Electron Spin Resonance Studies of Oxidative Processes of Quinones and Hydroquinones in Alkaline Solution; Formation of Primary and Secondary Semiquinone Radicals

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The oxidation of methyl substituted *para*- and *ortho*-hydroquinones and naphthohydroquinones or their corresponding quinones has been studied by e.s.r. spectroscopy. Improved spectral resolution has been obtained by a circulation technique for many primary and secondary semiquinones. Quinones having free quinonoid positions react with hydroxide ions resulting in the simultaneous formation of a semiquinone radical and a radical of a hydroxyquinone adduct which in turn serves as a precursor for the secondary hydroxylation products. Identical products are obtained from the corresponding hydroquinones *via* an autoxidation. All 11 *para*- and *ortho*-compounds studied yield secondary products with a 2-hydroxy-1,4-semiquinone structure.

THE characterization by means of e.s.r. spectroscopy of semiquinone free radicals, produced by air oxidation of quinols in alkaline solution, is of interest.[1] Most studies have focused on characterization of the semiquinones produced initially, either by oxidation of a parent hydroquinone or by reduction of the corresponding quinone. However, a number of recent studies have used e.s.r. as a tool in elucidating autoxidative reaction mechanisms.[2,3]

James *et al.*[4] suggested that *para*-quinones containing at least one hydrogen atom in the quinonoid ring are oxidized in alkaline media to the corresponding hydroxyquinones. E.s.r. studies have since demonstrated that the secondary radicals formed by autoxidation of some *para*- and *ortho*-hydroquinones correspond to the expected hydroxylation products.[1,2,5] Stone and Waters[2] and Ashworth and Dixon[5] did not, however, in all cases succeed in obtaining hydroxylation products.

To investigate the generality of the suggested mechanism, we have made a systematic e.s.r. study of the oxidation of hydroquinone and the complete range of methyl substituted hydroquinones or their corresponding quinones, as well as of catechol and the two monomethylcatechols. All become hydroxylated in an alkaline aqueous solution to 2-hydroxy-1,4-benzoquinones, which may be detected by e.s.r. as semiquinone free radicals. We have further studied 1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone, which are similarly oxidized to 2-hydroxy-1,4-naphthoquinones again detected as semiquinone free radicals.

A question which has received some attention is whether the secondary hydroxylation products have hydroxycyclohexadienyl radicals as precursors. No definite answer has as yet been given. However, starting from quinones, we have detected intermediate radicals with a hyperfine structure resembling that of the

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[1] B. Venkataraman and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1955, **77**, 2707.

[2] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1965, 1488.

[3] J. Pilař, I. Buben, and J. Pospišil, *Tetrahedron Letters*, 1968, 4203.

[4] T. H. James, J. M. Snell, and A. Weissberger, *J. Amer. Chem. Soc.*, 1938, **60**, 2084.

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

primary semiquinone of the parent compound except for the lack of one hyperfine coupling constant. We suggest that these radicals have a dihydroxycyclohexadienone structure, and that they in fact serve as precursors for the secondary hydroxylation products. When starting from a hydroquinone, hydroxylation products identical to those obtained from the corresponding quinone result from autoxidation. The precursors are suggested as having a peroxycyclohexadienone structure in this case.

EXPERIMENTAL

All quinones and hydroquinones studied were commercial, and a purification by sublimation was performed for *p*-benzoquinone only. The primary and secondary radicals were prepared at room temperature by atmospheric oxidation in an alkaline medium. Desired pH values were obtained from standardized NaOH solutions. Hydroquinones and most quinones were studied in water, whereas quinones slow to dissolve in water were first dissolved in a small volume of dimethylformamide and this solution then poured into the alkaline water.

For *para*- and *ortho*-compounds, we circulated the reaction mixture through an open reservoir and through the detection cell. This proved convenient for controlling the degree of air oxidation, and the open reservoir allowed changes in pH during the experiment. The spectra of the primary semiquinones were the first to be observed, and the spectra of the hydroxylation products appeared in most cases after continued circulation. In a few cases the spectra of the hydroxylation products were detectable only after the addition of a small amount of sodium dithionite. This observation indicates that the products were present in quinone form before the addition of the reductant.

Radicals from resorcinols, *i.e.*, *m*-benzosemiquinone radical anions, were detected by use of a flow system similar to the one described by Stone and Waters.[6] Potassium ferricyanide (10^{-2}M) was used as oxidizing agent for all the resorcinols studied.

The flow technique has been demonstrated to give rise to a linewidth broadening of about 0·3 G in the e.s.r. spectra, exempting smaller hyperfine coupling constants from detection.[2] No such broadening occurs when using the circulation technique.

Most e.s.r. spectra of the radicals were recorded on a Varian E-3 e.s.r. spectrometer with 100 kHz modulation. To avoid line distortions from the modulation side bands, high-resolution spectra were recorded on a Varian E-12 spectrometer with 10 kHz modulation.

