An E.s.r. Investigation of Radical Reactions of Some Sulphur-containing Phenolic Antioxidants

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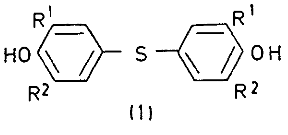
E.s.r. spectroscopy has been employed to detect radicals formed by the oxidation of some alkyl-substituted bis-(4-hydroxyphenyl) sulphides under a variety of conditions. Spectra described include those of the cation-radicals of the parent compounds (obtained by oxidation with Lewis acids) and those of sulphur-substituted phenoxyl radicals (from reaction of the parent compounds with Ce^{IV} or Pb^{IV}) and semiquinones (from reaction with Fe^{III} in basic solution). Secondary radicals detected in some instances include stable semiquinones and hydroxylated semiquinones formed in basic solution in the presence of oxygen. The mechanisms of their formation are discussed. Results of molecular orbital calculations on some of the sulphur-containing radicals are reported.

ALKYL-SUBSTITUTED bis-(4-hydroxyphenyl) and bis-(2-hydroxyphenyl) sulphides are more effective antioxidants than the analogous methylene-bridged compounds and simple alkyl-substituted phenols.[1,2] As with simpler phenolic antioxidants, the alkyl substituents play an important part in determining activity, and bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide (1; $R^1 = Me$, $R^2 = Bu^t$) is more effective than compound (1; $R^1 = R^2 = Bu^t$). Little is known about the reactions of these sulphides, although a few studies have been made of their oxidation. For example, their reaction with certain radicals (*e.g.* diphenylpicrylhydrazyl) has been studied,[3] and reactivity towards diphenylpicrylhydrazyl and antioxidant activity have been compared.



(1)

Radicals are formed during the electrochemical oxidation of (1; $R^1 = Me$, $R^2 = Bu^t$) in acetonitrile[4] and a one-electron polarographic oxidation step of the same compound in aqueous solution has been reported.[5]

We have previously described[6] spin-trapping experiments with some zinc dialkyl dithiophosphates and related antioxidants, and have compared[7] the extent of delocalisation of the unpaired electron in some aliphatic sulphide-, sulphoxide-, and sulphone-derived radicals. This investigation has been concerned with the properties (*e.g.* stability, extent of delocalisation) of radicals produced during oxidation of the antioxidant bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide and related compounds. Radicals have been detected and characterised by e.s.r., and molecular orbital calculations have been carried out.

RESULTS AND DISCUSSION

E.s.r. Results.—(a) *One-electron oxidations.* Some alkyl-substituted bis-(4-hydroxyphenyl) sulphides were treated with oxidants (concentrated sulphuric acid, trifluoromethanesulphonic acid, and aluminium trichloride in nitromethane) whose initial reaction with

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[1] L. Jirackova and J. Pospisil, *European Polymer J.*, 1972, **8**, 75.

[2] G. G. Knapp and H. D. Orloff, *Amer. Chem. Soc. Div. Petroleum Chem. Preprints*, 1960, **5**, 11.

[3] I. G. Arzamanova, A. S. Prashchikina, E. N. Gur'yanova, and A. E. Grinberg, *Vysokomol. Soedineniya, Ser. A*, 1968, **10**, 1829.

[4] Yu. V. Vodzinskii, A. A. Vasil'eva, G. A. Abakumov, and I. A. Korshunov, *Elektrokhimiya*, 1968, **4**, 1492.

[5] I. A. Korshunov, Yu. V. Vodzinskii, and A. A. Vasil'eva, *Elektrokhimiya*, 1970, **6**, 277.

[6] G. Brunton, B. C. Gilbert, and R. J. Mawby, *J.C.S. Perkin II*, 1976, 650.

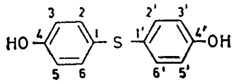
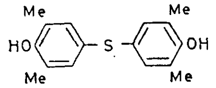
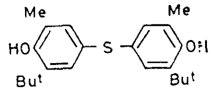
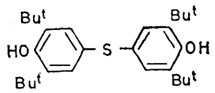
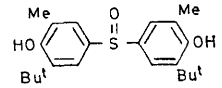
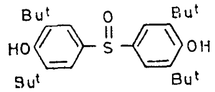
[7] P. M. Carton, B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 1245.

organic substances is thought to involve one-electron transfer (see references 8—10, respectively). The three methods all produced highly-coloured solutions which, for a given substrate, exhibited identical e.s.r. spectra (except that spectra obtained by using $AlCl_3$–$MeNO_2$ were usually better resolved than those using the other oxidants).

The spectrum from compound (1; $R^1 = R^2 = Bu^t$) had a(4 H) 0.145, a(2 H) 0.076 mT, g 2.007 0. With methyl-substituted bis(hydroxyphenyl) sulphides, the observed spectra were much more complicated, but computer simulation allowed complete analysis. The spectra are assigned to the cation-radicals of the corresponding sulphides (see Table 1), on the basis of their g values (which are consistent with there being significant spin-density on sulphur[11]) and the observed splittings which indicate that spin density is distributed symmetrically over both phenyl rings. Further, these results are consistent with Sullivan and Shine's assignment[12] of an e.s.r. spectrum to the cation-radical of the parent compound (1; $R^1 = R^2 = H$), formed in similar fashion in nitroethane at −50 °C (see Table 1); the assignment[12] of ring-proton splittings is confirmed.* The splitting from the hydroxyl proton is considerably reduced when a second t-butyl group is substituted in the 3-position, an effect which probably originates in the steric requirements of the t-butyl groups. The influence of steric and electronic effects on the spin distribution is considered in conjunction with the results of MO calculations in a later section.

