

827. *Aryloxy-radicals. Part III.*¹ *Electron Spin Resonance Spectra of Radicals from Some Substituted Resorcinols.*

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Short-lived radicals formed by the oxidation of resorcinols have been detected by means of electron spin resonance spectroscopy. The radicals produced by oxidation in alkaline solution are shown to be the *m*-benzosemiquinone radical-anions. Electron spin densities, calculated for a number of these radicals, indicate that *ca.* 82% of the spin density is associated with ring positions.

BENZOSEMIQUINONES produced by the oxidation of quinols have been well characterised by means of electron spin resonance (e.s.r.) spectroscopy;² those from catechols have been much less exhaustively studied, although the e.s.r. spectrum of *o*-benzosemiquinone is well

¹ Part II, *J.*, 1964, 408.

² Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworths, London, 1958.

known.³ However, the *m*-benzosemiquinones from resorcinol and its substituted compounds have not hitherto been detected. Although oxidation products of resorcinol and its alkyl-substituted compounds have been studied by means of e.s.r. by Adams *et al.*,³ who oxidised various resorcinols with air in an alkaline solution of water, acetone, ethanol, or mixtures thereof, they did not analyse their spectra for definite radical species, and it is clear from the data given that their spectra cannot easily be fitted with those expected from simple *m*-benzosemiquinones.

We have oxidised aqueous solutions of resorcinols both with an alkaline solution of potassium ferricyanide and with an acid solution of ceric sulphate, using the rapid-flow technique described in Part I.^{4*} The e.s.r. spectra of the radicals produced have been recorded and, in the case of radicals produced by alkaline oxidation, mathematical analysis clearly shows that they correspond to the *m*-benzosemiquinones (see Discussion section).

EXPERIMENTAL

The e.s.r. spectra were observed by using a Varian V4500 spectrometer. The flow system used was that previously described,⁴ in which the radicals are observed *ca.* 10^{-2} sec. after formation.

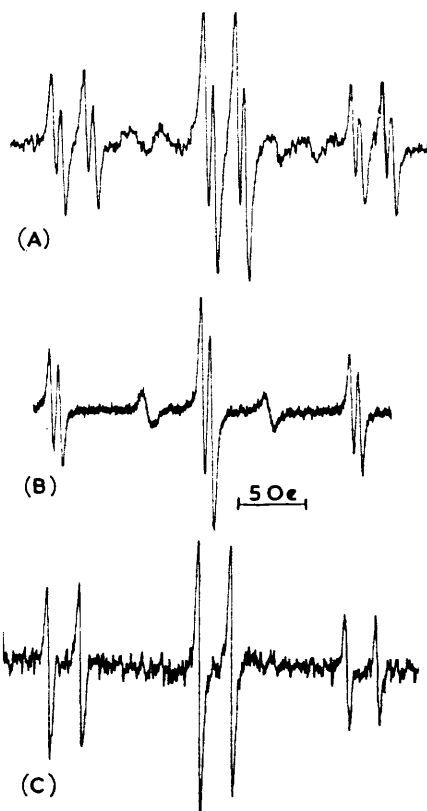


FIG. 1. E.s.r. spectra of radicals from the alkaline oxidation of (A) resorcinol, (B) resorcinol-5-carboxylic acid, and (C) resorcinol-2-carboxylic acid.

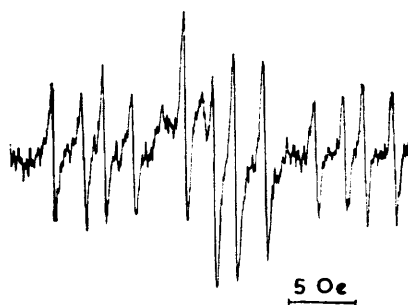


FIG. 2. E.s.r. spectrum of the radical from acid oxidation of resorcinol.

Both potassium ferricyanide ($10^{-2}M$) in $10^{-1}M$ -sodium hydroxide and ceric sulphate ($10^{-2}M$) in *m*-sulphuric acid were used as oxidants. The resorcinols ($10^{-2}M$) were dissolved in water or

* Corrigenda to Part I: ⁴

1. The equation on the last line of p. 217 should read: $a^H_o - a^H_m = 4.5 \pm 0.2$.

2. p. 218 line 12 should read: . . . α -CH groups coplanar with nuclear CH groups making a lesser contribution than CH groups at a large angle to it.

