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THERMAL RUNAWAY IN THE THERMAL EXPLOSION OF A LIQUID

J. Verhoeff and *P. J. van den Berg*

PRINS MAURITS LABORATORY TNO, P. O. BOX 45, 2280 AA RIJSWIJK;
LABORATORY FOR CHEMICAL TECHNOLOGY, DELFT UNIVERSITY
OF TECHNOLOGY, JULIANALAAN 136, 2628 BL DELFT, THE NETHERLANDS

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To study the thermal explosion of liquids a low pressure autoclave has been built. The first stage of a thermal explosion, the thermal runaway, has been studied. Evaluation of the temperature–time history results in kinetic data. Comparison with other thermal methods shows that the reliability of the method is better than with DTA.

Tertiary butylperoxybenzoate has been investigated in the temperature range of 330 K to 440 K. Decomposition starts with a short period of autocatalysis, up to a conversion of about 0.05. The subsequent decomposition can be described by a second order process in the first instance and by a first order process in the last resort. Induced decomposition occurs up to a conversion of about 0.95.

The description of exploding liquids is usually based on detonation or deflagration. However, many liquids do not detonate when shocked by an explosive and do not deflagrate when ignited by a flame. Yet an explosion can occur after a prolonged period of heating. This is called thermal explosion and is characterized by a considerable degree of self-heating or thermal runaway of the liquid before the larger part of the explosion energy is released. Actually an explosion comparable to a deflagration or detonation does not occur until after a drastic change in the physical state of the liquid by the thermal runaway process.

The theory of thermal explosion [1–3] is concerned with the competition between heat generation of the reacting system and heat dissipation by conduction, convection and radiation from the reacting mass to the outside. The tendency of the reacting system to rise above the ambient temperature due to self-heating is opposed by both the heat transfer to the surroundings and the heat consumption of the reactant. It is worth noting here that the thermal explosion theory tries to account for the onset of the explosive behaviour of energetic substances during storage or during batch-wise operation. Hence, a continuously stirred tank reactor is not considered.

To evaluate the temperature–time history for a thermal explosion and to gather reaction kinetic data a low pressure autoclave has been built. Tertiary butyl peroxybenzoate (TBPB) has been chosen as a model substance [4].

Experimental technique

The low pressure autoclave consists mainly of a heated sample compartment and an isothermal compartment in which the explosion products expand (Fig. 1). The inner volume is 0.01 m^3. The maximum working pressure is 4.0 MPa at a temperature of 473 K. The construction material is stainless steel.

The temperature of the insulated autoclave is kept at a constant value with the exception of the bottom which accommodates the sample vessel in a well. Around this well an electric heating wire has been fitted for heating the sample mass. Besides, this well is provided with a cooling jacket to make starting temperature below room temperature possible. The low pressure autoclave has a special form for two reasons.

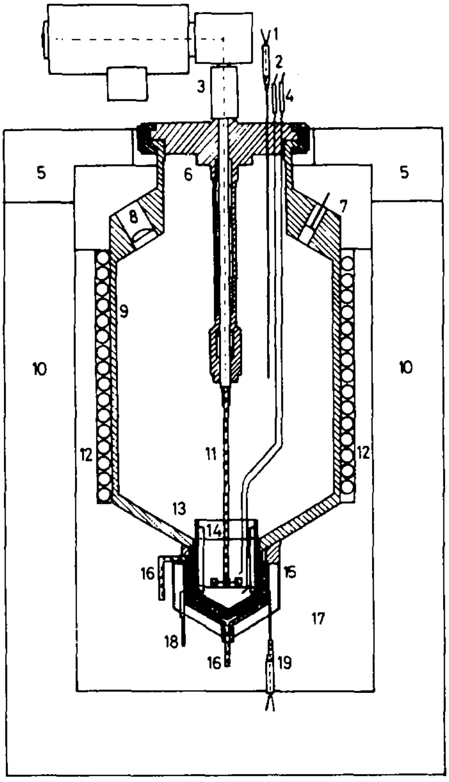


Fig. 1 Low pressure autoclave. 1. thermocouple autoclave, 2. thermocouple sample vessel, 3. stirring motor and transmission, 4. thermocouple sample vessel, 5. insulation cover filled with polyurethane, 6. cover of the autoclave, 7. pressure transducer, 8. safety membrane, 9. autoclave, 10. insulation jacket filled with polyurethane, 11. stirrer (flat-blade disk, $D_S = 30$ mm, 4 blades 5 X 6 mm), 12. cooling coil (thermostat), 13. sample vessel, 14. baffles, 15. cooling jacket (cryostat), 16. electric heating, 17. space around pressure vessel filled with insulation material, 18. platinum thermometer, 19. thermocouple

The sample part should be designed in such a way that explosions caused by self-heating can be investigated. Facilitating the heat transfer from the external heating coil to the sample during the heating period and hampering the heat transfer from the sample to the apparatus during the self-heating and explosion period calls for a compromise. Therefore a height/diameter ratio of about 1 has been chosen for the sample part of the autoclave while an air-space of 1 mm between inner sample vessel and the autoclave has been designed to obtain the required heat resistance. In order to prevent high pressures it was necessary to design a relatively large pressure vessel for the explosion products to expand. The low pressure autoclave is protected against too high a pressure by a bursting membrane of 4.5 MPa. Since oxygen from air may react with the hot explosion products the apparatus is purged with nitrogen before each test. For homogeneity of the sample mass during the self-heating period of the sample a 4-blade turbine stirrer has been mounted. During each test temperatures and pressure are monitored simultaneously.

Thermal runaway

As mentioned before a thermal explosion occurs if the transfer of heat from reactant to surroundings is insufficient. In this case self-heating may increase the temperature of the reactant to such an extent that finally an explosion occurs. The thermal explosion of liquids (Fig. 2) consists primarily of a period in which a thermal runaway reaction increases the temperature of the reactant exponentially and in the second place a period in which the explosion causes a fast pressure rise. Between thermal runaway and explosion lies the transition from a reactant which is homogeneous to one that is heterogeneous in temperature. At the end of the runaway stage temperature differences in the reacting liquid increase and result in a local initiation of a deflagration.

