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THERMAL STABILITY OF *TERT*-BUTYL PEROXYPIVALATE

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ABSTRACT

The thermal stability of *tert*-butyl peroxypivalate (TBPP) has been investigated in relation to peroxide—diluent compositions in the range 100—10% by weight of peroxide. TBPP was selected because the simple decomposition pattern of the pure product facilitates an interpretation of the concentration dependence. Differential thermal analyses, isothermal and adiabatic storage tests have been used for the analysis of the decomposition. From the experimental results it is found that the total heat of decomposition is proportional to the peroxide concentration, the activation energy is independent of concentration, and the reaction order varies slightly with concentration. The type of diluent influences the reaction rate. The results are applicable in the 290—360 K temperature range. For the determination of decomposition characteristics, a modified first order equation which takes into account the fraction of diluent can be used for TBPP—diluent compositions.

INTRODUCTION

Phlegmatization is often applied to reduce the dangerous aspects of some organic peroxides. The choice of the phlegmatizer *, an "inert" diluent with a high boiling and a high flash point, is rather complex. A suitable diluent, for instance, will improve the thermal stability of the mixture, where the term "thermal stability" is used to express the extent to which the product can be handled safely in a certain temperature range in so far as this is determined by its thermal properties. The exact temperature range for safe handling can be calculated with the aid of the product properties and the specifications of the container, such as size, heat transfer coefficient, etc. The thermal stability of a chemical compound is governed by the heat generation (decomposition rate), temperature and composition of the product, and in the second instance also by the pressure and reactivity of the product with respect to the construction material of the container. With the aid of modern test methods the heat generations can be measured directly. For the interpretation of the results and the extrapolations beyond the measuring range it is important to know the chemical kinetics of the decomposition reaction. In the literature [1—4] many investigations can be found on decomposition

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* According to the definition of the European transport regulations (e.g. ADR).

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kinetics. In principle all of them have been carried out with very diluted peroxides while the determination of the thermal stability for the safe handling of the product requires knowledge of the chemical kinetics in both the high concentration and low temperature range. In order to obtain more information on the latter problem a thermal analytical investigation has been performed on the decomposition of peroxides in the 100—10% assay range. A successful completion of such an investigation would make possible the calculation of the thermal stability of all intermediate compositions. Since such a study is a rather complex task, a peroxide showing a simple decomposition pattern has been selected. Preliminary investigations with a series of different peroxides showed that the decomposition of pure TBPP proceeds via approximate overall first order reaction kinetics. Therefore TBPP was selected in combination with two phlegmatizers, Shellsol T (a blend of synthetic isoparaffins with a very low content of aromatics, <0.5%) and di-*n*-butyl phthalate (DBP).

TERT-BUTYL PEROXYPIVALATE (TBPP)

TBPP is a peroxy ester with the following structure

$(CH_3)_3{-}C{-}C(O){-}O{-}O{-}C{-}(CH_3)_3$

having a molecular mass of 174. Peroxy esters decompose thermally into free radicals [5]

$$(CH_3)_3{-}C{-}C(O){-}O{-}O{-}C{-}(CH_3)_3 \rightarrow (CH_3)_3{-}C{-}O^{\bullet} + (CH_3)_3{-}C{-}C(O){-}O^{\bullet}$$

$$(CH_3)_3{-}C{-}C(O){-}O^{\bullet} \rightarrow (CH_3)_3{-}C^{\bullet} + CO_2$$

Simultaneous cleavage of two bonds apparently occurs in many cases, especially at higher temperatures. The free radicals may react with TBPP, with the diluent if present, or with one another. For very diluted TBPP only a small number of products was found [2,3], among which were carbon dioxide, *tert*-butyl alcohol, acetone and isobutane. The decomposition of technically pure TBPP yields a range of products, including some tar resulting from polymerization. The present investigation has been performed with two different samples, a technically pure sample prepared at laboratory scale and a commercial sample consisting of 75% w/w TBPP in Shellsol T (supplier

TABLE 1

Composition of the two samples used

	Technically pure	Commercially available
Peroxide content (%)	98.1	74—76
tert-butyl hydroperoxide content (%)	<0.02	<0.025
Inorg. and organic Cl$^-$ (%)	<0.01	<0.01
Pivalic acid content (%)	0.04	

AKZO Chemie B.V.). The composition of the samples is given in Table 1. The mixtures with DBP were prepared from the technically pure sample. For a comparison of the results it is necessary to verify that Shellsol T mixtures prepared from the technically pure sample have the same thermal properties as identical mixtures made with the commercial sample.

