

THERMAL DECOMPOSITION REACTIONS IN SOLIDS: COMPARISON OF THE CONSTANT DECOMPOSITION RATE THERMAL ANALYSIS WITH THE CONVENTIONAL TG METHOD

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ABSTRACT

The thermal decomposition of CaCO_3 was studied under high vacuum by means of both TG and the more recently developed constant decomposition rate thermal analysis (CRTA) which allows the monitoring of both reaction rate and the residual pressure over the sample. The reliability of the kinetic results seems to be much higher with the latter technique which actually allows the reduction of the reaction rate and therefore the heat and mass transfer effects over a broad range of sample size. For instance, it was necessary, by conventional TG started under a vacuum of $2 \cdot 10^{-6}$ torr with a heating rate of 0.5 K min^{-1} , to lower the amount of sample to 2 mg in order to obtain the same activation energy as that calculated from CRTA with various samples weighing up to 50 mg. The TG experimental conditions quoted above (and which are upper limits of mass and heating rate) are beyond the limit of sensitivity of most available conventional TG equipment.

INTRODUCTION

A pronounced influence of the experimental conditions on the thermal decomposition of CaCO_3 has been reported in a number of papers [1–4]. Recently, Gallagher and Johnson [2] have observed that, under an atmosphere of air, the activation energy of this reaction decreases when either the sample amount or heating rate are increased. They report, however, that under inert gases the decomposition rate increases in the same direction as the thermal conductivity of the environment, i.e., $\text{Ar} < \text{N}_2 < \text{He}$. It has been concluded [2] from these data that the thermal decomposition of CaCO_3 is controlled by thermal transport rather than a mass transfer effect. However, it has been pointed out in ref. 4 that the above results could also be interpreted in terms of a mass transport effect since, as is well known, the diffusivity of the gases increases when their molecular weights become lower. Hence, helium may be expected to be more effective in removing the CO_2 evolved in the reaction and, therefore, result in a higher decomposition rate

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of CaCO_3 , which is in accordance with Gallagher and Johnson's results [2]. Moreover, the influence of both the sample size and the heating rate on the kinetics of the thermal decomposition of CaCO_3 may be easily explained [4] by taking into account that at higher reaction rates it is more difficult to remove the self-generated CO_2 and following, for instance, the lines developed by Garn [5]. Therefore, in so far as the reaction is in progress, the CO_2 increase of pressure around the sample causes the TG curve to move towards higher temperatures. This mass transfer effect may cause a broadening of the TG diagram, which may explain the diminution of the activation energy observed in the literature [1,2].

From the above considerations we can conclude that the data reported in the literature about the influence of the experimental conditions on the kinetic parameters of the thermal decomposition of CaCO_3 do not allow an unambiguous determination of whether they are motivated by a mass transfer control or by a heat transfer control of the reaction. The scope of the present paper is to study the thermal decomposition of CaCO_3 in such a way that the effects of mass and thermal transport may be, if possible, separated. For that purpose, we decided to use the constant decomposition rate thermal analysis technique (CRTA) described elsewhere [6]. It allows the control, at the desired values, of both the residual pressure of CO_2 self-generated during the reaction in the close vicinity of the sample, and the decomposition rate (i.e., the amount of CO_2 generated per unit of time). The more conventional technique of vacuum TG was also used, with the aim of studying the influence of the pumping rate and sample size, the other experimental parameters being kept constant.

EXPERIMENTAL

Calcium carbonate of A.R. grade from d'Hermio was used. The experimental assembly (CRTA associated with TG) has been described elsewhere [6,7].

RESULTS

TG diagrams of CaCO_3 obtained with a starting vacuum of $2 \cdot 10^{-6}$ torr and a heating rate of 10 K min^{-1} , but using different sample sizes and/or pumping rates, are reported in Fig. 1. The pressure was recorded simultaneously with the weight change, as illustrated in Fig. 2 for one of the diagrams included in Fig. 1. In this case, where the initial sample weight was of 21,32 mg, the pressure increased up to about $4.7 \cdot 10^{-4}$ torr (235-fold increase!). It was necessary to lower the sample weight to 1.35 mg of CaCO_3 , with a heating rate of 0.5 K min^{-1} in order to obtain a pressure never exceeding $2 \cdot 10^{-6}$ torr. The corresponding TG curve is given in Fig. 3 (curve a). The sample mass, pumping rate and maximum pressure corresponding to these various experiments are listed in Table 1.

