

OBTAINING MORE, AND BETTER, INFORMATION FROM SIMPLE RAMPED TEMPERATURE SCREENING TESTS

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Abstract

Thermal screening of materials is a vital part of hazard assessment in the chemical industry. There is the need to identify the worst potential hazards and to further investigate these scenarios. Several screening methods are presented, and the subject of ramped temperature screening tests is studied in detail. Methods for the detection of exothermic reaction ‘onset’ temperatures are given. It is shown that, under some circumstances, the temperature data obtained during a simple controlled ramp heating experiment can be used to estimate the expected temperature rise that would occur under adiabatic conditions and the heat of reaction. The use of the data to obtain n^{th} order kinetic parameters is also demonstrated. Data obtained using the Thermal Screening Unit (TS^U) are compared to those obtained using other forms of apparatus. Heats of reaction and kinetic data have also been calculated and compare very well with data obtained using much more sophisticated adiabatic calorimeters.

Keywords: exotherm, hazard assessment, heat of reaction, kinetic data, runaway reaction, screening tests

Introduction

Hazard assessment is an important part of the development of any chemical process. Thermal screening tests are often a major constituent of the hazard assessment; it may be impractical or unnecessary to evaluate accurately every maloperation or incompatibility at each and every intermediate process stage, rather only the worst cases need to be more closely examined. Thermal screening involves stability testing of reactants, isolated intermediates, products and by-products at each stage of the process. There are many screening tools in use in the chemical industry, both commercially available and those built ‘in-house’. Some of the techniques and apparatus are described briefly below.

Differential scanning calorimetry (DSC) is commonly used for rapid screening of materials [1]. In this, a very small mass (typically 1–10 mg) of the sample is placed in a (usually) sealed test cell and is ramp heated at a fixed rate. A second cell with an

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inert sample is simultaneously heated at the same rate, and the heating power applied to each cell is measured. If exothermic activity occurs, less energy will be required to heat the cell containing the reaction mass, and the reaction power can be estimated from the drop-off in power required. From the data, an approximate 'onset' temperature and the heat of reaction can be measured. DSC techniques have some limitations in that there is no pressure measurement and the very small scale means that it may be difficult to obtain a representative sample, particularly of a multi-component mixture. The inability to measure pressure is a serious drawback: for instance, the hazard from an exothermic decomposition is almost always associated with the pressure that is developed rather than the temperature that is attained.

A similar technique is differential thermal analysis (DTA), where a fixed power is applied to each cell and thermal activity is indicated by the difference in the two cell temperatures. The insulated exotherm test [2] (IET) is an example of such a technique.

The Carius tube apparatus, as developed by ICI [3], uses a larger sample size, typically 10 g. The sample is placed in an unstirred, sealed glass test cell that has a re-entry thermocouple pocket in the bottom. A pressure transducer is attached to the test cell via a capillary tube that is often filled with oil. The cell is placed in an oven that is ramp heated at a predetermined rate. After an initial settling period, the sample temperature will follow the oven temperature at a linear rate, but lagging behind it a little, until thermal activity is encountered. The 'onset' of thermal activity can be determined by the point of deviation from the linear ramp. The Carius tube apparatus uses glass test cells, which typically fail at pressures of the order of 20–40 bar. If this happens the glass fragments are retained in the heating tube of the oven. The whole apparatus needs to be housed in a fume cupboard.

The Thermal Screening Unit (TS^U) [4] is a more recent development and is similar in principle to the Carius tube apparatus: it also should be used in a fume cupboard. The TS^U consists of a 1–10 cm³ stainless steel, hastelloy or glass test cell that is housed in a heating tube: the cell is unstirred. The heating tube acts as the sample oven and is wrapped in a resistance element that is used to produce a defined heating rate in the range of 0.1 K min⁻¹ to in excess of 15 K min⁻¹. The apparatus possesses two thermocouples, one located within the test cell to measure the sample temperature and a second located on the external wall of the oven to act as a reference and to provide a feedback measurement to the temperature control system. In a ramp test the sample temperature follows that of the oven temperature, but with an offset. Deviation of the sample temperature from the linear ramp rate of the oven indicates thermal activity: both exotherms and endotherms can be encountered. Following the reaction, the sample temperature will return to the background heating rate of the oven. The maximum temperature and the rate of change of temperature are used to identify the important characteristics of the exotherm. The graph in Fig. 1 shows typical temperature and pressure data from a TS^U experiment.

The techniques described above are also suitable for isothermal testing. In DSC techniques, any thermal activity is indicated by a change in the power required to maintain the sample cell at the isothermal temperature. In DTA, Carius tube and TS^U tests, the oven temperature can be held constant for a defined time period, and devia-

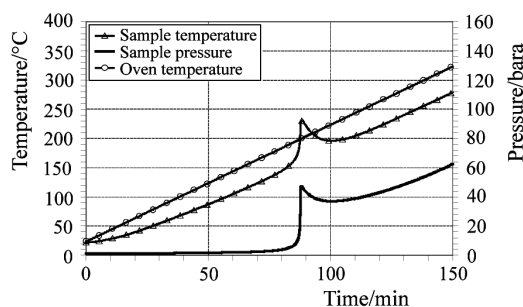


Fig. 1 Temperature and pressure vs. time; 20% DTBP in toluene: 2 K min^{-1} ramp rate, TS^U test

tions from isothermal conditions in the sample are an indicator of exothermic, or endothermic, activity. A change in sample pressure is also a useful indicator of gas generation or change in sample composition. This type of test is often used to verify safe storage temperatures and to check for induction times for exothermic activity that may, for instance, be attributed to autocatalytic kinetics.

