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Technical Information Sheet No 23

Reaction Engineering with the Accelerating Rate Calorimeter DTBP/Toluene data with 10-45% DTBP, Dial-a-ϕ

THT Technical Information Sheet No 21 describes heat losses and deviations from the fully adiabatic state in the Accelerating Rate Calorimeter and alternative calorimeters. THT Technical Information Sheet No 22 discusses of this into the thermal inertia or ϕ, the heat loss into the sample container. The discussion here is related to sample types that are usually processed in solution and how testing at various ϕ values affects the results. This is the application of accelerating rate calorimetry to reaction engineering or process optimisation. Such data, though, is generally useful to very many applications, with samples that may be solids or reactive liquids without solvent dilution.

The results here show the range of sample over which the Accelerating Rate Calorimeter may be used, the errors that may occur and how they may be quantified. The data indicates that it is possible to vary concentration to get whatever ϕ value is needed 'dial-a-ϕ' or to work at $\phi = 1$ if the concentration is adjusted by a few % to compensate for heat lost into the bomb. However this is discussed in detail in THT Technical Information Sheet No 24.

The conclusion is that the Accelerating Rate Calorimeter is highly suitable to work with samples in solution over a wide range of concentrations, the Accelerating Rate Calorimeterr is more suited to this than the low-ϕ vent sizing calorimeters. Thus the Accelerating Rate Calorimeter can be very usefully applied to scale up and all reaction engineering purposes.

Errors in Adiabatic Calorimetry.

Adiabatic calorimetry can never be performed absolutely by a laboratory scale instrument. Deviations from adiabaticity are primarily

Heat lost into the sample holder
Heat lost (or gained) to the sample holder.

But errors also can be obtained from temperature gradient within the same sample.

The first deviation is well-known as the phi (ϕ) of the test, the second is the error due to poor system adiabaticity, resulting normally in heat loss from the sample/container system. This might also be by sample reflux on cooler parts of the container.

It is generally agreed that the phi error may be corrected by using the equations below

Equation 1

$$\phi = 1 + \frac{M_b . c_{pb}}{M_s . c_{ps}}$$

Equation 2

$$\phi = 1 + \frac{M_b . c_{pb} + M_x . c_{px}}{M_s . c_{ps}}$$

In these equations m is the mass and c_p the specific heat. Actually the specific heat ought to be $\overline{c_v}$, the average specific heat at constant volume. The subscripts b, s and x represent the bomb, the sample and any other components which absorb heat (this may be a thermocouple clip or inert solvent, for example). Above the line is the heat absorbing parts, below the line the heat generating parts. Clearly ϕ = 1 represents a fully adiabatic, zero container mass or infinite sample, mass all-but impossible situation. This may be considered ‘worst case’ but a fire scenario would be heat addition to a system and then ϕ would be less than 1!

But correction for the unknown and undetermined heat loss from the sample/container system is not possible and may be a major cause of error.

What Really is the ϕ

However, what is the best ϕ? How reliable is it to correct for ϕ? How high can ϕ go?

The generally held view is that the ϕ to use in a bench scale test is the ϕ of the real situation, be it process, storage or transportation. Determination of the ϕ of a vessel is easier and quicker to do than usually realised. Maybe surprisingly most real scale situations have ϕ in the range 1.3-2.0, see, for example, Ref 1.

Some instrument manufacturers claim operation at ϕ of 1.05 and below. However such instruments may not be highly adiabatic due to the large sample size necessary. In addition to operate at such a low ϕ value very often, samples must be diluted and though they may give a '$\phi_{solution}$' of, for example, 1.05 in reality the '$\phi_{active\text{-}ingredient}$' may be near 10!

In fact it is easy to see that at such low ϕ values any adiabatic calorimeter cannot completely evaluate reactions with heats of reaction greater than approx. 100 cal/g (400 J/g) since the adiabatic temperature rise would be too great.

