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MECHANISMS OF ANTIOXIDANT ACTION:

AUTO-SYNERGISTIC BEHAVIOUR OF SULPHUR-CONTAINING PHENOLS

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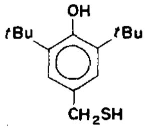
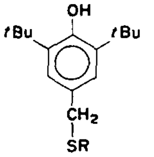
Abstract—The powerful antioxidant activity of 3,5-di-*tert*-butyl-4-hydroxybenzyl sulphides has been shown to be due to the generation of a Lewis acid catalyst which may destroy $>3 \times 10^5$ moles of hydroperoxide per mole of sulphur compound. The same catalytic species formed from a variety of benzylic sulphides and is believed to be an inorganic sulphur acid (probably SO_3). Dibenzyl monosulphide itself is not initially an antioxidant and one function of the hindered phenolic group in the auto-synergists is believed to be the removal of free radicals formed during the early stages of the reaction.

INTRODUCTION

Previous studies [1, 2] have shown that 3,5-di-*tert*-butyl-4-hydroxybenzyl mercaptan (**BHBM, I**) can be reacted with natural rubber latices to produce rubber-bound antioxidants with structure (**II**) in which R is the rubber chain.

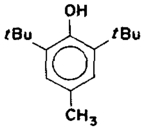


(**I**)

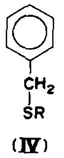


(**II**)

Low molecular weight antioxidants with structure (**II**) were found [2] to be more effective than an equimolar mixture of a simple hindered phenol (TBC, **III**) with the same antioxidant functional group and a non-phenolic sulphide (**IV**).



(**III**)



(**IV**)

It was suggested [2] that this effect was due to the Lewis acid peroxide decomposing activity of the sulphur moeity. However, the formation of the Lewis acid has been shown, in related studies of sulphide antioxidants, to involve a radical generating step which gives rise to pro-oxidant effects during the initial stages of the auto-oxidation involving sulphides [3–8] and it seems likely that the effectiveness of (**II**) results from the presence of the two antioxidant functions in the same molecule [2]. The purpose of the present study was to investigate the mechanisms of the peroxidolytic activity of 3,5-di-*tert*-butyl-4-hydroxybenzyl mercaptan (**I**) and derived monosulphides (**II**).

EXPERIMENTAL

Materials

Cumene hydroperoxide was purified by Kharasch's method [9]. 3,5-di-*tert*-butyl-4-hydroxybenzyl mercaptan (**BHBM, I**) was prepared by the method previously described [10], m.p. 27°; NMR data: aromatic protons 3.0 τ (singlet); methylenic protons, 6.0 τ (singlet); thiol protons, 7.2 τ (singlet). Bis-benzyl monosulphide (**IV**) and bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)monosulphide (V) were prepared from benzyl chloride and 3,5-di-*tert*-butyl-4-hydroxybenzyl chloride [10] by the previously described method [11]. (V), Mpt 142–3°C; NMR data: aromatic protons, 2.9 τ (singlet); *tert*-butyl protons, 8.6 τ (singlet); phenolic protons, 4.8 τ (singlet); methylenic protons, 5.6 τ (singlet). 3,5-di-*tert*-butyl-4-hydroxybenzyldodecyl sulphide was prepared by reacting dodecyl mercaptan with 3,5-di-*tert*-butyl-4-hydroxybenzyl chloride [10]. Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)monosulphide was a commercial antioxidant purified by recrystallization. 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol (**XI**), 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**XII**) and 2,6-di-*tert*-butyl-1,4-dibenzoquinone (**XIII**) were all obtained by the methods described by Pospisil [12].

Kinetic studies

Antioxidants were reacted with cumene hydroperoxide (CHP) in chlorobenzene solution under nitrogen at 70, 90, 100 and 110°. The CHP concentration ranged from 0.1 to 3 mole l^{-1} and concentrations of antioxidant between 1×10^{-4} and 1×10^{-3} mole l^{-1} were used. The decrease in CHP concentration was followed iodometrically [13] and the quantitative measurement of the decomposition products of CHP was carried out by GLC as described earlier [14]. Identification of the decomposition products of the phenolic sulphides was carried out by TLC [12].

