

THE THERMAL STABILITY OF *tert*-BUTYL HYDROPEROXIDE-ACID MIXTURES

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Summary

The behaviour of the *tert*-butyl hydroperoxide in presence of *p*-toluenesulphonic acid is studied under adiabatic conditions. The *tert*-butyl hydroperoxide molecule decomposes via C-O or O-O bond cleavage, depending on H⁺ attack. In the first case di-*tert*-butyl peroxide and hydrogen peroxide are produced, methyl alcohol and acetone in the second. Calorimetric measurements show an effect of the produced acetone on the stability of *tert*-butyl hydroperoxide. A simplified mathematical model is used to fit the experimental results.

Introduction

Di-*tert*-butyl peroxide (DTBP) is industrially produced from *tert*-butyl alcohol and hydrogen peroxide, in presence of acids at ambient temperature [1]. The reaction is exothermic and if the cooling system fails, hazardous situations arise. Plant explosions could happen with serious damage to people and equipment [3].

For DTBP production a complicated reaction network, involving ionic and radical mechanisms, occurs and the main reaction to the expected peroxide can be partially replaced by various side reactions [1,2]. Since some of the side reactions are more exothermic than the main reaction to the peroxide, the design of the reactor temperature control and of the emergency procedures must take in to account the main characteristics of the complete reaction network. Knowledge of the reaction mechanisms would assist in choosing the best operating conditions to minimize the explosion hazards and to maximize the process yield.

The first stage of the process [2] is the formation of *tert*-butyl hydroperoxide (TBHP) from *tert*-butyl alcohol. This hydroperoxide is well known to give a rapid exothermic decomposition reaction with a complex mechanism and many species can act as initiator or catalyst for this decomposition. Particu-

larly, acid species strongly reduce the decomposition temperature of the hydroperoxide to values close to the ambient temperature [4,5].

In this paper the detailed study of safety problems in the DTBP production process by investigating the behaviour of the TBHP/acid mixtures is described.

Experimental

All the mixtures tested in this study were prepared using tert-butyl hydroperoxide 70% in water solution and *p*-toluenesulphonic acid (solid 95%).

p-Toluenesulphonic acid was chosen in order to avoid, at least in the first stages of the reaction, the problems arising from the low solubility of TBHP in sulphuric acid, which is the acid most commonly used in the industrial practice.

The thermal decomposition of the TBHP/acid mixtures was studied under adiabatic conditions using the ARC and the Sikarex 3 calorimeters.

The accelerating rate calorimeter (ARC) has been used mainly to test the overall behaviour of different mixtures in a wide temperature range to determine, by using the heat/wait/search program [6], the temperature at which the runaway reactions begin. In order to avoid catalytic effects of the reactor surface and to have results comparable with those obtained in the Sikarex calorimeter, spherical glass bombs were used in all ARC runs. These bombs are open to the atmosphere so that the reaction mixture freely evaporates and no pressure increase is recorded.

The Sikarex 3 calorimeter was modified to act as a reaction calorimeter, simulating a well-mixed batch reactor. The scheme of the reactor used in this study is shown in Fig. 1. The reactor was provided with a glass stirrer, rotating at 500–600 rounds per minute. This stirrer gave a satisfactory mixing of the reaction mixture, even when two liquid phases were present. The heat pro-

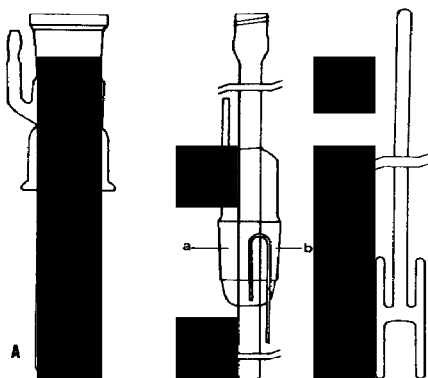


Fig. 1. The modified reactor for the Sikarex calorimeter: A, reactor vessel; B, reactant feeder; and C, stirrer.

duced by the mechanical mixing was compensated for thermal evaluations by choosing a suitable value of adiabatic deviation [7] during a calibration. This calibration was performed by putting only TBHP 70% in water solution in the stirred reactor.

