Journal of Thermal Analysis, Vol. 25 (1982) 299—311

THE USE OF TA – GLC – MS AS A QUANTITATIVE SPECIFIC EGA TECHNIQUE FOR THE INVESTIGATION OF COMPLEX THERMAL DECOMPOSITION REACTIONS: THE THERMAL DECOMPOSITION OF CALCIUM PROPANOATE

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(Received May, 22, 1982)

A versatile and flexible system is described for evolved gas analysis using a GLC, MS (mass scan and SIM modes) and GLC—MS. Gases evolved from materials in two differential thermal analysis units, a thermobalance or a micro-furnace linked directly to the MS or GLC can be analysed. Details are given of computer controlled data acquisition and processing. The techniques are applied to the thermal decomposition of calcium propanoate. Mechanisms are suggested to account for the observed decomposition products and the solid state process. Evidence is presented to support the view that the latter occurs via nucleation followed by two-dimensional growth with an activation energy of 315 kJ mol^{-1} and a pre-exponential factor of 4.8×10^{21}s^{-1}.

The value of thermoanalytical techniques in the study of thermal decomposition reactions is now widely recognised. Prior to detailed isothermal work DTA, DSC and TG are used frequently to identify both the number and temperature ranges of the thermal events experienced by a material on heating. An additional objective is to find conditions under which only one reaction occurs and where this is free from interferences caused by phase changes. Without this information the interpretation of decomposition kinetics is fraught with difficulty. The use of thermoanalytical techniques does not provide a complete solution however as it is not feasible to define the chemistry of the processes thus revealed without resorting to the use of a variety of ancillary techniques.

The classical approach to the problem of interpretation of thermoanalytical curves is to quench the sample, in a series of experiments, after each event and analyse the remaining solids using conventional chemical and instrumental methods. Whilst this is satisfactory in many cases a number of difficulties remain. For example high-temperature phase changes, if reversible, will not be detected at room temperature. The decomposition process might well reduce the crystallite size to a point where the products appear to be amorphous to X-rays. Solids produced by thermal decomposition often possess a large surface area and a high degree of reactivity, making them susceptible to reaction with oxygen, water and carbon dioxide in the atmosphere. Unless rigorous precautions are taken to exclude even traces of these gases the products observed on subsequent analysis may well be different from those produced in the original thermal decomposition.

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To overcome such experimental problems a number of simultaneous techniques have been developed. These have the added advantage that there can be little or no ambiguity in correlating the results of different techniques. While the simultaneous analysis of solid products is feasible by combination of DTA with high temperature XRD or IR such methods are rare due to the experimental difficulties involved. Fewer problems are found in analyzing the gases evolved during decomposition, a solution which has found favour with a number of workers. Given suitable EGA equipment one can improve considerably on the sensitivity of conventional TA methods. Furthermore, because of the specific response of many of the detectors used, detailed information can be obtained on the chemistry of the processes. This imparts the considerable advantage that where decompositions are complex and occur via more than one reaction it is possible to follow the course of each individual process. In such cases the use of classical weight-loss or pressure-increase methods in the study of kinetics is completely invalid. However specific EGA techniques can be used, if suitably designed, isothermally or otherwise, to follow kinetically the course of each separate reaction. In this way a much more detailed picture can be obtained for the entire thermal decomposition.

Many techniques have been used for EGA ranging from simple specific detectors such as an electrolytic hygrometer to detect water vapour [1] to infra-red spectroscopy [2] and gas-liquid chromatography [3]. While these and other techniques have been used successfully and have a variety of advantages none of them can be considered as universally applicable. Perhaps the most sensitive and versatile EGA detector is the mass spectrometer. Early workers using simple mass spectrometers with limited scan speeds and resolution established the potential of MS in this field. For example, Langer and Gohlke compared the relative advantages of heating the sample in the MS source, where identification of the evolved gases is instantaneous and there is no possibility of subsequent gas phase reactions, to using the MS to analyze gases evolved in a normal DTA. In the latter case a purge gas was used to sweep the gas-phase products into the MS. The advantage of this method is that the product gases are evolved under the atmospheric conditions in the DTA and as a result they are much more closely related to the shape of the DTA curve. The high vacuum in the MS source can affect very considerably the course of a decomposition giving little apparent correlation with DTA curves obtained at atmospheric pressure [4, 5].