³ Adams, Blois, and Sands, *J. Chem. Phys.*, 1958, **28**, 774.

⁴ Stone and Waters, *J.*, 1964, 213.

in as low a concentration of alkali as was necessary to effect solution. The use of more-concentrated alkaline solutions increased the likelihood of spurious peaks appearing in the spectra, although, even with a very low concentration, these occasionally appeared (*e.g.*, the two spurious peaks in Fig. 1B). These are possibly due to the formation of secondary radicals produced from oxidation products.

The comments made previously,⁴ concerning the use of rather higher microwave power and modulation amplitudes in the production of the spectra, apply also to the present work.

The coupling constants are estimated to have a maximum error of 3%.

RESULTS

In general, the spectra obtained from the acid oxidation of the resorcinols tended to be less well-resolved than those from alkaline oxidation. In the former case, the spectra were also somewhat asymmetric about the base-line (*e.g.*, Fig. 2). The coupling constants obtained from the resorcinols by oxidation with alkaline ferricyanide and with acid ceric sulphate are given in Table 1.

TABLE I.
Oxidation of substituted resorcinols.

Substituted resorcinol	Method of oxidation *	Number of spectral lines	Coupling constants (Oe)			
			$a_{H(2)}$	$a_{H(4,6)}$	$a_{Alkyl(4)}$	$a_{H(5)}$
Resorcinol.....	A	$3 \times 2 \times 2$	0.7	11.2 ₅		2.4
	B	$3 \times 2 \times 2$	3.8	9.8		2.2 ₅
2-CO ₂ H	A	3×2		11.2 ₅		2.3 ₅
	B	3×2		10.6 ₅		2.5
4-CO ₂ H	A	$2 \times 2 \times 2$	0.7	11.0		2.3
	B	$2 \times 2 \times 2$	4.6	9.9 ₅		1.9
5-CO ₂ H	A	3×2	0.7	11.3		
	B	3×2	3.9 ₅	9.8 ₅		
2-Me	A	3×6	1.0 †	10.9 ₅		2.2
	B	20	5.3 †	8.9		1.8 ₅
5-Me	A	$3 \times 4 \times 2$	0.8	11.1 ₅		2.3 ₅ ‡
	B	16	4.0	9.5 ₅		2.0 ‡
4-Et	A	4×2	?	10.5 ₅	10.5 ₅	2.3
	B	$4 \times 2 \times 2$	3.2	10.0		2.0 ₅
4-CH ₂ ·Ph	A	$4 \times 2 \times 2$	0.7	10.4	10.4	2.3
	B	22	3.2	9.1 ₅	8.1 ₅	2.1
4-[CH ₂] ₅ ·CH ₃	A	4×2		10.0	10.0	2.3
	B	$4 \times 2 \times 2$	3.2	8.6	8.6	2.0
2-NO ₂	A	3×2		11.5		2.6
	B	$3 \times 2 \times 3$	0.5 §	10.7		2.6
4-Cl	A	$2 \times 5 \times 2$	0.7	9.8	2.0 ¶	2.0
	B	4	7.5	7.5		

* A, Alkaline oxidation; B, acid oxidation. † $a_{Alkyl(2)}$. ‡ $a_{Alkyl(5)}$. § Coupling constant for N. ¶ Coupling constant for Cl.

Interpretation of the Spectra.—Resorcinol. The spectra obtained from alkaline and acid oxidation are shown in Figs. 1A and 2, respectively. Both consist of a large triplet splitting, each line of which is split into a doublet of doublets. This indicates interaction of the unpaired electron with two equivalent protons and with a further two non-equivalent protons. In the case of alkaline oxidation with the presumed formation of the *m*-benzosemiquinone, the protons at positions 4 and 6 would be equivalent and would give rise to the triplet splitting. The remaining two doublet splittings would correspond to protons at positions 2 and 5. In order to assign these positions unambiguously without the use of deuterium substitution, we have blocked each unassigned position in turn with the carboxyl group. Although the introduction of this group causes small changes in the coupling constants for positions on the ring,⁴ it is unlikely that their relative magnitudes would be appreciably altered.

