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THERMAL DECOMPOSITION OF TERTIARY-BUTYLPEROXYBENZOATE BY HEAT FLUX CALORIMETRY

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ABSTRACT

The use of a heat flux calorimeter for thermal hazard evaluation has been investigated using tertiary-butylperoxybenzoate as a 'model' substance. The results indicate a complex decomposition mechanism where the kinetic parameters depend on the temperature and extent of reaction. The results offer confirmation of the experimental and analytical procedures.

INTRODUCTION

Heat flux calorimetry is outstanding in its capacity to measure energy changes associated with slow reactions. The technique has been used increasingly to examine potentially thermally hazardous materials. It is in this context that we have evaluated the use of the Setaram heat flux calorimeter (Model C80). As a 'model' substance we used tertiary-butylperoxybenzoate, the thermal decomposition of which has already been investigated using isothermal and adiabatic storage tests, low pressure autoclave experiments and conventional thermal analysis [1]. The results of these investigations indicate a complex pattern of kinetic behaviour in which autocatalysis leads to a second order process, which in turn gives rise to a first order process.

The design of the Setaram C80 calorimeter is based on that of the Calvet microcalorimeters. The instrument signal is proportional to the thermal power, i.e. the rate of energy change, and thus the area enclosed by the curve of instrument signal vs. time is proportional to the total energy change. The instrument bears some resemblance to differential scanning calorimeters. It is 'differential' in operation, with sample and reference vessels placed side by side in cavities in a temperature-controlled calorimetric block. The heat flux between the vessels and the calorimetric block is measured by thermocouples which surround the two cavities and are connected in opposition. The temperature of the calorimetric block can be programmed to increase or decrease at a linear rate, subject to a maximum operating temperature of 573

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K. There are also major differences. The sample mass can be 100–1000 times greater than that used in conventional differential scanning calorimeters, and it is this which is partly responsible for the effectively high sensitivity. The calorimeter is thermally very stable but this is at the expense of the response time, which is much greater than that of conventional differential scanning calorimeters. Heating and cooling rates are slower, and experiments are far more time-consuming.

We investigated the calibration of the calorimeter under both isothermal and dynamic conditions, using electrical heating and chemical standards. Determination of the dynamic operating range was of particular importance. The size of the reaction vessels (15 cm^3) is appropriate to the study of large samples, whereas a prerequisite of hazard evaluation is the use of small samples. Gas evolution during the experiment may also necessitate the use of small samples if there is a risk of distortion to the reaction vessels through increased pressure. Such a risk exists in experiments with tertiary-butylperoxybenzoate where there is a considerable evolution of gas during decomposition. The calorimetric measurements were used to obtain the rate of decomposition as a function of temperature and extent of reaction. The starting point for the calculation of the latter is the assumption that there is a strict proportionality between the fractional extent of reaction and the isothermal energy change [2]. The experiments were carried out with the samples in air under dynamic conditions, and the kinetics investigated over a range of heating rates.

EXPERIMENTAL

Calibration of the calorimeter was carried out using electrical heaters each made of nichrome wire wound onto a support inside purpose-built calibration vessels. The external dimensions of the vessels were the same as those of conventional reaction vessels used in chemical experiments (diameter, 17 mm; length, 80 mm). Two calibration vessels were used, one in each of the cavities in the calorimetric block. The electrical heaters were connected in series to eliminate the effect of electrical heating in the leads. The resistance of the heaters was 530 Ω and 5 Ω; the total resistance of the four identical leads was < 0.1 Ω. The electrical current was supplied from a constant current source. The time for which the current flowed was measured using an electronic timer. During the heating period the resistance of the heaters and the current were measured. The differential electrical work was calculated using $w = I^2(R_1 - R_2)t$, where R_1 and R_2 are the resistances of the two heaters and t is the heating time. The current used in the experiments (5–20 mA) was small enough to ensure that the temperature rise of the calibration heaters was insufficient to cause a significant heat loss through the leads. The calibration factor was expressed as ϵ (in V W^{-1}) = peak area (in Vs)/differential electrical work (in J). Experiments were carried out over the working temperature range of the calorimeter under both isothermal and dynamic conditions.