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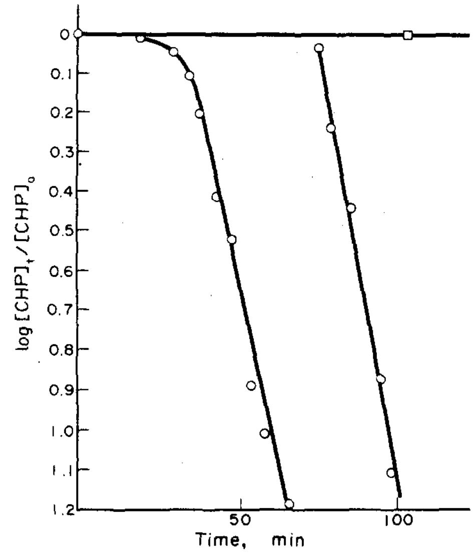
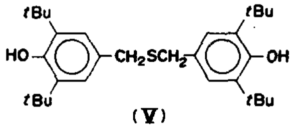


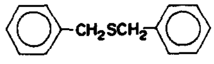
Fig. 1. Catalytic decomposition of CHP at 70°C; —o— in the presence of 3,5-di-*tert*-butyl-4-hydroxybenzyldodecyl sulphide (II) and —□—, 3,5-di-*tert*-butyl-4-hydroxyphenyl sulphide (VII) ([CHP] = 1×10^{-2} mole l^{-1}, [II] and [VII] = 1×10^{-3} mole l^{-1}).

RESULTS

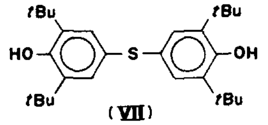
Compounds (**I**), (**II**) ($R{=}C_{10}H_{21}$), together with the bis-sulphides (**V**–**VII**), were examined as catalysts for the destruction of cumene hydroperoxide (CHP) at the same molar concentration (1×10^{-3} mole l^{-1}).



(**V**)



(**VI**)



(**VII**)

All except (**VII**) showed an induction period followed by a rapid pseudo first-order catalytic destruction of the hydroperoxide shown typically for (**II**) (molar ratio [CHP]: [II] = 10:1) in Fig. 1. The rate of decomposition of CHP at the same temperature but in the absence of catalyst is very low by comparison. Figure 1 also shows the effect of adding more hydroperoxide when the concentration of the initially added hydroperoxide has been reduced to a very low value. In each case the reaction recommenced at the same first order rate within the limits of experimental error but without an induction period. All the sulphur compounds, except (**VII**) (see Fig. 1) behaved in the same way and the first order rate constants (average values of the first and second stages of the reaction) are listed in Table 1 together with the induction periods measured in each case.

Table 1. Induction periods and pseudo first order rate constants for the destruction of CHP [0.01 M] by sulphur antioxidants [0.001 M] at 70°

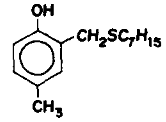
	Induction period (min)	$10^2 k\,s^{-1}$
I	25	3.4
II($R{=}C_{10}H_{21}$)	33	3.8
V	35	3.8
VI	28	3.7
VII	—	0.01

The first order rate constants were not independent of the concentration of the sulphur compounds and by varying both catalyst and hydroperoxide concentration separately the order of the reaction for both components was found to be 1. The catalytic rate was measured over the temperature range 90–110° for (**I**) and (**II**) and the Arrhenus plots are given in Fig. 2. The general equation for the rate constants are for (**I**) $\log k = (3.53 \pm 0.10) - (21.61 \pm 1.3)/2.3\,RT$, and for (**II**), $\log k = (3.0 - (16.29 \pm 1.16))/2.3\,RT$.

