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A description of kinetics of thermal decomposition of calcium oxalate monohydrate by means of the accommodated R*n* model

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Abstract

The choice of possible kinetic models for a solid state reaction should involve multi-parameters to reduce down specious models which are suggested by using single parameters. For this purpose, in the present work the activation energy estimated from the isoconversional plot was used to check models proposed by the degree of conversion at the maximum reaction rate for the thermal decomposition of calcium oxalate monohydrate. It was found that the basic D2 and D4 models are not a likely description of the kinetics of a three step decomposition. The R*n* model was also applied. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Kinetic model; Thermal decomposition; Solid state reactions; Calcium oxalate monohydrate

1. Introduction

A mechanistic interpretation is always required for understanding the process of solid state reactions. However, it suffers from an incomplete list of kinetic models [1]. Moreover, the current basic models are all over-simplified corresponding to certain physical limitation. Therefore, more advanced models have been derived to describe further aspects of actual reactions. On the other hand, even for the basic models, a complete procedure has not yet been established to distinguish their characteristics. Dollimore et al. have carried out important work in this respect [2–4]. They presented a useful scheme to classify the basic models by using the degree of conversion α_{max} at the maximum reaction rate. But, the scheme is somewhat rough, exact limits of α_{max} have not been given for definite models. For these reasons, the identification of probable models for an interested reaction is difficult and thus ambiguous. For example, kinetics of thermal decomposition of calcium oxalate monohydrate has not been described clearly so far. Elder proposed a D4 model both for the loss of water and for the loss of carbon dioxide, and R3 model for the loss of carbon monoxide [5,6]. Dollimore et al. also stated that the D4 model is favored over the R2 model for the thermal decomposition of calcium carbonate [3]. Recently, Anderson et al. summarized the results of the thermal decomposition of calcium oxalate monohydrate measured in 13 European laboratories using the *n*th-order model [7]. The use of various different models by different authors implies the absence of well-accepted procedure for deducing reaction mechanism.

Comparatively, the isoconversional method such as Flynn–Wall–Ozawa plot has been widely accepted and used to estimate activation energy irrespective

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of the reaction mechanism [8,9]. The value of activation energy obtained by the isoconversional plot should reasonably be expected to check the proposed model by comparing the similarity of the activation energy estimated by the model [10–12]. Nevertheless, it should be recognized that any identification made using a single parameter is not reliable. So, it is strongly suggested that a multi-parameter procedure should be used to eliminate specious mechanisms suggested by using any single parameter. In the present paper, we used two parameters simultaneously, i.e. the value of activation energy obtained by the isoconversional plot and the $\alpha_{\max}$ limit estimated accurately, and adopted the accommodated R*n* model proposed by Koga and Tanaka [13] to represent the probable kinetics of thermal decomposition of calcium oxalate monohydrate.

2. Theoretical

The differential Arrhenius equation and its integral form gives the apparent rate and degree of conversion of a solid state reaction being carried out at a specific heating rate β.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{e}^{-E/RT} f(\alpha) \tag{1}$$

$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T} \mathrm{e}^{-E/RT}\,\mathrm{d}T = \frac{AE}{\beta R} \frac{\mathrm{e}^{-x}}{x^2} h(x) \tag{2}$$

$$h(x) = \frac{x^4 + 18x^3 + 88x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{3}$$

where α is the degree of conversion, $T_0 = 0$ K, and $x = E/RT$. $f(\alpha)$ and $g(\alpha)$ are listed in Table 1 for the commonly used kinetic schemes. The temperature integral in Eq. (2) is expressed by the fourth Senum and Yang approximation [14] which gives an accurate fit better than $10^{-5}\%$ for $E/RT = 20$. When $h(x) = 1$, Eq. (2) can be rewritten as Eq. (4).

$$\ln\left(\frac{\beta}{T^2}\right) = \left[\ln\left(\frac{AR}{E}\right) - \ln g(\alpha)\right] - \frac{E}{RT} \tag{4}$$

This is an isoconversional plot. It gives an accurate estimate of the activation energy with an error below 0.68% at x greater than 15 [15]. And especially, the plot is model-independent since selection of kinetic models is not necessary in estimating the activation energy. Often, the estimate of activation energy varies with the degree of conversion. In some cases, compensation effect may be observed in the kinetic parameters of $\ln A$ and the E value. But, the mean estimate of activation energy obtained at various different degrees of conversion is always a good parameter characterizing the reaction under study. Usually the variation of the E values would at most be ±10% of the mean value from our observations.