The methodologies described below were developed from using the TS^U apparatus, and the data presented has been obtained using this equipment. However, the methodologies should be equally applicable to the data from any other similar testing technique, such as the Carius tube apparatus.

Data analysis

'Onset' temperature

It should be remembered that reactions do not start at a specific temperature, and therefore that there is no such thing as an 'onset' temperature. In practice the 'onset' temperature will be the lowest temperature at which an exotherm first becomes detectable. The greater the sensitivity of the measuring instrument, then the lower the detected 'onset' will be.

The data obtained from a ramped heating test may reflect the values of various parameters, but the only important variables for analysis are time, sample temperature and sample pressure. Oven temperature is largely unimportant for simple analysis, and is used for control purposes alone. However, in later sections of this paper a method is given for evaluation of heats of reaction based on the difference between sample and oven temperatures. During a ramped test, the oven temperature will rise steadily at the controlled rate, and the sample will start to heat, initially slowly, as the driving potential for heat transfer increases. After a relatively short time, the sample temperature will be increasing at a steady rate, with an essentially constant temperature offset (heat transfer driving potential) between the oven and sample. Any significant, or sudden, deviation from this steady rate is an indication of thermal activity. The rate of temperature rise can be found by differentiating the sample temperature with respect to time, and a plot of this vs. temperature will show deviations and the detected 'onset' temperature for any exotherm. As with all such experimental data,

some smoothing is likely to be necessary, and the smoothing algorithm should be carefully chosen so as not to mask the early stages of the exotherm.

It is possible that the exotherm will occur before a steady sample heat rate is established, and in this case it will be impossible to identify accurately the 'onset' from a heat rate vs. temperature plot. In such a test, the heat rate will initially be very low, and will increase as the difference between the oven and sample temperatures increases. The rate of change of the sample heat rate (i.e. d^2T/dt^2) will reduce as the temperature difference approaches a constant value and a steady ramp rate begins to be established. A plot of d^2T/dt^2 vs. temperature (or time) will show d^2T/dt^2 initially at a high value, but falling as the sample temperature increases. If a stable sample heat rate is established, then d^2T/dt^2 will become equal to zero. Any deviation from this is an indication of thermal activity. If a stable sample heat rate is not established, then a positive deviation from the falling d^2T/dt^2 curve is an indication of the 'onset' of thermal activity. Using this criterion, it is still possible to get a good indication of 'onset' temperature even though the sample heating may not have settled to a constant rate. Figure 2 shows data from such a situation. The detected 'onset' can be clearly seen from the local minimum of the data for the second derivative of temperature with time.

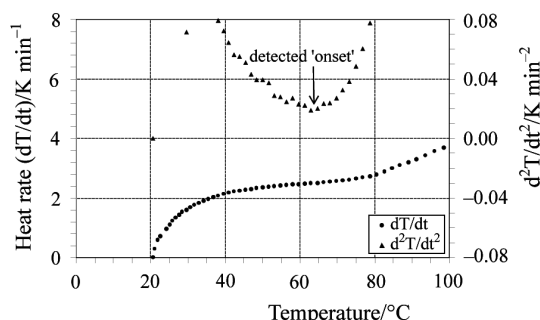


Fig. 2 Heat rate vs. temperature; pure TBPB: 3 K min^{-1} ramp rate, TS^U test

Obviously a lower oven ramp heating rate may give a more sensitive indication, but a compromise needs to be reached in terms of time and experimental throughput. The higher rate can give a much shorter test time and a greater sample throughput. In a screening apparatus, reducing sensitivity slightly but being able to process more samples may be an acceptable compromise. For standard tests we use heating rates of 2 or 3°C min^{-1} .

A further indication of activity may be able to be obtained from the pressure data. A case [4] has been presented where a DSC test gave no indication of exothermic activity, but further investigation showed that gas was being generated even at low temperatures. Any significant changes in pressure rise may indicate non-condensable gas generation. Further evidence can be gathered by plotting the logarithm of the pressure vs. the inverse absolute temperature. An essentially straight line indicates that the pressure is probably due largely to vapour pressure and that the vapour pressure of the sample follows an Antoine type dependency on temperature. Significant upward curvature with deviation from linearity is often an indication of non-condensable gas generation.

Heat of reaction

In addition to the exotherm 'onset' temperature, it is often useful to have an indication of the heat of reaction (or the potential temperature rise) that would be associated with the exotherm. In many cases ramped heating tests allow estimation of this, with a reasonable level of accuracy, by comparing the heat rate to the background heating rate and the difference between the sample and oven temperatures.