Owing to the fact that the term thermal explosion is used in a manner slightly different from that in literature the definition of this term is elucidated in the following scheme which gives different stages and respective features.

THERMAL EXPLOSION =	THERMAL RUNAWAY +	INITIATION +	EXPLOSION
time scale (seconds)	$10^4 - 1$	$10 - 0.1$	$1 - 10^{-3}$
main feature	uniform temperature	non-uniform temperature	propagating reaction zone through a running-away mass

Thermal runaway is defined as the stage during which the reacting liquid shows self-heating and a homogeneous temperature distribution. The feature of the subsequent initiation stage is the heterogeneity with respect to the temperature. The final explosion stage is characterized by a propagating reaction zone through a reactant that is already reacting.

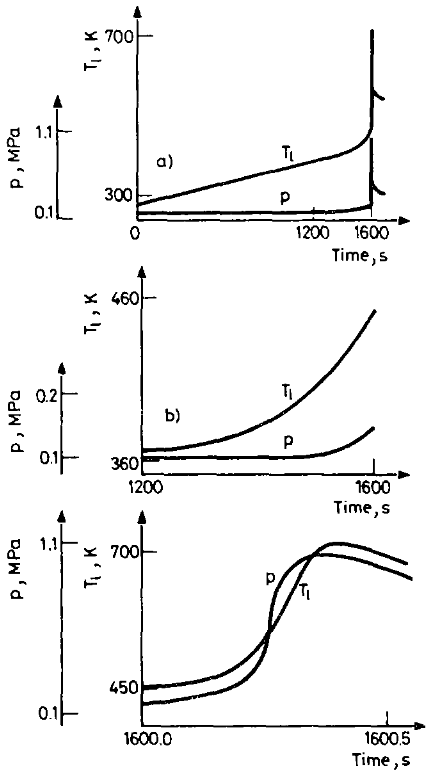


Fig. 2 Temperature and pressure course during a thermal explosion experiment in the low pressure autoclave at a prepressure of 0.1 MPa. a. linear heating followed by thermal explosion, b. thermal runaway stage of the thermal explosion, c. explosion stage of the thermal explosion

Reaction kinetic data from the thermal runaway curve

From evaluating the different modes of heat transfer it appears that the following equation describes approximately the heating rate of the sample

$$(mc_p)_t \frac{dT}{dt} = (hS)_w(T_w - T) - (hS)_g(T - T_g) \qquad (1)$$

where $(mc_p)_t$ = heat capacity of sample and sample vessel (JK^{-1}), $(hS)_w$ = heat transfer between sample and hot wall (WK^{-1}), $(hS)_g$ = heat transfer between sample and cold gas (WK^{-1}).

Equation (1) assumes that the temperature of the sample and the sample vessel are equal. This approximation is justified if the temperature does not rise too fast (e.g. less than 0.1 Ks^{-1}). Estimated values for $(hS)_w$ and $(hS)_g$ are 0.4 WK^{-1} and 0.2 WK^{-1} respectively.

The thermal runaway is preceded by the heating stage (constant heating rate) and starts when the temperature–time curve deviates from the linear curve which originates from external heating of the sample. In course of time the thermal runaway stage changes into the initiation stage.

For evaluation of the experimental results the upper boundary of the runaway stage has been defined as the lowest temperature at which a difference of 2 K is measured between the two sensors in the sample.

The heat resistance between the sample vessel and the autoclave is high as compared with the heat resistance between the reactant and the sample vessel. This means that the temperature difference between the sample and the sample vessel is negligible in the beginning of the thermal runaway curve. To judge if this simplification is allowed for the end of the thermal runaway curve as well, the time constant of the sample vessel has to be considered. With a heat capacity of 142 JK^{-1}, a heat exchange area of $15 \cdot 10^{-3}$ m^2 and a heat transfer coefficient of 800 to 2600 $Wm^{-2}K^{-1}$, which holds for most organic liquids, a time constant of 4 to 12 seconds is calculated. As this time constant is large compared with the time-scale of the thermal runaway curve, the temperature of the sample vessel must be calculated in order to determine the heat generation of the sample. Therefore the experimental data of the thermal runaway curve are processed with the following equations:

$$m_1 c_{p1} \frac{dT_1}{dt} = q_g - (hS)_{14}(T_1 - T_4) - (hS)_{12}(T_1 - T_2) \tag{2}$$

$$m_2 c_{p2} \frac{dT_2}{dt} = (hS)_{12}(T_1 - T_2) + (hS)_{32}(T_3 - T_2) - (hS)_{24}(T_2 - T_4) \tag{3}$$

$$T_3 = T_{3.0} + bt \tag{4}$$

and boundary conditions at $t = 0$:

$$q_g = 0$$

$$\frac{dT_1}{dt} = \frac{dT_2}{dt} = b$$

where T_1 = temperature of the sample, K; T_2 = temperature of the sample, K; T_3 = = temperature of the bottom of the autoclave, K; $T_{3.0}$ = temperature of the bottom of the autoclave at $t = 0$, K; T_4 = temperature of the upper part of the autoclave, K; hS = heat transfer value, WK^{-1}; q_g = heat generation of the sample, W and b = = heating rate at $t = 0$, Ks^{-1}.

