

Use of Solid Insertion Probe Mass Spectrometry and Constant Rate Thermal Analysis in the Study of Materials: Determination of Apparent Activation Energies and Mechanisms of Solid-State Decomposition Reactions

M. J. Tiernan,[†] P. A. Barnes,* and G. M. B. Parkes

Centre for Applied Catalysis, Materials Research Division, University of Huddersfield, Queensgate, Huddersfield HD1 3DH, U.K.

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Thermally induced reactions are of great importance in the manufacture and characterization of a very wide range of increasingly complex materials covering areas as diverse as ceramics and heterogeneous catalysts. Subsequently, there is a need for improved thermoanalytical methods that can provide enhanced resolution and a greater understanding of the energetics and mechanisms involved. This paper describes a new solid insertion probe mass spectrometer (SIP-MS) system that is designed to meet these needs by operating high vacuum with small sample masses. The SIP-MS system supports both conventional linear heating and a range of sample-controlled thermal analysis (SCTA) techniques including constant rate thermal analysis (CRTA). Its ability, in conjunction with the latter technique, to obtain reliable apparent activation energy measurements *throughout* a process under near-ideal experimental conditions is demonstrated. In addition, the system can discriminate between different reaction mechanisms and provide information on the often complex solid-state reactions found in calcination processes.

Introduction

Increasingly, materials manufactured by calcination have complex formulations and it is important to be able to understand, and quantify, the effects of the different components on the thermal decomposition reactions involved. To achieve these aims, high-resolution techniques are required to provide meaningful fundamental data.

Kinetic parameters for solid-state decomposition reactions have been widely investigated using methods based on the general kinetic equation:

$$\frac{d\alpha}{dt} = Af(\alpha) e^{-E/(RT)} \quad (1)$$

where A is the preexponential factor, T is the absolute temperature, t is the time, α is the fraction of sample decomposed, E is the activation energy, R is the gas constant, and $f(\alpha)$ is a function dependent on the reaction mechanism.

It is well-known that a number of factors are important in solid-state reactions in addition to the usual energy factors that relate to the chemistry involved. These include geometric considerations as well as nucleation, autocatalytic, and diffusion effects, all of which can produce significant deviations in the measured values of A and E for a given reaction.¹ In such circumstances, it is not appropriate to interpret E in terms of the usual energy barrier model of homogeneous chemical reaction kinetics and, for this reason, we prefer the term *apparent* activation energy.

One of the most widely investigated solid-state reactions is the decomposition of calcium carbonate² (CaCO_3). Reviews of the literature^{3–5} for this reaction have revealed significant variations in the measured values of E ranging from 142 kJ mol^{−1} to as high as 3828 kJ mol^{−1}. However, a critical analysis

of the reported values by Reading et al.³ indicated that a relatively reproducible value was obtained when only those studies that employed appropriate experimental conditions and calculation methods were considered. This led the authors to suggest that the activation energy of the thermal decomposition of CaCO_3 is in the range 210 ± 10 kJ mol^{−1} and that this value is meaningful in terms of the conventional energy barrier model of chemical reaction kinetics. Deviations from this value were attributed to the existence of mass or thermal transport influences under inappropriate experimental conditions with the measured value being particularly sensitive to the concentration of product gas (CO_2) in the vicinity of the reacting sample.^{2,3,5} It has been suggested that it is possible to measure the true activation energy for a solid-state decomposition provided care is taken to minimize such experimental influences³ or by employing a pressure correction term in the kinetic equation.²

One difficulty with conventional isothermal kinetics is that many experiments are required and, before the activation energy can be calculated, the reaction mechanism must be known or assumed. Nonisothermal techniques (i.e., linear heating thermal analysis) for the investigation of kinetic parameters have become popular because these take less time than a series of isothermal experiments at different temperatures.⁵ A relatively new development, constant rate thermal analysis (CRTA), when used in combination with the “rate-jump” method, has been recommended to provide measurements of the thermally activated step of a decomposition. This yields results that are much less dependent on experimental parameters than those obtained with conventional techniques,^{3,6,7} since the effects of heat and mass transfer are minimized.⁸ Our use of solid insertion probe mass spectrometer (SIP-MS) improves the experimental conditions by further reducing the temperature and concentration gradients within the sample, due to the low sample mass and high vacuum conditions employed.

