35. *Aryloxy-radicals. Part I. Electron Spin Resonance Spectra of Radicals from Some Substituted Monohydric Phenols.*

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A flow method has been used to obtain the electron spin resonance spectra of many aryloxy-radicals of very short life. It has been possible to analyse the hyperfine structures of most of these radicals and to evaluate coupling constants (which are listed) with hydrogen atoms present as aromatic ring substituents, in α-C–H groups of side-chains, or in attached methoxy-groups. Implications of these quantitative measurements are indicated.

FREE aryloxy-radicals are produced by the oxidation of phenols by one-electron-abstracting reagents. In 1958 Müller and his colleagues [1] described for the first time the electron spin resonance (e.s.r.) spectra of 2,4,6-trisubstituted phenoxy-radicals, which, when they contain bulky substituents having no α-hydrogen (*e.g.*, Me_3C), are entities of long free life. To obtain these radicals, solutions of the phenols were oxidised under nitrogen with alkaline ferricyanide or by a suspension of lead dioxide in benzene. Scott and his colleagues [2] have examined a number of less stable aryloxy-radicals by using a freezing technique but found that only secondary radicals were detected from phenols which contained less than two bulky *ortho*- or *para*-substituents. Another technique, due to Pannell,[3] involves the oxidation of phenols by t-butoxy-radicals formed within the e.s.r. apparatus by ultraviolet irradiation of cooled solutions containing t-butyl peroxide. This method too does not obviate secondary oxidations, which has been one of the main objectives of the present work.

As we have already indicated in outline,[4] free aryloxy-radicals can be examined, under steady-state conditions, within 10^{-2} sec. of their moment of formation by mixing flowing solutions of a phenol and an appropriate oxidant just before they enter the cavity of an e.s.r. spectrometer. In this way, free radicals with half-lives in the range 10^{-2}—10^{-5} sec. can be examined in sufficient detail for the analysis of the hyperfine line structure of their e.s.r. spectra and yet are removed too rapidly for the occurrence of secondary reactions. The typical spectra, illustrated by Figs. 1—6, show the resolution of the spectra of aromatic molecules which can thus be attained; as Tables 1 and 2 indicate, the limit of resolution is about 0·4 Oe, a figure mainly determined by the sensitivity of our Varian spectrometer.

EXPERIMENTAL

The e.s.r. spectra were observed by using a Varian V4500 spectrometer with a 6 in. magnet and 100 kc./sec. field modulation. The flow apparatus consisted of two 1-l. reservoirs leading to a mixing chamber, of the design described by Dixon and Norman,[5] which was inserted into a Varian V4548 aqueous-solution sample-cell. The dead volume between the mixing point of the reactants and the flat portion of the sample cell was *ca.* 50 $mm.^3$ and the maximum flow rate used was 5 ml./sec. Thus the radicals were observed, under regenerative conditions, *ca.* 10^{-2} sec. after formation.

Ceric sulphate (10^{-2}—10^{-3}M) in M-sulphuric acid was used as the oxidant; the phenol was dissolved in water, aqueous acetone, or aqueous sodium hydroxide. With sparingly soluble phenols, aqueous acetone was unsuitable since it is also a poor solvent for ceric sulphate; in most cases the best spectra were obtained by mixing alkaline aqueous solutions of the phenols (10^{-2}—10^{-3}M) with the oxidant in an excess of acid, but care had to be taken to maintain sufficient flow rates to ensure that any deposition of insoluble products took place well beyond the spectrometer cell.

[1] Müller, Ley, Scheffler, and Meyer, *Chem. Ber.*, 1958, **91**, 2682.
[2] Becconsall, Scott, and Clough, *Proc. Chem. Soc.*, 1959, 308; *Trans. Faraday Soc.*, 1960, **56**, 459.
[3] Pannell, *Chem. and Ind.*, 1962, 1797.
[4] Stone and Waters, *Proc. Chem. Soc.*, 1962, 253.
[5] Dixon and Norman, *J.*, 1963, 3119.

The most favourable conditions for observing e.s.r. spectra, *i.e.*, low microwave power, small modulation amplitude, and long sweep time, are difficult to attain in conjunction with the flow technique. Although the initial concentrations of the reagents might be *ca.* 10^{-2}M it was evident that the mean concentration of free radicals under observation was smaller by many powers of ten, and so relatively high microwave power and modulation amplitudes had to be used for the production of measurable spectra. As a result there are in some cases evident modulation broadening and asymmetry with respect to the horizontal base line of the spectra. Again the signal-to-noise ratio is somewhat lower than is usual with spectra obtained from stable radicals. For the recording of a complete spectrum of an aryloxy-radical during the consumption of 1 l. of each reagent the sweep rate normally used was 8 Oe./min. This magnetic field sweep was calibrated by using the radical potassium nitrosylsulphonate and was cross-checked with solutions of either *p*-benzosemiquinone or the positive ion of perylene. The splitting constants are estimated to have a maximum error of 3%.