The proton hyperfine splittings were directly observable in the spectra. Spectra with numerous lines or poor resolution were computer simulated to test the analysis.

RESULTS

The compounds studied and the proton hyperfine coupling constants for primary and secondary semiquinones are listed in Table 1. Also included are coupling constants for intermediate radicals, where they have been unambiguously assigned. We use the notation Q(*i*), SQ(*i*), and HQ(*i*), meaning quinone, semiquinone, and hydroquinone *i*, respectively. We shall further designate intermediate radicals by IRQ(*i*) if they arise from quinone *i*, and by IRH(*i*) if they arise from hydroquinone *i*.

p-*Benzosemiquinones*.—Starting from benzoquinone (I) in water, we have found a pH value of 11·0 or higher necessary for the formation of the semiquinone. The linewidth, measured to 300—350 mG immediately upon mixing, decreases to a value of about 100 mG after a few minutes. The rate of the narrowing process increases with increasing pH.

Below pH 11·8, the five-line spectrum of SQ(I) is the only one observed. At higher pH values an additional eight-line spectrum from a transient or intermediate radical IRQ(I) appears (Figure 1,B). Three coupling constants can be measured directly from this spectrum, and a small splitting of 45 mG can be detected under high resolution (see insert to Figure 1,B). Whether this splitting arises from a hyperfine coupling to a fourth proton or from the presence of isomers with slightly different *g*-values cannot be decided from the present results. The intermediate radical IRQ(I) is stable for several minutes. It is formed simultaneously with SQ(I) as observed if a solution of Q(I) in water is mixed in a flow apparatus with a strong alkaline solution and the e.s.r. spectrum is recorded under continuous flow. Figure 1,A shows the simultaneous production of SQ(I) and IRQ(I). Complete resolution of the spectrum of IRQ(I) is not possible when using the flow technique.

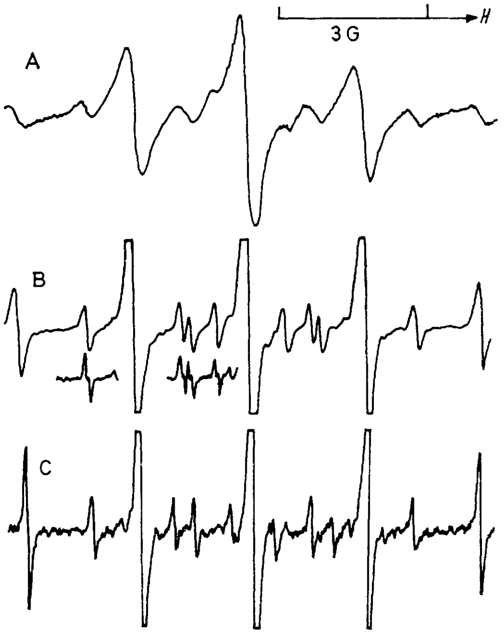

FIGURE 1 E.s.r. spectra of *para*-benzosemiquinone SQ(I) and of the intermediate radicals IRQ(I) and IRH(I). A and B, spectra of SQ(I) and IRQ)(I) with Q(I) as the parent compound. The spectra are recorded under continuous flow in A and under stationary conditions in B. Insert is part of the IRQ(I) spectrum under high resolution; C, spectra of SQ(I) and IRH(I) recorded under stationary conditions; ^{13}C satellites of SQ(I) are observed. HQ(I) is the parent compound

When the pH is raised to *ca.* 12·6, SQ(I) and IRQ(I) disappear during minutes, and a secondary spectrum with eight lines is then observed. This spectrum is identical to that obtained by oxidizing 1,2,4-trihydroxybenzene, HQ(II). We conclude that the secondary product is SQ(II).

Starting from hydroquinone HQ(I), we observe a number

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[6] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 4302.

TABLE 1

E.s.r. coupling constants/G of investigated semiquinones. Q(HQ) in the first column indicates the initial compound (quinone or hydroquinone). DMF indicates that the solvent contained 50% (v/v) of dimethylformamide. Coupling constants not definitely assigned are in parentheses. The numbering of the ring carbon atoms of the secondary product is such that the (methyl) substituents are in the same positions as in the primary compound. Methyl splitting constants are marked by an asterisk

