

EXPERIMENTAL DATA ON THE THERMAL KINETICS OF ORGANIC PEROXIDES

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ABSTRACT

The heat effects from the exothermic decomposition of concentrated organic peroxides have been investigated experimentally for three peroxy esters (*tert*-butyl peroxy benzoate, *tert*-butyl peroxy 2-ethyl hexanoate and *tert*-butyl peroxy pivalate). Four different calorimetric instruments were used: adiabatic and isothermal storage tests, differential thermal analysis and the low pressure autoclave. The heat generation values which could be measured with these instruments vary from 10^{-2} to 10^4 W kg⁻¹ (Watt per kilogram of peroxide). From the experimental data the following thermal kinetic information was obtained: total heat of decomposition, activation energy, heat generation factor, and the occurrence of induced decomposition. The storage/control temperatures and run-away data were calculated with these parameters. The calculated values agree with the experimental data for peroxides directly determined in the industrial 30-l container. The advantage of the computation by means of parameters is that the thermal conditions of practical situations as met, e.g., in production units can also be calculated. These thermal conditions can hardly be determined by direct experiments.

1. INTRODUCTION

The plastics industry widely uses organic peroxides in processes for the manufacture of high polymers, polyesters and natural rubbers. The free radical reactions for performing polymerization, curing and cross-linking are generally initiated with the aid of organic peroxides. In these chemical processes the peroxides act as a free radical source to start a chain of free radical reactions. The decomposition of peroxides into free radicals generally proceeds by thermal activation. A common denominator of the reactivity of the peroxide is its half-life time as a function of temperature. Only a low concentration of peroxide in the monomer, resin or compound is needed.

The thermal activation of the pure peroxide can cause safety problems. The decomposition reaction is exothermic so that self-heating of the product increases its reactivity and by repetition of this mechanism the decomposition can reach extremely high rates. Such a self-accelerating decomposition is accompanied by the formation of hot gaseous decomposition products and can at the end of its thermal run-away cause a fire or a thermal explosion. These hazardous events have to be avoided and appropriate precautions are to be taken.

Extensive safety precautions, primarily with respect to temperature control, are necessary during storage, transport and handling of the peroxides. Originally, safe temperatures for handling the peroxides were established by empirical tests. Experiments at actual scale were carried out to determine the temperature at which self-accelerating decomposition of the peroxide takes place. This temperature, diminished by a safety margin of 10–20°C, yields a safe temperature for handling. The above procedure is certainly reliable but becomes extensive when every deviating practical situation has to be tested and it becomes even unworkable in some cases, e.g., if safe temperatures for large containers filled with peroxide have to be determined. In order to arrive at a more general approach, thermal stability studies were undertaken.

The determination of safe handling temperatures for peroxides by calculation requires reliable data on the thermal decomposition kinetics of the pure or highly concentrated peroxides. The kinetic data are established by laboratory tests. Today many types of calorimetric instruments are available. A few examples are: differential scanning calorimetry (DSC), adiabatic storage test (AST), isothermal storage test (IST), differential thermal analyses (DTA), accelerating rate calorimeter (ARC) and others like Sikarex or SEDEX. All these instruments yield the caloric effect of an exothermal reaction. However, it is still complicated to derive the basic reaction parameters from the measured effects. The reaction rates and activation energies calculated from the results can differ markedly.

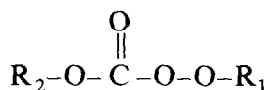
It is the aim of this article to determine a consistent set of thermal kinetic data for a selected group of organic peroxides in concentrated form. Reliability of the data is first pursued by using four different types of instruments to determine the data. Secondly, the data so obtained were used to calculate the storage temperature and the heat generation during run-away of some simple practical conditions. The predictions were compared with the outcome of the empirical tests. In this way it is secured that the thermal kinetic data can be used for practical applications.

2. DECOMPOSITION KINETICS

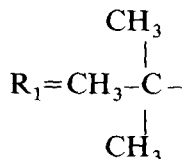
The four instruments used in this study are AST, IST, DTA and LPA (low pressure autoclave). The investigated peroxides are *tert*-butyl per-

oxybenzoate, *tert*-butyl peroxy 2-ethyl hexanoate and *tert*-butyl peroxy pivalate (75% in isododecane).

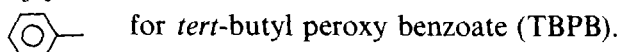
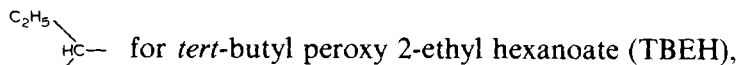
The three selected peroxides belong to the chemical group of peroxy esters



where, for the investigated peroxides

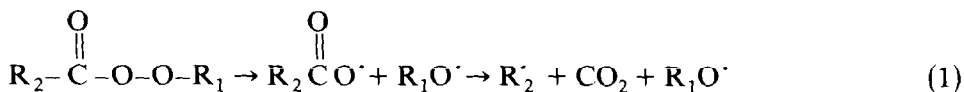


and $R_2 = R_1$ for *tert*-butyl peroxy pivalate (TBPP),



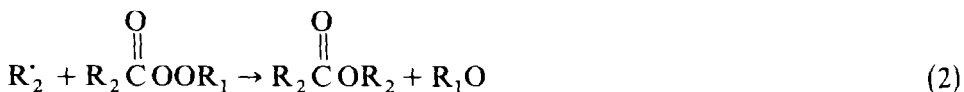
The decomposition of this type of molecules mainly proceeds in two ways:

(a) by thermal homolysis



It is found from the decomposition products that decarboxylation takes place to a very high extent.