TABLE 1

E.s.r. parameters of sulphur-containing radicals derived by oxidation of some bis-(4-hydroxyphenyl) sulphides (RH)

Substrate (RH)	Method of Oxidation [a–d]	Radical [e]	Proton hyperfine splittings (mT)							g
			a(2-H)	a(6-H)	a(3-H)	a(5-H)	a(OH)	a(3-Me)	a(5-Me)	
	a	$RH^{+\cdot}$ [f]	0.161(2,2′)	0.161(6,6′)	0.011 5(3,3′)	0.011 5(5,5′)	0.102			2.006 87 [f]
	b	R·	0.090	0.090	0.500	0.500				2.005 4
	c	$R(-H)^{-\cdot}$	[g]	[g]	0.213(3,3′)	0.213(5,5′				2.005 5
	a	$RH^{+\cdot}$	0.145(2,2′)	0.145(6,6′)			0.115	0.027 5(3,3′)	0.027 5(5,5′)	2.007 0
	d	R·	0.100	0.100				0.525	0.525	2.005 4
	c	$R(-H)^{-\cdot}$	[g]	[g]				0.213(3,3′)	0.213(5,5′)	2.005 5
	a	$RH^{+\cdot}$	0.145(2,2′)	0.112(6,6′)			0.112	0.027 5(3,3′)		2.007 0
	b	R·	0.102	0.102				0.505		2.005 4
	d	R·	0.118	0.118				0.556		2.005 4
	c	$R(-H)^{-\cdot}$	[g]	[g]				0.213		2.005 5
	a	$RH^{+\cdot}$	0.145(2,2′)	0.145(6,6′)			0.076			2.007 0
	d	R·	0.130	0.130						2.005 4
	c	$R(-H)^{-\cdot}$	0.081(2,2′)	0.081(6,6′)						2.005 5
	b	R·	0.188	0.188				0.725		2.005 4
	d	R·	0.135	0.135						2.005 4
	c	$R(-H)^{-\cdot}$	0.087(2,2′)	0.087(6,6′)						2.004 4

[a] $AlCl_3$ in $MeNO_2$. [b] $Ce(NH_4)_2(NO_3)_6$ in MeOH. [c] $K_3Fe(CN)_6$ in H_2O–MeOH. [d] PbO_2 in C_6H_6. [e] $RH^{+\cdot}$ = cation radical; (R−H) = semiquinone; R = phenoxyl radical (with splittings from one ring only: see text). [f] Data from ref. 12. [g] Splitting not resolved.

In contrast, one-electron electrochemical oxidation of compound (1; R^1 = Me, $R^2 = Bu^t$) gives[13] a radical with a(3 H) 0.690 and a(2 H) 0.160 mT; this has been assigned a phenoxyl structure. To confirm this assignment, we oxidised several bis-(4-hydroxyphenyl) sulphides with lead(IV) oxide in benzene[14] and with cerium(IV) ammonium nitrate in methanol[15] (systems which generate phenoxyl radicals from simple phenols).

The phenoxyl radical from the unsubstituted compound (see Table 1) could only be detected when a flow system and Ce^{IV} oxidation was employed, whereas reaction of the substituted phenols with lead(IV) oxide in benzene gave radicals which were stable enough to be detected in a static system. The radical from compound (1; R^1 =

* *Note added in proof.* Details of the spectra of the cation-radicals of some bis-(4-hydroxyphenyl) sulphides are also reported (P. D. Sullivan and L. J. Norman, *J. Magn. Resonance*, in the press); where comparison is possible, results are in close agreement with those reported here.

[8] M. C. R. Symons, *Adv. Phys. Org. Chem.*, 1963, **1**, 283.

[9] G. C. Yang and A. E. Pohland, *J. Phys. Chem.*, 1972, **76**, 1504.

[10] W. F. Forbes, P. D. Sullivan, and H. M. Wang, *J. Amer. Chem. Soc.*, 1967, **89**, 2705; W. F. Forbes and P. D. Sullivan, *ibid.*, 1966, **88**, 2862.

[11] A. J. Dobbs, Chem. Soc. Specialist Periodical Report, 'Electron Spin Resonance,' 1974, vol. 2, p. 281.

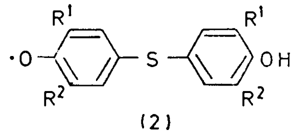
[12] P. D. Sullivan and H. J. Shine, *J. Phys. Chem.*, 1971, **75**, 411.

[13] Yu. V. Vodzinskii, A. A. Vasil'eva, I. A. Korshunov, and G. A. Abakumov, *Elektrokhimiya*, 1971, **7**, 24.

[14] C. Steelink, *J. Amer. Chem. Soc.*, 1965, **87**, 2056.

[15] J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 1446, and refs. therein.