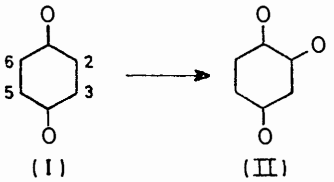
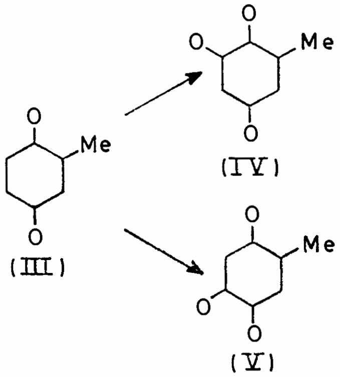
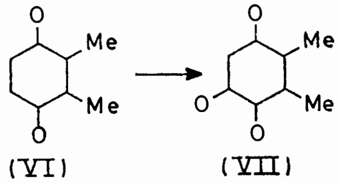
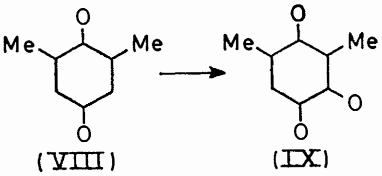
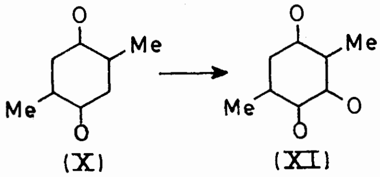
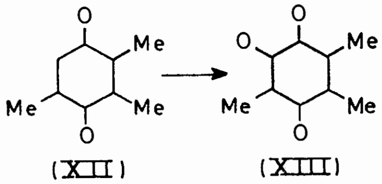
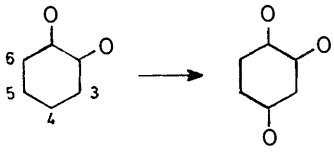
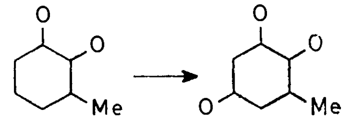
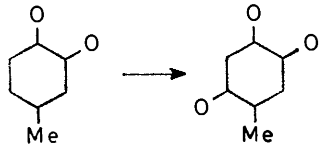
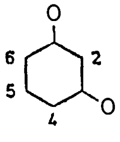
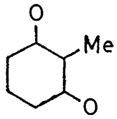
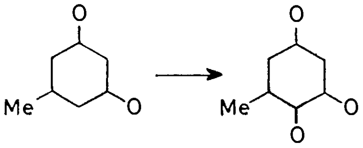
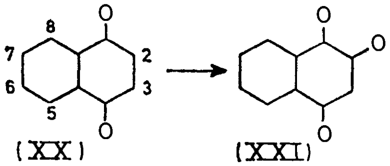
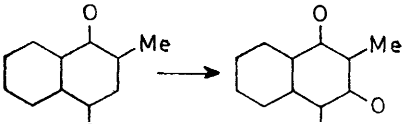
Exptl. condns.	Oxidation process (schematic)	Radicals observed	Position (*para*-compounds)			
			2	3	5	6
	Benzosemiquinones					
Q,HQ		SQ(I)	2·33	2·33	2·33	2·33
		IRQ(I)		2·60	1·91	2·09
		IRH(I)		2·85	1·66	2·08
		SQ(II) [a]		0·60	4·81	1·33
Q,HQ		SQ(IV) [a]	0·93 *	3·98	0·55	
		SQ(III) [b]	2·10 *	1·70	2·55	2·37
		SQ(V) [a]	4·91 *	0·66		0·58
Q,DMF		SQ(VI)	1·69 *	1·69 *	2·54	2·54
		SQ(VII)	4·60 *	0·62 *		0·47
Q,DMF		SQ(VIII)	2·12 *	1·87	1·87	2·12 *
		SQ(IX) [a]	0·93 *		0·76	5·08 *
HQ		SQ(X)	2·36 *	1·70	2·36 *	1·70
		SQ(XI) [a]	0·93 *		0·98 *	4·15
HQ		SQ(XII) [b]	2·33 *	1·91 *	1·76 *	1·94
		SQ(XIII) [a]	0·84 *	4·56 *	0·62 *	

TABLE 1 (*Continued*)

			Position (*ortho*-compounds)					
			3	4	5	6		
HQ	 (XIV) (II)	SQ(XIV)[c]	0·74	3·66	3·66	0·74		
		SQ(II)[a]	0·60		4·81	1·33		
HQ	 (XV) (IV)	SQ(XV)	0·63 *	(2·85)	(4·09)	0·28		
		SQ(IV)[a]	0·93 *	3·98		0·55		
HQ	 (XVI) (V)	SQ(XVI)[c]	0·10	4·80 *	3·85	0·95		
		IRH(XVI)	0·47	4·36 *		0·75		
		SQ(V)[a]	0·66	4·91 *		0·58		
			Position (*meta*-compounds)					
			2	4	5	6		
HQ	 (XVII)	SQ(XVII)[d]	0·63	11·30	2·40	11·30		
HQ	 (XVIII)	SQ(XVIII)	0·98 *	10·98	2·25	10·98		
HQ	 (XIX) (IV)	SQ(XIX)	0·75	11·20	2·37 *	11·20		
		SQ(IV)[a]	0·55		0·95 *	4·05		
	Naphthosemiquinones		Position					
			2	3	5	6	7	8
Q,HQ	 (XX) (XXI)	SQ(XX)[e]	3·11	3·11	0·55	0·63	0·63	0·55
		IRQ(XX)		2·35	(0·42)	(0·61)	(0·78)	(0·53)
		SQ(XXI)		0·25	(0·08)	(1·96)	(0·16)	(1·53)
Q	 (XXII) (XXIII)	SQ(XXII)[e]	3·01 *	2·34	0·66	0·59	0·73	0·66
		SQ(XXIII)	0·51 *		(0·12)	(1·97)	(0·12)	(1·54)

