Electron Spin Resonance Spectra of Radicals derived from Arylhydroquinones

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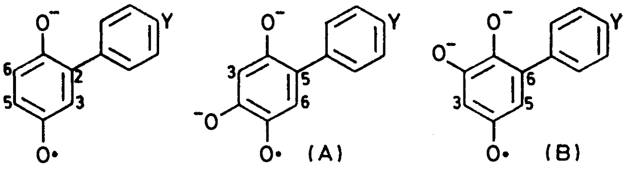
The e.s.r. spectra of radicals formed in the autoxidation of arylhydroquinones show hyperfine splitting from protons attached to the aryl group, showing that the odd electron is delocalised over both rings. Substituents on the phenyl group influence the various proton coupling constants in a way which is related to their electron-donating or electron-withdrawing properties.

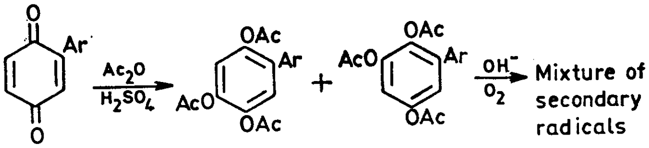
We have reported how several different types of radical intermediate can be observed during the autoxidation of alkylhydroquinones and quinones.[1,2] In addition to semiquinones, radicals derived from 1,2,4-trihydroxybenzenes can be seen by means of e.s.r. spectroscopy. A parallel series of radicals are formed during the autoxidation of arylhydroquinones, showing that the aryl groups have little effect on the reactivity of the quinone nucleus, although the hyperfine splittings of aryl protons indicate that the odd electron is delocalised on to the second ring to some extent. Substituents on the aryl group have only a small effect on the coupling constants although the trends are reasonably definite.

The parent quinones were made by direct arylation of *p*-benzoquinone *via* the diazonium salts,[3] and the ease with which this reaction could be made to yield the arylquinone varied somewhat from one case to another. The primary radicals were generated easily in dilute alkaline solutions and the secondary radicals from more concentrated alkali. The latter were always obtained initially as a mixture of two isomeric radicals, (A) and (B). This contrasts with the behaviour of alkylhydroquinones which could be made to yield one or other isomer depending on the conditions. However, when the solutions were left the (B)-type radical decayed, often leaving a pure spectrum from type (A). Improved spectra of the secondary radicals could be obtained by acetylating the arylquinones followed by alkaline hydrolysis (Scheme 1). The e.s.r. spectra were in general well resolved and although there was a mixture of secondary radicals both spectra could be analysed because the overlap between them was minimal (see Figure 1). Difficulties arise in a few cases because the smaller splittings are of the same



(A) (B)

Primary radical Secondary radicals



Scheme 1

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[1] P. Ashworth and W. T. Dixon, *Chem. Comm.*, 1971, 1150.

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

[3] P. Brassard and P. L. Écuyer, *Canad. J. Chem.*, 1958, **36**, 700.

order as the line-widths, and since we observe the first derivative of the absorption spectrum, overlapping of maxima and minima can lead to reductions of apparent intensity or even total annihilation of some lines. This leads, in the case of *p*-nitrophenylsemiquinone to some uncertainty in the smaller coupling constants (see Figure 2).

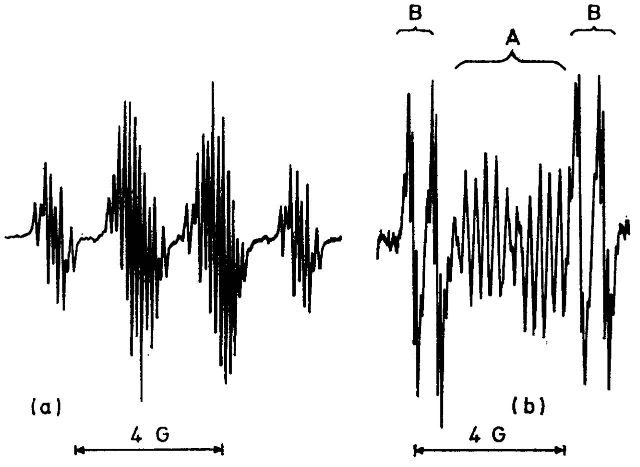


FIGURE 1 E.s.r. spectra of radicals from *m*-chlorophenylhydroquinone, (a) primary radical (in 50% aqueous ethanol, 0·5% sodium hydroxide; (b) secondary radicals (in 7·5% sodium hydroxide)

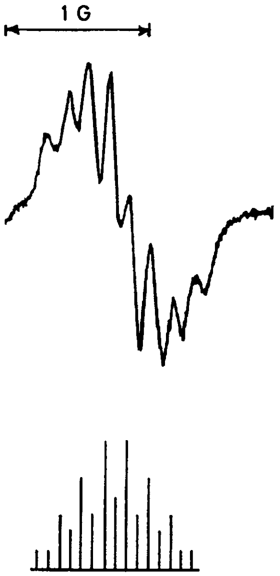


FIGURE 2 One of the side bands of the e.s.r. spectrum of *p*-nitrophenylsemiquinone, with the reconstructed ' stick ' spectrum (alternate lines are ' missing ')

