	$E/(\mathrm{kJ\,mol}^{-1})$	$A/(\mathrm{s}^{-1})$	R	S_{xy}	S_b
Integral method						
0	A2	246.7	4.54E + 20	0.9963	7.25E − 2	2439
	A1.5	331.9	3.51E + 28	0.9964	7.10E − 2	3037
0.3	A2	220.3	7.46E + 20	0.9961	5.85E − 2	2515
	A1.5	299.7	8.46E + 25	0.9962	7.32E − 2	3149
0.5	A2	202.8	3.02E + 16	0.9995	3.68E − 2	1302
	A1.5	273.4	1.01E + 23	0.9995	3.14E − 2	1112
	F1	414.7	4.11E + 32	0.9995	5.02E − 2	1773
0.8	A2	182.2	2.78E + 14	0.9966	5.55E − 2	2361
	A1.5	249.8	1.17E + 21	0.9967	6.87E − 2	2923
1.0	A2	170.7	1.70E + 13	0.9972	5.39E − 2	1680
	A1.5	230.6	8.81E + 18	0.9973	6.64E − 2	1877
Differential method						
0	A2	200.6	1.81E + 16	1.000	0.3446	14757
	A1.5	285.9	1.43E + 24	0.9996	6.21E − 2	2657
0.3	A2	181.3	2.61E + 14	0.9987	0.2971	10562
	A1.5	256.1	1.97E + 21	0.9989	6.23E − 2	2685
0.5	A2	165.1	9.02E + 12	0.9966	0.2728	9650
	F1	377.2	2.96E + 32	0.9991	6.17E − 2	2372
	D3	895.2	4.12E + 52	0.9991	0.1314	4648
0.8	A2	151.6	1.81E + 11	0.9942	0.2560	8792
	D3	817.5	9.69E + 47	0.9991	6.17E − 2	2626
1.0	A2	139.5	3.73E + 10	0.9902	0.2434	7320
	D3	756.1	5.97E + 40	0.9994	0.1170	3199

Key: E is the activation energy; A is the frequency factor; R is the R-squared or regression factor; S_{xy} is the standard error of the y estimate; S_b is the standard error of the x coefficient. The testing mechanism is A2, $f(\alpha) = 2(1-\alpha)(-\ln(1-\alpha))^{1/2}$; $E = 200\ \mathrm{kJ\,mol}^{-1}$, $A = 1.6\mathrm{E} + 16\ \mathrm{s}^{-1}$.

different values reported in the literature. Likewise, different results can be obtained under different experimental conditions, leading to discrepancies in the mechanism. In fact, this occurs for many solid materials.

Therefore, these kinetic results can be attributed to the non-linear relationship between the sample temperature and the time. It is found that the sample temperature and time maintain the linear relationship very well during the initial decomposition period of the material. Therefore, it seems that using the initial decomposition data to perform the kinetic analysis might provide a solution.

Recall eqn. (2)

$$T = T_0 + \beta t + C \ln(a/(a - \alpha))$$

In commercially available TG instrumentation, the error in measuring the temperature is 1 *C*. Therefore it is reasonable to assume that the sample temperature has a linear relationship with time when the temperature difference between the sample and furnace is smaller than 1 *C*. Based on this assumption, the linear range of the *T–t* curve can be determined. From

$$C \ln(a/(a-\alpha)) < 1 \tag{10}$$

and rearranging

$$\alpha < a[1 - \exp(-1/C)] \tag{11}$$

The α range used in the kinetic analysis can be estimated using eqn. (11). For example, suppose one has a substance, of which $Q = 1000\ \mathrm{J\,g^{-1}}$, $C_p = 0.2\ \mathrm{J\,g^{-1}\,{}^\circ C^{-1}}$, $\mu = 0.001$ (μ can be estimated from the nature of the gas evolved and the value of the atmospheric gas flow) and $a = W_0/(W_0 - W_f) = 2.5$, which can be calculated directly from the TG curve. Then

$$C = \mu Q/C_p = (0.01 \times 1000\ \mathrm{J\,g^{-1}})/(0.2\ \mathrm{J\,g^{-1}\,{}^\circ C^{-1}}) = 50^\circ\mathrm{C}$$

and

$$\alpha < a[1 - \exp(-1/C)] = 2.5(1 - \exp(-1/50)) = 0.05$$

Therefore, for this substance, the useful information can be obtained by performing the kinetic analysis at $\alpha < 0.05$. Table 4 shows the ranges of useful α values with varying the *C* and *a* values. It can be seen from Table 4 that when *C* is small and *a* is large enough, the whole α range can be used to perform the kinetic analysis. However, when *C* is large, or *a* is small, the useful α range is small.