To illustrate this, considered DTBP; ΔH=-43 Kcal/mol, molecular weight 146, specific heat = 0.5 call/g°CΔH=BTϕCp, then if ϕ =1.1, the ΔT=535 °C, and the final temperature is near 650°C!
If the test was done at 15% DTBP in toluene the true $\phi_{peroxide}$ equals:

$$\phi_{peroxide} = 1 + \frac{M_b . c_{pb} + M_{toluene} . c_{ptoluene}}{M_{peroxide} . c_{pperoxide}}$$

$\phi_{peroxide} = 6.66$ even if the bomb mass was 0g.

A 15% solution is easy to test but $\phi > 6.66$. In addition as said earlier there are the two heat loss possibilities: the heat lost into the container can be corrected for with a good deal of certainty, but the heat lost from the sample/container is almost impossible to correct. And minimising one error (e.g. ϕ) by going to larger samples will always result in increasing the other error. There is a trade-off that cannot be overcome. In the Accelerating Rate Calorimeter for example the original aim, successfully achieved, was to maximise system adiabaticity but this meant smaller samples and thus rather large ϕ values, correction would therefore be necessary. This is further discussed in Ref 2.

The ϕ correction has often been considered to be a disadvantage of the Accelerating Rate Calorimeter, but in reality to be able to operate within a range of 1.2 to 5 or 10 is indeed an advantage. Only at high ϕ values can very exothermic reactions be followed over their full reaction range and thus be evaluated.

Mechanism Change and Heat Loss

With low ϕ instruments their use is mainly for materials in solution, solids are often tested as a suspension. However with such equipment there is only a 'window of opportunity' or usability within a certain concentration range. Too high a percentage or concentration results in spontaneous explosive-type reaction and thus often the real concentration cannot be tested.

In most samples it is generally known that the exothermic decomposition reaction begins with the normal self-heating behaviour. At this stage all of the sample is rising in temperature at the same rate - but as the reaction rate accelerates; 10°C/min, 20°C/min, 50°C/min, the mechanism will usually change to the spontaneous explosive-type reaction. Here a branching decomposition mechanism occurs and the reaction finishes in microseconds, this is observed by a rapid temperature rise over several seconds as heat is transferred out of the sample to the thermocouple (an artifact of the heat transfer through the system. It is of course impossible to follow reactions with rates almost infinitely high. This is usually not necessary, the rate is so large that little heat can be lost from any system in so short a time - and indeed this is usually not of much interest since by this stage there is no safety information to gain, the reaction has gone too far.

At the high energy release reactions there are problems which have been discussed above but with low energy released problems there are also problems.

Here the exotherm may be so low that the heat rate may have significant error due to baseline uncertainty. A high sensitivity instrument is of most value and the lower the baseline error (i.e. amount of temperature drift observed when no reaction occurs) the better. Typically the Accelerating Rate Calorimeter has a baseline better than ±0.005°C/min and thus can readily detect exotherms from this level. The experimental data will have this much uncertainty in all reaction rate values, and thus this error is only significant below, say, 0.2 °C/min. However other instruments have a detection threshold near 0.05 °C/min and thus not only cannot detect very low energy reactions but also will cause greater significance error, at rates up to 1-2 °C/minute.

Accelerating Rate Calorimetry With a Range of DTBP Concentrations in Toluene

How an adiabatic calorimeter will observe a reaction at various ϕ values is shown in Fig. 1. Here the self-heating rates of a number of DTBP/toluene tests are shown, they are from experiments carried out with an Accelerating Rate Calorimeter.