(b) by induced decomposition



The cleavage of the oxygen-oxygen bond occurs at relatively low temperatures. For the three peroxides the differences in reactivity are due to the structure of R_2 .

The half-life time values at 100°C are 4 min for TBPP, 20 min for TBEH and 700 min for TBPB.

The reactivity data refer to very dilute solutions of the peroxides. For the non-diluted or highly concentrated peroxides the start of the decomposition is important. The most important characteristic safety parameter for the onset of a potential hazardous decomposition is the self-accelerating decomposition temperature (SADT). The specific SADT values are 20°C for TBPP, 35°C for TBEH and 55°C for TBPB. The order of thermal stability is

clearly TBPB > TBEH > TBPP, which is, as expected, the reverse of their reactivity order.

A better description of the thermal stability of peroxides and of such phenomena as self-accelerating decomposition requires more information on the thermal kinetics of the peroxide decomposition. A complete kinetic study of the decomposition reactions is quite complicated. The common reaction rate for diluted peroxy esters reads [1]

$$-d[P]/dt = k_d[P] + k_i[P]^{3/2} \quad (3)$$

where k_d and k_i are the reaction rates for the thermal homolytic and induced decomposition, respectively.

For concentrated peroxides the reaction rate will be more complicated, e.g.

$$-d[P]/dt = \sum_i k_i [P]^{n_i} ([P_0] - [P])^{m_i} \quad (4)$$

as indeed, autocatalyses and first- and second-order reactions have been observed.

Reactions of this kind have different activation energies. The whole decomposition pattern becomes extremely complex. For industrial purposes, however, only a limited conversion range, about 15%, is of interest. The first reason for this is that the decomposition of the organic peroxide during regular handling has to be very limited in order to meet the product specifications. Secondly, non-diluted peroxides contain so much energy that under run-away conditions the temperature rise will become uncontrollable before a conversion of 10% has been reached. For the description of such a limited conversion range one can start with a simple expression, e.g., zero- or first-order kinetics, and add more terms if necessary.

The general expression to describe the thermal effects reads [2-4]

$$q = k_0 c_0^{n-1} (-\Delta H) (1 - \xi)^n (\xi + \kappa)^m \exp(-E/RT) \quad (5)$$

where it is assumed that the volume of the peroxide will not change during decomposition since ξ is less than, say, 0.15.

The introduction of only one activation energy is based on the assumption that rupture of the oxygen-oxygen bond is the rate-determining step. The practical approach is therefore to determine experimentally the heat production as a function of temperature.

The degree of conversion is calculated from the experimental data by use of the relation

$$\xi = \frac{1}{\Delta H} \int_{t_0}^t q dt \quad (6)$$

In the present work heat measurements are performed at constant temperature and the heat production is studied as a function of conversion. The change in q at constant T (see eqn. 5) gives information about the reaction

order or the influence of induced decomposition. Next, the heat production is measured over a wide temperature range. From these measurements changes in the reaction pattern caused by the reaction temperature can be studied.

Finally, the kinetic parameters are derived which most adequately describe the experimental data.

3. SHORT DESCRIPTION OF THE TEST METHOD

The heat generation measurements have been carried out using four different instruments: adiabatic storage test (AST), isothermal storage test (IST), differential thermal analysis (DTA) and low pressure autoclave (LPA). The self-accelerating decomposition temperature (SADT), from which the storage temperature of a peroxide is deduced, has been determined with the heat accumulation storage test (HAST). The run-away decompositions of the peroxides in a commercial 30-l package have been carried out at true scale.

The measuring techniques for the AST, IST and DTA are described in a previous publication [2]. In Table 1 the characteristic technical features are summarized. Most DTA experiments were performed at constant oven temperature (isothermal mode).

The low pressure autoclave (LPA) is a test method in which a peroxide sample of 100 cm³ is heated at a constant rate until a thermal explosion occurs. The sample is contained in a beaker (50 mm diameter, 100 mm height) situated at the bottom of a 10-l closed pressure vessel. Pressure and temperatures are recorded. The maximum allowable pressure amounts to 4.0 MPa at 473 K. The upper part of the pressure vessel is maintained at a constant temperature of 300 K. The sample is usually stirred at 300 rpm to obtain an even temperature throughout the sample.

When the temperatures measured 1 cm above and below the agitator differ more than 2 K the sample is considered to be no longer homogeneous, which makes it impossible to calculate the heat generation accurately (see also ref. 5).

The heat accumulation storage test (HAST), which is called in German "Wärmestauverfahren", has been developed by the German Institute for

TABLE 1

Technical data of test methods

	AST	IST	DTA (isothermal)
Sample mass (kg)	1.0	50×10^{-3}	50×10^{-6}
Temperature range (K)	273–473	293–343	173–773
Detection limit (m W kg ⁻¹)	15	5	500
Duration of test (h)	350	150–450	1–24

Material Research (BAM). The HAST consists of a Dewar vessel with a capacity of 500 cm³ filled with 400 cm³ of the organic peroxide formulation. The Dewar vessel with closure is placed in an oven which is kept at constant temperature. The product temperature is monitored for 7 days after it has reached the oven temperature. The heat loss rate of the Dewar corresponds with that of a commercial 30-l package. The test is carried out at intervals of 5 K. The lowest temperature at which a run-away occurs is called the self-accelerating decomposition temperature (SADT). A full description of the test method is given in ref. 6.