THEORY

The careful selection of TBPP on account of its simple decomposition pattern allows the application of straightforward kinetics to the analysis of the thermal data obtained from the experimental investigations. For a first analysis of the experimental data the reaction rate will be assumed to depend on the peroxide concentration only. Secondly, it will be assumed that the temperature dependence is given by the Arrhenius equation so that the reaction mechanism is given by the equation

$$-\frac{1}{V}\frac{\mathrm{d}n}{\mathrm{d}t} = k_0\left(\frac{n}{V}\right)^{\beta}\exp(-E_a/RT) \tag{1}$$

For a given solution of n_0 molecules the fraction of molecules decomposing per unit of time is given by $n_0^{-1}\,\mathrm{d}n/\mathrm{d}t$. The heat generation of the solution per unit of weight can then be written

$$q = \Delta H'\frac{1}{n}\frac{\mathrm{d}n}{\mathrm{d}t} \tag{2}$$

where $\Delta H'$ is the total heat of decomposition per kg of the solution at constant pressure.

Combining eqns. (1) and (2) yields

$$q = \Delta H' k_0(1-\alpha)^{\beta}(n_0/V)^{\beta-1}\exp(-E_a/RT) \tag{3}$$

where $\alpha = 1 - n/n_0$ is the fraction of molecules decomposed. For first order reactions the term $(n_0/V)^{\beta-1} = 1$. In the case of higher order reactions it will be assumed that the volume of the solution does not change during the decomposition, so that $V = V_0$. Introducing the starting concentration $c_0 = n_0/V_0$, eqn. (3) can be written

$$q = \Delta H'(c_0)^{\beta-1}(1-\alpha)^{\beta}\,k_0\exp(-E_a/RT) \tag{4}$$

The concentration defined here is connected with the practical weight fraction A by

$$A = \frac{n_0 M}{V_0\rho_0} = c_0 M/\rho_0 \tag{5}$$

Isothermal measurements

If the generated heat is adequately transferred to a heat sink and the temperature of the sample is kept constant, isothermal conditions are obtained and eqn. (5) can be written as

$$\ln q = \beta \ln(1 - \alpha) + \ln k_T + \ln \Delta H' c_0^{\beta-1} \qquad (6)$$

with

$$k_T = k_0 \exp(-E_a/RT)\,, \qquad (7)$$

k_T is constant during the isothermal measurement.

According to eqn. (6) a plot of ln q vs. ln $(1 - \alpha)$ yields a straight line, the slope of which is equal to the order of the reaction, β, and the intersect at $\alpha = 0$ yields k_T. The relevant parameters $\Delta H'$, q and α are obtained from isothermal measurements by measuring the heat flow as a function of time and with the aid of two relations derived from eqn. (2)

$$-\alpha = \frac{1}{n_0} \int_{n(t_0)}^{n(t)} \mathrm{d}n = -\frac{1}{\Delta H'} \int_{t_0}^{t} q\, \mathrm{d}t \quad \text{and} \quad \Delta H' = \int_{t_0}^{t=\infty} q\, \mathrm{d}t \qquad (8)$$

Frequently $\Delta H'$ is also determined from the left-hand side of eqn. (8) by measuring the value of α at the end of the experiment with the aid of chemical analysis.

Adiabatic measurements

If heat losses from the peroxide sample to the surroundings are avoided so that an adiabatic system is obtained, then eqn. (4) can be written in the form

$$q = (c_w/m)\, \mathrm{d}T/\mathrm{d}t = k_0\, \Delta H' c_0^{(\beta-1)} (1 - \alpha)^{\beta} \exp(-E_a/RT) \qquad (9)$$

where c_w is the heat capacity of the insulated system. From the observable parameters, the temperature of the sample as a function of time, one can determine T, $\mathrm{d}T/\mathrm{d}t$, and α. The latter is given by

$$\alpha = \frac{1}{\Delta H'} \int_{t_0}^{t} q\, \mathrm{d}t = \frac{1}{\Delta H'} \int_{T_0}^{T} (c_w/m)\, \mathrm{d}T \qquad (10)$$

Addition to this set of the parameters $\Delta H'$ and β, as determined in the isothermal measurements, enables the calculation of the rate constant k_0 and the activation energy from eqn. (9). In adiabatic experiments it is generally assumed that the heat capacity, c_w, made up of the capacity of the Dewar and the specific heat of the substance, does not change with temperature and conversion. Since in adiabatic experiments the degree of conversion, α, is small and the temperature range (about 50 K) is limited, this is justified.

MEASURING TECHNIQUES

Isothermal as well as adiabatic measuring techniques have been developed at TNO [6,7]. The two extremely sensitive instruments enable heat generation measurements in the low temperature range at which peroxides have to be stored. With the aid of the two tests safe storage temperatures can be determined so that the tests have been called the isothermal storage test (IST) and the adiabatic storage test (AST).