The kinetic analysis of the TG curves has been carried out, assuming first-

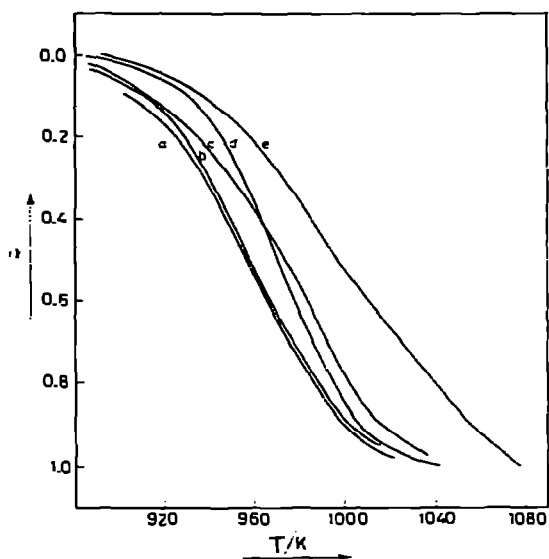


Fig. 1. TG curves for CaCO_3 recorded at 10 K min^{-1} and with a starting vacuum of $2 \cdot 10^{-6}$ torr. Sample amount and pumping rates: a, 5.32 mg and 46 l/s; b, 2.05 mg and 46 l/s; c, 21.32 mg and 46 l/s; d, 5.23 mg and 23 l/s; e, 20.83 mg and 23 l/s.

order kinetics, using Coats and Redfern's method [8]

$$\ln \ln \frac{1}{1-\alpha} - 2 \ln T = \ln \frac{AR}{E\beta} - \frac{E}{RT} \quad (1)$$

where α is the molar extent of reaction referred to the starting amount of carbonate, β is the heating rate, and the other parameters have their usual meaning. The reason for assuming first-order kinetics is given elsewhere [9].

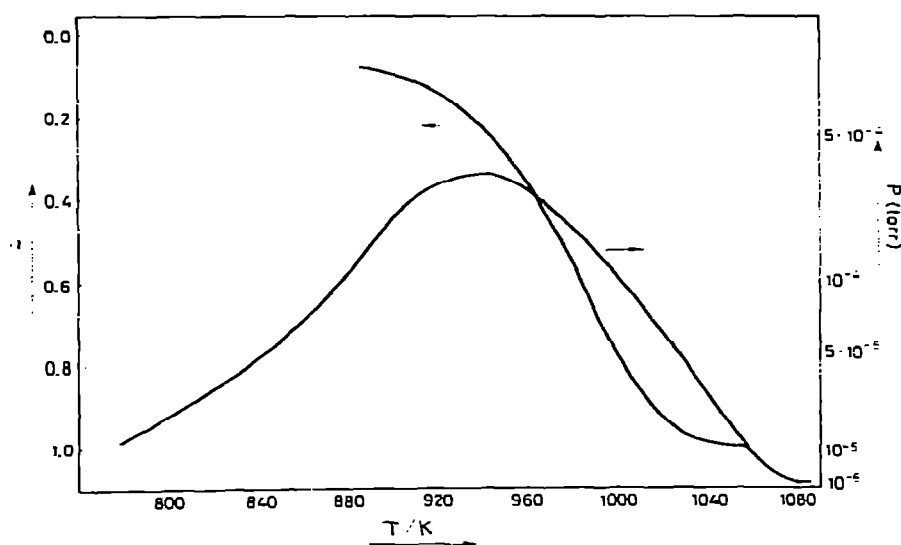


Fig. 2. Simultaneous recording of weight and pressure during the TG experiment quoted c in Fig. 1.