In our case, with $a = 1.5$ and $C = 25$, 15, 10, −10, −20, the useful α ranges is below approximately 0.07. We performed the kinetic analysis using the information obtained in the range $0.005 < \alpha < 0.065$; identical

TABLE 4

The α range [a] of the TG and DTG curves with varying *C* and *a* values

a	*C*						
	1.0	5.0	10.0	15.0	20.0	30.0	40.0
1.0	0.632	0.181	0.105	0.064	0.049	0.033	0.025
2.0	1.0	0.362	0.211	0.129	0.098	0.066	0.049
3.0	1.0	0.543	0.315	0.193	0.147	0.098	0.074
4.0	1.0	0.724	0.420	0.258	0.196	0.131	0.099
5.0	1.0	0.905	0.525	0.322	0.245	0.164	0.124

[a] α ranges from zero to the values indicated.

TABLE 5

The probable mechanism and kinetic parameters calculated by the differential and integral methods ($0.005 < \alpha < 0.065$, $C = -10$, $\beta = 20°\mathrm{C\,min^{-1}}$)

Mechanism	$E/(\mathrm{kJ\,mol^{-1}})$	$A/(\mathrm{s^{-1}})$	R	S_{xy}	S_b
Integral method					
A4	97.1	5.56E + 06	1.0000	1.04E − 3	131
A3	132.4	1.06E + 10	1.0000	7.03E − 3	884
A2	203.1	3.18E + 16	1.0000	2.86E − 2	3596
A1.5	273.8	8.52E + 22	1.0000	3.62E − 2	4548
P3	200.5	1.79E + 16	1.0000	1.79E − 2	2250
R2	412.5	4.12E + 32	1.0000	4.06E − 2	5111
R3	413.4	4.12E + 32	1.0000	4.31E − 3	5421
F1	415.1	4.10E + 32	1.0000	4.45E − 2	5593
D1	828.8	2.05E + 32	1.0000	4.51E − 2	5665
D2	832.4	2.04E + 32	1.0000	4.54E − 2	5720
D3	835.7	2.04E + 32	1.0000	4.62E − 2	5810
D4	832.3	2.04E + 32	1.0000	4.60E − 2	5779
Differential method					
A4	93.8	3.89E + 06	1.0000	1.11E − 3	135
A3	129.2	6.62E + 09	1.0000	6.97E − 3	853
A2	200.0	1.61E + 16	1.0000	1.84E − 2	2255
A1.5	270.8	3.49E + 22	1.0000	2.83E − 2	3463
R2	407.0	2.18E + 34	1.0000	3.51E − 2	4290
R3	408.8	2.13E + 34	1.0000	3.91E − 2	4775
F1	412.4	1.38E + 35	1.0000	4.12E − 2	5044
D1	821.0	1.74E + 38	1.0000	4.24E − 2	5187
D2	826.4	1.70E + 38	1.0000	4.30E − 2	5250
D3	840.8	1.71E + 38	1.0000	4.43E − 2	5408
D4	828.3	1.71E + 38	1.0000	4.32E − 2	5284

Key: E is the activation energy; A is the frequency factor; R is the R-squared or regression factor; S_{xy} is the standard error of the y estimate; S_b is the standard error of the x coefficient. The testing mechanism is A2, $f(\alpha) = 2(1-\alpha)(-\ln(1-\alpha))^{1/2}$; $E = 200\,\mathrm{kJ\,mol^{-1}}$, $A = 1.6\mathrm{E} + 16\,\mathrm{s^{-1}}$.