The power output from a reaction at any point can be estimated from

$$\text{Power} = \frac{dh}{dt} = \phi mc_p \frac{dT}{dt} \quad (1)$$

Therefore, if c_p is assumed to be independent of temperature

$$\int \frac{dh}{dt} dt = \phi mc_p \int \left(\frac{dT}{dt} \right) dt = \Delta h \quad (2)$$

and

$$\Delta H = \frac{\Delta h}{m} = \phi c_p \int \left(\frac{dT}{dt} \right) dt \quad (3)$$

where dT/dt is evaluated above a reference, or baseline, value that corresponds to zero thermal activity of the sample, i.e. it is the heat rate due to reaction without the oven heating, and ϕ is the thermal inertia of the cell given by

$$\phi = 1 + \frac{mc_{p_{\text{cell}}}}{mc_{p_{\text{sample}}}}$$

Strictly, the ϕ factor is not truly applicable in the case of systems with external heating, as the test cell wall will transfer heat to the sample rather than the other way round. However, when the sample undergoes an exotherm, the steady ramped state is augmented and the ϕ factor does become an important factor. This method has been successfully used to estimate the heat of reaction for a number of different systems.

The enthalpy of reaction can be estimated by integration of the heat rate (above the reference value) with respect to time, and from knowledge of the heat capacity of the sample and the factor ϕ for the sample and test cell. The lower limit for integration can be taken as any time between where a steady sample heat rate has been obtained and before the heat rate first deviates from the baseline value (the time at the 'onset' temperature): the upper limit should correspond to the time at which sample cooling first starts and the heat rate becomes negative (i.e. the time at the local maximum temperature). It may be that some reaction is still occurring during cooling, but it is assumed that the contribution of such reaction to the total enthalpy is likely to be very small.

An alternative, and that used in the subsequent calculations in this paper, is to take the upper limit of integration as the value where the sample temperature starts to increase following cooling and to evaluate the cumulative enthalpy by integrating over all temper-

atures up to this point. The enthalpy of reaction is then taken as the peak value of this integral. This takes into account the heat of reaction released during cooling of the sample.

Arguably, the adiabatic temperature rise is of equal importance to the heat of reaction. Again if c_p is assumed to be independent of temperature, the adiabatic temperature rise can be estimated from:

$$\Delta T_{\text{ad}} = \frac{\Delta H}{c_p} = \phi \int_{t_{\text{onset}}}^t \frac{dT}{dt} dt \quad (4)$$

where t is the time at any point during the exotherm and dT/dt is the rate of temperature rise above the baseline reference value at time t .

Heat transfer reference calculation

Definition of the reference baseline requires that the sample temperature ramp rate reach a steady value before any exotherm (or endotherm) starts. This will be an initial or 'inert' baseline value, $(dT/dt)_{\text{'inert'}}$. Once an exotherm starts, the sample temperature will rise, and the driving potential for heat transfer between the oven and the sample cell will reduce. The heat input to the cell, and therefore the background heating rate, will therefore also reduce. A point may exist where the sample and oven temperatures eventually become identical, and at this point there will be no net heat transfer. In this case the sample heating must be due to exothermic reaction and its associated self-heating. If the heat transfer coefficient is assumed to remain constant, then interpolation between these two points gives the sample heat rate due to oven heating at any difference in temperature between the oven and sample.

A modified baseline (the heat transfer reference line) can then be described by Eq. (5). This can be extrapolated to points where the sample is at a higher temperature than the oven (and where the sample is therefore losing heat to the oven) and will result in the heat transfer reference line at this time having a negative value. This means that the heat rate due to reaction is actually greater than that measured within the sample, and this should be incorporated into the estimated enthalpy release and temperature rise calculated from Eqs (3) and (4).

The modified heat transfer reference line at any temperature T therefore becomes

$$\left(\frac{dT}{dt} \right)_{\text{reference}} = \left[\frac{(T_{\text{oven}} - T)}{(T_{\text{oven}} - T)_{\text{'inert'}}} \right] \left[\left(\frac{dT}{dt} \right)_{\text{'inert'}} \right] \quad (5)$$

The heat rate due to reaction is then

$$\left(\frac{dT}{dt} \right)_{\text{reaction}} = \left(\frac{dT}{dt} \right)_{\text{measured}} - \left(\frac{dT}{dt} \right)_{\text{reference}} \quad (6)$$

Integrating $(dT/dt)_{\text{reaction}}$ with respect to time, between the limits of the reaction (i.e. the times corresponding to T_{onset} and T_{max}) will yield an adiabatic temperature rise, ΔT_{ad} . The data will certainly not be as accurate as those obtained using adiabatic calorimetry, but can be used for comparing different substances and identifying

'worst cases' amongst a number of contenders. When doing this, the ramped temperature testing should all be carried out at a constant oven ramp rate.

