thermal hazard technology

Thermal Hazard Technology, 1 North House, Bond Avenue, Bletchley MK1 1SW, England.
Phone: +44 1908 646700 Fax: +44 1908 645209 E-mail: science@easynet.co.uk Web: www.science.org.uk

Technical Information Sheet No 100

Accelerating Rate Calorimeter Sample Data: DTBP / Toluene

Di-Tertiary Butyl Peroxide (DTBP) is a well-known and very well characterised organic peroxide. It is widely available in pure form. DTBP has always been used as the ‘standard’ sample for showing the performance of the Accelerating Rate Calorimeter - and more recently other calorimeter manufacturers have used DTBP as their standard sample.

Early work with DTBP in the Accelerating Rate Calorimeter was with a relatively small sample in a sample container of heavy mass. More recently there has been an aim to reduce the thermal inertia (ϕ, heat lost to the container). In light-weight (or high volume) containers using a pure sample only a small sample mass can be used if rupture of the container was to be avoided. Therefore most recent work with DTBP has been with a solution in toluene. Data from a series of DTBP/toluene tests with different concentrations of DTBP is given in THT Technical Information Sheet No 23.

Here it was shown that uniquely in the Accelerating Rate Calorimeter it is possible to work with concentration from 10- 100% DTBP. However from approximately 30% DTBP with bombs of low mass, it is necessary to reduce sample size to prevent spontaneous reaction that can cause container rupture. This is not the case with other equipment. For example, vent sizing instruments may really only be used in the range 10-20% DTBP.

Samples of 20% by volume DTBP are used for the standard test to verify correct operation of an Accelerating Rate Calorimeter. A 6gram sample is contained in an

8gram ‘bomb’ and the test started at 80°C. Heat steps of 3°C are used and the onset sensitivity set at 0.02°C/min. The wait time used is 15 minutes and an end temperature of 220°C. Reaction is usually recorded from 115-195°C with a maximum rate near 10°C/min.

A typical set of DTBP/toluene data is shown here. Toluene was of analytical reagent grade but it may be noted that there are several manufacturers of DTBP and the level of stabilisers they add varies and thus the start of self-heating may be slightly variable. However fresh DTBP from all sources is of 98% purity.

In this test the sample was 20.0% by weight DTBP in toluene, the sample mass was 6.001g in a titanium bomb of mass 7.582g. With specific heats of both chemicals estimated at 2.09J/g°C or 0.5cal/g°C, this gives a ϕ for the sample mixture of 1.32 but of course the ϕ for the peroxide component alone is much higher, it calculates as 6.64. The test conditions used were those detailed above.

The exotherm was recorded at the 114°C heat step, the first data point having the temperature 115.61°C. Prior to this there was indication of self-heating before the exotherm commenced, by a temperature rise in the seek period above the baseline thus: at 111°C, the seek value showed 0.011°C/min , at 108°C, the seek value showed 0.006°C/min and at 105°C the self heating was 0.002°C/min. Therefore prior to the start of recording of the exotherm there was some of the DTBP lost - but considering the time at these temperatures and the self-heating rates observed the amount of lost heat was well below 0.5%.

The seek values immediately after the conclusion of the exotherm were: 0.000°C/min, 0.000°C/min, -0.002°C/min, -0.001°C/min and -0.001°C/min. A very clear indication that there is no heat loss in the Accelerating Rate Calorimeter by reflux. Similar seek values were recorded above the exotherm indicating no reflux condensation - a problem which exists in adiabatic calorimeters that use large sample volumes.