If T_1 at $t = 0$ is chosen from the experimental curve, T_2 as well as T_3 at $t = 0$ ($T_{3.0}$) can be calculated with the help of equations (2) and (3). With these initial values a further evaluation of the experimental T_1 versus t curve (thermal runaway curve) is obtained by a stepwise calculation of T_2 and q_g by using equation (5):

$$T_2(i+1) = T_2(i) + 0.5\left\{\left(\frac{dT_2}{dt}\right)_i + \left(\frac{dT_2}{dt}\right)_{i+1}\right\}\{t(i+1) - t(i)\} \tag{5}$$

At $T_1(i+1)$ the rate of temperature rise $(dT_2/dt)_{i+1}$ is calculated with equations (3), (4) and (5). Thereafter $T_2(i+1)$ and $q_g(i+1)$ are determined with equations (5) and (2) respectively.

A trial and error method is necessary to determine the activation energy of the runaway reaction. Suppose that the reaction can be described by

$$q_g = q_m \cdot m_0 = Cm_0(1-\xi)^n \exp\left(-\frac{E}{RT}\right) \tag{6}$$

A convenient method is to take a value for n and to check after that if the experimental set of (T_1, q_g, ξ) values obey equation (6). This procedure is repeated until $\ln\{q_g \cdot (1-\xi)^{-n}\}$ becomes a linear function of T_1^{-1}. Although such a method is fundamentally correct, difficulties arise in judging the best value for n. Owing to the small conversion range it is even rather difficult to discriminate between zero, first and second order processes. Therefore the activation energy of the thermal runaway is determined by assuming a zero order reaction during this stage. The fault that is introduced by making this assumption is relatively small. A simple calculation shows that the activation energies for different reaction models mostly differ less than ten percent.

Table 1 Influence of parameter values on the calculated values for the heat generation and conversion as functions of temperature

Set of parameters	$T_1 = 394.0$ K		$T_1 = 411.7$ K		$T_1 = 433.7$ K	
	q_g, W	ξ	q_g, W	ξ	q_g, W	ξ
1	90.6	0.0406	415.1	0.0809	1928	0.1249
2	80.4	0.0365	362.2	0.0720	1636	0.1096
3	100.9	0.0455	451.5	0.0900	2005	0.1365
4	91.4	0.0412	417.4	0.0817	1930	0.1258
5	88.7	0.0399	400.3	0.0790	1839	0.1211
6	91.0	0.0408	416.7	0.0812	1929	0.1252
7	91.1	0.0410	416.8	0.0814	1929	0.1254
8	90.6	0.0406	415.1	0.0809	1928	0.1249

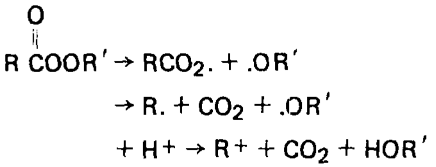
Set of parameters	m_1c_{p1}, JK^{-1}	m_2c_{p2}, JK^{-1}	$(hS)_{14}$, WK^{-1}	$(hS)_{12}$, WK^{-1}	$(hS)_{32}$, WK^{-1}	$(hS)_{24}$, WK^{-1}	T_4, K
1	200	142	0.05	30	0.32	0.17	300
2	160	x	x	x	x	x	x
3	x	200	x	x	x	x	x
4	x	x	0.08	x	x	x	x
5	x	x	x	20	x	x	x
6	x	x	x	x	0.35	x	x
7	x	x	x	x	x	0.19	x
8	x	x	x	x	x	x	320

x means: same value as used in set 1.

The sensitivity of the calculation procedure for the heat generation and conversion as functions of temperature with respect to the parameter values of equations (2) to (4) is shown in Table 1. One experimental $T_1 - t$ curve has been evaluated using different parameter values. Although it appears from Table 1 that mc_p values strongly influence the q_g and ξ values, further calculations indicated that differences in activation energies determined from the calculated q_g, ξ values are smaller than 3 kJ mol^{-1}.

Decomposition rate of tertiary butylperoxybenzoate (TBPB)

Tertiary butylperoxybenzoate (TBPB) belongs to the group of peroxyesters which may decompose via a single or multiple bond-breaking process [5]. It is widely used as a source of free radicals for polymerization. Peroxyesters show a spectrum of mechanisms ranging from oxygen–oxygen bond homolysis through the two-bond homolytic fragmentation with varying degrees of polar character of the transition state, to an ionic process. This is illustrated by the following scheme:



$$\begin{aligned} R\overset{\overset{O}{\|}}{C}OOR' &\rightarrow RCO_2. + .OR' \\ &\rightarrow R. + CO_2 + .OR' \\ &+ H^+ \rightarrow R^+ + CO_2 + HOR' \end{aligned}$$

These mechanisms operate in the peroxyesters of tertiary alcohols. Cyclic concerted decomposition occurs with peroxyesters of primary and secondary alcohol. Also metal-catalyzed decomposition may occur.

In general it is rather difficult to distinguish between one-bond and multiple-bond cleavage because in many systems the decarboxylation step

$$RCO_2. \rightarrow R. + CO_2$$

is relatively fast. Moreover induced decomposition may occur, which means that a faster decomposition rate is measured as a consequence of the interaction between radicals and unreacted peroxyesters. TBPB shows induced decomposition. Higher concentrations increase the decomposition rate, while the addition of radical scavengers reduces the rate increase [6]. Induced decomposition often occurs at concentrations above 0.1–0.2 *M*. Therefore reaction kinetic measurements are preferably performed with diluted samples.

Several investigators have shown that TBPB is a one-bond radical initiator [5, 7]. Reported first order rate constants for TBPB in alkane solvents vary from $5.97 \cdot 10^{-5}$ s^{-1} to $7.21 \cdot 10^{-5}$ s^{-1} at 388 K [7]. Blomquist [6] reports an activation energy of 144 kJ mol^{-1} for the homolysis of TBPB in the temperature range 383 K – 403 K.

An extensive kinetic study of the stability of TBPB and para-substituted peroxybenzoates has been performed by means of differential scanning calorimetry [8–10].