The "thermal explosion test in package" is a full-scale experiment. The tests were performed with commercial packages consisting in a composite packaging of a polyethylene inner receptacle placed in a cardboard outer packaging. At the top of the inner receptacle a relief opening was provided. The contents of the packaging (25 kg) was heated by means of a specially shaped heating coil until complete decomposition of the peroxide took place. The temperature of the contents was measured by means of a thermocouple placed in the centre of the receptacle.

4. RESULTS

4.1. Induced decomposition

The influence of induced decomposition is derived from the heat generation at constant temperature. The heat generation values obtained are

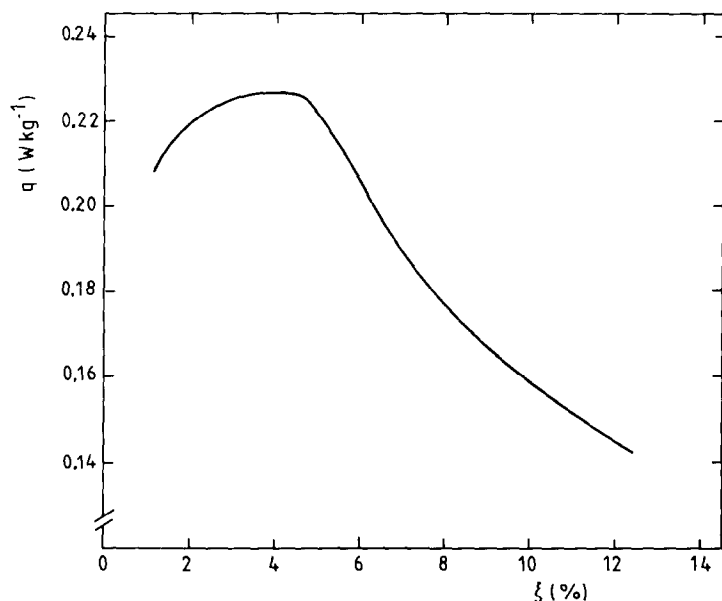


Fig. 1. Influence of conversion on the heat generation of *tert*-butyl peroxy benzoate (technically pure) at 62.8°C (335.8 K). (Derived from an IST measurement.)

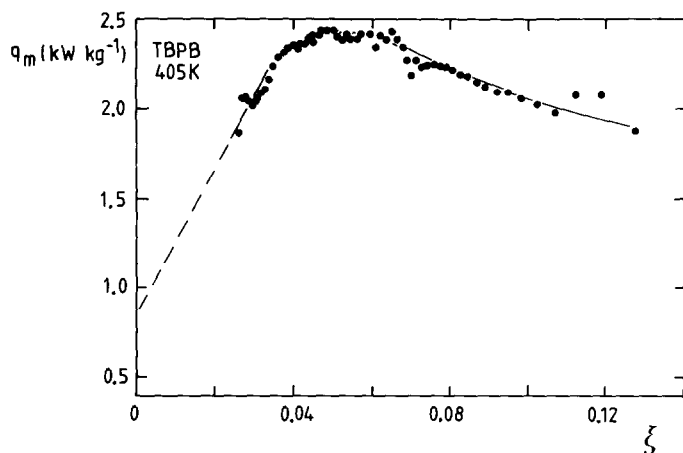


Fig. 2. Influence of conversion on the heat generation of *tert*-butyl peroxy benzoate (technically pure) at 132°C (405 K). (Calculated from an LPA experiment.)

plotted as a function of the peroxide conversion in Figs. 1–4. The results shown in Figs. 1, 3 and 4 come from isothermal test measurements. Figure 2 has been obtained from an LPA measurement in the temperature rate 383–427 K by recalculating the heat generation for the average temperature of 405 K (see ref. 5), using the activation energy as determined from the same LPA experiment. Figures 1 and 2 show the induced decomposition

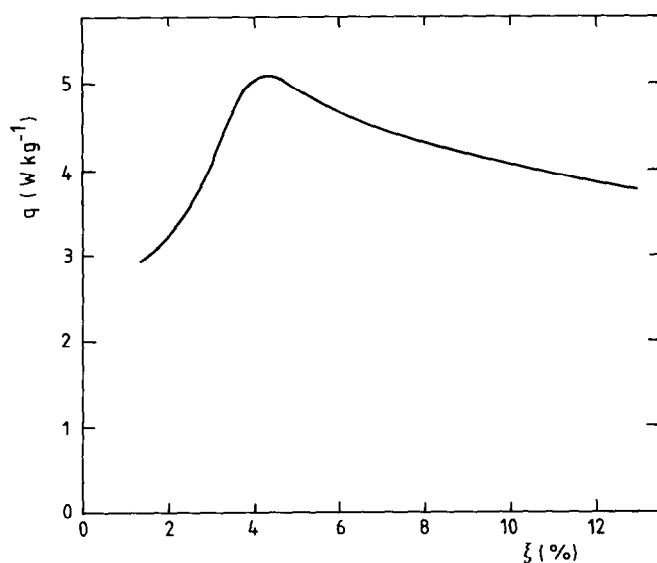


Fig. 3. Influence of conversion on the heat generation of *tert*-butyl peroxy 2-ethyl hexanoate (technically pure) at 60°C (333 K). (Derived from an isothermal DTA experiment.)