Isothermal storage test (IST)

With the IST the heat generation produced by reacting or decomposing substances is determined as a function of time at a constant temperature. The IST consists of a large heat sink (an aluminium block), which is kept at a constant temperature. At the bottom of the two holes drilled in the heat sink a heat flow meter (e.g. a peltier element) is placed. A heat flow through such an element results in a voltage signal which is proportional to the heat flow. The voltage difference resulting from the difference in heat flow between the sample and an inert substance is monitored as a function of time. The holders are identical and each has a capacity of 50×10^{-6} m^3. The amount of substance (sample as well as reference) is 20 g. The holders are made of glass and the sample holder is provided with a long capillary tube which prevents pressure build-up in the holder and inhibits evaporation of volatile components from the sample. A schematic set-up of the IST is shown in Fig. 1.

Measurements can be performed in the temperature range of 250—450 K (below 320 K a special regulating system is used). For kinetic measurements the temperature rise due to heat generation and the thermal resistance between holder and heat sink should not exceed 0.3 K. The sensitivity of the apparatus covers a range of heat generations from 5 mW kg^{-1} to 1500 mW kg^{-1}. The heat of decomposition can be calculated from the surface beneath the heat generation—time graph.

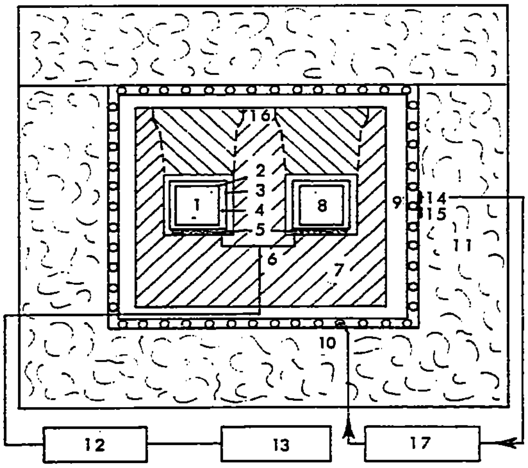

Fig. 1. Arrangement for isothermal storage test. 1, Sample; 2, sample vessel; 3, cylindrical holder; 4, air space; 5, peltier elements; 6, electrical circuit; 7, aluminium block; 8, inert material; 9, air space; 10, heating wires; 11, glass wool; 12, amplifier; 13, recorder; 14, platinum resistance sensor for temperature control; 15, platinum resistance sensor for safety control; 16, platinum resistance thermometer; 17, temperature controller.

Adiabatic storage test (AST)

With the AST the heat generation produced at nearly adiabatic conditions by reacting or decomposing substances can be determined as a function of temperature (see Fig. 2). 1×10^{-3} m^3 of the substance is introduced into a Dewar vessel with a capacity of 1.5×10^{-3} m^3, which is closed by means of a glass cover. The Dewar vessel is placed in an oven whose temperature is kept equal to the temperature of the substance in the Dewar vessel, thus minimizing heat losses in order to create an almost adiabatic condition. To prevent pressure build-up in the Dewar vessel a capillary tube (PTFE) passes through the cover of the vessel, which inhibits evaporation of volatile components.

The substance can be heated to the desired starting temperature by means of internal heating. By using a constant electric power for this heating the specific heat of the substance can be calculated. The temperature rise of the substance caused by self-heating is monitored as a function of time. When the specific heat and mass of the sample are known the heat generation can

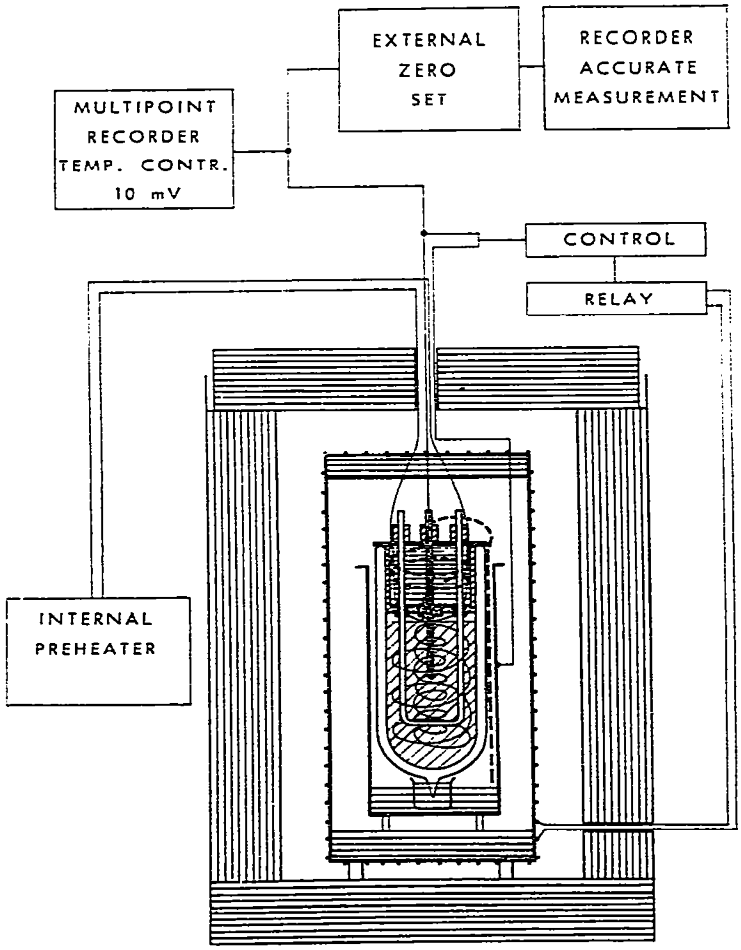

Fig. 2. Arrangement for adiabatic storage test.