By varying the ratio of CHP to antioxidant, it was attempted to measure the stoichiometric coefficient (v) for the peroxide decomposition. It was found to be very high for both compounds and for compound (**II**)

$$v = \frac{[\mathrm{ROOH}]_0 - [\mathrm{ROOH}]_t}{[\mathrm{AH}]_0}$$

($R{=}C_{12}H_{25}$) it was $> 3 \times 10^5$ to be compared with the previously reported value of $v \simeq 1.5 \times 10^3$ for the ortho analogue (**VIII**) of (**II**) [15].



(**VIII**)

DISCUSSION

These results confirm the view that the powerful antioxidant activity of BHBM (**I**) and its adducts (**II**) is primarily due to their ability to destroy hydroperoxides. By analogy with the thiodipropionate esters [4–7], it may be assumed that the first stage involves the formation of an unstable sulphoxide which subsequently undergoes thermolysis to give sulphur oxy-

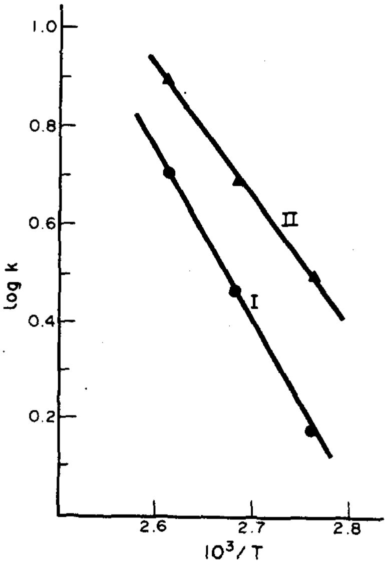
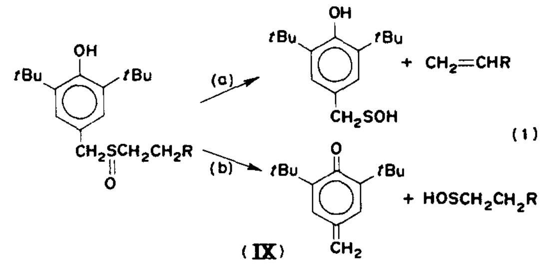


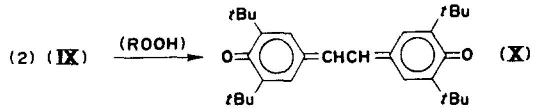
Fig. 2. Arrhenius plots for the catalytic decomposition of CHP by 3,5-di-*tert*-butyl-4-hydroxybenzyl mercaptan (**I**) and 3,5-di-*tert*-butyl-4-hydroxybenzyldodecyl sulphide (**II**).

acids. The fact that the bis-benzyl monosulphide also gives rise to the same catalyst suggests that the concerted elimination to give the corresponding olefin (1a) is not involved since the reaction cannot occur with (V) and yet the latter gives an almost identical induction period and rate constant to (II). Furthermore, the

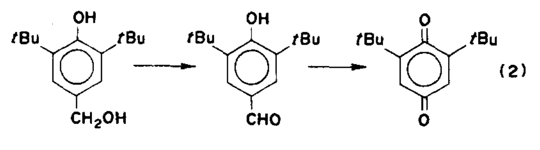


fact that bis-benzylmonosulphide (VI) appears to give rise to the same catalyst with equal facility indicates that the alternative formation of sulphenic acid (1b) does not occur.

The red stilbene quinone (X) was identified as a very minor product during the reaction of (II) with hydroperoxides confirming that 1(b) is not a major route to the sulphenic acid since (X) is always formed from (IX) under these conditions [16].

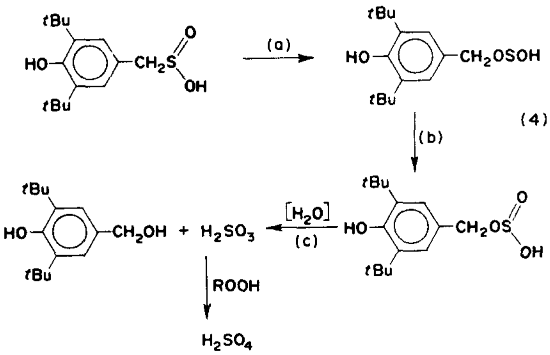


Major products formed from BHBM (I) and the bisphenol sulphide (V) were 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol (XI) and the further oxidation products (XII) and quinone (XIII) [12].