Further analysis

From the data calculated above, self-heat rates over a wide temperature range can be obtained. This opens up possibilities of calculating a number of properties of the reaction, notably kinetic data including reaction order and the Arrhenius activation energy and pre-exponential factor. However, it is important to stress that there is no substitute for rigorous adiabatic calorimetry when accurate calculation of such parameters is required.

Kinetic evaluation

For an n^{th} order reaction, the paper by Townsend and Tou [5] shows how the 'pseudo' rate coefficient, k , can be derived from adiabatic data.

$$k = \frac{dT/dt}{(T_f - T_o)[(T_f - T)/(T_f - T_o)]^n} \quad (7)$$

where dT/dt is the self-heat rate at temperature T , T_f is the final adiabatic temperature, T_o is the initial starting temperature of the exotherm and n is the reaction order. Strictly this equation only applies for a single reaction with an enthalpy of reaction that is independent of temperature.

A plot of $\ln k$ vs. the reciprocal measured sample temperature (absolute) should yield a straight line, with gradient $-E/R$ if the chosen n^{th} order reaction model is an adequate description of the chemistry. Alternative choices of n may give better straight line fits to the experimental data.

An analogous evaluation can be performed using data from a ramped screening test. A rate of reaction and a fractional conversion (in terms of temperature) are needed. From the heat of reaction data, Eq. (6), the heat rate due to reaction at a specific temperature is known. Additionally, integration of Eq. (6) allows calculation of the adiabatic temperature rise above the 'onset' at each temperature point and consequently the overall adiabatic temperature rise due to reaction. The fractional conversion at any point can then be calculated as the ratio of these two values. Equation (7) should be rewritten, replacing $T_f - T_o$ with the adiabatic temperature rise (ΔT_{ad}), and $T_f - T$ can be replaced with $\Delta T_{\text{ad}} - T_{\text{ad}}$.

$$k = \frac{(dT/dt)_{\text{reaction}}}{(\Delta T_{\text{ad}})[(\Delta T_{\text{ad}} - T_{\text{ad}})/(\Delta T_{\text{ad}})]^n} \quad (8)$$

where T_{ad} is the adiabatic temperature rise at the point where $(dT/dt)_{\text{reaction}}$ is measured, i.e. the integral of Eq. (6) between the limits of T_o and T_{ad} .

Again, a plot of $\ln k$ vs. the reciprocal absolute temperature should yield a straight line, with gradient $-E/R$.

It may be worth noting for convenience that,

$$\frac{(\Delta T_{\text{ad}} - T_{\text{ad}})}{\Delta T_{\text{ad}}} = 1 - \frac{T_{\text{ad}}}{\Delta T_{\text{ad}}} \quad (9)$$

i.e. Eq. (8) becomes,

$$k = \frac{(dT/dt)_{\text{reaction}}}{\Delta T_{\text{ad}} [1 - (T_{\text{ad}}/\Delta T_{\text{ad}})]^n} \quad (10)$$

Evaluation and comparative testing using the TS^U

Three reactive systems have been run in the TS^U for evaluation.

- The decomposition of di-tert butyl peroxide (DTBP) at 20% on a mass basis in toluene solvent
- The decomposition of N-nitroso-N-methyl-*p*-toluene sulfonamide (NMTS) at 20% on a mass basis in 1,4 dioxane
- The decomposition of tertiary butyl peroxybenzoate (TBPB)

These reactions were chosen as they are well documented and have been used previously as standard reactions in a thermal screening context. Additionally, relevant results from adiabatic testing in the PHI TEC calorimeter have been published [7].

DTBP decomposition

A series of tests were carried out using 1 g of DTBP in 4 g of toluene (4.8 g of the mixture was charged to the test cell). The samples were ramp heated in the TS^U at various rates from 0.5 to 10 K min⁻¹. The data have been analysed using HEL's iQ data analysis software. The detected onset temperatures, together with those obtained in the PHI-TEC adiabatic calorimeter are given in Table 1. Typical data showing the experimental history and detected 'onset' are also given in Figs 1 and 3.

Table 1 'Onset' data for 20% DTBP in toluene

Ramp rate/K min ⁻¹	Detected 'onset' temperature/°C
0.5	118
1.0	115
2.0	115
3.0	112
5.0	132
10.0	138
PHI-TEC II*	110–120

*PHI-TEC 'onset' temperature normally in the range indicated when a temperature increment of 10°C is used

It can be seen that there is only a very small variation in the detected 'onset' temperatures at rates up to 3 K min⁻¹. At these rates, the TS^U gives 'onset' data comparable with

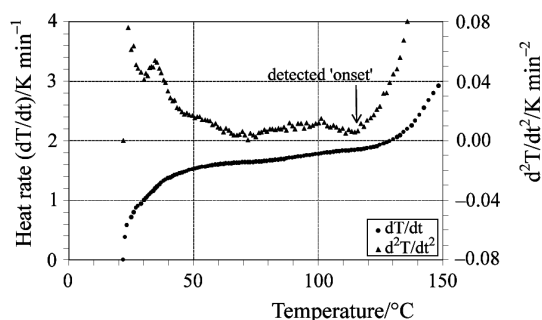


Fig. 3 Heat rate vs. temperature; 20% DTBP in toluene: 2 K min⁻¹ ramp rate, TS^U test

much more sophisticated adiabatic calorimeters. At higher rates, the detected 'onsets' are higher, but still provide an excellent estimation from a very rapid test. The so-called '100 degree rule [6]' is based on having a DSC test run at 10 K min⁻¹. This now discredited rule of thumb states that any substance that does not exhibit an exotherm in a DSC test at a temperature within 100°C above the maximum process temperature needs no further testing. Hofelich and Thomas [6] make it clear that it is not safe to rely this rule, and that if strong exotherms are present then testing in a more sensitive calorimeter should be carried out.