The assignments given in Tables 1 and 2 are based on the rules adopted in our previous paper [2] on alkyl semiquinones and which are in agreement with the results of previous workers.[4-6] These rules may be summarised thus: (1) coupling constants of protons *para* to a substituent on the semiquinone nucleus are large; (2) coupling constants of protons *ortho* to an electron-donating substituent are small. As an example, consider structure (I). Position 5 is *para* to X; positions 5 and 6 are *ortho* to O^-; position 3 is *ortho* to O^- and to X. Hence $a_3 < a_6 < a_5$; (3) the influence of the group X decreases along the series $O^- \gg Bu^t > Me > Ph > Cl > H$.

TABLE 1

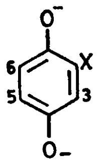
Coupling constants of primary radicals

	Coupling constants/G				
	a_2				
Aryl group	a_{ortho} a_{para}	a_{meta}	a_3	a_5	a_6
Ph	0·27	0·16	1·99	2·56	2·12
p-OH	0·32	0·14	1·38	2·53	2·33
p-OMe	0·30	0·15	1·85	2·56	2·16
p-Me	0·28	0·16	1·88	2·55	2·13
p-Ph	0·28	0·20	1·98	2·58	2·10
m-Cl	0·27	0·15	2·00	2·52	2·13
p-Cl	0·28	0·16	2·10	2·54	2·10
p-CO_2H	0·27	0·17	2·10	2·56	2·10
p-CO_2Me	0·29	0·18	2·26	2·56	1·95
p-NO_2	0·30 a_N = 0·75	0·15	2·38	2·50	1·92
2,5-Diphenyl	0·25	0·14	2·20		2·20
2,5-Di-*p*-Cl	0·31	0·16	1·78		1·78

TABLE 2

Coupling constants/G of secondary radicals

	Secondary radical (A)				Secondary radical (B)			
		a_5					a_6	
Aryl group	a_3	a_{ortho} a_{para}	a_{meta}	a_6	a_3	a_5	a_{ortho} a_{para}	a_{meta}
Ph	0·50	0·54	0·31	1·08	0·67	4·52	0·12	0·12
p-OH	0·53	0·65	0·27	0·53	0·63	4·00	0·14	0·10
p-OMe	0·53	0·59	0·29	0·90	0·65	4·40	0·12	0·12
p-Me	0·50	0·58	0·31	0·90	0·67	4·42	0·13	0·13
p-Ph	0·50	0·58	0·33	1·12	0·66	4·52	0·12	0·12
m-Cl	0·52	0·54	0·29	1·19	0·67	4·62	0·12	0·12
p-Cl	0·48	0·59	0·31	1·16	0·68	4·58	0·12	0·12
p-CO_2H	0·48	0·58	0·32	1·17	0·67	4·66	0·12	0·12
p-NO_2	0·45	a_{ortho} =0·60 a_{para} a_N =0·15	0·30	1·48	0·70	4·86	0·12	0·12



(I)

In the case of primary radicals we expect substitution into the phenyl ring to affect H-3 more than H-5, and we

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[4] B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, 1959, **30**, 1006.

[5] A. Fairbourn and E. A. A. Lucken, *J. Chem. Soc.*, 1963, 258.

[6] K. A. K. Lott, E. L. Short, and D. N. Waters, *J. Chem. Soc.* (B), 1969, 1232.

assign the larger splitting to H-3 in two cases: (a) Y = $\mathrm{NO_2}$ and (b) Y = $\mathrm{CO_2Me}$ (see Table 1).

The coupling constants of protons on the phenyl ring were assigned by reference to unambiguous cases (*e.g.*, *m*-chlorophenyl) and in the primary radicals and the secondary radicals of type (A) the *ortho*- and *para*-proton splittings were of the order of twice the *meta*-proton coupling constants.