The temperature sensor (Pt-100) was placed in the bottom of the reactor (Fig. 1A) where an axial housing was arranged. After the sensor was placed in the housing, this was closed by a teflon stopper to insulate the sensor from the oven atmosphere. A reservoir for liquids (a, Fig. 1B) was fitted on the top of the reactor to allow the continuous or pulsed feeding of liquid reactants, at the same temperature as the reacting mixture. The siphon b (Fig. 1B) allowed the reactants to be fed from the reservoir into the reactor. This reactor modification was absolutely indispensable in allowing the use of the Sikarex 3 calorimeter in this study.

In fact, also at ambient temperature the mixture reacted at a noticeable rate so that a separate pre-heating of the two reactants to the desired initial temperature was necessary, prior to mixing. *p*-Toluenesulphonic acid was put in the reactor and the TBHP solution in the reservoir. Once the temperature inside the calorimeter had attained the desired value, the TBHP solution, in a single pulse, was fed to the reactor and the stirrer was started up.

All the gases evolved during each Sikarex run were collected. In the line from the reactor outlet a carbon dioxide-snow trap allowed the separate collection of the condensable vapors.

Some of the Sikarex runs were stopped at different times to analyze the reacting liquid mixtures. To do this the reactor content was quenched to stop the reactions.

For the analysis of the liquid phases a Mega 5360 gas-chromatograph with a fused silica capillary column was used. The injection of the samples were injected "on column". The operating conditions used were: Capillary column SPB-1, length 30 m, I.D. 0.32 mm, film thickness 1 μm ; initial temperature 30°C, final temperature 90°C, heating rate 10°C/min; carrier gas, helium (2.0 ml/min).

For gas analysis a Hewlett Packard HP 5700A gas-chromatograph with a packed column was used. The operating conditions were: Poropak Q packed column, length 2 m, 1/8 "SS; initial temperature 80°C, final temperature 170°C, heating rate 8°C/min; carrier gas, helium (20 ml/min).

For GC-MS analysis, an HP 5890 gas-chromatograph and a Hewlett-Packard MS spectrometer were used.

Results and discussion

Temperatures recorded during three preliminary runs made with the ARC calorimeter at different molar ratio TBHP/*p*-toluenesulphonic acid (*R*), in the initial mixture are reported. In Fig. 2 it appears that the mixture reactivity

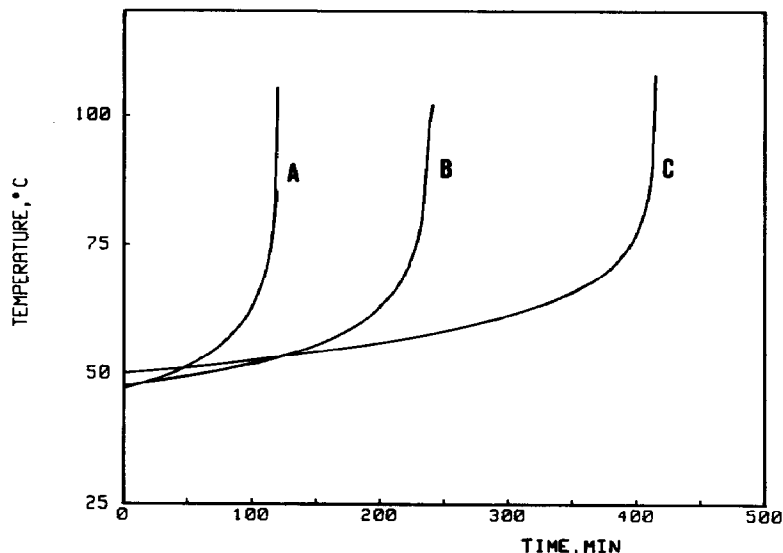


Fig. 2. Temperature-time plot for different molar ratio R : A, $R=1.2$; B, $R=1.5$; and C $R=3.0$.

strongly depends on the ratio R . In fact as the molar ratio R increases from 1.2 to 3.0 the time to maximum rate (TMR) increases from nearly 120 to 410 minutes. The simplified analysis, suggested by Townsend and Tou [6] and automatically carried out by the ARC processor, gave results similar to those shown in Fig. 3 in which the data for curve C in Fig. 2 are reported.

