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On the suitability of controlled transformation rate thermal analysis (CRTA) for kinetic studies. Part 3. Discrimination of the reaction mechanism of dolomite thermolysis

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Abstract

The ability to discriminate the most probable reaction mechanism of a solid-state reaction is analysed and discussed. It is shown that the analysis of a single CRTA experiment (like any other single, conventional, thermal analysis experiment) is not sufficient absolutely to select the reaction mechanism, because several of them (three in the case of dolomite thermolysis) give an excellent fit with the CRTA curve. Fortunately, fully independent information is provided by the CRTA "rate-jump" method, from which a truly model-free activation energy is derived and which still keeps under control (like any CRTA experiment can do) the heat and gas transport processes (which is not the case with conventional TG). Among the three mechanisms selected, only one (with no possible doubt) is consistent with the "rate-jump" activation energy (197.8 kJ mol^{-1}) which clearly shows that the thermolysis of ground dolomite, under vacuum, follows a first-order F_1 mechanism (random nucleation unimolecular decay law).

Keywords: Activation energy; CRTA; Mechanism; Rate jump

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1. Introduction

Determining the mechanism of a solid-state reaction by means of either isothermal or non-isothermal studies is still, quite often, a matter of controversy. The number of papers published for a given reaction, the number of methods available with which to analyse the data and the final discrepancy often arrived at, are all somewhat unsatisfactory.

Among the reasons for this situation includes the fact that a single conventional experiment (either isothermal or with constant heating rate) does not provide enough information to determine the kinetic law. It has indeed been shown [1,2] that any theoretical TG curve calculated with the assumptions of a linear heating programme and of a particular kinetic law necessarily satisfies the other kinetic equations proposed in the literature for the description of solid-state reactions (Table 1). At this stage, the knowledge and comparison of the energies of activation calculated from either isothermal or non-isothermal experiments are helpful [3,4], because they result in the same activation energy only when the correct kinetic model is assumed. This provides, in theory, the kinetic mechanism provided the sample temperature and environment (in the case of a solid–gas reaction) are uniform and well-known, which is unfortunately very rarely the case because of the temperature and pressure gradients produced by the reaction itself. In order to solve these problems, controlled transformation rate thermal analysis (CRTA) [5] is especially useful.

In a previous paper [6], we showed that, for the thermolysis of dolomite, the "rate-jump" method was able to provide meaningful activation energies, independent of the sample mass (contrary to what is observed by conventional TG). Moreover,

Table 1
Algebraic expression of the $f(\alpha)$ function for common mechanisms operating in solid-state reaction

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

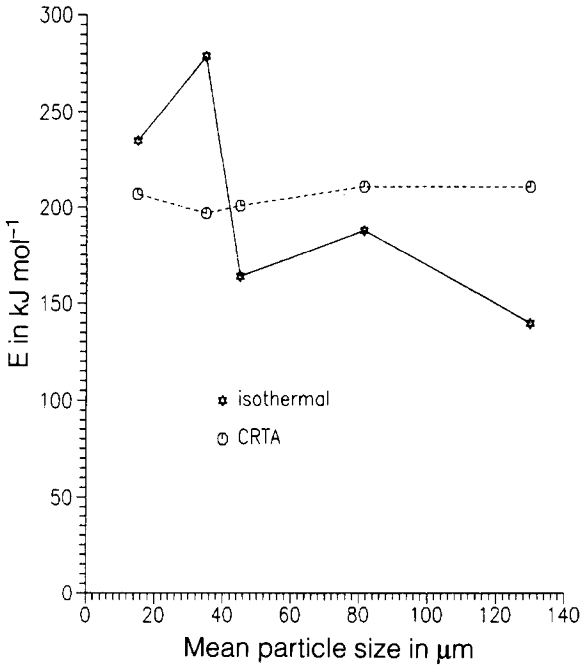

Fig. 1. Activation energies as a function of particle size for the thermal decomposition of dolomite [8].

in this special case of dolomite, it was shown [7] that the activation energy was practically independent of the sample grain size, see Fig. 1.