[a] See ref. 8. [b] B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, 1959, **30**, 1006. [c] J. Pilař, *J. Phys. Chem.*, 1970, **74**, 4029. [d] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 4302. [e] M. R. Das, H. D. Connor, D. S. Leniart, and J. H. Freed, *J. Amer. Chem. Soc.*, 1970, **92**, 2258.

of experimental features which differ from those observed when starting from Q(I). Thus, a pH of 11·7 or higher is a necessary condition for the formation of SQ(I), indicating that dissociation of both hydroxy-protons takes place before the oxidation HQ(I) $\longrightarrow$ SQ(I) (pK_1 = 9·85 and pK_2 = 11·4).[7] No initial line-broadening is observed for the semiquinone, and the eight-line spectrum of the intermediate radical IRH(I) differs from that of IRQ(I) (*cf.* Figures 1,B and 1,C). No splitting corresponding to the 45 mG splitting from IRQ(I) is observed for IRH(I). The amount of IRH(I) formed depends on the oxygen content in the solution. In a partly degassed solution, no trace of the intermediate radical is detected, whereas a solution saturated with oxygen gives an intense spectrum of IRH(I). As for Q(I), the secondary product SQ(II) is detected a few minutes after the pH is raised to *ca.* 12·6.

Toluquinone Q(III) and methylhydroquinone HQ(III) contain three non-equivalent protons accessible for oxidative attack. Three secondary products are thus expected. However, only two equally intense signals from two different radicals are detected in water at pH 13·3. These are identified as SQ(IV) and SQ(V) by comparing the measured coupling constants with those recently published by Lott *et al.*[8] for these radicals. No trace of 3-methyl-2-hydroxy-1,4-benzosemiquinone is observed.

For the three dimethyl *p*-benzoquinones (VI), (VIII), and (X) we have obtained completely resolved spectra for the primary radicals by using the circulation technique. Only one secondary hydroxylation product is formed from each of the compounds, as expected from their structures (see Table 1). By comparing the coupling constants of the products with the results by Lott *et al.* for the methyl substituted 1,2,4-trihydroxybenzenes,[8] the products, when starting from quinones (VI), (VIII), and (X), are identified as SQ(VII), SQ(IX), and SQ(XI), respectively. For the trimethylhydroquinone (XII) we have obtained the spectrum in Figure 2,A of the primary radical. The radical is unstable at the pH used (pH 13·0). The spectrum of the secondary radical is shown in Figure 2,B. Lott *et al.*[8] obtained an identical spectrum from a sample of HQ(XIII), from which we conclude that our product is SQ(XIII).

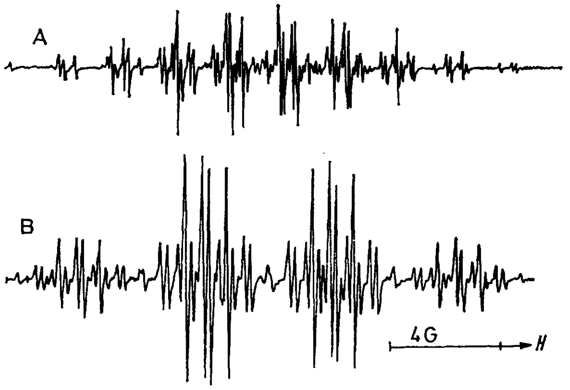


FIGURE 2 A, E.s.r. spectrum of the primary trimethyl-1,4-benzosemiquinone (XII); B, e.s.r. spectrum of the secondary radical 2-hydroxy-3,5,6-trimethyl-1,4-benzosemiquinone (XIII) recorded some time after the disappearance of A. Both spectra demonstrate the high resolution which has been obtained for nearly all primary and secondary spectra observed. A slight decay of the radical is observed in A

An unambiguous identification of intermediate radicals from methyl substituted benzoquinones was not possible because of the large number of overlapping lines from the primary radicals of these compounds.

o-*Benzosemiquinones*.—Using the circulation technique and water at pH 12, we obtained fairly stable radicals of catechol (XIV). In a stationary system with water at pH 13, a secondary radical is detected after *ca.* 10 min from mixing. It has an eight-line spectrum identical to the one obtained from *p*-benzoquinone (I) and it is, as expected, SQ(II).