R, S_{xy} and S_b values were obtained for all the mechanisms. This is because all the reaction mechanisms can be reduced to a zero-order reaction mechanism when α is small enough. Table 5 shows the regression results obtained by both the integral and differential methods. It is impossible to distinguish between these mechanisms, and it is also impossible to select the right values of the kinetic parameters. Therefore there seems no way to obtain the correct mechanism and correct values of the kinetic parameters from only a single TG and DTG curve when only a small portion of initial decomposition information is used. The Ozawa [6] and Friedman methods [7] are based on multi-heating-rate TG and DTG curves, and the calculation of the activation energy E is independent of the reaction mech-

TABLE 6

Kinetic parameters calculated for the A2 mechanism by the differential and integral methods ($f = 0$, $0.005 < \alpha < 0.065$)

Heating rate/(°C min^{-1})	C	E/(kJ mol^{-1})	A/(s^{-1})	R	S_{xy}	S_b
Integral method						
10	−20	207.0	7.78E + 16	0.9999	3.18E − 2	4065
	−10	203.2	3.18E + 16	1.0000	2.85E − 2	3596
	0	200.0	1.61E + 16	1.0000	5.53E − 3	871
	10	195.9	6.38E + 15	1.0000	2.84E − 2	3457
	15	194.1	4.29E + 15	1.0000	3.02E − 2	3636
	25	190.7	1.97E + 15	0.9999	3.27E − 2	3876
1	−10	203.5	3.23E + 16	1.0000	2.75E − 2	3483
5		202.9	2.98E + 16	1.0000	3.35E − 2	3467
10		203.2	3.18E + 16	1.0000	2.85E − 2	3596
20		203.3	3.21E + 16	1.0000	2.95E − 2	3487
40		203.1	3.01E + 16	1.0000	2.80E − 2	3469
Differential method						
10	−20	200.1	1.62E + 16	1.0000	2.36E − 2	2932
	−10	200.0	1.61E + 16	1.0000	1.85E − 2	2269
	0	200.0	1.60E + 16	1.0000	5.23E − 3	798
	10	200.1	1.61E + 16	1.0000	2.06E − 2	2531
	15	200.0	1.61E + 16	1.0000	1.92E − 2	2241
	25	200.0	1.61e + 16	1.0000	2.29E − 2	2630
1	−10	200.0	1.61E + 16	1.0000	1.17E − 2	1067
5		200.0	1.61E + 16	1.0000	1.81E − 2	1656
10		200.0	1.61E + 16	1.0000	1.85E − 2	2269
20		200.0	1.60E + 16	1.0000	1.91E − 2	2262
40		200.0	1.61E + 16	1.0000	1.84E − 2	2255

anism. Therefore, the Ozawa and Friedman methods were first used to calculate the value of E; then another kinetic analysis was performed on each single-heating-rate TG and DTG curve. The specific mechanism whose E value as obtained from the single heating-rate curve was closest to the value of E obtained by the Ozawa and Friedman methods, was considered as a correct reaction mechanism. Tables 6–8 show the E and A values for the A2 mechanism obtained from a single TG and DTG curve using the integral and differential methods. It can be seen the calculated values of E are all around 200 kJ mol^{-1} for the cases $f = 0$, 1.0 and 0.5. From Table 5, it can be seen that the E values for all other mechanisms are either significantly smaller or larger than 200 kJ mol^{-1}. Table 9 shows the values of E calculated by the Ozawa and Friedman methods for the cases $f = 0$, 1.0 and 0.5, when $a = 1.5$ and $C = -10$, and the heating rates are 1, 5, 10, 20, 40°C min^{-1} respectively. The values of E in Table 9 are also around 200 kJ mol^{-1}. As a result, the A2 mechanism was chosen as the correct

TABLE 7

Kinetic parameters calculated for the A2 mechanism by the differential and integral methods ($f = 1.00$, $0.005 < \alpha < 0.065$)