Heat of reaction

Using the data from the above tests, the heat of reaction can be calculated. The ϕ -factor has been estimated using the mass and heat capacity of the stainless steel test cell.

$$\phi = 1 + \frac{15.3 \cdot 0.42}{4.8 \cdot 2.1} = 1.64$$

The heats of reaction are given in Table 2.

Most of the data show good agreement with the expected heat of reaction, see the data obtained in the PHI-TEC II. The values at 2, 3, 5 and 10 K min⁻¹ are very close to the expected range, and provide excellent agreement for a simple screening test.

Table 2 Heat of reaction for DTBP decomposition

Ramp rate/K min ⁻¹	ΔT_{ad} /K (from Eq. (4))	$-\Delta H_r$ /J g ⁻¹ (from Eq. (3))
0.5	58.7	123
1.0	99.4	208
2.0	116.8	245
3.0	126.6	265
5.0	129.7	272
10.0	119.9	251
PHI-TEC II ($\phi=1.1$)	127.1	267

At very low ramp rates, the effects of heat losses from the sample during exothermic activity become significant, and this is seen with the low measured heat of reaction at 0.5 and 1 K min⁻¹. This also shows that some care must be taken in interpretation of data. The data at other rates all give good estimations and fall within 10% of the value obtained from the adiabatic test.

Enthalpy of reaction data that is evaluated from experiments for which the exotherm is mild, and the temperature range over which it occurs is broad, are also likely to have large errors.

Kinetic fits

Kinetic analysis of the data at various ramp rates has been performed and the results are given in Table 3. A first order Arrhenius fit has been assumed. (Figure 4 shows a typical kinetic plot, with a ramp rate of 2 K min⁻¹.)

Table 3 Kinetic data for DTBP decomposition

Ramp rate/K min ⁻¹	Activation energy/kJ mol ⁻¹	lnA
0.5	192.3	46.3
1.0	170.3	39.9
2.0	161.7	37.7
3.0	171.5	40.2
5.0	162.3	38.0
10.0	149.5	34.6
PHI-TEC II	156.2	36.2

The TS^U data show excellent agreement with the adiabatic PHI-TEC II results. The TS^U was never intended to provide data that could be used for kinetic modelling and a spread of values may be expected. The data shows that with the possible exception of the test run at 0.5 K min⁻¹, the data provide good estimations of the Arrhenius parameters (activation energy and pre-exponential factor) from what are simple screening tests.

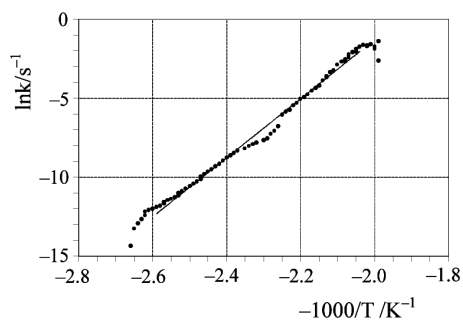


Fig. 4 lnk vs. (-1000/T); 20% DTBP in toluene: 2 K min⁻¹ ramp rate, TS^U test

NMTS decomposition

A series of tests were carried out with ramp heating of a mixture of NMTS in 1,4-dioxane. Mass concentrations of 5, 10 and 20% NMTS were studied, with a ramp rate of 2 K min⁻¹. An additional test was run with 20% NMTS at 10 K min⁻¹. The resultant data have been compared to both published data and testing using the PHI-TEC adiabatic calorimeter.

Table 4 ‘Onset’ data for NMTS decomposition, 20% in 1,4-dioxane

Ramp rate/K min ⁻¹	Detected ‘onset’/°C
2	73.0
10	75.0
PHI-TEC I	61.0
ARC* ⁵	71.2

*Data for 20% NMTS in diethyl ether

The detected ‘onset’ temperatures for the 20% solutions are given in Table 4.

From the above data, it can be seen that the TS^U detection limits compare very well with the more sophisticated adiabatic calorimeters.

Heats of reaction

The heats of reaction for the 2 K min⁻¹ ramps in the TS^U have not been calculated as the termination conditions of the test were set to prevent a violent second exotherm (to prevent excess pressure and possible damage to the TS^U). As such the data will not be for the full exotherm and will underestimate the heat of reaction. The severity of the second exotherm can be seen in Fig. 5, the test run at 10 K min⁻¹, where the pressure exceeded 200 bara following cessation of the oven heating.