Resorcinol carboxylic acids. On alkaline oxidation of resorcinol-5-carboxylic acid, the spectrum shows a large triplet, each component of which is split into a doublet of 0.7 Oe (Fig. 1B). The 2-carboxylic acid, similarly, shows a large triplet, with a doublet splitting of 2.35 Oe [Fig. 1(C)]. The 4-carboxylic acid shows a large doublet with further doublet splittings of 2.3 and 0.7 Oe. These results indicate that the two doublet splittings of 2.4 and 0.7 Oe in the spectrum

from the alkaline oxidation of resorcinol can be assigned to the 5- and the 2-position, respectively. Similarly, in the acid oxidation of the 2- and 5-carboxylic acids, the spectra each consist of a triplet with doublet splitting, but in this case the larger of the two double splittings is assigned to the 2-position. The 4-carboxylic, on acid oxidation, shows a doublet further split into a doublet of doublets.

Alkylresorcinols. The spectra of 2- and 5-methylresorcinol both confirm the assignments made above. Alkaline oxidation of the 2-methyl compound gives a spectrum consisting of a triplet of doublets, each line being split further into 4 lines of coupling constant 1.0 Oe, corresponding to interaction with 3 methyl protons at the position giving the smallest proton coupling constant in the unsubstituted compound. Similarly, 5-methylresorcinol shows a splitting for the methyl protons of the same order as that of the proton assigned to position 5 in the unsubstituted compound. The 4-alkyl resorcinols fit into the suggested scheme, with the α -protons giving rise to large coupling constants.

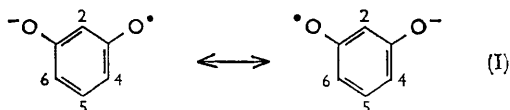
4-Chlororesorcinol. Alkaline oxidation gave rise to a spectrum with the expected splittings from the ring protons, but showing, in addition, further splitting which could only be interpreted on the basis of a 1 : 1 : 1 : 1 splitting of 2.0 Oe from the chlorine atom ($I = 3/2$). The only other recorded observation⁵ of chlorine splitting in an aromatic system is that of 0.24 Oe in the anion of *p*-chloronitrobenzene. The spectrum of the *p*-chlorophenoxy-radical, referred to in Part I,⁴ has now also been analysed, and shows a chlorine splitting of 1.6 Oe. Only a weak, badly resolved spectrum was obtained on acid oxidation of 4-chlororesorcinol.

2-Nitroresorcinol. The spectrum obtained on alkaline oxidation showed only a broad triplet of doublets, and no splitting due to the nitrogen atom could be detected; however, a small nitrogen splitting was observed on acid oxidation.

Phloroglucinol. Alkaline oxidation gave a 1 : 3 : 3 : 1 quartet spectrum, due to the three equivalent protons at positions 2, 4, and 6. A strong but unanalysable spectrum was obtained on acid oxidation.

DISCUSSION

The primary alkaline-oxidation products, by the loss of one electron, of the di-anions of quinols and catechols are the *p*- and *o*-benzosemiquinones, respectively. Similarly, it is to be expected that the primary oxidation product of the di-anion of resorcinol will be *m*-benzosemiquinone (I).



The e.s.r. spectrum of *m*-benzosemiquinone cannot be obtained in the manner used for the *o*- and *p*-benzosemiquinones, but can only be obtained by using a rapid-mixing technique. The spectrum clearly fits that expected from a species such as (I), with the protons at positions 4 and 6 being equivalent, and two non-equivalent protons at positions 2 and 5. The coupling constants of these latter protons have been unambiguously assigned by using the carboxylic acids, as described in the Results section. Spin densities at the carbon atoms of the benzene nucleus may be calculated by using equation (A), where $Q_{\text{CH}^{\text{H}}}$ has the value -23.7 Oe.⁶

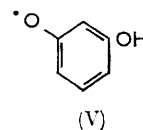
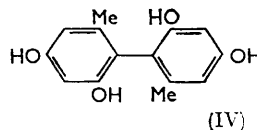
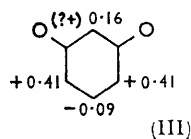
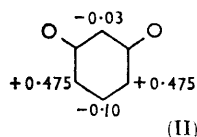
$$a_i^{\text{H}} = Q_{\text{CH}^{\text{H}}}\rho_i^{\pi} \quad (\text{A})$$

Ignoring, in the first instance, the signs of the coupling constants and of $Q_{\text{CH}^{\text{H}}}$, the following values for the spin densities in the *m*-benzosemiquinone radical are obtained: $\rho_4^{\pi} = \rho_6^{\pi} = 0.475$; $\rho_2^{\pi} = 0.03$; $\rho_5^{\pi} = 0.10$. It will be seen that even if there is no spin density associated with the oxygen atoms, the sum of the above spin densities is greater than unity. Clearly, either the spin density at position 5, or at both positions 5 and 2, must be negative.

