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ANTIOXIDANTS AND STABILIZERS—XCVII*

THE MECHANISM OF ACTION OF A PROCESSING ANTIOXIDANT, 4,4′-THIOBIS(2-METHYL-6-t.BUTYLPHENOL) IN THE DECOMPOSITION OF t.BUTYL HYDROPEROXIDE

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Abstract—By an investigation of the effect of 4,4′-thiobis(2-methyl-6-t.butylphenol) (**I**) on the decomposition of t.butyl hydroperoxide (TBH) at 85°, analysis of the composition of the reaction mixture and by the determination of the effect of primary transformation products of **I** on the decomposition of TBH, the mechanism of deactivation of the latter was determined as a model for the reaction of an antioxidant with polymeric hydroperoxide. In the region of an accelerated decomposition of TBH, formation of SO_2, H_2SO_4 and a sulphonic acid was established; the peroxidolytic character was confirmed by carrying out the reaction in presence of calcium carbonate.

INTRODUCTION

Phenolic sulphides contain two active sites and are able to act as chain-breaking antioxidants and hydroperoxide decomposers [1]. A series of reactions with t.butyl hydroperoxide leads to transformations on sulphidic sulphur; one part of the products thus formed possesses chain-breaking activity and/or is able to decompose hydroperoxides. A preliminary study at 75° with 4,4′thiobis(2-methyl-6-t.butylphenol) (**I**) and TBH as a model for poly(propylene hydroperoxide) indicated [2] gradual transformation of **I** to the corresponding phenolic sulphoxide **II** and sulphone **III**. We examined this reaction, which models the deactivation of hydroperoxides in polyolefins, in detail at 85°; this temperature was somewhat closer to the processing temperature of polyolefins and allowed us to investigate chemical transformations of antioxidant **I** accompanying the process. Our main attention was directed to the formation of compounds which effectively accelerate the decomposition of TBH.

EXPERIMENTAL

Materials

t.Butyl hydroperoxide (TBH) was purified by distillation *in vacuo*. The fraction with b.p. 36–37°/2.4 kPa containing 98% TBH was used. 4,4′-Thiobis(2-methyl-6-t.butylphenol) (**I**, Aldrich Chem. Co.) was recrystallized from heptane (m.p. 125–126°). 4,4′-Sulphinylbis(2-methyl-6-t.butylphenol) (**II**), m.p. 179–180° (with decomposition) and 4,4′-sulphonylbis(2-methyl-6-t.butylphenol) (**III**), m.p. 238–240° were prepared by the oxidation of sulphide **I** with H_2O_2 in acetic acid [3]. 4-Hydroxy-3-methyl-5-t.butylbenzenesulphonic acid (**IV**) (i.r. of Na^+ salt: $\nu_{SO_2} = 1052\,cm^{-1}$, $1210\,cm^{-1}$ in KBr disc) was a product of the hydrolysis of sulphochloride prepared by the sulphochlorination of 2-methyl-6-t.butylphenol [4].

Analytical methods

The TBH content was determined iodometrically according to a published procedure [5] (variant with Cu_2Cl_2). The contents of **I**, **II**, **III** in the reaction mixtures were determined by liquid chromatography (LC) using an LC Chrom 50 chromatograph (Laboratory Instruments, Prague) with detection by means of a differential flow u.v. detector 254 nm [6]. A metal column 250 × 6 mm with a silica gel packing Separon SI VSK (Laboratory Instruments, Prague), particle size 10 μm was used; elution system hexane–isopropyl alcohol (9:1), flow rate 64 ml/hr, pressure 1 MPa. Concentrations of the compounds were determined after calibration with standards. Qualitative changes in the reaction mixture were detected by thin-layer chromatography (TLC) on Silufol u.v. 254 (silica gel precoated Al foils with fluorescent indicator). A chloroform–acetone mixture (10:1) was the elution agent, an u.v. 254 nm lamp and ferricyanide agent were used for detection.

The evolution of SO_2 was proved by employing a published procedure [7]. Filtration paper was impregnated with a mixture of saturated solution of K_2CrO_4, LiCl and water (10:1:9), dried and placed in a desiccator over a glycerol–water mixture (1:1). The presence of SO_2 in the gas leaving the reactor was demonstrated by the detection paper turning brown.