The data from the 10 K min⁻¹ test (Fig. 5) indicate an adiabatic temperature rise for the first exotherm of 92°C. Assuming a sample heat capacity of 1.93 kJ kg⁻¹ K⁻¹ (based on the 1,4-dioxane solvent heat capacity) gives a ϕ -corrected (i.e. $\phi=1$) adiabatic temperature rise of 157°C. This is higher than the ARC data (120°C) but this

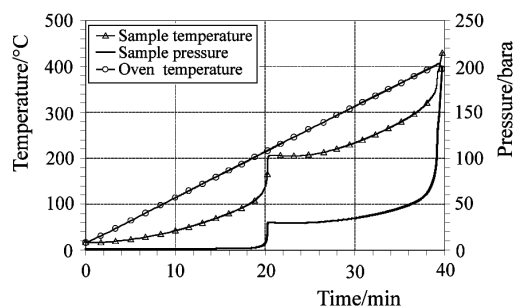


Fig. 5 Temperature and pressure vs. time; 20% NMTS in 1,4-dioxane, 10 K min⁻¹ ramp rate, TS^U test

should not be unexpected, as there was no steady heating rate established in the TS^U before the runaway: therefore some contribution to the estimated heat of reaction would come from the ramp heating.

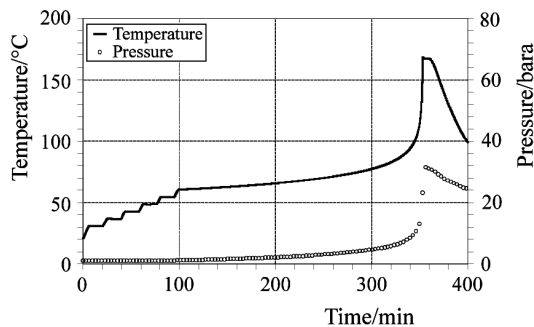


Fig. 6 Temperature and pressure vs. time; 20% NMTS in 1,4-dioxane, adiabatic PHI-TEC I test

An interesting feature of thermal screening tests is that much higher final temperatures are usually studied than are obtained from adiabatic testing. Figure 5 shows that a second exotherm was observed at $\sim 270^\circ\text{C}$. Tests such as the ARC or PHI-TEC I (Fig. 6), which have relatively high ϕ factors are often terminated following the exotherms, and second exotherms at higher temperatures can easily be overlooked.

Kinetic evaluation

The kinetic evaluation for these tests is again complicated by the early termination of the experiment. A first order kinetic fit is therefore not possible. Zero order fits have been applied. For the 10 K min^{-1} test, the reaction was allowed to continue and a first order fit has been used. The kinetic plot for this experiment is shown in Figs 7 and 8 shows similar data from the PHI-TEC test. The data are given in Table 5.

Table 5 Activation energy for decomposition of NMTS in dioxane

Test	Activation energy/ kJ mol^{-1}
5% NMTS, 2°C min^{-1}	122.0
10% NMTS, 2°C min^{-1}	114.0
20% NMTS, 2°C min^{-1}	122, 120 (repeat test)
20% NMTS, $10^\circ\text{C min}^{-1}$	118.0
PHI-TEC I data	112.5
ARC data ^{*3}	116.5

*Data for 20% NMTS in diethyl ether

Again, the TS^U data is very close to those values obtained using more sophisticated adiabatic calorimetry.

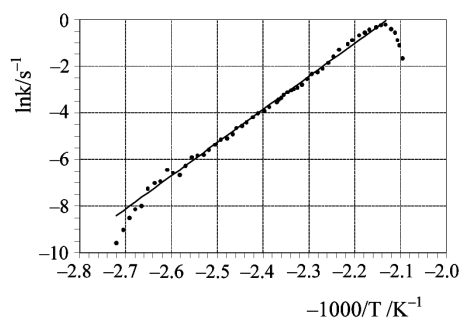


Fig. 7 $\ln k$ vs. $(-1000/T)$; 20% NMMS in 1,4-dioxane, 10 K min^{-1} ramp rate, TS^U test

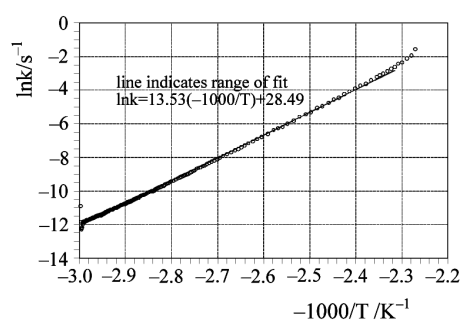


Fig. 8 $\ln k$ vs. $(-1000/T)$; 20% NMMS in 1,4-dioxane, adiabatic PHI-TEC I test

Note

Often the data from a TS^U test early in the exotherm are noisy. This is due to very low reaction rates at these temperatures, and the fact that the sample is being heated. Very small fluctuations in rate of temperature rise due to reaction can be swamped by a small variation in ramped heating rate. At higher temperatures, the heating rate due to reaction becomes a much more significant component of the observed heating rate and the noise is reduced. In other words, unlike the PHI-TEC, where the kinetic data early in the exotherm are usually the best for kinetic evaluation, in the TS^U , this early data should be largely ignored. This appears bad at first, in that part of the exotherm temperature range is ignored, but better estimates of the kinetic parameters do result.

