935. *Electron Spin Resonance Studies of Oxidation. Part IV.*[1]
Some Benzenoid Compounds.

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The electron spin resonance spectra of the radicals formed by the inter-action of acidified solutions of titanous ion and hydrogen peroxide in the presence of a number of benzenoid compounds are described. Interpret-ation of the spectra shows that benzene and trimesic acid give adducts (sub-stituted cyclohexadienyl radicals) with the hydroxyl radical, while phenol, *p*-cresol, quinol, and toluene undergo abstraction of a hydrogen atom to give the corresponding phenoxy, semiquinone, and benzyl radicals. Conclusions are drawn from the values of the hyperfine splitting constants about the relative spin densities at the carbon atoms in these radicals, and the results are compared with calculated spin densities. An attempt to observe the phenyl radical by the one-electron reduction of the benzenediazonium cation gave a spectrum which is tentatively ascribed to the benzenediazonium radical.

WE have previously described and discussed the electron spin resonance spectra of free radicals derived from the reactions of aliphatic compounds with the hydroxyl radical. generated by the interaction of titanous ion and hydrogen peroxide in acid solution.[1-3] In the present Paper we first describe the spectra obtained in this way from a number of benzenoid compounds and then discuss the hyperfine splitting constants of these radicals with reference both to those of other aromatic radicals and to theoretical calculations of unpaired spin densities in some of these systems.

Descriptions and Assignments of the Spectra.—The spectrum from benzene, its ascrip-tion to the radical (I), and the assignments of the coupling constants have been reported in a preliminary Note.[4] Improvement in the resolving power of the spectrometer and its calibration by reference to ·CH$_2$OH in the flow system as secondary standard and to semiquinone in a static system as primary standard [2] have led to minor adjustments in the coupling constants, and the revised values are shown in (I). Assignments were based previously on comparisons of the spectrum from benzene with those of the phenoxy [5] and cyclohexadienyl [6] radicals, and further evidence for these has now been obtained by studying trimesic acid. This gave a spectrum consisting of a widely split doublet ($|a| = 24\cdot4$ gauss) each line of which was a triplet ($1:2:1$)($|a| = 2\cdot6$ gauss), and this can be unambiguously assigned to the radical (II). The similarity in the splitting due to the *meta*-protons in (II) and the smaller triplet in (I) reinforces the arguments on which our previous assignment was made.

Phenol and *p*-cresol gave spectra similar to those reported for the corresponding phenoxy radicals obtained by the oxidation of the phenols with ceric ion,[5] but with slightly different coupling constants [phenol: see (III) below; *p*-cresol: $|a_H|$ (methyl), $12\cdot3$; $|a_{o-H}|$, $6\cdot1$; $|a_{m-H}|$, $1\cdot4$ gauss]. Quinol gave the semiquinone radical ($|a_H|$, $2\cdot4$ gauss).

Toluene gave a complex spectrum which consisted of three sets of triplets ($1:2:1$) ($|a| = 16\cdot4$, $5\cdot1$, and $1\cdot6$ gauss) and one doublet ($|a| = 6\cdot3$ gauss). This is inconsistent with the radical's being an adduct of toluene and hydroxyl for there is no quartet splitting due to the methyl group, but the pattern of splittings is that expected for the benzyl radical, formed by abstraction of hydrogen from the side-chain. Further, the triplet splittings of $5\cdot1$ and $1\cdot6$ gauss and the doublet splitting of $6\cdot3$ gauss are related, respectively, to the corresponding splittings for the phenoxy radical (III) by factors which are the same within the experimental accuracy of the measurements ($\pm0\cdot3$ gauss). This is not

[1] Part III, preceding Paper.
[2] Dixon and Norman, *J.*, 1963, 3119.
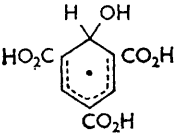[3] Dixon, Norman, and Buley, *J.*, 1964, 3625.
[4] Dixon and Norman, *Proc. Chem. Soc.*, 1963, 97.
[5] Stone and Waters, *Proc. Chem. Soc.*, 1962, 253.
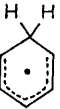[6] Fischer, *J. Chem. Phys.*, 1962, **37**, 1094.

surprising since the benzyl and phenoxy radicals are isoelectronic, and helps to justify the assignments given in (IV).