Heating rate/(°C min^{-1})	C	E/(kJ mol^{-1})	A/(s^{-1})	R	S_{xy}	S_b
Integral method						
10	−20	194.0	4.31E + 15	1.0000	3.09E − 2	4124
	−10	197.2	8.51E + 15	1.0000	2.79E − 2	3587
	0	200.0	1.61E + 16	1.0000	5.53E − 3	871
	10	202.9	2.95E + 16	1.0000	2.78E − 2	3398
	15	204.1	5.25E + 16	1.0000	3.11E − 2	3576
	25	206.7	7.97E + 15	0.9999	3.31E − 2	3901
1	−10	197.3	8.62E + 15	1.0000	2.81E − 2	3483
5		197.1	8.45E + 15	1.0000	3.21E − 2	3467
10		197.2	8.51E + 15	1.0000	2.76E − 2	3592
20		197.3	8.61E + 15	1.0000	2.85E − 2	3480
40		197.2	8.52E + 15	1.0000	2.82E − 2	3467
Differential method						
10	−20	190.1	1.82E + 15	1.0000	2.29E − 2	2891
	−10	193.5	4.15E + 15	1.0000	1.90E − 2	2302
	0	200.0	1.60E + 16	1.0000	5.16E − 3	798
	10	202.1	2.75E + 16	1.0000	2.12E − 2	2430
	15	204.0	5.21E + 16	1.0000	1.81E − 2	2198
	25	207.0	8.05E + 16	1.0000	2.18E − 2	2641
1	−10	193.7	4.36E + 15	1.0000	1.17E − 2	1067
5		193.6	4.28E + 15	1.0000	1.81E − 2	1656
10		193.5	4.15E + 15	1.0000	1.90E − 2	2302
20		193.5	4.14E + 16	1.0000	1.91E − 2	2262
40		193.4	4.09E + 16	1.0000	1.84E − 2	2255

reaction mechanism, with $E = 193$–$207\ \mathrm{kJ\ mol^{-1}}$ and $A = 4.29\mathrm{E} + 15$–$7.38\mathrm{E} + 16$. The actual mechanism is A2, with $E = 200\ \mathrm{kJ\ mol^{-1}}$ and $A = 1.61\mathrm{E} + 16$, which we consider to be the correct interpretation of the kinetic data.

CONCLUSIONS

(1) The reaction heat has a significant effect on the T–t, TG and DTG curves. The Arrhenius parameters calculated and the reaction mechanisms identified by both the differential and integral methods are all different from the ideal case.

(2) A new approach has been developed to obtain the correct mechanism and kinetic parameters. This approach includes the estimation of the useful α range for performing the kinetic analysis, and the application of both single- and multi-heating-rate methods.

TABLE 8

Kinetic parameters calculated for the A2 mechanism by the differential and integral methods ($f = 0.5$, $0.005 < \alpha < 0.065$)

Heating rate/(°C min^{-1})	C	E/(kJ mol^{-1})	A/(s^{-1})	R	S_{xy}	S_b
10	−20	200.1	1.61E + 16	1.0000	3.18E − 2	4065
	−10	200.2	1.63E + 16	1.0000	2.85E − 2	3596
	0	200.0	1.61E + 16	1.0000	5.53E − 3	871
	10	199.5	1.52E + 16	1.0000	2.84E − 2	3457
	15	198.4	1.28E + 16	1.0000	3.02E − 2	3636
	25	197.7	1.02E + 16	0.9999	3.27E − 2	3876
1	−10	200.1	1.61E + 16	1.0000	2.75E − 2	3483
5		200.2	1.61E + 16	1.0000	3.35E − 2	3467
10		300.1	1.61E + 16	1.0000	2.85E − 2	3596
20		200.1	1.61E + 16	1.0000	2.95E − 2	3487
40		200.0	1.61E + 16	1.0000	2.80E − 2	3469
Differential method						
10	−20	195.1	9.02E + 15	1.0000	2.36E − 2	2932
	−10	197.9	1.12E + 15	1.0000	1.85E − 2	2269
	0	200.0	1.60E + 16	1.0000	5.23E − 3	798
	10	201.8	2.61E + 16	1.0000	2.06E − 2	2531
	15	203.1	4.52E + 16	1.0000	1.92E − 2	2241
	25	204.5	5.01E + 16	1.0000	2.29E − 2	2630
1	−10	197.4	9.97E + 15	1.0000	1.17E − 2	1067
5		197.5	1.01E + 16	1.0000	1.81E − 2	1656
10		197.9	1.12E + 16	1.0000	1.85E − 2	2269
20		197.9	1.13E + 16	1.0000	1.91E − 2	2262
40		198.0	1.13E + 16	1.0000	1.84E − 2	2255

TABLE 9

The activation energy E/(kJ mol^{-1}) obtained from the Ozawa and Friedman methods ($0.005 < \alpha < 0.065$, $C = -10$, $a = 1.5$)

Ozawa				Friedman			
f	α			f	α		
	0.02	0.04	0.06		0.02	0.04	0.06
0	203.5	203.8	204.2	0	200.6	200.5	200.6
1.0	197.2	196.9	196.5	1.0	198.2	198.1	197.8
0.5	199.3	199.0	199.2	0.5	199.5	199.4	199.0

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