Kinetic parameters of thermolysis in several solvents are given. Investigations were carried out in the temperature range 373 K – 413 K. The conclusion is that the free activation enthalpy is a specific characteristic of the thermal stability. This parameter is recommended instead of the activation energy and the pre-exponential factor of the Arrhenius relation in evaluating the effect of aromatic ring substituents on stability. If the Arrhenius relation is applied to describe the experimental results the following values hold for TBPB in the range 373 K – 413 K:

$E = 139.0 \pm 1.7$ kJ mol^{-1} (activation energy)

$\ln k_0 = 33.3 \pm 0.4$ ((pre-exponential factor of a first order decomposition, s^{-1})

For our purposes it is sufficient to use the Arrhenius relation due to the accuracy of the experimental results. A useful application of the Eyring relation requires discrimination between activation energies which differ about 1 kJ mol^{-1}.

Finally the total amount of heat, which is the sum of the enthalpies of the different reactions during decomposition of TBPB, has been reported for decomposition in several solvents [10]. Values for di-*n*-butylphthalate, diphenylether, tri-isopropylbenzene and di-*n*-octyl adipate are – 318, – 259, – 280 and – 285 kJ mol^{-1} respectively.

One-bond homolysis of TBPB in a solvent (SH) occurs according to the following scheme [8]:

$C_6H_5{-}C(O)OOC(CH_3)_3 \rightarrow (CH_3)_3CO. + C_6H_5{-}C(O)O.$

$(CH_3)_3CO. + SH \rightarrow (CH_3)_3COH + S.$

$(CH_3)_3CO. \rightarrow (CH_3)_2C{=}O + CH_3.$

$CH_3. + SH \rightarrow CH_4 + S.$

$C_6H_5{-}C(O)O. + SH \rightarrow C_6H_5C(O)OH + S.$

$C_6H_5{-}C(O)O. \rightarrow CO_2 + C_6H_5.$

$C_6H_5. + SH \rightarrow C_6H_6 + S.$

Decomposition rates by other methods

Decomposition rate measurements of technical pure TBPB have been performed with the adiabatic storage test (AST), the isothermal storage test (IST), differential thermal analysis (DTA) and the low pressure autoclave (LPA). The AST, IST and DTA, which are complementary, are described by Barendregt [11] who used these techniques for several substances. Each test method has its specific advantages. The isothermal and adiabatic storage tests are the most sensitive, which means that reaction kinetic data are determined for the lowest possible temperature range. From investigating the thermal stability of tertiary butylperoxypivalate [12] the conclusion has been drawn that the test results of these methods agree surprisingly well for this substance in a rather broad concentration and temperature range. A similar, more extensive comparison is given here for tertiary butylperoxybenzoate.

The influence of the degree of conversion on the rate constant has been determined by consecutive AST experiments. Twenty-five tests were necessary to decompose the peroxide completely.

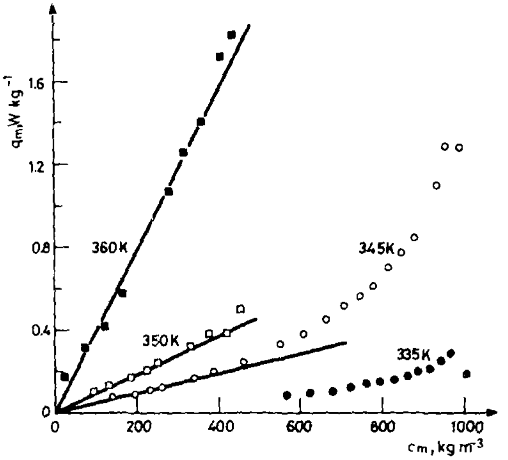


Fig. 3 Heat generation of TBPB as a function of concentration at different temperatures as measured with the help of the AST

Evaluation of the heat generations measured at a certain temperature in successive tests results in the concentration dependence of the rate of decomposition. The results of this evaluation are given in Figure 3 for four temperatures: 335, 345, 350 and 360 K. From this Figure it is concluded that below concentrations of about 500 kg m^{-3} the decomposition of TBPB is a first order process. The reaction rate constant is:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{7}$$

where $k_0 = 2.819 \cdot 10^{15}$ s^{-1}, $E = 144.65$ kJ mol^{-1}, temperature range: 345–360 K.

In the concentration range 500–900 kg m^{-3} the decomposition of TBPB can be described by a second order process. This is shown in Fig. 4. In this case the heat generation is:

$$q_m = k_0 Q c_{m,0} (1 - \xi)^2 \exp\left(-\frac{E}{RT}\right) \tag{8}$$

where $k_0 = 1.02 \cdot 10^{12}$ m^3 kg^{-1} s^{-1}, $E = 139.5$ kJ mol^{-1}, $Q = 1380$ kJ kg^{-1}, $c_{m,0} = 1040$ kg m^{-3}, temperature range: 335 K – 355 K.

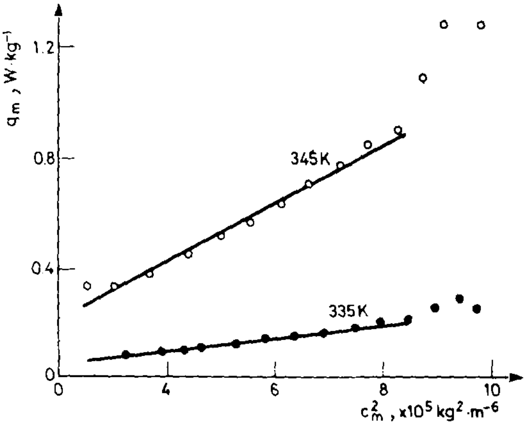


Fig. 4 Heat generation of TBPB as a function of quadratic concentration at two temperatures measured with the help of the AST

In the concentration range 900–1040 kg m^{-3} the decomposition of TBPB follows a high-order (above 2) process, which points to autocatalysis.