R^2 = Bu^t) proved to be particularly stable. The attribution[13] to the radical (2; R^1 = Me, R^2 = Bu^t) of a signal detected during the electrochemical oxidation of compound (1; R^1 = Me, R^2 = Bu^t) is confirmed (though the magnitudes of the splittings appear to be solvent dependent). The unpaired electron is not delocalised to any significant extent across the sulphur atom into the second ring and, as judged by the *g* values, there is considerably less spin density on sulphur than in the corresponding cation-radicals. Nevertheless, a radical-stabilising effect of the *para*-arylthio substituent (possibly *via* steric and electronic effects) is indicated by the stability of the substituted radicals.



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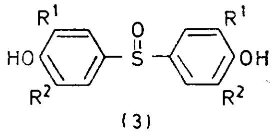


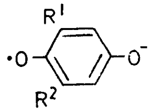
(3)

Alkyl-substituted sulphoxides of the type (3), whose formation is described later, were also oxidised by lead(IV) oxide or cerium(IV) to the corresponding phenoxyl radicals (see Table 1). The radicals were less long-lived than the corresponding sulphur-bridged species [the phenoxyl radical from compound (3; R^1 = Me, R^2 = Bu^t) could only be detected in a flow system]. Ring-proton and substituent splittings are greater for the sulphoxide-derived than the sulphide-derived radicals, indicating that the –S(O)Ar group is less effective at delocalising the unpaired electron than is –SAr. This has been noted previously for some alkyl radicals with alkylthio and sulphinyl groups attached to the radical centre[7] and for some 4-substituted phenoxyl radicals.[16]

(b) *Oxidation under basic conditions.* A preliminary study of the autoxidation of compound (1; R^1 = Me, R^2 = Bu^t) has been reported[17] but the radicals responsible were not characterised. We have investigated the oxidation of some bis-(4-hydroxyphenyl) sulphides under a variety of autoxidative conditions (including, for example, the oxidation under basic conditions with molecular oxygen, a system known[18] to produce semiquinones[19] from hydroquinones). The radicals formed varied with the concentration of substrates and the oxidation system used, and the sequence of reactions is best illustrated by considering in detail the radicals formed from compound (1; R^1 = Me, R^2 = Bu^t).

Aerial oxidation of a solution of compound (1; R^1 = Me, R^2 = Bu^t) in ethanolic 2M-sodium hydroxide led to a complex e.s.r. spectrum which, slowly, or rapidly on addition of further sodium hydroxide, simplified to an eight-line signal with *a*(3 H) 0.205, *a*(1 H) 0.155 mT, *g* 2.004 7. The initial spectrum could be resolved into spectra from two radicals, the eight-line signal mentioned above and a spectrum with *a*(3 H) 0.256, *a*(1 H) 0.152, *a*(1 H) 0.166 mT, *g* 2.004 5. The latter is evidently[20,21] from 2-methyl-6-t-butyl-*p*-benzosemiquinone (4; R^1 = Me, R^2 = Bu^t). The radical which remains is believed to be the hydroxylated semiquinone of structure (5; R^1 = Me, R^2 = Bu^t), on the basis of the slightly higher *g* value and the presence of only a single hydrogen-atom splitting: hydroxylation presumably takes place at the ring position adjacent to the methyl group. Further, the action of aqueous ethanolic sodium hydroxide and molecular oxygen on 2-methyl-6-t-butyl-*p*-benzoquinone led to the same two radicals, the spectrum from (5; R^1 = Me, R^2 = Bu^t) developing after a few hours.

Semiquinones were also detected in the oxidation of substituted bis-(4-hydroxyphenyl) sulphides but not in the reaction of the parent compound; the sulphide (1; R^1 = R^2 = Me) gave a radical with *a*(8 H) 0.20 (±0.01) mT, *g* 2.004 5, assigned[21] to 2,6-dimethylbenzosemiquinone, and compound (1; R^1 = R^2 = Bu^t) gave the corresponding 2,6-di-t-butylbenzosemiquinone [*a*(2 H), 0.113 mT, *g* 2.004 5[21]].



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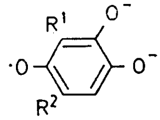
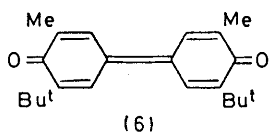


(5)

In order to obtain further information about the modes of formation of semiquinones in these systems, oxidation was carried out with potassium hexacyanoferrate(III) in aqueous methanolic sodium hydroxide in a flow system. With compound (1; R^1 = Me, R^2 = Bu^t) (*ca.* 7 × 10^{-3}M), two radicals were detected: the spectrum of one had *a*(6 H) 0.213 mT, *g* 2.005 5, and a large linewidth (0.094 mT); that of the second (*g* 2.003 9) comprised a large number of sharper lines (ΔH 0.025 mT). When the flow was slowed or stopped, the broader spectrum disappeared and the second spectrum became completely resolved; it had *a*(6 H) 0.169, *a*(4 H) 0.076 mT. This is assigned to the diphenosemiquinone [(6)$^{-\cdot}$], and the same spectrum was obtained by reaction of the parent diphenoquinone with aerated aqueous ethanolic sodium hydroxide. When the oxidation of compound (1; R^1 = Me, R^2 = Bu^t) was carried out under conditions of fast flow, with a lower concentration of organic substrate, only the broad-line spectrum was detected. This spectrum has splittings and a *g* value which suggest that unpaired electron density is delocalized onto S and over both rings and is accordingly assigned to the anion-radical (7). Sulphur-bridged semiquinones from



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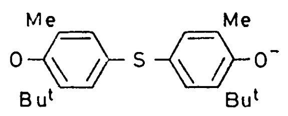

(7)

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[16] H. B. Stegmann, K. Scheffler, and E. Müller, *Annalen*, 1964, **677**, 59.