be calculated. When the decomposition rate of the substance is too high the measurement is stopped by cooling the substance with the aid of a cooling coil made of glass. In this investigation the sample contacts only glass. Measurements can be performed in the temperature range 250 K—500 K. The smallest temperature rise that can be detected corresponds to a heat generation of 10 mW kg^{-1}. The upper limit is determined by the capacity of the cooling coil allowing a maximum heat generation of 500 W if water is applied as coolant. The heat losses amount to a maximum of 10 mW.

Isothermal DTA

Differential thermal analyses at constant temperatures were performed with the aid of a Mettler 2000 B apparatus. Isothermal DTA is a technique whereby the temperature difference between a sample and an inert material is monitored as a function of time. The temperature difference is converted to a heat flow with the aid of a calibration factor [8]. However, the size of the measuring sample is rather small, viz. 2×10^{-4} kg, and measurements are only possible at relatively high temperatures compared with IST and AST. Special high-pressure crucibles made of nickel—chromium alloy were used as sample holders. The crucible is provided on the inside with a tight-fitting glass vessel to prevent catalytic decomposition of the sample by the alloy. The crucible is pressure-tight so that the system is isochoric.

RESULTS

Isothermal measurements

The heat generation of technically pure TBPP and the different concentrations of TBPP in Shellsol T have been measured at three different temperatures with the isothermal storage test. The result of a typical measurement is given in Fig. 3. Points of low degree of conversion deviate from the straight line because it takes some time — about 12 h — before the instrument reaches equilibrium after the experiment has started. The results obtained at 303 and 313 K could be used for a calculation of β and k_T. The heat generation measured at 323 K gives rise to a self-heating of the sample of more than 0.3 K and had to be rejected for β and k_T determinations. The IST measurements also showed that the results obtained for mixtures prepared from technically pure TBPP do not deviate from those obtained for identical mixtures prepared from the commercial 75% w/w TBPP in Shellsol T sample. The relevant data of the combined IST measurements and the parameters derived from it are given in Table 2. The activation energies listed have been calculated using the results of two measurements at different temperatures. It follows from eqns. (6) and (7) that at equal degree of conversion the two isotherms are related by the equation

$$\ln q(T_1) - \ln q(T_2) = (E_a/R)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{11}$$

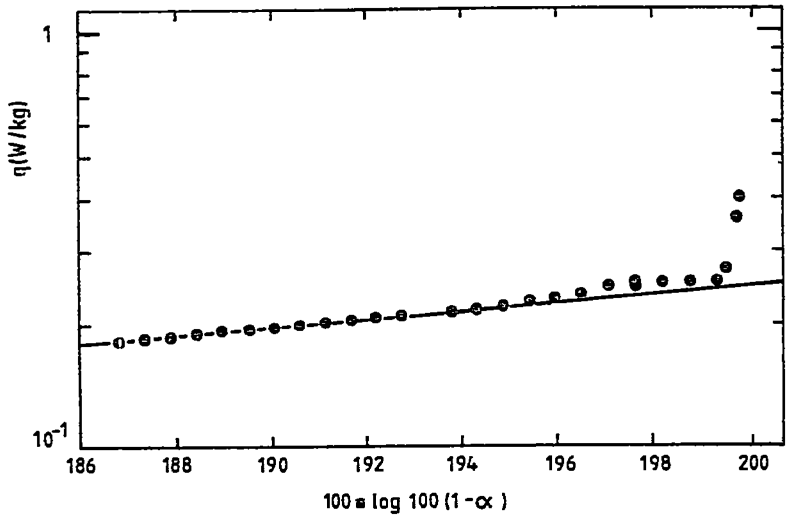

Fig. 3. Heat generation, q, under isothermal conditions as a function of conversion, α, for a 50% w/w solution of TBPP in Shellsol T.