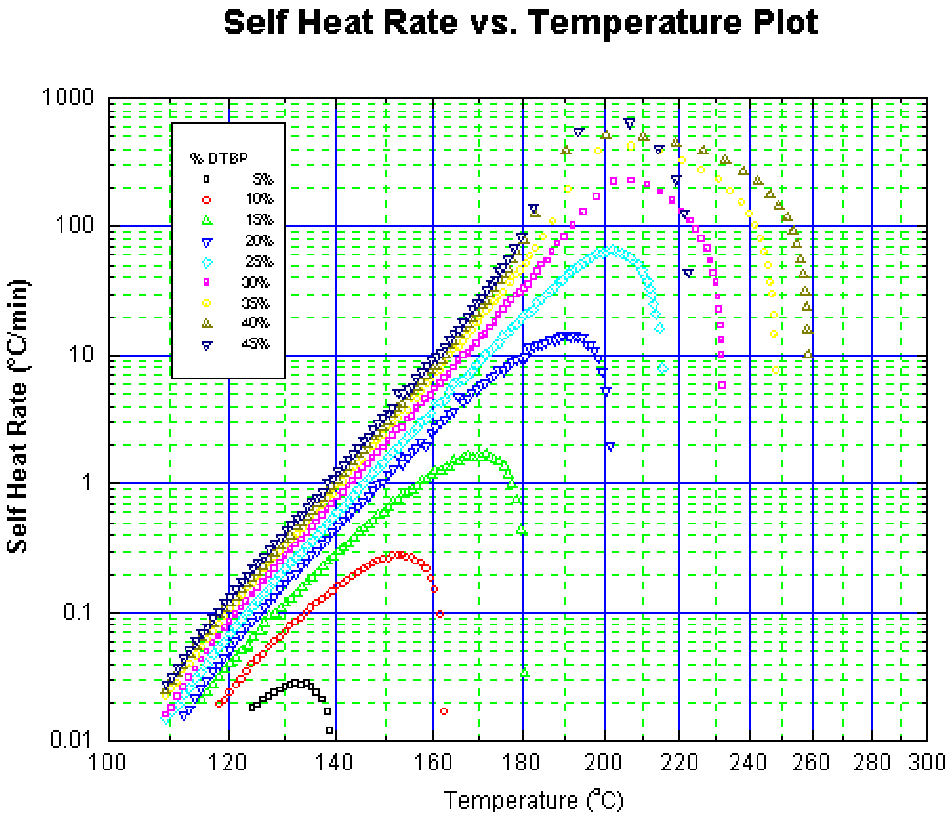

Fig. 1.

An accelerating rate calorimetry test with 20% DTBP/toluene typically will show reaction from 115-200°C, between 100-115°C some heat generation is observed, see Fig. 1. Calculation of the heat loss below the onset of reaction, which may be taken as the rate of self-heating multiplied by the time at each temperature step and summing the heat step prior to reaction, shows that less than 1% of heat is lost. Also tests in the Accelerating Rate Calorimeter show no heat input or loss at temperatures above the exotherm. The self-heat rates return to the near-zero baseline after the exotherm. This often is not the case with large sample/low ϕ instruments. Reflux on the lid of the container has been widely reported as a major source of heat loss with negative self-heat rates (indicating heat loss) subsequent to the exothermic of -1 °C/min.

The tests carried out with data reported in Fig. 1 were all carried out with a 6 gram sample in an 8 gram sample container. The ϕ could be reported for each as 1.33. However the $\phi_{peroxide}$ using Equation 2 on page 2 is given in Table 1.

Similarly it can be observed that if a 20% solution was to be used even if there was a zero weight container, the $\phi_{peroxide}$ would still be $\phi = 4$. Considering the self-heat rate data at below 10% DTBP the amount of heat observed is low and thus errors may be significant. Also from 30% the change in mechanism to a spontaneous completion of the reaction is apparent. Therefore the accelerating rate calorimetry data is likely to be reliable in the range 10-30%.

Table 1

% DTBP	ϕ-solution	ϕ-peroxide
2	1.33	69.3
5	1.33	26.9
10	1.33	13.5
15	1.33	8.97
20	1.33	6.73
25	1.33	5.38
30	1.33	4.49
35	1.33	3.89
40	1.33	3.36
45	1.33	2.99
50	1.33	2.69

Table 2 (at the end) summarises the data. The self-heat rates determined after correction for ϕ show little variation at lower temperatures but at higher temperatures deviation occurs. This is to be expected since at higher temperature there is depletion of sample and because the order of reaction is not zero. This decomposition is understood to be a first order reaction.