A direct method to measure the concentration dependence of the heat generation is found in the isothermal storage test (IST). With this technique the heat generation of a sample of 0.01 kg is measured as a function of time by heat flow sensors. Some results for TBPB are given in Fig. 5. These measurements clearly show autocatalysis at the beginning of the decomposition of technical pure TBPB. Further elaboration of the results reveals that the conversion must be about 20% before the decomposition

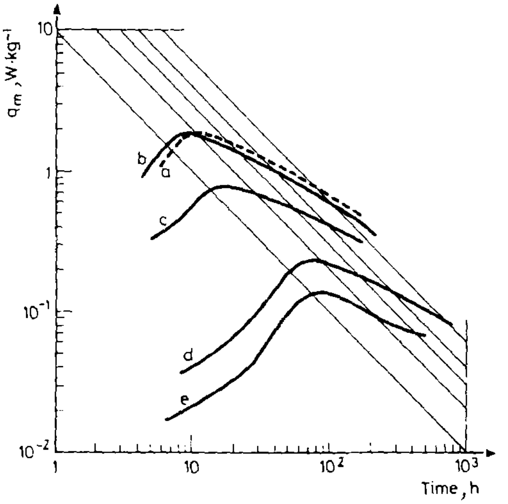


Fig. 5 Heat generation of TBPB as a function of time at different temperatures as measured with the help of the IST. a. 348.2 K; b. 347.7 K; c. 342.2 K; d. 335.8 K; e. 330.1 K

obeys a second order process. This agrees with the AST results. Up to a conversion of about 20% the activation energy amounts to 163±6 kJ mol^{-1}. Chemical analysis after the test (which is normally not performed until complete conversion) makes it possible to determine the heat of reaction.

Non-isothermal differential thermal analysis is a technique that provides data from which both the temperature and concentration dependence of the heat generation can be found. Due to the small amount of sample (milligrams), decomposition rate data are determined at considerably higher temperatures than those covered by AST and IST. The DTA experiments have been performed in pressuretight nickel–chromium sample vessels provided with an inner glass vessel. The nett volume of the vessel is $0.5 \cdot 10^{-6}$ m^3. Evaluation of the DTA curves has been carried out by means of the following equations (see also [11]:

$$q_m = \frac{yK_1}{m} \tag{9}$$

$$T_1 = T_{\mathrm{ov}} - \tau_{\mathrm{v}}\dot{T}_{\mathrm{ov}} + \frac{y}{K_2} \tag{10}$$

where y = DTA signal, V; K_1 = calibration constant, indium sensitivity, WV^{-1}; T_1 = = temperature of the liquid sample, K; T_{ov} = oven temperature, K; $\dot{T}_{\mathrm{ov}}$ = heating rate of the oven, Ks^{-1}; τ_{v} = time constant of the sample vessel, s; K_2 = sensor sensitivity constant, VK^{-1}.

In opposition to the evaluation procedure of AST measurements, where a zero order approach is permitted owing to the small changes in concentration during one AST experiment, the evaluation method of a non-isothermal DTA experiment has to take account of both temperature and concentration changes during the experiment. A possible solution is to make use of the general heat generation equation [6] and to solve it by trial and error.

Other solutions are discussed in [11]. The trial and error method assumes the order n and subsequently calculates $q_m/(1-\xi)^n$ as a function of T_1 from the measured DTA curve. Graphical representation of $\ln q_m/(1-\xi)^n$ versus $1/T_1$ reveals whether the assumed order is acceptable for the observed DTA curve.

The results of three DTA runs with TBPB under different experimental conditions are given in Table 2 and one run in Fig. 6. From Table and Figure it is apparent that it is extremely difficult to conclude about reaction order and activation energy. The general picture from the DTA experiments agrees broadly with the aforementioned results from AST and IST: a second order decomposition preceded by an autocatalytic process and followed by a first order decomposition. However, the activation energies resulting from the three DTA runs differ markedly. The presence of oxygen seems to influence the decomposition process as appears from the values of the heat of reaction and the activation energy. Heat generation values in the temperature range 370 K – 385 K in experiment DTA-1 (nitrogen) exceed the values of DTA-2 (air) by a factor of 2 to 4. Obviously oxygen inhibits the decomposition of TBPB.