⁵ Ayscough, Sargent, and Wilson, *J.*, 1963, 5418.

⁶ Chesnut, *J. Chem. Phys.*, 1958, **29**, 43; Fesenden and Schuler, *ibid.*, 1960, **33**, 936; Karplus and Frankel, *ibid.*, 1961, **35**, 1312.

If, as seems likely, the molecule can be described as a state which has a node through C-2 and C-5, simple theory will predict zero spin density at these positions. It is well known that negative spin densities are likely to occur when simple theory predicts zero spin densities.⁷ In this case, the spin-density distribution in *m*-benzosemiquinone is as shown in (II).



It can be seen that a very large proportion of the spin density is associated with C-4 and C-6, and only some 18% with both oxygen atoms and the carbon atoms to which they are attached. These values are quite different from those for *o*- and *p*-benzosemiquinones, which have *ca.* 65 and 60%, respectively, of the spin density associated with the two oxygen atoms.

The spin densities of the two methyl-substituted *m*-benzosemiquinones are shown in Table 2. The spin densities at the carbon atoms with the attached methyl groups have been calculated by using an equation analogous to equation (A) and taking $Q^{\text{H}_{\text{C-CH}_3}}$ as 27.2 Oe.⁶ Although the presence of a methyl group causes small changes in individual spin densities, the total spin density at the ring carbon atoms remains constant. Other substituents, such as carboxyl and nitro-groups, cause changes in individual coupling constants, but these are too small to warrant any quantitative discussion.

TABLE 2.
Spin densities for radicals from resorcinols.

Radical from	Method of oxidation *	Spin densities			
		ρ_2	ρ_4	ρ_5	$\rho_2 + 2\rho_4 + \rho_5$
Resorcinol	A	-0.03	0.475	-0.10	0.82
	B	-0.16	0.41	-0.095	0.565
2-Methylresorcinol	A	+0.16	0.41	-0.095	0.88
	B	-0.04	0.46	-0.09	0.79
5-Methylresorcinol	A	-0.195	0.375	-0.08	0.475
	B	+0.195	0.375	-0.08	0.87
	A	-0.035	0.47	-0.09	0.815
	B	-0.17	0.40	-0.075	0.555
	or	+0.17	0.40	-0.075	0.89

* Oxidation in: A, alkaline solution; B, acid solution.

Considering the very high spin density at the 4- and 6-positions, it is to be expected that further oxidation products of resorcinol and its mono-substituted compounds would occur by the dimerisation of the primary radicals at one of these two positions to form a biphenyl compound. The dimer (IV) has been obtained as a minor product from the oxidation of orcinol (5-methylresorcinol), although further coupling occurs to give a mixture of polymers.⁸

The form of the radical produced by the oxidation of resorcinol in acid solution is less obvious than that of the radical from the alkaline oxidation discussed above. The spectra from the acid oxidation indicate that the same number of interacting hydrogen nuclei are involved, and it is thus likely that these nuclei correspond to the four ring protons. Since the anion (I) would not exist in a strongly acid solution, we suggest that the spectrum of the protonated radical (V) is then observed. That no splitting from the hydroxyl proton is observed, could be due either to the coupling being less than *ca.* 0.3 Oe, which would

⁷ Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, 1962, ch. 6.

⁸ Musso, *Angew. Chem.*, 1963, **75**, 965.

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probably not be observed with the flow technique, or to rapid exchange of the proton with the solvent.

The prediction of the sign of the spin densities in a molecule such as (V) is more difficult, owing to the lack of symmetry. A radical of this structure is more comparable with a phenoxy-radical, and so the spin density at C-2 might be expected to be positive and that at C-5 negative, as these positions are *ortho* and *meta* to the phenoxy-oxygen, respectively.⁴ The values of the spin densities at the ring positions, calculated using both negative and positive spin densities for C-2, are shown in Table 2 [and also in (III) for the unsubstituted radical], and it can be seen that the total spin density at the ring positions is constant only if a positive spin density at C-2 is assumed.

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