Trends in the Coupling Constants.—There seems to be a small but definite relationship between the electron-donating power of the substituent on the phenyl ring and the coupling constants of the various protons. For example, the rules applying to the protons attached to the original quinone nucleus are as follows. For protons *ortho* to the aryl group, the coupling constants decrease with increasing electron-donating power of Y, as shown in Table 3. Protons *meta* to the aryl group have coupling constants which increase with increasing electron-donating power of Y, as shown in Table 4. Protons *para* to the aryl group are little affected by the substituent Y, if anything the trend is similar to that for *ortho*-substituents, as shown in Table 5. When the overall spin density in the aryl ring is large the *ortho*- and *para*-proton coupling constants are of the order of twice those of the *meta*-protons, but as this overall coupling decreases the splittings become more equal. The difference between the coupling constants of the *ortho*- and *meta*-protons is apparently increased somewhat by electron-donating substituents in the *para*-position, as shown in Table 6. Addition of the proton coupling constants gives us a measure of the amount of spin associated with carbon atoms attached to hydrogen, provided that the splittings all have the same sign. If this is the case, then it appears that electron-donating substituents on the phenyl ring tend to decrease the probability of the odd electron being on carbon atoms attached to hydrogen. It, therefore, appears to be probable that the $>$C–Y group tends to 'attract' spin density more when Y releases electrons more easily. We can rationalise this in terms of valence-bond approach to radicals in which the odd electron is largely associated with oxygen. The only canonical structures which have reasonably low energies and can lead to delocalisation of the odd electron are those having a double bond to, or a negative change on, the oxygen, *i.e.*, for phenoxyl or semiquinone radicals the main canonical structures are of types (i), (ii), and (iii). The odd electron density will be greater on positions which yield electrons more easily, for the canonical structures in which the odd electron is associated with these positions will have higher probabilities owing to contributions of canonical structures of type (II). The delocalisation of the odd electron to the phenyl group must occur largely through structures such as (II)—(IV) and that explains why the spin density on the *ortho*- and *para*-positions is generally greater than that on the *meta*-positions.

TABLE 3

Y	O$^-$	OMe	Me	H	Cl	$\mathrm{CO_2Me}$	$\mathrm{NO_2}$
a_{ortho}							
Primary	1·38	1·85	1·88	1·99	2·10	2·26	2·38
Secondary (A)	0·53	0·90	0·90	1·08	1·16		1·48
Secondary (B)	4·00	4·40	4·42	4·52	4·58		4·86

TABLE 4

Y	O$^-$	OMe	Me	H	Cl	$\mathrm{CO_2Me}$	$\mathrm{NO_2}$
a_{meta}							
Primary	2·33	2·16	2·13	2·12	2·10	1·95	1·92
Secondary (A)	0·53	0·53	0·50	0·50	0·48		0·45

TABLE 5

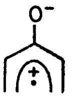
Y	O$^-$	OMe	Me	H	Cl	$\mathrm{CO_2Me}$	$\mathrm{NO_2}$
a_{para}							
Primary	2·53	2·56	2·55	2·56	2·54	2·56	2·50
Secondary (B)	0·63	0·65	0·67	0·67	0·68		0·70

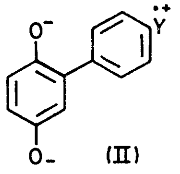
TABLE 6

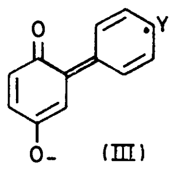
	Primary		(A)		(B)	
Y	O$^-$	Cl	O$^-$	Cl	O$^-$	Cl
a_{ortho}	0·32	0·28	0·65	0·59	0·14	0·12
a_{meta}	0·14	0·16	0·27	0·31	0·10	0·12

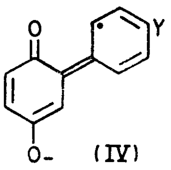

(i)


(ii)


(iii)


(II)


(III)


(IV)

Similarly on the hydroquinone nucleus, the trends of the coupling constants of protons *meta* to phenyl substituents probably arises from the lack of conjugation between the two positions and also, perhaps, from the influence of the phenyl group on the adjacent oxygen atom.

By difference, these trends are opposite to those at the *ortho*- and *para*-positions, which, from the usual valence-bond viewpoint, are more directly affected by the substituents, although the observed changes at the *para*-position are very small.

Finally the extra stability of the radicals of type (A) compared with corresponding radicals (B) is probably due not so much to the fact that there is greater delocalisation of the odd electron in type (A), but more to the availability of a position of high spin density for further attack in the type (B) radicals.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E4 instrument. To obtain the primary radicals a solution of the arylhydroquinone (0·01M) in ethanol was mixed with an equal volume of 1% sodium hydroxide solution, both flow and static methods being used. The secondary radicals were obtained by adding an aqueous solution of the hydroquinone (0·05M) to an equal volume of 15% sodium hydroxide solution.

Materials.—The arylquinones were obtained by direct arylation of *p*-benzoquinone *via* the diazonium salts according to the method of Brassard and L'Écuyer.[3] In certain cases, where appreciable amounts of the diarylquinone tended to be formed, it was convenient to use a large excess of the *p*-benzoquinone. The arylquinone was much easier to separate from the excess of starting material than from the diaryl compound. Reaction of the arylquinone in aqueous acetone with further diazonium salt produced the 2,5-diaryl compound in moderate yield.[3]

The triacetoxy-derivatives were prepared by heating the quinone with acetic anhydride and a little concentrated sulphuric acid at 80 °C.

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