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AN IMPROVED METHOD FOR THE USE OF DSC IN THE ISOTHERMAL MODE TO MONITOR EXOTHERMIC REACTIONS *

J.M. BARTON

Materials and Structures Department, Royal Aircraft Establishment, Farnborough, Hampshire, GU14 6TD (Gt. Britain)

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ABSTRACT

When DSC is used in the isothermal mode to monitor exothermic reactions a horizontal baseline is usually assumed. The true non-linear baseline can be obtained from a second run on the fully reacted sample. This method was evaluated using the reaction of phenylglycidyl ether and 2-ethyl-4-methylimidazole in a 2:1 molar ratio. The assumption of horizontal baselines gives an apparently decreasing heat of reaction over the temperature range 80–151 °C, while the use of experimentally determined non-linear baselines gives a constant heat of reaction, 459.7 J g^{-1} with standard deviation 17.3 J g^{-1}.

INTRODUCTION

The value of differential scanning calorimetry (DSC) instruments used in the isothermal mode to monitor the rates of exothermic reactions is well established. This method has been used, for example, to study the bulk polymerisation [1,2] and copolymerisation [3] of unsaturated monomers, and the curing reactions of polyester [4] and epoxy [5–7] resins.

The method involves the insertion of the sample within its container into the DSC cell which has previously been equilibrated at the required temperature. A small sample is used so that the temperature rise within the sample, due to the reaction exotherm, may be neglected. After an initial period of stabilisation the heat flow output signal becomes exothermic and then as the reaction reaches completion the heat flow signal approaches a final steady-state level. The conventional method involves the assumption of a horizontal baseline on the heat flow–time curve at the final steady-state value. The intersection of this baseline with the heat flow–time curve is taken as the starting point of the reaction, and the difference between the baseline and the heat flow signal is taken as the heat flow due to the reaction at any given

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time. Errors can be introduced by this assumption of a horizontal baseline, especially at higher temperature where significant reaction is occurring during the initial period of instrument equilibration.

In the present work it is shown that the true baseline is non-linear and that improved isothermal data can be obtained by the use of the true baseline. The reaction of phenylglycidyl ether (PGE) and 2-ethyl-4-methylimidazole (EMI), to form a 2 : 1 molar adduct, was used to evaluate the method. This reaction involves the formation of an adduct [8] of PGE and EMI, as shown in Fig. 1, and it has been investigated previously using DSC in the isothermal mode, by the conventional method [9].

EXPERIMENTAL

The instrument was the Du Pont 990 thermal analyser with the 910 DSC cell, operating in a nitrogen atmosphere (50 cm^3 min^{-1}). The DSC was calibrated from temperature scans on a disc of pure alumina, as the enthalpy standard, over the temperature range of interest. A Hewlett-Packard 9835 computer was interfaced with the instrument through a Solartron 7055 digital voltmeter and analogue scanner, for data acquisition and processing.

The 2-ethyl-4-methylimidazole (97%) was obtained from Aldrich and the phenylglycidyl ether was Koch-Light puriss grade (~ 99%). The reaction mixture was prepared as batches of about 2 g total weight by dissolving the imidazole in the appropriate quantity of phenylglycidyl ether to give a molar ratio of 1 : 2. Samples in the range 2–10 mg were accurately weighed into DSC sample pans which were then hermetically sealed.

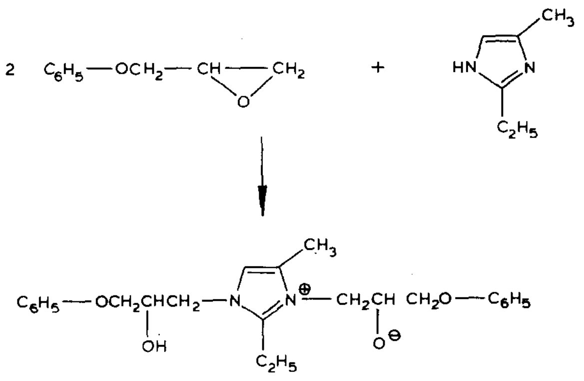

Fig. 1. The reaction of phenylglycidyl ether and 2,4-ethylmethylimidazole.