[†] School of Chemical Sciences, Dublin City University, Ireland.

TABLE 1: Algebraic Expressions ($f(\alpha)$) for Common Reaction Mechanisms Operating in Solid-State Reactions

mechanism	symbol	$f(\alpha)$
one-dimensional diffusion	D1	$(1/2)\alpha$
two-dimensional diffusion	D2	$1/[-\ln(1 - \alpha)]$
three-dimensional diffusion (Jander equation)	D3	$3(1 - \alpha)^{2/3}/\{2[1 - (1 - \alpha)^{1/3}]\}$
three-dimensional diffusion (Ginstein–Brounshtein equation)	D4	$(3/2)[(1 - \alpha)^{-1/3} - 1]$
random nucleation; unimolecular decay law (first order)	F1	$(1 - \alpha)$
phase-boundary-controlled reaction (contracting cylinder)	R2	$(1 - \alpha)^{1/2}$
phase-boundary-controlled reaction (contracting sphere)	R3	$(1 - \alpha)^{2/3}$
two-dimensional growth of nuclei (Avrami–Erofeyev equation)	A2	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$
three-dimensional growth of nuclei (Avrami–Erofeyev equation)	A3	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$

Theory

Kinetic interpretation of thermal analysis data for solid-state decomposition reactions is normally carried out using methods based on eq 1. The aim is to determine the kinetic model that gives the best description of the reaction being studied and allows the calculation of meaningful values for the parameters E and A .

The most frequently cited kinetic models,⁹ listed in Table 1, can be categorized as diffusion-controlled processes (D1, D2, D3, D4), boundary-controlled or n -order reactions (F1, R2, R3), or processes involving random nucleation and subsequent growth of nuclei (A2, A3).^{10,11} It has been shown that the shape of CRTA curves can be used to distinguish between each of these three categories, but differences between similar models within each group are small and difficult to select unambiguously.^{11,12} Other methods to determine $f(\alpha)$ include those based on a prior determination of E , which can then be used to determine the kinetic model and calculate the remaining kinetic parameters.¹⁰

In the present study, activation energies for the decomposition of sodium hydrogen carbonate (NaHCO_3) were measured using both conventional linear heating and CRTA rate-jump techniques. This was done in order to contrast the different experimental conditions used by each technique and to confirm the validity of the latter. A further set of activation energies were also obtained for the thermal decomposition of CaCO_3 .

The additional ability of CRTA to provide an insight into the kinetic model (i.e., $f(\alpha)$) for each decomposition is demonstrated, and all results are discussed in relation to values, found using a variety of techniques, reported in the literature.

Linear Heating Rate Methods. Two similar methods that have been recommended¹⁰ for the determination of E from linear heating rate experiments are those developed by Ozawa¹³ and Kissinger.¹⁴ Data analysis for linear heating rate experiments in the current study was based on these methods.

Kissinger Method. This uses the following equation derived from the condition for the maximum rate on a thermoanalytical curve:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(-f(\alpha) A \frac{R}{E}\right) - \frac{E}{RT_m} \quad (2)$$

where β is the heating rate (K min^{-1}) and T_m is the temperature (K) of maximum reaction rate. E can be calculated from the slope of a plot of $\ln(\beta/T_m^2)$ vs $1/T_m$ for various heating rates. Although the first term on the right-hand side of eq 2 is only constant for first-order processes, it has been claimed that the error in the activation energy determined by this method for other kinetic models does not exceed 5%.¹⁰