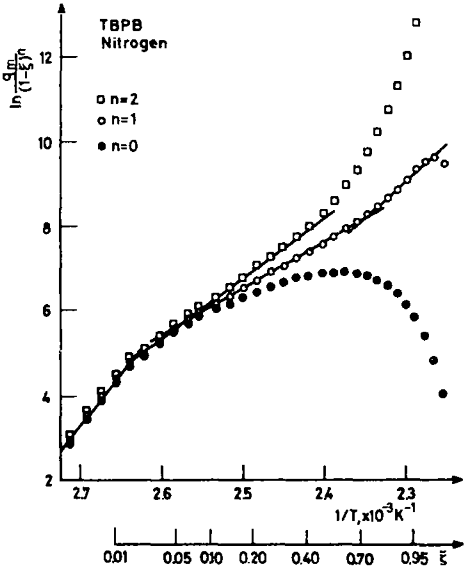


Fig. 6 Results of DTA-1

Table 2 DTA results for TBPB in a pressuretight sample vessel

Conditions	DTA–1		DTA–2		DTA–3	
$\dot{T}_{ov}$, mK s^{-1}	33.1		33.3		3.33	
m, mg	4.91		5.05		46.03	
Atmosphere	nitrogen		air		nitrogen	
Sample vessel	NiCr, glass		NiCr, glass		NiCr, glass	
Results						
Q, kJ mol^{-1}	229		274		232	
	E, kJ mol^{-1}	C, W kg^{-1}	E, kJ mol^{-1}	C, W kg^{-1}	E, kJ mol^{-1}	C, W kg^{-1}
$\xi \approx 0.01$ $n = 0$	206	$3.1 \cdot 10^{30}$	270	$6.0 \cdot 10^{38}$	264	$1.2 \cdot 10^{39}$
$\xi \approx 0.20$ $n = 2$	118	$2.3 \cdot 10^{18}$	164	$2.2 \cdot 10^{24}$	110	$1.2 \cdot 10^{17}$
$\xi \approx 0.30$ $n = 1$						
$\xi \approx 0.40$ $n = 1$	93	$1.0 \cdot 10^{15}$				
$\xi \approx 0.60$ $n = 1$			101	$1.4 \cdot 10^{16}$	109	$6.0 \cdot 10^{16}$
$\xi \approx 0.85$ $n = 1$	148	$5.5 \cdot 10^{21}$				
Calculated	q_m at 400 K, W kg^{-1}		q_m at 400 K, W kg^{-1}		q_m at 400 K, W kg^{-1}	
$\xi = 0.20$	570		540		330	
$\xi = 0.30$	500		630		220	
$\xi = 0.40$	430		540		190	
$\xi = 0.60$	290		360		140	
$\xi = 0.85$	39		140		52	

The differences between DTA-1 and DTA-3 may partly be attributed to the slightly different temperature ranges and are manifest if heat generations at corresponding conversions are compared for one temperature. Several values are given in Table 2 for a temperature of 400 K. This temperature lies in the measuring range of both experiments, which means that extrapolation from the measured conditions to the respective conversions at 400 K is rather small. Nevertheless considerable differences in heat generations occur between DTA-1 and DTA-3. The explanation of these differences must be sought in the simplified calculation procedure of the heat generation as a function of temperature from the original DTA signal, in the different mass of sample and in decomposition in the gas phase.

Thermal runaway of tertiary butylperoxybenzoate

This paragraph deals with the results of various experiments with tertiary butylperoxybenzoate (TBPB) in the LPA. First of all the results of a series of "standard" tests with 100 g of TBPB are discussed. The experimental procedure for these tests has been given before. For practical reasons the temperature–time curve is not evaluated directly from point T_1 $(t = 0)$ where the curve begins to deviate from the linear heating curve. The first measuring point is the point which deviates 5 K from the extrapolated linear heating line. The conversion ξ at that point is estimated by means of the actual heat generation and the time from T_1 $(t = 0)$. The "end point" of the thermal runaway curve is determined by the moment when the difference between the two thermocouples exceeds 2 K. The results of seven identical experiments with TBPB in the LPA are as follows:

Experimental conditions:

$\dot{T} \approx 40$ mK s^{-1}	$T_g = 300$ K
$m = 100$ g	$\omega = 5$ s^{-1}
nitrogen	$P_0 = 0.1$ MPa

Results: zero order:

$E = 127.8$ kJ mol^{-1}, standard deviation 2.0 kJ mol^{-1}

$C = 7.53 \cdot 10^{19}$ W kg^{-1}, standard deviation $4.06 \cdot 10^{19}$ W kg^{-1}

The relatively large standard deviation of the heat generation factor is caused by the fact that a mutual dependency exists between E and C. Determination of the spread in heat generation requires recalculation of C values after application of the same (mean) activation energy.

With a value of 128 kJ mol^{-1} a mean C value of $7.35 \cdot 10^{19}$ W kg^{-1} with a standard deviation of $0.10 \cdot 10^{19}$ W kg^{-1} has been obtained. Therefore the heat generation of TBPB can be summarized by the following formula

$$q_m = 7.4 \cdot 10^{19} \exp -\frac{128000}{8.314\,T} \tag{11}$$

temperature range: 380–430 K, pressure range: 0.1–0.15 MPa, conversion range: 0–12.

In Fig. 7 a logarithmic plot of q_m versus the reciprocal temperature is given as an example of the results of an LPA experiment. In Fig. 8 an isothermal curve at 405 K is shown. This plot has been obtained by converting all the data points shown in Fig. 7 to the temperature of 405 K by using the Arrhenius relation and the activation energy that follows from the zero order approximation. Figure 8 clearly shows the autocatalytic behaviour of TBPB up to a conversion of about 0.05.

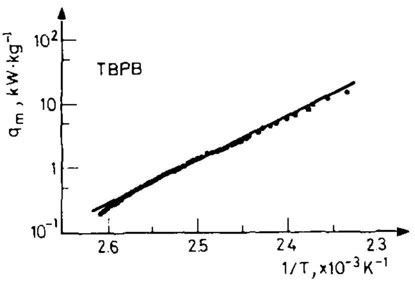


Fig. 7 Heat generation of TBPB as a function of temperature

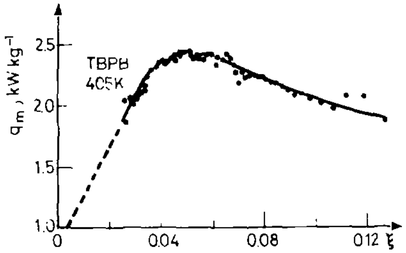


Fig. 8 Heat generation of TBPB as a function of conversion at a constant temperature

A series of experiments with TBPB has been performed at different prepressures within the range 800–10 kPa. The results of this series is summarized in Table 3. If the prepressure is larger, a higher activation energy is found. This is illustrated by the heat generation values. As the temperature increases the influence of the prepressure becomes more pronounced: at 430 K and a prepressure of 800 kPa the heat generation is more than 3 times as high as at 10 kPa. An explanation for these phenomena is found in the heat consuming process of evaporation of decomposition products and of TBPB. From the composition of the decomposition products it follows that a maximum amount of about 70 g of products with an atmospheric boiling