From Eq. (1), Eq. (5) is derived at the maximum reaction rate.

$$-\frac{1}{\mathrm{d}f(\alpha)/\mathrm{d}\alpha} = -\frac{1}{f'(\alpha_{\max})} = \frac{A}{\beta}\frac{RT_{\max}^2}{E} \exp\left(-\frac{E}{RT_{\max}}\right) \tag{5}$$

The subscript "max" denotes the variables at the maximum reaction rate. Then, combining Eq. (2) with Eq. (5) gives

$$g(\alpha_{\max}) \times f'(\alpha_{\max}) = -h\left(\frac{E}{RT_{\max}}\right) \tag{6}$$

Table 1
Basic models of solid state reactions[a]

Model	$f(\alpha)$	$f'(\alpha)$	$g(\alpha)$
A*n*	$n(1-\alpha)[-\ln(1-\alpha)]^{1-(1/n)}$	$(n-1)[-\ln(1-\alpha)]^{-1/n} - n[-\ln(1-\alpha)]^{1-(1/n)}$	$[-\ln(1-\alpha)]^{1/n}$
R*n*	$n(1-\alpha)^{1-(1/n)}$	$(1-n)(1-\alpha)^{-1/n}$	$1-(1-\alpha)^{1/n}$
D2	$-[\ln(1-\alpha)]^{-1}$	$-(1-\alpha)^{-1}[-\ln(1-\alpha)]^{-2}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1/2-(1-\alpha)^{-1/3}][1-(1-\alpha)^{1/3}]^{-2}$	$[1-(1-\alpha)^{1/3}]^2$
D4	$(3/2)(1-\alpha)^{1/3}[1-(1-\alpha)^{1/3}]^{-1}$	$(-1/2)(1-\alpha)^{-2/3}[1-(1-\alpha)^{1/3}]^{-2}$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$
F1	$1-\alpha$	-1	$-\ln(1-\alpha)$
F*n*	$(1-\alpha)^n$	$-n(1-\alpha)^{n-1}$	$[1-(1-\alpha)^{1-n}]/(1-n)$

[a] Where $f'(\alpha) \equiv \mathrm{d}f(\alpha)/\mathrm{d}\alpha$; $g(\alpha) \equiv \int_0^{\alpha}\mathrm{d}\alpha/f(\alpha)$; $n = 2$, 3, and 4 for A*n*; $n = 2$ and 3 for R*n*; $n \neq 1$ or 0 for F*n*.

Table 2
The theoretical limits[a] of $\alpha_{\max}$ of solid state reactions in the basic models

Model	$\alpha_{\max}$	Model	$\alpha_{\max}$	Model	$\alpha_{\max}$	Model	$\alpha_{\max}$
A2	0.612–0.627	R3	0.669–0.696	R2	0.720–0.743	D2	0.783–0.823
A3	0.619–0.629	D3	0.629–0.687	D4	0.715–0.763		
A4	0.622–0.630						

[a] Corresponding to $E/RT_{\max} = 15$ to $E/RT_{\max} = 70$.

Eq. (6) indicates that $\alpha_{\max}$ value depends only on $E/RT_{\max}$ value for a definite kinetic model. This quantitative relation can be applied to estimate the limits of $\alpha_{\max}$ for various kinetic models and then classify them by the magnitude of $\alpha_{\max}$. This is because ordinary reactions have $E/RT = 15$ to $E/RT = 70$, correspondingly $h\ (E/RT) = 0.8910$–0.9729. The limits of $\alpha_{\max}$ thus calculated are listed in Table 2. It is seen that the basic models are classified into four groups.