The chemical experiments were carried out using liquid tertiary-butylperoxybenzoate (95% pure). Samples (10–500 mg) were weighed into an aluminium crucible, which was then sealed inside the reaction vessel. The reference was a small sample of calcined alumina, also contained in an aluminium crucible. The isothermal base-line signal was recorded with the calorimeter at laboratory temperature (~ 293 K). The temperature of the calorimeter was raised to 425 K and the decomposition curve recorded. The residues from some of the experiments were heated over the same temperature range to obtain the heat capacity curve. A range of heating rates from 2 to 9 K h^{-1} was used. The instrument signal was recorded using a microcomputer. The sample vessel and contents were weighed at the end of the experiments to confirm that no loss of material had occurred.

RESULTS AND DISCUSSION

The results of the electrical calibration experiments are shown in Fig. 1. Unlike modern differential scanning calorimeters, the instrument signal was not linearized, and the calibration 'constant' shows a significant temperature dependence. The calibration for our instrument was supplied by Setaram as a fourth order polynomial in temperature. This is shown in Fig. 1 as the full curve. Our results under both isothermal and dynamic conditions were in excellent agreement with this curve. Repeat determinations in which the current and time of heating were varied gave an experimental error (standard deviation of six results) of 1–2%. We confirmed that there was no asymmetry in the operation of the calorimeter by reversing the positions of the two heaters in the calorimetric block. Measurements were made over the signal amplification range of the instrument (10^2–10^5). The dynamic operating range of the calorimeter was confirmed over four orders of magnitude of energy.

In the chemical calibration experiments the peaks resulting from the fusion of pure substances were recorded, a technique used in conventional differential scanning calorimetry. The samples were contained in an aluminium crucible in the conventional reaction vessel. Setaram recommend that with small samples special reaction vessels should be used which support the sample nearer the centre of the thermocouples. Even so, we were surprised at the magnitude of the discrepancy between our chemical calibrations and the values obtained electrically. Some results for indium are shown in Fig. 1. With sufficiently large samples the calibration from the electrical experiments can be reproduced, but the critical mass varies from one substance to another: for indium it was about 10 g, whereas for benzoic acid