The average value of the heat of decomposition, ΔH, is 250 kJ mole^{-1} with a standard deviation of 33 kJ mole^{-1}. The results obtained from the isothermal DTA measurements are given in Table 3. The combined IST and DTA results have been used to evaluate the order of the decomposition reaction as a

TABLE 2

IST results for TBPP in Shellsol T

TBPP (% w/w)	T (K)	α_t (%)	ΔH (kJ mole^{-1})	E_a (kJ mole^{-1})	β (—)	k_T
26.4	302.5	26	249	112	0.87	2.643×10^{-7}
24.4	313.0	85	211		0.97	1.155×10^{-6}
26.4	313.3	57	236		1.05	1.283×10^{-6}
26.4	322.9	93	285			
27.2 *	322.9	92	257			
48.2	293.4	9	229	124	0.84	8.310×10^{-8}
48.2	296.7	37	189		0.87	2.106×10^{-7}
52.5	302.5	26	287		1.05	3.366×10^{-7}
52.5	313.3	64	241		1.03	1.682×10^{-6}
52.5	322.6	95	209			
49.9 *	322.9	94	263			
74.6	293.5	15	206	117	0.70	1.263×10^{-7}
74.8	302.7	25	300		1.10	3.981×10^{-7}
74.8	313.2	69	235		1.17	2.080×10^{-6}
74.8	322.9	96	265			
72.7 *	322.9	95				
98.1 *	293.5	13	246	126	1.04	8.832×10^{-8}
97.2 *	302.8	22	297		1.34	5.059×10^{-7}
97.2 *	313.2	75	250		1.14	2.487×10^{-6}
97.2 *	322.7	96	250			

* Technically pure TBPP or prepared from the technically pure product.

TABLE 3

DTA results for TBPP in Shellsol T

TBPP (% w/w)	T (K)	α_t (%)	β (—)	k_T
26.4	343	90	0.68	6.909×10^{-5}
	358	95	1.10	6.784×10^{-4}
	358	98	0.52	2.737×10^{-4}
27.2 *	343	83	0.66	7.484×10^{-5}
	358	99	0.84	4.679×10^{-4}
	358	94	1.13	6.485×10^{-4}
52.5	328	46	1.10	1.357×10^{-5}
	328	51	1.37	1.267×10^{-5}
	338	76	0.84	5.074×10^{-5}
	348	97	0.60	1.696×10^{-4}
49.9 *	328	46	0.75	1.423×10^{-5}
	328	57	1.22	1.267×10^{-5}
	338	63	1.30	5.089×10^{-5}
	338	69	1.20	5.634×10^{-5}
	348	97	0.77	2.016×10^{-4}
74.8	328	31	0.96	1.567×10^{-5}
	338	42	0.99	6.160×10^{-5}
	343	49	0.94	1.193×10^{-4}
	343	46	1.36	1.276×10^{-4}
72.7 *	328	44	1.60	1.488×10^{-5}
	328	48	1.62	1.568×10^{-5}
	338	55	1.36	3.960×10^{-5}
	343	45	1.11	1.235×10^{-4}
	343	46	1.21	1.082×10^{-4}

* Prepared from technically pure TBHP.

TABLE 4

Summary of reaction order values for TBPP in Shellsol T

Test method	TBPP concentration (% w/w)			
	25	50	75	100
IST β	0.96	0.98	1.14	1.24
$S^*(\beta)$	0.04	0.05	0.02	0.05
DTA β	0.82	1.07	1.12	
$S^*(\beta)$	0.25	0.25	0.17	
Estimated	1.00	1.05	1.15	1.25

TABLE 5

AST results for TRPP in Shellsol T

TBPP (% w/w)	c_p (kJ kg^{-1} K^{-1})	β (—)	T_s (K)	k_{Ts}	T_c (K)	k_{Tc}	α_t (%)	E_a (kJ mole^{-1})
12.4 *	1.86	1.0	311	5.896×10^{-7}	343	3.132×10^{-5}	53	110.10
	1.96	1.0	310	5.577×10^{-7}	333	1.236×10^{-5}	40	115.62
	1.87	1.0	310	5.293×10^{-7}	336	1.280×10^{-5}	42	106.10
15.7	1.83	1.0	308	3.602×10^{-7}	341	3.034×10^{-5}	38	117.31
	1.84	1.0	311	6.101×10^{-7}	339	2.208×10^{-5}	37	112.35
24.4	2.04	1.0	305	2.707×10^{-7}	332	1.309×10^{-5}	28	120.93
26.4	2.03	1.0	304	2.184×10^{-7}	331	8.421×10^{-6}	21	113.16
26.4	1.86	1.0	309	4.436×10^{-7}	328	5.985×10^{-6}	15	115.41
48.2	2.06	1.05	298	1.482×10^{-7}	320	3.507×10^{-6}	13	114.02
48.2	1.88	1.05	303	2.876×10^{-7}	317	2.406×10^{-6}	8	121.16
52.5	2.05	1.05	299	1.343×10^{-7}	327	7.132×10^{-6}	9	115.32
52.5	1.81	1.05	300	1.657×10^{-7}	320	3.224×10^{-6}	8	118.44
74.6	1.85	1.15	299	1.856×10^{-7}	321	4.820×10^{-6}	7	118.13
74.6	1.90	1.15	295	8.764×10^{-8}	319	3.378×10^{-6}	6	119.05
74.8	1.58	1.15	294	6.789×10^{-8}	328	9.367×10^{-6}	7	116.18
74.8	1.50	1.15	295	7.749×10^{-8}	310	8.143×10^{-7}	4	119.23
98.1 *	1.87	1.25	289	3.856×10^{-8}	310	1.235×10^{-6}	5	122.96

* Technically pure TBPP or prepared from the technically pure product.

function of concentration. Table 4 shows that β gradually increases with increasing TBPP concentration.

