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MASS SPECTROMETRIC DETERMINATION OF KINETIC PARAMETERS FOR SOLID-STATE DECOMPOSITION REACTIONS. PART 2. CALCIUM CARBONATE *

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ABSTRACT

The thermal decomposition of calcium carbonate has been investigated using a non-isothermal mass spectrometric thermal analysis technique. A small sample size and rapid removal of evolved CO_2 minimised gas–residue interaction. Initial experiments showed that T_{max}, at which the maximum rate of CO_2 evolution occurred at a given heating rate, fluctuated over a 20°C range. Experiments conducted 12 months later had an even greater fluctuation range of 90°C. Evidence is presented that the decomposition temperature of $CaCO_3$, in vacuum, is controlled by two major factors, namely, ageing and the extent of chemisorbed water.

A linear compensation plot of log A vs. E was obtained despite the wide fluctuation in the T_{max} values used to evaluate A and E. The reasons for this are discussed.

INTRODUCTION

There are numerous reports concerned with kinetic studies of the thermal decomposition of calcium carbonate (calcite) both under isothermal and non-isothermal conditions. There is strong evidence that the reaction

$$CaCO_3 \rightarrow CaO + CO_2$$

takes place at an interface between calcite and residual oxide [1]. In reviewing reported values of the activation energy for calcite decomposition, Beruto and Searcy [2] find that most are close to the dissociation enthalpy. They suggested that if product gas removal is not rapid and complete, readsorp-

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* For Part 1, see ref. 21a.

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tion of CO_2 on residual oxide may establish dissociation equilibria within the pores and channels of the layer of residual phase. Others [3,4] have supported this idea and stated that where large samples of reactant are used and/or where CO_2 withdrawal is not rapid or complete, the rate of calcite decomposition can be controlled by the rate of heat transfer or CO_2 removal. The decrease in the activation energy value reported by Altorfer [5] from 234 in nitrogen to 155 kJ mol^{-1} in vacuum confirms the importance of the reverse reaction and also the effect of the sample size in altering the values of the kinetic parameters obtained. Caldwell et al. [6] considered the effect of the thermal conductivity of inert gas to be the 'crucial factor in determining the reaction temperature. Thomas and Renshaw [7] concluded that decomposition in deformed calcite crystals can be initiated at particular dislocations only, namely those which glide on 100 and $2\bar{1}\bar{1}$ planes but not those which glide on $11\bar{1}$ planes. From the shape of decomposition nuclei, it was concluded that $1\bar{1}$, 11 and 110 planes are of some significance in the preferred growth of the product, CaO, within the parent lattice. However, their kinetic studies indicated that the activation energies computed from initial rates of decomposition may be lower than those derived from constant rates at higher fractions decomposed. This is tentatively interpreted to mean that the intrinsic energy of a dislocation contributes to the energy of activation. Shannon [8], using activated complex theory, obtained reasonable agreement between experimental and theoretical rate coefficients. This was achieved by considering an activated complex containing one O–C–O group free to rotate about an axis perpendicular to the plane of the solid surface.

The combination of various factors controlling the kinetics of decomposition of calcium carbonate together with the development of different methods for calculating the kinetic parameters from non-isothermal data has led to very different values being reported for the kinetic parameters and, consequently, different mechanistic conclusions being drawn. Indeed, the problems which arise in the interpretation of the kinetic parameters are nowhere more apparent than in the totally unreasonable spread of values of log A (2–69) and E (108–1600 kJ mol^{-1}) summarized by Zsako and Ars [9] and collated by us in Table 1. As a contribution to the elucidation of this situation we herein report a study of the decomposition kinetics of pure calcium carbonate using the mass spectrometric thermal analysis technique (MSTA) developed in this laboratory [21]. This approach utilises very small sample sizes together with very rapid removal of product gases from the reaction zone by the fast pumping system. Thus gas–residue and ion–molecule reactions are significantly reduced. It was hoped that this "simplification" of the reaction conditions would lead to a more reproducible decomposition behaviour.