Ozawa Method. This is based on the following equation:

$$\log \beta = -0.4567\left(\frac{E}{RT}\right) + C \quad (3)$$

where C is a constant. As for the Kissinger method, a series of

experiments are carried out using different linear heating rates and E is then calculated from the slope of a plot of $\log \beta$ vs $1/T$ for a given value of α . E is calculated for a range of values of α , thereby allowing any variations with the fraction of sample reacted to be determined. This method combines the advantages of allowing the calculation of E at various stages throughout the reaction without requiring prior knowledge of the kinetic model.^{5,7}

With both the Kissinger and Ozawa methods, it is important to ensure that the plots obtained are linear across the entire range of heating rates employed. Furthermore, experimental conditions should minimize temperature and pressure gradients during the reaction.^{5,7} These criteria require the use of low sample masses and pressure gradients for which our SIP-MS system is ideal, especially when using CRTA.

CRTA “Rate-Jump” Method. CRTA is one of a family of related techniques, given the generic name sample-controlled thermal analysis (SCTA), where the heating rate is not predetermined but rather governed by some function of the measured reaction rate of the process being studied. In CRTA the reaction is forced to proceed at a constant (and low) reaction rate by appropriate control of either the temperature⁸ or, for certain systems, the concentration of a reactant gas.¹⁵ Thus, rather than setting the heating rate at a predetermined value, the reaction rate is predetermined.¹⁶ Adopting this approach enables temperature and pressure gradients to be greatly reduced throughout the sample, minimizing the effects of heat and mass transfer.^{3,8,17}

CRTA can be modified to give the “rate-jump” method for determining kinetic parameters. Here, the rate of reaction is made to alternate between two preselected values, while the changes in sample temperature required to achieve this are monitored.^{8,18} Provided the reaction rate is allowed to reach equilibrium at the two successive rates, the corresponding temperature measurements can be used to calculate a value of E for the reaction using the following form of the Arrhenius equation:

$$E = R\left(\frac{T_1 T_2}{T_2 - T_1}\right) \ln\left(\frac{C_2}{C_1}\right) \quad (4)$$

where T_1 and T_2 are the temperature measurements corresponding to the two preset reaction rates C_1 and C_2 at the same value of α (extent of reaction).^{7,10}

The “rate-jump” method has the great advantage that the calculation of the apparent activation energy is independent of any assumptions regarding the mechanism of the process. However, as it assumes that any changes in $f(\alpha)$ during each temperature jump are negligible, the time taken to execute each jump must be as small as possible in comparison to the total duration of the experiment.³

A typical rate-jump measurement is illustrated in Figure 1. The temperature required to maintain a constant reaction rate is found to vary with the extent of reaction, depending on the

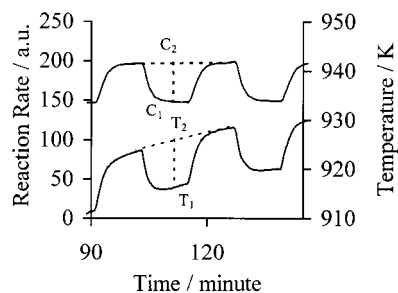


Figure 1. Temperature and gas-phase concentration profiles for a typical “rate-jump” experiment showing the construct used to obtain T_1 , T_2 , C_1 , and C_2 for the calculation of the activation energy E .

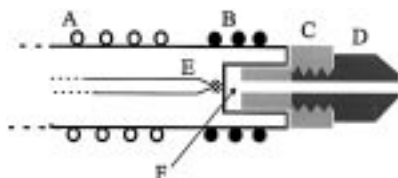


Figure 2. Schematic cross section of the solid insertion probe: A, water-cooling coil; B, thermocoax heating element; C, Nichrome plug; D, ceramic tip; E, thermocouple; F, sample cavity.