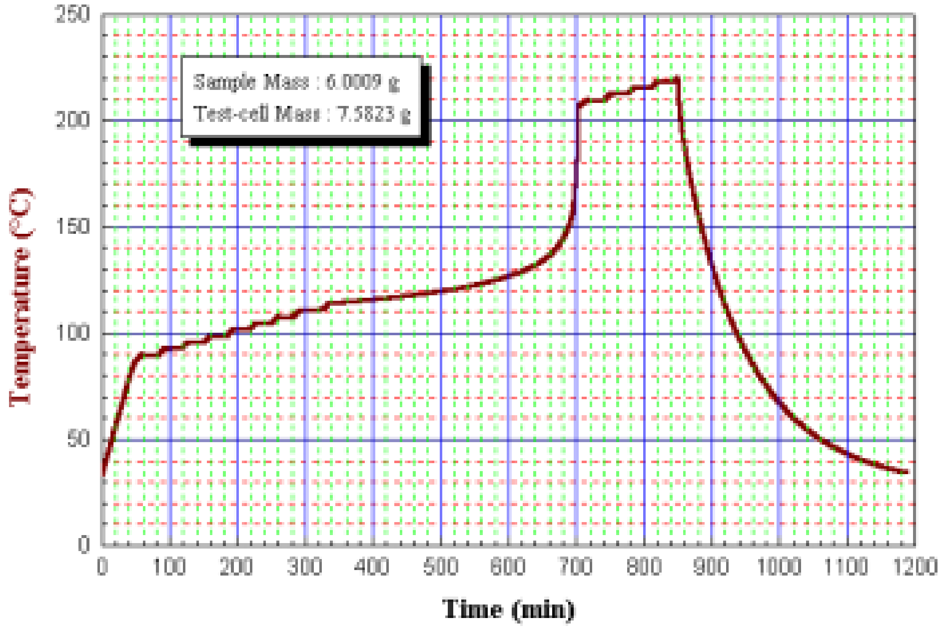
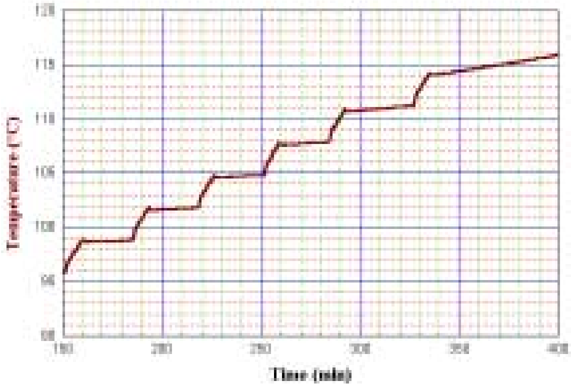


Fig 1



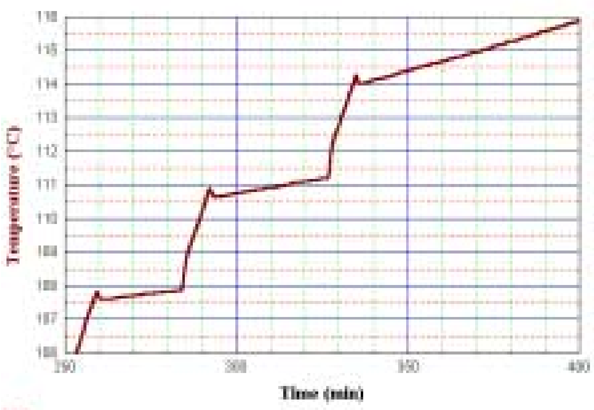


Fig 2

Fig 3

The real time curve of temperature against time is shown in Fig. 1. Fig 2 and Fig 3 enlarge the data to show 'reaction' prior to the exotherm being recorded and the quality of data. Fig 4 shows the data after exotherm, indicating stability of the instrument. Fig 5 shows pressure data prior to exotherm.

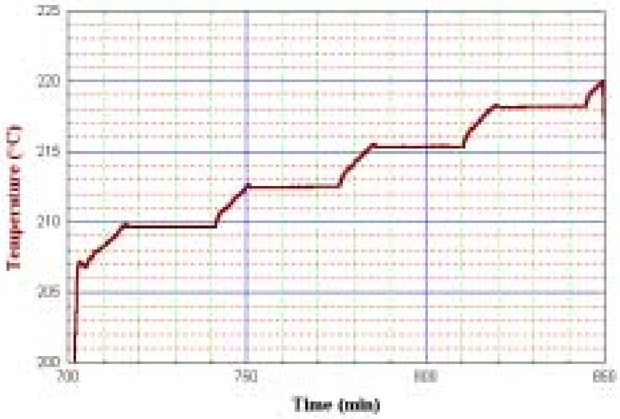


Fig 4

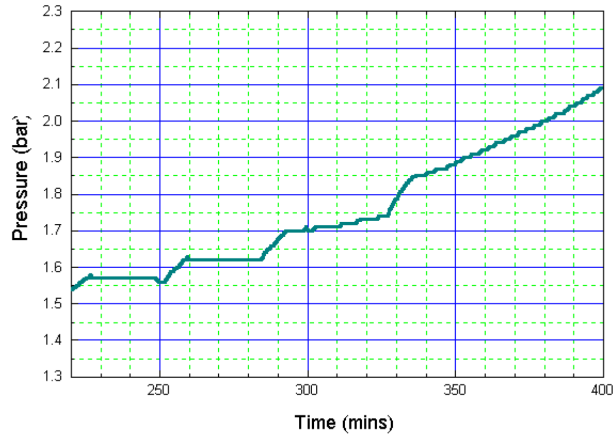


Fig 5

Fig 6 and later figures show just the exotherm data. Fig 6 shows the temperature and pressure rise as a function of time.