TABLE 1

Some reported activation energy values for the thermal decomposition of $CaCO_3$

Atmosphere	Order	Dynamic (D) or isothermal (I)	E (kJ mol^{-1})	Ref.
Air	0.46	D	216	10
Air	0.67	I	170	11
Air	1	I	397	12
Air	0–1	D	155–742	9
O_2	0.5	D	142–297	13
O_2	0.5	I	175–208	13
CO_2	1	D	135–288	14
CO_2	0.5	I	201–950	6
CO_2	0.5–2	D	213–2142	6
CO_2	2/3	D	565–3828	15
N_2	–	I	172	16
N_2	0.2	D	184	17
N_2	0.17	D	228	5
He	0.2–1.53	D	220–348	5
vacuum	0.8	D	153	5
vacuum	0.58–0.72	I	146–176	18
vacuum	1	I	159	19
–	0.5–2/3	D	184–197	20

EXPERIMENTAL

Reagent grade calcium carbonate (BDH) was sieved and the 30–60 μm fraction selected for study. The mass spectrometric thermal analysis technique and procedure were as previously described [21]. For each experiment, the 1–5 mg sample was located in the ion source region and then left overnight in order that any surface adsorbed material was pumped away. The decomposition at the chosen heating rate, β, was then initiated. Experiments were conducted in the heating rate range 1–10°C min^{-1}.

RESULTS

A typical ion current/temperature profile obtained for CO_2 evolution (i.e., at m/z 44) is shown in Fig. 1. The profile clearly exhibits the long induction period which we also observed in the second stage of the calcium oxalate decomposition [21]. However, the first few kinetic experiments on the decomposition of $CaCO_3$ showed drastic changes in the appearance of onset and peak temperatures (about 20°C) even when the same heating rate was applied. Figure 2 shows the scatter of points observed when Ozawa's

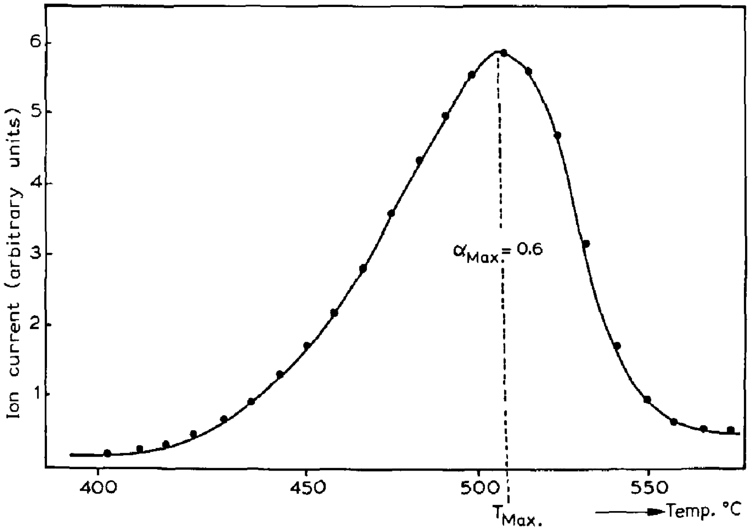

Fig. 1. Ion current/temperature profile for the decomposition of $CaCO_3$; heating rate (β) = 10°C min^{-1}.

equation for the maximum rate is applied to the experimental data [21,22].

$$\log \beta = -0.4567\frac{E}{RT_{\max}} - 2.315 + \log\frac{E}{Rg(\alpha)} \tag{1}$$

Here, $T_{\max}$ represents the temperature at which the maximum rate of reaction is observed (i.e., peak temperature in MSTA experiments), $g(\alpha)$ is a