The non-linear behaviour observed for all the tested reaction orders suggests that more than a single reaction is necessary to simulate the behaviour of the reacting mixture.

To identify the main reactions occurring in TBHP/acid mixtures, the temperature and the composition pattern of the reacting system, including the analysis of the evolved gases and vapours, had to be measured for each experimental run.

The Sikarex runs were thus programmed to give some insight in the reaction mechanisms. For this detailed analysis a molar ratio R equal to 3.0 and an initial temperature T of 50°C were chosen. Typical results obtained are shown in Fig. 4, where the pattern of the temperature of the TBHP and DTBP concentrations are reported as functions of the time elapsed since the initial mixing of the acid and TBHP. The GC analysis indicated that the main product was di-tert-butyl peroxide, whose maximum yield, in the reaction conditions of Fig. 4, was 32.5%, corresponding to the 56.0% of the reacted THBP and to an adiabatic temperature rise of 35°C.

In these reaction conditions, the main reaction to DTBP is coupled to other reactions to some by-products. In fact, at temperature of about 60°C, the for-

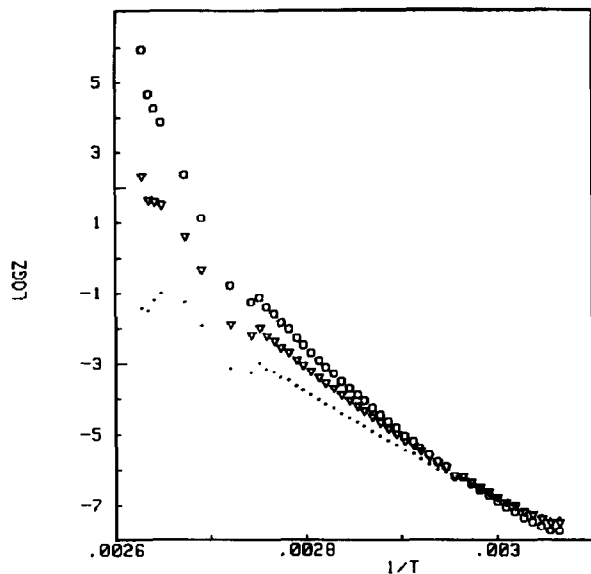


Fig. 3. Townsend and Tou plots for different reaction orders n : \circ , $n=0$; ∇ , $n=1$; \bullet , and $n=2$.