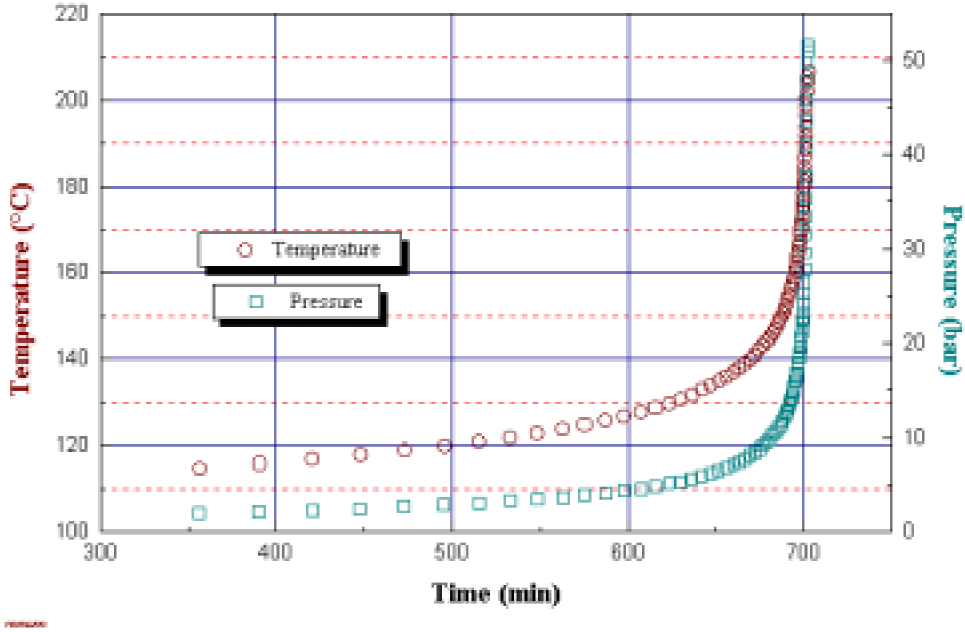


Fig 6

The expected single reaction, simple mechanism profile is shown, the reaction starting above 110°C and finishing near 200°C. This profile is better seen in the Self-Heat Rate plot, Fig 7.

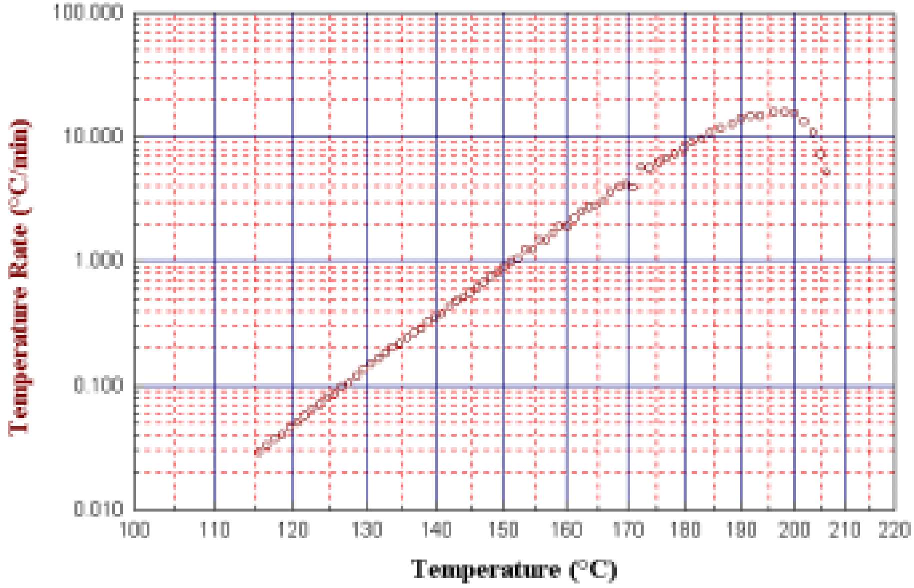


Fig 7

From this data the thermodynamic Heat of Reaction may be obtained and a kinetic information may be obtained utilising the modelling software that is part of the ARCCal package. This is detailed later. Fig 8 and Fig 9 show pressure data . Pressure may be plotted on linear axes or log/reciprocal axes. A straight line on the former indicates the presence of non-condensable gas, a straight line on the latter indicates presence of condensable gas.