Both methods have unique advantages and ideally both should be used in any investigation. However most later workers have opted for either one or the other approach. Price *et al.* [6] used a temperature programmed solid insertion probe in a time-of-flight MS to study the decomposition of cadmium oxalate. Smith and Johnson [7] working on the thermal analysis of natural material developed a simultaneous TG – DTG – DTA – EGA technique in which the thermal analysis equipment was coupled externally to a small quadrupole MS.

While such techniques are ideal for measuring simple mixtures of low molecular weight gases, problems of the interpretation of the mass spectra arise with complex mixtures of larger molecules.

One approach to this problem has been to use chemical ionisation (CI) rather than electron impact (EI) to minimize fragmentation and thus simplify the mass spectra very considerably. An advantage of this approach, developed by Baumgartner and Nachbaur [8] is the higher source pressure (100 Pa) which leads to fewer problems in interfacing the MS with thermal analysis equipment. Other workers have exploited high resolution MS [9] in conjunction with GLC and on-line data processing [10].

The object of the work described here was to develop a low-cost versatile system capable of use in both single and complex thermal decompositions utilising to the full the advantages of gas-liquid chromatography, mass spectroscopy and modern micro-computer control, data acquisition and processing facilities. A prime aim has been to do this using standard commercially available equipment linked using inexpensive components which can easily be modified to retain maximum versatility. The system first developed employed either coupled simultaneous DTA – MS or TG – MS [11]. Work with more complex materials demonstrated the need for a preliminary separation of evolved gases prior to presentation to the MS and an on-line GC – MS system was developed [12]. Recently the system has been modified to include greatly improved computing facilities which have proved invaluable in kinetic studies.

The preparation of symmetrical ketones by heating the calcium salt of a corresponding carboxylic acid appears to be one of the standard techniques of preparative organic chemistry, which was first reported in 1858 [13]. However it was not until the work of Sichels *et al.* [14] in 1961 and Hites *et al.* in 1972 that is was realized that the simple mechanisms proposed for the reaction were ill-founded. The latter proposed a series of free radical reactions which accounted for the formation of the symmetrical ketone and the corresponding alkanes and alkenes. From the parent radical an homologous series of lower ketones could be produced as the former broke down to give smaller alkyl radicals. Despite the usefulness of such reactions little detailed investigation has been carried out on the calcium salts of the monocarboxylic acids higher than ethanoic acid using modern techniques. Chaudhuri's investigation of the kinetics of decomposition of calcium propanoate was slightly marred by a rapid initial temperature rise of some 25 K and the results of Charbonnier and Gobert-Ranchoux [16] differ in some respects from those of Ferloni who used different experimental conditions. In view of the paucity of authoritative literature it was felt that a study of the kinetics of decomposition of calcium propanoate by coupled simultaneous TA – GLS – MS was justified.

Experimental

A block diagram of the system is shown in Fig. 1; full details of the interfaces have been described elsewhere [12]. In essence one can use a variety of thermoanalytical equipment (Stanton Redcroft DTA 671B (77 – 780 K) Stanton Redcroft DTA 673 (300 – 1300 K), Stanton Redcroft TG 750 (300 – 1300 K) and a small micro-furnace (300 – 1300 K)). The latter is particularly useful for kinetic work as the sample container is in direct physical contact with the temperature measuring thermocouple thus assuring satisfactory control and measurement of the sample temperature. This is achieved at the expense of TG information which is redundant however as the α values can be found from the EGA profile as a fraction of the total amount of the gas lost. A further advantage is that the sample can be viewed through an observation port via a low-power stereo microscope.

