THERMAL HAZARDS: CALCULATING ADIABATIC BEHAVIOUR FROM DIFFERENTIAL SCANNING CALORIMETRY (DSC) DATA

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Abstract
   Temperature-time data under adiabatic conditions is required for the safe use of substances which decompose exothermically. Such data can be measured directly by adiabatic calorimetry but not by DSC. However, here it is shown that the kinetic and thermodynamic data from a carefully designed DSC experiment (using high pressures or pressure-tight pans to minimise vaporisation) can be transformed using simple physical chemistry to predict the course which the reaction would follow under adiabatic conditions. The procedure is illustrated for the decomposition of di-tert-butyl peroxide and tert-butyl peroxybenzoate, and the predictions are compared with data from an adiabatic calorimeter.

1. INTRODUCTION

   Substances which decompose exothermically (eg. organic peroxides and nitro compounds) require special care during use or storage because they can enter a state of accelerating-rate decomposition, leading to explosion. This becomes possible when the rate of heat production from the decomposition exceeds the rate of heat loss. In such a situation, the underlying physico-chemical laws lead to a temperature-time profile in which there appears to be an induction period before the temperature rises suddenly. It should be emphasised that this is usually a consequence of the mathematical form of the curve and not due to the reaction being suppressed by an inhibitor. (An example of the latter phenomenon occurs when an oil containing an oxidation inhibitor is held in oxygen at a high temperature: the DSC signal is zero until the inhibitor becomes depleted, then a highly exothermic free-radical oxidation is seen. DSC is ideally suited to the measurement of induction times for such inhibited reactions and details can be found elsewhere [1,2].)

   For an exothermic decomposition, the possibility of the reaction proceeding at apparently insignificant rates and then entering a potentially explosive phase makes it essential to know the temperature-time profile, focusing on the worst-case: a reaction under adiabatic conditions. One of the most widely used instruments for acquiring this data is the Columbia Scientific Accelerating Rate Calorimeter (ARC) [3,4], which in effect isolates the sample adiabatically at a chosen temperature and then monitors its temperature rise. However, an ARC is restricted to hazards investigations, and experiments are relatively lengthy.

In contrast, DSC, with high-pressure inert gas or pressure-tight pans to minimise vaporisation, is a cheaper, quicker, more generally useful and available technique but in the field of hazards studies has so far been limited to measuring heats of reaction or approximate onset temperatures. Some attempts have been made to relate the onset temperatures from DSC to those from the ARC [5,6] but these have been statistical correlations with little reference to the underlying physical chemistry.

However, here it will be shown that data from a carefully designed DSC experiment can be transformed to predict the course the reaction would follow under adiabatic conditions. This is done by fitting the data to a kinetic equation and applying some simple physical chemistry, implemented on a computer. The procedure is illustrated for the decompositions of di-tert-butyl peroxide (DTBP) and tert-butyl peroxybenzoate (TBPB), and the adiabatic predictions are compared with data from ARC experiments.

2. DESIGNING THE EXPERIMENT

If the sample vaporises during an experiment, the DSC signal will be the sum of this endothermic effect and the exothermic decomposition, making the data unsuitable for kinetic analysis. There are two means of suppressing vaporisation: using a pressure-tight pan to contain the internal pressure of vapour and decomposition products, or using a sealed pan with a pinhole in the lid in an atmosphere of high pressure inert gas. The latter option (referred to here as p-DSC) is experimentally simpler and was used for this study; however, the calculation procedure described below is just as valid for data from experiments using pressure-tight-pans.

Commercial p-DSCs typically operate to 70 bar and 600°C; pressure-tight pans are usually designed to withstand internal pressures of 100 bar or higher at temperatures up to 500°C.