Accuracy, Validity and Reproducibility of Accelerating Rate Calorimeter Data

There has been much published research on the decomposition of DTBP and this has shown variation in thermokinetic parameters. The paper by Tou and Whiting (Ref 3) suggests best values for heat of reaction and activation energy are -43 Kcal/mole and 38 Kcal/mole. This heat of reaction would suggest an adiabatic temperature rise of 600°C for the pure peroxide. The summary of data from the tests carried out here is given in Table 2. This shows that within the range 10-25% the heat of reaction values agree closely with the published data. At lower and higher concentrations there is error. The maximum heat rate of more concentrated solutions show heat loss but in these tests since there has been spontaneous ending of the reaction. The maximum self-heat rate has gone into the range 200-1000°C/min. Although the Accelerating Rate Calorimeter cannot readily follow such rapid reactions, the heat loss is not specifically due to this but because the rates here recorded after change of mechanism are artefactual, basically showing heat transfer from the sample to the thermocouple.

Fig. 2 shows two 20% DTBP tests, they illustrate the reproducibility of the Accelerating Rate Calorimeter.

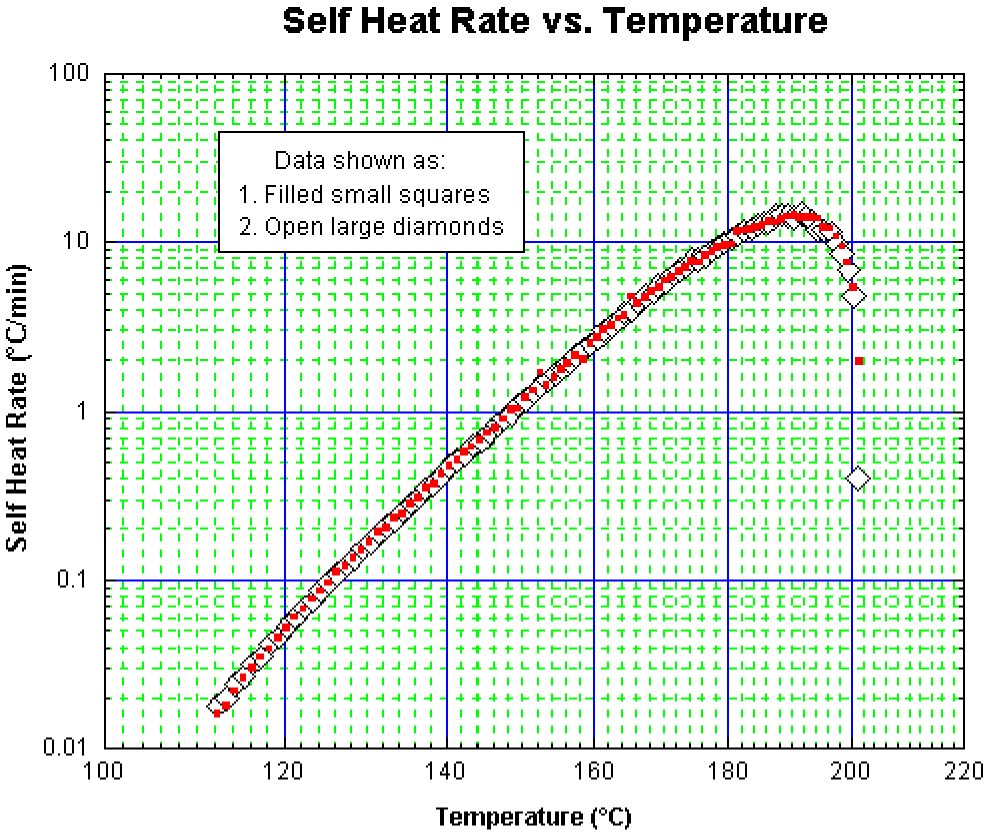

Fig 2

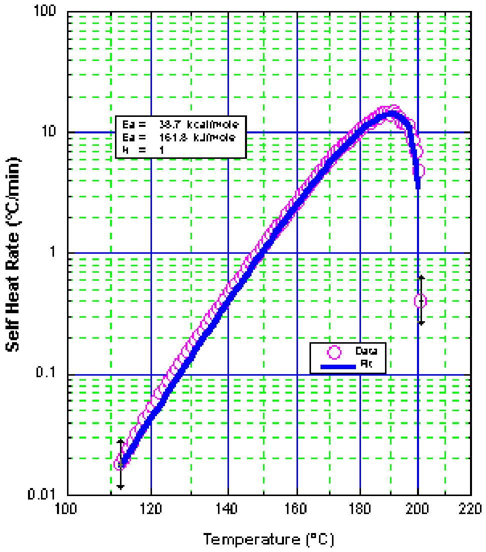

Fig. 3.

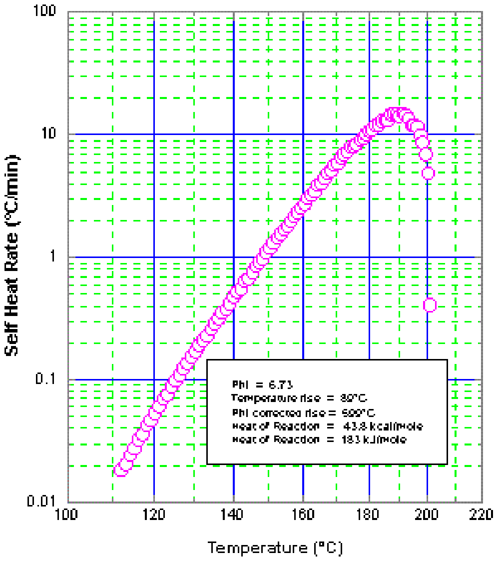

Fig. 4.

Fig. 3 shows the kinetically modelled predicted self-heat rate curve and Fig. 4 for the thermodynamic heat of reaction. Clearly these show excellent comparison with the expected data. For further and more detailed results from DTBP/toluene see THT Technical Information Sheet No 100, which is a set of 'specimen results' from this sample.

<u>'Dial-a-phi', the Use of the Accelerating Rate Calorimeter at ϕ = 1 or any Chosen ϕ.</u>