The mass spectrometer, which has been described in detail previously, has a useful mass range of up to 500 with a maximum scan speed of 0.1 s. Of particular interest is the selected ion monitoring mode of operation (SIM) under which the accelerating potential is rapidly switched (0.025 s) between four values enabling a virtually continuous readout to be obtained of up to four m/e values. Thus the rates of evolution of up to four different gases can be followed so that the progress of individual reactions can be studied in the presence of other gas-evolving processes.

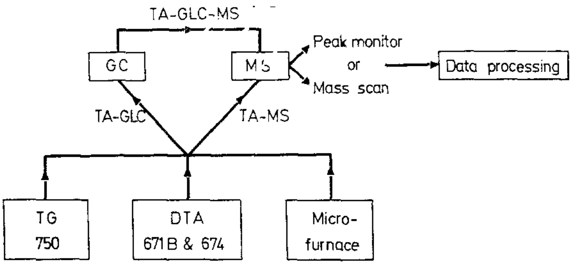

Fig. 1. Schematic diagram of the TA – GLC – MS system

The gases evolved can be analyzed by a number of different routes. For simple systems TA – MS, either using rapid mass scans or SIM can be used. In cases where the complexity of the gases warrants it GLC can be used either alone or in combination with the MS which can be used in the mass scan or SIM mode.

In a typical investigation a series of mass spectra is taken during the course of a TG experiment when the equipment shows a weight loss process is occurring.

An alternative approach is to pass the gases through the on-line sampling loop, a 50 cm spiral of 4 mm external diameter glt or stainless steel, which is connected to the GLC via a 6-way valve. Rapid 'injections' from the loop to the GLC can be made, the frequency of which is limited only by retention times of the products on the column. In this way evolved gas profiles can be built up, the MS being used as each material is eluted from the column to identify it. If the separation under the conditions required to give the small retention times required by this mode of operation is insufficient or if trace products are sought, the sampling loop can be cooled in liquid nitrogen. When sufficient products have been accumulated, the contents of the trap can be flash heated onto the GLC column and the MS used on-line in conventional mass scan or SIM modes to identify the individual components.

Once the products have been identified using one of the above techniques, SIM is used in subsequent experiments to follow the rates of evolution of up to four gases simultaneously in either isothermal or temperature programmed work. This enables studies to be made of the kinetics of complex reactions where a number of processes occur at the same time or perhaps overlap.

The voltage outputs of the thermobalance, DTG unit, DTA, GLC and the four channels of the MS operating in the SIM mode are fed into an 8-channel 12-bit analogue to digital converter (ADC) made commercially for Holdene Ltd. The ADC is capable of 12-bit accuracy (1 part in 4096) and can operate at sampling speeds of up to 500 Hz. It is controlled by a CBM 4032 microcomputer which can be used to select the number of channels required, to adjust the sensitivity of each, to select a uni- or bipolar input for each, to control the number of samples taken per output value (for noise averaging) and to select the delay between output values. The latter parameter is adjusted to obtain between 200 and 500 readings per channel per experiment so that the kinetic curves and sample temperatures can be adequately defined. The readings are held initially in the CBM 4032 RAM and transferred subsequently to a CBM 4040 disc unit for permanent storage. From the data α – time values are calculated and the results treated by the usual methods involving the kinetic expressions commonly used to analyse thermal decomposition reactions. Hard copy can be obtained using an Epson MX80 F/T type II printer using an Aculab Centronics – IEEE interface. The CBM 4032 is fitted with a high resolution board capable of a resolution of 200×320 pixels so that the validity of the various kinetic functions can be examined on the screen and retained via the printer. True high resolution curves (0.1 mm) can be obtained via a Honeywell 66 mainframe computer to which the CBM is linked via an acoustic coupler.