However, three complications should be considered. Firstly, pressure-tight pans usually have a high heat capacity and this can lead to distortion of the heat flow signal and the data cannot then be used for kinetic modelling. This problem is minimised if low heating rates are used. Secondly, if the reaction is significantly affected by pressure, the increasing pressure during an experiment in a pressure-tight pan will make kinetic modelling complicated, while the high constant pressure in a pressure-DSC may give data which does not exactly reflect the conditions of interest in the investigation. However, for a pressure sensitive reaction, there will be problems in interpreting data from any technique. Thirdly, it is important that the atmosphere is chosen to correspond to the problem of interest. For example, an air atmosphere is likely in the head space of a storage vessel but unlikely in a high-temperature chemical reactor where combustion is a risk. Where air is the choice, pressure-tight pans are preferred to p-DSC as the amount and pressure of O_2 in a p-DSC is high enough to lead to combustion.

Pressure-tight pans are also preferred for very volatile samples, eg. ethylene oxide.

3. EXPERIMENTAL

3.1. Samples

The samples used in the DSC and ARC experiments were as follows: DTBP 98% from BHD Ltd; TBPB 98% from Aldrich Co. Ltd. Both were stored at 5°C in a fridge.

3.2. Pressure-DSC

A Mettler pressure-DSC20 was used with an atmosphere of 50 bar N_2 and a flowrate of 100 ml/min (STP) through the cell. The apparatus was pressurised and depressurised with N_2 several times to remove oxygen before the experiment. The DSC was calibrated under conditions as close as possible to those in the experiments. This involved putting 7 mg pieces of In and Pb in a 150 μl aluminium pan, adding 60 mg of squalane, crimping on the lid, piercing the lid to give as small a hole as possible (in practice approx. 0.1 mm diam), and heating at 1°C/min in 50 bar N_2. Both melting points were used for the temperature calibration, and the In value was used for the enthalpy calibration. The squalane was added to simulate the heat transfer conditions in the actual samples.

The relatively low heating rate of 1°C/min was chosen because the heat flux signal is then within the linearity range of the instrument (<60 mW). Under these conditions, the signal is not distorted by heat capacity or thermal resistance effects, therefore there is no need to deconvolute the curve.

3.3. Heat capacities

The heat capacities of DTBP and TBPB were measured using a Mettler DSC30, calibrated for temperature using In, Pb and Zn, and for enthalpy using In. A 60 mg disc of sapphire was used as the heat capacity standard. Samples (60 mg) were sealed in the aluminium pans mentioned above and heated at 10°C/min from -40°C to 100°C. Data in the range 20-80°C was used because it is above the melting point and below the point of significant reaction or vaporisation of the sample into the head space in the pan.

3.4. Data analysis

The kinetic analyses were performed using Mettler GraphWare TA72.5, which has options for fixing the order or calculating it by multiple linear regression. The Mettler software also offers several choices for constructing the baseline to compensate for the small gradual changes in heat capacity during experiments. The subsequent transformation of the rate data to predict adiabatic behaviour (as described below) was made with the authors' programme in the Appendix, which will run in any C environment.

3.5. ARC experiments

The conditions for the ARC experiments were: 2-2.5 g sample in a Hastalloy bomb of mass ~70 g. The head space in the vessel was air for the experiment with DTBP, which is the usual practice for ARC experiments. However, for TBPB the presence of air markedly affects the reaction mechanism and gives the type of complicated Arrhenius plots widely found in the literature [7,8]. In

contrast, if the headspace is thoroughly purged with N_2 to remove O_2, the ARC data shows a single mechanism for the decomposition of TBPB and can be readily modelled; this was the approach adopted here.

The operation of the ARC has been described in detail elsewhere [4], but it should be noted that there is a complication in interpreting the temperature-time data: the heat capacity of the sample vessel is large compared to that of the sample so most of the heat of reaction enters the vessel. Townsend [4] has described a procedure for converting the data to values expected for a vessel with zero heat capacity and that procedure is used here.

