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MASS SPECTROMETRIC DETERMINATION OF KINETIC PARAMETERS FOR SOLID STATE DECOMPOSITION REACTIONS. PART 1. METHOD; CALCIUM OXALATE DECOMPOSITION

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ABSTRACT

A description is given of an experiment in which a time-of-flight mass spectrometer is used to monitor the thermal decomposition of solid samples placed in the ion source region. Because the mass spectrometer can both identify and quantify the gaseous products, the technique yields direct insight into the decomposition mechanism as well as values for kinetic parameters. An assessment of the technique is given and its application illustrated by a study of anhydrous calcium oxalate decomposition "in vacuo". The decomposition occurred in two stages, the kinetic parameters determined being

1st Stage: $A = 6.3 \pm 0.5 \times 10^{21}\ \mathrm{s}^{-1}$; $E = 283 \pm 12$ kJ mole^{-1}

2nd Stage: $A = 6.0 \pm 0.5 \times 10^{14}\ \mathrm{s}^{-1}$; $E = 231 \pm 12$ kJ mole^{-1}

The decomposition mechanism is found not to be simple and thus the selection of calcium oxalate as a "model" compound to show the applicability of a particular method of analysing kinetic data obtained in vacuum is questioned.

INTRODUCTION

It has long been recognised that in order to make definitive statements about a chemical decomposition, the products must be identified and their relative quantities determined. This has led to the coupling of instruments capable of supplying this information to the more traditional methods of thermal analysis. Mass spectrometers are known as one of the most accurate and reliable instruments which can be used for evolved gas analysis in conjunction with the conventional thermal analysis techniques such as TG and DTA, etc [1].

It is possible, however, to obtain kinetic and mechanistic information for a solid decomposition reaction, in which gas is evolved, directly from the mass spectrometric data thus obviating the need for a TG instrument. This approach has been discussed by Wendlandt [1], Shulman [2], Friedman [3] and most recently by Smith [4].

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The basis of the experiment is that provided the ion current (H) measured for a characteristic mass spectral ion is proportional to the rate of gas evolution from the decomposing solid, i.e. the rate of weight loss, then the fraction α of the sample decomposed at time x is given by

$$\alpha_x = \frac{\Sigma_0^\infty H_x - \Sigma_x^\infty H_x}{\Sigma_0^\infty H_x}$$

thus the value of α against time (t), or temperature (T) for the rising temperature experiment can be determined from the area under the ion current against time (or temperature) curve. Thus conventional α/t or α/T curves can be obtained directly from the mass spectrometric data. Figure 1 compares the type of curve obtained when the ion current signal is plotted against either time or temperature with the conventional α/T curve obtained from a TG instrument.

This paper reports the development of a time-of-flight mass spectrometer to monitor the thermal decomposition of solid samples placed in the ion source region and the application of this equipment to a kinetic study of the decomposition of anhydrous calcium oxalate.