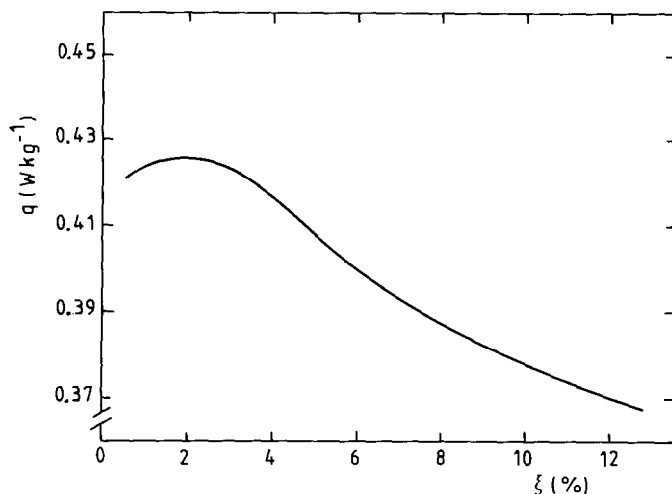


Fig. 4. Influence of conversion on the heat generation of *tert*-butyl peroxy pivalate (75% solution in isododecane) at 29.7°C (302.7 K). (Derived from an IST experiment.)

effect for TBPB at 63 and 132°C, respectively. Apparently, the induced decomposition pattern does not change very much with temperature.

From the three investigated peroxy esters the induced decomposition effect is very distinct for TBPB and TBEH, whereas it is less distinct for 75% TBPP in isododecane. The experimental results reported in ref. 2 has already shown that TBPP closely follows a first-order reaction mechanism. For the 75% concentration of TBPP the estimated reaction order is 1.15. The detailed analysis of the TBPB measurements given in ref. 5, indicating that for this substance the decomposition starts with autocatalysis (induced decomposition), which changes into a second-order reaction at 20% conversion and becomes first order at about 50% conversion. Within the conversion range which is relevant in practice the induced decomposition effects thus play an important role. In Table 2 the characteristic parameters for induced decomposition are summarized.

4.2. Heat generation as a function of temperature

As a consequence of autocatalytic effects the calculation of activation energy from thermal measurements requires some care. In the case of

TABLE 2

Characteristics of the induced decomposition effect for TBPB, TBEH and TBPP-75%

Substance	TBPB	TBEH	TBPP-75%
ξ_m (%) ^a	4–5	4	2.5
q_m ^b	2.5	1.7–2.4	1.0–1.1

^a Conversion at maximum heat generation.

^b Ratio between maximum heat generation and heat generation at zero conversion.

isothermal measurements it is sufficient to plot the heat generations which occur at the same degree of conversion as a function of temperature in a $\ln q$ vs. $1/T$ graph. In this study the maximum heat generations are taken. It follows from Figures 1 and 2 that these maxima take place at the same degree of conversion (4% for TBPB). In the case of temperature scanning measurements (LPA, AST and DTA-scan) the situation is more complicated. Generally the measured heat generation values are corrected for conversion by assuming a first-order reaction mechanism. The corrections are small for measurements covering a limited conversion range as is the case for AST and LPA where the conversion is less than 15%. The corrected values are close to the maxima in heat generation (see Figs. 2–4) with the exception of

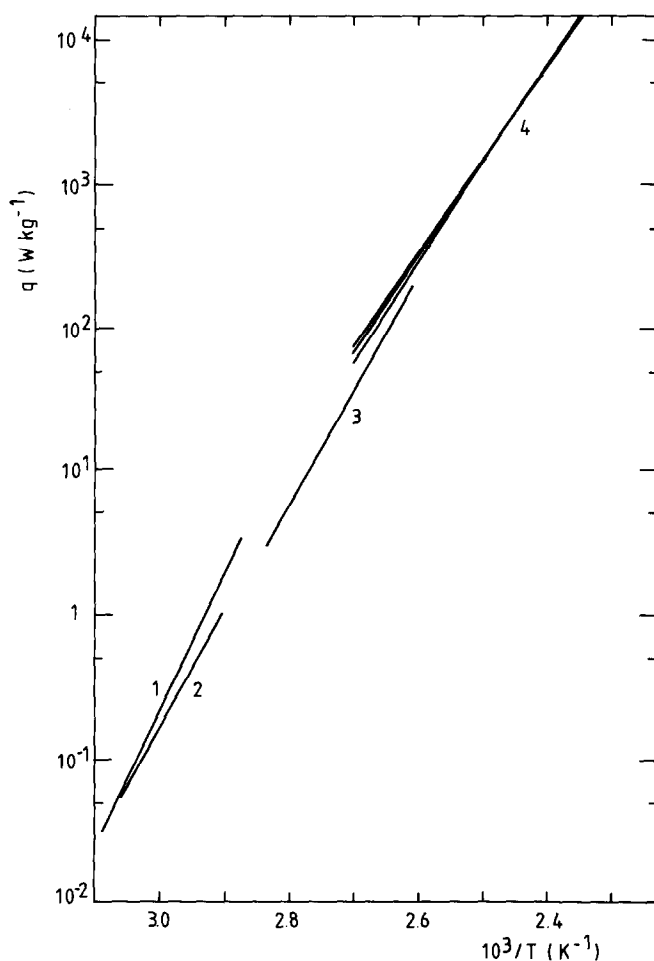


Fig. 5. Heat generation of TBPB (technically pure) determined over a wide temperature range (conversion less than 12%). (1) AST results, (2) IST results, (3) isothermal DTA results, (4) LPA results.