Mass spectra were recorded with an AEI MS 901 spectrometer. I.R. spectra were measured in KBr discs or with the bulk substance using a Perkin–Elmer 457 spectrometer. Elemental analysis was performed by means of a Perkin–Elmer 240 apparatus.

Investigation of the reaction between TBH and antioxidants

The decomposition of TBH with **I**, **IV** and H_2SO_4 was carried out in a closed stirred reactor at 85° in chlorobenzene; the reactions with **II**, **III** and H_2SO_4 were performed in a mixture chlorobenzene–t.butyl alcohol (5:1 by vol.). The initial concentrations of **I**, **II**, **III** were 0.02 mol/l, the TBH concentration was 0.2 mol/l, that of H_2SO_4 and

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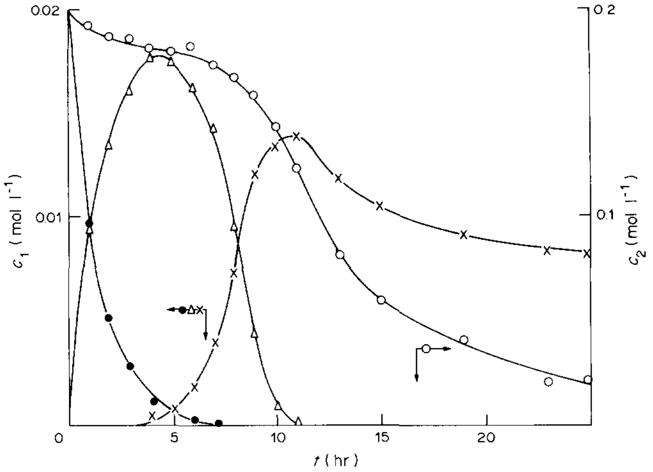
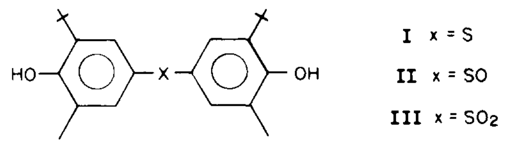


Fig. 1. Changes in the concentrations of **I**, **II**, **III** (c_1) and TBH (c_2) during the reaction of TBH (0.2 mol/l) at 85° in chlorobenzene with sulphide **I** (0.02 mol/l): (●) **I**; (△) **II**; (×) **III**; (○) TBH.

sulphonic acid **IV**, cf. Fig. 5. During the reaction, samples were taken at intervals for iodometric titration and for LC and TLC. To achieve isolation of some transformation products of **I**, **II**, **III** by column chromatography and to identify SO_2, experiments were also carried out with 5-fold starting concentrations of TBH and **I**, **II** or **III**. The effect of temperature on the reaction between TBH and sulphone **III** was studied at 75 and 100°. Some experiments involving **II** and **III** were performed in the presence of $CaCO_3$ (0.025 mol/l). The thermal stability of sulphoxide **II** was investigated in a chlorobenzene–t.butyl alcohol mixture (5:1 by vol.) at 85° in the same apparatus.

RESULTS AND DISCUSSION

Phenolic sulphides act as chain-breaking antioxidants and decomposers of hydroperoxides [1]. The ability of 4,4′-thiobis(2-methyl-6-t.butylphenol) (**I**), 4,4′-sulphinylbis(2-methyl-6-t.butylphenol) (**II**) and 4,4′-sulphonylbis(2-methyl-6-t.butylphenol) (**III**) to decompose t.butyl hydroperoxide (TBH) in chlorobenzene at 85° and the mechanism of participation of antioxidants **I–III** in this process were investigated. To make **II** and **III** soluble, a mixture of chlorobenzene with t.butyl alcohol (5:1 by vol.) was used. The reaction was followed by simultaneous iodometric determination of the TBH content and of the contents of **I–III** by liquid chromatography [6]. The time-dependence of the loss of reactants and of the formation of some products is demonstrated in Figs 1 and 2. A blank test carried out in the absence of the antioxidant showed that under the given experimental conditions about 5% of TBH was decomposed after 50 hr. A larger loss of TBH in the presence of antioxidants is therefore due to the action of these compounds alone or to their transformation products.