The monohydrated calcium oxalate has often been used as a model com-

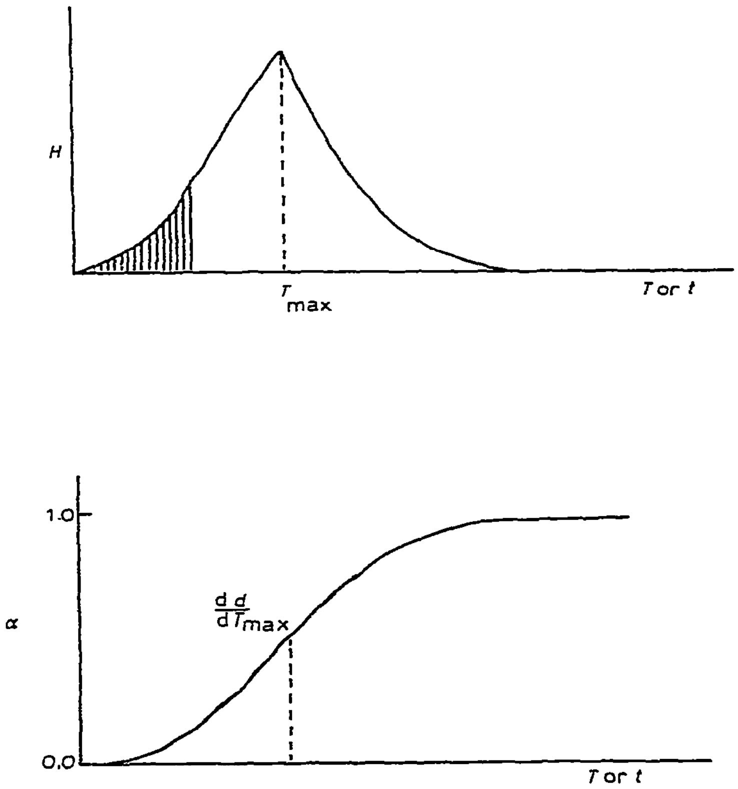


Fig. 1. (a) Mass spectrometric peak height (H) vs. temperature (T) or time (t) obtained from non-isothermal experiment. (b) α vs. temperature (T) or time (t) curve obtained via conventional non-isothermal thermogravimetric experiment.

pound to check the validity of a particular kinetic method. It is known that during the thermal decomposition of $CaC_2O_4 \cdot H_2O$ the following equilibrium reactions occur

$$CaC_2O_4 \cdot H_2O \rightleftharpoons CaC_2O_4 + H_2O \tag{I}$$

$$CaC_2O_4 \rightleftharpoons CaCO_3 + CO \tag{II}$$

$$CaCO_3 \rightleftharpoons CaO + CO_2 \tag{III}$$

Several authors have studied the kinetics of reactions (I) and (III) [5—8] and (II) [5,8—10] by means of TG, DTA and IR disc techniques. Most of these experiments were carried out under a static air atmosphere when reaction (II) is immediately followed by the heterogeneous exothermic reaction

$$CO + \tfrac{1}{2}\,O_2 \rightleftharpoons CO_2 \tag{IV}$$

which is often able to occur at the carbon monoxide formation temperature due to the catalytic effect of such crucible materials as, for example, platinum.

On the other hand, one of the characteristic features of the decomposition of alkaline earth oxalates is the formation of carbon dioxide via the disproportionation reaction