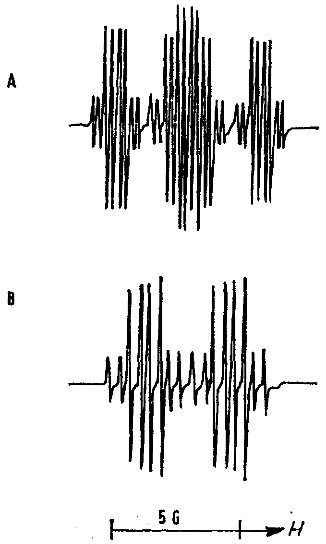


FIGURE 3 A, E.s.r. spectrum of 3-methyl-1,2-benzosemiquinone (XV); B, e.s.r. spectrum of the secondary product 2-hydroxy-6-methyl-1,4-benzosemiquinone (IV) obtained after circulating the solution for 15 min

In their study of alkyl substituted catechols, Stone and Waters [2] were unsuccessful in detecting a secondary product from 3-methylcatechol (XV). Their use of the flow technique further precluded observation of the small coupling constant at position 6 of the primary radical, which is expected to be less than 0·3 G. This radical SQ(XV) is completely stable in water at pH 13 when using the circulation technique. The well resolved spectrum is shown in Figure 3,A. It furnishes the smallest hyperfine coupling constant, α_6 = 0·28 G. A strong secondary spectrum is observed *ca.* 15 min after mixing, namely that of SQ(IV) shown in Figure 3,B.

For 4-methylcatechol (XVI) we have obtained results similar to those published by Stone and Waters.[2] A non-decaying spectrum of SQ(XVI) is obtained by use of the flow technique. One of the hyperfine splittings is masked by the line-broadening of 0·3 G. However, this splitting is resolved on stopping the flow, and a spectrum from an unstable intermediate radical IRH(XVI) is observed. The intermediate radical exhibits coupling to two protons and one methyl group. A similar pattern is observed in the spectrum of the secondary radical SQ(V). That they are in fact different species is apparent from the coupling constants (Table 1).

m-*Benzosemiquinones*.—The *m*-benzosemiquinones are unstable and could be detected only by the flow technique.

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[7] C. A. Bishop and L. K. J. Tong, *J. Amer. Chem. Soc.*, 1965, **87**, 501.

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

Starting from orcinol (XIX), a secondary spectrum is observed *ca.* 1 min after stopping the flow. This spectrum is identical to the secondary spectrum observed from 3-methylcatechol (XV), and the radical responsible is thus identified as SQ(IV) by the coupling constants. SQ(IV) is in fact the only possible product with a 2-hydroxy-1,4-semiquinone structure which can be obtained. No effort was made to obtain secondary products from the other two resorcinols studied.

1,4-*Naphthosemiquinones*.—To see whether extended ring-systems are oxidized in a manner analogous to that of simple benzoquinones, we have studied 1,4-naphthoquinone (XX) and 2-methyl-1,4-naphthoquinone (XXII).

The unsubstituted 1,4-naphthosemiquinone SQ(XX) gives in a 1 : 1 dimethylformamide–water solution the spectrum shown in Figure 4,A. The three expected coupling constants are easily measured, and the difference between the two smaller ones amounts to 80 mG. A spectrum of an intermediate radical IRQ(XX) is partly obscured by the spectrum of the primary radical SQ(XX) (Figure 4,A). The spectrum of IRQ(XX) consists of 26 lines of equal intensity and three lines with twice that intensity (*cf.* the simulation shown in Figures 4,B and 4,C). IRQ(XX) thus exhibits coupling to five non-equivalent protons with constants close to five of those of the parent radical SQ(XX) (Table 1).

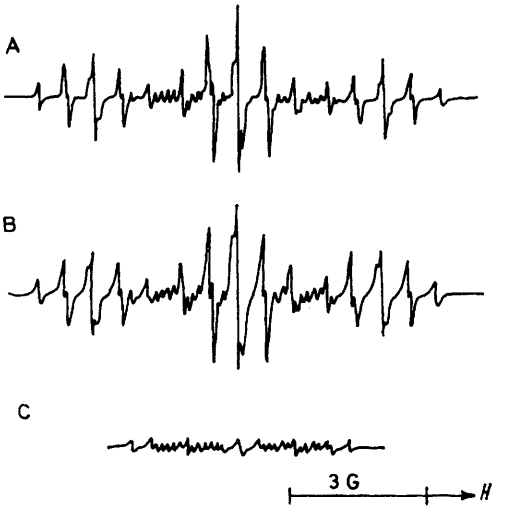

FIGURE 4 E.s.r. spectra of 1,4-naphthosemiquinone (XX) and the intermediate radical IRQ(XX); A, experimental spectra of both radicals superimposed, the spectrum of IRQ(XX) is partly obscured; B, spectra of both radicals simulated from data in Table 1, constant linewidth being assumed; C, simulated spectrum of IRQ(XX)

After increasing the pH value and circulating the solution we observe the spectrum of a secondary product. An identical spectrum is obtained starting from a sample of 2-hydroxy-1,4-naphthoquinone (XXI), which shows that the secondary radical is SQ(XXI).

Using the circulation technique we obtain a well resolved e.s.r. spectrum of the primary radical SQ(XXII) from 2-methyl-1,4-naphthoquinone (XXII). Of the six coupling constants expected, five are immediately obtainable from the spectrum. The sixth constant is equal to one of the others within the linewidth of 50 mG (Table 1).