Table 3 Thermal runaway data of TBPB. Temperature range: 380 K–430 K, Conversion range: 0–0.12, Experimental conditions: $\dot{T} \approx 40$ mK s^{-1}, $T_g = 300$ K, $\omega = 5$ s^{-1}, nitrogen

p_0, kPa	E, kJ mol^{-1}	C, W kg^{-1}	q, kW kg^{-1} 380 K	390 K	400 K	410 K	420 K	430 K
800	135	$6.63 \cdot 10^{20}$	0.2	0.5	1.6	4.2	10.7	26.4
400	133	$3.76 \cdot 10^{20}$	0.2	0.6	1.6	4.3	10.8	26.2
100	128	$7.40 \cdot 10^{19}$	0.2	0.5	1.4	3.6	8.9	20.9
60	122	$1.19 \cdot 10^{10}$	0.2	0.5	1.4	3.4	8.0	18.0
40	106	$8{,}38 \cdot 10^{16}$	0.2	0.5	1.2	2.6	5.5	11.1
20	101	$1.88 \cdot 10^{16}$	0.2	0.6	1.2	2.5	5.2	10.1
10	96	$3.77 \cdot 10^{15}$	0.2	0.5	1.1	2.2	4.3	8.2

point below 430 K is formed from 100 g of TBPB. If the heat of evaporation is assumed to be 500 J g^{-1} it follows that evaporation of 11 g s^{-1} is necessary to account for the decrease of 5.5 kW kg^{-1} at 100 kPa with respect to 800 kPa at 430 K.

From the heat generation of 26.4 kW kg^{-1} at 430 K follows a maximum evaporation of 13 g s^{-1}. The discrepancy of 11 g s^{-1} is caused by two other phenomena, viz. accumulation of decomposition products in the liquid during the thermal runaway and condensation at the upper steel part of the sample vessel which is in contact with the relatively cold gas phase.

To enable a comparison between DTA and LPA results four tests have been performed with a 40% w/w solution of TBPB in dibutylphthalate. The results calculated on the assumption of a 0.6 conversion of TBPB are:

$$q_m = 2.0 \cdot 10^{18}(1-\xi)\exp -\frac{118000}{8.314\,T} \tag{12}$$

$E = 117.9$ kJ mol^{-1}, standard deviation 4.3 kJ mol^{-1}

$C = 2.0 \cdot 10^{18}$ W kg^{-1}, standard deviation $0.1 \cdot 10^{18}$ W kg^{-1}

temperature range: 395–445 K, pressure range: 0.1–0.15 MPa, conversion range: 0.60–0.74.

Finally the thermal runaway of TBPB has been measured in air instead of nitrogen in the LPA. The results obtained are similar as for nitrogen.

Discussion

Heat generations

In the preceding paragraphs many heat generation equations have been given for the decomposition of TBPB. A variety of experimental conditions have passed in review. The results are conveniently arranged in Fig. 9. From this Figure a careful comparison can be made with the results obtained with AST, IST, DTA and LPA.

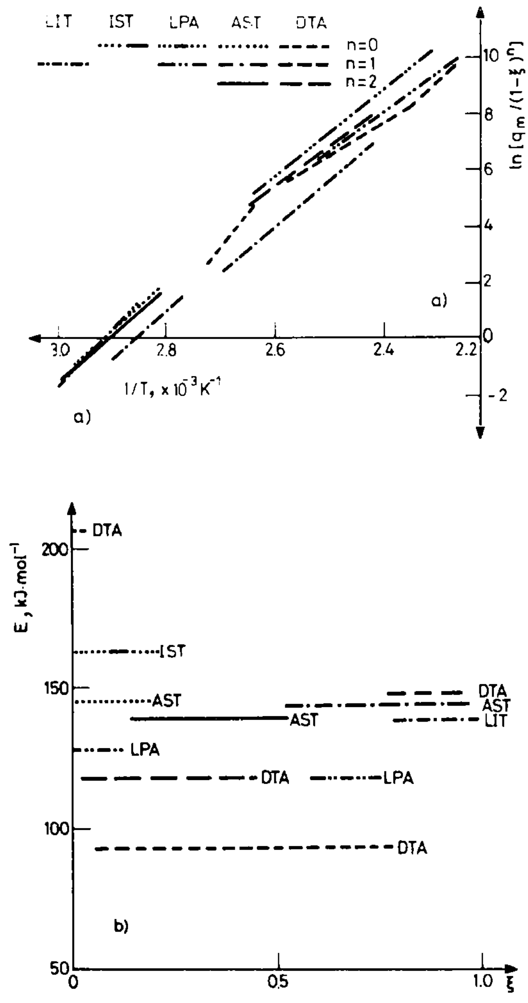


Fig. 9 Comparison of test results of TBPB

Notwithstanding the wide temperature range, which extends from 330 K to 440 K, there is a surprisingly good agreement between the different test results with respect to heat generation q_m as a function of temperature. A relatively narrow band covers all the results plotted in Fig. 9a. At one temperature the $q_m/(1-\xi)^n$ values differ by a factor of not more than 6. If the respective ξ and n values of the individual lines are taken into account the q_m values appear to agree very well. However, the activation energies differ markedly.

Autocatalytic range

In the very beginning of the decomposition of TBPB, up to conversions of about 0.03 (DTA) and 0.05 (LPA), autocatalytic decomposition occurs, resulting in a very high apparent activation energy of at least 200 kJ mol^{-1} (DTA). Each separate test proves an autocatalytic decomposition of TBPB in the initial phase. An eminent test for studying the autocatalytic behaviour of TBPB is the isothermal storage test (IST) because this phenomenon only occurs in a very narrow conversion range in the beginning of decomposition. Its eminence especially springs from its sensitivity, which is sufficiently high to measure at temperatures at which the rate of decomposition is so low that conversion during the temperature equilibration after inserting the sample is small in relation to the conversion range of autocatalytic behaviour. An isothermal DTA experiment is inadequate because a substantial part of autocatalytic decomposition occurs before the sample has attained its measuring temperature. No more useful is non-isothermal DTA because the autocatalytic decomposition is completed in a very small temperature range, which causes an inaccurate activation energy. Moreover the actual heat transfer from the sample to the measuring sensor is so complex that evaluation of such a very small part of the DTA curve is at least doubtful.