On the other hand, Eq. (2) can be rewritten as Eq. (7) if the kinetic model of the reaction under study is known. The plot of $\ln g(\alpha)$against $\ln\beta$ at the same temperature for several different heating rates should show a straight line with the constant slope equal to unity as illustrated in Table 3.

$$\ln g(\alpha) = \left[\ln\left(\frac{AE}{R}\right) + \ln\left(\frac{\mathrm{e}^{-x}}{x^2}\right) + \ln h(x)\right] - \ln\beta \tag{7}$$

However, if the $g(\alpha)$ is a wrong model, the isotemperature plot will not show good linearity and/or its slope will not be equal to unity as expressed by Eq. (8).

$$\ln g(\alpha) = \left[\ln\left(\frac{AE}{R}\right) + \ln\left(\frac{\mathrm{e}^{-x}}{x^2}\right) + \ln h(x)\right] - s\ln\beta \tag{8}$$

By dividing both sides of Eq. (8) by the slope, the plot of $\ln[g(\alpha)]^{1/s}$ versus $\ln\beta$ has a slope equal to unity. The function $[g(\alpha)]^{1/s}$ thus becomes a possible model for the reaction at this stage. Whether the $[g(\alpha)]^{1/s}$ is a probable model should be identified by the magnitude of the $\alpha_{\max}$ at the maximum reaction rate. Here, let $m = 1/s$, $G(\alpha) \equiv [g(\alpha)]^m$, and similarly $G(\alpha) \equiv \int_0^\alpha \mathrm{d}\alpha/F(\alpha)$, $F'(\alpha) \equiv \mathrm{d}F(\alpha)/\mathrm{d}\alpha$. We obtain

$$F(\alpha) = \frac{1}{m}[g(\alpha)]^{1-m} f(\alpha) \tag{9}$$

$$G(\alpha_{\max}) \times F'(\alpha_{\max}) = \frac{1-m}{m} + \frac{1}{m} g(\alpha_{\max}) \times f'(\alpha_{\max}) \tag{10}$$

Besides, we still have

$$G(\alpha_{\max}) \times F'(\alpha_{\max}) = -h\left(\frac{E}{RT_{\max}}\right) \tag{11}$$

The theoretical limit of $\alpha_{\max}$ for the accommodated model $F(\alpha)$ can be calculated from Eq. (11) after m is determined from Eq. (8).

Koga and Tanaka have derived the accommodation function $a(\alpha)$ for the Rn model [13]. The n value of the model Rn can have non-integral values. This was supported by microscopic views of the irregularly

Table 3
The isotemperature plots of $\ln g(\alpha)$ vs. $\ln\beta$ at 670 K on the basic models with use of the theoretically designed α–T data of D3 model at $E = 220$ kJ/mol, $A = 1.25 \times 10^{15}$/min[a]

β (K/min)	α	Model	The fitted function from the plot	R^2
1	0.75863	A2	$y = -0.2789x + 0.1625$	0.9993
2	0.60592	A3	$y = -0.1859x + 0.1083$	0.9993
3	0.52157	A4	$y = -0.1394x + 0.0812$	0.9993
5	0.42566	R2	$y = -0.4731x - 0.6643$	0.9998
10	0.31699	R3	$y = -0.5x - 0.9745$	1.0000
15	0.26476	D2	$y = -0.8906x - 0.8308$	0.9991
20	0.23239	D3	$y = -x - 1.9490$	1.0000
		D4	$y = -0.9268x - 2.2069$	0.9996

[a] R^2 is correlation coefficient of linear regression.

shaped reaction interfaces. It has been reported that a sample of $CaCO_3$ was decomposed by a R1.8 model [16], and the dehydration of $MgC_2O_4{\cdot}H_2O$ was done by R1.6 model [17]. Furthermore, they assumed that the rate behavior of interface advancement could be described by the *p*th-order law instead of the preliminary assumption of the constant rate of advancement of the reaction interface in the basic R*n* model.