Continued circulation of the solution leads to a secondary spectrum. This spectrum yields four coupling constants. A small 1 : 2 : 1 triplet of 0·12 G arises from two protons having the same coupling constants within the linewidth of 60 mG (Table 1). Hollocher *et al.*[9] obtained a spectrum identical to ours starting from a sample of 2-hydroxy-3-methyl-1,4-naphthoquinone (XXIII). We thus conclude that our secondary spectrum arises from SQ(XXIII).

Miscellaneous Quinones.—To see whether quinones which do not yield hydroxylation products are reduced to their corresponding semiquinones without the presence of a reductant, we have studied duroquinone (tetramethyl-1,4-benzoquinone), 2,5-dihydroxy-1,4-benzoquinone, 2,3-dimethyl-1,4-naphthoquinone, acenaphthenequinone, and anthraquinone. None of these yields semiquinone spectra within the time-scale of the measurement (*ca.* 30 min) unless a reducing agent such as sodium dithionite is added. This negative result for duroquinone is at variance with the observation by Fomin *et al.*[10] who detected an e.s.r. spectrum of the durosemiquinone in an alkaline water–ethanol solution. However, a subsequent investigation by Golubev *et al.*[11] showed that the radical formation of tetrasubstituted quinones occurs as a result of quinone reduction by organic substances present (*e.g.*, alcohol, dioxan, or acetone), that is, by a process quite different from that discussed here.

DISCUSSION

We adopt previously published assignments of the coupling constants for primary and secondary radicals as indicated in Table 1. For intermediate radicals, assignments are based on molecular orbital calculations described below. For a few radicals, no assignment was made.

It appears from Table 1 that methyl substituted quinones with free quinonoid positions are oxidized (hydroxylated) exclusively at the free position having the largest spin density in the primary semiquinone. Identical hydroxylation products are formed, whether the parent compound is a quinone or the corresponding hydroquinone. However, the hydroxylation process follows different pathways in the two cases.

Oxidation of Quinones.—We shall divide alkyl substituted quinones into two groups. The first group contains the quinones having at least one free quinonoid position. They become hydroxylated in alkaline aqueous solutions. The second group contains quinones with alkyl substituents occupying all quinonoid positions. These quinones do not become hydroxylated under similar alkaline conditions.

Two observations are essential for an understanding of the oxidation of the quinones. Hydroxide ions add to group 1 quinones forming hydroxyquinone adducts.[7,12] Moreover, we have shown that these quinones are reduced to their corresponding semiquinones immediately upon being dissolved in the alkaline solution. The presence of a reducing agent in the otherwise oxidative milieu is immaterial.

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[9] T. C. Hollocher, N. M. Tooney, and R. Adman, *Nature*, 1963, **197**, 74.

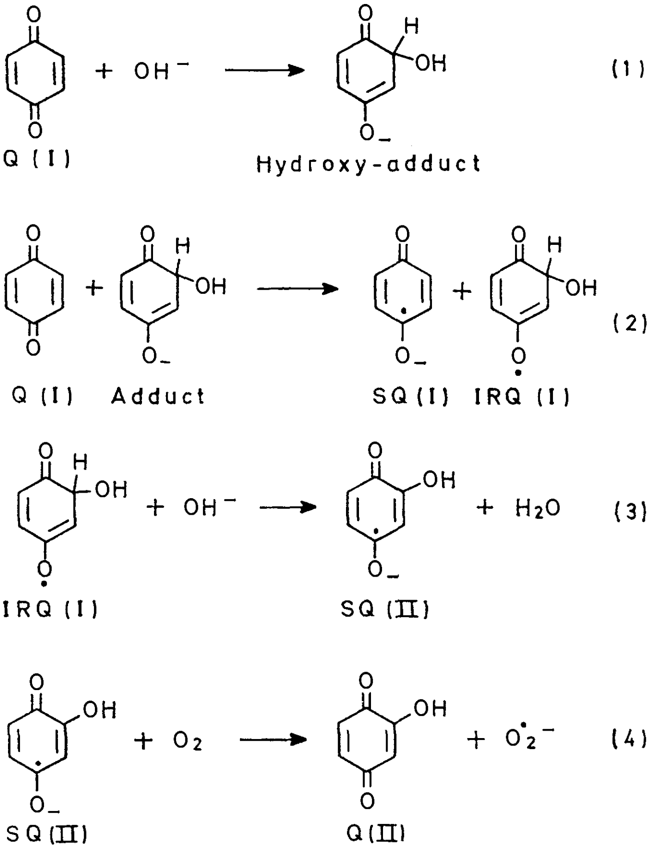
[10] G. V. Fomin, L. A. Blyumenfel'd, and B. I. Sukhorukov, *Doklady Akad. Nauk S.S.S.R.*, 1964, **157**, 1199.

[11] V. B. Golubev, L. S. Yaguzhinskii, and A. V. Volkov, *Biofizika*, 1966, **11**, 572.

[12] M. Eigen and P. Matthies, *Chem. Ber.*, 1961, **94**, 3309.