the very low conversion points. These points are, however, mostly disregarded as they occur at the start of the experiment where heat equilibrium has not been achieved. The correction procedure works satisfactorily for the three peroxy esters because the induced composition arises at such low conversions and its effect on the heat generation is limited. The procedure is less reliable for DTA-scan measurements which extend up to 50% conversion. For TBPP, which is almost first order, the DTA results are still accurate.

Although the corrected heat generations obtained by the scanning methods come close to the true values, the activation energy derived from one measurement can have a disturbing systematic error. The error is caused by the changing degree of conversion during measurement and the unknown

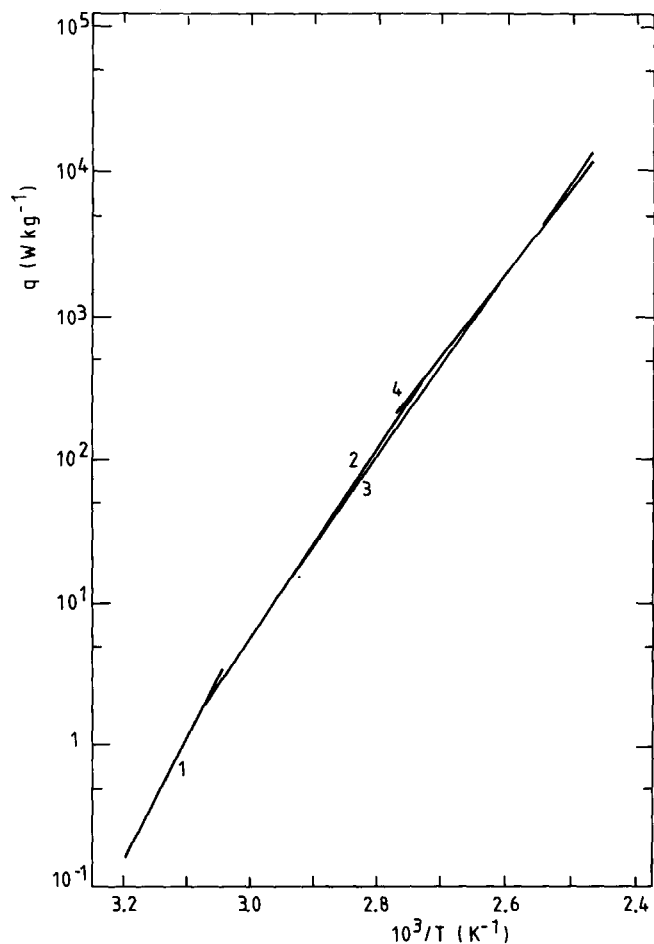


Fig. 6. Heat generation of TBEH (technically pure) determined over a wide temperature range (conversion less than 12%). (1) AST results, (2) DTA results, (3) isothermal DTA results, (4) LPA results.

kinetic parameters n , m and k in eqn. (5). The error can be greatly avoided if the activation energy is derived from several measurements with different test methods which together cover a large temperature range. This procedure will be followed here.

The heat generation values measured with the four different test methods are shown in Figs. 5–7 for TBPB, TBEH and TBPP-75%, respectively. No kinetic corrections have been applied to AST, IST and isothermal DTA results. First-order kinetic corrections have been applied to the LPA and DTA-scan results. Second-order kinetic corrections have been tried out for the LPA results of TBPB. The results neither improved nor became more reproducible in the limited conversion range covered by the LPA.