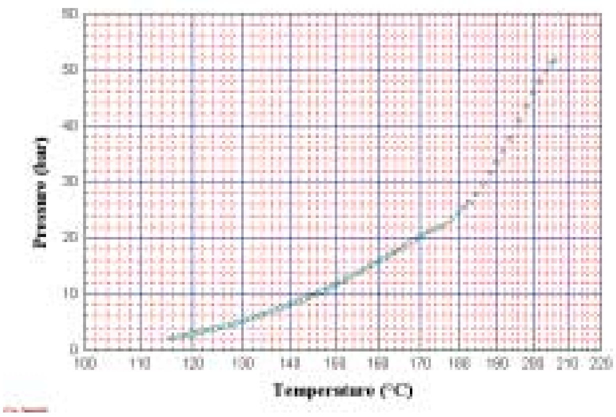


Fig 8

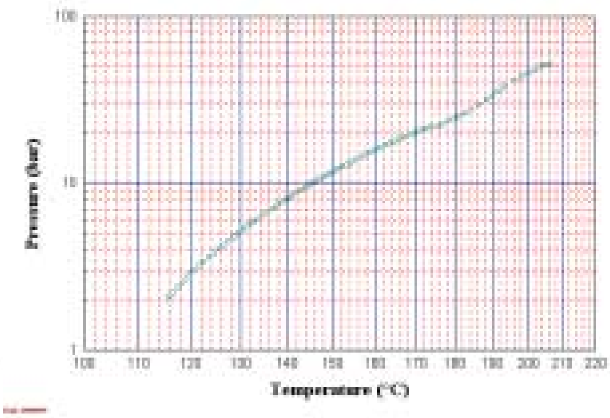


Fig 9

The final ‘raw data’ representation of the result is the Time to Maximum Rate plot. This is shown in Fig 10 and of course is used to determine maximum safe temperatures as well as times to explosion. This curve is always corrected for the ϕ error – and is often extrapolated.

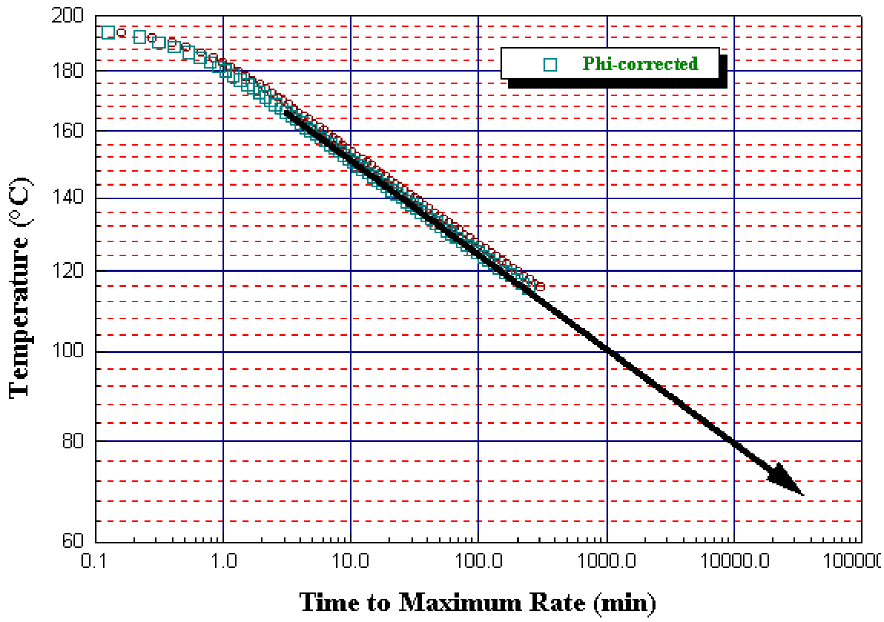


Fig 10

Mathematical analysis of the data performed with this sample (assuming first order kinetics gives the results shown in Fig 11. The Activation Energy has been calculated as 161kJ/mol (38.3kcal/mol) which compares with ‘accepted’ and published data (Ref 1), and the Heat of Reaction 250J/g (of the 20% solution) is equivalent to 182kJ/mol (43.3kcal/mol) again in excellent agreement.