Results

Calcium propanoate (ex Wilkinson Vickers Ltd.) was crystallized from boiling methanol, washed and dried at 330 K for 10 hours. Replicate analysis for calcium by titration with standardised EDTA solution by the method described in Vogel gave a value of 21.18% (theoretical 21.52). The purified sample was a white powder which completely passed a 200 mesh sieve.

X-ray powder diffraction (Debye-Scherrer) analysis showed the samples as prepared were amorphous to X-rays but after heating through a small irreversible exotherm at 490 K and cooling, the pattern matched fairly closely that reported by Charbonnier *et al.* [16].

DTA, using a purge of N_2, showed (Fig. 2), in addition to the exotherm mentioned above, a sharp endotherm at 673 K which was confirmed as melting by visual observation. A broad endothermic peak next occurred due to decomposition of the calcium propanoate, which at higher temperatures was complicated by a series of sharp spikes as the product gases were released from the bubbling melt. In air the decomposition became highly exothermic due to the oxidation of the organic prod-

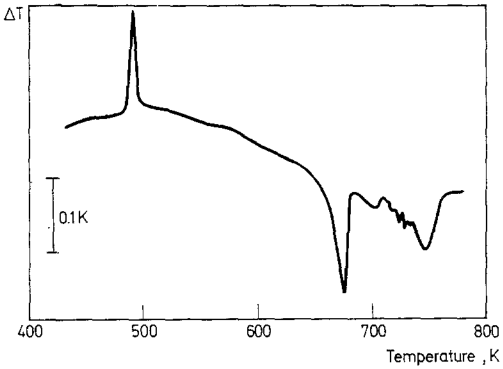

Fig. 2. DTA curve for calcium propanoate using the Stanton Redcroft DTA 673, with high sensitivity head. Sample mass — 1.4 mg, heating rate — 10 degree min^{-1}, atmosphere — N_2 flowing at 200 cm^3 min^{-1}

ucts. In both cases the solid remaining at 800 K was shown to be $CaCO_3$ by XRD.

For TG (Fig. 3) small sample weights (700 μg) were used to minimize the effects of bubbling. In helium two main weight losses were observed. The first was due to decomposition of the calcium propanoate to the carbonate which subsequently de-

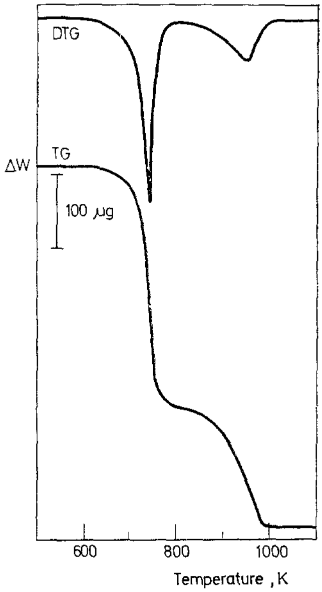

Fig. 3. TG and DTG curves for calcium propanoate. Stanton Redcroft TG 750. Sample mass — 0.69 mg, heating rate — 30 degree min^{-1}, atmosphere flowing helium (50 cm^3 min^{-1})

composed to form CaO as confirmed by XRD. At fast heating rates (30 K min^{-1}) the TG results agreed closely with the scheme

$$Ca(C_2H_5CO_2)_2 \rightarrow CaCO_3 \rightarrow CaO,$$

the weight losses being respectively 46.1 % (theoretical 46.2 %) and 23.5 % (theoretical 23.7 %). At lower heating rates (down to 1 K min^{-1}) some carbon was formed as the gaseous products underwent a slow partial oxidative degradation with the oxygen present, at a very low level, in the helium purge stream. The results can be explained by assuming the rate of this process is limited by the rate of oxygen supply so that at low heating rates the extent of the reaction is greater. The carbon thus formed burnt off slowly between the two major weight loss processes.