Adiabatic measurements

As pointed out earlier, adiabatic measurements yield heat generation values as a function of two simultaneously varying parameters, the temperature and the degree of conversion. With the aid of eqn. (9) and the values of $\Delta H'$ and β obtained from isothermal measurements, the rate constants as a function of temperature and the activation energy can be determined from one experiment. The results are presented in Table 5. The rate constants at the temperature where the measurement started, T_s, and ended, T_e, have been tabulated. The accuracy in the activation energy determination amounts to about 4%. It can therefore be concluded from Table 5 that for TBPP—Shellsol T mixtures the activation energy is independent of the TBPP concentration. The average value for the activation energy is 117 kJ mole^{-1} with a standard deviation of 3 kJ mole^{-1}.

TBPP in DBP (di-n-butyl phthalate)

The decomposition of TBPP has also been investigated in solutions of another common phlegmatizer, DBP. Two solutions of technically pure TBPP in DBP, 27.2 and 49.9%, respectively, have been measured in the IST at two different temperatures. Isothermal measurements have also been performed with two concentrations at three different temperatures in the iso-DTA. The results are presented in Table 6. It is found that the mean value for the heat of decomposition of pure TBPP in the mixture is 248 kJ mole^{-1}. As is to be expected, this value is almost equal to the value obtained for TBPP in Shellsol T, being 250 kJ mole^{-1}. Finally it can be concluded from Table 6 that the overall order of the decomposition reaction for TBPP—DBP mixtures does not deviate from the order found for corresponding concentrations of TBPP—Shellsol T mixtures.

TABLE 6

IST and DTA results for TBPP in DBP

Test method	TBPP (% w/w)	T (K)	t (h)	α_t (%)	ΔH (kJ mole^{-1})	β (—)	k_T
IST	27.2	313.1	168	77	223	1.03	2.467×10^{-6}
	27.2	323.0	168	99	253	1.00	8.117×10^{-6}
	49.9	313.1	168	76	242	1.01	2.338×10^{-6}
	49.9	322.8	168	93	264		
DTA	27.5	343	5.8			0.93	1.193×10^{-4}
	27.5	358	1.7			1.07	7.640×10^{-4}
	63.0	338	2.8			1.35	4.995×10^{-5}
	63.0	348	2.6			1.12	2.654×10^{-4}

COMPARISON OF RESULTS

Influence of concentration

A direct comparison of the results obtained with the various test methods can be carried out by means of the rate constants for decomposition as derived from each measurement. With reference to the theory given earlier, it is recalled that each isothermal measurement yields one value for the reaction rate, k_T [eqns. (6) and (7)]. Each adiabatic measurement yields directly all the reaction rate constants for temperatures within the measuring range provided that the order of the reaction and the heat of decomposition are known [see eqn. (9)]. As an example the reaction rate constants as determined with the three different measuring techniques are plotted as a function of the temperature in Fig. 4 for the 75% w/w concentration in Shellsol T. In the logarithmic plots the discrete points represent the isothermal data from IST and iso-DTA. Line A represents adiabatic measurements: two measurements have been performed which coincide in the plot. Data analysis showed that the reaction rates of all three concentrations could be well described with one value for the activation energy, $E_a = 117\ 360$ J mole^{-1}. The expressions for the rate constants, represented by line B in the