Coupling constants (gauss)

	(I)	(II)	(III)	(IV)
$a_{H \text{ (methylene)}}$	36·0	24·4	—	16·4
a_{o-H}	9·2	—	6·9	5·1
a_{m-H}	2·8	2·7	1·9	1·6
a_{p-H}	13·4	—	10·1	6·3

Two reactions employing one-electron reducing agents were carried out in an attempt to observe the spectrum of the phenyl radical. The interaction between aqueous benzene-diazonium sulphate and titanous ion in the flow system did not give rise to the spectrum of an organic radical, but when sodium dithionite was substituted for titanous ion there appeared five broad lines, of relative intensities approximately 1 : 2 : 3 : 2 : 1, together with a more intense line slightly displaced from the centre of the quintet. The pattern of the quintet corresponds to interaction of the unpaired electron with two nitrogen nuclei ($|a_{N1}| = |a_{N2}| = 9·3$ gauss), and the spectrum is assigned to the benzenediazonium radical,

Ph–N=Ṅ ◀━▶ Ph–N̈⁺=N̄. The broadening of the lines may have resulted from there being slight differences between the couplings of the two nitrogens and possibly also from the occurrence of weak, unresolved interactions with the aromatic protons.

Coupling Constants.—Certain inferences may be drawn from the values of the hyperfine splittings in the radicals (I)—(IV), together with corresponding data for the cyclohexa-dienyl radical (V). Of the two sets of splitting constants which have been published for (V), those of Fessenden and Schuler[7] were obtained from a more fully resolved spectrum.

Coupling constants (gauss)

	Fischer[6]	Fessenden and Schuler[7]
$a_{H \text{ (methylene)}}$	50	47·71
a_{o-H}	10·6	8·99
a_{m-H}	2·6	2·65
a_{p-H}	10·6	13·04

(a) The ratios $a_{o-H} : a_{m-H} : a_{p-H}$ are constant within the limits of accuracy of the experimental method for the phenoxy, benzyl, cyclohexadienyl (values from ref. 7), and hydroxy-cyclohexadienyl radicals. If the reasonable assumption is made that the same Q-value[8] is appropriate to the *ortho-*, *meta-*, and *para-*protons in each (*cf.* ref. 6), the relative values of the unpaired spin densities at the *ortho-*, *meta-*, and *para-*carbon atoms are the same. The systems may be treated as odd-alternant hydrocarbon radicals, so that the spin densities at the *ortho-* and *para-*carbon atoms should be positive and that at the *meta-*carbon should be negative.

(b) The aromatic-proton splittings in (I) and (V) are considerably larger than those in (III) which in turn are larger than those in (IV), so that if the same Q-value applies, the unpaired spin densities at the aromatic carbons decrease in the order (I) ~ (V) > (III) > (IV). Looked at from a simple viewpoint, it would appear that an exocyclic methylene group takes a greater fraction of unpaired electron density from the nucleus than does exocyclic oxygen and that a saturated group in the ring takes only a small fraction of the total spin density.

(c) The hyperfine splittings of the aromatic protons in (I) and (II) are the same within experimental error as those reported for (V) by Fessenden and Schuler,[7] and it is therefore

[7] Fessenden and Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.
[8] Symons in " Advances in Physical Organic Chemistry," Vol. 1, ed. V. Gold, Academic Press, 1963, p. 284.

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likely that the spin densities associated with the aliphatic groups in (I), (II), and (V) are also similar. In view of this it is interesting that there is so large a difference between the splittings due to each of the two methylene protons in (V) and the single aliphatic protons in (I) and (II).

A possible explanation for the difference between (V) and (I) can be suggested from a consideration of the mechanism of hyperconjugative coupling.[9,10] A methylene group is usually treated in terms of bonding between sp^3-hybridised carbon orbitals and the hydrogen 1s-orbital, but an alternative approach may be followed. This consists of setting up molecular orbitals using linear combinations of the hydrogen orbitals: one of these combinations, which has σ-symmetry, $\frac{1}{\sqrt{2}} [H(1s)_1 + H(1s)_2]$, forms a three-centre bond with an appropriately hybridised orbital of carbon (sp), and the other, which has π-symmetry, $\frac{1}{\sqrt{2}} [H(1s)_1 - H(1s)_2]$, may be combined with the $2p_z$-orbital of carbon. It is the latter orbital which can lead to an extension of the π-electron system when the methylene group is attached to an unsaturated centre, and this type of interaction is evidently important in cyclohexadienyl, as judged by the magnitude of the hyperfine splitting. When one hydrogen atom is replaced by hydroxyl in this radical, orbitals with approximately σ- and π-symmetry may be constructed from the hydrogen (1s) orbital and the appropriately hybridised orbital of the oxygen in the hydroxyl group (Figure): these are,
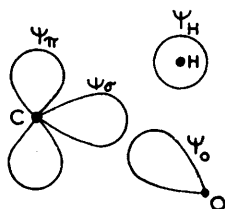
Orbital scheme for the >CH(OH) group of the radical (I). $\psi_H = H(1s)$; $\psi_0 =$ approximate tetrahedral hybrid of the oxygen atomic orbitals; $\psi_\sigma =$ appropriate hybrid orbital of carbon (sp); $\psi_\pi = C(2p_z)$.