RESULTS AND DISCUSSION

When a sample is introduced into the DSC cell previously equilibrated at a set temperature, there is a perturbation in the heat flow and sample temperature output signals before temperature control is re-established. As the temperature approaches its set value the heat flow signal for an inert sample follows a retarded recovery to the equilibrium (zero) level. For a sample undergoing an exothermic reaction the initial exothermic heat flow due to the reaction will be superimposed on this retarded recovery, or baseline, curve.

The raw data for the reaction of a 2.46 mg sample of the PGE–EMI mixture in a hermetically sealed pan at a set temperature of 151°C are shown in Fig. 2. It is seen that after insertion of the sample the temperature drops by about 45°C, and returns to the isothermal value of 151°C after about 1 min. The solid line shows the heat flow output signal which becomes exothermic after about 0.3 min, develops the exothermic peak attributed to the reaction, and finally reaches a steady state after completion of the reaction. The sample was removed from the instrument and cooled to room temperature. The instrument was equilibrated at the same set temperature and the experiment was repeated with the reacted sample. This gave the baseline output signal shown as a dashed line in Fig. 2.

The start of the reaction was assumed to be the onset of the major exotherm 0.4 min after beginning the experiment, shown as A in Fig. 2.

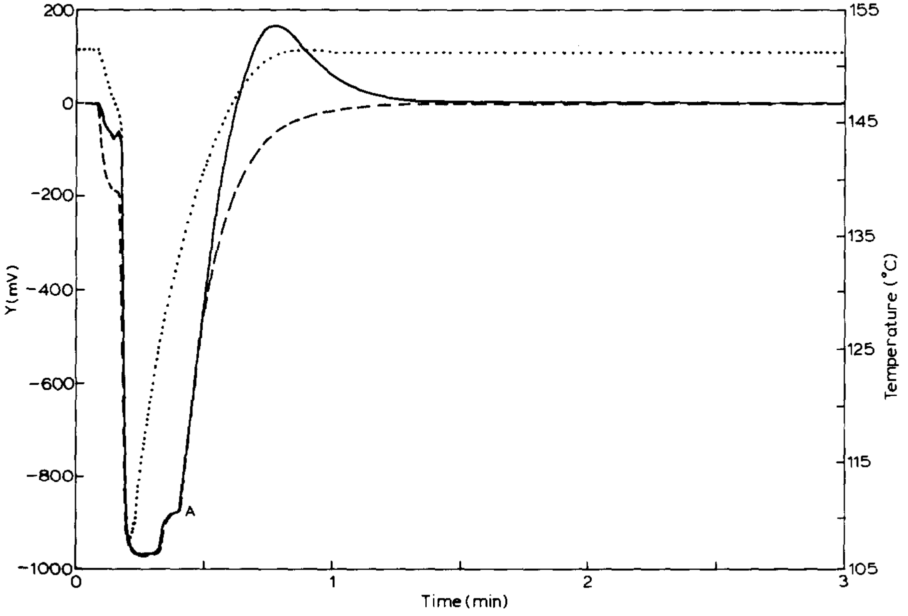

Fig. 2. Raw data for the reaction at 151°C. Reaction (————); baseline, (- - - - -); temperature (· · · · · ·).