The next stage in the investigation was to analyse the evolved gases. Using a helium carrier gas stream of 70 cm^3 min^{-1} and heated glass lined capillary tubes to connect the TG750 to the gas sampling loop and the GLC – MS, the gases evolved over the first decomposition were trapped by cooling the sampling loop in liquid nitrogen (Fig. 4). At the end of the experiment the contents of the loop were flash-heated onto the GLC column, a 2.1 m × 4 mm i.d. glass column packed with Poropaq Q. A 50 : 50 splitter was used to direct the column effluent in equal amounts to the Katharometer detector of the Pye 204 GLC and the jet separator of the MS. Mass scans were taken at the maximum of each GLC peak. The chromatogram,

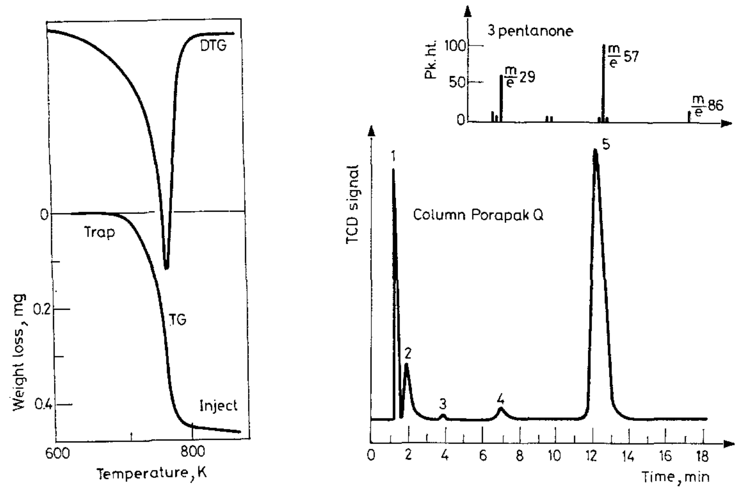

Fig. 4. TG, DTG and TG – GLC – MS of calcium propanoate. The gas – liquid chromatogram is shown of the volatiles trapped — as indicated — during the first weight loss process, the decomposition of calcium propanoate to calcium carbonate. A typical mass spectrum of one of the components is shown as is the identify of the remaining materials giving GLC peaks. Sample mass — 1 mg, heating rate — 30 degree min^{-1}, atmosphere — flowing helium (70 cm^3 min^{-1}) 1. H_2O, 2. CO_2, 3. C_2H_5CHO, 4. $C_2H_5COCH_3$, 5. $C_2H_5COC_2H_5$

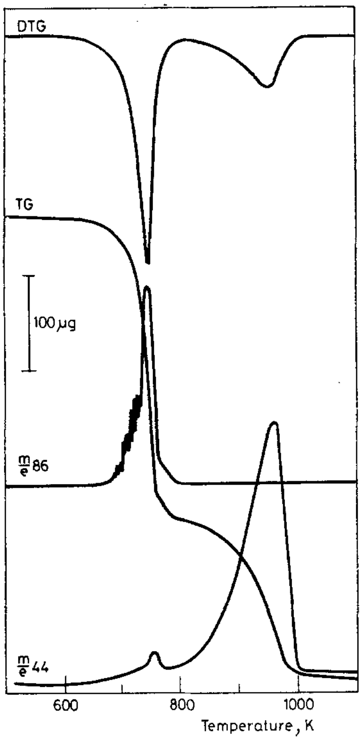

Fig. 5. TG and DTG with simultaneous MS (SIM) with continuous monitoring of the m/e 86 and m/e 44 peaks of calcium propanoate (3-pentanone and CO_2 respectively). Sample mass — 0.69 mg, heating rate — 30 degree min^{-1}, atmosphere — flowing helium (50 cm^3 min^{-1})

a typical mass spectrum and the identity of the various components are also shown in Fig. 4. The major component, 3-pentanone, accounted for over 90% of the total evolved gases. In order to check that the other products were not due to degradation of the 3-pentanone in the furnace of the TG 750 or in transit to the MS via the various heated lines, a sample of the pure material was injected into the pre-heated furnace, trapped, flash heated and analysed by GLC–MS as before. Although no organic molecules, other than 3-pentanone, were found, there was some indication of CO_2 and H_2O at variable, low, levels due possibly to minute air leaks in the system.