Results and Analysis of Spectra.—The phenols listed in Table 1 gave mainly well-defined spectra from which the coupling constants associated with both nuclear and side-chain α-hydrogen atoms could be computed. In some cases these coupling constants differ slightly from those given in our preliminary communication,[4] mainly because an increase in sensitivity has now been attained with the Varian instrument.

TABLE 1.

Coupling constants of substituted phenoxy-radicals.

Substituent			Coupling constants (Oe) *				
2	4	6	$a_{H(2.6)}$	$a_{Alkyl(2.6)}$	$a_{H(4)}$	$a_{Alkyl(4)}$	$a_{H(3.5)}$
H	H	H	6·65		10·1		1·8
H	Me	H	6·0			11·95	1·45
H	Et	H	6·0			10·15	1·5
H	Pr^n	H	6·1			8·7	1·45
H	CH$_2$Ph	H	6·1			8·7	1·45
H	Pr^i	H	6·0			6·0	$\leqslant$1·4 †
H	Bu^s	H	6·0			4·3	$\leqslant$1·4 †
H	Bu^t	H	6·0			—	$\leqslant$1·4 †
H	CO$_2$H	H	6·8				2·2
H	CO$_2$Et	H	6·8				2·3
H	COMe	H	7·0				2·3
H	CHO	H	6·8				2·2
H	SO$_3$Na	H	6·8				2·2
H	NO$_2$	H	7·0			2·35 ‡	2·35
H	F	H	6·5			27·4 §	1·6
F	H	H	6·05	17·0 §	10·1		2·1/1·5
Me	H	Me		6·5	9·5		1·65
Et	H	Et		5·7	9·35		1·65
Pr^i	H	Pr^i		3·7	9·5		1·8
Bu^t	H	Bu^t		—	9·6 ¶		2·0 ¶
Me	Me	Me		6·0		11·95	1·4
Me	Et	Me		6·0		9·1	1·45
Me	Pr^n	Me		6·0		8·3	1·35
Me	CH$_2$Ph	Me		6·0		8·5	1·35
Me	Bu^t	Me		6·1 **		—	1·8 **
Me	CO$_2$H	Me		6·8			2·2
Me	COPh	Me		7·0			2·2
H	H	CO$_2$H	7·5		10·8		2·2/1·3
3-CO$_2$H			7·5/6·65		10·15		2·0

* Absolute coupling constants given; *meta* coupling constants are probably positive, *ortho* and *para* negative. † Values not accurately known, see text. ‡ Coupling constant for N. § Coupling constant for fluorine. ¶ Taken from ref. 3 for comparison. ** Taken from ref. 2 for comparison.

The spectra of the radicals from *p*-isopropyl-, *p*-s-butyl, and *p*-t-butyl-phenol were incompletely resolved and only the coupling constants from the *ortho*- and *para*-hydrogen atoms could be measured with certainty; with radicals having substituents such as CHO, COMe, CO$_2$H, or CO$_2$Et no splitting was observed from the hydrogen atoms contained in these groups. Some such hyperfine splittings have been observed by others[6] but are usually so small that they would not have been detected under our conditions.