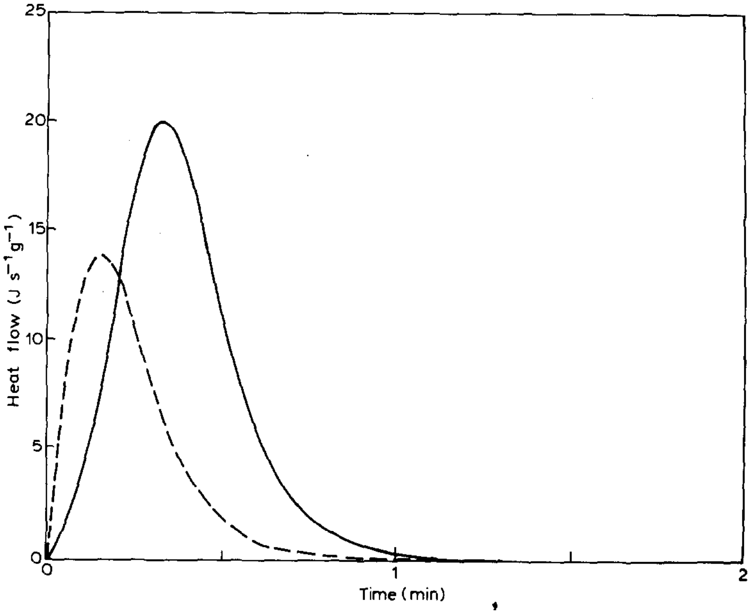

Fig. 3. Heat flow against time at 151 °C. From non-linear (————), and horizontal (- - - - -) baseline.

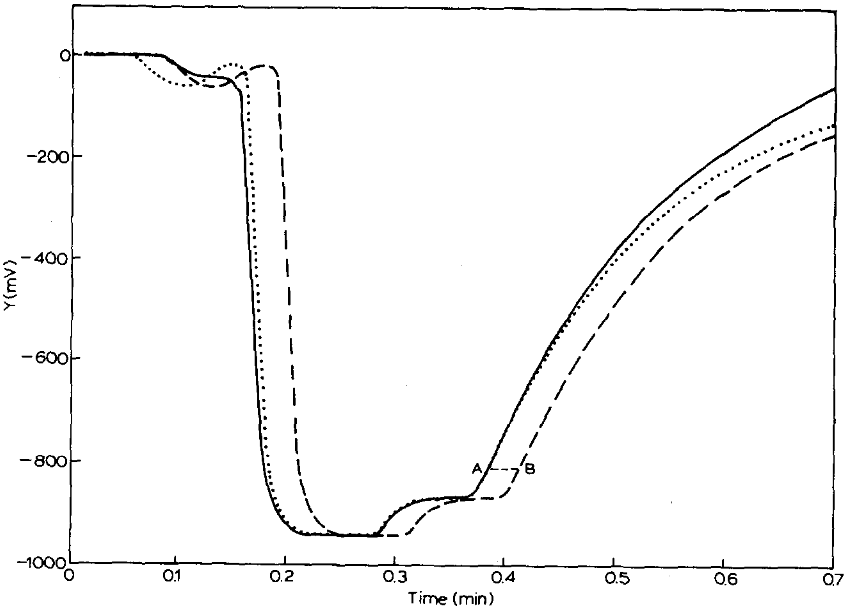

Fig. 4. Raw data for the reaction at 122°C. Reaction (————); baseline (- - - - - -); time-shifted baseline (· · · · · ·).

Between this starting point and the completion of the reaction, heat flow data (dq/dt) were calculated as

$$dq/dt = C(Y - Y_b)/M \qquad (1)$$

where dq/dt is the heat flow (J s^{-1} g^{-1}), C is the calibration constant (J s^{-1} mV^{-1}), Y is the output in mV, Y_b is the corresponding output at the same time for the baseline, obtained by linear interpolation, and M is the sample mass in g. The heat of reaction, Q, was obtained by numerical integration of the heat flow as a function of time. As a comparison, heat flow data were also obtained by the conventional method using eqn. (1) with $Y_b = Y_f$, where Y_f is the horizontal baseline value of Y, determined as the average of the final five experimental points.

The results of the two methods are shown as plots of heat flow against time in Fig. 3. From the peak areas in Fig. 3, the heat of reaction, Q, is 455.1 J g^{-1} from the non-linear baseline, and 258.4 J g^{-1} from the horizontal baseline.