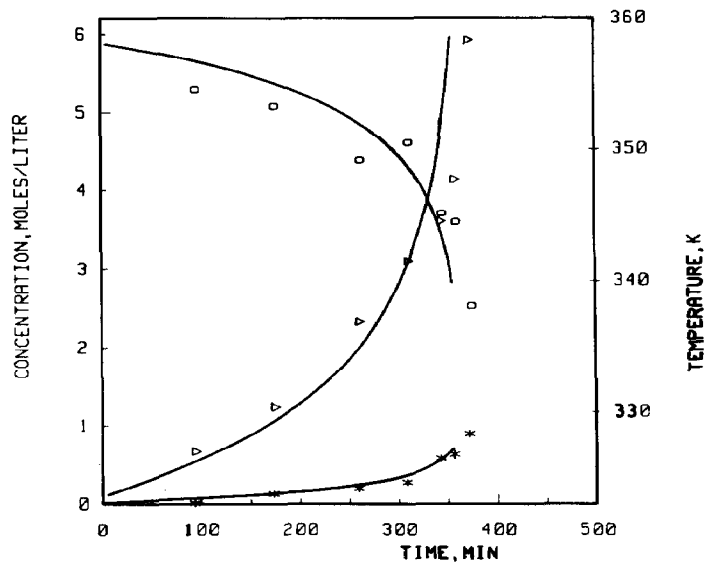
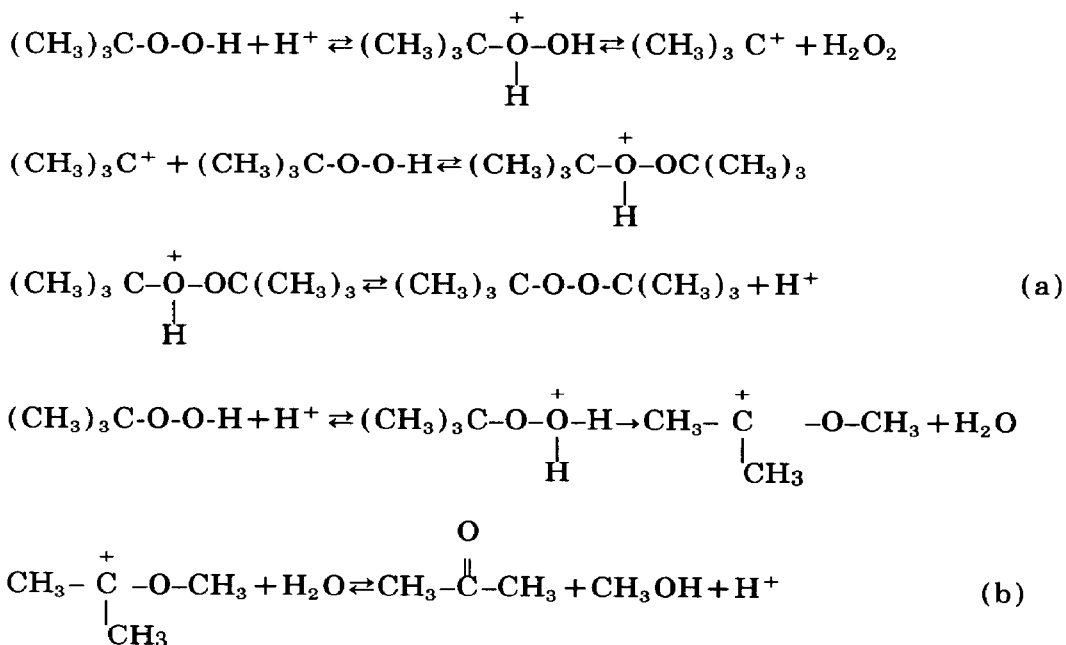


Fig. 4. Experimental results from Sikarex runs and model results: \circ , TBHP; *, DTBP; ∇ , Temperature; —, model.

mation of yellow coloured substances was observed and GC-MS analysis indicated the presence in the liquid mixture of high-molecular weight compounds, showing parent peaks in the 250–350 mass range. At a temperature of 70°C in

the reacting system, two phases were evident and small amounts of methyl alcohol were detected. Furthermore at that temperature, some gases, mainly carbon dioxide, were evolved. Once the temperature rose further to about 90°C, it kept nearly constant and the gas production rate was much higher than that observed at lower temperature. The gas analysis indicated the presence of methane, iso-butylene and very small amounts of propylene in the evolved gases.

The above mentioned results suggest that the formation of the main product, di-tert-butyl peroxide, and of methyl alcohol and other by-products can be described by the following reactions:



which are characterized by a different initial attack of the hydrogen ion on either of two oxygen atoms of hydroperoxide molecule.

The two above-mentioned reactions indicate that acetone and hydrogen peroxide are also produced. Nevertheless, no traces of acetone have been indicated by GC analysis. This happens because, in accordance with reported ketone behaviour [9], the acetone reacts quickly with the TBHP in the prevailing conditions. The peroxycarbonate (perketal) resulting from acetone-TBHP reaction is very reactive [10] and undergoes thermal decomposition to free