$$2\,CO \rightleftharpoons CO_2 + C \tag{V}$$

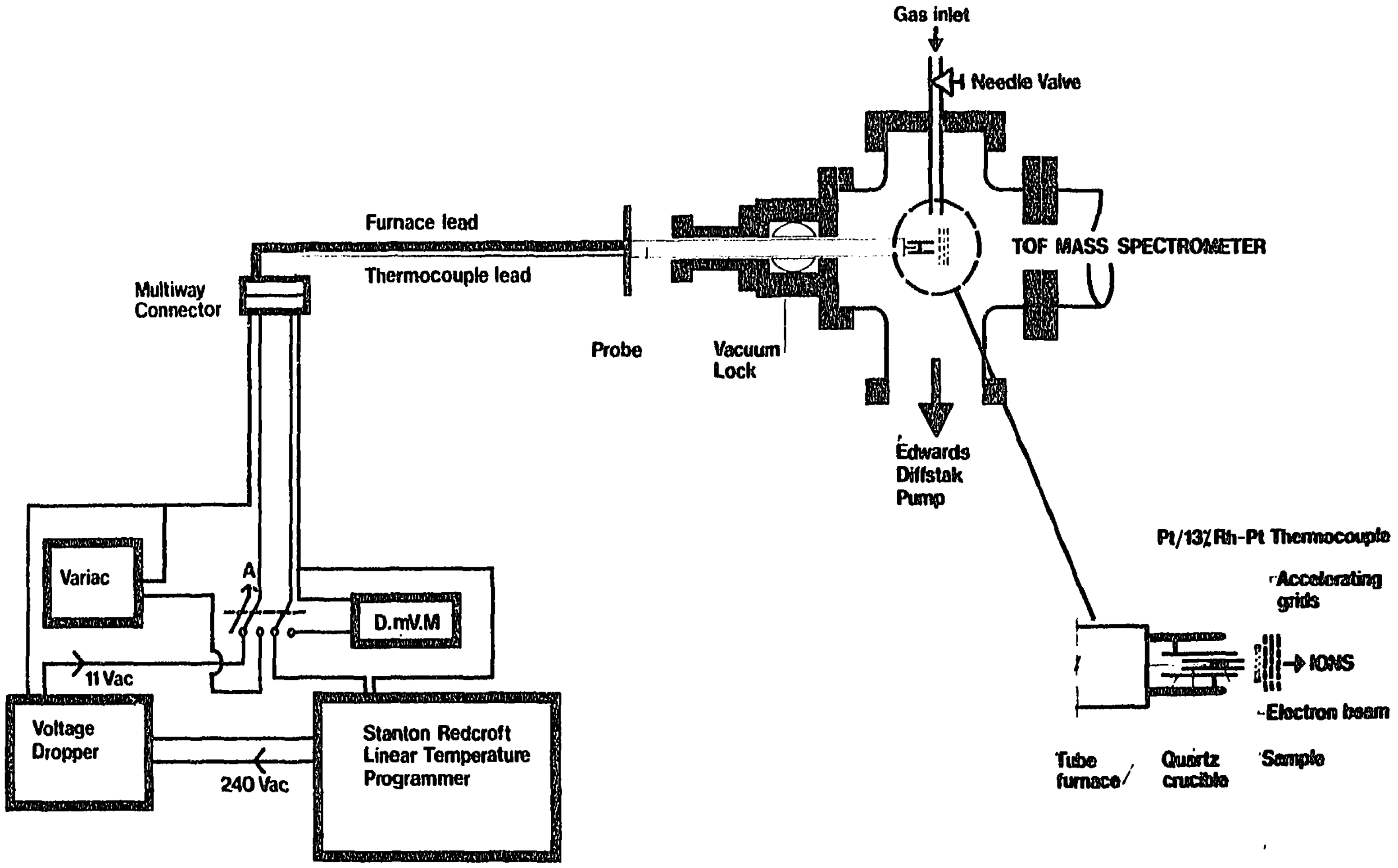
The extent of reaction (V) is reported to vary widely with the environmental conditions.

This feature was clearly demonstrated in the work by Passalis [11] who studied the thermal decomposition of strontium oxalate under various conditions. The importance of this disproportionation reaction of carbon monoxide has been neglected by many research workers (e.g. refs. 9, 10 and 12) who have used calcium oxalate as a model compound to test the validity of their kinetic method. We report results which clearly demonstrate that, although the decomposition of anhydrous CaC_2O_4 in "vacuum" produces good straight line Arrhenius plots, the mechanism of reaction can by no means be regarded as simple, and further studies are required to completely clarify the situation.

EXPERIMENTAL

Figure 2 shows a schematic diagram of the experiment. The ion source of the mass spectrometer is situated above an Edwards 100/300 Diffstak diffusion pump which is backed by a high speed rotary pump. Using Santovac 5 diffusion pump oil, this is capable of producing pressures below 10^{-6} Torr (i.e. 10^{-4} Nm^{-2}) during the decomposition.

Two inlet systems are available, the gas inlet system can be used to introduce calibration gases and also vapours or gases produced from an external unit, e.g. TG, DTA, GLC etc., whilst the Bendix Model 843 A direct insertion probe permits the introduction of solid materials into the ionisation region via the vacuum lock system which enables the probe to be inserted or



(A: TOFMS recorder 'on' switch)

Fig. 2. Schematic representation of mass spectrometric experiment.

withdrawn from the mass spectrometer without the latter being let up to atmosphere pressure.

The original Bendix thermocouple and furnace (tungsten—rhenium filament) systems have been changed to a 1 mm diameter Pt/13% Rh—Pt thermocouple and a special tube furnace. The tube furnaces were manufactured from 50 mm lengths of high purity alumina ("ALSINI" tubes 3.5 mm outer diameter and 2.5 mm inner diameter, open both ends) which were spattered with platinum to give a resistance of approximately 2—3 Ω over the whole length. The 50 mm lengths were then cut in half to yield two furnaces.