For the example given above the experiment and baseline data at the exotherm onset were found to synchronise within 0.2 s. However, the time taken to manually insert the sample pan into the DSC cell can vary and this usually results in a small mis-match in the time base between the two runs. This is illustrated by Fig. 4 which shows the early parts of the data for the experiment at 122°C, using a 4.55 mg sample. The exotherm onset was arbitrarily assigned to the point A on Fig. 4, and the digitising facility of the

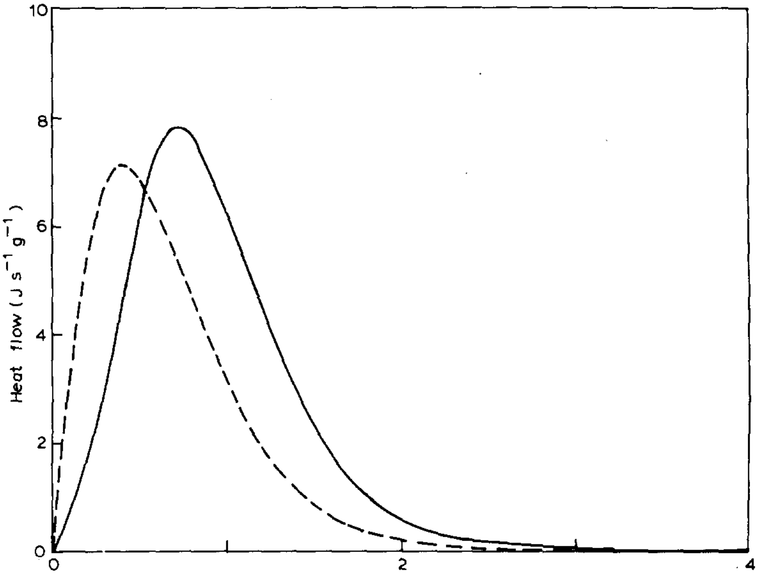

Fig. 5. Heat flow against time at 122°C. From non-linear (————), and horizontal (- - - - -) baseline.

plotter was used to determine the times at point A on the experiment curve and point B at the same output level on the baseline curve. The time difference, AB, was 1.71 s, and this value was subtracted from the baseline time data array to give the shifted baseline in Fig. 4. The resulting plot of heat flow against time is given in Fig. 5, and the peak area corresponds to a heat of reaction of 477.4 J g^{-1}. Also shown in Fig. 5 is the corresponding data obtained assuming a horizontal baseline which results in a value of 384.5 J g^{-1} for the heat of reaction.

Results from experiments in the temperature range 80–151°C are given as plots of apparent heat of reaction against temperature, for the two methods, using either non-linear or horizontal baselines, in Fig. 6. The use of the non-linear baseline gives the approximately constant value for the heat of reaction of 459.7 J g^{-1}, with a standard deviation of 17.3 J g^{-1}. In contrast, the conventional assumption of a horizontal baseline indicates an approximately linear decrease in apparent heat of reaction with increasing temperature, from 450.7 J g^{-1} at 79.8°C to 258.4 J g^{-1} at 151.4°C.

At temperatures below 100°C the combined results from the two methods give the average value for Q of 459.4 J g^{-1}, with a standard deviation of 17.2 J g^{-1}, which indicates that the error due to the assumption of a horizontal baseline is not very significant at these lower temperatures. The average value for Q found in the earlier investigation [9], using the horizontal baseline in the temperature range 80–120°C, was about 342 J g^{-1}. This is lower than the corresponding present data. The reason for this difference is