Having established that the major component in the evolved gases is 3-propanone a further temperature programmed TG–MS (SIM) experiment (Fig. 5) confirmed that the evolution of this material took place in a single step. The m/e 44 trace proves that the minor reaction which occurs between the two major weight-loss processes mentioned previously is due to the evolution of CO_2. The extent of the carbonisation reaction which eventually gives rise to this CO_2 can be assessed by

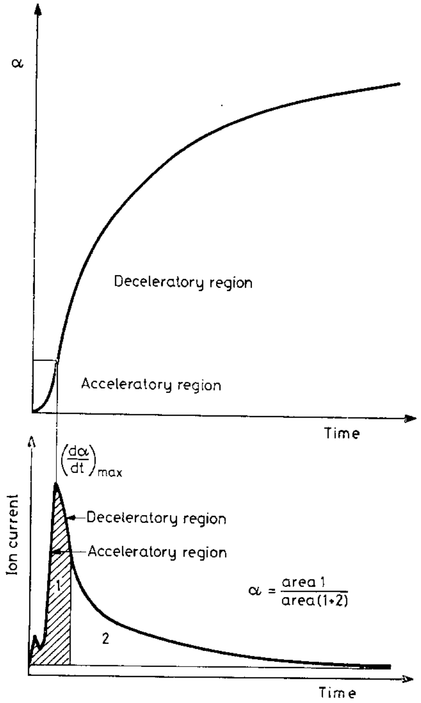

Fig. 6. An evolved gas profile showing the two processes found in the decomposition of calcium propanoate and the derived α-time curve

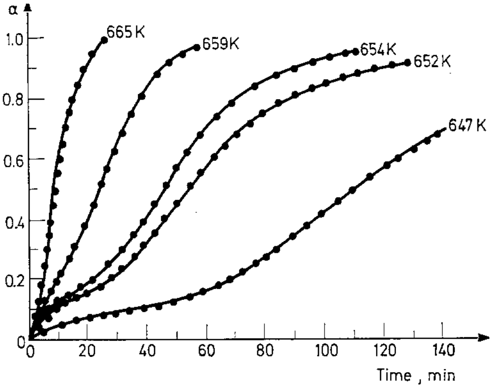

Fig. 7. α-time curves for the isothermal thermal decomposition of calcium propanoate. The reaction was carried out in the separate microfurnace linked directly to the jet separator of the MS. The MS was set to monitor the *m/e* 86 (-pentanone) peak. Nominal sample masses — 0.3 mg, atmosphere — flowing helium (150 cm^3 min^{-1})

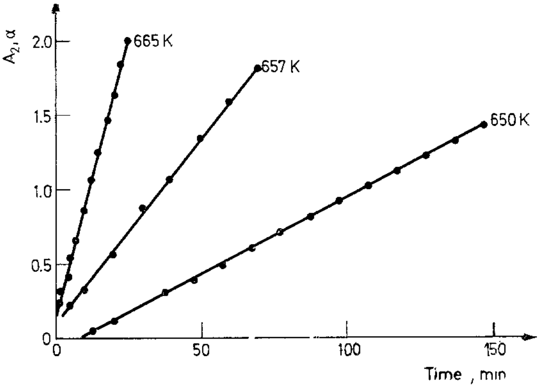

Fig. 8. Typical Avrami—Erofeev ($n = 2$) plots for the isothermal decomposition of calcium propanoate. α and time values were corrected to zero for the start of this, the second process. α values were calculated from the SIM (m/e 86) data

comparing the size of the first CO_2 peak to that of the second, which is due to the decomposition of $CaCO_3$. From the relative peak areas the results indicate that, in this case, approximately 0.8% of the 3-pentanone was broken down. At slower heating rates the spikes on the m/e 86 peak, due to bubbling, were found to be absent. Comparison of the DTG and m/e 86 peaks illustrates the virtually instantaneous response of the MS system.