The decomposition of TBH in the presence of sulphide **I** proceeds in two stages (Fig. 1). In the first

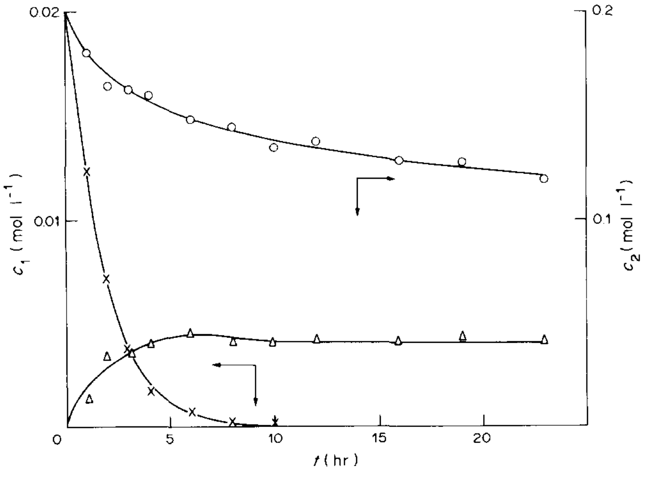


Fig. 2. Changes in the concentration of **II**, **III** (c_1) and TBH (c_2) during the reaction of TBH (0.2 mol/l) with sulphoxide **II** (0.02 mol/l) at 85° in the mixture of chlorobenzene–t.butyl alcohol (5:1 by vol.): (×) **II**; (△) **III**; (○) TBH.

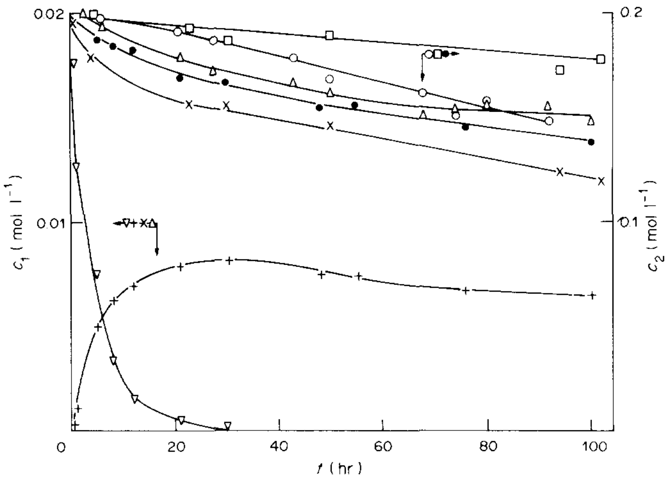


Fig. 3. Changes in the concentrations of **II**, **III** (c_1) and TBH (c_2) during the reaction of TBH (0.2 mol/l) at 85° in the mixture chlorobenzene–t.butyl alchol (5:1 by vol.). (a) With sulphoxide **II** (0.02 mol/l) in presence of $CaCO_3$ (0.025 mol/l): (▽) **II**; (+) **III**; (●) TBH. (b) With sulphone **III** (0.02 mol/l) in presence of $CaCO_3$ (0.025 mol/l): (×) **III**; (□) TBH. (c) With sulphone **III** (0.02 mol/l) without $CaCO_3$: (△) **III**; (○) TBH.

and slower stage, the loss of TBH corresponds approximately stoichiometrically to the content of consumed sulphide **I** and to sulphoxide **II** and sulphone **III** formed from **I**. Sulphoxide **II** is formed from the onset of oxidation; sulphone **III** is formed only after *ca* 90% transformation **I** into **II**. Hence, the formation of sulphone requires a considerable concentration of **II**. Sulphide **I** readily reacts with TBH. Its content decreases in the first stage of decomposition of TBH very quickly to zero, while the concentration of forming sulphoxide **II** reaches a maximum. The second stage, immediately following the first, starts with a fast decomposition of TBH which is slowed down after all sulphoxide **II** has reacted. This decomposition may be regarded as catalytic with respect to the number of moles of TBH decomposed in the presence of the amount of sulphoxide **II** formed. In this part of the reaction, the concentration of sulphoxide **II** drops very quickly to zero, and the content of sulphone **III** also decreases to a limiting value after having reached a maximum. The amount of sulphur, given by the instantaneous total concentration of **II** and **III** is smaller than that in the starting sulphide **I**. For this reason, sulphur must still be present in the reaction mixture in the form of other compounds. A similar but slower course of reaction between **I** and TBH was also observed in a preliminary investigation at 75° [2].