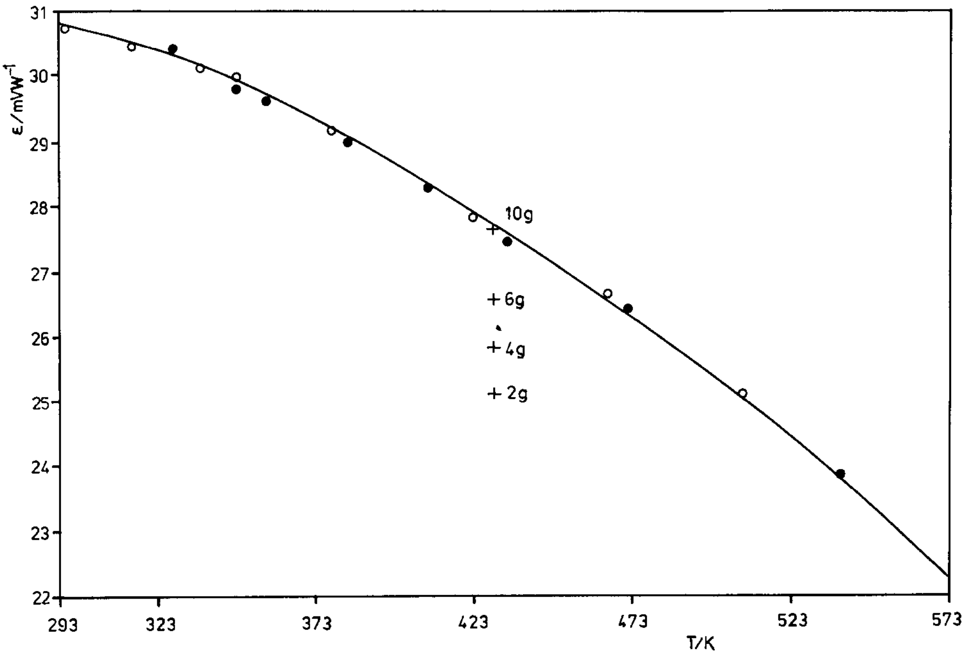

Fig. 1. Calibration curves: ———, manufacturer's calibration; ● and ○, electrical calibrations under isothermal and dynamic heating conditions respectively; +, chemical calibrations with indium.

it was 1.5 g. Figure 2 shows the results we obtained with a modified reaction vessel in which the crucible containing the samples of indium was supported on stainless steel cylinders. Agreement with the electrical calibration was obtained with samples of mass $\geqslant$ 100 mg. Confirmation of the consistency of our measurements was obtained by using two samples of different mass in the sample and reference vessels. The measured calibration constant was in agreement with that calculated from individual values relevant to the different masses. We also carried out mixing experiments in which tris(hydroxymethyl)methylamine (Tris) was dissolved in 0.1 mol dm^{-3} aqueous HCl. In these experiments the calorimeter was rotated so that the heat evolution was distributed over the entire surface area of the reaction vessel. Under these conditions the calibration constant agreed with the electrical value. For the more usual 'static' experiments it is essential that small samples be studied using either the special reaction vessel or a modified version of the conventional reaction vessel. It is desirable to employ a range of sample masses, to confirm that the effect of instrumental 'heat loss' is negligible.

The time constant for the calorimeter is conveniently derived from the rise and decay of the instrument signal when the electrical heater is switched on or off. We have found that most of the rise and decay can be represented by a single exponential term. We define the rise and decay times as

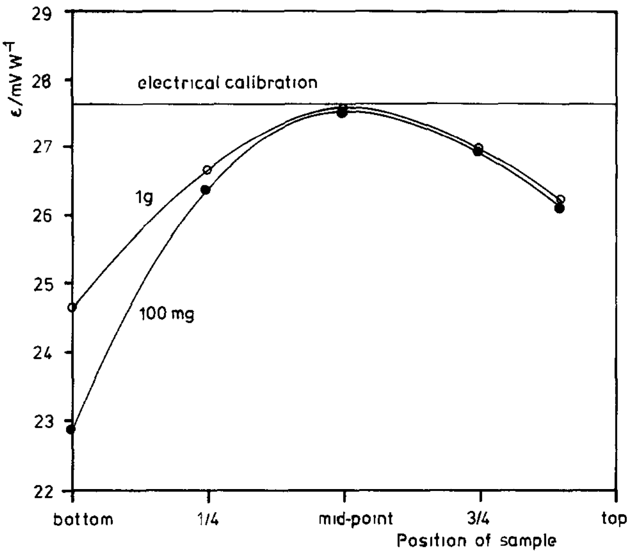

Fig. 2. Calibration results using samples of indium supported at different vertical positions in the reaction vessel.

$t_r^{-1} = \mathrm{d}\ln \Delta S/\mathrm{d}t$ and $t_d^{-1} = -\mathrm{d}\ln \Delta S/\mathrm{d}t$, respectively, where $\Delta S = S - S_f$ is the instrument signal measured from the final steady-state values (S_f). The value obtained for the response time was $t_s = t_r \simeq t_d \simeq 300$ s. We defer a detailed consideration of the response characteristics to a future publication: signal correction (deconvolution) was unnecessary in the chemical experiments with tertiary butylperoxybenzoate where the reaction time was > 10–20 t_s.