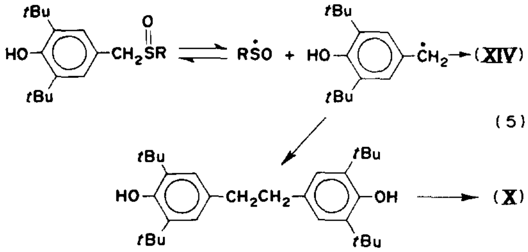


The formation of these products and the absence of sulphur in any of the isolated end products is evidence for the elimination of sulphur either as sulphur dioxide or sulphur trioxide and is in accord with present views on the function of sulphur-containing antioxidants [7]. The products formed from CHP when the sulphur compounds are present as catalysts are exclusively phenol and acetone. No α-methylstyrene, the expected radical product [7] was detected under these conditions. The following reactions are consistent with the experimental findings.

When R is itself a benzyl residue, then complete elimination of the sulphur may occur.



There is evidence from previous studies of the re-arrangement of benzyl sulphoxides to sulphenate esters (3a) that radical intermediates are involved [17–19]. This reaction (5) would give rise to pro-oxidant species before the generation of the Lewis acid and would account for the formation of a small amount of stilbene quinone (X) under these conditions.

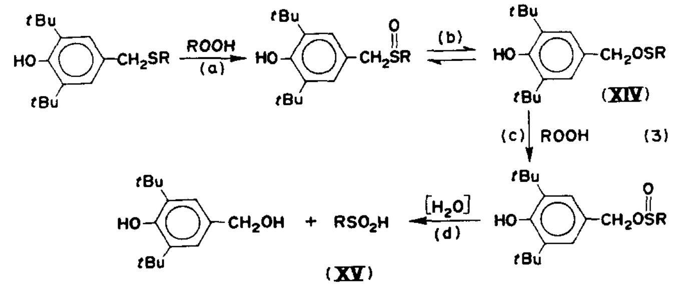


When R is an alkyl group, the sulphinic acid (XV) behaves as a powerful decomposing antioxidant under the conditions being considered, but at higher temperatures this can also eliminate SO_2 [20].

$$\underset{\text{(XV)}}{RSO_2H} \longrightarrow RH + SO_2 \xrightarrow{ROOH} SO_3 \qquad (6)$$

The facility of the above re-arrangement and elimination reactions is associated with the benzylic sulphide structure since the analogous phenyl mono-sulphides do not undergo similar elimination reactions. Bis-3,5-di-*tert*-butyl-4-hydroxyphenylmonosulphide (VII) was found to react very slowly with cumene hydroperoxide at 70° but at 95° it gave a good yield of the corresponding sulphoxide which was stable at this temperature and had no peroxidolytic activity.

It has been shown that the intermediate sulphinic acids (e.g. XV) undergo redox reactions with hydroperoxides in parallel with their Lewis acid decomposi-



tion of hydroperoxides [20]. This reaction (7) in addition to (5) leads to the formation of free radicals, with consequent pro-oxidant effects particularly during the initial stages

$$RSO_2H + R'OOH \rightarrow R'S\dot{O}_2 + H_2O + R'\dot{O} \quad (7)$$

of peroxide initiated thermal oxidative reactions [7]. Consequently bis-benzyl monosulphide (**VI**) does not behave initially as an antioxidant in tetralin at 80° [2], and in rubber [21] and polypropylene [22] this compound has been found to be a pro-oxidant. The phenolic bis-benzyl monosulphide (V) on the other hand is a very effective antioxidant and is more effective on a molar basis than a related 2,6-di-*tert*-butylphenol (**III**) which does not contain benzylic sulphur. It seems then that the hindered phenolic grouping in the molecule plays an important role during the early stages of thermal oxidation in scavenging free radicals produced in reactions (5) and (7). In the later stages, the powerful pseudo-first-order catalytic destruction of hydroperoxides is the dominant antioxidant process although doubtless the phenolic antioxidant will also complement this function at this stage also.

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