4. RATE EQUATIONS

Before considering the prediction of adiabatic behaviour, the data must be fitted to a rate equation. The data required for this is the curve of heat flowrate to the sample dq/dt (energy per unit time) versus temperature at a fixed heating rate, under the conditions specified above. Where the reaction is complete, the area under the curve is the heat of reaction $\Delta H_{rxn,tot}$ (understood to be per unit mass in this paper) and the fraction reacted x at any temperature can be calculated as:

$$x = \Delta H_{rxn}(T)/\Delta H_{rxn,tot} \tag{1}$$

where $\Delta H_{rxn}(T)$ is the heat of reaction from the start of reaction to temperature T. Equation 1 is a useful approximation based on the assumption that the stoichiometry of the reaction does not change over the temperature range of the DSC curve. For the measurement of this area, the start of reaction is taken as the first noticeable deviation from the baseline. Note that the thermodynamic convention gives a -ve sign to ΔH for an exothermic reaction.

Where $\Delta H_{rxn,tot}$ cannot be obtained, an estimate can be used, and a review by Grewer [9] is a good starting point for values.

The following rate equation can then be used:

$$dx/dt = A.(1-x)^n.\exp(-E_a/RT) \tag{2}$$

where t is time, A is the pre-exponential factor, n is the order, E_a is the activation energy, and R is the gas constant.

The parameters E_a and A are calculated by taking the log of both sides of Equation 2, fixing the value of n (usually to 1), rearranging, and performing linear regression. Alternatively, if software is available for multiple linear regression, E_a, A and n can be calculated, although this can sometimes give physically uninterpretable values for n.

5. PREDICTING ADIABATIC BEHAVIOUR

The system to be modelled here is a substance isolated adiabatically at initial temperature T_0 at time zero in a container with zero heat capacity. The fraction of space occupied by the liquid is assumed to be same as in the DSC experiment. The aim is to predict the temperature-time profile of the system up

to the time at which the temperature rises very steeply (eg > 10° C/min), which corresponds to the so-called induction time.

The starting point in deriving the calculation procedure is the rate [Buation expressed in the form of Equation 2 and data on the specific heat capacity C_p of the sample. Ideally the calculation requires C_p as a function of temperature and the fraction reacted; in practice, for the calculation of induction times, a mean value for the temperature range of interest is adequate and this is the approximation used here. If a measured value of C_p is not available, a useful estimate is 2 J K-1 g-1.

For a reaction occurring in an adiabatic system, the enthalpy change for the system (dH_{sys}) is zero by definition, and the heat of reaction raises the temperature of the system according to the following thermodynamic equation :

$$0 = dH_{sys} = dH_{rnx}(T) + C_p.dT \tag{3}$$

Equation 3 can be integrated between T_0 and T to give:

$$-\Delta H_{rxn}(T) = C_p.(T-T_0) \tag{4}$$

and this can be combined with Equation 1 to give:

$$x = -C_p.(T-T_0)/\Delta H_{rxn,tot} \tag{5}$$

which expresses the fraction reacted as a simple function of temperature for an adiabatic system only. In fact the relationship is linear, ranging from x = 0 at T_0 to x = 1 at the final adiabatic temperature T_f given by:

$$T_f = T_0 - \Delta H_{rxn,tot}/C_p \tag{6}$$

The next step is to differentiate Equation 5 by time and rearrange to give:

$$dT/dt = -(\Delta H_{rxn,tot}/C_p).(dx/dt) \tag{7}$$

where dT/dt is known as the self-heating rate.

The final step is to recognise that the time is related to the self-heating rate by:

$$t(T) = \int_{T_0}^{T}(1/(dT/dt)).dT \tag{8}$$

The procedure can be implemented simply by numerical integration using a computer, and a programme is given in the Appendix. The sequence of steps is to start at $T=T_0$ and increment by a finite dT; for each T, calculate x by Equation 1, dx/dt by Equation 2, and dT/dt by Equation 7; the time is calculated as the current value of Equation 8 used as a summation. The data (t,x,T,dT/dt) is saved to a file and the calculation can be stopped at a chosen

value of dT/dt (eg 10˚C/min $\equiv$ 0.16˚C/s). Other useful parameters can be derived from dT/dt, eg. the rate of heat production.

