On the suitability of controlled transformation rate thermal analysis (CRTA) for kinetic studies.
Part 2. Comparison with conventional TG for the thermolysis of dolomite with different particle sizes

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Abstract

The thermal decomposition of dolomite is studied, both conventionally (isothermal or constant heating rate experiments) and by controlled transformation rate thermal analysis (CRTA) using the "rate-jump" method. A comparative study was carried out in order to determine carefully the effects of particle size on the activation energy of the reaction. The reliability of the kinetic results seems to be much higher with the "rate-jump" method whose results are practically independent of grain size. This is because CRTA allows both a close control of the pressure in the sample surroundings and the use of reaction rates low enough to keep temperature gradients and, therefore, heat or mass transfer problems at a negligible level.

It is shown that the activation energy of the thermal decomposition of dolomite obtained from the CRTA method is largely independent of particle size, always remaining in the neighbourhood of $200 \, \text{kJ} \, \text{mol}^{-1}$.

INTRODUCTION

The conventional "dynamics" techniques of thermal analysis offer attractive ways to determine kinetic parameters. There is obvious convenience and economy in making a single set of measurements in a short time but these advantages are actually counterbalanced by experimental uncertainties leading to apparent activation energies, depending on the experimental conditions.

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It has been shown abundantly in the literature that experimental parameters such as sample mass, particle size and the atmosphere in the close vicinity of the sample strongly affect the values of the kinetic constants (see, for example, refs. 1–3). Also the heating rate often affects the shape of the dynamic curves [4] and, consequently, the apparent activation energy. The existence of these significant effects has led several authors to conclude that there is a real limit to our kinetic understanding and to consistent interpretations of solid-state reactions.

It has been argued, for instance [5], that the existence of mass and heat transfer effects in rising temperature experiments of the solid–gas type precludes any meaningful measurement of the activation energy corresponding to the chemical process. Attempts to derive meaningful kinetic data are generally based on experiments in which very small sample masses and heating rates are used because any unknown gradient in temperature and gas composition (or pressure) is a real limit to the kinetic study.

However, in the isothermal method, one compares the behaviour of two samples corresponding to the same extent of conversion and assumed to be identical, although this is uncertain because they were obtained at different temperatures. Moreover, the temperature differences within the sample must be kept to a negligible level as compared with the temperature difference between the experiments used for the calculation. The above difficulties encountered with the analysis of conventional isothermal or rising temperature experiments are virtually eliminated if the experiments are carried out by CRTA [6] using the "rate-jump" procedure. Here, indeed, the transformation can take place, if needed, at a very low and constant rate. In this way, one indirectly controls any gradient which originates from the rate of reaction itself, so that the reaction can take place simultaneously within the whole sample.

A comparison between dynamic TG methods and the "one-curve" CRTA method was made by Criado et al. [7–9]. A striking conclusion in the context of the influence of sample size is that the results obtained using CRTA were not greatly influenced by sample size and that both methods tend to give the same kinetic results, provided the mass of sample in the TG experiment is decreased to 20 mg (instead of 500 mg for the CRTA experiment). A broader comparison was carried out by Dollimore et al. [10] and showed that the safest and most rewarding way to use CRTA in kinetics is to introduce a "modulation" of the rate of reaction by applying the "rate-jump" method.

In an earlier paper (Part 1) [11], we studied the thermal decomposition of dolomite and showed that the "rate-jump" results are independent of both the sample mass and the nature of the $f(\alpha)$ function, regardless of the range of temperature used. This paper reports the influence of the particle size on this reaction and evaluates the validity or effectiveness of CRTA and of the more conventional approaches.

EXPERIMENTAL

Material

The dolomite sample used was supplied by S.A.E. (Productos Dolomiti-cos, Spain). Its analysis by atomic absorption spectrophotometry gave the following results: MgO, 21.05% (21.70); CaO, 30.20% (30.50); Al_2O_3 and Fe_2O_3, 63%; loss on ignition, 46.44% (47.72). (The figures in parentheses are the theoretical values for dolomite.)

All experiments are carried out under a vacuum of approx. 2×10^{-5} mbar using gravimetric equipment (Mettler thermoanalyser) which can be oper-ated either conventionally or in the CRTA mode by controlling the rate of gas evolution [12]. The dolomite sample was sieved between 30 and 160 μm.