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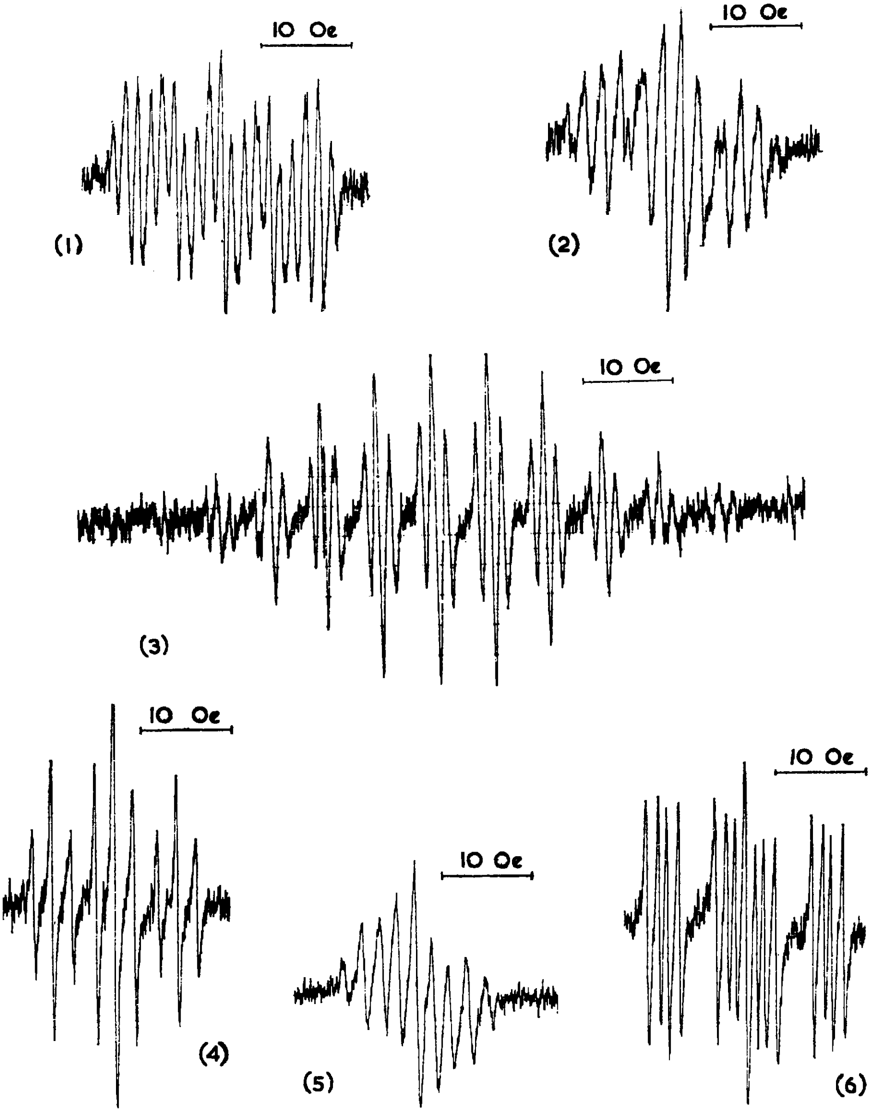
[6] Maki and Geske, *J. Amer. Chem. Soc.*, 1961, **83**, 1852.

Amongst compounds related to those listed in Table 1, biphenyl-4-ol gave a radical exhibiting only a broad singlet. This is analogous to the spectrum from the aryloxy-radical of 2,6-di-*t*-butylbiphenyl-4-ol in which no fine structure could be observed.[7] The alkylphenoxy-radicals for which we report spectral analysis all have a plane of symmetry. Whilst mono-*o*-alkylphenols and α- and β-naphthols have also been oxidised and give radicals with e.s.r. spectra (for β-naphthol, see Fig. 1) showing a considerable amount of hyperfine structure, it has not been possible for us to analyse these mathematically.



FIGS. 1—6. E.s.r. spectra of radicals from (1) β-naphthol, (2) *p*-chlorophenol, (3) 2,4,6-trimethylphenol, (4) *p*-hydroxybenzoic acid, (5) 4-methoxy-3-t-butylphenol, and (6) *o*-hydroxybenzoic acid.

For the *p*-nitrophenoxy-radical the coupling constant of the nitrogen atom was measured; for *o*- and *p*-fluorophenoxy-radicals, coupling with the fluorine nucleus dominated the appearance of the e.s.r. spectrum. The spectrum from the oxidation of *p*-chlorophenol (Fig. 2)

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[7] Müller, Schick, and Scheffer, *Chem. Ber.*, 1958, **91**, 2670.

shows 12 major lines; if splitting due to chlorine, which has a low nuclear moment, is not significant, then the *p*-chlorophenoxy-radical should show only a 9-line spectrum (a triplet of triplets), whilst even if there were significant splitting due to chlorine it should give an intensity pattern different from that observed. Similarly the spectrum from the oxidation of 2,6-dichloro-4-nitrophenol has more lines than anticipated. Perhaps these oxidations do not follow a simple course.

The coupling constant of the fluorine nucleus in either the *ortho*- or the *para*-position is 2·6—2·7 times that of the coupling with a proton. This is larger than that found either by Maki and Geske[6] for the radical-ion of *p*-fluoronitrobenzene, or by Rieger and Fraenkel[8] for the anion from 4-fluoroacetophenone.

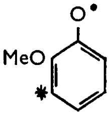
Table 2 lists the coupling constants of alkoxyphenoxy-radicals. The corresponding spectra (*e.g.*, Fig. 5) have rather broader lines than those given by the alkylated phenols. Hyperfine coupling with the hydrogen atoms of the methoxy-group has been detected, the coupling constant for *p*-OCH_3 being 2·0 ± 0·1 Oe. With these *p*-alkyloxyphenols the coupling constants for nuclear hydrogen atoms in *ortho*- or *para*-positions are both about 20% less than those for the unsubstituted phenoxy-radical and in many cases coupling with *meta*-hydrogen can scarcely be detected. With *o*-alkoxyphenols discrimination between positions 3 and 5 can be made, but coupling with only one of these positions is detectable. This appears to be that marked * which is adjacent to the alkoxy-group since the radicals from both guaiacol (I) and isovanillin (II) show splitting due to the same number of *meta*-hydrogen atoms, though with the acid (III) splitting due to hydrogen in both positions 3 and 5 is observed.