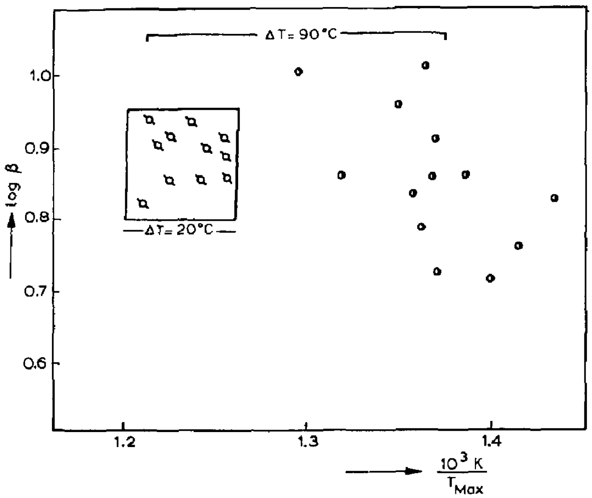

Fig. 2. Ozawa equation plot for CO_2 evolution from $CaCO_3$: (○) data from initial series of experiments; (◑) data obtained 12 months later.

term which is mechanism dependent ($-\ln(1-\alpha)$ for the first-order decay type mechanism), E and R are the activation energy and gas constant, respectively. Many experiments were carried out in order to clarify this situation by systematically altering the degassing time, the initial sample weight, the dimensions of the crucible and operating at very low heating rates. None of these changes gave a clear explanation for the observed drastic fluctuation in onset and peak temperatures.

In order to be able to study if "ageing" affected the decomposition temperature, a sample bottle containing pure calcium carbonate was kept for one year in a desiccator. Figure 2 compares the maximum reaction points originally obtained with those obtained 12 months later. It can be seen that the shifts of temperature in some cases are as high as 90°C. This decrease in the appearance of peak temperatures was further investigated by considering the behaviour of characteristic ion peaks other than m/z 44, during the decomposition of $CaCO_3$. This showed that, in spite of the ageing effect, traces of water, monitored at m/z 17 and 18, were evolved at high temperatures, above about 300°C, just before the decomposition. In addition, the m/z 17 peak was more intense than would have been expected if it were due to the fragmentation of H_2O^+. This indicates that some of the adsorbed water dissociated and was evolved as the OH species. The evolution of these water molecules could not be related to impurities (e.g., H_2CO_3, etc.), since their appearance did not coincide with that of any other characteristic ion peaks. Furthermore, it was found that the evolution of H_2O became more distinct when the salt had been subjected to ageing.

DISCUSSION

Based on the observations reported in this study, it became evident that there were two major factors controlling the decomposition temperature of $CaCO_3$ in vacuum, namely, the effect of adsorbed water molecules and ageing. The fact that the evolution of water molecules commenced at relatively high temperatures (i.e., > 300°C) indicates the possibility of a chemical (or valence) bond between adsorbate molecules (i.e., H_2O) and the surface of the anhydrous salt. This is confirmed by the observation that some of this water dissociated and evolved as the OH species. This phenomenon is indeed typical of the chemisorption process where relatively high temperatures are needed for desorption of the adsorbed gas.

Chemisorption, being a chemical process, frequently requires an activation energy and so proceeds at a limited rate which increases with rising temperature or pressure. Studies with clean metal wires have shown that chemisorption can be rapid even at low temperatures. Roberts [23] found that hydrogen was taken up rapidly by tungsten filaments both at room temperature and at liquid air temperature to give a saturated layer even at very low pressure (10^{-4} Torr). The heat of adsorption for this process was reported to be about 142 kJ mol^{-1}. Analogous results were obtained with oxygen, the initial heat of adsorption being as high as 460 kJ mol^{-1}.

It is feasible to assume that when the sample bottle containing pure $CaCO_3$ was exposed to the atmosphere, the chemisorption process for those particles situated at the surface is favoured by the period of ageing. Further exposure of new particles, by shaking of the sample bottle or when taking samples from it, etc., and/or introduction of fresh traces of airborne water vapour, by opening the sample bottle, will naturally increase the possibility of such chemisorption. When such a sample is subjected to heat the chemisorbed water molecules escape from the surface of the solid material, giving rise to the newly exposed surfaces. This increase in surface area apparently has a significant effect in increasing the possibility for early decomposition of the solid material. There are numerous reports concerned with the effect of the dehydration process on the decomposition of solid inorganic materials (e.g., refs. 24 and 25) and it is well known that the number of surface cracks, holes, dislocations, etc., is often crucially dependent upon the amount of water molecules present and the mode of heat treatment. It can thus be anticipated that, when the aged $CaCO_3$ was subjected to the linear heating rate in our experiments, the chemisorbed water molecules escaped, thus increasing the number of potential nucleus-forming sites at the surface of the solid and, hence, the decomposition