Constant heating rate experiments

The kinetic analysis of the TG curves was carried out using the Ozawa method [13] which combines the advantages of allowing the calculation of the activation energy without any prior knowledge of the reaction mecha-nism and of determining this kinetic parameter point-by-point on the thermoanalytical curve. The following expression was used

$$\log(\beta/\text{K min}^{-1}) = -0.4567 \frac{E}{RT} + C \tag{1}$$

where β is the heating rate and C a constant.

A series of rising temperature experiments at different heating rates, $0.5 \leqslant \beta \leqslant 4$ K min^{-1}, were carried out. For a given value of the reacted fraction, a plot of $\log(\beta/\text{K min}^{-1})$ against $1/T$ allows the activation energy to be derived via eqn. (1). Such calculations were made for different values of the reacted fraction. Heating rates above 4 K min^{-1} were shown to give results which departed significantly from the straight line of the Ozawa plots obtained with a lower heating rate. The heating rates used in these experi-ments are low enough to reduce the influence of temperature gradients and to minimize the effect of heat and/or mass transfer phenomena.

Isothermal experiments

The kinetic analysis of a series of isothermal experiments at temperattures ranging from 750 to 810 K was carried out by means of the general kinetic equation

$$g(\alpha) = kt \tag{2}$$

where k is the rate constant of the reaction. The term describing the

TABLE 1

Algebraic expression of the $g(\alpha)$ function for common mechanisms operating in solid-state reactions

Mechanism	Symbol	$g(\alpha)$
Random nucleation, unimolecular decay law	F1	$-\ln(1-\alpha)$
Phase boundary controlled reaction (two-dimensional contracting cylinder)	R2	$2[1-(1-\alpha)^{1/2}]$
Phase boundary controlled reaction (three-dimensional contracting sphere)	R3	$3[1-(1-\alpha)^{1/3}]$
Two-dimensional growth of nuclei (Avrami–Erofeev equation)	A2	$[-\ln(1-\alpha)]^{1/2}$
Three-dimensional growth of nuclei (Avrami–Erofeev equation)	A3	$[-\ln(1-\alpha)]^{1/3}$
One-dimensional diffusion	D1	α^2
Two-dimensional diffusion	D2	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (Jander equation)	D3	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstling–Brounshtein equation)	D4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

dependence of reaction rates on T is usually assumed to follow an Arrhenius-type equation

$$K = A \exp(-E/RT) \tag{3}$$

where α is the reacted fraction and $g(\alpha)$ a function depending on the kinetic law obeyed by the reaction. Table 1 summarizes the algebraic expression of the $g(\alpha)$ functions for common mechanisms operating in solid-state reactions.

Rate-jump experiments

A series of rate-jump diagrams were recorded between two predetermined reaction rates conveniently chosen with a ratio of 4, i.e. $C_1/C_2 = (d\alpha/dt)_1/(d\alpha/dt)_2 = 4$, and under a controlled residual pressure of 2×10^{-5} mbar. The activation energy in the CRTA experiments was calculated from the equation

