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THE ELECTRON SPIN RESONANCE SPECTRA OF RADICALS FORMED IN THE AUTOXIDATION OF PHENOLS

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Hexamethyl phosphoramide (HMPA) is much more stable towards base than other commonly available aprotic solvents which are also highly polar[1]. Its inert quality in this respect makes this solvent especially suitable for autoxidation studies which are generally catalysed by base, and a variety of intermediate radicals have been generated and observed by means of electron spin resonance spectroscopy[2,3].

These radicals often appear only after several steps, the first being the formation of a negative ion, the second, oxygenation by molecular oxygen[2], subsequent stages leading to products which can give radicals either by reduction or by direct interaction with O_2.

Hexamethyl phosphoramide is a particularly suitable solvent for studying semiquinones because the concentration of base can be kept low by using an alcohol salt, e.g. sodium methoxide, which is sparingly soluble, at the same time the concentration of acidic protons is also very low.

Direct autoxidation of α- and β-naphthol: In aqueous or in alcoholic solutions it is not generally possible to detect evidence of appreciable autoxidation of the naphthols or of their sodium salts over a period of an hour or so. In HMPA we obtain from both naphthols, strong e.s.r. signals due to 1,2-naphthosemiquinone, which, in the case of α-naphthol, decays after some minutes to leave weaker spectrum due to 1,4-naphthosemiquinone (see Table 1). The same spectra can be obtained directly from the corresponding naphthoquinones, or from the two corresponding dihydroxy naphthalenes. The coupling constants are rather different from those observed in aqueous solution[4,5].

Autoxidation of dihydroxy naphthalenes: In some cases the dihydroxynaphthalenes behave as simple extensions of the naphthols, for example 1,5-dihydroxynaphthalene gives rise to the same e.s.r. spectrum as juglone showing preferred oxidation in the 4-position, perhaps due to the extra stability provided by the peri-hydrogen[6] (see Table 1) or to extra stability of 1,4-semiquinones. Similarly oxygenation of the 4-position takes place with the 1,6- and 1,7-isomers. In the latter case, in which the two oxygen atoms are conjugated with respect to each other, a transient signal can be observed which decays in about 5 minutes and which we attribute to a primary radical. The coupling constant of 0.93 mT is the largest we have observed for an aromatic proton in a static system. A transient signal, ascribed to a primary radical, is also observed in the case of the 1,5-isomer in which the two oxygen atoms are similarly conjugated.

Table 1

E.S.R. parameters (a/mT) of radicals from autoxidation of naphthols in HMPA in the presence of NaOMe or $KOBu^t$

Position of oxygens (i) in radical	(ii) in precursor*	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
1,2-	1;2; 1,2-			0.038	0.405	0.075	0.152	0.038	0.115
1,2,4-	1,3-; 1,2,4-			0.035		0.060	0.245	0.060	0.155
1,2,3,4-	1,3-					0.095	0.122	0.122	0.095
1,2,6-†	1,6-; 2,6-			0.035	0.525	0.110		0.010	0.190
1,2,7-†	1,7-; 2,7-			0.048	0.460	0.0	0.268		0.085
1,4-	1; 1,4-		0.330	0.330		0.025	0.065	0.065	0.025
1,4,5-≠	1,5-; 1,4,5-		0.245	0.420			0.085	0.065	0.100
1,4,6-	1,6-; 1,7-		0.330	0.220		0.048		0.096	0.048
2,6-	2,6-	0.425		0.130	0.070	0.425		0.130	0.070
1,7-	1,7-		0.020	0.345	0.135	0.0	0.120		0.930
1,5-	1,5-		0.380	0.055	0.525		0.380	0.055	0.525

* Where a precursor is autoxidised to a mixture of 1,2- and 1,4-naphthosemiquinones the signal from the 1,4-semiquinone is seen after the decay of the spectrum of the 1,2-semiquinone.

† Obtained using $KOBu^t$/HMPA only: use of NaOMe gives sodium splittings, a_{Na}=0.040.

≠ a_H = 0.035 (peri-hydrogen)[4].

Weak, indistinct spectra are obtained from the 1,8- and 2,3-dihydroxynaphthalenes and the results from the other dihydroxynaphthalenes are given in Table 1.