The calorimetric curve for the thermal decomposition of tertiary butylperoxybenzoate is shown in Fig. 3. The sample mass was 250 mg, the heating rate 4.5 K h^{-1} and the amplification 5×10^2. The total time taken for the experiment, including the time taken for the calorimeter to cool to laboratory temperature, was about 2 days. Also shown are the curves for the heat capacity of the tertiary butylperoxybenzoate and the reaction products over the temperature range of the decomposition (340–410 K). The former was obtained by extrapolating the instrument signal recorded before decomposition of the sample became apparent. The principle of the analysis is illustrated in the inset diagram: the fractional extent of reaction α at temperature T_r is assumed to correspond to the ratio area ABC/area ABCDE, where area ABCDE is proportional to the energy change for the complete isothermal reaction at temperature T_r. The reaction rate can be derived from the instrument signal by making allowance for the contribution of the instantaneous heat capacity $\mathrm{d}\alpha/\mathrm{d}t = (S - \beta C(\alpha))/\Delta U$, where S is the instrument signal (in W) incorporating the calibration constant, β is the heating rate, ΔU is the energy change for the isothermal reaction (in J) and

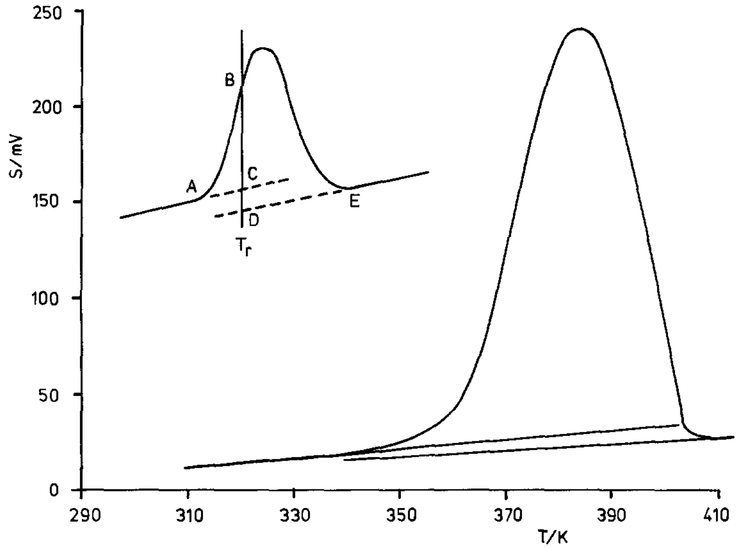

Fig. 3. Decomposition of tertiary-butylperoxybenzoate in air. Sample mass, 250 mg; heating rate, 4.5 K h^{-1}.

$C(\alpha)$ is the heat capacity corresponding to the fractional extent of reaction α, and is calculated from the heat capacity curves for the reactant and products. At this stage the calculation becomes similar to that suggested by Brennan et al. [3].

We estimated the significance of the heat capacity corrections in the present experiments by comparing the results with those based on the conventional approach of a straight base-line to the peak. Our calculations incorporated the temperature dependence of the calibration. The change in heat capacity was small, often scarcely discernible, and the effect on the calculation of both the fractional extent of reaction and reaction rate was $< 1\%$. The experimental error in the heat capacity measurements and the wide temperature range over which the heat capacity of tertiary-butyl peroxybenzoate was extrapolated led to very large uncertainties in the calculations (greater than the magnitude of the corrections). It is a moot point whether it is better to use a treatment which is formally erroneous where the results are likely to be slightly in error, or a valid approach which incorporates large experimental uncertainties. For the present experiments we elected to ignore the heat capacity correction. It is important to assess the likely errors: the 'straight line' approach effectively disguises the experimental uncertainties in the base-line, and neglect of the thermodynamically valid approach can lead to very significant errors in energy changes and the derived kinetic constants [3].