$$(r_0 - r)^p = kt \tag{12}$$

where r_0 and r are the radii of reactant at $t = 0$ and $t = t$, respectively, and k refers to the apparent rate constant. Taking account of the reaction geometry, they obtained the kinetic model function,

$$h(\alpha) = f(\alpha) \times a(\alpha) = \frac{n(1-\alpha)^{1-(1/n)}}{p[1-(1-\alpha)^{1/n}]^{p-1}} \tag{13}$$

and the accommodation function $a(\alpha)$ is

$$a(\alpha) = \frac{1}{p}[1-(1-\alpha)^{1/n}]^{1-p} \tag{14}$$

Based on the suggestion of Koga and Tanaka, we calculated the limits of $\alpha_{\max}$ for the R*n* model at various non-integral *n* values. The results are listed in Table 4. Furthermore, when we substituted $f(\alpha)$ and $g(\alpha)$ for the R*n* model (as seen in Table 1) into Eq. (9), the same expression as Eq. (13) was obtained. Therefore, we can apply Koga and Tanaka's assumption into Eq. (9) for accommodation of the R*n* model. The p value in Eq. (12) can then be determined from Eq. (8). In another word, the quantity m in Eq. (9) is the quantity p in Eq. (12), and the function $1/m[g(\alpha)]^{1-m}$ of Eq. (9) is the $a(\alpha)$ of Eq. (14) for R*n* model.

Again, taking $h(x) = 1$, Eq. (15) is derived from Eq. (2) for a single heating rate β.

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \left[\ln\left(\frac{AR}{E}\right) - \ln\beta\right] - \frac{E}{RT} \tag{15}$$

If $g(\alpha)$ is the wrong model, similar value of activation energy to that estimated from the isoconversional plot (Eq. (4)) could not be obtained from Eq. (15). After accommodation of the proposed model is then performed, the activation energy can be recalculated from the plot of $\ln[G(\alpha)/T^2]$ versus $1/T$.

Table 4
The theoretic limits[a] of $\alpha_{\max}$ value of solid state reactions on R*n* model at various non-integral *n* values

n	$\alpha_{\max}$	n	$\alpha_{\max}$
1.1	0.920–0.926	2.1	0.712–0.736
1.2	0.869–0.880	2.2	0.705–0.729
1.3	0.833–0.847	2.3	0.699–0.723
1.4	0.806–0.822	2.4	0.693–0.718
1.5	0.785–0.802	2.5	0.688–0.713
1.6	0.767–0.786	2.6	0.684–0.709
1.7	0.752–0.773	2.7	0.680–0.705
1.8	0.740–0.761	2.8	0.676–0.702
1.9	0.730–0.752	2.9	0.672–0.699
2.0	0.720–0.743	3.0	0.669–0.696

[a] Corresponding to $E/RT = 15$ to $E/RT = 70$.

3. Experimental

Thermal decomposition of calcium oxalate monohydrate $CaC_2O_4{\cdot}H_2O$ (of special grade, Kanto Chemicals, Japan) was carried out in a thermogravimetric analyzer (Shimadzu, TGA-60, Japan). The selected heating rates were 2, 4, 6, 8, 10, and 20 K/min. Purge gas was nitrogen gas of high purity, flowing at 50 cm^3/min. The sample cells are platinum pans. Sample weights were around 10 mg. Sampling interval of time for recording sample weight loss was kept at 1 s.

For convenience, we denote the three step decomposition of calcium oxalate monohydrate as step 1 for the loss of water, step 2 for the loss of carbon monoxide, and step 3 for the loss of carbon dioxide as the order of temperature increases.

4. Results and discussion

The experimental $\alpha_{\max}$ values of the decomposition of the calcium oxalate monohydrate were found to be about 79.0, 72.9, and 81.6%, respectively for the step 1, step 2 and step 3. From Table 2, it is therefore deduced that step 1 and 3 both have D2 mechanism, and step 2 have R2 or D4 mechanism. The other models in Table 2 are not possible. Next, whether the deduction is right or not was checked from the value of activation energy.

The isoconversional plot of Eq. (4) was used to calculate activation energies of the three steps of decomposition. The results are given in Table 5. Meanwhile, for comparison the values of activation energy were

Table 5
The values of activation energies (kJ/mol) of thermal decomposition of calcium oxalate monohydrate estimated by the isoconversional plots of $\ln(\beta/T^2)$ vs. $1/T$[a]

α	E_1	E_2	E_3
0.1	70.4	212.1	180.1
0.2	70.2	207.9	178.7
0.3	69.7	203.8	177.7
0.4	69.3	202.0	176.0
0.5	69.2	200.4	175.0
0.6	68.9	199.3	174.0
0.7	68.4	198.3	173.0
0.8	67.3	197.1	171.8
0.9	64.6	195.8	169.9
Ave.	68.7	201.9	175.0

[a] E_1, E_2 and E_3 refer to the step 1, step 2 and step 3 of the thermal decomposition of calcium oxalate monohydrate, respectively. The ave. stands for the mean value of activation energy.

estimated on the proposed models by use of the single heating rate plots of Eq. (15). The results are shown in Table 6. It is obvious, except for the values obtained from the R2 model that the other values in Table 6 are far different from (more than two times) those of Table 5. This indicates that the proposed models of D2 and D4 are not correct.