Power to the furnace is supplied via two platinum wires affixed at each end, good electric contact being ensured by a coating of platinum paste (N758, Johnson Matthey Metals Ltd.) which was cured by heating in a muffle furnace to 800—850°C. The completed furnace is positioned between two heater supply terminals so that the thermocouple is exactly in the middle. The leads from the heater terminals and the thermocouple are connected to a LVP/CA10/R/SP Stanton—Redcroft temperature controller. Because of the low thermal capacity of the furnace (approximately 1—2 Ω), the controller was especially modified by the manufacturer to give lower than normal current outputs. This is used in conjunction with an "in-house" voltage dropper (nominal output 10 Vac) to provide constant heating rates in the range 0.5—10°C min^{-1} with an accuracy of temperature control within 1°C. The temperature reading on the Stanton—Redcroft controller unit is taken as the crucible temperature, calibration experiments having shown that this was correct to within 0.5°C.

The sample crucibles are made from quartz tubing (1.2—1.5 mm diameter and about 2.5 cm length) which enabled samples to be heated up to 800°C. The crucibles are sealed in the middle so that they can be filled with sample from one end and then easily rested on the thermocouple from the other end. About 1—5 mg of sample is loosely packed in the quartz crucible which is then placed at the end of the probe. The sample is introduced into the ion source region of the mass spectrometer by passing the probe through the vacuum lock and left for sufficient time (e.g. overnight) so that any surface adsorbed material is pumped away. The sample is then subjected to a linear temperature rise and the required mass spectrometric information recorded during the decomposition. The ion current vs. temperature profiles can be obtained either by repeated scanning of the mass spectral region of interest or by continuous monitoring of a single characteristic peak. These are then used to calculate the α/T curve and hence kinetic parameters for the decomposition reaction.

The monohydrated calcium oxalate was prepared by dissolving 16.64 g of anhydrous calcium chloride in 1 l of deionised water. The precipitation was then made by drop-wise addition of 0.5 N oxalic acid solution (10 ml min^{-1}) whilst the solution was stirred rapidly at a constant temperature of 50°C. The white precipitate obtained was dried in a vacuum oven over the P_2O_5 at room temperature and then converted to the anhydrous material by heating in a TG 750 furnace at a heating rate of 10°C min^{-1} under flowing nitrogen gas. The weight loss was carefully recorded and when the dehydration was complete, the sample was cooled to room temperature under flowing nitrogen atmosphere and then placed in a storage bottle and kept in a vacuum desiccator until used. The TG measurement showed an 11.77% weight loss for the dehydration process which corresponds to 0.95 mole water of crystallization in the original calcium oxalate sample. Subsequent decomposition of the anhydrous salt gave a final weight loss value of 31.02% which is in good agreement with the expected value. The IR spectrum obtained when a sample of the anhydrous calcium oxalate was examined in a KBr disc was in good agreement with that previously reported [14]. Conventional analysis using standard $KMnO_4$ solution was also used to check sample purity and to confirm the absence of oxalic acid.

RESULTS

The anhydrous CaC_2O_4 samples were decomposed at various heating rates (4—10°C min^{-1}) and the characteristic ion peaks at *m/e* 28 and 44 were recorded using the continuous scanning mode of the mass spectrometer over the appropriate range. The ion current measured at *m/e* 28 is a composite of contributions from carbon monoxide, the background nitrogen and a major fragment ion of CO_2. The background contribution was determined from spectra taken immediately before the decomposition was initiated, whilst the CO_2 contribution was calculated from the *m/e* 44 ion current using an H_{28}/H_{44} calibration ratio previously determined for pure CO_2 gas. Thus ion current vs. temperature profiles for both CO and CO_2 produced via the decom-