mechanism of the reaction. In some cases an initial gradual fall is replaced by a slow increase at higher α values. For other reactions, e.g., the thermal decomposition of NaHCO_3 , there is a different relationship with a continual rise in the temperature required to achieve a constant reaction rate. As a result of this variation of T with α , it is necessary, in many cases when performing rate-jump experiments, to estimate the temperature corresponding to a given rate of reaction by extrapolating back to the same value of α at which C_1 was measured, as indicated in Figure 1. In practice the extrapolation is performed using best-fit curves drawn through the higher and lower levels of successive “jumps” for both temperature and concentration. Furthermore, when a number of such rate-jump measurements are made, any variation in E throughout the reaction can be quantified.^{8,12}

Experimental Section

Equipment. Samples were analyzed using the SIP-MS system,^{19,20} which has been modified to provide improved temperature measurement, and to incorporate computerized data acquisition, and to control software²¹ capable of performing both linear heating and a range of SCTA techniques, including CRTA and rate-jump experiments.

The SIP, shown schematically in Figure 2, comprises a cylindrical microfurnace (12 mm \times 5 mm) positioned at the end of a water-cooled stainless steel rod that can be located, via airlock valves, directly into the source chamber of a VG Micromass 7070HS mass spectrometer. Temperature measurement is via a thermocouple (type K, chrome–alumel) located at the base of the sample holder to place it in virtually direct contact with the sample itself. The SIP can be heated electrically to a temperature of 1300 K via a Thermocoax winding. Samples in the mass range 10 μg to 10 mg can be analyzed depending on the density of the material under study.

The mass spectrometer is a very sensitive and stable double-focusing magnetic sector instrument with a resolving power of 25 000. For the current work, the instrument was operated in “peak select” mode in conjunction with an MID (multiple ion detector) unit using field switching, which allows direct measurement of up to 64 selected m/z values to give evolved gas profiles for each species selected. Switching the magnetic

TABLE 2: Experimental Conditions Employed for CRTA “Rate-Jump” Experiments

run	sample	sample mass (mg)	C_1 (mol CO_2 min^{-1})	C_2 (mol CO_2 min^{-1})	no. of rate jumps
A	NaHCO_3	10.0 ± 0.2	1.2×10^{-7}	1.5×10^{-7}	50
B	CaCO_3	5.0 ± 0.2	1.3×10^{-7}	1.6×10^{-7}	24

fields is preferable to changing the accelerating potential, since it avoids the mass discrimination effect inherent in the latter technique. This simplifies the acquisition of accurate data, which is invaluable when carrying out background subtraction. The use of a laminated magnet gives a maximum scanning speed of 100 ms/decade, providing the rapid response required for accurate control of the reaction rates.

The system utilizes software, developed by the authors and running under Windows 95 (Microsoft), for data acquisition and control, which provides a range of experimental techniques including conventional linear heating and a wide variety of SCTA methods such as CRTA.¹⁶ Voltages corresponding to the relative concentration of the species being measured are acquired from the MID unit via a 16-bit analog-to-digital converter (ADC, Strawberry Tree Dyna-Res). These values, together with the sample temperature, are processed and stored by a PC (P-II, 233 MHz, Viglen) and the required heating rate (for CRTA experiments) calculated, using a three-term PID algorithm to ensure good control of the reaction rate, as a series of temperature set points. These set point values are then sent to the furnace programmer (Eurotherm 818P), connected to the computer via an RS232C serial interface, which controls the power applied to the SIP Thermocoax windings.

In the current application, two ions, $m/z = 18$ (water) and $m/z = 44$ (carbon dioxide), were monitored alternatively for 500 ms each with the furnace temperature being modified every 1000 ms.

The combination of small sample mass, which reduces temperature gradients, and high vacuum (10^{-5} Pa), which minimizes diffusion problems and the possibility of back reaction between the solid product and the evolved gases, makes the SIP-MS ideal for kinetic studies of calcination and decomposition processes. These benefits are further increased when used with SCTA, and CRTA in particular, which allow measurements to be made in controlled pseudo-equilibrium conditions, thereby improving the quality and fundamental significance of the data obtained.