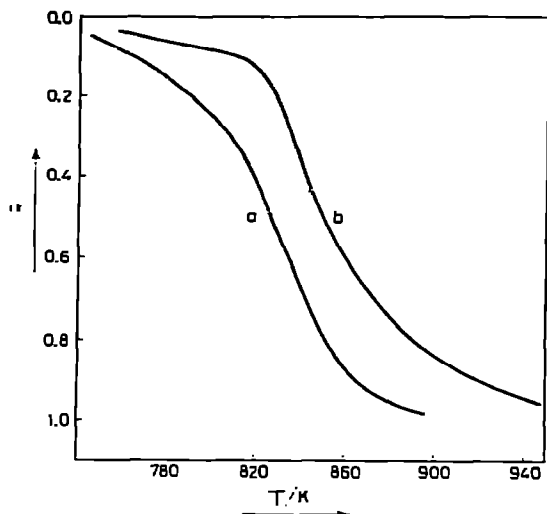


Fig. 3. a, TG curve for CaCO_3 ($m_0 = 1.35$ mg; $\beta = 0.5$ K min^{-1}); b, CRTA curve for CaCO_3 ($m_0 = 22.1$ mg; $P = 4 \cdot 10^{-5}$ torr; $C = 0.005$ min^{-1}).

The plot of the left-hand side of eqn. (1) vs. $1/T$ gives a straight line whose slope supplies the activation energy. The values of this parameter, as calculated from the data given in Figs. 1 and 3, are given in Table 1. We can see that the greater the sample size, the higher the pressure around the sample and the lower the apparent activation energy.

On the other hand, a series of CRTA diagrams were recorded using constant decomposition rates, C (measured in mg of gas evolved per mg of starting per min, and therefore expressed in min^{-1}) ranging from 0.0070 to 0.0015 min^{-1} and controlled residual pressures ranging from $4 \cdot 10^{-5}$ to 10^{-3} torr. As an example, curve b of Fig. 3 was obtained at $C = 0.005$ min^{-1} with a controlled pressure of $4 \cdot 10^{-5}$ torr. The kinetic analysis of these curves was also carried out with the assumption of first-order kinetics. Since the thermal

TABLE 1

Influence of experimental conditions on the kinetic parameters of thermal decomposition of CaCO_3 as calculated from conventional TG curves after assuming a first-order kinetics law

Fig.	Curve	m_0 (mg)	Pumping rate * (l s^{-1})	Pressure at peak (torr)	E (kcal mole^{-1})
1	c	21.3	46	$4.7 \cdot 10^{-4}$	46
1	e	20.83	23	$1.2 \cdot 10^{-3}$	44
1	a	5.32	46	$1.9 \cdot 10^{-4}$	56
1	d	5.23	23	$6.0 \cdot 10^{-4}$	67
1	b	2.05	46	$8.5 \cdot 10^{-5}$	57
3	b	1.35	46	$2.0 \cdot 10^{-6}$	35

* At 10^{-4} torr, after instruction manual of Mettler Thermoanalyzer.