As will become clear below, for an adiabatic system, only a small (~0.1) fraction need react to cause the system to enter the explosive phase. Hence it is important to optimise the kinetic model of the DSC data over this range of fraction reacted rather than over the complete reaction.

6. RESULTS

6.1. Heat capacities

Duplicate experiments to determine the heat capacities of DTBP and TBPB agreed within ±2% and gave the following results:

DTBP: Cp(J K-1 g-1) = 1.20 + 2.77e-3T(K)   (9)
TBPB: Cp(J K-1 g-1) = 1.03 + 2.13e-3T(K)   (10)

Values of 2.3 and 1.9 J K-1 g-1, at 130˚C, respectively were used for the calculations.

6.2. Kinetic parameters from p-DSC data

Table 1 summarises the results of kinetic analyses of data from three experiments on DTBP and three on TBPB. Figure 1 shows the DSC curve for experiment DTBP/DSC/1, and Figure 2 shows the corresponding Arrhenius plot for the data over the region x=0.05-0.15 with n=1. As explained above, the data over the initial part of the reaction dictates the value of the induction time, and

TABLE 1
Kinetic parameters and heats of reaction from p-DSC in the range x =0.05-0.15 and with n=1.

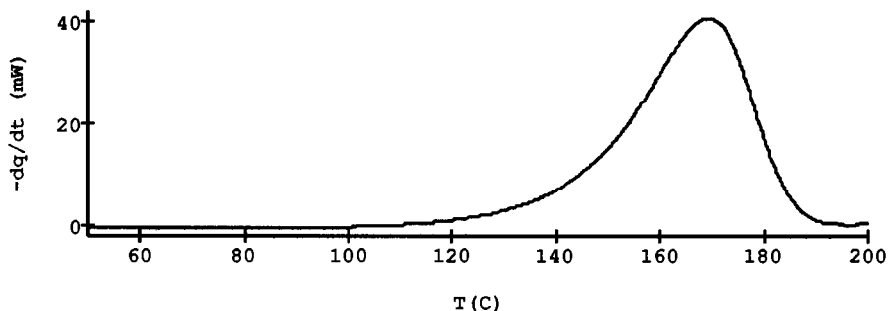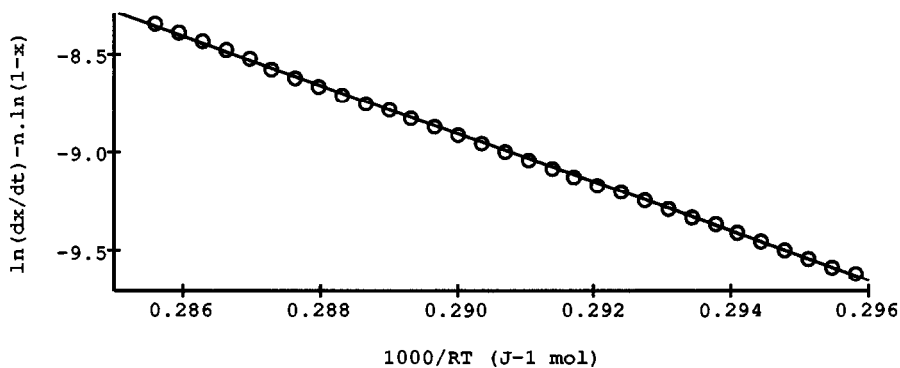| Experiment	mass (mg)	-ΔH (J/g)	E_a (kJ/mol)	ln(A/(s-1))
DTBP/DSC/1	57	1211	122.1±0.8	26.51±.23
DTBP/DSC/2	57	1189	124.8±0.5	27.28±.14
DTBP/DSC/3	50	1181	119.3±1.1	25.72±.31
TBPB/DSC/1	90	1294	103.7±0.6	23.41±.15
TBPB/DSC/2	70	1263	102.5±0.4	23.04±.13
TBPB/DSC/3	72	1286	101.5±0.4	22.72±.13

FIGURE 1. The DSC curve for DTBP/DSC/1.