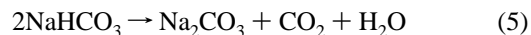
Materials. NaHCO_3 (BDH, AnalaR grade reagent) and CaCO_3 (Fisons, 99.9%) were used as supplied.

Experimental Conditions. Linear heating experiments on NaHCO_3 were performed using 4 ± 0.2 mg of sample at a series of heating rates of between 2 and 7 K min^{-1} .

The experimental conditions used for CRTA “rate-jump” experiments are shown in Table 2. Maximum and minimum heating and cooling rates of +10 and -10 K min^{-1} , respectively, were used with the rate being continuously varied under software control between these limits in order to alternate between the preselected CO_2 evolution rates C_1 and C_2 .

Results and Discussion

Decomposition of Sodium Hydrogen Carbonate. The decomposition reaction of NaHCO_3 in the range 373–453 K is represented by the equation²²



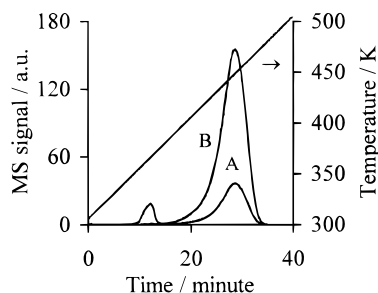


Figure 3. Decomposition of NaHCO_3 at a linear heating rate of 5 K min^{-1} : H_2O evolution profile (A) and CO_2 evolution profile (B). Note that the MS signal is directly proportional to the rate of reaction.

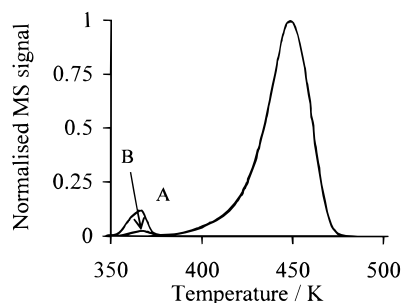


Figure 4. Decomposition of NaHCO_3 at a linear heating rate of 5 K min^{-1} , showing the degree of coincidence of the H_2O (A) and CO_2 (B) profiles after normalization.

A typical decomposition profile obtained under linear heating rate conditions is shown in Figure 3. [Note that the magnitude of the peaks is directly proportional to the rate of the reaction.] After a small initial peak, possibly associated with decomposition of surface groups, the evolution of CO_2 and H_2O occurs simultaneously throughout the main decomposition process.²³ This can be seen more clearly if the two profiles are brought exactly into coincidence by normalization (on a scale 0 and 1) to allow for the difference in response of the mass spectrometer to the two evolved species (Figure 4). The difference in the signals for the small initial peak is attributed to the loss of physically adsorbed water. Thereafter the two gases are evolved simultaneously and exactly in phase, showing that differences in phase found with other materials are not due to experimental problems.

For the range of linear heating rates investigated, a Kissinger plot of $\ln(\beta/T_m^2)$ vs $1/T_m$ was found to be a straight line with a linear regression coefficient (r^2) of 0.9984. Using eq 2, E was calculated to be 104 kJ mol^{-1} from the slope of this line.

The isoconversional Ozawa plots, obtained by plotting $\log \beta$ vs $1/T$ at the same degree of conversion (α) for various values of α , are shown in Figure 5. In general, the plots are parallel straight lines yielding similar values for E throughout the entire

TABLE 3: Activation Energies for the Decomposition of NaHCO_3 Calculated from the Data Shown in from Figure 5 by the Ozawa Method

α	E (kJ mol^{-1})	linear regression coefficient ^a
0.1	86	0.9999
0.2	80	0.9983
0.3	84	0.9889
0.4	91	0.9882
0.5	92	0.9852
0.6	89	0.9888
0.7	92	0.9909
0.8	92	0.9899
0.9	92	0.9936
average	89	0.9915
SD	4.4	

^a For isoconversional lines in Figure 5.

