Thermochimica Acta, 163 (1990) 25-32
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

ON THE SUITABILITY OF CONTROLLED TRANSFORMATION RATE THERMAL ANALYSIS (CRTA) FOR KINETIC STUDIES

I/ DETERMINATION OF THE ACTIVATION ENERGY BY THE RATE-JUMP METHOD

A. ORTEGA[1], S. AKHOUAYRI, F. ROUQUEROL[2] and J. ROUQUEROL
Centre de Thermodynamique et de Microcalorimétrie du CNRS, 26 rue du 141° RIA, 13003 Marseille (France)
[1]Departamento de Quimica Inorganica, Universidad de Sevilla, Apdo. 553, 41071 Sevilla (Spain)
[2]Université de Provence, Place Victor Hugo, 13331 Marseille Cedex 3 (France)

ABSTRACT

The rate-jump method is introduced and illustrated in the case of the thermolysis of dolomite Ca $Mg(CO_3)_2$. It is shown that it leads to a value of the apparent energy of activation which is practically independent, all at once, from the function $f(\alpha)$, from the sample size (20 to 200 mg) and from the rate ratio (4 to 20). This may be considered as an interesting step towards the assessment of kinetic parameters characteristic of the reaction proper.

INTRODUCTION

The nature and a number of possibilities of Controlled transformation Rate Thermal Analysis were recently reviewed (ref. 1). Following the recent advice of the Nomenclature Committee of the International Confederation on Thermal Analysis, we are using this name to designate a general thermoanalytical method where a physical or chemical property "X" of a substance is modified following a predetermined programme X = f(time), under the appropriate action of temperature, which is recorded. This approach is in some respect the "opposite" or the "image" of conventional thermal analysis where the predetermined programme is that of temperature whereas the resulting value of X is simply recorded.

Shortly said, Controlled Rate Thermal Analysis (CRTA) usually allows to significantly enhance the resolution of any thermal analysis equipment. This is because one also indirectly controls all the gradients (temperature, pressure) which originate from the rate of reaction itself. In these conditions the reaction may take place simultaneously within the whole sample. The literature data (ref. 2-4) have widely shown that experimental parameters such as the sample size or the ambient atmosphere can affect significantly the calculated values of the kinetic parameters. It may therefore be expected that the CRTA

0040-6031/90/$03.50

method enables to virtually eliminate any errors arising from mass and energy transport problems, since it allows to keep, if wanted, both the rate of decomposition and the pressure of the gaseous products at a low value.

CRTA has been already widely used in order to characterize processes of thermal preparation of solids. It leads to an improved sensitivity and resolution of the thermal analysis curve as it has been reported in several publications (ref. 5-7). On the other hand, papers concerning the use of CRTA in kinetic studies are scarce, although this is possibly the field in which CRTA is most novel and powerful.

Since CRTA may be expected to fulfill the criterion of independence from the sample size, we wanted to check it, together with other features of the method, for the determination of the activation energy of the thermolysis of dolomite. This sample has indeed been widely studied (ref. 8-10) owing to its technological importance because the oxide mixture produced by its decomposition under controlled conditions has been shown to be a promising getter to remove sulfur oxides from gases (ref. 12). The solid products of dolomite decomposition depend on the pressure of CO_2, since in fact two different decomposition reactions occur. In a CO_2 atmosphere (> 50 mbar) dolomite produces $CaCO_3$ following the reaction :

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \qquad (1)$$

but under lower partial pressures of CO_2 dolomite directly decomposes into CaO :

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \qquad (2)$$

In this work the constant rate decomposition is carried out under low pressure so that reaction eqn. (2) takes place and MgO and CaO are produced simultaneously.

It is the purpose of this paper to carefully determine the effects of sample size and reaction rate upon a well defined thermal decomposition, using the rate-jump method, in order to determine the suitability of this approach for kinetic analysis.