[17] N. N. Kalibabchuk, Ya. A. Gurvich, A. E. Grinberg, and V. D. Pokhodenko, *Zhur. org. Khim.*, 1971, **7**, 339.

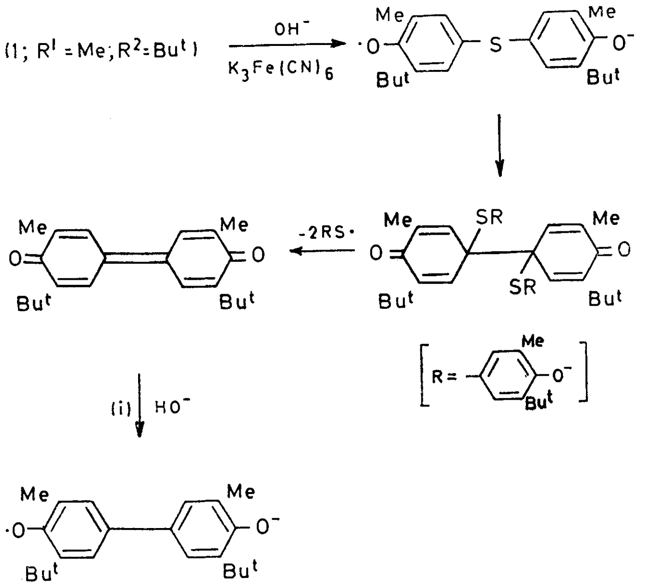
[18] P. B. Ayscough, 'Electron Spin Resonance in Chemistry,' Methuen, London, 1967.

[19] M. Adams, M. S. Blois, and R. H. Sands, *J. Chem. Phys.*, 1958, **28**, 774.

[20] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.

[21] J. A. Pedersen, *Mol. Phys.*, 1974, **28**, 1031.

other substrates were also characterized (see Table 1); only in the case of compound (1; $R^1 = R^2 = Bu^t$) was a spectrum from the corresponding diphenosemiquinone also observed [this radical has *a*(4 H) 0.081 mT, *g* 2.003 9, and it was also generated from the parent diphenoquinone by the method described above].

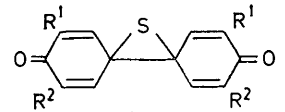


SCHEME 1

Oxidation of bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphoxide (*ca.* 10^{-2}M) with potassium hexacyanoferrate(III) under flow system conditions yielded the anion-radical of (6); at lower substrate concentrations, no radicals were detected. The e.s.r. spectrum of 3,3′,5,5′-tetra-t-butyldiphenosemiquinone was also observed during the oxidation of bis-(4-hydroxy-3,5-di-t-butylphenyl) sulphoxide (*ca.* 10^{-2}M) but at lower concentrations of substrate (*ca.* 10^{-3}M) the sulphinyl(SO)-containing semiquinone [*cf.* (7)] was detected (Table 1). The fact that the *g* value for this radical is lower than that for (7) may be attributable to the reduced ability of the sulphinyl group for electron delocalisation.

Mechanism of the Oxidations.—A possible mechanism for the oxidation by potassium hexacyanoferrate(III) of, for example, compound (1; $R^1 = Me$, $R^2 = Bu^t$) involves (Scheme 1) dimerisation of the semiquinone followed by loss of the sulphur-containing groups, probably in homolytic fashion, to give the diphenoquinone. [This compound was isolated when the parent compound was treated with lead(IV) oxide in benzene; see Experimental section.] We note that, for example, 4-methyl-2,6-di-t-butylphenoxyl, when generated photolytically in CCl_4, exhibits initial second-order decay (k 1.5×10^8 l mol^{-1} s^{-1}) and that dimerisation *via* the 4-position is though to be involved.[22] A similar mechanism to that in Scheme 1 may explain[23,24] the production of diphenoquinones in the oxidation of 4-halogeno-2,6-di-t-butylphenols, where homolysis of the carbon–halogen bond in the dimer might also be expected. The final steps [summarized as reaction (i)] are presumably analogous to those involved in the production of semiquinones from quinones under basic conditions[20,25] (reaction is thought to involve hydroxide-ion attack on the quinone and electron transfer from an anionic intermediate to a second molecule of quinone).

A possible alternative route to the diphenoquinone involves formation, *via* two-electron oxidation, of the dispirothiiran (8) followed by extrusion of sulphur: a related dispirocyclopropanone has been proposed[26] as an intermediate in the formation of the corresponding diphenoquinone from the anaerobic oxidation of 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butylbenzophenone with $K_3Fe(CN)_6$.



