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Influence of pressure on the shape of TG and controlled transformation rate thermal analysis (CRTA) traces

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Abstract

The influence of pressure on the shape of both TG and controlled transformation rate thermal analysis (CRTA) traces is theoretically and experimentally illustrated. It is shown that this shape can be explained on the basis of kinetic considerations and consequently thermoanalytical data can be used to perform kinetic analysis of solid state reactions contrary to Paulik's statement.

However it has been shown that CRTA traces are more sensitive than conventional non-isothermal curves to the effect of pressure of the gases self-generated in the reaction. This may be considered as an interesting argument to explain the advantages of the CRTA technique for discriminating between overlapping processes.

LIST OF SYMBOLS

A	pre-exponential factor
C	constant decomposition rate
E	activation energy
ΔH	heat of reaction
P_{eq}	equilibrium pressure
P_g	pressure of the gas generated in the reaction
P_0	constant of the van't Hoff equation
R	gas constant

Greek letters

α	reacted fraction at time t
β	heating rate

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INTRODUCTION

The kinetic analysis of solid-state reactions from non-isothermal data has been the subject of considerable numbers of publications, probably because of its simplicity with respect to isothermal methods.

In conventional thermal analysis (TG, DTA, DSC, EGA, etc.) three basic parameters are measured simultaneously as Fig. 1 shows, the sample temperature T (by the "thermometer"), the time t (by the "chronometer") and the physical property "X" which depends on the technique selected (by the "X-meter"). The first two parameters are associated by means of the heating control loop in order to follow a predetermined T versus t program ($T = f(t)$) which is most often linear and which is therefore not necessarily recorded. The corresponding value of X is recorded versus t or T to deliver the proper thermal analysis curve.

Nevertheless another approach has been advocated and used in recent years to study the thermal behavior of a substance. This approach is very close to thermal analysis but is in some respects "the opposite" as Fig. 2 shows. Here the physical property "X" is brought to follow a predetermined

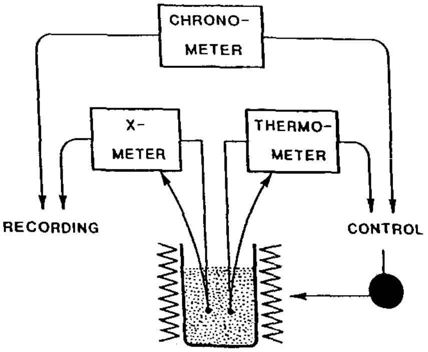

Fig. 1. Principle of conventional thermal analysis (TG).

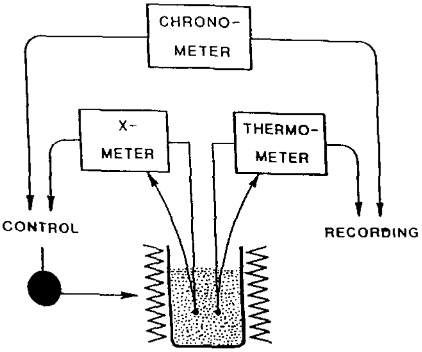

Fig. 2. Principle of controlled rate thermal analysis (CRTA).

program and therefore controls the heating of the sample ($X = f(t)$); for this the Nomenclature Committee of ICTA has suggested the name controlled transformation rate thermal analysis (CRTA).

Comparison between the CRTA approach and conventional non-isothermal methods has been systematically carried out and is reported in several papers [1–4]. The advantages of the CRTA technique can be summarized as follows:

(i) to reduce the influence of mass and transfer phenomena;
(ii) to obtain kinetic parameters which are independent of the starting sample mass.

The kinetics of solid state reactions is probably the most recent field in which CRTA has been applied [5]. It is well known that the validity and significance of kinetic analysis of solid state reactions depends on our exact knowledge of both the "influencing parameters" and of their values at any point of the reacting system. This means that any unknown gradient in temperature, gas composition (or pressure), etc., is a real limit to our kinetical understanding of the forward reaction. It has been shown that CRTA allows considerably better control of the heat and mass transfer phenomena than conventional methods [6].

However Paulik and Paulik [7] have carried out a comparison of the shape of both TG and quasi-isothermal quasi-isobaric curves corresponding to reactions of the type

$$A(s) \rightarrow B(s) + C(g) \qquad (1)$$

According to these authors the $\alpha - T$ plots yielded by the CRTA technique occur at a nearly constant temperature while the corresponding TG curves extend over a broad temperature range. Paulik and Paulik [7] conclude from this finding that every $\alpha - T$ point on a TG trace represents the value of α at which the equilibrium pressure corresponding to reaction (1) at the temperature T has been reached and therefore that, "the correctness of reaction kinetic calculation on the basis of curves obtained by dynamic thermoanalytical methods is rather questionable" [7].