Group 2 quinones, on the other hand, do not undergo an initial reduction unless a reducing agent such as sodium dithionite is added. Baxendale and Hardy[13] did not observe adducts for duroquinone below pH 13·3, from which it may be inferred that quinones in group 2 do not form hydroxyquinone adducts as long as the pH is kept below 13·3.

These observations have led us to suggest the reaction Scheme 1 for group 1 quinones, here depicted for *p*-benzoquinone. The reaction starts with the formation of a hydroxyquinone adduct [step (1)]. This adduct acts as the reductant, and the reduction results in simultaneous formation of the semiquinone SQ(I) and the intermediate radical IRQ(I) [step (2) and Figure 1,A]. The line-broadening observed initially (Figure 1,A) may arise from complex formation between SQ(I) and IRQ(I). The secondary radical 2-hydroxy-1,4-benzosemiquinone SQ(II) is formed by subsequent proton abstraction [step (3)], and if the solution is circulated, the oxidation proceeds to 2-hydroxy-1,4-benzoquinone Q(II) [step (4)].



Scheme 1

Structure of the Intermediate Radical.—The key compound in the above discussion is the intermediate radical IRQ(I) [step (2)]. This radical is stable in alkaline solutions (Figure 1,B) and has the coupling constants 1·91, 2·09, and 2·60 G (Table 1), all close to the *p*-benzosemiquinone (I) constant of 2·33 G. This indicates that the radical is of the semiquinone type. We suggest that IRQ(I) is the radical of 2,4-dihydroxycyclohexa-3,5-dienone [step (2)].

In assigning the coupling constants of IRQ(I) we have made use of a Hückel molecular orbital (HMO) calculation including the McLachlan SCF modification.[14] The results are summarized in Table 2. We employed an inductive model with an inductive parameter δ_C^2 introduced in the usual way in the Coulomb integral for C-2. We found the spin densities ρ_3, ρ_5, and ρ_6 to be linear functions of δ_C^2, when the latter was taken in the range 0·0—0·2. 'Experimental' spin densities, calculated from the McConnell equation,[15] $\rho_i = a_i/Q$ with Q = 19·4 G, give a good correlation with the theoretical spin densities, if δ_C^2 is taken as 0·1 (Table 2).

TABLE 2

Spin densities for intermediate radicals

Radical	Position	Theory [a]	Experiment [d]
IRQ(I)	3	0·1317 [b]	0·1340
	5	0·0949	0·0984
	6	0·1085	0·1078
IRH(I)	3	0·1496 [c]	0·1470
	5	0·0873	0·0856
	6	0·1077	0·1072

[a] $\alpha_X = \alpha + h_X\beta$, $h_O = 2{\cdot}1$, h_C (posn. 2) $= \delta_C^2$, $h_C = 0$ otherwise. $\beta_{xy} = k_{xy}\beta$, $k_{12} = k_{23} = 0{\cdot}9$, $k_{CO} = 1{\cdot}85$, $k_{xy} = 1$ otherwise. McLachlan constant $\lambda = 1{\cdot}2$. [b] $\delta_C^2 = 0{\cdot}100$. [c] $\delta_C^2 = 0{\cdot}155$. [d] Experimental spin densities calculated from the McConnell equation $\rho_i = a_i$ (expt)/Q with Q = 19·4 G. This Q-value and the heteroparameters in *a* are similar in magnitude to those of ref. 8.

From this calculation, no information about the aliphatic proton coupling constant at C-2 can be gained. Our experiments show that a possible coupling constant is less than 50 mG. This finding is in contrast to the observation of large coupling constants of the methylene protons in hydroxycyclohexadienyl radicals.[16,17] The lack of a large coupling may be explained in terms of two opposing mechanisms. For an in-plane proton in a π-electron radical, the indirect coupling through the C–H bond gives rise to a spin polarization responsible for a negative spin density in the hydrogen 1*s* orbital.[18] Moving the proton out of the plane introduces an overlap between the 1*s* orbital of the hydrogen atom and the odd π-orbital, which results in a positive spin density in the 1*s* orbital. For some orientation of the proton, the two contributions cancel, resulting in a zero or near-zero spin density. Small negative and positive spin densities at methylene protons have in fact been observed experimentally by n.m.r.[19]

Oxidation of Hydroquinones.—We obtain the same hydroxylation product from a hydroquinone as from the corresponding quinone. The assumption has been

