

Secondary Radicals in the Autoxidation of Hydroquinones

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Summary Strongly alkaline solutions of hydroquinones, shaken in air, may give e.s.r. spectra corresponding to radicals other than the expected semiquinones; secondary or even tertiary stages of the autoxidation may thus be observed.

THE autoxidation of hydroquinones in alkaline solution is well known to be a radical process involving initial formation

of *p*-semiquinone radicals,¹ which are short-lived in aqueous solution, but can be kept for much longer periods in strongly alcoholic media. The relative stability of these 'primary' radicals in alcoholic solution² has, to a certain extent, precluded further investigation of what appears to be a complex autoxidation process.

The autoxidation of 4-methylcatechol in aqueous alkali has been found to give a secondary radical, in which an

additional oxygen is bonded to the aromatic ring.³ This extends our knowledge of the autoxidation process in that particular case, and now, using e.s.r. spectroscopy, we have found rather similar results for some substituted hydroquinones and *p*-quinones.

In contrast to the situation in ethanolic solutions, more than one type of radical may be observed in largely aqueous solutions of certain hydroquinones or *p*-quinones, depending on the conditions. For example, in 1% sodium hydroxide solution, simple *p*-semiquinone radicals are usually observed, but after a relatively short time, their e.s.r. spectra disappear. In more concentrated alkali (5–20% NaOH), totally different e.s.r. spectra are obtained (apart from cases where we might expect strong steric hindrance), corresponding to 'secondary' radicals. These arise from substitution of an aromatic hydrogen, probably by hydroxyl, to give radicals derived from the 1,2,4-trihydroxybenzene system.

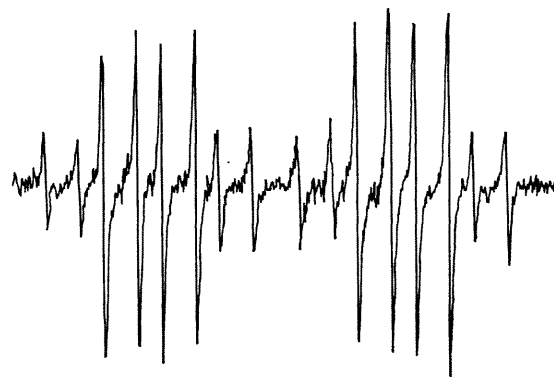


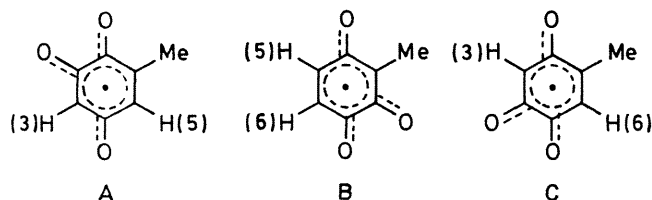
FIGURE. E.s.r. spectrum of secondary radical from methylhydroquinone.

Coupling constants in the e.s.r. spectra of the observed radicals

Hydroquinone or <i>p</i> -quinone	Proton	Primary (weak alkali)	Coupling Constants (Gauss)			
			Secondary (strong alkali)			
Unsubstituted	2	2.38 ^a				
	3	2.38				
	5	2.38				
	6	2.38				
2-Methyl-	2	2.12 ^b				
	3	1.75				
	5	2.54	0.55 (H)	0.95 (Me)	0.56 (H)	0.66 (H)
	6	2.45	4.15 (H)	0.55 (H)	5.18 (Me)	0.56 (H)
2,5-Dimethyl-	2	2.32 ^c				
	3	1.84	0.98 (Me)	0.88 (Me)		
	5	2.32	4.31 (H)			
	6	1.84	0.88 (Me)	0.98 (Me)		
2,6-Dimethyl-	2	2.15 ^c				
	3	1.98	0.97 (Me)			
	5	1.98	5.20 (Me)			
	6	2.15	0.72 (H)			
2,5-Di- <i>t</i> -butyl	2					
	3	2.09				
	5					
	6	2.09				

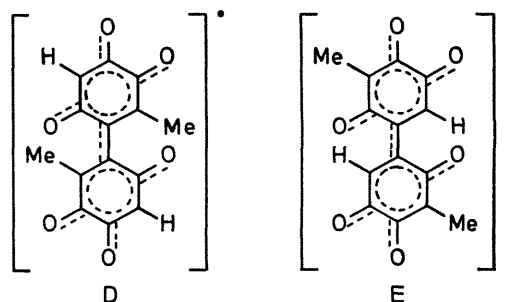
^a Aqueous solution. ^b 1:1 H₂O–EtOH. ^c 1:1 H₂O–DMF. ^d 3:1 H₂O–DMF.

One characteristic of the ensuing radical is that the coupling constants of methyl or aromatic protons *para* to an oxygen atom (*i.e.* on C-5), are much larger than in the original *p*-semiquinone radical (Table).



It is clear that competing reactions in these solutions are finely balanced, for changes of solvent have a marked effect on the ease of formation and lifetimes of the observed radicals and also, in one case, that of methylhydroquinone, at least two secondary radicals can be observed depending on the conditions (A–C).

(a) In cold sodium hydroxide (5–20%) radical A (or radical B, which would be expected to have similar coupling



constants) was observed (Figure); (b) in hot, strong alkali radical C, the same as that observed by Stone and Waters from 4-methylcatechol, was obtained; and (c) in mildly

alkaline aqueous DMF a spectrum corresponded to a mixture of both radicals was obtained.

In the case of methylhydroquinone a 'tertiary' radical was obtained in very strong, cold alkali (30% NaOH). The resulting spectrum appears to correspond to a biphenyl derivative, D or E, where there is conjugation between the two rings, the coupling constants being approximately half those in the secondary radical (A or B) from which it would be formed.

The formation of this dimer is apparently favoured by the high spin-density on the position *para* to an oxygen (*i.e.* on C-5), and the presence of a replaceable hydrogen at that position.

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² G. K. Fraenkel and B. Venkataraman, *J. Chem. Phys.*, 1959, **30**, 1006.

³ T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1965, 1488.