For reaction engineering, where there is a reactive material in solution, it may be appropriate to experiment at ϕ = 1 or other ϕ value. This can readily be done with the Accelerating Rate Calorimeter. Essentially all that is needed is to compensate for the thermal capacity of the bomb by a reduction of an appropriate amount of solvent.

There are essentially 4 methods to get to a ϕ = 1 situation: (1) Adjust the solution concentration to compensate from the heat lost into the bomb (as described here); (2) use a heater inside or on the outer surface of the sample container; (3) employ a light bomb or a bomb within a bomb approach and (4) use a very, very large sample container. Method (1) is simplest to perform, in most cases is very appropriate and perhaps least prone to problems.

This again may be illustrated by considering DTBP in toluene.

The process may be 15% DTBP and the process vessel may be very large. The phi of the vessel may not the known, and therefore it may be best to test as close to ϕ = 1 as possible.

To test at ϕ = 1 in an accelerating rate calorimetry test simply increase the % concentration as described - only 1-3% more concentrated solution is needed.

In a test similar to that reported earlier, the sample container may be 5g, the sample weight may be 8g. The $\phi_{15\% \text{ solution}}$ = 1.12 about the lowest possible by accelerating rate calorimetry, unless non-standard bomb types are used.

However in this container, ϕ_{peroxide} = 7.50

$$\phi = 1 + \frac{5 \times 0.1 + 8 \times 0.85 \times 0.5}{8 \times 0.15 \times 0.5}$$

If there was no container, ϕ_{peroxide} = 6.67

$$\phi = 1 + \frac{8 \times 0.85 \times 0.5}{8 \times 0.15 \times 0.5}$$

This is the ϕ value for a ϕ = 1 or containerless 15% DTBP solution.

To simulate this in the Accelerating Rate Calorimeter extra peroxide is required according to the equation below:

$$6.67 = 1 + \frac{5 \times 0.1 + 8 \times (1 - x) \times 0.5}{8 \times (x) \times 0.5}$$

$$x = 16.87\%$$

A 16.87% solution in a 5 gram Accelerating Rate Calorimeter bomb will be equivalent to a test than with a 15% solution in a zero gram bomb.