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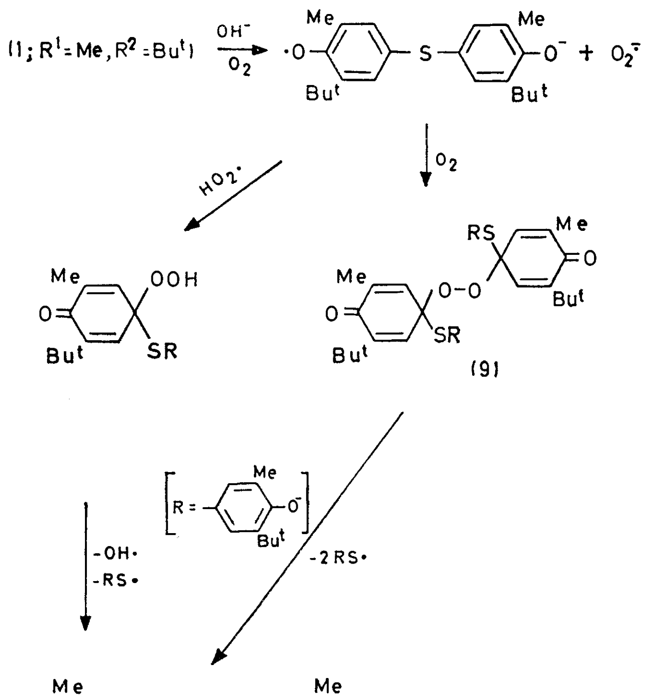

SCHEME 2

The formation of the semiquinone (4; $R^1 = Me$, $R^2 = Bu^t$) in the base-catalysed autoxidation of compound (1; $R^1 = Me$, $R^2 = Bu^t$) may well proceed (see

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[22] E. J. Land and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2016.

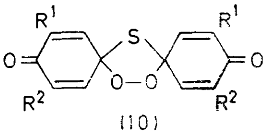
[23] K. Ley, E. Müller, R. Mayer, and K. Scheffler, *Chem. Ber.*, 1958, **91**, 2670.

[24] E. R. Altwicker, *Chem. Rev.*, 1967, **67**, 475.

[25] J. A. Pedersen, *J.C.S. Perkin II*, 1973, 424.

[26] S. M. Colegate, F. R. Hewgill, and G. B. Howie, *Austral. J. Chem.*, 1975, **28**, 343.

Scheme 2) through a first-formed sulphur-bridged semiquinone (formed by electron-transfer from the dianion to oxygen) which could then react at the 4-position in the phenoxyl-like ring with either oxygen itself or $HO_2\cdot$ (from $O_2^{-\cdot}$). Analogous reactions previously proposed include that undergone by 2,4,6-tri-t-butylphenol under similar conditions to give a bicyclohexadienone peroxide, structurally similar to (9), which decomposes to give, *inter alia*, 2,6-di-t-butylbenzoquinone, and the reaction between $Bu^tO_2\cdot$ and 4-methyl-2,6-di-t-butylphenol to give a cyclohexadienone peroxide [27] (see also ref. 24). A further possibility is that, by analogy with the mechanism proposed [26] for the aerobic oxidation of a 4,4′-dihydroxybenzophenone to the corresponding *p*-benzoquinone, a cyclic peroxide (10) is involved. As explained above, the route from 2-methyl-6-t-butyl-*p*-benzoquinone to the semiquinone [reaction (ii)] is analogous to that followed by other quinones,[20,21] as is the hydroxylation of the quinone to give the other radical detected [(5; $R^1 = Me$, $R^2 = Bu^t$)]



(10)

Summary.—The results suggest that the mechanism of oxidation inhibition by alkyl-substituted bis-(4-hydroxyphenyl) sulphides is analogous to that for simpler phenols: in a chain-terminating step, a sulphur-substituted phenoxyl (or semiquinone) radical is produced which, on account of its steric and electronic properties, has considerable stability. Under certain conditions, further reactions can remove oxygen and peroxyl radicals from the system to give compounds (*e.g.* quinones) which are themselves inhibitors of radical reactions.[28] In particular, it is interesting that the diphenoquinone (6) is known to act as a synergistic agent when used with alkyl-substituted bis-(4-hydroxyphenyl) sulphides to inhibit the oxidation of polyethylene.[29] Alkyl-substituted bis-(4-hydroxyphenyl) sulphides also react with hydrogen peroxide to give the corresponding sulphoxides: the Experimental section describes details of the appropriate reactions of compounds (1; $R^1 = Me$, $R^2 = Bu^t$) and (1; $R^1 = R^2 = Me$). As indicated above, these sulphoxides undergo oxidation under appropriate conditions to phenoxyl radicals, semiquinones, and, presumably *via* diphenoquinones, diphenosemiquinones. It thus seems likely that bis-(4-hydroxyphenyl) sulphides can function as hydroperoxide decomposers as well as chain-terminating agents and that products of this molecular oxidation pathway can themselves function as oxidation inhibitors.

Molecular Orbital Calculations.—Sullivan and Shine [12] have previously determined a set of parameters for Hückel molecular orbital [30] calculations, employing the McLachlan [31] modification, on the cation-radical of the parent bis-(4-hydroxyphenyl) sulphide: these are h_S 1.11, k_{CS} 0.65, h_O 2.0, k_{CO} 1.11. Although we have tested alternative parameters for sulphur (*e.g.* h_S 1.25, k_{CS} 0.57, as used for calculations on phenothiazine cation-radicals [32]), together with a variety of parameters for oxygen, the earlier set of parameters gives optimum agreement.

We have carried out a series of calculations designed to simulate changes in spin-density [as judged by the magnitude of *a*(H) and *a*(Me), both of which should be proportional to the π-electron spin density, ρ_π, on the ring carbon atom to which the substituents are attached] when alkyl groups are introduced into the cation-radical of the parent (see Table 1).