decomposition, which confirms that the activation energy calculated is independent of both α (at least for $\alpha > 0.3$) and β in the heating range investigated in the current study. Table 3 shows E values calculated from each of these straight lines using eq 3. The average value is 89 kJ mol^{-1} with a standard deviation (SD) of 4.4 kJ mol^{-1} . Ortega et al.⁵ reported that the activation energy for NaHCO_3 decomposition determined using the Ozawa method was independent of both α and β (for linear heating rates between 2 and 10 K min^{-1}). For α values of 0.3 and below, slightly lower values of E were determined. However, this phenomenon was not apparent in CRTA “rate-jump” results discussed below and may be associated with an overlap of the initial and main decomposition processes in linear heating experiments (see Figure 3). With the CRTA “rate-jump” method, the two processes are more completely resolved and the measurements are strictly associated with the main decomposition process.

Figure 6 shows a “rate-jump” experiment (run A in Table 2) on NaHCO_3 . The product gases, H_2O and CO_2 , are again seen to be evolved simultaneously and in phase throughout the main decomposition step in confirmation of the linear heating results. The temperature trace in Figure 6 shows how the sample heating rate was varied by the computer program in order to alternate between the two preselected target CO_2 evolution rates throughout the main decomposition process. E was calculated for each individual jump (Table 4). It appears that, in agreement with previous results,⁵ E is independent of α in that, while there is some scatter, there is no obvious trend. It is interesting to note that, under the conditions employed, the CRTA rate-jump experiments gave a lower standard deviation (2.5 vs 4.4) than the Ozawa model.

One of the most important criteria in determining the significance and validity of measured E values for solid-state decomposition reactions is the establishment of an independence from experimental conditions such as atmosphere, sample mass,

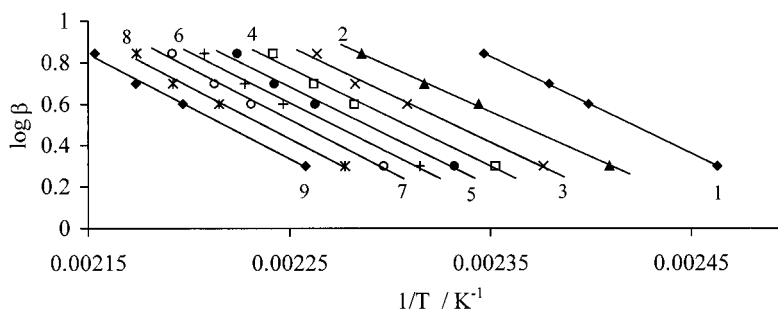


Figure 5. Isoconversional Ozawa plots for the thermal decomposition of NaHCO_3 at heating rates, β , of 2, 4, 5, and 7 K min^{-1} . Curves 1–9 represent plots calculated for α values of 0.1–0.9 at intervals of 0.1.

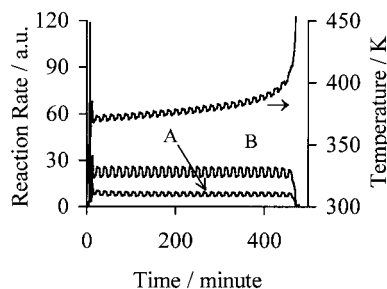


Figure 6. Decomposition of NaHCO_3 under CRTA "rate-jump" conditions (run A) with control on CO_2 evolution: H_2O evolution profile (A); CO_2 evolution profile (B).

TABLE 4: Activation Energies for the Decomposition of NaHCO_3 Calculated from CRTA "Rate-Jump" Experiments

α	E (kJ mol^{-1}) run A ^a
0.1	104
0.2	101
0.3	102
0.4	103
0.5	104
0.6	98
0.7	98
0.8	101
0.9	98
average	101
SD	2.5

^a For experimental details see Table 2.

heating rate, and experimental method.³ Table 5 compares our results using the Ozawa, Kissinger, and CRTA rate-jump methods (all using the SIP-MS) with other values found in the literature. It can be seen that the various techniques give results falling into two main groups. The methods of Ozawa and Friedman gave an average value of E of 90.3 kJ mol^{-1} , which is ca. 10% lower than that obtained from the Kissinger, Romero, and CRTA rate-jump methods (average value of $100.0 \text{ kJ mol}^{-1}$). In view of the inherent advantages of both the SIP-MS and CRTA, we contend that the latter values more closely represent the chemical activation stage of the process.