Isothermal kinetic studies of the decomposition of calcium propanoate were carried out using the separate micro-furnace attached directly to the jet separator inlet of the MS. Great care was taken to minimise the minute air leaks mentioned previously. The sample weights used were of the order of 300 μg to eliminate effects due to diffusion of gaseous products through the mass of the sample. All reaction temperatures were below the melting point, as indicated by the DTA melting peak temperature, a conclusion supported by microscopy. The fact that the DTA curve

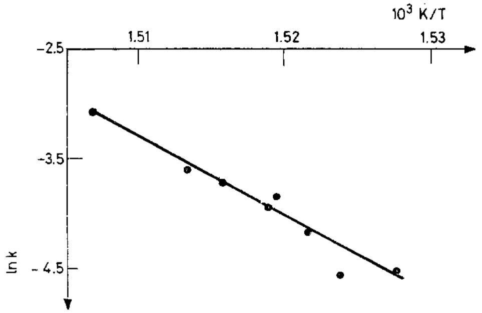

Fig. 9. Arrhenius plot for the rate constants derived from the Avrami—Erofeev equation with $n = 2$, for the isothermal decomposition of calcium propanoate as determined by EGA (SIM on m/e 86)

(Fig. 2) appears to show a decomposition after the melt is due to the dynamic nature of the technique. A close examination of the DTA curve prior to the melting endotherm reveals an increasingly sloping baseline from approximately 600 K onwards, which the isothermal EGA work shows to be due to decomposition.

Under the conditions used for this isothermal work simultaneous monitoring of the *m/e* 44 peak showed the breakdown of the 3-pentanone to CO_2 to be less than 0.5%.

The evolved gas profiles consisted of two major regions, as illustrated in Fig. 6, which also shows how the α-time curves are generated from the evolved gas profiles. The initial process, the extent of which varied with temperature from $\alpha = 0.1$ to $\alpha = 0.20$, proved difficult to analyse as it occurred during the first few minutes of the reaction during which the sample was reaching reaction temperature. Measurements show that the reaction temperature is achieved in much less than a minute which is still an appreciable percentage of the initial reaction time. For this reason the major process was treated separately and the α and time values rescaled to zero at the minimum in the EGA curve between the two reactions. Such a procedure can be justified for consecutive processes which are well resolved.

Some of the rescaled α-time curves for the second process are shown in Fig. 7. These sigmoidal curves were best described by the Avrami-Erofeev equation with a value of $n = 2$ where plots of $F(\alpha)$ against time gave straight lines in the range of $0.01 < \alpha < 0.9$ to 1.0 (Fig. 8). Regression analysis of the Arrhenius plot, using values of rate constants derived from slopes of the Avrami-Erofeev plots, with $n = 2$ (Fig. 9) gave a correlation coefficient of 0.98, an activation energy of 315 kJ mol^{-1} and a pre-exponential factor of $4.8 \times 10^{-21} s^{-1}$.

Discussion

Mechanism

Following the free radical mechanism of Hites and Biemann [17], proposed for the decomposition of the calcium salts of monocarboxylic acids we suggest that the initial stage in the decomposition of calcium propanoate can be represented as:

$$Ca(C_2H_5COO)_2 \rightarrow CaCO_3 + \dot{C}_2H_5^{\cdot} + C_2H_5\dot{C} = 0\ ,$$

Combination of the two free radicals results in the formation of the major product, 3-pentanone:

$$C_2H_5\dot{C} = 0 + C_2H_5^{\cdot} \rightarrow C_2H_5 - CO - C_2H_5$$

The other trace products observed, 2-butanone and propanal, can be accounted for by disproportionation reactions involving the ethyl radical:

$$C_2H_5^{\cdot} + C_2H_5^{\cdot} \rightarrow C_3H_7^{\cdot} + CH_3^{\cdot}$$

and

$$C_2H_5^{\cdot} \rightarrow C_2H_5 + H^{\cdot}$$

The methyl and hydrogen radicals so produced may react with the large excess of the original propanoyl radicals to give 2-butanone and propanal respectively.