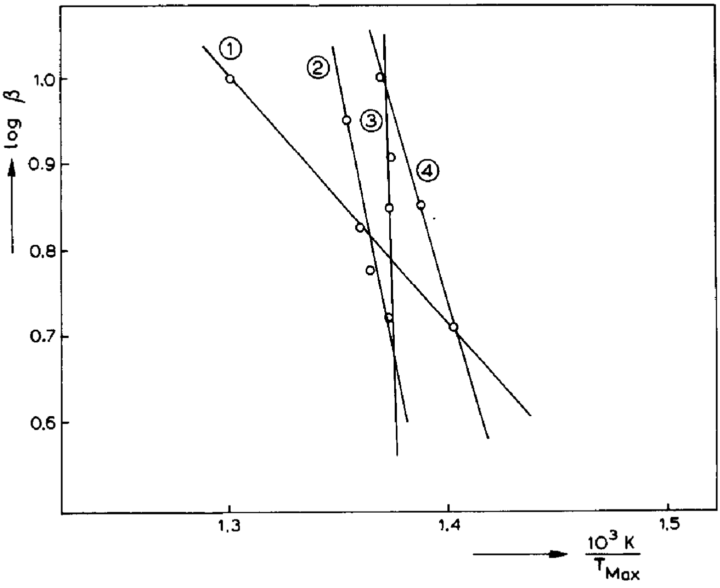

Fig. 3. Straight lines of negative slope drawn through appropriate data points taken from Fig. 2.

temperature decreased. The number of these potential nucleus-forming sites will be dependent upon the number of water molecules originally adsorbed on the surface of the solid. Also, since the samples for study were usually taken from the particles situated at the surface of the powder material, the degree to which the decomposition temperature increases, or decreases, will also be dependent upon how and where the samples were taken from the particular sample bottle.

In conclusion, it should be stated that, based on the present investigation, it is impossible to make any propositions for the decomposition mechanism (or kinetics) of the $CaCO_3$ since the ageing and adsorption phenomena were found to be responsible for the fluctuations of the obtained onset and peak temperature data.

Zsako and Arz [9] and others [13,15,26] have discussed the possibility of compensation behaviour for the decomposition of $CaCO_3$. This possibility was also taken into consideration here by further analysis of our data obtained on the aged material. To do this, only those points in Fig. 2 which could exhibit a straight-line fit (giving a negative slope) were considered (Fig. 3). From the slope and intercept of the various lines drawn, the corresponding E and A factors were evaluated assuming a first-order type mechanism and taking $\alpha = 0.6$ for all the maximum rates of reaction points. The values obtained are given in Table 2. Figure 4 shows the straight line obtained when these values are plotted according to the compensation equation.