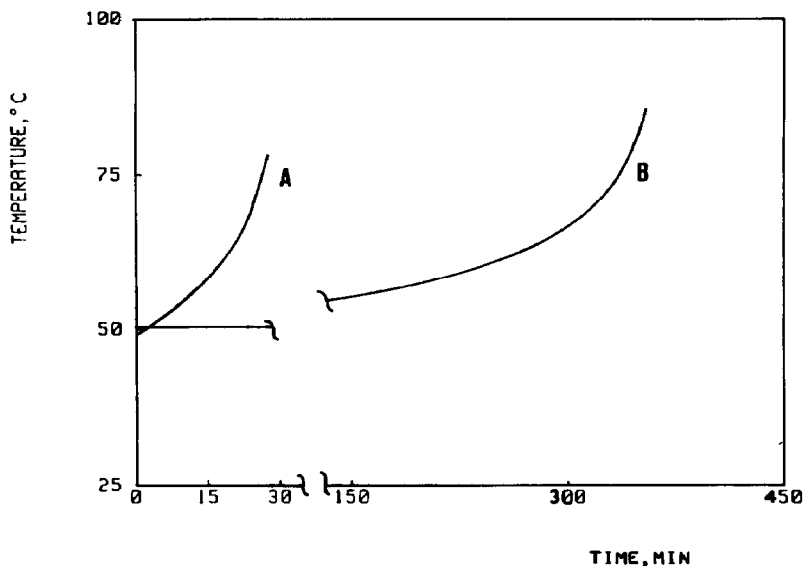


Fig. 5. Effect of acetone on the reactivity of the system: A, with acetone; and B, without acetone.

radicals [1,10], which induce a further decomposition of the peroxides present in the system.

In order to confirm this hypothesis two ARC tests were made using two mixtures of TBHP and *p*-toluenesulphonic acid: with 2% acetone and without. Both runs were performed at the same TBHP/acid ratio used in the Sikarex experiments ($R=3.0$). It appears that the presence of acetone considerably enhances the reactivity of the system. In fact, acetone reduced the temperature at which the first reactivity appears from 49.5 to 31.0°C.

The same reaction mixtures were also tested in the Sikarex calorimeter. In Fig. 5 the temperature versus time plot obtained is shown. The two curves show dramatic difference in reactivity. In the run with acetone, stopped at 78°C, the degree of conversion of TBHP was 39% and the 14% yield of di-*tert*-butyl peroxide was measured. The gas-chromatographic analysis indicated that no other peroxyc compounds were present. In a run without acetone, stopped at 74.3°C, about the same degree of conversion of TBHP (38%) was found but the yield of DTBP was greater: 23.5%.

The lower yield of di-*tert*-butyl peroxide in the run with acetone can be justified by the reaction between TBHP and acetone. From the material balance it can be inferred that 35.8% of the reacted TBHP produces DTBP, 12.2% produces perketal, whereas the remaining 52.0% decomposes with a reaction induced by radicals from perketal. On the contrary, without acetone, 62% of the reacted TBHP gives DTBP whereas 38% decomposes.

The hydrogen peroxide acts as an oxidant and no traces of this product is found in the system. This is in accordance with the experimental results re-

TABLE 1

Kinetic parameters

Reaction	ΔH cal/mol	A	E cal/mol	n
(a)	7,500	2.5×10^{14} min^{-1}	26,500	1.0
(b)	23,750	7.0×10^{17} $\text{min}^{-1} \text{mol}^{-1}$	32,500	1.5

ported by Kozhukhar and co-workers [11]. In fact the methyl alcohol produced is partially oxidized to formaldehyde and then to carbon dioxide, which has been detected in our experiments.

For a first quantitative analysis of the experimental data, the previously described reactions have been lumped in only two parallel reactions: DTBP formation from TBHP (a) and the decomposition of TBHP itself to various by-products (b). The kinetic parameters of these two reactions, reported in Table 1, were estimated to give the best fit to the experimental data. The thermodynamic data for reaction (a) were obtained from Refs. [12,13] and from the experimental adiabatic temperature rise for reaction (b). In Fig. 4 the curves represent the results for this simple model. Good agreement is observed. However, owing to the complicated network prevailing in the reaction system, it cannot be recommended to scale-up these results to industrial plants by means of this oversimplified mathematical model.

Conclusions

From the preliminary results, the following can be concluded:

(1) The TBHP/*p*-toluenesulphonic acid mixtures undergo exothermic reactions of possible runaway potential, and the temperature at which the first reactivity appears is as low as 50°C. The adiabatic temperature rise, in the open reactor, is about 40–50°C.

(2) The chemical behaviour of the studied system is very complex, ionic or free radical reactions predominate when reaction conditions (e.g. the temperature or the mixture composition) are varied.

(3) The stability of the system is strongly influenced by the presence of acetone. This is a very important result because acetone itself can be produced as by-product in the di-*tert*-butyl peroxide synthesis.

These conclusions confirm that, for a complete understanding of the safety problems relating to the DTBP production process, a detailed knowledge of the mechanism, operating in the system, under normal and anomalous conditions, is required.

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