A particularly interesting result is that obtained from 2,6-dihydroxynaphthalene which gives an intense spectrum to <u>amphi</u>-naphthosemiquinone. The corresponding quinone is destroyed in hydroxylic solvents.[7]

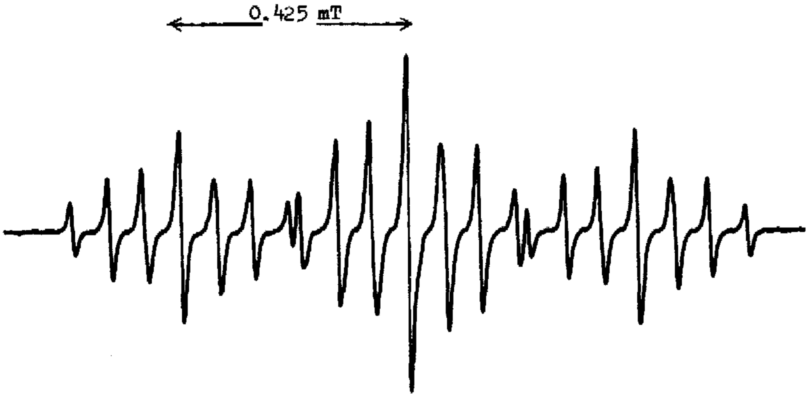


Figure: e.s.r. spectrum of 2,6-naphthosemiquinone

Direct autoxidation of phenol and resorcinol: The successful autoxidation of α- and of β-naphthols led us to investigate a corresponding possibility for phenol itself. As with the hydroxynaphthalene compounds a definite sequence of events occurs after shaking a mixture of phenol in HMPA with sodium methoxide or potassium *t*-butoxide in air, prior to transfer to the e.s.r. aqueous cell. First there is a broad e.s.r. absorption but later sharp-lined spectra of *o*- or of *p*-benzosemiquinone can be observed.

Table 2

E.s.r. parameters (a/mT) of semiquinones produced by autoxidation in HMPA in the presence of NaOMe or $KOBu^t$

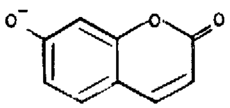
Radical		Coupling constants
1,2-benzosemiquinone	phenol, catechol, 1,2-benzoquinone	0.35 (x2) 0.11 (x2)
1,4-benzosemiquinone	phenol, hydroquinone, 1,4-benzoquinone, 1,3- and 1,4-dihydrobenzene	0.24 (x4)
2-hydroxy-1,4-benzosemiquinone	resorcinol, 1,2,4-trihydroxybenzene	0.055, 0.14, 0.49 (after addition of H_2O)
1,2-naphthosemiquinone	1- and 2-naphthol, 1,2-dihydroxynaphthalene, 1,4-naphthoquinone	0.038 (x2), 0.075, 0.405, 0.152, 0.115
1,4-naphthosemiquinone	1-naphthol, 1,4-dihydroxynaphthalene, 1,4-naphthoquinone	0.025 (x2), 0.065 (x2), 0.33 (x2)
9,10-anthrasemiquinone	9,10-anthraquinone, 9,10-dihydroxyanthracene, anthrone, 9,10-dihydroanthracene	0.10 (x4), 0.024 (x4)
pyrene-1,2-semiquinone	1,2-dihydropyrene	0.015 (x2), 0.086 (x2), 0.207 (x2), 0.330 (x2)

In the case of resorcinol a sharp lined spectrum is observed only after the HMPA solution is diluted with water, when the semiquinone from 1,2,4-trihydroxybenzene can be identified.

A number of dihydrobenzene derivatives can also be autoxidised using the HMPA/alkoxide combination and the derived semiquinones observed, showing the introduction of two oxygens into the ring systems (see Table 2).

Discussion: Where no primary radicals are observed, there is an induction period of up to an hour or even more. A characteristic of such cases is that the sudden rise in radical concentration after the induction period is accompanied by a fluorescence which roughly parallels the intensity of the e.s.r. spectrum, though it dies away somewhat before the signal decays. [Both the e.s.r. signal and the fluorescence can be regenerated by shaking with more oxygen]. None of the starting material, nor any of the products were fluorescent, and neither were the observed radicals, which could also be made directly from the corresponding quinones or dihydroxy compounds, (on which case there was no fluorescence). From these observations it appears that the fluorescence was probably due to some precursor of the radicals, especially since its colour was characteristic of the starting material, e.g. blue for α- or β-naphthol, red for 1,3-dihydroxynaphthalene.

A likely intermediate is the complex I, between the negative ion of the starting material and oxygen. This is not unreasonable, because molecules of the coumarin type II, are well known to be fluorescent and substitution of electron donor substituents leads to a shift to lower frequency[8]. Intermediates analogous to I have been postulated to account for the formation of semidiones[2] during the autoxidation of aliphatic ketones.



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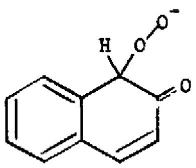

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