The scope of this paper is to analyze the influence of pressure on the shape of thermoanalytical curves (TG and CRTA) in order to elucidate if these data can be explained on the basis of kinetic considerations and not only from the point of view of thermodynamic equilibrium as Paulik and Paulik [7] suggest.

THEORETICAL

The reaction rate of solid state process can be described by the well known general kinetic law

$$\frac{d\alpha}{dt} = Af(\alpha)\exp(-E/RT) \qquad (2)$$

If the reaction is carried out under a pressure P_g eqn. (2) becomes, after taking into account the microreversibility principle

$$\frac{d\alpha}{dt} = Af(\alpha)\left[1 - \frac{P_g}{P_{eq}}\right]\exp(-E/RT) \tag{3}$$

According to the van't Hoff equation, P_{eq} is given by the expression

$$P_{eq} = P_0 \exp(-\Delta H/RT) \tag{4}$$

If the thermoanalytical trace was recorded at a heating rate $\beta = dT/dt$, eqn. (3) could be integrated by using as lower integration limit of temperature the value T_0 at which the equilibrium pressure became equal to P_g. Thus we obtain

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{dt} = \frac{A}{\beta}\left[\int_{T_0}^{T} \exp(-E/RT)\, dT - \frac{P_g}{P_0}\int_{T_0}^{T} \exp\left(-\frac{E-\Delta H}{RT}\right) dT\right] \tag{5}$$

If the process is carried out under vacuum $P_g/P_{eq} \approx 0$ and eqn. (5) can be simplified to

$$g(\alpha) = \frac{A}{\beta}\int_{T_0}^{T} \exp(-E/RT)\, dT \tag{6}$$

If the thermoanalytical curve is obtained at a constant decomposition rate C ($C = d\alpha/dt$), according to the CRTA method eqn. (3) becomes

$$C = Af(\alpha)\exp(-E/RT) \tag{7}$$

EXPERIMENTAL

Calcium carbonate of AR grade from d'Hemio was used. The X-ray diffraction pattern indicated that the product is mainly calcite. The Mettler thermobalance modified in order to obtain CRTA traces has been described elsewhere [8]. The Q-derivatograph developed by Paulik and Paulik is illustrated in ref. 9.

It was shown in a previous paper [10] using the same sample that the activation energy of the thermal decomposition of calcite determined from CRTA experiments was independent of the sample mass in the range investigated (2–300 mg).

RESULTS AND DISCUSSION

The thermal decomposition of calcite has been chosen as a "model" reaction because its equilibrium pressure P_{eq} at different temperatures has been reported in the literature [11]. Therefore, it can easily be deduced from previously reported data that between 500 and 1000°C its behavior is fitted very closely by the equation