The mean energy change $\Delta U = -1.70 \pm 0.10$ kJ g^{-1} (ca. -330 kJ mol^{-1}) was obtained with samples weighing 10–500 mg using heating rates of 4.5–9 K h^{-1}. With the small samples (10 mg), uncertainty in determining the precise onset of the reaction made reliable area calculations difficult. Measurements made using differential scanning calorimetry (Perkin–Elmer DSC 4) gave an onset temperature of 370 K. The energy change $\Delta U = -1.44 \pm 0.05$ kJ g^{-1} (ca. -279 kJ mol^{-1}) was obtained with samples (1.5–3.0 mg) sealed in aluminium crucibles. The result is close to the value -274 kJ mol^{-1} measured by differential thermal analysis [1]. Our results are for the sample heated in air, with the volume of air in the reaction vessels of the Setaram calorimeter being considerably greater than that in the aluminium crucibles used in a conventional thermal analyser. There is evidence that the reaction products may depend on the precise experimental conditions. The agreement between the results obtained with the Setaram calorimeter over the mass range of the samples (10–500 mg) offers some validation of the calibration curve used in the calculations. Even with quantities as small as 10 mg, the measurements are still well within the resolution of the Setaram calorimeter.

We have adopted two strategies for the analysis of the kinetic data. Both assume that the rate of reaction may be expressed as separable functions of temperature and extent of reaction. One is based on the approach of Borchardt and Daniels [4] and the other is more classical. In the former, we examine the simultaneous effects on the reaction rate of temperature and extent of reaction. We chose to investigate the rate law $d\alpha/dt = A(1-\alpha)^n \exp(-E/RT)$, with $n = 0$, 1 and 2. Graphs of $\ln[(1-\alpha)^{-n}\, d\alpha/dt]$ (in s^{-1}) plotted against T^{-1} (in K^{-1}) (Fig. 4) gave shallow curves to which it was tempting to assign straight lines consistent with first and second order kinetics at high and low temperatures, respectively. The graphs have a shape similar to that obtained by differential thermal analysis [1], from which Verhoeff and van den Berg [1] were able to identify both first order and second order regimes in the decomposition. Our results relate to a lower

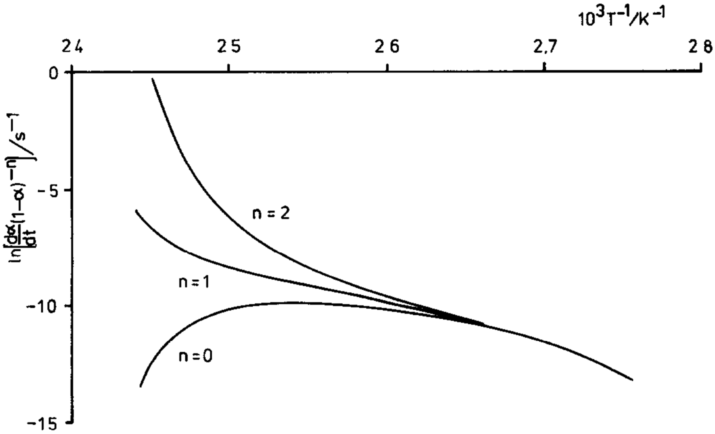

Fig. 4. Kinetic analysis using the Borchardt and Daniels approach. Sample mass, 10 mg; heating rate, 4.5 K h^{-1}.