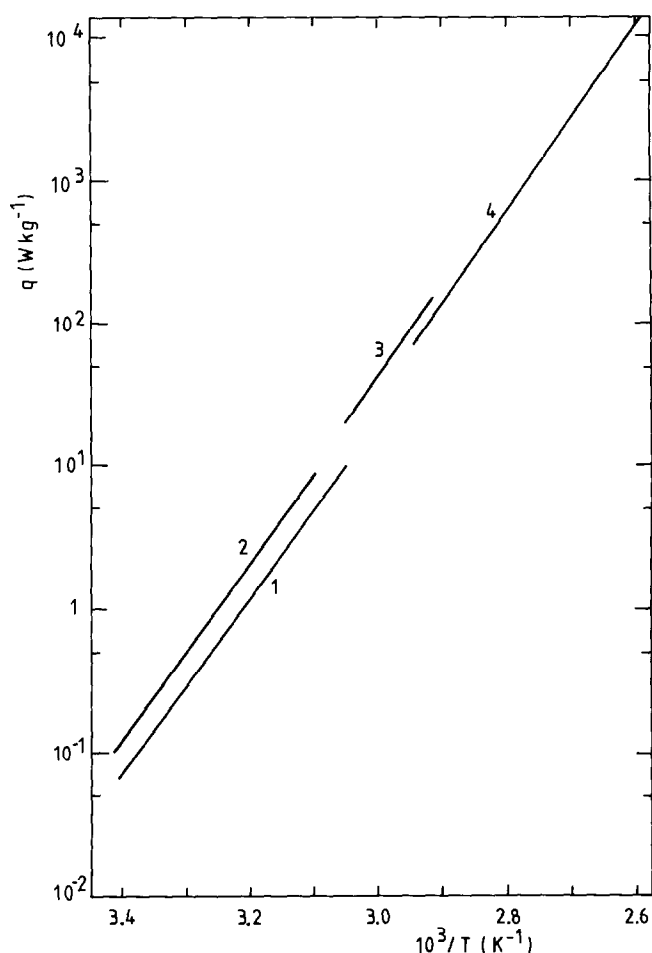


Fig. 7. Heat generation of TBPP (a 75% solution in isododecane) determined over a wide temperature range (conversion less than 12%). (1) AST results, (2) IST results, (3) isothermal DTA results, (4) LPA results.

The Figures nicely illustrate the temperature regimes covered by the different test methods. AST and IST for the low temperature measurements, LPA for the high temperature range, and DTA for the intermediate range. This combination of test methods covers a temperature range of about 120 K and heat generation values varying from as low as 10^{-2} W kg⁻¹ to as high as 10^4 W kg⁻¹. The thermal kinetic parameters obtained with each individual test method are given in Table 3. The parameters represent the average heat generation values of several test runs. The AST results for TBPB and TBEH (see the No. 1 curves in Figs. 5 and 6 and the respective numerical values in Table 3) yield very high activation energy values (E_a). This is clearly due to the induced decomposition effects which dominate the limited conversion range covered by the AST. The increasing heat generation causes a steeper slope. TBPP does not show this effect because it hardly exhibits autocatalysis (see Fig. 4). For TBPB a recalculation of the AST results by selecting a conversion range of 4–7% instead of 0–7% reduces the activation energy significantly ($E_a = 153$ instead of $E_a = 185$ kJ mol⁻¹). By using the 4–7% range the heat increasing effect shown in Figs. 1 and 2 is eliminated. The low 100 kJ mol⁻¹ activation energy for TBPP as obtained with the LPA stems from the relatively high volatility of this product. Increasing evaporation due to the temperature rise during the LPA measurement causes heat losses which affect the heat generation. An elevated pressure (0.6 MPa) from an inert gas in the vapour space of the LPA practically eliminates this effect and leads to an E_a of 123 kJ mol⁻¹. Similar effects, though much less pronounced, have been found for the LPA results of TBPB [5].

The total enthalpy of decomposition for the three peroxy esters as obtained with the various test methods are given in Table 3 as well. The values are given in kJ per kg of product, a 75% assay in the case of TBPP.

4.3. Recommended thermal kinetic data

The values given in Table 3 for E_a and $\ln C$ represent the outcome of the experimental data obtained with each particular test method. Since each of these methods is applicable over a restricted temperature range, the question arises whether the data can be combined and parameters can be found which describe the thermal data of one peroxide over the whole temperature range. As can be seen from Figs. 5–7, the data of the various test methods constitute a fairly straight line, which indicates that a simple description is feasible. A straightforward averaging of the E_a and $\ln C$ values leads to erroneous results because the two parameters are interrelated and contain some systematic deviations due to the induced decomposition effect (see Section 2). These errors are circumvented if the heat generation values themselves are used and the optimal parameter fit is made. Figure 8 illustrates the procedure for TBEH. The heat generation values obtained

TABLE 3
Results of three peroxy esters

Substance	Test method	Number of tests	E_a^a (kJ mol ⁻¹)	Mean values for ln C^b (C in W kg ⁻¹)	Temperature range (K)	Conversion range (%)	Enthalpy of decomposition (kJ kg ⁻¹)
TBPB	AST	6	184.9	65.17	323-353	7	-
		6	153	53.68	323-353	4-7	-
	IST	5	163	56.98	330-348	56	1350 ± 150
	DTA	4	154.3	53.68	353-383	ca. 40	1250
	LPA	3	128.0	45.75	380-430	12	-
TBEH	AST	2	171.0	64.00	310-331	7	-
	IST	1			313.5	-	-
	DTA	5	127.9	47.88	323-363	40	1140
	s-DTA	5	122.2	45.90	341-383	50	1070 ± 15
	LPA	3	111.0	42.44	360-405	12	-
TBPP 75% in isododecane	AST	4	117.2	45.30	294-328	7	-
	IST	5	117.8	46.06	293-323	15-96	1080 ± 140
	DTA	4	121.5	47.56	325-343	31-49	-
	LPA	3	100.0	30.14	340-395	12	-
	LPA*	2	123.0	47.81	340-395	12	-

^a E_a means activation energy.

^b C stands for the pre-exponential Arrhenius factor.

LPA* prepressurized LPA-experiment (prepressure is 0.6 MPa).