We have used an inductive model to simulate the effect of alkyl substitution in the cation-radicals:[30] h_C is lowered for the carbon atom to which the alkyl group is attached. Best agreement between observed splittings for [(1; $R^1 = R^2 = Me)^{+\cdot}$] and those calculated by using a variety of h_C values (together with Q^H_{CH} −2.7 mT, $Q^H_{CCH_3}$ 3.0 mT,* λ 1.2) was obtained for $h_{C(3,5)}$ −0.1 (see Table 2): the lowering of ρ(C-2) and raising of ρ(C-3), in comparison with the values calculated for the parent radical (for which all h_C were taken as 1), is marked. The value chosen for k_{CO} (1.11) reflects the expected extensive conjugation between the lone pairs on the oxygen atoms and the π-system; this overlap is presumably maximised when the OH bonds are in the same plane as the atoms in the aromatic rings. The dominant contribution to *a*(OH) will then be that arising from spin-polarisation of electrons in the O–H bonds by unpaired electron density on oxygen (giving a negative splitting) rather than that arising *via* hyperconjugation involving spin density at C-4 (this would give a positive contribution to the splitting, but would not be significant unless the OH bonds occupied out-of-plane conformations to any extent; *cf.* ref. 33). The hydroxy-proton splittings in the cation-radicals [(1; $R^1 = R^2 = H)^{+\cdot}$] and [(1; $R^1 = R^2 = Me)^{+\cdot}$] are probably negative: if this is so, the greater value of *a*(OH) for the latter may reflect an increased value of ρ_O (calculated ρ 0.030 3), in comparison with that for the former (calculated ρ 0.026 8), which stems from the inductive effect of the methyl groups.

The fact that *a*(2-H) is the same for the cation-radicals

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* There appears to be no accepted value for $Q^H_{CCH_3}$ in radicals of this type: methyl-proton splittings in charged aromatic free radicals probably depend on the charge on the ion as well as on the spin density on the adjacent ring carbon atom.[8] The value for $Q^H_{CCH_3}$ chosen here is based on the observation [7] that for a variety of sulphur-conjugated aliphatic radicals $\cdot CH(CH_3)X$, $a(CH_3)$ is in each case slightly greater than *a*(H), so that $Q^H_{CCH_3} > Q^H_{CH}$.

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$[1;\ R^1 = R^2 = \mathrm{Me})^{+\cdot}]$ and $[(1;\ R^1 = R^2 = \mathrm{Bu^t})^{+\cdot}]$ could indicate that the value of −0.1 for h_C for the methyl-substituted carbon atoms in the former is also appropriate for the ring carbon atoms bearing substituents in the latter, although the inductive effect of t-butyl is generally expected to be greater than that for methyl. However, a more likely explanation is that in the latter example an increased inductive effect (for $\mathrm{Bu^t}$) is coupled with an increased angle of twist between the O–H bonds and the plane of the aromatic carbon atoms, and hence reduced conjugation between the rings and the hydroxy-groups. In support of this suggestion, we find that reducing h_C (to −0.3) *and* k_{CO} (to 0.95) reproduces the required trend (see Table 2). Further, the lower value of *a*(OH) for the cation-radical $[(1;\ R^1 = R^2 = \mathrm{Bu^t})^{+\cdot}]$ than for $[(1;\ R^1 = R^2 = \mathrm{Me})^{+\cdot}]$ is then understandable in terms of an increased positive contribution to an overall negative splitting as the O–H bonds move out of plane. These results also suggest that suitable parameters for the cation-radical $[1;\ R^1 = R^2 = \mathrm{Me})^{+\cdot}]$ could include the combination h_C −0.2 (for C-3 and C-5: this would be close to the values normally used for carbon atoms bearing methyl substituents) and $0.95 < k_{CO} < 1.11$ (*i.e.* to simulate a small extent of twisting).

TABLE 2

Results of Hückel–McLachlan molecular orbital calculations on some bis-(4-hydroxyphenyl) sulphide cation-radicals [a]

	$[(1;\ R^1 = R^2 = \mathrm{Me})^{+\cdot}]$			$[(1;\ R^1 = R^2 = \mathrm{Bu^t})^{+\cdot}]$			$[(1;\ R^1 = \mathrm{Me},\ R^2 = \mathrm{Bu^t})^{+\cdot}]$		
	Parameters: $h_{C\text{-}3,\text{-}5}$ −0.1; k_{CO} 1.11			$h_{C\text{-}3,\text{-}5}$ −0.3; k_{CO} 0.95			$h_{C\text{-}3}$ −0.2, $h_{C\text{-}5'}$ −0.3; k_{CO} 1.09		
Position	ρ	*a*(calc.) [b]	*a*(obs.) [b]	ρ	*a*(calc.)	*a*(obs.)	ρ	*a*(calc.)	*a*(obs.)
1	0.056 90			0.049 88			0.057 36		
2	0.053 30	(−)0.144	0.145	0.054 28	(−)0.147	0.145	0.055 36	(−)0.150	0.145
3	0.009 10	(+)0.027	0.027 5	0.001 88			0.008 96	(+)0.027	0.027 5
4	0.101 14			0.128 01			0.118 14		
5	0.009 10	(+)0.027	0.027 5	0.001 88			0.015 69		
6	0.053 30	(−)0.144	0.145	0.054 28	(−)0.147	0.145	0.079 11	(−)0.106	0.112
O	0.030 33		(−)0.115(OH)	0.025 45		(−)0.076(OH)	0.034 47		(−)0.112(OH)
S	0.373 13			0.368 72			0.341 82		

[a] For other parameters and *Q* values, see text. [b] Splitting from α-proton or methyl-group protons (mT).