Higher values of E have been reported when the atmosphere used has contained CO_2 (a product of the reaction), which makes it more difficult for the reaction to proceed in the forward direction.²² This emphasizes the importance of controlling product gas concentrations in the vicinity of the sample in order to make meaningful kinetic measurements.^{3,4}

To the best of our knowledge, this is the first study that reports both the use of an SIP-MS system for the study of calcination processes and the application of the CRTA "rate-jump" method to the kinetics of NaHCO_3 decomposition.

In other studies,^{7,11} the switching of the reaction rate in "rate-jump" techniques has been achieved by alternatively increasing

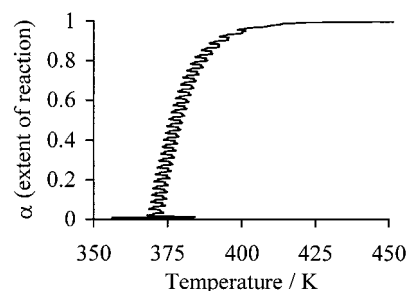


Figure 7. α vs temperature plot for the decomposition of NaHCO_3 under CRTA "rate-jump" conditions (run A).

and decreasing the rate at which product gas is removed from the sample with the result that sample reaction rate, and hence temperature, must increase to maintain the same residual partial pressure. In the present study, although the product gas pressure is not controlled in this way, the magnitude of the change in sample reaction rate is kept very small and, in combination with the high-vacuum conditions prevailing, minimizes any back reaction and diffusion-related problems.

The decomposition of NaHCO_3 has been reported to follow a first-order kinetic model, labeled F1 in Table 1, under linear heating rate conditions in an inert atmosphere.^{5,22,24} Figure 7 shows a plot of α vs temperature for the decomposition of NaHCO_3 under CRTA "rate-jump" conditions. The shape of this plot indeed confirms that the decomposition mechanism follows an " n -order" type of kinetic model (models F1, R2, and R3 in Table 1), although distinguishing between these three models¹¹ would require further work.

Decomposition of Calcium Carbonate. The decomposition of CaCO_3 (eq 6) has been widely investigated in thermal analysis studies:^{1,3,6,24}



The kinetics of this reaction have also been found to be highly sensitive to heat- and mass-transfer effects,^{3,4} and measured values of E are found to be particularly sensitive to the concentration of the product gas, CO_2 . Consequently, values of E reported in the literature^{3,25–27} range from under 200 to over 950 kJ mol^{-1} .

Table 6 shows the E values obtained in a "rate-jump" experiment (run B in Table 2) in the current study. The corresponding decomposition profile is shown in Figure 8. A low rate of reaction was purposefully chosen, and again, the change in reaction rate at each jump was minimized to limit the effects of CO_2 concentration. The average value of E from measurements made for each of the "rate jumps" in Figure 8 was $220.3 \text{ kJ mol}^{-1}$ ($\text{SD} = 5.9 \text{ kJ mol}^{-1}$). Dollimore and co-workers measured values of E for this reaction of between 200