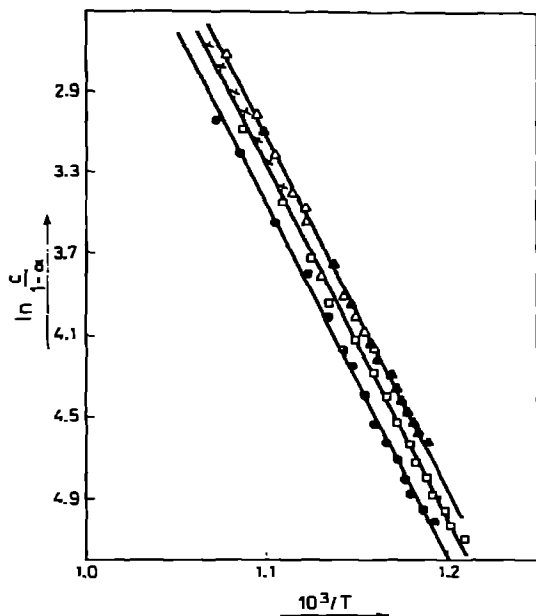


Fig. 4. Plots of CRTA data of CaCO_3 following eqn. (2): $m_0 = 21.2$ mg, $P = 8 \cdot 10^{-5}$ torr, $C = 0.0097$ min^{-1} (Δ); $m_0 = 21.0$ mg, $P = 10^{-4}$ torr, $C = 0.0070$ min^{-1} (\blacktriangle); $m_0 = 22.1$ mg, $P = 4 \cdot 10^{-5}$ torr, $C = 0.0050$ min^{-1} (\square); $m_0 = 52.0$ mg, $P = 10^{-3}$ torr, $C = 0.015$ min^{-1} (\times); $m_0 = 23.1$ mg, $P = 4 \cdot 10^{-5}$ torr, $C = 0.0047$ min^{-1} (\bullet).

decomposition rate is kept constant ($C = d\alpha/dt$), we can write

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

The plot of the left-hand side of eqn. (2) vs. the reverse of temperature is expected to be a straight line whose slope gives the activation energy.

From the CRTA diagrams, values of $\ln C/(1-\alpha)$ were calculated for various temperatures, and plotted (in Fig. 4) vs. $10^3/T$, according the eqn. (2). From any of these plots an activation energy of 34 kcal mole^{-1} was obtained.

DISCUSSION

Figure 1 shows that the TG traces of CaCO_3 , obtained at a heating rate of 10 K min^{-1} , move towards higher temperatures when the sample size is increased, while maintaining a constant pumping rate (series a, b, c at the first pumping rate; series d, e, at the second pumping rate). It is worth pointing out that, under these experimental conditions, the larger the sample size, the higher the pressure recorded around the sample. Moreover, in the TG curve recorded with a sample of 21.3 mg and a pumping rate of 46 l s^{-1} (Fig. 1, curve c), the weight loss starts at lower temperatures than in the run obtained using a much smaller sample (5.2 mg), but a pumping rate of only 23 l s^{-1} (Fig. 1, curve d), which explains a somewhat higher maximum pressure in the latter experiment (cf. Table 1).

It may also be seen from Fig. 1 and Table 1 that if the pumping rate is decreased while maintaining the sample size and heating rate constant (i.e. two important parameters in the control of heat transfer), the CaCO_3 TG traces move towards higher temperatures, while the CO_2 pressure around the sample increases. If the thermolysis was heat-transfer controlled, the increase in pressure (and therefore in surrounding thermal conductivity) would cause the TG curves to move towards lower temperatures (which is not observed). We therefore tend to conclude that, even in our "vacuum" experimental conditions, the residual pressure is a major rate-controlling parameter which does not act through a heat-transfer process but through the control of a reversible reaction, and maybe also through a mass transfer (i.e., diffusion) process.

On the other hand, as shown in Table 1, the experimental conditions at which TG diagrams are recorded exert a pronounced effect what must be called the "apparent" activation energy of the thermal decomposition of CaCO_3 . However, no correlation was found in these conventional experiments between this parameter and either the sample weight or the pumping rate.

The data obtained by means of the CRTA technique show that the activation energy of the thermal decomposition of CaCO_3 is independent of both the CO_2 residual pressure (in the $4 \cdot 10^{-5}$ – 10^{-3} torr range) and the constant decomposition rate within the range investigated. This behaviour seems to indicate that in the experimental conditions used here the reaction is not influenced by any mass transfer, heat transfer or equilibrium pressure phenomenon. These results are surprising if we bear in mind the strong effect exerted by the pumping rate on the kinetic parameters as calculated from the TG curves recorded, apparently, in a similar pressure range.

The above results seem to indicate that the pressure recorded simultaneously with the TG diagrams is actually much lower than that really surrounding the sample. However, in the extreme case of a sample size (1.35 mg) and heating rate (0.5 K min^{-1}) small enough to avoid any detectable increase in the initially low pressure along the experiment, then the activation energy value obtained from conventional TG (cf. Table 1, last line) agrees with the single value given by the various CRTA experiments.

In summary, the results reported here indicate that in our "vacuum" experimental conditions the CRTA technique leads to more reliable kinetic data than the TG method. This is because the former allows both a good control of the pressure in the sample surroundings and the use of reaction rates low enough to avoid any heat, or mass transfer problem.

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