respectively, $(1 + \lambda^2)^{-\frac{1}{2}}[H(1s) + \lambda\psi_{OH}]$ and $(1 + \lambda^{-2})^{-\frac{1}{2}}[H(1s) - \lambda^{-1}\psi_{OH}]$. For a particular value of λ, the first of these will result in zero overlap with the $2p_z$-orbital of the adjacent carbon, while the second can lead to overlap and hence delocalisation of the unpaired electron. For the same electron density in the group orbitals in (I) and (V), the spin density on the proton in (I) will differ from that on the methylene protons in (V) because λ will differ from unity, and this could account for the observed difference in the hyperfine splittings.

The difference between the splitting constants for the aliphatic protons in (I) and (II) may arise from steric interactions in (II) between the *ortho*-carboxyl groups and the substituents on the aliphatic carbon. If the hydroxyl group were thereby forced downwards from the plane of the aromatic system the methylene proton would adopt a position nearer to the molecular plane in which it is less favourably cited for hyperconjugative interaction.[3]

Comparison of Coupling Constants with Calculated Spin Densities.—The spin-density distribution of the benzyl radical has been evaluated by a number of methods,* as follows:

	Calculated spin densities				
Method	Methylene carbon	C_1	o-C	m-C	p-C
Simple Hückel M.O.	0·571	0	0·143	0	0·143
Self-consistent M.O.[11]	0·770	−0·102	0·161	−0·063	0·137
M.O. with five excited-orbital configurations[12]	0·634	−0·121	0·200	−0·072	0·231

* A valence-bond treatment [13] used an incorrect wave function [14] and is therefore excluded.

[9] Coulson and Crawford, *J.*, 1953, 2052.
[10] Chesnut, *J. Chem. Phys.*, 1958, **29**, 43.
[11] McLachlan, *Mol. Phys.*, 1960, **3**, 233.
[12] Atherton, Land, and Porter, *Trans. Faraday Soc.*, 1963, **59**, 818.
[13] Dearman and McConnell, *J. Chem. Phys.*, 1960, **33**, 1877.
[14] Pullman, *Discuss. Faraday Soc.*, 1947, **2**, 26.

The hyperfine splitting observed for the *meta*-protons in this radical points to the inadequacy of the simple Hückel theory. Insofar as experiment indicates that there is a higher spin density at the *para*- than at the *ortho*-carbon, the M.O. treatment which includes five excited-orbital configurations gives a more satisfactory fit then the self-consistent M.O. method, and indeed the ratios of the splitting constants of the *ortho*-, *meta*-, and *para*-protons, neglecting signs (1 : 0·3 : 1·2) are approximately equal to the ratios of the spin densities at the corresponding carbon atoms calculated by the excited-orbital method (1 : 0·36 : 1·15).

The spin densities in the phenoxy-radical, calculated by a molecular-orbital treatment which included configurational interaction and with the parameters $\alpha_O = \alpha_C + 2\beta_{CC}$, $\beta_{CO} = \beta_{CC}$, are shown in (VI).[12] Agreement with experiment is much less satisfactory in this case.

(VI)
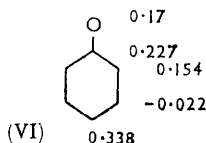
EXPERIMENTAL

The flow system and the procedure for the generation and observation of the radicals have been described.[2] Because of the low solubilities of benzene and toluene in water, the amplitudes of the spectra from these compounds were initially very small. This difficulty was satisfactorily overcome by using warm solutions and, in the case of toluene, by adding pyridine as co-solvent (1 : 1) to the reactant solution containing titanous ion. Very high microwave powers were necessary for these compounds, but despite this there was no indication of saturation, possibly because of the short life-times of the radicals.

In the attempt to observe the phenyl radical, the reactant solutions contained, respectively, sodium dithionite (5 g.) in water (2 l.) and diazotised aniline prepared from aniline (20 ml.), concentrated sulphuric acid (60 ml.), and sodium nitrite (17·5 g.) in water (2 l.).