For step 2, the values of activation energy from the R2 model are similar to those obtained from the isoconversional plots. This suggests that a non-integral Rn model describes the kinetics of step 1 and 3. Based on Table 4, we selected R1.5 for the step 1 and R1.4 for the step 3. The activation energies estimated on the non-integral Rn model are summarized in Table 7. It can be seen that the values of the step 1 and the step 3 are also relatively similar to those in Table 5. So the extended Rn model is a better description of the kinetics of the three step decomposition.

Furthermore, to consider the value of the activation energy of the isoconversional plots further, the accommodation of the Rn model was applied. The results are shown in Table 8. It was found that the values of p were between 0.8–0.9, and not 1.0. p value of unity means that the rate of advancement of the reaction interface is constant as assumed in the basic Rn model,

Table 6
The values of activation energies (kJ/mol) of thermal decomposition of calcium oxalate monohydrate estimated from the single heating rate plots of $\ln[g(\alpha)/T^2]$ vs. $1/T$ and using models D2, R2, D4 and D2[a]

β (K/min)	E_1 on D2	E_2 on R2	E_2 on D4	E_3 on D2
2	178.5	255.3	508.5	432.8
4	165.3	265.6	532.5	442.4
6	152.5	247.9	498.0	435.7
8	164.2	237.1	473.6	424.6
10	164.5	248.8	496.5	420.3
20	158.8	239.5	481.7	413.0

[a] E_1, E_2 and E_3 refer to the step 1, step 2 and step 3 of the thermal decomposition of the calcium oxalate monohydrate, respectively.

Table 7
The values of activation energies (kJ/mol) of thermal decomposition of calcium oxalate monohydrate estimated by the single heating rate plots of $\ln[g(\alpha)/T^2]$ vs. $1/T$ on the extended Rn model[a]

β (K/min)	E_1	E_2	E_3
2	86.6	255.3	206.9
4	79.7	265.6	211.4
6	73.0	247.9	207.9
8	79.2	237.1	202.4
10	79.3	248.8	200.2
20	76.1	239.5	196.3
Ave.	79.0	249.0	204.2

[a] E_1, E_2 and E_3 refer to the step 1, step 2 and step 3 of the thermal decomposition of the calcium oxalate monohydrate, respectively. And $n = 1.5$ for E_1; $n = 2.0$ for E_2; $n = 1.4$ for E_3. The ave. stands for the mean value of activation energy.

Table 8
The values of activation energies (kJ/mol) of thermal decomposition of calcium oxalate monohydrate estimated by the single heating rate plots of $\ln[G(\alpha)/T^2]$ vs. $1/T$ on the accommodated Rn model, i.e. Rn, m model[a]

β (K/min)	E_1	E_2	E_3
2	74.5	204.5	175.8
4	68.5	212.9	179.6
6	62.6	198.5	176.6
8	68.0	189.7	171.8
10	68.1	199.1	169.9
20	65.3	191.5	166.5
Ave.	67.8	199.4	173.4

[a] E_1, E_2 and E_3 refer to the step 1, step 2 and step 3 of the thermal decomposition of the calcium oxalate monohydrate, respectively. And $n = 1.5$, $m = 0.87$ for E_1; $n = 2.0$, $m = 0.81$ for E_2; $n = 1.4$, $m = 0.86$ for E_3. The ave. stands for the mean value of activation energy.