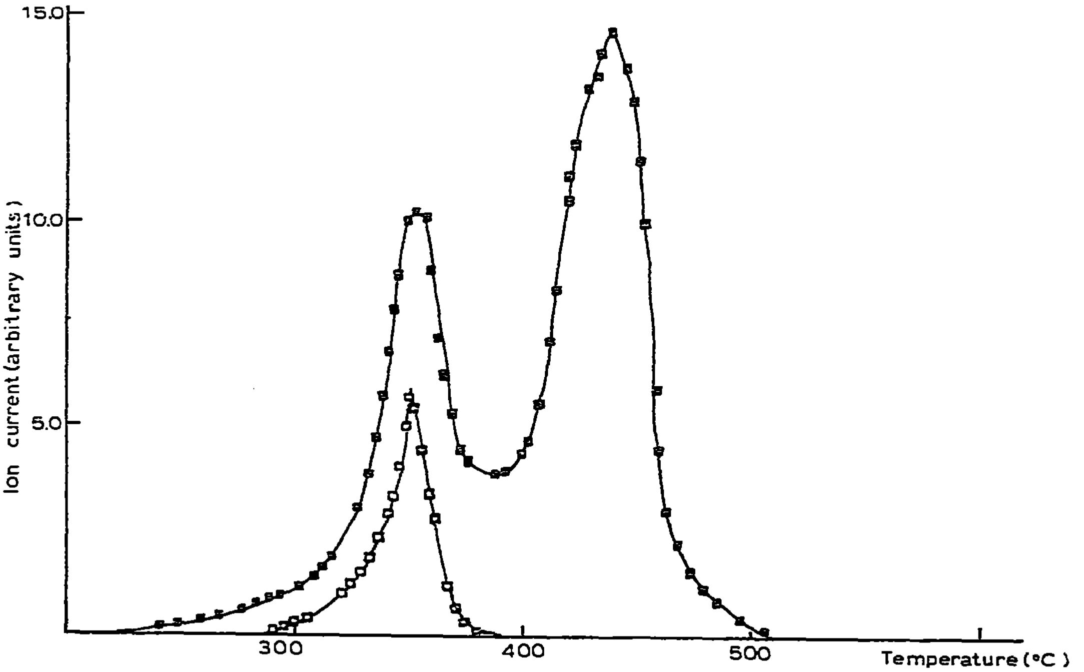


Fig. 3. Ion current vs. temperature profiles obtained for CaC_2O_4 decomposition. Linear heating rate 8.175°C min^{-1}. ▪, CO_2; □, CO.

position of CaC_2O_4 were obtained; Fig. 3 is typical of all the heating rates investigated. The profiles indicate that the decomposition occurs in two stages, in the first of which both CO and CO_2 are produced whilst only CO_2 results from the second. Calculation of α, from the areas under the H_{CO} vs. temperature curves obtained, showed that it had a maximum value of 0.6 ± 0.05, independent of heating rate, corresponding to the points at which the CO evolution is at a maximum. This may be regarded as an indication that the mechanism of the first decomposition stage remains isokinetic regardless of the different CO/CO_2 ratios being produced.

Evidence that the CO_2 produced during the first stage of the decomposition could be due to the disproportionation reaction (V) was investigated by experiments in which the furnace was switched off at the point where the CO_2 evolution reaches a minimum. Clear indications of black carbon traces were observed on visual inspection of the cooled residue; this was confirmed by X-ray analysis. It was not possible to quantify the extent to which reaction (V) occurred.

The values of the activation energy (E) and pre-exponental A-factor for both decomposition stages were calculated using the method of Ozawa [12] which is based on the equation

$$\log\beta = -0.4567\,\frac{E}{RT_\mathrm{m}} - 2.315 + \log_{10}\left[\frac{AE}{Rg(\alpha)}\right] \tag{1}$$

where β is the linear heating rate, T_M is the temperature at the maximum of the ion current/temperature profile, R is the universal gas constant, and $g(\alpha)$ is a functional form of α representing the mechanism. Figure 4 shows the plots obtained of $\log\beta$ vs. $1/T_\mathrm{M}$. From the slopes of these two straight lines, activation energies of 283 ± 12 kJ mole^{-1} and 231 ± 12 kJ mole^{-1} were calculated for the first and second stages of the decomposition of CaC_2O_4,