$$E = R \frac{T_1 T_2}{T_1 - T_2} \ln \frac{C_1}{C_2} \tag{4}$$

where T_1, T_2, C_1 and C_2 are illustrated in Fig. 1 for a typical rate-jump diagram.
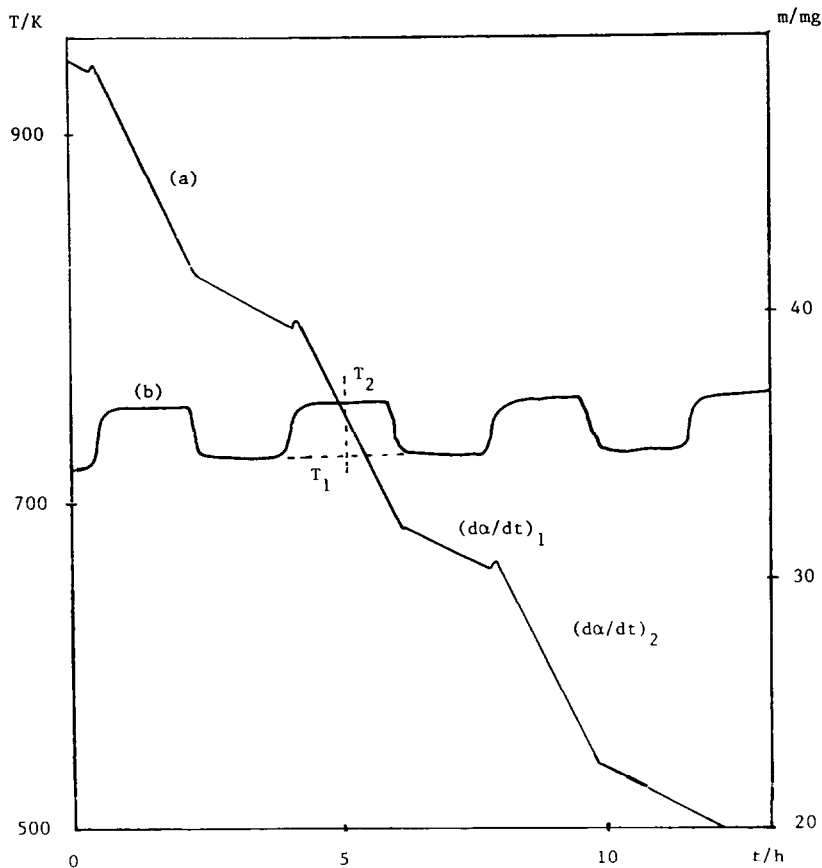
Fig. 1. Typical rate-jump diagram for dolomite thermolysis. Curve (a), m vs. t; curve (b), T vs. t.

RESULTS AND DISCUSSION

Table 2 shows the activation energies calculated from the kinetic analysis of TG data for the thermal decomposition of dolomite using the method of Ozawa and a heating rate ranging from 0.5 to 4 K min^{-1}. The results in

TABLE 2

Activation energies (kJ mol^{-1}) for the thermal decomposition of dolomite as a function of the particle size (μm)

Method	$100 \leqslant d \leqslant 160$	$53 \leqslant d \leqslant 100$	$40 \leqslant d \leqslant 50$	$30 \leqslant d \leqslant 40$	$d \leqslant 30$
Rate-jump	211 ± 20	211 ± 15	201 ± 12	197 ± 12	207 ± 14
Isothermal	140 ± 2	188 ± 6	164 ± 5	279 ± 7	235 ± 16
Dynamic (Ozawa)	91 ± 8	190 ± 7	144 ± 8	270 ± 30	80 ± 5

TABLE 3

Kinetic analysis by Ozawa's method of the thermolysis of the fraction of dolomite sieved between 63 and 160 μm

α	$E/\text{kJ mol}^{-1}$	$(A/g(\alpha))/\text{s}^{-1}$	Regression coefficient
0.100	188	1.9×10^9	0.9953
0.200	185	4.7×10^8	0.9972
0.300	180	1.4×10^8	0.9981
0.400	186	2.4×10^8	0.9961
0.500	188	2.1×10^8	0.9938
0.600	186	1.3×10^8	0.9965
0.700	195	3.6×10^8	0.9975
0.800	198	4.2×10^8	0.9956
0.900	204	6.7×10^8	0.9931

Table 2 reveal considerable scatter in the values of the activation energies, which indicates that the activation energies calculated by Ozawa's (dynamic) method are largely dependent on the particle size in the range 30–160 μm and that they change with the particle size in an apparently random fashion. Although the dependence of the kinetic constant upon experimental conditions is not new, in these experiments it has been carefully determined over a wide range and with smaller heating rates than those previously employed. Table 3 shows, for instance, the results obtained by Ozawa's method for the fraction of dolomite sieved between 63 and 100 μm. We can see that all the results are in good agreement and it is worth pointing out that a good linear regression coefficient is obtained over the whole range of α and that the activation energy does not change in the course of the reaction. Although they are not shown here, for the sake of brevity, similar results were obtained for the other particle sizes.