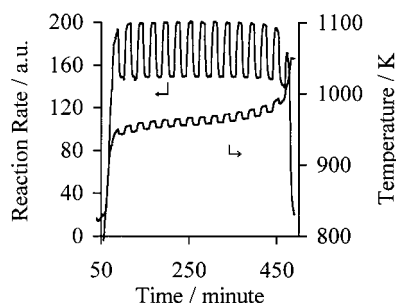
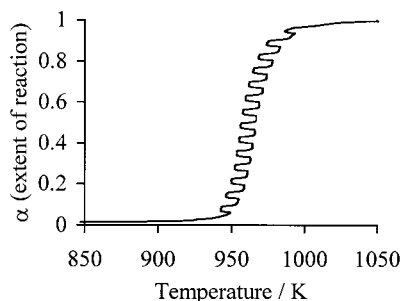
TABLE 5: Comparison of Activation Energies for the Decomposition of NaHCO_3 Found in This Work and in the Literature

source	E (kJ mol^{-1})	sample mass (mg)	atmosphere	heating rate (K min^{-1})	method
Oretega et al. ⁵	94	<i>a</i>	N_2	1.0–10.0	Ozawa
Heda et al. ²²	87	15–25	N_2	2.0–16.0	Friedman
	91	15–25	N_2	2.0–16.0	Ozawa
Romero et al. ²⁴	99	10	N_2	0.6–11.0	Romero
this work	89	4	vacuum	2–10	Ozawa
this work	104	4	vacuum	2–10	Kissinger
this work	101	8	vacuum	$\pm 10^b$	"rate-jump"
this work	96	4	vacuum	$\pm 10^b$	"rate-jump"

^a Not reported. ^b Maximum and minimum heating rate limits.

TABLE 6: Activation Energies for the Decomposition of CaCO₃ Calculated from CRTA “Rate-Jump” Experiment Run B

α	E (kJ mol ⁻¹) run B ^a
0.1	220
0.2	227
0.3	229
0.4	228
0.5	219
0.6	218
0.7	213
0.8	217
0.9	212
average	220
SD	6.3

^a For experimental details see Table 2.**Figure 8.** Decomposition of CaCO₃ under CRTA “rate-jump” conditions with control on CO₂ evolution (run B).**Figure 9.** α vs temperature plot for the decomposition of CaCO₃ under CRTA “rate-jump” conditions (run B).

and 230 kJ mol⁻¹ using various CRTA, linear heating, and isothermal techniques,⁶ while Romero et al. reported a value of E of 209 kJ mol⁻¹ under linear heating conditions in a flowing N₂ atmosphere.²⁴ Rouquerol et al. also reported a mean value of 209 kJ mol⁻¹ from a CRTA “rate-jump” experiment performed under vacuum.¹⁸ Such values, along with that determined in the current study, support the contention of Reading et al.³ that the true activation energy for this decomposition is about 210 kJ mol⁻¹, SD = 10 kJ mol⁻¹, with good agreement with values measured under near-equilibrium experimental conditions.

Figure 9 shows the plot of α vs temperature obtained for the decomposition of CaCO₃ under CRTA “rate-jump” conditions. The shape of this plot indicates that the decomposition mechanism follows an “ n -order” type of kinetic model (models F1, R2, and R3 in Table 1), although as mentioned above, distinguishing between these three models would require further work. Previous studies^{2,24} have also reported that the reaction mechanism is described by an order type model, although the apparent order obtained depended greatly on the experimental conditions.⁴

Conclusions

We describe a SIP-MS system using low-mass samples that are heated under high vacuum to provide near-ideal experimental conditions for the measurement of apparent activation energies and the study of mechanisms of solid-state decompositions that produce a gas, or gases. These benefits are enhanced when combined with SCTA techniques such as CRTA, which further reduce errors caused by variations in the sample temperature and the gas-phase concentration. However, many other factors that are sample-dependent may influence the apparent activation energy of thermal processes, for example, the grain size, crystallinity, purity, and thermal history of the material.

The SIP-MS system was used with both linear heating and CRTA techniques to study the decomposition of sodium hydrogen carbonate and calcium carbonate. Apparent activation energies of 101 kJ mol⁻¹, SD = 2.5 kJ mol⁻¹, and 220 kJ mol⁻¹, SD = 6.3 kJ mol⁻¹, respectively, were obtained from CRTA “rate-jump” experiments. The mechanisms of both reactions were found to be described by an n th-order expression where nucleation or diffusion are not the rate-controlling factors.

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