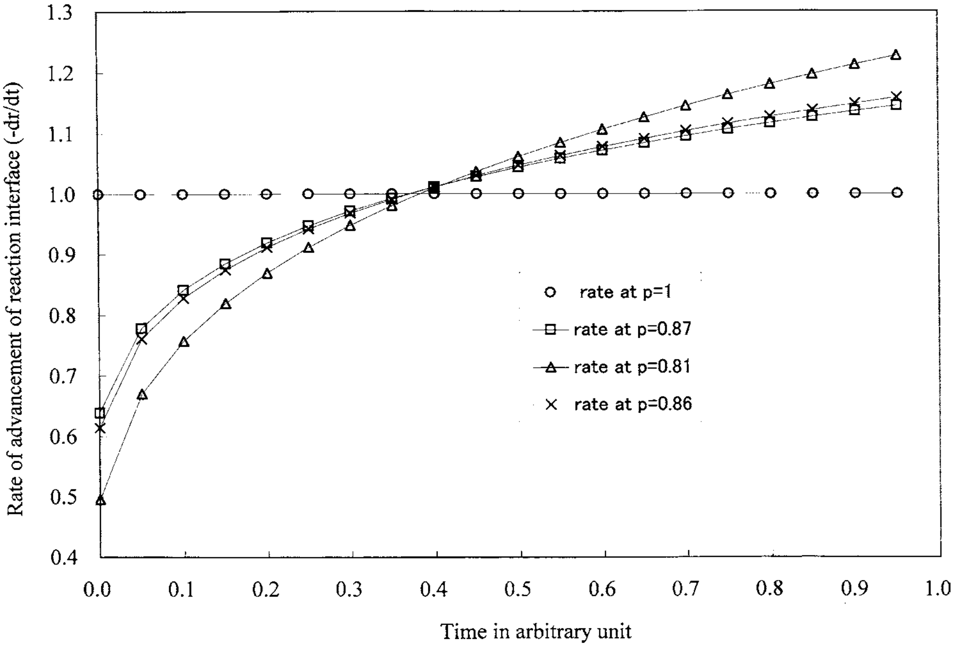

Fig. 1. The calculated rates of advancement of reaction interfaces for the thermal decomposition of calcium oxalate monohydrate based on Eq. (12) supposing $r_0 = 1$, $k = 1$.

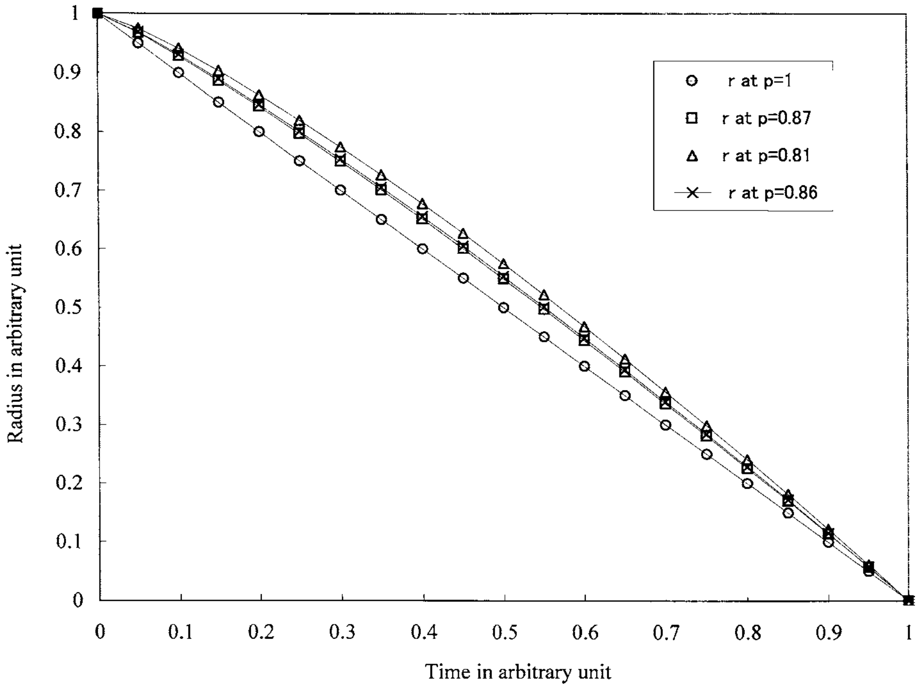

Fig. 2. The decrease of radii of reactants with time in the thermal decomposition of the calcium oxalate monohydrate calculated from Eq. (12) supposing $r_0 = 1$, $k = 1$.

and when the p value deviates from unity, the rate of the advancement is not constant as shown in Fig. 1. The rate increased from an initial low value to a higher value. The smaller the p value, the larger was the increase of rate of advancement of the reaction interface. The decrease in radii at each p value is shown in Fig. 2.