The decomposition of TBH in the presence of sulphoxide **II** is illustrated in Fig. 2. Compared with the reaction with sulphide **I**, its rate is higher at the beginning, but after some 5 hr it is considerably slowed down. Owing to this, the residual concentation of TBH in the reaction mixture is larger starting from the tenth hour of the reaction than in the experiment with sulphide **I**. This surprising findings may be explained by the presence of t.butyl alcohol which made possible solubility of **II** in the reaction medium. t.Butyl alcohol slows down the decomposition of TBH as shown in the experiments with H_2SO_4 (Fig. 5). The content of sulphoxide **II** decreases very quickly within the first 4 hr; the decrease is then markedly slowed down, but sulphoxide **II** disappears from the reaction mixture after 10 hr. The reactivity of **II**, characterized by the rate of its consumption in the reaction, is the same as in the case of **II** arising by the oxidation of **I** (Figs 1 and 2). Sulphone **III**, the oxidation transformation product of **II**, is formed from the onset of the reaction, but the increase in its concentration is smaller than the decrease in the concentration of sulphoxide **II**. Its maximal concentration amounts only to 22% of the initial concentration of sulphoxide **II**. Thus, under the reaction conditions, some further sulphur compounds must be formed.

In discussion of the mechanism of the action of sulphur decomposers of hydroperoxides, it is stated that an aliphatic sulphone is unable to decompose hydroperoxide [8]. On the other hand, however, under conditions analogous to those used by us, 2,2′-sulphonylbis(4,6-dit.butylphenol) was found to be able to decompose TBH [9]. We investigated the reaction between isomeric phenolic sulphone **III** and TBH in some detail (Fig. 3). The decomposition of TBH was very slow and was not very significant for the times recorded for **I** and **II** in Figs 1 and 2. During the first few hours, the rate of its decomposition is almost on the level of the blank test and increases only later. After 90 hr, 25% TBH was decomposed. Due to the amount of reacted sulphone **III**, the decomposition was again catalytic and moreover probably slowed down in the reaction medium by t.butyl alcohol present in it. The sulphone concentration gradually decreases during the experiment, reaching 75% of the starting value after 100 hr. When following the temperature dependence of the reaction between **III** and TBH (75, 85 and 100°), we observed that the rates of decomposition of TBH and of transformation of sulphone **III** depended upon the temperature.

Analysis of the results of quantitative LC determination of **I**, **II** and **III** carried out during their reaction with TBH indicated indirectly formation of other compounds, not identifiable by the LC method.

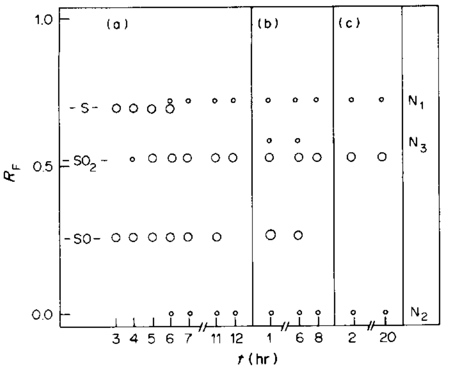
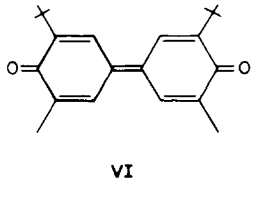


Fig. 4. Chromatogram (TLC) of an important part of the time dependence of the reaction mixture composition in the reaction of TBH (a) with sulphide **I**, (b) with sulphoxide **II** and (c) with sulphone **III** at 85° in chlorobenzene or in the mixture chlorobenzene–t.butyl alchol (5:1 by vol.).

The reaction mixtures formed in the oxidation of **I–III** with TBH were therefore qualitatively analyzed in detail by TLC. The resulting reaction mixture was fractionated by column chromatography and the individual components were determined more exactly by spectral methods. If necessary, the experiment was carried out in the same volume of solvent, but with a 5-fold concentration of the reactants.