In the present work we wish to derive the relevant kinetic law from the analysis of a single CRTA curve in the light of the above energies of activation.

2. Experimental

2.1. Material

The dolomite sample used was supplied by S.A.E. (Productos Dolomiticos, Spain). Its analysis by atomic absorption gave the following results: MgO, 21.05% (21.7%): CaO, 30.20% (30.50%); Al_2O_3, Fe_2O_3, 0.63%; loss on ignition, 46.44% (47.72%). (The figures in parentheses are theoretical values for dolomite.)

All experiments were carried out under a vacuum of 2×10^{-5} mbar using gravimetric equipment (Mettler thermoanalyser) which could be operated either conventionally or in the CRTA mode by controlling the rate of gas evolution [8]. The dolomite sample was sieved between 30 and 160 µm in order to provide several fractions with narrow particle size distributions.

2.2. *Constant rate experiments and corresponding kinetic analysis*

The kinetic analysis of CRTA curves was carried out by means of the general kinetic equation

$$\frac{d\alpha}{dt} = Af(\alpha)\exp(-E/RT) \qquad (1)$$

where α is the fraction of sample reacted at time t and $f(\alpha)$ is a function depending on the reaction mechanism.

Because the CRTA experiments were done with a constant decomposition rate, $C = d\alpha/dt$, Eq. (1) becomes, after taking the logarithm

$$\ln\frac{1}{f(\alpha)} = \ln\frac{A}{C} - \frac{E}{RT} \qquad (2)$$

Table 1 summarizes the algebraic expressions of $f(\alpha)$ for common mechanisms operating in solid-state reactions. The plot of the left-hand side of Eq. (2) as a function of the reciprocal of the temperature leads to a straight line whose slope yields the activation energy of the process, provided the proper $f(\alpha)$ function has been selected.

The CRTA "rate-jump" temperature traces 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 same as that used in the simple CRTA experiments). The corresponding activation energy was calculated from the equation

$$E = R\frac{T_1 T_2}{T_1 - T_2}\ln\frac{C_1}{C_2} \qquad (3)$$

where T_1 and T_2 are the two temperatures corresponding to reaction rates C_1 and C_2.

3. Results and discussion

The CRTA curve in Fig. 2 shows the values of the reacted fraction α as a function of the temperature obtained at a constant reaction rate of 6×10^{-6} s^{-1} and at a controlled pressure of 2×10^{-5} mbar with a sample made of a fraction of dolomite sieved between 30 and 40 μm and weighing 50 mg.

The kinetic analysis of the above CRTA curve was carried out by means of Eq. (2) with the assumption of the various kinetic models included in Table 1. The resulting activation energies and corresponding linear regression coefficients are reported in Table 2. As one can see, the activation energies obtained are heavily dependent on the kinetic law assumed for performing the calculation. A first selection of the most appropriate kinetic models can be carried out from the value of the regression coefficient: the three first mechanisms, labelled F1, R2 and R3, are clearly those to be selected. Nevertheless, using a single CRTA trace (like any other

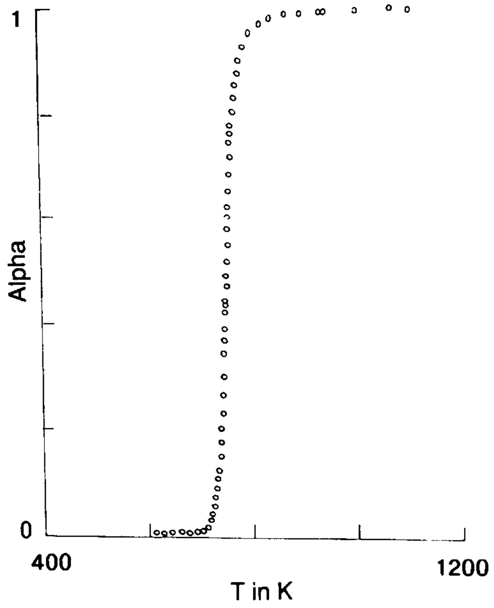

Fig. 2. CRTA curve for the thermolysis of dolomite sieved between 30 and 40 μm.