In the calculations on the cation-radical of $(1;\ R^1 = \mathrm{Me},\ R^2 = \mathrm{Bu^t})$ two different inductive parameters were used [h_C (Me) −0.2, h_C ($\mathrm{Bu^t}$) −0.3]. From a variety of values chosen for k_{CO}, best agreement was obtained with k_{CO} 1.09, with assignment of proton splittings in the sense *a*(2-H) 0.145, *a*(6-H) 0.112 mT (see Table 2). The value of k_{CO} corresponds to a nearly in-plane conformation for the O–H bonds (they are presumably *syn* to the methyl rather than to the t-butyl groups) and the value of *a*(OH) observed is in the region expected on this basis.

Calculations were also undertaken for the phenoxyl radical from $(1;\ R^1 = R^2 = \mathrm{H})$, the observed splittings for which are *a*(3- and 5-H) 0.500, *a*(2- and 6-H) 0.090 mT (with no evidence for significant delocalisation into the second, phenolic ring). The parameters used were as follows: h_S 1.11, k_{CS} 0.65 (as before), for the phenolic oxygen $h_{\ddot{O}}$ 2.0, k_{CO} 1.11, and for the phenoxyl oxygen k_{CO} 1.11, $h_{\dot{O}}$ 0.6—1.0. The closest agreement with experiment was obtained with $h_{\dot{O}}$ 0.7: the calculated ring splittings are then, for the phenoxyl ring, (−)0.606 and (+)0.078 mT (2- and 5-H, and 3- and 6-H, respectively) and, for the second ring, *a*(2′- and 5′-H) (+)0.130, *a*(3′- and 6′-H) (+)0.031 mT. The magnitude of *a*(2′- and 5′-H) is clearly overemphasised; it is possible that further variation of some of the parameters (*e.g.* k_{CS}, to simulate reduction of conjugation across sulphur as a consequence of ring twisting) would enable closer agreement to be achieved.

EXPERIMENTAL

The e.s.r. spectrometer, the procedure for measuring splittings (±0.005 mT unless stated otherwise) and *g* values, and details of the three-way flow system have been described previously.[6,7] For the oxidations with hexacyanoferrate, the three solutions contained potassium hexacyanoferrate(III) (*ca.* 5×10^{-3}M), sodium hydroxide (*ca.* 2.5×10^{-1}M) in aqueous methanol, and the bis-(4-hydroxyphenyl) sulphide (5×10^{-4}—10^{-2}M). For oxidation with cerium(IV) ammonium nitrate a two-way flow system and conditions described previously [15] were employed.

Cation-radicals were prepared by methods described previously.[8–10] Most of the spectra were generated with the $AlCl_3$–$MeNO_2$ system, as follows. The diaryl sulphide (*ca.* 5 mg) was placed in one arm of a three-armed cell which contained $AlCl_3$ (*ca.* 20 mg) in a second arm. The cell was attached to a vacuum line and evacuated. Nitromethane (0.5 ml; previously degassed *via* a number of freeze–thaw cycles) was distilled into the arm containing $AlCl_3$. This arm was cooled (to −196 °C) and the cell was evacuated and sealed off. The solution containing $AlCl_3$ was then mixed with the substrate and poured into the e.s.r. cell, which was attached to the third arm. The resulting solution, diluted where necessary by distillation of solvent into the e.s.r. tube, was then examined at room temperature by e.s.r. A similar technique was used for the oxidations with lead(IV) oxide–benzene, although a nitrogen purge replaced the evacuation–outgassing procedure. Autoxidation reactions were carried out *in situ* in Varian aqueous sample cells.

Bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide was a gift from Dr. R. W. Glyde, Esso Research Centre, Abingdon, and was recrystallised from petroleum prior to use. Bis-(4-hydroxyphenyl) sulphide was prepared according to the method described in reference 34. The method used for the preparation of *bis-(4-hydroxy-3,5-dimethylphenyl) sulphide* was similar to that described [35] for the preparation of bis-

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[34] A. J. Neale, P. J. S. Bain, and T. J. Rawlings, *Tetrahedron*, 1969, **25**, 4583.

[35] Ethyl Corp., B.P. 898,028 (*Chem. Abs.*, 1962, **57**, 15013b).