FIGURE 2. Arrhenius plot for DTBP/DSC/1;
          x=0.05-0.15, n=1.

that explains the choice of x=0.15 as the upper limit. The lower limit was set at
0.05 since the linearity of the signal and the choice of the base line make the
data less reliable at lower values of x. The error levels and the linearity of the
Arrhenius plots support the first order assumption for both DTBP and TBPB,
and the resulting values of E_a and lnA are consistent within the three
experiments on each. TBPB shows a particularly well-behaved first order
reaction and the Arrhenius plot is linear over the entire reaction, giving
optimal fits with orders of n=1.06,0.96 and 0.99 by multiple linear regression
over the range x=0.01-0.99 for the three experiments.

   The heats of reaction by DSC were -1190±10 J/g for DTBP and -1280±20 J/g
for TBPB.

6.3. Kinetic parameters from ARC data

The kinetic parameters from one ARC experiment on DTBP and two on TBPB are summarised in Table 2.

TABLE 2
Kinetic parameters from ARC experiments

Experiment	E_a (kJ/mol)	a	b
DTBP/ARC/1	113.2	12789.3	-29.05
TBPB/ARC/1	106.3	12164.6	-29.95
TBPB/ARC/2	106.6	11915.3	-29.36

Coefficients for data fitted to:
$\ln(t_{ind}(\min)) = a/T(K) + b$

Townsend [4] has shown that data from a single ARC experiment can be processed to give the equation:

$$\ln(t_{ind}) = a/T_0(K) + b \tag{11}$$

where t_{ind} is the induction time for a sample isolated adiabatically at T_0. Equation 11 is based on the assumption of a zero order reaction and therefore is applicable only at low values of x; however, that is the region of relevance here. The activation energies, which were also calculated over the initial part of the reaction using a procedure described by Townsend [4], are close to those obtained by DSC but are less than the usually quoted values. For DTBP and TBPB, the literature values [7,8,10] are fitted to data for the complete range of the reaction and not for the region of most relevance as here, and for TBPB there is the additional complication that O_2 will markedly change the mechanism, so only data obtained in an O_2-free atmosphere can be compared.

7. PREDICTIONS

To allow a comparison of ARC and DSC data, induction times were calculated for DTBP isolated adiabatically at 60, 80 and 100°C, and for TBPB at 40,60 and 80°C. The calculations from the DSC data were made using the programme in the Appendix and data in Table 1 , and the calculations from the

ARC data used Equation 11. The results are summarised in Table 3 together with $T_{0.005}$, the temperature at which the self-heating rate is 0.005 °C/min,

TABLE 3

Predictions for DTBP calculated from data in Tables 1&2

Experiment	$T_{0.005}$ (°C)	Induction time (min) at		
		60 °C	80 °C	100 °C
DTBP/DSC/1	75	11000	1100	130
DTBP/DSC/2	77	14000	1200	140
DTBP/DSC/3	74	9300	910	120
DTBP/ARC/1	77	12000	1300	190