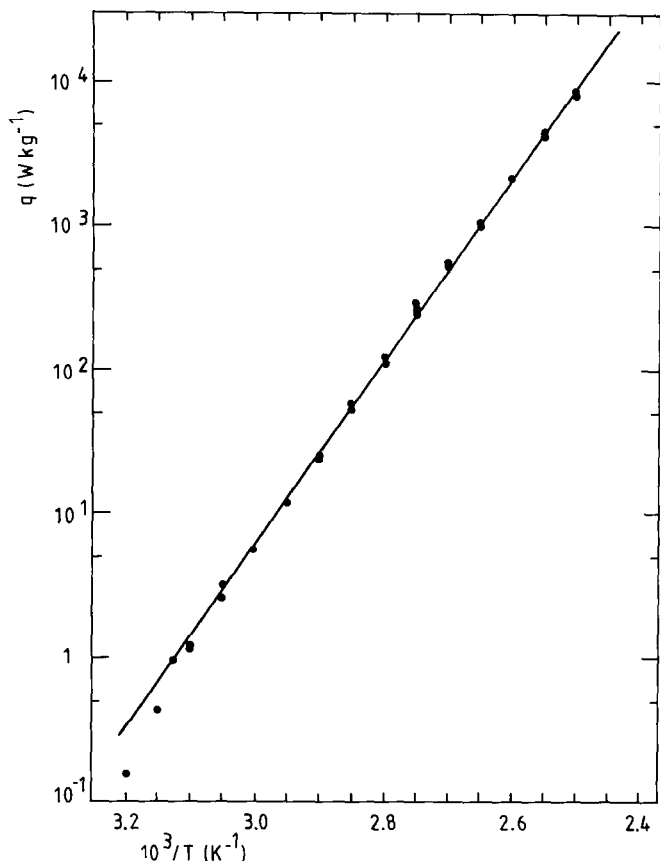


Fig. 8. Determination of the working parameter from the measured data for *tert*-butyl peroxy 2-ethyl hexanoate

with the different test methods are plotted at equal intervals of $0.5 \times 10^{-4} \text{ K}^{-1}$ for $1/T$. The parameters are determined by a least-squares fit through the points. In this way the recommended set of working parameters listed in Table 4 was obtained. The corresponding working equations read

$$q = C \exp(-E/RT) \quad (7)$$

at $\xi = 0.04$ for TBPB and TBEH and at $\xi = 0.02$ for TBPP-75%

If conversion is to be taken into account an approximate equation can be used

$$q = C(1 - \xi) \exp(-E/RT) \quad (8)$$

in the conversion range $0.04 < \xi < 0.15$ and the temperature range $300 \text{ K} < T < 400 \text{ K}$.

In the range $0.00 < \xi < 0.04$ the heat generation obtained by eqns. (7) and (8) can be much too high for TBPB and TBEH because of induced decomposition.

TABLE 4
Recommended thermal kinetic data

	E (kJ mol ⁻¹)	ln C (C in W kg ⁻¹)	Literature value	
			E (kJ mol ⁻¹)	Ref.
TBPB	145.6	51.11	139–144	7–10
TBEH	120.8	45.45	123–126	^a
TBPP-75%	123.1	47.91	122	11

^a Calculated as outlined in ref. 12.

As noted before the conversion range covered by eqn. (8) is the most important one for the practical application of concentrated peroxides.

The parameter values presented in Table 4 compare favourably with those reported in the literature. According to Blomquist and Ferris [7], the activation energy of the homolytic one-bond cleavage of TBPB amounts to 144 kJ mol⁻¹ while more recently a value of 139.0 ± 1.7 kJ mol⁻¹ has been reported [8–10]. For the homolytic one-bond cleavage of TBEH the literature values vary between 126 and 133 kJ mol⁻¹. TBPP has been extensively investigated by Buback and Lendle [11]. They arrived at 122.3 ± 3.0 kJ mol⁻¹ in the temperature range 338–378 K. They also reported first-order kinetics for TBPP, and their rate constants agree well with the values given in ref. 2. The working parameters in ref. 2 describe the whole conversion range and are also valid for different concentrations. The present values are the best fit for the 75% concentration of TBPP.

4.4. Comparison with practical data

The working parameters can be used to calculate thermal conditions encountered in practice. Such a condition is the control temperature prescribed for the transport of peroxides by the regulatory bodies. These temperatures are listed in the so-called orange book "Transport of Dangerous Goods" [6], issued by a Committee of Experts on the Transport of Dangerous Goods of the United Nations. The values are derived from the SADT values which can be determined with, e.g., the HAST. On the other hand the SADT values can be calculated with the working parameters. The calculation procedure is given in ref. 3. In Table 5 the experimental United Nations values for the SADT are compared with the calculated values. The temperatures compare favourably, in particular if one takes into account that the experimental SADT values have been determined at 5 K intervals. TBEH just does not show a thermal run-away at 30°C and so the official UN SADT is 35°C.

The working parameters can also be used to calculate the thermal conditions of a peroxide in its commercial 30-l package during a run-away.