THEORETICAL

Any kinetical analysis of the thermoanalytical data must start from the general expression of the reaction rate of the thermal decomposition of a solid :

$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \exp(-E/RT) \qquad (3)$$

where α, the reacted fraction at time t, is defined as $\alpha = \dfrac{m_0 - m}{m_0 - m_\infty}$

m_0 is the initial mass of dolomite

m the instantaneous mass

m_∞ the mass at the end of the reaction

and $f(\alpha)$ a function depending on the mechanism assumed for the transformation. Various relationships, taken from the literature, dealing with reactions controlled by Diffusion (D1, D2, D3, D4), Phase-boundary (R1, R2, R3), Random-Nucleation (F1) and Nucleation and Growth of nuclei are summarized in Table 1. Provided that the CRTA diagrams are obtained at a constant decomposition rate, i.e. $d\alpha/dt = C$, eqn. (3) becomes :

$$\ln \frac{1}{f(\alpha)} = \ln \frac{A}{C} - \frac{E}{R.T} \tag{4}$$

TABLE 1

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

Mechanism	Symbol	$f(\alpha)$
Phase boundary controlled reaction (contracting area)	R2	$(1-\alpha)^{1/2}$
Phase boundary controlled reaction (contracting volume)	R3	$(1-\alpha)^{2/3}$
Unimolecular decay law	F1	$(1-\alpha)$
Avrami-Erofeev equation	Am	$m(1-\alpha)[-\ln(1-\alpha)]^{1/m}$
Two-dimensional diffusion	D2	$1/-\ln(1-\alpha)$
Three dimensional diffusion (Jander equation)	D3	$\dfrac{3(1-\alpha)^{2/3}}{2[\ 1-(1-\alpha)^{1/3}\ ]}$
Three dimensional diffusion (Ginstlein-Brounshtein equation)	D4	$\dfrac{3}{2[(1-\alpha)^{-1/3} - 1]}$

The activation energy may then be derived in several ways :

a) From eqn. (4) : the kinetic parameters can be obtained from the plots of the left hand side of this equation *vs* the reciprocal of the temperature.

b) From eqn. (3) : a series of experiments must be carried out at different constant decomposition rates, so that, for a given value of α (the same in each experiment) a plot of :

$\ln(C_i)$ against $1/T_i$

also gives the activation energy.

c) From the Rate-Jump method : here the rate of transformation is brought to swing between two pre-selected values conveniently chosen, say, for instance, with a ratio of 1 to 4. Correspondingly, the heating control loop changes the sample temperature in such a way that the desired rates are successively obtained. The resulting mass and temperature recordings (in case a thermobalance is used) are illustrated in Fig 1. Any set of 2 successive rates of transformation together with the 2 corresponding temperatures allows, for a sample whose experimental conditions are otherwise virtually unchanged (atmosphere composition and pressure, extent of reaction etc...) allows to calculate an activation energy by making use of eqn. (4) :

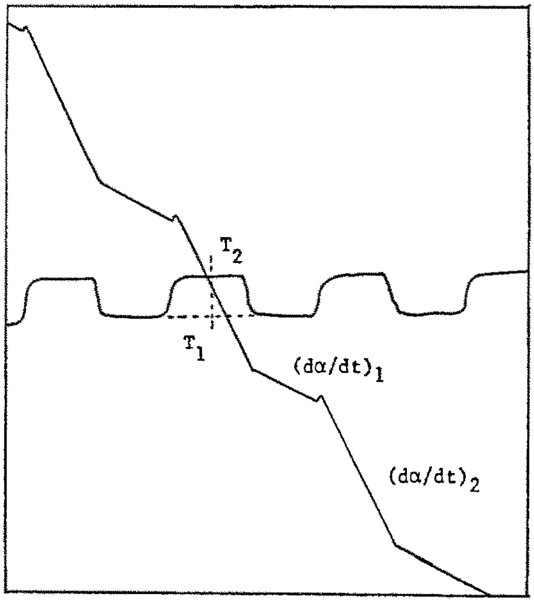

Fig. 1 Principle of the Rate-Jump method (two different rates in a constant ratio $a = C_1/C_2$ and the two corresponding temperatures T_1, T_2).

$$E = R \frac{T_1 \cdot T_2}{T_1 - T_2} \ln \frac{C_1}{C_2} \qquad (5)$$

EXPERIMENTAL

Material

The dolomite used was supplied by "S.A.E. de Productos Dolomiticos" (Spain). Its analysis by atomic absorption gives the following results (in brackets : the theoretical composition) :

MgO : 21.05 % (21.70 %)
CaO : 30.20 % (30.50 %)
Al_2O_3, Fe_2O_3 : 0.63 %
loss of ignition : 46.44 % (47.72 %)

This sample was sieved and the fraction with a grain size ranging from 30 to 40 µm was selected for the present work.