The plot of Eq. (15) on the accommodated Rn model, i.e. Rn, m model, agrees excellently with the isoconversional plot of Eq. (4) for that value of the activation energy (see Tables 5 and 8). The n values for the Rn, m models were determined from the experimental $\alpha_{\max}$ values (see Table 4) and the m values from Eq. (8). However, after the parameter m was determined, the Rn, m models were reinvestigated to establish the corresponding $\alpha_{\max}$ limits for comparison with the experimentally observed $\alpha_{\max}$ values. Table 9 lists the theoretic $\alpha_{\max}$ limits calculated from Eq. (10) for the Rn, m models. It appears that the introduction of the m parameter did not change the limits determined from n values only, and it was concluded that the accommodated Rn model, i.e. Rn, m model, can meet simultaneously the demands for the activation energy and the experimental $\alpha_{\max}$ value.

In addition, if we ignore the difference in activation energy of any proposed model from one of the iso-

Table 9
The theoretical limits[a] of $\alpha_{\max}$ value estimated for the thermal decomposition of calcium oxalate monohydrate on the accommodated Rn model, i.e. Rn, m model

n	m	$\alpha_{\max}$
1.5	1.00	0.785–0.802
1.5	0.90	0.787–0.803
1.5	**0.87**	0.788–0.803
1.5	0.30	0.801–0.806
2.0	1.00	0.720–0.743
2.0	0.90	0.724–0.744
2.0	**0.81**	0.726–0.744
2.0	0.30	0.742–0.748
1.4	1.00	0.806–0.822
1.4	0.90	0.808–0.823
1.4	**0.86**	0.809–0.823
1.4	0.30	0.821–0.825

[a] Corresponding to $E/RT = 15$ to $E/RT = 70$.

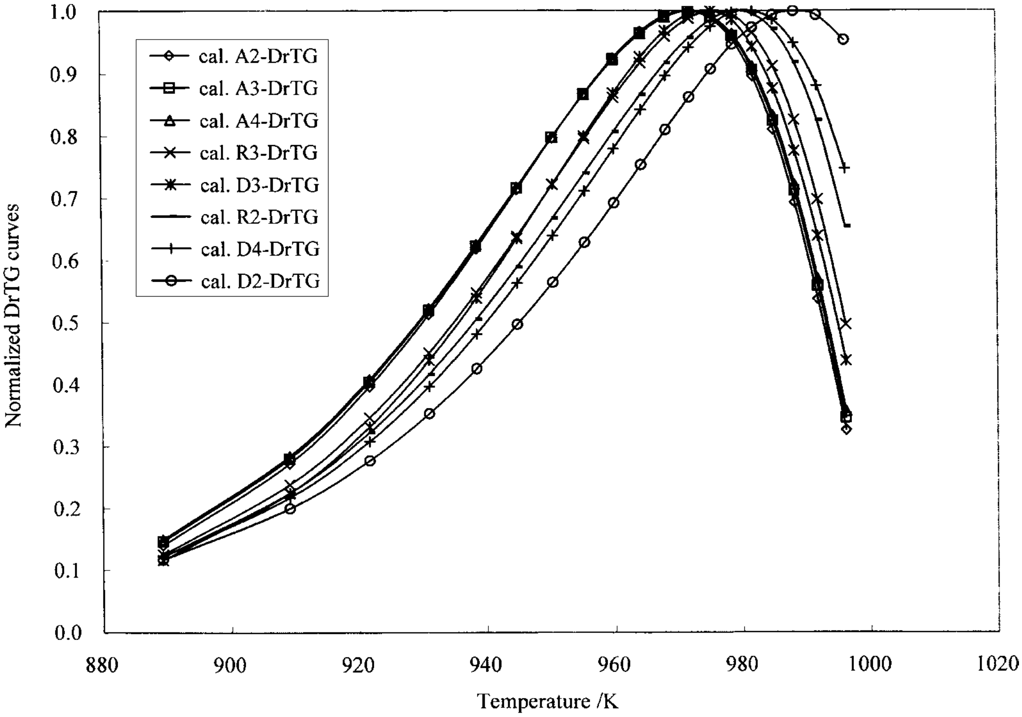

Fig. 3. The calculated differential TG curves for the step 3 of the decomposition of the calcium oxalate monohydrate at $\beta = 8$ K/min on the various kinetic basic models.