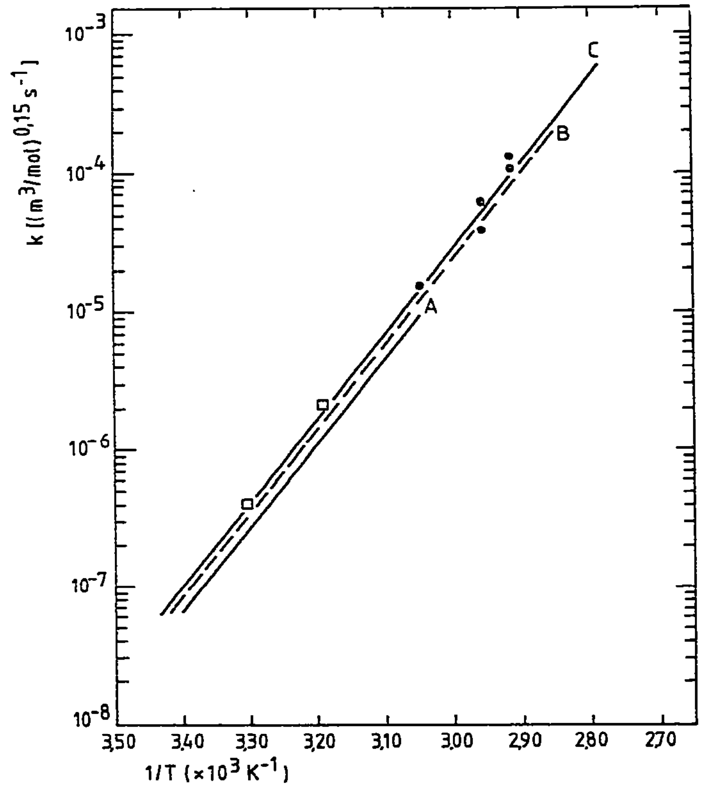

Fig. 4. Reaction rate constants, k, as a function of the reciprocal temperature for 75% w/w TBPP in Shellsol T. A, AST; B, $\ln k_T = 31.740 - 117\ 360/RT$; C, eqn. (12). □, IST; ●, DTA.

plot, and the corresponding order of reaction are then given by

12.5% TBPP in Shellsol T: $\ln k_T = 31.045 - 117\,360/RT$; $\beta = 1.00$

25% TBPP in Shellsol T: $\ln k_T = 31.218 - 117\,360/RT$; $\beta = 1.00$

50% TBPP in Shellsol T: $\ln k_T = 31.669 - 117\,360/RT$; $\beta = 1.05$

75% TBPP in Shellsol T: $\ln k_T = 31.740 - 117\,360/RT$; $\beta = 1.15$

100% TBPP (technically pure): $\ln k_T = 32.093 - 117\,360/RT$; $\beta = 1.25$

The expressions show that the pre-exponential Arrhenius factor, k_0, is dependent on the Shellsol T concentration.

Analysis of the experimental data as performed here is quite complex and the reverse operation, the calculation of the heat generations for intermediate concentrations from the chemical kinetic data, is difficult to perform. Nevertheless, in practical applications one would like to make predictions about the thermal stability of intermediate concentrations without having to measure all of them. We have therefore deduced with the aid of the above conclusions an empirical formula for the heat generation. The facts that the activation energy is independent of concentration, the heat of decomposition is constant when calculated per mole of pure product, and the pre-exponential factor depends on the Shellsol T concentration have been incorporated in a modified reaction rate equation. An optimal description of the experimental results within the above constraints was obtained with

$$q = k'_T(1 - \alpha)\,\Delta H' \tag{12}$$

and

$$k'_T = -3.538 \times 10^{13}(1.309S - 2.309)\exp(-117360/RT)$$

where S represents the weight fraction of solvent ($0 \leqslant S < 1$). In this way an analysis of the experimental data has led to two theoretical representations of the data: a rigorous chemical kinetic representation given by eqn. (4) with

TABLE 7

Ratios of measured and calculated heat generations for IST results with TBPP in Shellsol T at 313 K as a function of conversion

TBPP (% w/w)	T (K)	Conversion (%)							
		5		10		20		60	
		Eqn. (4)	Eqn. (12)	Eqn. (4)	Eqn. (12)	Eqn. (4)	Eqn. (12)	Eqn. (4)	Eqn. (12)
25	313.0	1.07	0.82	1.06	0.81	1.07	0.80	1.08	0.81
	313.4	1.39	1.04	1.36	1.02	1.36	1.02	1.32	0.98
50	313.3	1.12	1.04	1.08	1.01	1.08	1.01	1.07	0.94
75	313.2	1.26	1.08	1.24	1.06	1.21	1.00	1.23	0.95
100	313.2	1.19	1.26	1.15	1.22	1.18	1.18	1.20	1.00

the numerical values given before and a modified equation representation given by eqn. (12).

At this point it is interesting to work backwards and to see how well the two representations describe the experimental data. In Table 7 the two representations are compared with the results of the IST which is regarded as the most accurate measuring technique. The ratio of measured and calculated heat generation values are given for four concentrations of TBPP at several degrees of conversion. The modified reaction rate equation gives a better approximation of the measured values. Similar comparisons for iso-DTA and AST showed that the modified reaction representation corresponds better with the experimental DTA data and is only slightly worse for the AST data. Finally, it is remarked that eqn. (12) yields a simple relationship between the heat generations of two different mixtures at equal temperature and degree of conversion

$$q(c_1)/q(c_2) = (1.309S_1 - 2.309)(S_1 - 1)/1.309S_2 - 2.309)(S_2 - 1)$$

because $\Delta H'_1/\Delta H'_2 = (S_1 - 1)/(S_2 - 1)$. One thus finds, for instance, that the heat generation of a 25% w/w mixture is 0.22 times that of a 75% w/w mixture.