TBPB decomposition

A third system, the decomposition of tertiary butyl peroxybenzoate has been partially studied. Tests using $\sim 1.9 \text{ g}$ of TBPB have been performed at ramp rates between 2 and 10 K min^{-1} , and in a PHI-TEC I adiabatic experiment. There is more data for comparison for this system [2, 8]. The detected onset and heat of reaction data are given in Table 6. Much of the data in this table are extracted from [2, 8].

From the published data above, it can be seen that generally, a lower ramp rate gives a lower 'onset'. The figure for the SIKAREX is slightly lower than alternative methods published at the time, and this was attributed to the much longer heating

time and autocatalytic effects. The PHI-TEC data shows that some reaction was occurring at much lower temperatures (adiabatic storage 'orange book' tests have shown onsets of $\sim 55^\circ\text{C}$, using 24 h hold periods).

Table 6 Experimental and literature data for TBPB decomposition

Test method	Ramp rate/ K min^{-1}	Detected 'onset' temperature/ $^\circ\text{C}$	$-\Delta H_r$ / J g^{-1}	E / kJ mol^{-1}
DSC (Perkin Elmer)	10	122	1335	
DSC (Perkin Elmer)	1	93	1441	
ARC	–	82	721.8	
SEDEX	0.5	84	–	
SIKAREX	0.125	72	682.8	
IET	0.5	80	816.6	150 ²
PHI-TEC I ($\phi=4.98$)	–	50	1269	
TS^U	2	73	1380	166
TS^U	3	65	1174	160
TS^U	5	83	1098	161
TS^U	10	87	1562	153

The TS^U data shows that at 2 or 3 K min^{-1} , the exotherm was detectable at temperatures of 70°C or less, and that even with faster ramp rates of 5 or 10 K min^{-1} , there was little compromise in terms of sensitivity. The difference in experimental duration between the SIKAREX and the TS^U experiment (at 2 K min^{-1}) would be sixteen fold, yet both tests yield similar 'onset' data.

The heat of reaction data indicate that the majority of the ramped tests gave low heat outputs. Some mass loss is indicated in the references for the ARC, IET and SIKAREX tests [6], and this would undoubtedly result in underestimation of the heat of reaction. The theoretical heat of reaction calculation based on product analysis is given as $1380 \pm 150 \text{ J g}^{-1}$ [2]. The TS^U tests give a good approximation to this value. At a ramp rate of 10 K min^{-1} , no steady sample ramp rate was established prior to the exotherm and the calculated heat of reaction would therefore be expected to be an overestimate.

Kinetic evaluation is difficult for these TS^U tests (Figs 9–11): the reaction does not appear to be a simple single stage reaction, and two straight lines are possible on the kinetic plots, Figs 9–11. The PHI-TEC test gave an initially exponential rising curve for a zero order plot (Fig. 12) before levelling off at $\sim 170^\circ\text{C}$ ($-1000/T = -2.26 \text{ K}^{-1}$). It has been suggested [2] that TBPB exhibits autocatalytic decomposition, and the adiabatic PHI-TEC test does have some features which might indicate this. Zero order kinetic fits have been applied to the TS^U data, and these give good agreement with the only published data (also zero order). This was calculated from an IET test, where the reaction self-heat rate is assumed to be that above the reference cell heat rate. This should be a good approximation in the early stages of reaction where the reaction rate is low. Only a

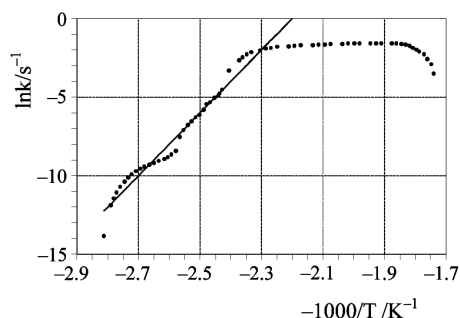


Fig. 9 $\ln k$ vs. $(-1000/T)$; pure TBPB: 2 K min⁻¹ ramp rate, TS^U test

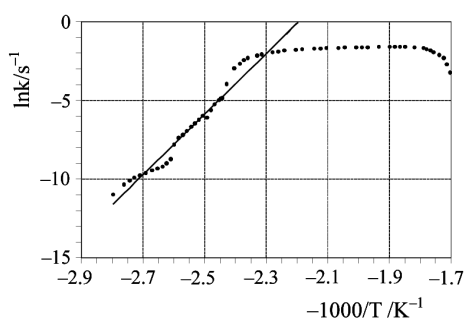


Fig. 10 $\ln k$ vs. $(-1000/T)$; pure TBPB: 3 K min⁻¹ ramp rate, TS^U test

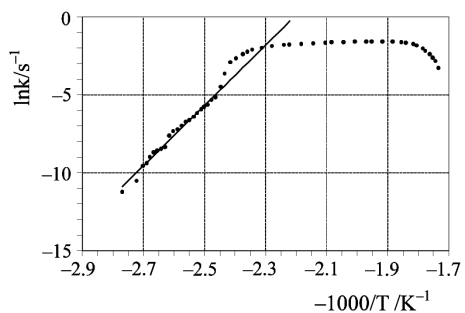


Fig. 11 $\ln k$ vs. $(-1000/T)$; pure TBPB: 5 K min⁻¹ ramp rate, TS^U test

zero order kinetic fit can be applied to such data. Figures 9 to 11 also show the consistency of the data obtained, despite the varying ramp rates.