which is the lower limit of detection for the ARC. Figure 3 shows the temperature-time and x-time profiles for a starting temperature of 60 °C calculated using the programme in the Appendix from data for sample DTBP/DSC/1. The temperature-time profile illustrates the sudden rise in temperature after the so-called induction time, and the corresponding x plot shows a value of ~0.1 at this point.
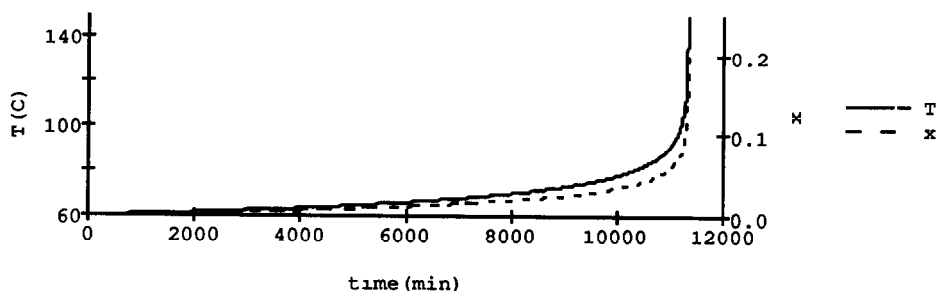

FIGURE 3. Computer-calculated adiabatic behaviour using kinetic data from DTBP/DSC/1.

To put the results in Tables 3&4 into context, it should be recognised that there is no definitive technique for obtaining data to predict thermal hazards and that the conditions used in each technique can be significantly different.

TABLE 4
Predictions for TBPB calculated from data in Tables 1&2

Experiment	$T_{0.005}$ ($^\circ$C)	Induction time (min) at		
		40°C	60°C	80°C
TBPB/DSC/1	44	2900	300	40
TBPB/DSC/2	44	2700	280	39
TBPB/DSC/3	43	2500	280	39
TBPB/ARC/1	52	7400	720	91
TBPB/ARC/2	52	6100	620	81

This point is made in a review by Verhoeff and Berg [7] who show that induction times can vary by 500% between techniques. Against that background, the agreement between the predicted induction times from p-DSC and the ARC is encouraging, as is the closeness of the $T_{0.005}$ values. As for the repeatability within each technique/procedure, that appears to be good in both cases.

8. FUTURE WORK

The procedure described and illustrated here will be explored further using both p-DSC and pressure-tight pans, and only then will a proper assessment of its value be possible. However, this initial study suggests this could be a significant advance in the application of DSC to safety investigations and could be a useful addition to commercial kinetics software.

9. ACKNOWLEDGEMENT

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APPENDIX

A programme in C to calculate adiabatic behaviour from kinetic and
thermodynamic data from DSC. The notation follows the text as closely as
possible.

```c
#include <stdio.h>
#include <math.h>
#define R 8.3144 /* gas constant */
#define dT 0.1 /* temperature increment for integration */
#define dT_dt_threshold 0.2 /* threshold self-heat rate C s-1*/

main()
{
double T, T_0, dT_dt=0.0 , t=0.0, Cp;
double x, n, lnA, A, Ea, delta_H, dx_dt;
FILE *output;

printf("\n\n\n\n\n\n\n\n");
printf("Give Ea (kJ mol-1): ");
scanf("%lf",&Ea);
printf("Give lnA (A in s-1): ");
scanf("%lf",&lnA);
printf("Give n: ");
scanf("%lf",&n);
printf("Give delta H (J g-1; -ve for exothermic): ");
scanf("%lf",&delta_H);
printf("Give mean Cp (J g-1 K-1): ");
scanf("%lf",&Cp);
```

```
printf("Give initial temperature (C): ");
scanf("%lf",&T_0);

A = exp(lnA);
T_0 += 273.0;
Ea *= 1000.0;

output=fopen("hazards.txt","w");

    for(T=T_0;dT_dt < dT_dt_threshold; T += dT)
    {
        x = -Cp*(T-T_0) / delta_H;
        dx_dt = A*pow((1.0-x),n)*exp(-Ea/R/T);
        dT_dt = -(delta_H / Cp)*dx_dt;
        t += dT / dT_dt;
        fprintf(output,"%g %g %g %g\n",
                t/60.0, x, T-273.0, dT_dt*60.0);

                /* units: min none C C/min */
    }

fclose(output);
}
```