Influence of diluent

The measurements of the TBPP—DBP system show some interesting similarities with the TBPP—Shellsol T system. Several parameters are the same for both systems: the activation energies have the same value, the heats of decomposition are identical and linear in concentration, and the orders of the decomposition reaction are the same for corresponding concentrations. Only the reaction rate constants are different for both systems. It follows from the above observations that the two systems can be described with the same set of equations, i.e. eqn. (4) and its numerical values or eqn. (12), with the exception of the pre-exponential Arrhenius factor which is larger for the TBPP—DBP system than for the TBPP—Shellsol T system. This conclusion confirms the assumption made earlier that the influence of the concentration and type of diluent is reflected in the parameter k_T'. For DBP the diluent coefficient in eqn. (12), which is 1.309 for Shellsol T, becomes about 2.2.

DISCUSSION

In this paper the thermal stability of highly concentrated peroxide solutions has been analysed using simple reaction kinetics. After performing the analysis it is important to verify the validity of the theoretical framework adopted for the thermal phenomena that have been measured. In other words, do deviations from the theory occur, do some experimental observations directly confirm the theory, have assumptions been violated, etc? Before going into details one should realize that the observed thermal phenomena do not give detailed information on the reaction mechanism.

One rather observes an overall phenomenon that those processes which are accompanied by the largest heat effects play a dominant role. The underlying kinetics and undoubtedly numerous free radical reactions remain unresolved. For our purpose these are not important. We are seeking a consistent overall reaction pattern describing the measurements and enabling reliable extrapolations.

If we compare theory and experiment the first thing that strikes us is that the measured values for the total heat of decomposition are remarkably constant. In Tables 2 and 6 the heat of decomposition is expressed as the energy per mole of pure peroxide, which is obtained from the measured values by use of the equation

$$\Delta H = \Delta H' \rho / c_0$$

This expression is independent of the adopted theory. A constant H value shows that for all concentrations and investigated diluents the major final products of the reaction are the same. However, the reaction mechanism and the rate constants may still be different. Secondly, a reaction mechanism of variable order is introduced for the analysis of the results. The analytical procedure is applied to the results of three different test methods: IST, isothermal-DTA and AST, and yields a constant value for the activation energy which is the same for all concentrations (see Tables 2 and 5). The major reaction responsible for the heat generation is apparently the same in all concentrations.

Finally, it is found that the reaction is first order in peroxide concentration for low TBPP content mixtures and increases slightly with TBPP content to a value of about 1.25 for pure TBPP. Although it is assumed that the reaction depends on the TBPP concentration only — eqn. (4) — the calculated values of k_0 are dependent on the composition of the mixture. This fact combined with the almost first order reaction mechanism has led to the composition of a modified rate equation — eqn. (12) — which is first order in peroxide concentration and has a diluent dependent parameter k_T'. In this respect it should be remarked that the theory is insufficient in so far as it does not take into account the small but experimentally noticeable influence of solvent concentration. The effect is very distinct if one compares the DBP results with those of Shellsol T. Chemically the higher rate constant for DBP may be explained by noticing that hydrogen abstraction reactions by the free peroxide radicals formed is easier on a DBP molecule than on the aliphatic Shellsol T molecules.

To conclude, a remark concerning the assumption made in the derivation of eqn. (4). The factor $(c_0)^{\beta-1}$ has been introduced for $(n_0/V)^{-1}$. During decomposition the volume will change so that the factor (n_0/V) varies while a constant c_0 has been used in the analysis. Since the exponent $(\beta - 1)$ is almost zero for TBPP this will not affect the analysis to a great extent. For other peroxides which show a significantly higher reaction order than 1 the correct factor will have to be used.

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LIST OF SYMBOLS

A	fraction of peroxide in mixture	
c	concentration of peroxide	mole m^{-3}
c_0	original concentration of peroxide	mole m^{-3}
c_p	specific heat	J kg^{-1} K^{-1}
c	total heat capacity	J K^{-1}
E_a	activation energy	J $mole^{-1}$
ΔH	heat of decomposition	J $mole^{-1}$
$\Delta H'$	heat of decomposition	J kg^{-1} solution
k_0	decomposition rate constant at $T = \infty$	$(m^3)^{-1}/(mole)^{\beta-1}$ s
k_T	decomposition rate at constant temperature T	$(m^3)^{-1}/(mole)^{\beta-1}$ s
M	molecular mass of peroxide	kg $mole^{-1}$
m	mass	kg
n	number of molecules	
q	heat generation	W kg^{-1}
R	gas constant	J $mole^{-1}$ K^{-1}
S	fraction of solvent	
S^*	standard deviation	
T	temperature	K
t	time	s
V	capacity — volume	m^3
α	conversion	
α_t	total conversion	
β	order of decomposition kinetics	
ρ	density	kg m^{-3}

Subscripts

s	start of the measurement
e	end of the measurement

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