TABLE 4

Isothermal results derived from eqn. (2) for dolomite sieved between 63 and 160 μm

Mechanism	$E/(\text{kJ mol}^{-1})$	A/s^{-1}	Regression coefficient
F1	188	8.5×10^8	0.9939
R2	188	5.4×10^8	0.9939
R3	188	6.2×10^8	0.9939
A2	188	4.9×10^8	0.9939
A3	188	3.5×10^8	0.9940
D1	188	3.5×10^8	0.9939
D2	188	2.7×10^8	0.9939
D3	187	1.0×10^8	0.9938
D4	187	7.2×10^7	0.9938

The series of isothermal experiments covered a temperature range that was broader than 60°C. The activation energies calculated by means of eqn. (2) from the isothermal curves obtained for dolomite at 755, 764, 791 and 812 K, for different particle sizes, are summarized in Table 2. Table 4 shows, as an example, the results obtained from the kinetic analysis of the isothermal data for the fraction of dolomite ranging from 63 to 100 μm. We can see that a good linear regression coefficient can be obtained over the whole range of temperature investigated (755–812 K). Although they are not shown here, for the sake of brevity, similar results were obtained for the other particle sizes. Moreover the results reported in Table 4 demonstrate that the isothermal data fulfil all the kinetic equations quoted in Table 1. This is in agreement with previous findings [14, 15] which demonstrated that the isothermal kinetic data of solid-state reactions show a good fit to eqn. (2) regardless of the nature of the $g(\alpha)$ function, and that the activation energy obtained from the Arrhenius law is quite independent of the kinetic model assumed.

This result, therefore, explains why the activation energies for the isothermal decomposition of dolomite as calculated by a number of authors for different kinetic models are so consistent with each other [16, 17]. However, Table 2 shows that the activation energies calculated by the isothermal method depend on the particle size, although there is no clear relationship between the variation of this parameter and the measured activation energy, despite the wide range of grain size used (30–160 μm). From Fig. 2, it can
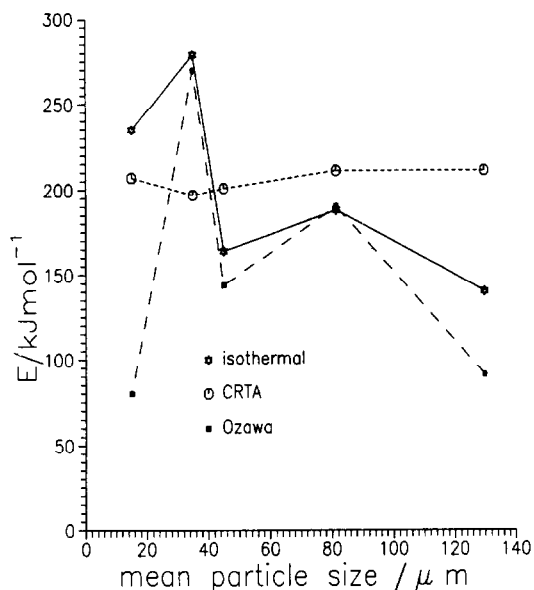

Fig. 2. Activation energies as a function of the particle size for the thermal decomposition of dolomite.

be seen that the activation energy changes in an apparently random fashion; a similar behaviour is clearly evident from the dynamic results. These trends were not observed with CRTA experiments, as Fig. 2 shows. The results obtained by means of the rate-jump method and summarized in Table 2 show that the activation energies have the same values despite the wide range of particle size used. The small differences are within experimental errors.

A comparison of the results obtained from CRTA (rate-jump) and conventional methods included in Table 2 and Fig. 2 leads to the conclusion that the rate-jump results are independent of the particle size, in contrast to conventional techniques (rising temperature or isothermal). Conventional thermoanalytical curves give distorted pictures of the course of the transformation. This results from the heat and mass transport phenomena that primarily reflect the experimental conditions under which the curve was obtained.

CONCLUSIONS

The results obtained in this comparative investigation indicate that constant rate thermal analysis (rate-jump) leads to more reliable kinetic data than the conventional techniques. This is because CRTA allows both a good control of partial pressure in the sample surroundings and the use of reaction rates low enough to limit at will the disturbing effect of heat or mass transfer. We finally conclude that whatever its particle size in the $30–160 \, \mu$m range, the activation energy of dolomite thermolysis remains equal to $200 \pm 10 \, \text{kJ mol}^{-1}$.

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