TABLE 5

Comparison of UN and calculated SADT values

Substance	SADT (°C)	
	Measured	Calculated
TBPB	55	53
TBEH	35	29
TBPP-75%	20	20

These thermal conditions are experimentally determined using the “thermal explosion test in package” described in Section 3. The test has been carried out with TBPB and TBPP-75%. From the temperature recorded inside the package the heat generation during the run-away reaction has been calculated. These heat generations are compared with the results of the working

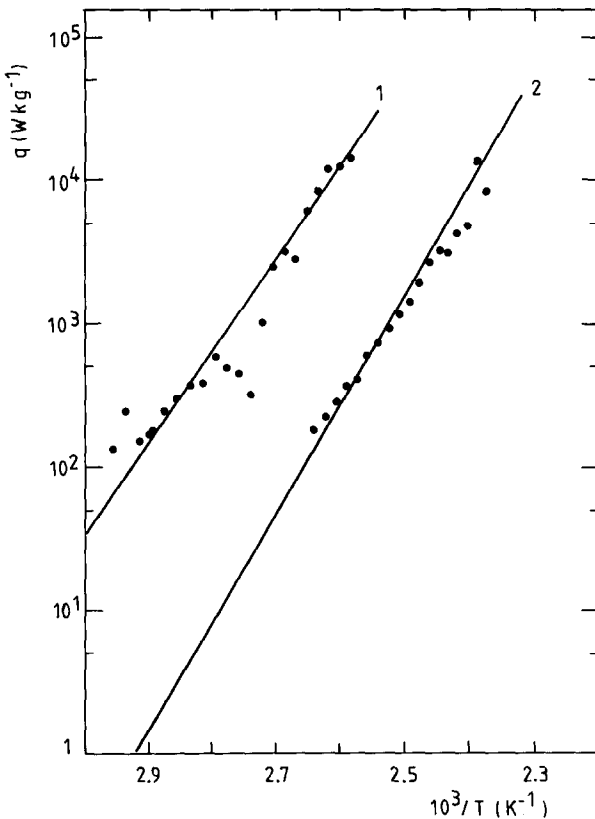


Fig. 9. Comparison between the heat generations calculated with the thermal kinetic parameters (lines) and those determined from a thermal run-away of a peroxide in a 30-l container (points). (1) *tert*-butyl peroxy pivalate, 75% in isododecane (2) *tert*-butyl peroxy benzoate, technically pure.

parameters in Fig. 9. The parameter description fits the experimental values very well. The deviation of the experimental points at $1/T = 2.8 \times 10^{-3} \text{ K}^{-1}$ for TBPP is caused by the opening of the pressure relief, as was observed in the video pictures. The sudden release of pressure resulted in evaporation of the low boiling point decomposition products. The accompanying heat losses give rise to low heat generation values. A similar effect is mentioned in Section 2 for the LPA measurements of TBPP. Since the working parameters describe the practical conditions so well one can reverse the procedure and predict the temperature rise during a run-away with the aid of the parameters. These predictions are important for practical situations which cannot be tested but still need control and emergency temperatures.

5. DISCUSSION

The working parameters for the three peroxy esters give a good description of the thermal kinetics of the peroxide decomposition. The parameters are applicable over a wide temperature range, more than 100 K.

The range of conversion is restricted to 15%, but is amply sufficient for conversions which are of practical interest. The parameters are based on many measurements with different laboratory instruments. It has furthermore been verified that the parameters give a good description of some practical situations which could be tested at full scale. Consequently it can be concluded that the phenomenological effects are properly covered. From a fundamental point of view it is interesting to know whether any information about the underlying chemical kinetics has been obtained. For pure peroxides induced decompositions have to be expected and are indeed observed (see Section 4.1). The theoretical calculations on autocatalysis given in ref. 3 showed that its influence has to be quite large before it becomes noticeable in thermal experiments. Increasing heat generation in the isothermal measurements of TBPB and TBEH indicates that induced decomposition might even be the dominant reaction. Analyses of the experimental data in terms of first- and second-order reactions might therefore have no basic meaning other than providing a phenomenological description of the decomposition.

TBPP is an exception. The kinetic data reported in ref. 2 for concentrated solutions agree with those found by Buback and Lendle [11] for very dilute solutions. For future work it will be worthwhile to analyse the data of the other peroxides in terms of induced decomposition reactions making use of eqn. (5).

With respect to activation energies the situation is more favourable. The values obtained for the pure peroxides agree very well with those reported in the literature for diluted peroxides (see Table 4). This is probably due to the fact that the temperature dependence of the oxygen-oxygen bond cleavage

is most dominant. In this respect it is important to note that the activation energies have been derived from the temperature dependence of the heat generation values by keeping the degree of conversion constant. As the AST results illustrate a varying conversion can lead to apparent high activation energies (see Table 3).

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LIST OF SYMBOLS

c	concentration	mol m^{-3}
E_a	activation energy	J mol^{-1}
$(-\Delta H)$	enthalpy of decomposition	J kg^{-1}
κ	reaction rate constant	
K	criterion for autocatalysis	
m	order of reaction	
n	order of reaction	
p	peroxide concentration	mol m^{-3}
q	heat generation	W kg^{-1}
R	gas constant	$\text{J mol}^{-1}\text{K}^{-1}$
t	time	s
T	temperature	K
ξ	conversion	

Indices

d	decomposition
i	induced decomposition
max	maximum
0	original, or in the case of time, zero

Abbreviations

AST	adiabatic storage test
DTA	differential thermal analysis
HAST	heat accumulation storage test

IST	isothermal storage test
LPA	low pressure autoclave
SADT	self-accelerating decomposition temperature
TBPB	<i>tert</i> -butyl peroxy benzoate
TBEH	<i>tert</i> -butyl peroxy 2-ethyl hexanoate
TBPP-75%	75% solution of <i>tert</i> -butyl peroxy pivalate in isododecane

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