The low pressure autoclave (LPA) and the adiabatic storage test (AST) are more useful than DTA but less suitable than IST for studying the autocatalytic decomposition of TBPB. Owing to the change in both the temperature and the conversion of the sample during experimentation the influence of the two variables has to be derived from the temperature–time curve. In fact it is necessary to solve one equation with two unknown variables. Therefore LPA and AST results are less useful for the study of the influence of the conversion on the decomposition than IST is.

First order and second order range

The above mentioned factors elucidate the fact that the zero order lines of Fig. 9a show the least similarity. When the first and second order lines in the low temperature regime (AST) are extrapolated to higher temperatures the agreement is excellent, except for the literature data in [9]. The low position of the literature line can be explained by the phenomenon of induced decomposition which often occurs at concentrations above 0.2 *M* (roughly equivalent to conversions below 0.96). A comparison of the LPA results from 40% w/w TBPB in dibutylphthalate with the literature line reveals that q_m increases with a factor of about 2 by induced decomposition. It appears from Fig. 9a that the zero order AST line after extrapolation covers the zero order LPA line. The difference between both lines is their activation energy. The same holds for the first order AST line and the first order LPA line. In both cases the activation energy has its lowest value for the LPA results which originate from the highest temperature range. As pointed out in the previous paragraph this is caused by evaporation. If evaporation is reduced, for example by increasing the prepressure of the LPA test, the activation energy is also in accordance with the AST value.

Interpretation of DTA curves

It has already been concluded that the DTA results agree with the other tests because they are covered by a narrow band in Fig. 9a. The activation energies of the DTA experiments differ markedly from the other test results. Moreover there exist considerable differences between different DTA experiments. A comparison of DTA-1 and DTA-3 shows that the results are affected by heating rate and sample mass. A distinct advantage of a non-isothermal DTA run is that it covers the whole conversion range. At the same time this has the consequence that the method is rather insensitive for the determination of reaction kinetic parameters of a substance like TBPB that shows a changing reaction mechanism. Nevertheless DTA activation energies are significantly lower than LPA values. Also considerable differences occur between the heat generations calculated at 400 K from the results of DTA-1 and DTA-3.

A first explanation of these results is the simplified calculation of the heat generation values from the DTA signal by means of the equations used. Heat transfer from the sample to the measuring sensor has to overcome several resistances: sample/glass, glass/steel and steel/sensor. Approximation of these resistances by one calibration constant K_2 to correct the sample temperature is too simple. Owing to the gaseous reaction products the heat transfer coefficient from sample to glass decreases substantially in the course of the test. The pressure inside the vessel, which changes if another sample mass is used, also influences the heat transfer coefficients inside the vessel.

A second explanation concerning the deviating DTA results is found in the possibility of decomposition in the gas phase of the sample vessel. At higher temperatures decomposition of gaseous TBPB is more probable. Experiment DTA-2 shows that air instead of nitrogen in the gas phase in the sample vessel has a marked influence. Further investigations into these aspects are recommended so as to obtain a better evaluation method for DTA curves of substances like TBPB.

Conclusions

Thermal runaway, the first stage of a thermal explosion of a liquid, is characterized by a uniform temperature of the liquid or liquid–gas dispersion. Evaluation of the temperature–time history from a thermal explosion of 100 g of sample in the low pressure autoclave (LPA) results in reaction kinetic data for tertiary butylperoxybenzoate (TBPB) which are in very good agreement with the other test results treated in this article, and with literature. As is apparent from independent calibration experiments the accuracy of the LPA results is such that the reliability rises above the results of differential thermal analysis (DTA).

Technical pure TBPB has been investigated in the wide temperature range of 330 K to 440 K. Decomposition starts with a short period of autocatalysis, up to a conversion of about 0.05. The subsequent decomposition can be described by a second order process in the first instance and by a first order process in the last resort. Induced decomposition occurs up to a conversion of about 0.95. Excellent agreement exists for the adiabatic storage test (AST) results in the 330–360 K range and the LPA results in the 380–440 K range.

Depending on the pressure, thermal runaway of TBPB is to a greater or less extent accompanied by evaporation of TBPB and decomposition products.

Development of a more realistic evaluation method for non-isothermal DTA curves of substances like TBPB is strongly recommended. This should preferably be performed by means of a model substance whose kinetic data have been determined accurately by means of LPA experiments.

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Zusammenfassung — Zur Untersuchung der thermischen Explosion von Flüssigkeiten wurde ein Niederdruckautoklav konstruiert. Es wurde das erste Stadium der thermischen Explosion, das thermische "Durchgehen" untersucht. Die Auswertung des Temperatur–Zeit-Geschehens ergibt kinetische Daten. Vergleiche mit anderen thermischen Methoden zeigen, daß diese Methode zuverlässiger als die DTA ist. Tertiär-Butylperoxybenzoat wurde im Temperaturbereich von 330–440 K untersucht. Die Zersetzung verläuft zu Beginn eine kurze Zeit bis zu einer Konversion von etwa 0.05 autokatalytisch. Die folgende Zersetzung kann in erster Linie als ein Prozeß zweiter Ordnung und letztlich als ein nach erster Ordnung verlaufender Prozeß angesehen werden. Eine induzierte Zersetzung erfolgt bis zu einer Konversion von 0.95.

Резюме — Для изучения термического взрыва жидкостей был построен автоклав низкого давления. Изучена первая стадия термического взрыва-термического пробега. Проведена оценка результатов температура-время по данным кинетики реакции. Сравнение этого метода с другими термическими методами показало его лучшую надежность по сравнению с ДТА. Перекись трет-бутилбензоата исследована в области температур 330–440 К. Разложение начинается с короткого периода автокатализа, протекающего со степенью превращения около 0,05. Последующее разложение может быть описано реакцией второго порядка для первого примера, а в крайнем случае-реакцией первого порядка. Индуцированное разложение протекает со степенью превращения около 0,95.