Composition of the reaction mixture during decomposition of TBH with sulphide **I** investigated by TLC is shown in Fig. 4a. Results (Fig. 1) confirm that, in the first stage of decomposition of TBH, only sulphoxide and sulphone are formed; in the second stage (characterized by the catalytic decomposition of TBH) two further compounds, N_1 and N_2, appear in the TLC diagram at the same moment; these compounds are present in the reaction mixture until the end of the investigated interval (25 hr). They were detected first when the concentration of sulphide **I** was already very low; hence, it is quite probable that they are not formed directly from this sulphide.

The resulting reaction mixture was fractionated on a silica gel column. 2-Methyl-6-t.butyl-1,4-benzoquinone (**V**) ($M^+ = 178\,m/e$, $\nu_{C=O} = 1652\,cm^{-1}$) was identified in fraction N_1 by means of spectroscopy and i.r. analysis; in N_2, a compound was identified which after comparison between its i.r. spectrum and that of a standard, was attributed the structure **IV**. After extraction of the reaction mixture with water, sulphuric acid was obtained from the water fraction as $BaSO_4$. 3,3′-Dimethyl-5,5′-dit.butyl-4,4′-diphenoquinone (**VI**), the main product of the reaction between **I** and cumyl hydroperoxide at 120° [10], would not be detected even in an experiment involving high concentrations of reactants (investigated by i.r., MS and TLC). This fact rules out the intermediate formation of 2-methyl-6-t.butylphenol followed by its coupling reaction and oxidation.