The experiments were all carried out with a vacuum thermobalance (Mettler Thermoanalyser I). The way to use the latter in the CRTA mode was described elsewhere (ref. 12-13). The residual pressure (or "vacuum") in the close neighbourhood of the sample was kept constant at the value of 2.10^{-5} mbar (controlled with a Penning gauge).

RESULTS AND DISCUSSION

Effect of the experimental method

The values of the reacted fraction α as a function of temperature for two different reaction rates $\left((d\alpha/dt)_1 = 3.10^{-6}\,s^{-1} \text{ and } (d\alpha/dt)_2 = 10^{-5}\,s^{-1}\right)$, under a constant pressure of 2.10^{-5} mbar and with a sample mass of 50 mg are shown in Fig. 2. The activation energies calculated from method B $\left(\ln(d\alpha/dt)_i \text{ vs.} 1/T_i\right)$ in the interval of α from 0.1 to 0.9 are shown in Table 2. The mean value is $E = 197\ kJ.mol^{-1}$. The internal agreement is quite satisfactory except for the first value, which is lower (for $\alpha = 0.1$).

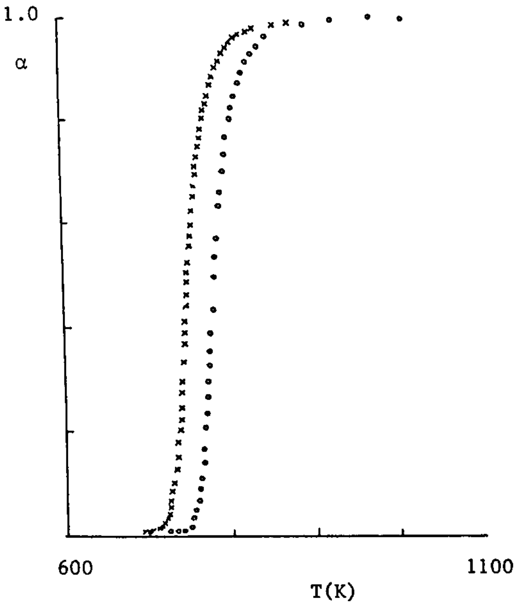

Fig. 2 CRTA diagrams obtained at two constant reaction rates ($C = 10^{-5}\,s^{-1}$ and $C = 3.10^{-6}\,s^{-1}$) for the thermal decomposition of dolomite.

TABLE 2

Activation energies of thermal decomposition of dolomite calculated at two different constant rate (CRTA) for a series of values of α. A mean value of 197 kJ.mol is obtained.

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
E / kJ.mol^{-1}	182	197	193	204	205	193	201	196	201

An actual trace now corresponding to the Rate-Jump method (but, here again, α *vs* T) is represented in Fig. 3. The dots are the experimental points

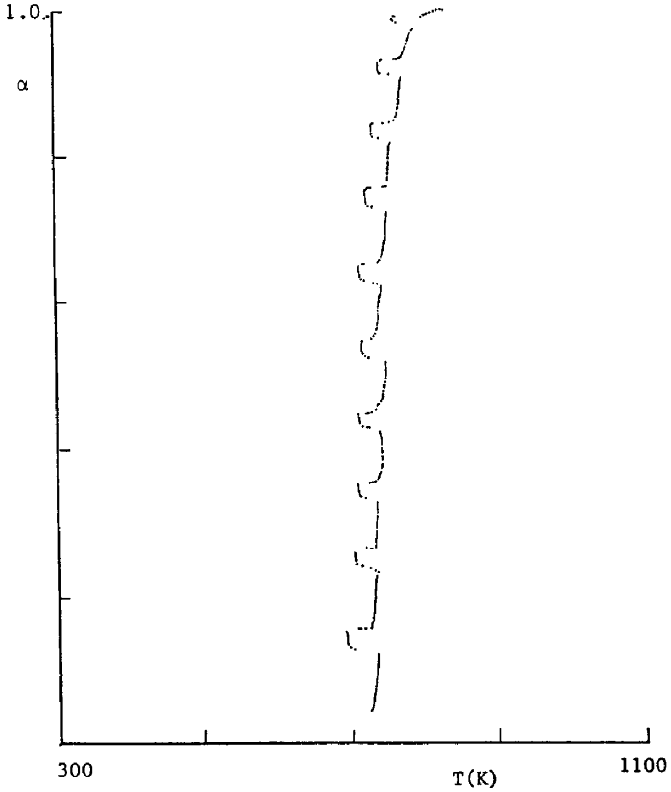

Fig. 3 Typical Rate-Jump diagram for the thermal decomposition of dolomite.

collected by the microcomputer during the experiment. The mean value of the activation energies obtained from these data by applying method C is 194 ± 13 $kJ.mol^{-1}$, i.e. in good agreement with the result from method B.