Limitations of ramped screening methods

A potential disadvantage is the possibility of detection of false exotherms due to the presence of an earlier endotherm. Once an endotherm occurs, the temperature difference between the oven and sample increases, hence increasing the 'driving potential' for heat transfer to the sample. Once the endotherm is complete this can lead to a trace

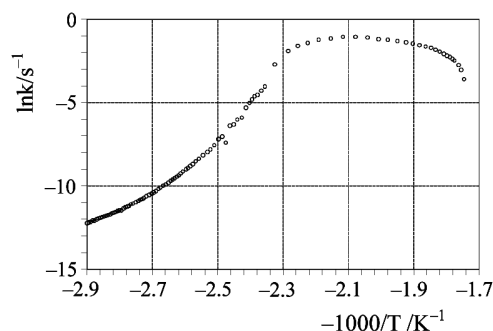


Fig. 12 $\ln k$ vs. $(-1000/T)$; pure TBPB: adiabatic PHI-TEC I test

that gives the appearance of an exotherm, and care must be taken with data analysis. As long as the user is aware of this phenomenon, there should be little problem. In any case, ramped heating tests should be regarded as an initial screening process, and it is better to further examine a false exotherm than to miss an exotherm altogether.

Obviously the n^{th} order global kinetic model presented above may not be applicable to every situation. There may be reactions with induction times, multiple reactions, both exothermic and endothermic reactions occurring simultaneously but independently, or reactions where the heat capacity changes significantly during reaction. Such behaviour will give similar problems with all calorimetric methods, and full understanding may require many isothermal experiments or other calorimetric measurement.

Conclusions

There is the need for rapid thermal screening of samples from industrial processes, in order to identify where potential hazards exist. From the screening tests decisions can be made as to where further, more detailed testing and analysis are required.

Like the Carius tube apparatus, the TS^U was developed as a simple screening tool for exothermic reaction hazards. The data presented shows that with good analysis techniques, the TS^U is very sensitive for exotherm detection; indeed, it can give similar data to much more refined and expensive adiabatic calorimeters. Even at relatively high ramp rates, good indications of exotherm 'onset' temperatures are obtained. The high ramp rates allow a fast turnaround of samples, with a 10 K min^{-1} ramp rate allowing an experiment to be completed in about an hour.

Another very important advantage is the measurement of pressure, allowing what is usually the dominant hazard of overpressure (non-condensable gas generation or high vapour pressure) to be identified. In many situations exothermic activity may be identified from the pressure trace alone before it is evident by eye from the temperature traces. Plotting the pressure data in the form of an Antoine type relationship ($\ln P$ vs. $-1000/T$) may enable the onset of non-condensable gas generation to be identified.

Additionally, the temperature data obtained from a TS^U experiment can be further analysed to give an estimation of the expected adiabatic temperature rise, and subsequently the heat of reaction. An estimate of the parameters of an n^{th} order kinetic model

can also be obtained. Although there are limitations to the accuracy, the availability of more data can help in making decisions over where more detailed analysis and testing should be performed. It should be stressed that despite the possibilities of extracting much more information, ramped heating tests, and indeed all screening tests, should be regarded as tools to identify (rather than accurately characterize) thermal hazards.

Nomenclature

A	pre-exponential Arrhenius factor/(s ⁻¹ (m ³ mol ⁻¹) ⁿ⁻¹)
c_p	heat capacity/J kg ⁻¹ K ⁻¹
E	activation energy/J mol ⁻¹
H	reaction energy release/J
Δh	enthalpy of reaction/J
ΔH	specific enthalpy of reaction/J kg ⁻¹
k	pseudorate constant/s ⁻¹
m	mass/kg
n	global reaction order
R	universal gas constant/=8.314 J mol ⁻¹ K ⁻¹
t	time/s
T	temperature/K
T_{ad}	adiabatic temperature due to reaction at any time/K
T_f	final temperature due to reaction (adiabatic)/K
T_o	'onset' temperature for kinetic calculation/K
T_{oven}	oven temperature/K
ΔT_{ad}	overall adiabatic temperature rise from reaction/K
ϕ	thermal inertia due to sample cell mass/' ϕ -factor'

Subscripts

cell	property of test cell
'inert'	pertaining to that which would be obtained if no reaction was present
reaction	pertaining to reaction alone
sample	property of sample within test cell

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