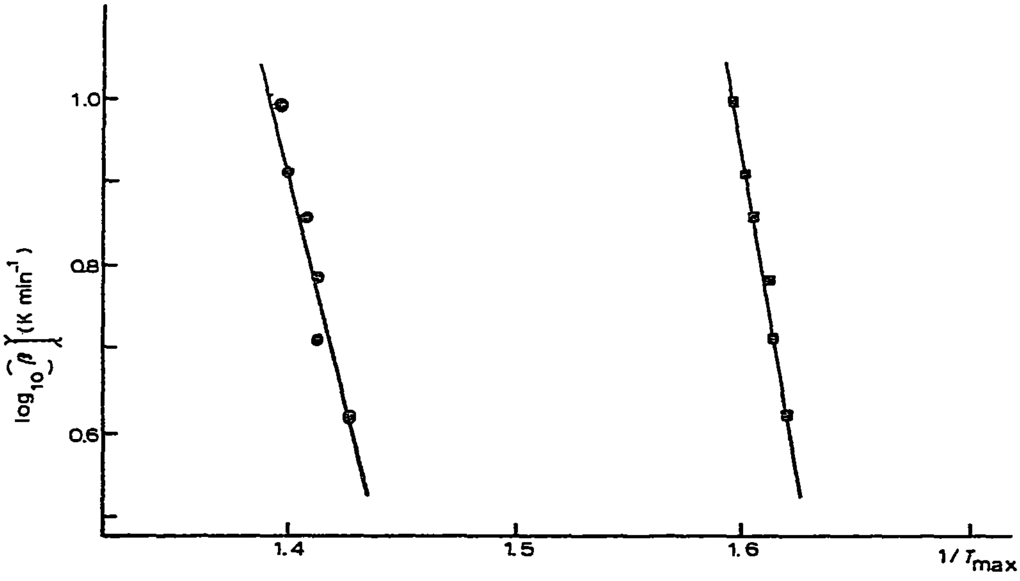


Fig. 4. Plots of $\log\beta$ vs. $1/T_\mathrm{max}$ obtained for CaC_2O_4 decomposition. ■, 1st stage; ●, 2nd stage.

respectively. Assuming the decompositions to be first order (see Ozawa [12]), then the intercept of the plots in Fig. 4 may be written from eqn. (1) as

$$\text{Intercept} = -2.315 + \log_{10}\left[\frac{-AE}{2.302R\,\log_{10}(1-\alpha)}\right] \qquad (2)$$

Thus the values of the A-factor were found to be $6.3 \pm 0.5 \times 10^{21}\ s^{-1}$ and $6.0 \pm 0.5 \times 10^{14}\ s^{-1}$ for the first and second stages of the CaC_2O_4 decomposition, respectively, but the assumption of a first order mechanism must be kept firmly in mind when assessing these values.

DISCUSSION

CaC_2O_4 decomposition

Most workers have studied the decomposition of $CaC_2O_4 \cdot H_2O$ at atmospheric pressure in either flowing or static air and naturally much emphasis has been placed on the possible oxidation of the CO evolved under these conditions. The present study, however, can be regarded as unique since the anhydrous CaC_2O_4 decomposition has been studied under high vacuum conditions with the simultaneous analysis of the evolved decomposition product gases. The first stage of the decomposition process results in the evolution of both CO and CO_2, and from the data plotted in Fig. 3 two significant features are evident. First, the initial CO_2 peak faithfully follows the CO peak and second, the two CO_2 peaks are well resolved. It is difficult to conceive that much of the CO_2 formed in the first part of the decomposition comes from carbonate decomposition, reaction (III), and it must be considered much more likely, in view of the detected presence of carbon in the solid phase, that it stems from the disproportionation reaction (V) taking place heterogeneously and sufficiently rapidly. The second stage is essentially the decomposition of calcium carbonate and this occurs at a somewhat lower temperature than that observed in air at atmospheric pressure (see for example ref. 13). This could be because the calcium carbonate resulting from the decomposition of calcium oxalate "in vacuo" is in either microcrystalline or amorphous form. The increased activity of materials in this form is well known and could be responsible for the lower decomposition temperature observed for the calcium carbonate produced in these experiments.