Analysis Results for D971119

T.M.R. | Plot Model | Print | Printer Options | Report

Sample Identity :	D971119
Sample Mass (g) :	6.0009
Sample Cp (J/gK) :	2.1
Sample Density (g/l) :	800
Sample RMM (g/mol) :	146
Test-cell type :	ARCTC-Ti-LCE
Test-cell Mass (g) :	7.5823
Test-cell Cp (J/gK) :	0.418
Phi-factor :	1.2515
Onset Temp (°C) :	115.61
Onset T.Rate (°C/min) :	0.029
Max Rate Temp (°C) :	196.15
Max T.Rate (°C/min) :	15.777
Max P.Rate (bar/min) :	27.66667
Final Temp (°C) :	206.27
Max Pres (bar) :	51.51
Adiab Temp Rise (°C) :	90.66
Total Enthalpy (J) :	1429.82528
Heat of Reaction (J/g) :	238.26847

Fig 11

Plotting the calculated data will show the quality of the fitting. Fig 12 indicates the kinetic fit and the validity of the reaction order. This 'pseudo-zero order plot' should give a straight line only if the order has been chosen correctly. The Self-Heat Rate raw data and model data comparison indicates the model fitting over the range of the data, Fig 13.

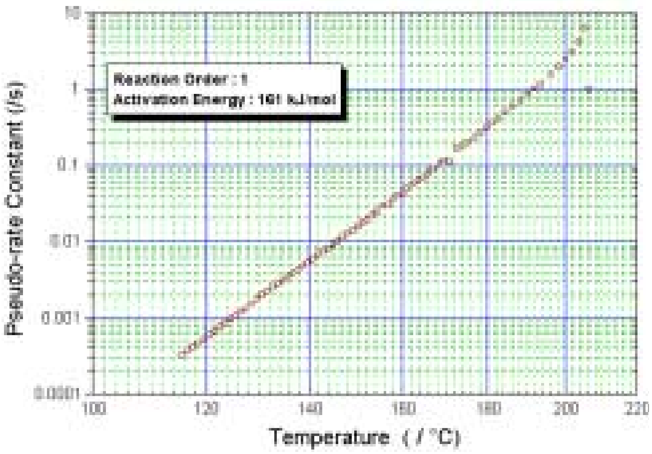


Fig 12

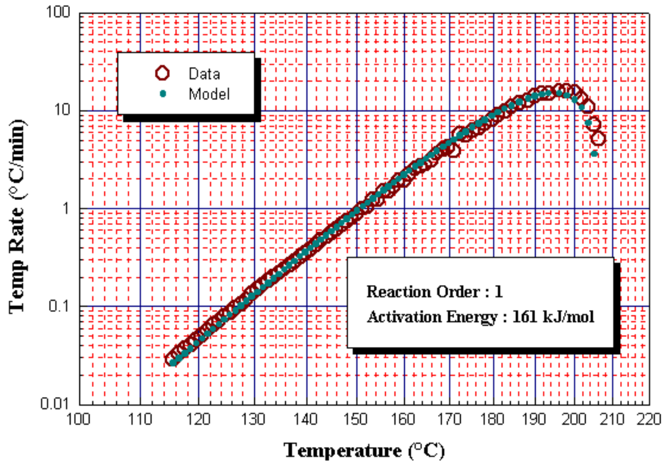


Fig 13

Finally Fig 14 is a plot of Time to Maximum Rate using the model reaction. This data representation is often preferred to using that of the raw data.

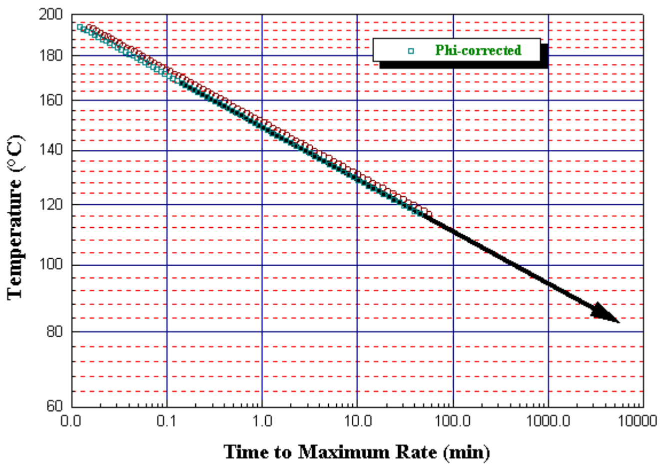


Fig 14

This data though simply one of very many produced with many Accelerating Rate Calorimeter systems over many years can be taken as specimen data. DTBP from another supplier may show a slightly different onset, but for verification of any Accelerating Rate Calorimeter or for comparison with data from other adiabatic calorimeters this data may be considered to be ‘standard’.

A complete test report , in the format standard for THT Accelerating Rate Calorimeter tests, from this sample is available on request.

Reference 1.   Tou J C and Whiting L F,   Thermochimica Acta 48 21, 1981.