Table 2
Mean activation energies of the thermal decomposition of dolomite, sieved between 30 and 40 μm, calculated from one CRTA curve (Fig. 2) by assuming various reaction mechanisms

Mechanism	F1	R2	R3	A2	A3	D1	D2	D3	D4
E/kJ mol^{-1}	**197**	98	131	90	55	136	213	314	248
Regression coefficient	0.9942	0.9942	0.9942	0.8655	0.6532	0.8856	0.9492	0.9806	0.9652

single, conventional, thermoanalytical curve) still leaves the choice between several mechanisms. This is why we are looking for independent information provided by a CRTA "rate-jump" experiment. The corresponding diagram is reported in Fig. 3, which shows the reacted fraction as a function of temperature, with a rate-jump ratio of 4 and a sample mass of 100 mg. This trace was analysed by means of Eq. (3), which leads to the results presented in Table 3. It can be seen that the eight independent values obtained for eight selected values of α, ranging from 0.1 to 0.9, are relatively consistent with each other. An average value of the activation energy of 197.8 kJ mol^{-1} can be derived. It should be recalled that the CRTA "rate-jump" method for determining the activation energy of a solid-state reaction does not require any prior knowledge of the reaction mechamism. Moreover, as has been demonstrated [9], it enables the virtual elimination of errors arising from mass and energy transport problems. For these reasons, it makes sense to use this energy of

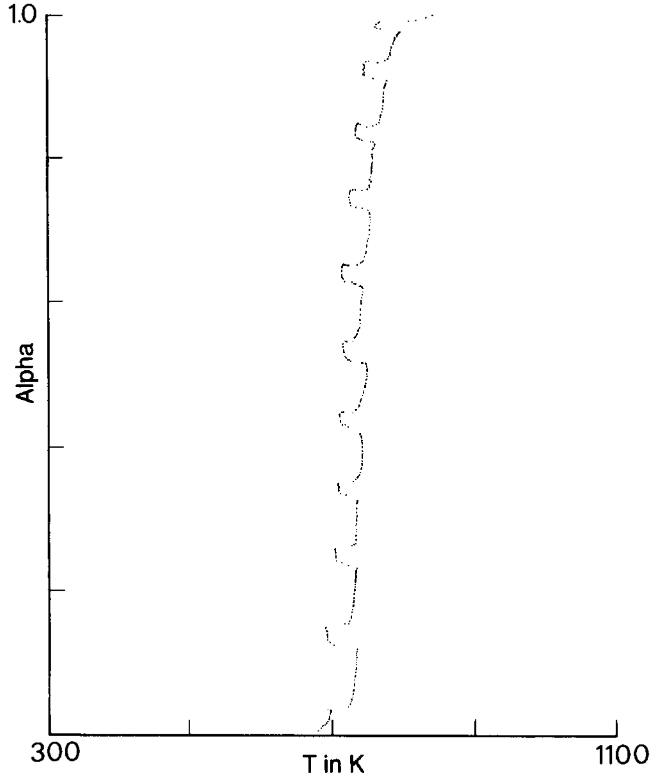

Fig. 3. Rate-jump diagram for the thermal decomposition of dolomite sieved between 30 and 40 μm obtained using a rate jump ratio of 4.

Table 3
Activation energies of the thermal decomposition of dolomite, sieved between 30 and 40 μm, obtained from the rate-jump method (Fig. 3) for various degrees of reaction α

α	0.18	0.28	0.38	0.49	0.60	0.70	0.80	0.89
E/kJ mol^{-1}	184	190	185	202	205	203	204	200
Mean value	**197.8**							

activation as the "discriminating factor". Looking back at Table 2 shows that only mechanism F1 (random nucleation unimolecular decay law) provides an activation energy (calculated from the single CRTA curve of Fig. 2) consistent with that provided by the CRTA "rate-jump" experiment. Let us finally stress that experimental results obtained with other particle sizes ($100 \leq d \leq 160$ μm, $63 \leq d \leq 100$ μm, $40 \leq d \leq 50$ μm, and $d \leq 30$ μm), which we do not report here for the sake of brevity, lead to the same kinetic law.

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