$$P_{eq}\,\text{mbar} = 7.9 \times 10^7 \exp(-173/RT) \tag{8}$$

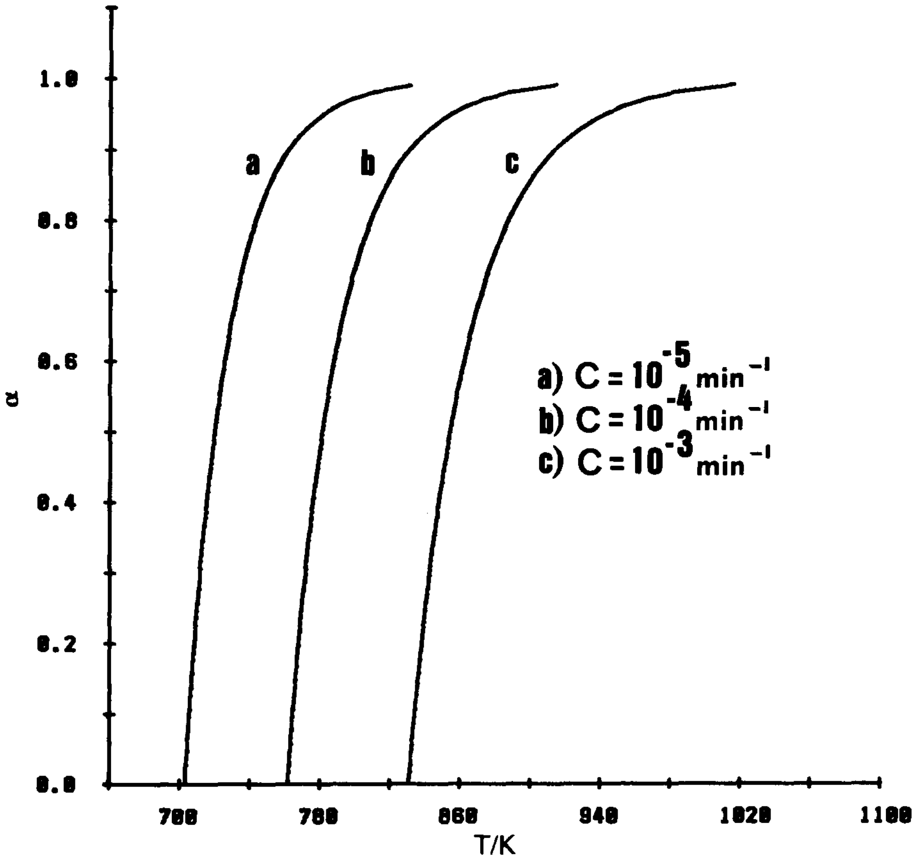

Fig. 3. Effect of reaction rate C on CRTA theoretical curves.

Figures 3 and 4 show the series of CRTA and TG theoretical curves calculated under a high vacuum for the thermal decomposition of $CaCO_3$ (i.e. $1 - P_{CO_2}/P_{eq} \approx 1$).

The series of TG curves shown in Fig. 4 for different heating rates β have been constructed by integrating eqn. (6) by means of Simpson's procedure with an error lower than $10^{-3}\%$. The CRTA diagrams in Fig. 3 have been obtained from eqn. (7). We have assumed the kinetic parameters ($E = 163\ \mathrm{kJ\ mol^{-1}}$; $A = 2 \times 10^{8}\ \mathrm{min^{-1}}$) and the reaction mechanism (phase boundary controlled reaction, contracting volume) determined previously [12] for the thermal decomposition under high vacuum of the same $CaCO_3$ sample used here.

An examination of Fig. 3 shows that CRTA diagrams shift to higher temperatures upon increasing the reaction rate C. Moreover the temperature range over which the reaction takes place increases upon increasing the reaction rate C. We can see that the effect of the reaction rate on the shape of CRTA traces is similar to the influence of the heating rate β on the shape

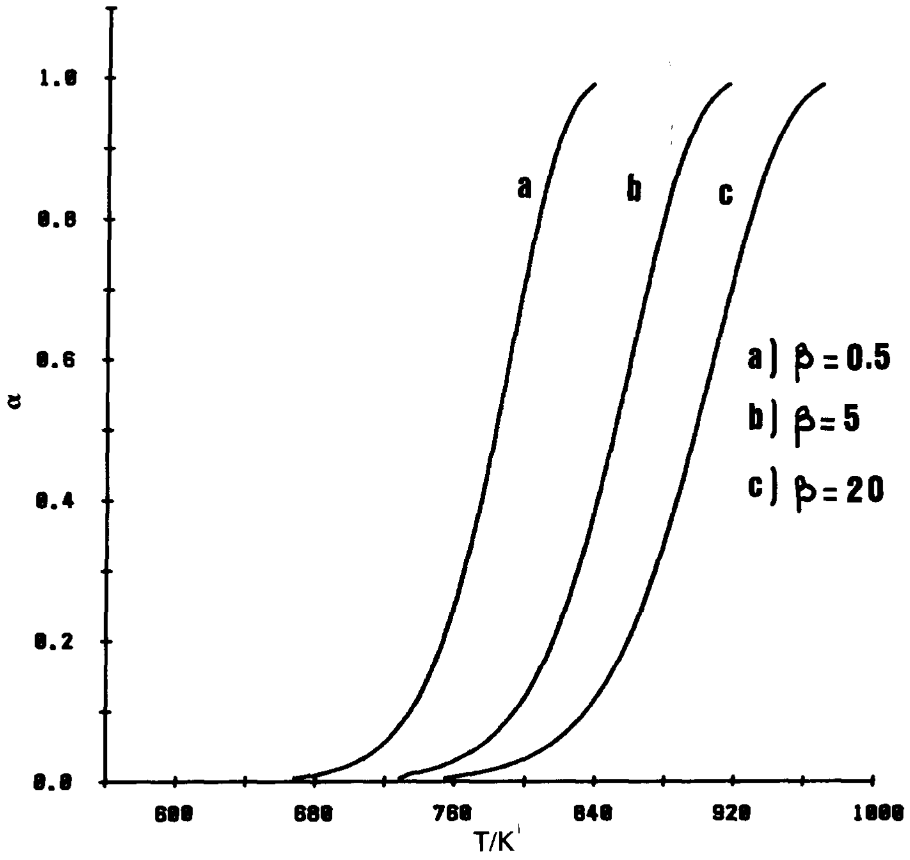

Fig. 4. Effect of heating rate β on TG theoretical curves.

of TG curves as shown in Fig. 4. The results included in Figs. 3 and 4 indicate that the shape of thermoanalytical curves can be defined by the kinetics obeyed by the reaction, provided that there is effective control of heat and mass transfer phenomena, i.e. if the reaction takes place far from equilibrium.