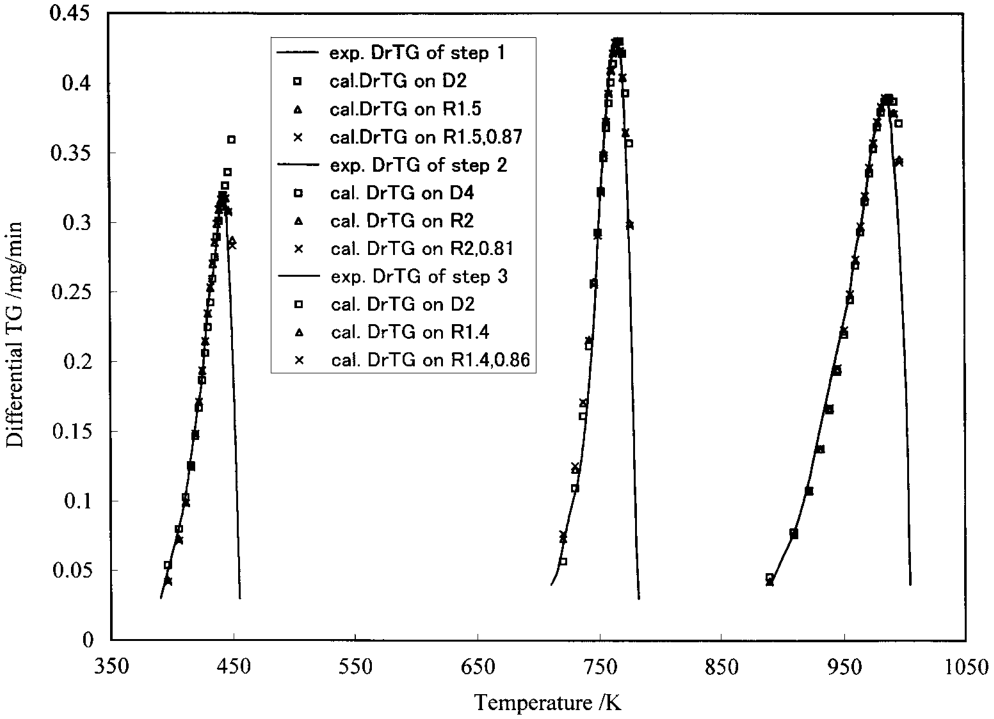

Fig. 4. The comparison of the calculated differential TG curves on the proposed models with the experimental ones recorded at $\beta = 8$ K/min.

conversional plot, the differential TG (Dr TG) curves can be drawn for every proposed model. In calculation, we use the set of the E value and $f(\alpha)$ of each model, in which the E value is estimated from the corresponding $g(\alpha)$ function using Eq. (15). An example is given in Fig. 3. It is evident that the peak positions of those models is distributed in order of the theoretic $\alpha_{\max}$ magnitudes as given in Table 2. Similarly, the calculated Dr TG curves of the three steps of decomposition are drawn in Fig. 4 in comparison with the experimental Dr TG curves. It is seen that the proposed models based on $\alpha_{\max}$ values reproduce the experimental Dr TG curves except for the case of the D2 model for the step 1 of the decomposition.

5. Conclusions

We strongly recommend that the experimental $\alpha_{\max}$ values and the activation energy estimated from the isoconversional plot should be applied simultaneously to determine the kinetic mechanisms for solid state reactions.

Theoretic limits of $\alpha_{\max}$ of various kinetic models are given for simple reactions for which $E/RT = 15$ to $E/RT = 70$.

The kinetics of thermal decomposition of calcium oxalate monohydrate is described by means of the accommodated R*n* model proposed by Koga and Tanaka. Based on the model, the rate of advancement of reaction interface in the thermal decomposition of the calcium oxalate monohydrate is not constant, but increasing monotonously with decomposition progressing at every step of the whole decomposition.

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