Table 1 collates the values of the kinetic parameters determined in this study with those previously reported in the literature. Our value of the activation energy for reaction (II) is in good agreement with that of Freeberg et al. [14], being some 20—40 kJ $mole^{-1}$ lower than the other values. The A-factor at $6.3 \times 10^{21}\ s^{-1}$ is closer to that of Gurrieri et al. [9] than that of Ozawa [12]. The activation energy currently reported for reaction (III) agrees closest with that of Abou-Shaaban and Simonelli [10].

In conclusion, it may be said that despite the very good agreement between the kinetic parameters obtained in this work and those reported by Freeberg et al. [14], the mechanism of reaction can by no means be regarded

TABLE 1

Kinetic parameters for CaC_2O_4 decomposition

Technique	Conditions	Reaction	E (kJ mole^{-1})	A (s^{-1})	Ref.
Mass Spectrometry	High vacuum $<10^{-4}$ Nm^{-2}	II (V overlaps) III	283 231	6.3×10^{21} 6.3×10^{14}	This work
TG/DTA/IR	Atm.	II	284	9.3×10^{14}	14
TG	Air; atm.	II	326	7.3×10^{26}	12
TG	Air; atm.	II III	310 163		5
DTG/DTA	Air; N_2 Static; flowing	II III	314 174	3.85×10^{19} 7.3×10^{5}	9
TG/DTG	Flowing N_2	II III	300 275		10

as simple. The increased amount of carbon being produced as a result of the disproportionation reaction might be expected to have a significant effect in altering the subsequent rates of decomposition in various regions of the solid material and also to increase or decrease the decomposition temperature of the $CaCO_3$ formed. The reported E and A values for both the first and second stages of decomposition are highly questionable unless the exact effect of catalytic carbon formation, sample size and vacuum conditions on the kinetic parameters are studied. Furthermore, it should be emphasised that the selection of CaC_2O_4 as a "model" compound to show the applicability of a particular method of analysing the kinetic data obtained in vacuum cannot be justified.

Assessment of experimental method

The advantages of using mass spectrometry for a direct study of a solid decomposition are that in addition to giving instantaneous evolved gas analysis (EGA), an α/T curve is obtained for each gaseous product and no knowledge of the initial sample weight, mass spectrometer sensitivity or non-volatile residue is necessary. Also, because of the very small sample size and the rapid removal of product gases by the fast pumping system, gas—residue reactions are significantly reduced. In this respect the decomposition conditions are very different from those of the conventional TG experiment.

The ability of the time-of-flight mass spectrometer to give simultaneous multicomponent analysis [15] at high sensitivities makes it a very powerful method for the study of complex decomposition reactions. This point is also emphasised in the paper by Smith [4] based on his studies on *trans*-dichlor-(ethylene) (pyridine) platinate(II). However, the value of the technique does depend upon the detailed behaviour of the compound under study. Ideally when the decomposition proceeds via one or more steps these will be well resolved and the mass spectrometric technique will then yield a series of sequential α/T curves from which the kinetic parameters of each step can be calculated. On the other hand, if the temperature regions for the various decomposition steps overlap under high vacuum conditions the interpretation of such curves to yield separate α/T curves, and hence kinetic parameters, for each step can be very difficult and often impossible. The problem will be further complicated if the parent species itself is significantly volatile and if its mass spectrum overlaps with that of the decomposition product.

The "in vacuo" conditions may lead to substantial pressure gradients within the sample with a consequent effect upon the kinetics [16—19]. Further, actual "blow-out" of the sample may occur, an effect which may be counteracted by means of a glass-wool pad or glass frit. Lower heating rates can help to reduce both these problems.

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