Now considering the data shown here, it is clear that such a test could be carried out easily in the Accelerating Rate Calorimeter. Thus it is simple to compensate for heat lost into the bomb without any error. Also to simulate fire situations, ϕ values well below 1 could be tested or of course higher ϕ scenarios could also be tested.

Considering the solution ranges used generally in the Chemical Processing Industry and the heats capacity of the Accelerating Rate Calorimeter bombs, this Dial-a-ϕ approach is appropriate and can be applied to concentrations up to 90%.

Accelerating Rate Calorimeter Pressure Data

Shown in Fig. 5 is the pressure data for these tests and Fig. 6 the pressure rate data.

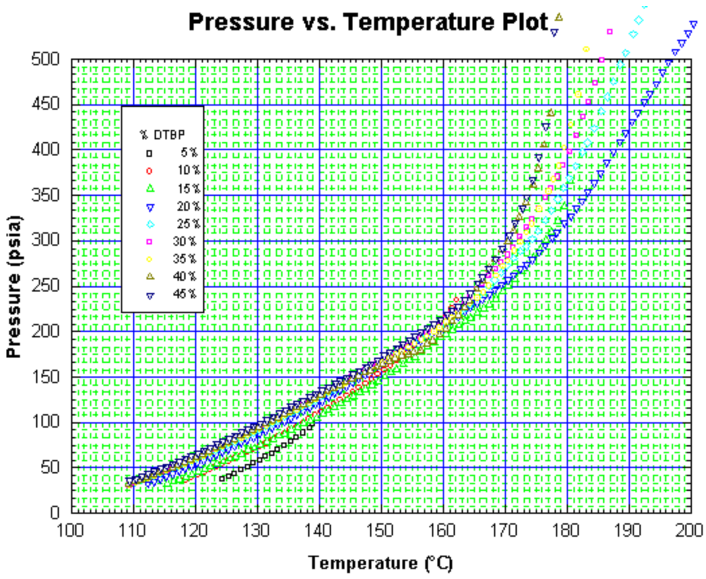

Fig 5

It is interesting to note that at temperatures up to 160°C, the pressure generated by each solution is similar. This may be expected since the pressure generated is the vapour pressure of the toluene and a contribution from gas generated by the reaction. Gas generated from the reaction would contribute to the total pressure and this would cause a reduction in the contribution from the vapour pressure of toluene. Further testing by accelerating rate calorimetry can provide pressure data and pressure rate

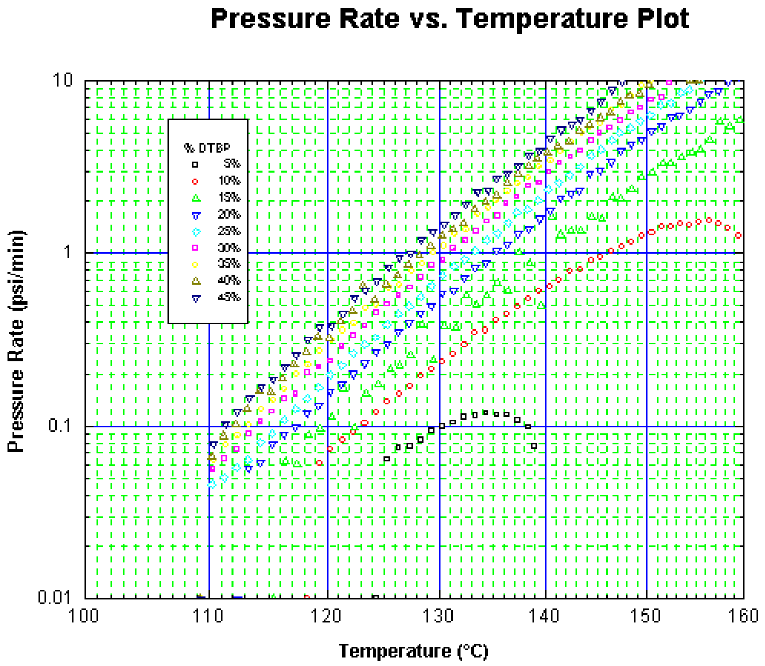

Fig 6

data that can be used for vent size calculations. This can be done in the T.H.T Accelerating Rate Calorimeter using a special option, the VSU or for simple closed cell tests Thermal Hazard Technology produces low ϕ test cells.