$$\ln A = aE + b \tag{2}$$

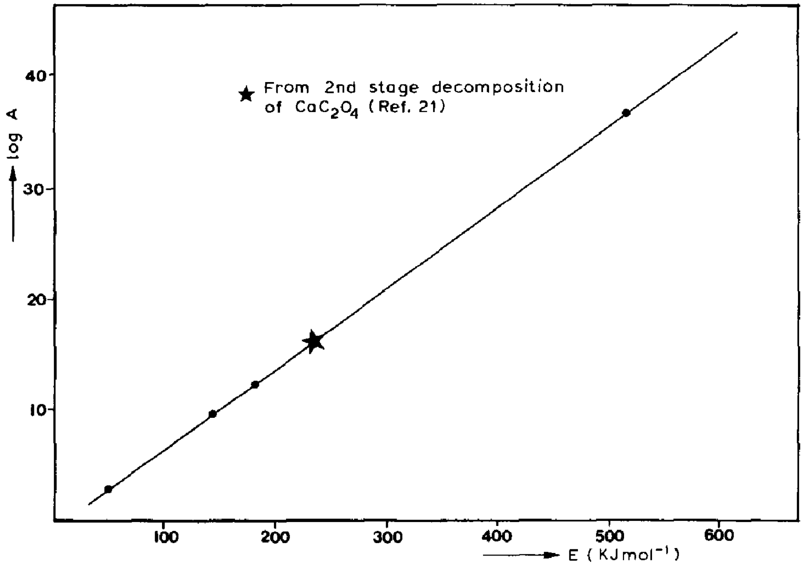

Fig. 4. Compensation plot for the decomposition of $CaCO_3$; data taken from Table 2.

TABLE 2

T_{max} for $CaCO_3$ decomposition at various heating rates together with E and log A values obtained for cases 1–4 of Fig. 3

Line	β (°C min^{-1})									E (kJ mol^{-1})	log A
	10.000	9.071	8.053	7.245	7.145	6.733	6.041	5.333	5.146		
Case 1	773.39	–	–	–	–	736.38	–	–	714.03	48.78	2.97
Case 2	–	740.85	–	–	–	736.38	733.14	728.54	–	180.92	12.29
Case 3	733.14	–	729.93	731.00	–	–	–	728.54	–	513.96	37.00
Case 4	733.14	–	–	–	721.81	–	–	–	714.03	192.59	9.73
Values taken from the second stage decomposition of CaC_2O_4 [21a]										231.08	16.55

The following compensation parameters were evaluated from the slope and intercept.

$a = 0.073$ mol kJ^{-1}; $b = -0.685$

It is interesting to note that even when the A and E values obtained for the second stage of decomposition of CaC_2O_4 [21a] were considered, the point was found to be exactly aligned with those for pure $CaCO_3$. Since the lines shown in Fig. 3 are drawn through the scattered points on an entirely optional basis, and regardless of the validity of such points, the perfect compensation plot with a linear regression of 0.9999 can merely be regarded as an artefact.

According to Garn [27] the kinetic compensation effect is only an apparent effect and it is due to the form of the Arrhenius equation which can be written in the following manner.

$$\log A = \frac{E}{2.303RT} + \log k \tag{3}$$

Thus, log A will be a linear function of E, and, comparing eqns. (2) and (3), the compensation parameters a and b are given by

$$a = \frac{1}{2.303RT} \text{and } b = \log k \tag{4}$$

The perfect linearity of the log A vs. E plot (Fig. 4) is a natural consequence of the fact that the Ozawa equation (1) is obtained utilising the Arrhenius expression.

That this is so can be further corroborated by using Garn's expression [4] to estimate a as the reciprocal of $2.303R\overline{T}$ where $\overline{T}$ is the mean of the $T_{\max}$ range given in Table 2, i.e., $\overline{T} = 744$ K. This gives $a = 0.070$ mol kJ^{-1} which is almost the same as that determined from the experimental plot. This new evidence endorses Garn's suggestion [27] that the linearity of the compensation equation can be due to the form of the Arrhenius equation and on this basis one cannot assign with certainty any physical significance to the obtained compensation parameters. This is in contradiction to the statements made by Zsako and Arz [9] and others [13,15,26].

The broad generalisation of an alternative theory based on a variety of reactions occurring simultaneously at a reaction interface, each with its own characteristic activation energy and pre-exponential term, also leads to a linear compensation effect (e.g., refs. 28 and 29). However, it does not necessarily follow that an experimentally observed compensation effect would be due to either the alternative theory mentioned immediately above or the theory based on the form of the Arrhenius equation discussed previously. It would seem, however, upon consideration of the manner in which the data shown in Fig. 4 were collected, that the discussion based on the form of the Arrhenius equation is most pertinent and the observed compensation plot is an artefact based on the data obtained.

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