On the basis of these results, the advantages and kinetical interest of the Rate-Jump method may already be summarized as follows :

⇒ First of all, the Rate-Jump method allows to assess an activation energy without knowing the kinetic model, i.e., regardless of the nature of the $f(\alpha)$ function assumed in eqn. (3).

⇒ Unlike in conventional methods, closely similar states of the same sample can be compared. The crystalline structure and porous structure of these states may therefore be very similar.

⇒ The residual pressure remains constant, which increases the meaning of the energy of activation measured, since we know it often depends on the pressure.

⇒ It is possible during a single experiment to perform a number of successive and independent measurements of the activation energy and then to follow the variation of this parameter over the whole range of α.

Taking into account these advantages, it is the Rate-Jump method which we use in the following.

Effect of the sample mass

We compare in Table 3 the activation energies calculated with different sample masses (20, 50, 100 and 200 mg) and with a rate jump ratio kept between 3 and 5. One sees that the sample size does not influence significantly the value of the activation energy. The scatter is the largest for the smallest sample (± 26 $kJ.mol^{-1}$). This is because the duration of the jump is not any more negligible as compared with the duration of the whole experiment, so that the sample is undergoing some detectable changes during one jump.

TABLE 3

Activation energies of thermal decomposition of dolomite calculated from Rate-Jump method as a function of sample size (a = rate ratio).

mg	20	50	100	200
a	3.7 - 5.5	3.4 - 5.0	3.2 - 4.2	3.5 - 4.5
$E\ /\ kJ.mol^{-1}$	201 ± 26	194 ± 13	190 ± 13	180 ± 15

Effect of the rate ratio

We report in Table 4 the activation energies calculated for 2 very different rate ratios. As we see, the results are still remarkably close to each other.

TABLE 4

Activation energies of thermal decomposition of dolomite obtained from Rate-Jump method as a function of the rate ratio a.

a	4	20
E /kJ.mol^{-1}	197 + 12	196 + 11

The general consistency of the results obtained with the Rate-Jump method shows that, in spite of the relatively wide range of mass (20 to 200 mg) and rate ratio (4 to 20) used, it is possible, by this method, to assess a value of the activation energy which seems to be relatively insensitive to experimental artefacts : it may be infered that this -although again "apparent"- activation energy is likely to be more closely related to the chemical reaction proper than the energies of activation depending on the sample mass, heating rate and temperature often obtained by other methods.

REFERENCES

1 J. Rouquerol, Thermochimica Acta, 144 (1989) 209.
2 P.K. Gallagher and D.W. Johnson, Thermochimica Acta, 6 (1973) 67.
3 D.T.Y. Chen, J. Thermal Analysis, 7 (1975) 61.
4 J. Simon, J. Thermal Analysis, 5 (1973) 271.
5 J. Rouquerol and M. Ganteaume, J. Thermal Analysis, 11 (1977) 201.
6 M.J. Torralvo, Y. Grillet, F. Rouquerol and J. Rouquerol, J. Chimie Physique, 77 (1980) 125.
7 J. Rouquerol, in Proceedings 1st Franco-Venezuelian Symposium on Catalysis, (1984), Caracas, Intevep (Ed.), pp. 247-254.
8 G. Spinolo and D Beruto, J. Chem. Soc. Faraday Transactions I, (1982) 78.
9 H. Hashimoto, E. Komaki, F. Hayashi and T. Uematsu, J. of Solid State Chemistry, 33 (1980) 181.
10 E.K. Powell and A.W. Searcy, J. American Ceramic Society, 61 (1978) 216.
11 E.P. O'Neil, D.L. Keairns and W.F. Kittle, Thermochimica Acta, 14 (1976) 209.
12 J. Rouquerol, in "Thermal Analysis", F.F. Schwenker and P.D. Garn (Eds.), Academic Press, New York, 1969, 281 and J. Thermal Analysis, 5 (1973) 203.
13 F. Rouquerol, S. Regnier and J. Rouquerol, in "Thermal Analysis", Vol. 1, E. Buzagh (Ed.), Akademiai Kiado, Budapest (1975) 313.