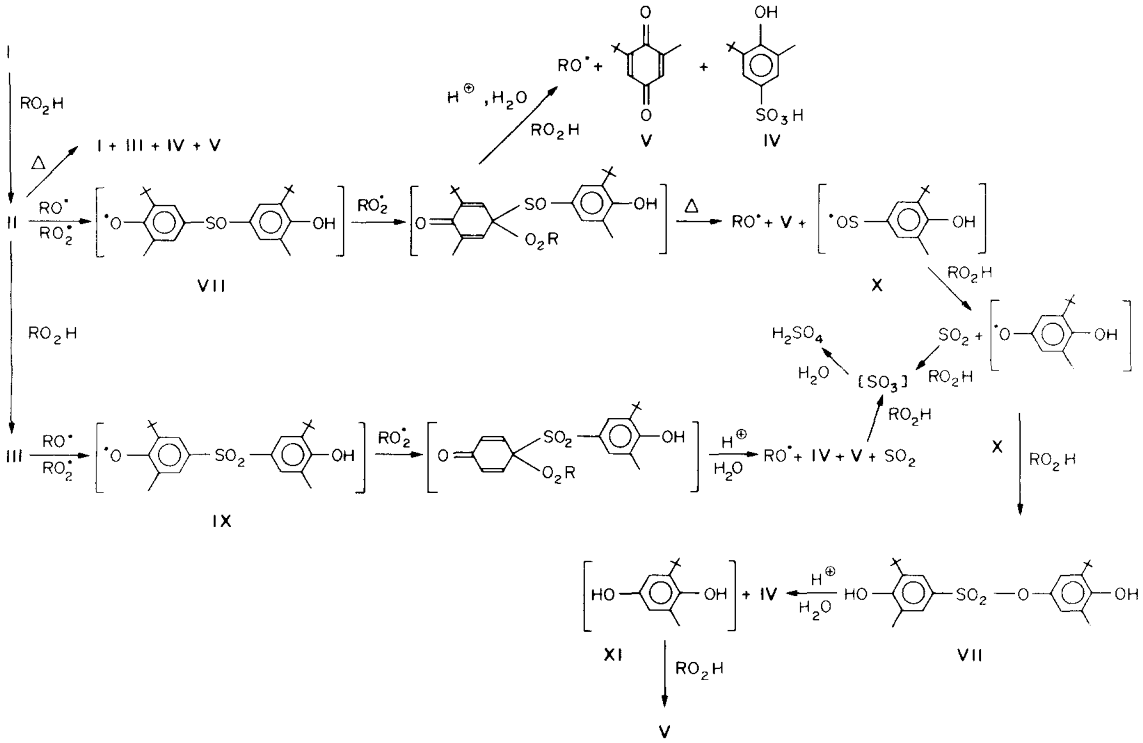
VI

Simultaneous TLC characterization of the reaction between TBH and sulphoxide **II** confirms the formation of sulphone **III** right from the beginning, as well as the relatively fast disappearance of sulphoxide from the reaction mixture (Fig. 4b). In addition, two spots were detected due to compounds present over the whole period under investigation (N_1, N_2), along with a third spot which could be perceived only up to the sixth hour of the reaction (parallel presence with sulphoxide **II**). After separation on the SiO_2 column, the components N_1, N_2 and N_3 were analyzed. The first two are identical with **IV** and **V**; in fraction N_3 a compound was detected with m.p. 203.5–204.5° (crystallized from benzene) with i.r. spectrum ($\nu_{SO_2} = 1180$ and $1365\,cm^{-1}$, further also $\nu = 1110\,cm^{-1}$ and $\nu = 1260\,cm^{-1}$) and $M^+ = 406\,m/e$ corresponding to 4-hydroxy-3-methyl-5-t.butylphenyl ester of 4-hydroxy-3-methyl-5-t.butylbenzene sulphonic acid (**VII**) [3]. H_2SO_4 was also found in the reaction mixture. The cause of formation of **IV** and **V** in this experiment may consist in the thermal decomposition of sulphoxide **II** or its oxidation. From the product analyses, it may be deduced indirectly that under our experimental conditions sulphoxide **II** is thermally stable: Diphenoquinone, whose formation from sulphoxide **II** at 120° is connected with the instability of **II** at this temperature [10], was not detected among our reaction products. The thermal stability of **II** at the temperature of our TBH decomposition measurements (85°) was verified in an independent experiment. After 150 hr the concentration of **II** decreased only insignificantly. After 100 hr the TLC analysis revealed the presence of sulphide **I** and sulphone **III** in the reaction mixture, thus indicating the disproportionation of sulphoxide **II**. Within the following 50 hr, **IV** and **V** were also detected and attributed to spots in TLC on the basis of a comparison of their R_f values with standards. In view of the long-term stability of sulphoxide **II** at 85°, the formation of **IV** and **V** observed from the onset of oxidation of sulphoxide **II** with t.butyl hydroperoxide is probably a consequence of the formation of the phenoxyl radical **VIII**, the mesomeric cyclohexadienonylic form of which after further transformations gives rise to acid **IV** and quinone **V**, either directly or after hydrolysis of the transitionally formed ester **VII** (Scheme 1).

TLC analyses of the reaction mixture during the decompostion of TBH in the presence of sulphone **III** confirmed its ability to react with TBH while giving rise to sulphonic acid **IV** and quinone **V** (Fig. 4c). This ability was also observed at 75°, but the reaction is of course slower, and the products from sulphone **III** were detected only after 20 hr (at 85° after 2 hr). Similarly to the reactions of sulphide **I** and sulphoxide **II**, H_2SO_4 was detected in the reaction mixture, while diphenoquinone **VI** was not detected even at a 5-fold concentration of the reacting compounds. The cause underlying formation of **IV** and **V** from sulphone **III** can be seen in the formation of the phenoxyl radical **IX**, generated through a radical reaction with $RO^\cdot$ and $RO_2^\cdot$ (Scheme 1, $RO_2^\cdot$ is formed via

$$ROOH \rightarrow RO^\cdot \xrightarrow{ROOH} 2\,RO_2^\cdot.$$

The $RO^\cdot$ radicals may arise in a small amount by



Scheme 1

thermal decomposition of TBH and/or by the splitting of TBH with acid phenolic protons of **III**, due to the increased acidity of the latter compared with **I** and **II** [11].

The formation of sulphuric acid is connected with the release of sulphur dioxide during the reaction of sulphuric antioxidants with hydroperoxide. Hawkins [12] interpreted the high efficiency of diphenyldisulfide in terms of the formation of sulphur dioxide. SO_2 was identified in the thermolysis of 4-hydroxy-3,5-dit.butylphenyl ester of 4-hydroxy-3,5-dit.butylbenzenethiosulphonic acid [10]. We successfully gave a qualitative colorimetric proof of the formation of SO_2 in samples of the gaseous phase taken from the reactor also in the oxidation of **I–III** with t.butyl hydroperoxide in experiments carried out with a 5-fold concentration of the initial compounds.