The pressure data given has not been normalised for the void volume above the sample. This is necessary for interpretation. However it is interesting to note the comparison of the results for the series of DTBP/peroxide tests, this is shown in Table 3 below.

Table 3

DTBP	Pressure Rate	at 130°C	Pressure Rate	at 140°C
%	raw	ϕ corrected	Raw	ϕ corrected
5	-	-	-	-
10	0.25	3.4	0.65	8.7
15	0.38	3.4	1.3	11.7
20	0.57	3.8	1.7	11.8
25	0.71	3.8	2.3	12.4
30	0.92	4.1	2.8	12.6
35	1.1	4.2	3.3	12.6
40	1.2	4.0	3.8	12.7
45	1.3	3.8	4.3	12.8

At 130°C the ϕ-corrected pressure rates for 20-45% DTBP show a rate of 4.0±0.2 psi/min (5% error). Again within a 5% error at 140°C all results with DTBP at 15-45% show a pressure rate of 12.3 ±0.6psi/min. The indication here is that the pressure rate is independent of DTBP concentration, which may be a result of pressure produced by gaseous species of reaction being compensated for by reduction in toluene partial pressure.

Ref 1. Townsend D I, Ferguson H D and Kohlbrand H T, Int Symp Runaway Reactions, Orlando 1992

Ref 2. THT Technical Information Sheet No 22

Ref 3. Tou J C & Whiting L F: Thermochimica Acta 48, 21 (1981)

Table 2

DTBP	ϕ	Onset Temp	Max Rate	Temp max rate	Temp mechan change	Final Temp	Heat of ΔT raw	Reaction ΔT ϕ-corr	Heat At Raw	rate 120°C ϕ-corr	Heat at raw	rate 130°C ϕ-corr	Heat at raw	rate 140°C ϕ-corr	Heat at raw	rate 150°C ϕ-corr	Heat at raw	rate 160°C ϕ-corr
%		°C	°C/min	°C	°C	°C	°C	°C	°C/min	°C/min	°C/min	°C/min	°C/min	°C/min	°C/min	°C/min	°C/min	°C/min
5	26.91	123	0.03	135	-		16	430	0.010	0.269	0.026	0.699	-	-	-	-	--	-
10	13.46	117	0.27	153	-		44	592	0.025	0.337	0.071	0.956	0.160	2.15	0.260	3.50	0.142	2.01
15	8.97	114	1.7	172	-		66	592	0.040	0.359	0.110	0.987	0.286	2.56	0.620	5.56	1.20	10.7
20	6.73	111	15	188	-		89	599	0.050	0.336	0.162	1.09	0.444	2.99	1.10	7.40	2.61	17.6
25	5.38	108	65	201	-		108	581	0.063	0.338	0.214	1.15	0.580	3.12	1.57	8.45	3.95	21.2
30	4.49	108	227	206	194		125	561	0.080	0.359	0.263	1.18	0.746	3.35	2.02	9.07	5.10	33.9
35	3.84	108	417	206	190		140	538	0.098	0.376	0.312	1.20	0.900	3.47	2.51	9.64	6.90	26.5
40	3.36	108	505	200	182		151	507	0.115	0.386	0.362	1.22	1.05	3.52	2.96	9.95	8.05	28.5
45	2.99	108	644	206	179		**	-	0.124	0.372	0.410	1.23	1.19	3.57	3.40	10.2	9.14	28.3
100								589*										

* Based upon ΔH = 43kcal/mol, c_p = 0.5 cal/g°C (Ref 3)

** Bomb rupture