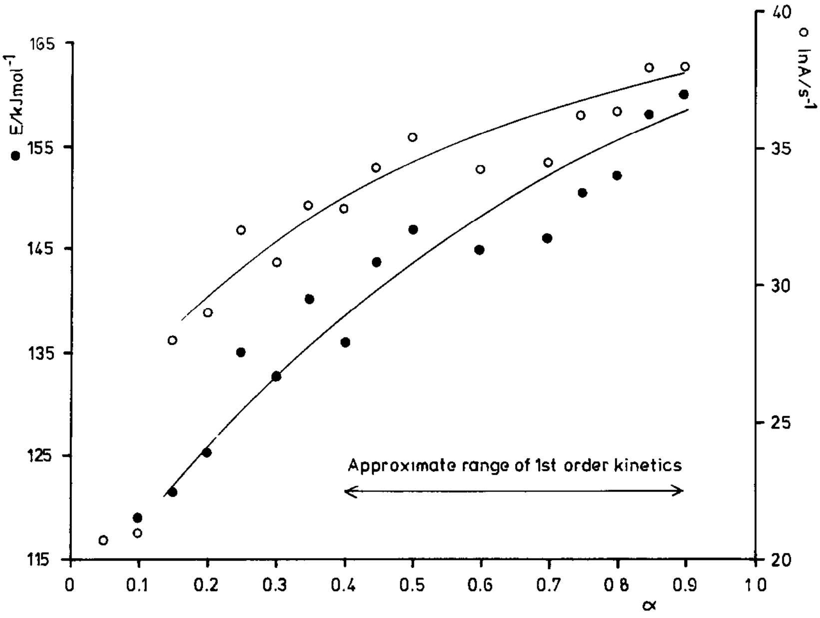

Fig. 5. Summary of kinetic results.

temperature range. The straight line portions of our graphs were not clearly delineated, and the analysis highlights the inadequacy of the approach for representing the decomposition of tertiary-butylperoxybenzoate. Any attempt to derive kinetic parameters is without firm foundation, since the entire basis of the calculation of fractional extents of reaction is called into question. There is no unequivocal method of apportioning the experimental signal between component reactions without first postulating a model of the reaction sequence which can be validated. The present results endorse the view of the authors of ref. 1 regarding the complexity of the decomposition.

In the alternative strategy we examined the dependence of the rate of reaction on the temperature independently from the effect of the extent of reaction. S-shaped curves were obtained for the fractional extent of reaction plotted against temperature for different heating rates. We examined the application of the Arrhenius equation at constant values of the extent of reaction. Graphs of $\ln[d\alpha/dt]$ (in s^{-1}) against T^{-1} (in K^{-1}) gave reasonably good straight lines (correlation coefficients of 0.991–0.999), and established a gradation in the activation energy and pre-exponential factor as the reaction proceeded to completion. Similarly, graphs of $\ln[d\alpha/dt]$ (in s^{-1}) plotted against $\ln[1-\alpha]$ gave a series of straight lines (correlation coefficients of 0.990–0.995) in which the gradient n changed with temperature. Our results are summarized in Fig. 5: the curves are a tentative interpretation of the scattered results. Reservations similar to those associated with the Borchardt and Daniels treatment, regarding the derivation of the kinetics of separate reaction stages, pertain: the status of our results is that of a convenient representation of experimental data.

The present results parallel those reported previously [1]. Measurements with the heat flow calorimeter allowed the decomposition to be detected at a lower temperature than with the differential scanning calorimeter, but this was at the expense of a considerably longer experimental time. The discrepancy between the energy changes obtained by the two techniques appears to be due to the different environment of the samples. Thus we obtained the value $\Delta U = -1.50 \pm 0.05$ kJ g^{-1} using the heat flux calorimeter for a sample enclosed in an aluminium crucible as used for differential scanning calorimetry. Our results vindicate the use of the Setaram calorimeter for the investigation of reaction kinetics at low temperatures, an aspect integral to the evaluation of thermal hazards. The results present a consistent description of the kinetics but not one which is simple to apply, since the kinetic parameters change with temperature and extent of reaction. In effect, the results cast doubt on the original premise that the reaction rate can be expressed as separate functions of temperature and extent of reaction. A key aspect in hazard evaluation is the extrapolation of rate data to conditions outside those of the measurements. Often this has to be done against the background of a limited amount of information, further experimentation being too expensive in time. In these situations the need for kinetic parameters may necessitate the use of values which may be approximate or of uncertain status. In this connection, our results yield a description of the first order regime which is in good agreement with that obtained from the more extensive investigation of Verhoeff and van den Berg using adiabatic storage tests [1]. Thus over a major part of the decomposition ($\alpha = 0.4$–0.9), where our results indicate a predominantly first order regime, we obtain the mean values $E \simeq 148$ kJ mol^{-1} and $\ln A \simeq 35.2\ s^{-1}$.

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