$$C_2H_5\dot{C} = O + CH_3^{\cdot} \rightarrow C_2H_5COCH_3$$

and

$$C_2H_5\dot{C} = O + \dot{H} \rightarrow C_2H_5CHO$$

The $\dot{C}_3H_7$ may combine with any of the other radicals or may disproportionate. In any event there was no evidence for compounds larger than 3-propanone. However on close examination of the GC curves there were indications of a very small peak before that due to CO_2 which could be attributed to low molecular weight alkanes and alkenes.

Kinetics

The α-time curves show, especially at the lower temperatures, the classical shape characteristic of surface decomposition with the formation and spread of nuclei on the surface of the crystallites. During the deceleratory region of this reaction the surface becomes covered in product followed, possibly after an induction period, by the advance of the reactant-product interface into the bulk of the solid. The initial reaction accounts for approximately 8% of the entire process, a value which rises as the temperature is increased in a series of isothermal experiments. The temperature range of the decompositions is only just below the melting point of the solid and a rapid increase in the number of defects would be expected at the higher temperatures. This would result in more nuclei being formed and so could account for the increased extent of the first reaction as the temperature approaches the melting point.

The major part of the reaction obeyed the Avrami-Erofeev equation, with $n = 2$, which can be interpreted as two dimensional growth of nuclei into the bulk of the solid. This is consistent with the fact that the starting material appeared as thin platelets under the optical microscope. Thus the evidence would seem to support a nucleation and 2-dimensional growth mechanism.

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The authors gratefully acknowledge the provision of an equipment grant and Research Studentships to G.S. and S.B.W. by the SERC.

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Zusammenfassung — Ein vielseitiges und flexibles System zur Analyse von gebildeten Gasen wird beschrieben, das GLC, MS (in Massen-scanning und SIM Betriebsweise) und GLC—MS umfaßt. Damit können die in zwei differentialthermoanalytischen Einheiten, einer Thermowaage oder einem direkt mit dem MS- oder GLC-Gerät gekoppelten Mikroofen aus den zu untersuchenden Substanzen entwickelten Gase analysiert werden. Einzelheiten der komputerkontrollierten Datengewinnung und Steuerung werden angegeben. Die Techniken werden zur Untersuchung der thermischen Zersetzung von Calciumpropionat herangezogen. Mechanismen werden vorgeschlagen, die die beobachteten Zersetzungsprodukte und die Festkörperreaktion erklären. Beweise werden dafür erbracht, daß bei letzterer eine Keimbildung und darauffolgendes zweidimensionales Wachstum vor sich geht, wobei die Aktivierungsenergie 315 kJ $\cdot$ mol^{-1} und der präexponentielle Faktor $4.8 \cdot 10^{21} \cdot s^{-1}$ beträgt.

Резюме — Описана многостороняя и гибкая система анализа выделяющегося газа на основе использования газо-жидкостной хроматографии (ГЖХ), масс-спектрометрии (МС) и совмещенного метода ГЖХ и МС. Термовесы или микропечь соединены прямо с масс-спектрометром или газо-жидкостным хроматографом, что позволяет анализировать газы, выделяющиеся из веществ в этих двух различных термических аналитических блоках. Приведены детали сбора и обработки данных с помощью ЭВМ. Метод был использован для изучения термического разложения пропионата кальция. Предложен механизм реакций образования продуктов разложения и твердотельных процессов. Предсравлены доказательства в пользу того, что твердотельные процессы происходят через стадию образования центров кристаллизации, за которой следует двухразмерный рост с энергией активации 315 кдж.моль$^{-1}$ и предэкспоненциальным фактором $4{,}8 \cdot 10^{21}$ сек$^{-1}$.