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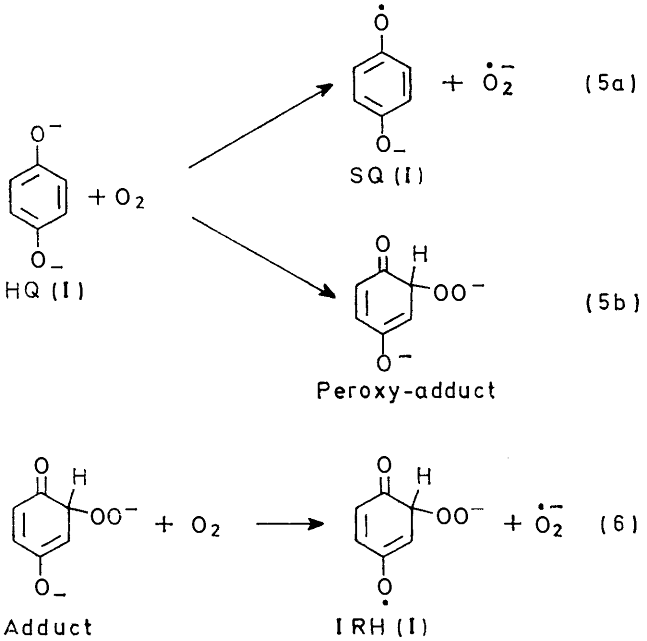
made[2,20] that the hydroquinone is first oxidized to its corresponding quinone and that the subsequent reactions are the same as when starting from the quinone. The following observations indicate that this does not hold. Since *meta*-quinones corresponding to resorcinols do not exist, the formation of the secondary radical SQ(IV) by oxidation of orcinol (XIX) necessarily follows a route different from that depicted in the steps (1)—(3). Further, when starting from hydroquinone (I), no line-width broadening in the spectrum of the primary radical is observed initially, as was the case for *para*-quinone (I), and the eight-line spectrum observed from the intermediate radical IRH(I) is clearly distinct from that of IRQ(I) (Table 1). In fact, both radicals IRH(I) and IRQ(I) have been observed simultaneously in an experiment starting with equal amounts of Q(I) and HQ(I). Finally, the amount of IRH(I) formed depends strongly on the oxygen content of the solution, and no splitting corresponding to the 45 mG splitting in the IRQ(I) spectrum has been observed.

We suggest that the main autoxidative reactions for hydroquinones are as shown in Scheme 2. Molecular oxygen either oxidizes the hydroquinone to the corresponding semiquinone [step (5a)] or adds to the hydroquinone to yield the quinol hydroperoxide (5b). The existence of such adducts in some t-butylresorcinols has been demonstrated by Musso *et al.*[21a,b] In our case the adduct is further oxidized to the radical IRH(I) [step (6)], which in turn yields the hydroxysemiquinone SQ(II).



Scheme 2

As for the radical IRQ(I), we have performed HMO calculations for the radical IRH(I), taking $\delta_O{}^2$ as the only parameter to be varied. We obtained an excellent correlation between experimental and theoretically determined spin densities by taking $\delta_O{}^2 = 0{\cdot}155$ and $Q = 19{\cdot}4$ G as before (Table 2). An attempt to extend the calculations to the intermediate radicals IRH(XVI) and IRQ(XX) by employing the same set of heteroparameters for the oxygen atoms was unsuccessful. This is not surprising since it has been shown that different sets of oxygen parameters are required for *para*-semiquinones and *ortho*-semiquinones.[22] However, the assignment of coupling constants for most intermediate radicals of the type discussed here is straightforward by use of the following observation. The hyperfine coupling constants of SQ(I) and of IRQ(I) [or IRH(I)] are very similar except that one constant is lost in the transition SQ(I) ⟶ IRQ(I). The assumption that the intermediate radical in general has a hyperfine constant pattern similar to the semiquinone pattern of its parent compound (one constant missing) leads to the assignment of the constant of IRH(XVI) shown in Table 1. Similarly, for IRQ(XX) the large constant of 2·35 G can be assigned to C-3, while no definite assignment of the remaining four constants can be made without further information.

Conclusion.—From the present e.s.r. study of the oxidation in alkaline solution of methyl substituted quinones and hydroquinones the following general features emerge. (i) A quinone having an unsubstituted quinonoid position is in general reduced spontaneously to its semiquinone whether or not a reductant is present. In contrast, reduction of anthraquinones, 2,3-disubstituted naphthoquinones, and tetrasubstituted benzoquinones, *i.e.*, of quinones lacking a free quinonoid position, requires a reducing agent. (ii) Hydroxylation products with a 2-hydroxy-1,4-quinonoid structure are obtained from hydroquinones having free quinonoid positions *via* an autoxidation and from their corresponding quinones through a nucleophilic substitution by hydroxide ions. (iii) For *p*-benzosemiquinones, hydroxy-substitution produces an increase (by a factor 2 or more) of the spin density at the *para*-carbon atom relative to the new substituent, whereas the spin densities at the *ortho*- and *meta*-positions are about halved. This feature is of great assistance in determining the structure of the secondary products. For *o*-benzosemiquinones, no similar change in the hyperfine pattern is introduced by the hydroxylation.

The above results do not necessarily apply to hydroquinones or their corresponding quinones having other than alkyl substituents. Thus 2,5-dihydroxy-1,4-benzoquinone, even though it has free quinonoid positions, is not reduced to its semiquinone unless a reductant is added. Likewise, the autoxidation of 4-carbonylcatechols has been demonstrated to yield products with a pyrogallol structure.[2]

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