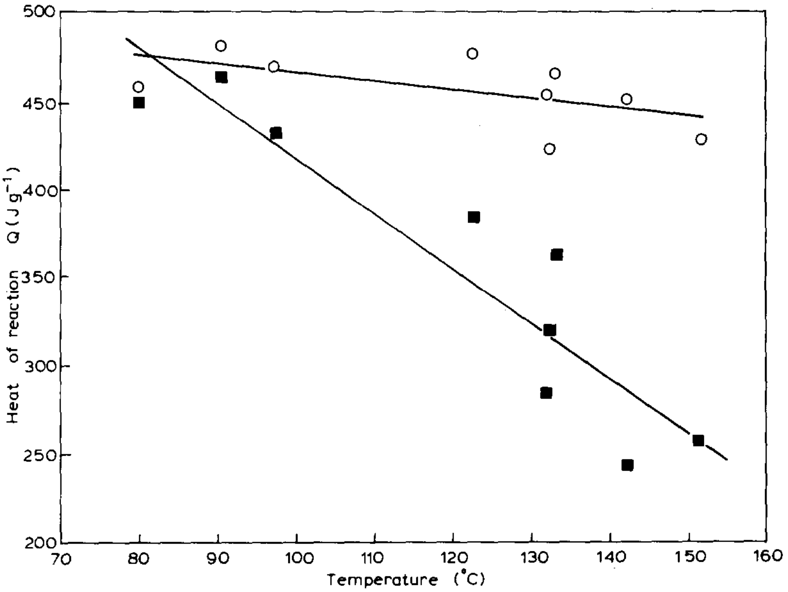

Fig. 6. Heat of reaction as a function of temperature. Data from non-linear (○), and horizontal (■) baseline.

TABLE 1

Temperature deviations

Temp. (°C)		Fractional conversion at ΔT	
Final	Onset	5	2
80	77	–	0.001
90	84	< 0.001	0.007
97	90	< 0.001	0.003
122	107	0.03	0.08
132	120	0.05	0.13
142	126	0.10	0.23
151	135	0.11	0.23

not clear, but the earlier data were obtained on different batches of the reagents, with a different instrument, and using open rather than sealed sample pans.

During the experiments the temperature of the DSC sample thermocouple was monitored, and this showed that the reaction exotherm onset occurs before isothermal conditions are established. This temperature deviation in the early part of the reaction becomes greater with increasing temperature. The results are shown in Table 1.

The instrument temperature was within 1°C of the isothermal level at a conversion of less than 1% for the experiments at 80–97°C. However, at the

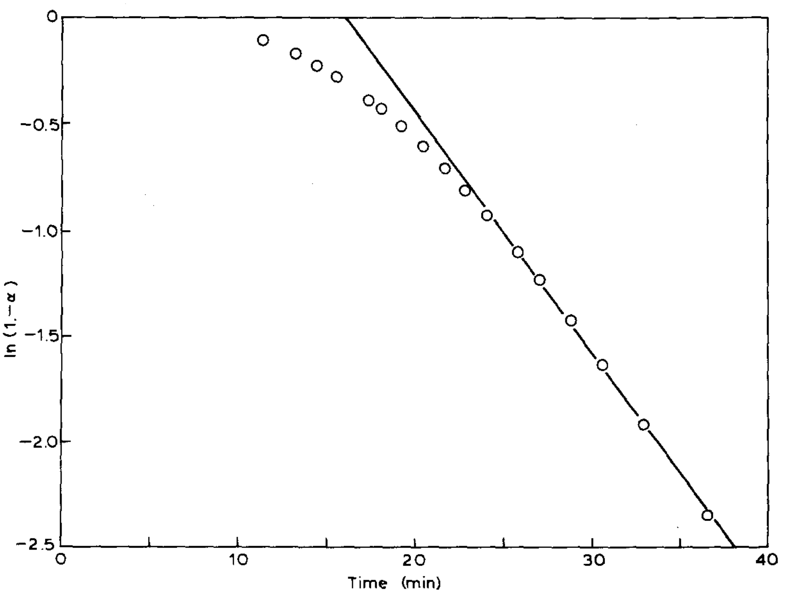

Fig. 7. First-order kinetic plot for data at 151°C.

higher temperatures isothermal control is not established until a significant amount of reaction has occurred. This effect is likely to produce some distortion of the kinetic data in the early stages of reaction at the higher temperatures. In general the degree of conversion before isothermal equilibrium is reached at a given temperature will depend on the kinetics of the particular reaction under study.

For first-order kinetics a plot of $\ln(1-\alpha)$ against time should be linear with a slope equal to $-k$, where k is the rate constant. The data from the reaction at 151°C are plotted in this form in Fig. 7. Linearity is apparent for fractional conversion greater than about 0.55, with a slope corresponding to $k = 0.113\ \mathrm{s}^{-1}$. In this case the recorded temperature was within 2°C of the set value at a fractional conversion of 0.23, so that some of the deviation from first-order kinetics may be due to complexity in the reaction mechanism. A more detailed study of the kinetics of this reaction is in progress.

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