Note that the CRTA diagram of the forward reaction does not take place at a defined temperature and in a quasi-isothermal manner but under non-equilibrium conditions. This is in agreement with the experimental results reported previously [12].

In contrast the experimental results obtained by Paulik and Paulik [7] for a series of inorganic materials by the quasi-isothermal quasi-isobaric technique show that the chemical transformation takes place at a constant temperature. This behavior could be explained as arising from the special experimental conditions created by using the so-called labyrinth crucible. This crucible leads to a self-generated atmosphere of the gases

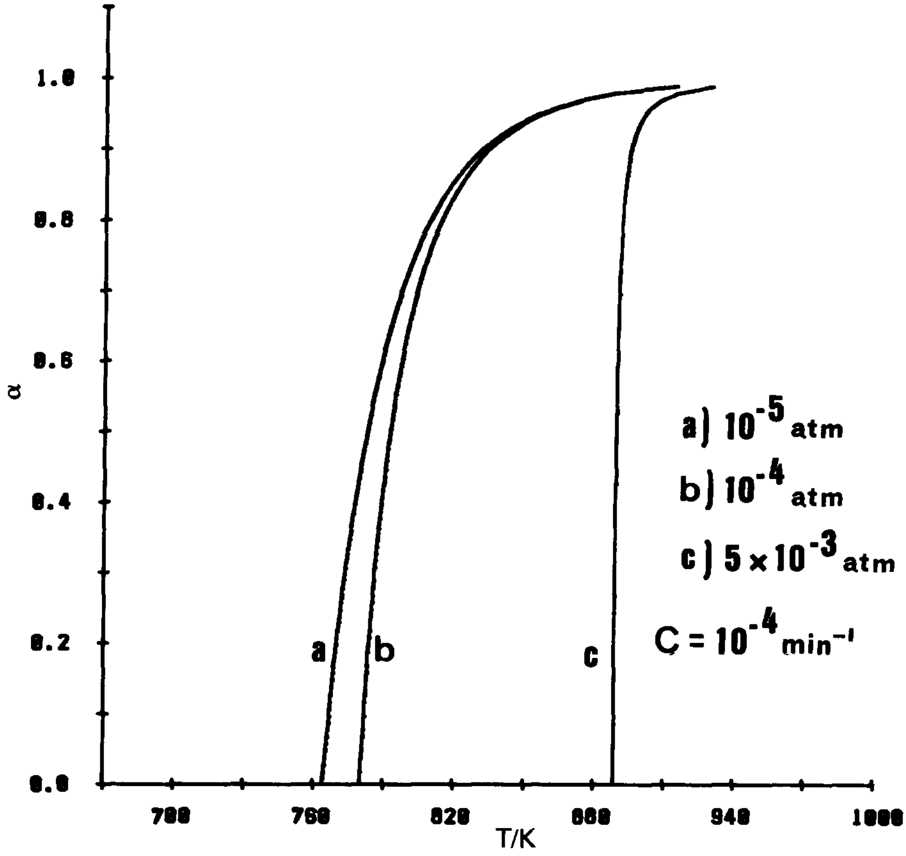

Fig. 5. Effect of pressure on CRTA theoretical curves.

yielded in the reaction that significantly influence the shape of thermoanalytical curves.

In order to check the validity of the above assumption and to show that the vapor pressure in the close vicinity of the sample plays an important part in determining the shape of thermoanalytical curves, we have constructed in Fig. 5 the CRTA diagrams calculated by assuming a constant rate $C = 10^{-4}$ $\min^{-1}$ and several values of the CO_2 pressure. Figure 5 shows that the curves become narrower as the CO_2 pressure is increased and at $P_{CO_2} \approx 4$ mbar, the conversion takes place without any change in temperature i.e. isothermally.

However the conventional TG curves constructed in Fig. 6 at a heating rate of $\beta = 6$ K $\min^{-1}$ are almost insensitive to the variation of CO_2 pressure within the range considered above (0–4 mbar).

To summarize, the results reported here allow us to conclude that the shape of conventional and CRTA thermoanalytical curves can be explained