(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide. To 2,6-dimethylphenol (12.2 g) in benzene (100 ml) was slowly added a solution of sulphur dichloride (5.10 g) in benzene (25 ml). The mixture was stirred overnight and then the solvent was removed *in vacuo*. The resulting viscous oil was dissolved in petroleum and cooled to 0 °C. The precipitate was filtered off and reprecipitated from petroleum (yield 6.10 g); m.p. 122—123 °C (Found: C, 73.75; H, 8.55. $C_{22}H_{30}O_2S$ requires C, 73.75; H, 8.35%). This method was unsatisfactory for preparing bis-(4-hydroxy-3,5-di-t-butylphenyl) sulphide [36] and the following procedure was employed. 2,6-Di-t-butylphenol (10.3 g) was dissolved in glacial acetic acid (50 ml) and bromine (8.00 g) was added slowly (the temperature of the solution was not allowed to rise significantly above room temperature). After stirring for 1.0 h, the yellow solution was heated under reflux for 2.0 h. When the mixture (colourless) was cooled, a precipitate of 4-bromo-2,6-di-t-butylphenol was formed. This was filtered off and washed with glacial acetic acid. To 4-bromo-2,6-di-t-butylphenol in propan-2-ol (100 ml) and water (50 ml) was added sodium sulphide (6.00 g). The solution was heated under reflux for 4.0 h and then cooled. The precipitate was filtered off and recrystallized from acetone–water (yield 2.50 g); m.p. 137—138 °C (lit.,[36] 138—140°). *Bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphoxide* was prepared by a method which is known readily to oxidise a sulphide to a sulphoxide group.[37,38] Bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide (3.56 g) in acetone (25 ml) was treated with 30% hydrogen peroxide (1 ml). The solution was stirred overnight at room temperature and ether (100 ml) was then added to precipitate the product. This was filtered off, washed with ether, and recrystallized from acetone–ether (yield 3.00 g); it decomposed on heating at 149—150 °C (Found: C, 70.7; H, 8.45. $C_{22}H_{30}O_3S$ requires C, 70.6; H, 8.0%); $\nu_{S=O}$ 980 cm^{-1} (Nujol). *Bis-(4-hydroxy-3,5-di-t-butylphenyl) sulphoxide*, prepared similarly, also decomposed on heating (181—183 °C) (Found: C, 73.55; H, 9.0. $C_{28}H_{40}O_3S$ requires C, 73.4; H, 9.2%). Attempts to prepare bis-(4-hydroxyphenyl) sulphoxide and bis-(4-hydroxy-3,5-dimethylphenyl) sulphoxide resulted in the production of oils which could not be further purified.

An initial attempt was made to prepare 2-methyl-6-t butylquinone by the method of Hewitt.[39] A solution of 4-bromo-2-methyl-6-t-butylphenol [prepared from 2-methyl-6-t-butylphenol (1.64 g) by the method described above] in water (50 ml) was treated with a solution of Fremy's salt [40] (5.00 g) and sodium acetate (10.0 g) in water (250 ml), and the mixture was stirred overnight. Extraction with ether yielded a bright red material which was not the desired 2-methyl-6-t-butylquinone.

An indirect method involving the following transformations was more successful. To a solution of 2-methyl-6-t-butylphenol (3.00 g) in absolute ethanol (25 ml) was added concentrated hydrochloric acid (2 ml) and the solution was cooled to −5 °C. A solution of sodium nitrite (1.10 g) in water (5 ml) was gradually added with vigorous stirring, care being taken to ensure that the temperature did not rise above 0 °C. The solution was stirred for a further 0.5 h and then poured into ice–water. The precipitated oxime was filtered off, washed with water, dried, and used without further purification (yield 3.80 g). To a solution of the oxime (3.80 g) and sodium hydroxide (2.00 g) in water (70 ml) was added, at 40 °C, sodium dithionite (20.0 g). White crystals of the corresponding 4-aminophenol were formed. These were filtered off, washed with water, and dissolved in glacial acetic acid (35 ml). To the solution was added chromium(VI) oxide (6.00 g) in water (100 ml). The mixture was stirred for 1.0 h and then steam distilled. The distillate was extracted with ether and the ether layer was then dried ($MgSO_4$) and evaporated *in vacuo* to give 2-methyl-6-t-butyl-*p*-benzoquinone as a yellow oil (0.90 g), which was used without further purification. 3,3′-Dimethyl-5,5′-di-t-butyldiphenoquinone was prepared as follows.[41] To a solution of 2-methyl-6-t-butylphenol (2.00 g) in benzene (50 ml) was added lead(IV) oxide (10.0 g). The solution was stirred overnight at room temperature and then the excess of lead(IV) oxide was filtered off; the solvent was removed *in vacuo*. The residue of 3,3′-dimethyl-5,5′-di-t-butyldiphenoquinone was contaminated with some lead(IV) oxide, but was used without further purification. A similar method was used for the preparation of 3,3′,5′,5′-tetra-t-butyldiphenoquinone.

3,3-Dimethyl-5,5′-di-t-butyldiphenoquinone was also formed in the oxidation of bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide by lead(IV) oxide. To the sulphide (1.00 g) in benzene (20 ml) was added lead(IV) oxide (3.00 g). The solution was stirred for 12.0 h and the excess of lead(IV) oxide was filtered off. The filtrate was evaporated to dryness under reduced pressure and the resulting solid was purified by silica-gel column chromatography (dichloromethane as eluant). The red solid obtained by removal of the dichloromethane under reduced pressure was recrystallized from ethanol to give red crystals of 3,3′-dimethyl-5,5′-di-t-butyldiphenoquinone (0.30 g), m.p. 195—196 °C (lit.,[41] 196—198 °C).

Satisfactory elemental analyses were obtained for all the compounds mentioned above: these were performed by Mr. R. B. Girling of this Department using a Perkin-Elmer 240 Elemental Analyser. M.p.s were determined with a Kofler micro-heating stage (Reichert).

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