The effects of H_2SO_4 and of sulphonic acid **IV** on the decomposition of TBH in chlorobenzene were investigated by an independent test (Fig. 5). One can see strong catalytic effect of both acids also at concentrations lower by an order of magnitude than those of sulphuric compounds in the preceding experiments. A rise in the concentration of H_2SO_4 leads to further acceleration of decomposition. Because the reaction of TBH with **II** and **III** was investigated in a mixture of chlorobenzene with t.butyl alcohol, the effect of H_2SO_4 was studied also in this medium. The rate of decomposition of TBH was markedly lower than in pure chlorobenzene. The importance of H_2SO_4 and **IV** formed *in situ* in the decomposition of TBH with sulphur-containing phenolic antioxidants was checked by another model experiment. Addition of $CaCO_3$ to the reaction mixture TBH-sulphoxide **II** reduces the rate of decomposition of TBH (Fig. 3) compared with the experiment illustrated by Fig. 2. In the time interval under investigation, the decomposition of TBH is slowed down to almost the value corresponding to the blank test. The process has some further characteristic features. The presence of $CaCO_3$ slows down the conversion **II** into **III** and the concentration of sulphone **III** reaches higher values (its maximum is about 40% of the starting concentration of sulphoxide **II**). By means of TLC, the formation of **IV**, **V** and **VII** together with another unidentifiable compound was demonstrated along with the formation of **III**.

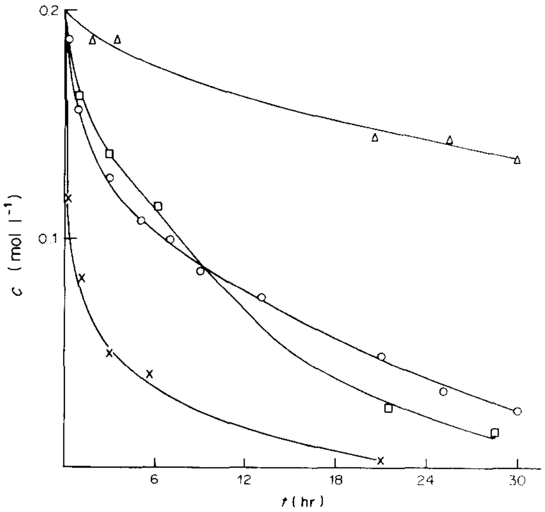


Fig. 5. Decrease in the concentration of TBH (c) during the reaction of TBH (0.2 mol/l). (a) At 85° in chlorobenzene: (○) with sulphonic acid **IV** (0.0023 mol/l); (□) with H_2SO_4 (0.0036 mol/l); (×) with H_2SO_4 (0.01 mol/l). (b) (△) With H_2SO_4 (0.01 mol/l) at 85° in chlorobenzene–t.butyl alchol (5:1 by vol.).

The reaction of TBH with sulphone **III** in the presence of $CaCO_3$ corresponds to the blank test within the limits of experimental error (Fig. 3). The concentration of sulphone **III** decreases over the whole period more quickly, however, and does not trend to a limiting value. Thus, the base present in the mixture has a positive effect on the rate of its transformation, as can be seen particularly at the onset of the reaction. In spite of this, however, the loss of sulphone is so small that the reacted amount of TBH in a stoichiometric reaction with sulphone **III** is lower than the error of its determination.

CONCLUSIONS

The results of the experiments elucidate the mechanism of action of sulphide **I** in the processing of polyolefins. Its high efficiency in the decomposition of hydroperoxides, as confirmed by a model reaction with TBH, is due to the formation of peroxidolytic species of acid character. These species do not arise directly from sulphide **I**: the latter is first oxidized to sulphoxide **II** which is their main source. In addition, however, they are also formed from sulphone **III**, so that the latter too is capable of decomposing hydroperoxides, though this ability is much weaker than that of compounds **I** and **II**. Under the experimental conditions, the cause of formation of peroxidolytic compounds does not lie in the thermal instability of sulphoxide **II** and sulphone **III**, but probably in the transitional formation of phenoxyl radicals **VIII** and **IX** as a result of the homolytic decomposition of TBH. The observed effect of $CaCO_3$ on the mechanism of stabilizing action of phenolic sulphide and its transformation products indicates differences in the stabilizing power of sulphuric antioxidants in polyolefins filled with microground calcite.

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