TABLE 2.

Coupling constants of alkoxyphenoxy radicals.

Substituent					Coupling constants (Oe)							
2	3	4	5	6	$a_{H(2)}$	$a_{H(6)}$	$a_{CH_3(2)}$	$a_{CH_3(6)}$	$a_{H(3)}$	$a_{H(5)}$	$a_{H(4)}$	$a_{CH_3(4)}$
H	H	OMe	H	H	5·0	5·0			?	?		2·0
H	Bu^t	OMe	H	H	3·9 *	5·8 *			?	?		2·1
Bu^t	H	OMe	H	H	—	5·4			0·6 †	?		1·9
Bu^t	H	OMe	Bu^t	H	—	4·0			?	—		2·0
H	H	O·CH_2Ph	H	H	4·9	4·9			?	?		2·1
Me	H	OMe	H	Me			4·7	4·7	?	?		2·0
H	H	OPh	H	H	5·2	5·2			0·5	0·5		— ·
OMe	H	H	H	H		4·2	1·8		1·8 †	?	8·3	
OMe	H	CHO	H	H		4·3	2·2		2·2 †	?	—	
OMe	H	H	CHO	H		5·4	1·8		1·8		7·8	
OMe	H	H	H	OMe			1·5	1·5	1·5	1·5	8·3	
OMe	H	CO_2H	H	OMe			1·65	1·65	1·65	1·65	—	

*† Coupling constant not conclusively assigned between two * *ortho*- and † *meta*-positions.



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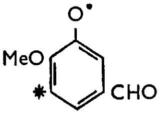

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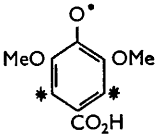
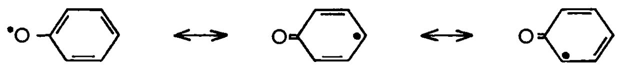


(III)

DISCUSSION

Aryloxy-radicals are mesomeric systems (IV) in which, from the magnitudes of the e.s.r. coupling constants, as well as from knowledge of chemical reactivity, it is evident that the unpaired electron must be largely associated with the π-electron system of the aromatic ring. Now, for protons directly bonded to the carbon atoms of the benzene



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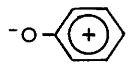

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[8] Rieger and Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2811.

nucleus[9] one may write equation (A), where $a_{\mathrm{i}}^{\mathrm{H}}$ is the proton coupling constant, in Oersteds, for the proton at position i, and ρ_{i}^{π} is the electron spin density at the carbon

$$a_{\mathrm{i}}^{\mathrm{H}} = Q_{\mathrm{CH}}^{\mathrm{H}}\rho_{\mathrm{i}}^{\pi} \quad (\mathrm{A}); \qquad a_{\mathrm{CH_3}}^{\mathrm{H}} = Q_{\mathrm{CCH_3}}^{\mathrm{H}}\rho^{\pi} \quad (\mathrm{B})$$

atom i; equation (B) holds for directly attached methyl groups, $a_{\mathrm{CH_3}}^{\mathrm{H}}$ being the coupling constant with the methyl-hydrogen atoms and ρ^{π} the electron spin density at the corresponding aromatic carbon centre. On theoretical grounds the factors $Q_{\mathrm{CH}}^{\mathrm{H}}$ and $Q_{\mathrm{CCH_3}}^{\mathrm{H}}$ have been assigned values of —23·7 and 27·2 Oe, respectively.[10] Using these values we can derive from the figures in Table 1 the spin densities at *ortho-*, *meta-*, and *para*-positions to the oxygen atom of aryloxy-radicals, as illustrated in Table 3.

TABLE 3.

Spin densities for aryloxy-radicals.

Radical from	Spin densities			
	ρ_o	ρ_m	ρ_p	$\rho_p + 2(\rho_o + \rho_m)$
Phenol	0·28	−0·075	0·42	0·83
p-Cresol	0·25	−0·06	0·44	0·82
2,6-Dimethylphenol	0·24	−0·07	0·40	0·74
2,4,6-Trimethylphenol	0·22	−0·06	0·44	0·76

The spin densities in Table 3 differ considerably from those which have been calculated from theoretical models of radicals. The simplest of these, due to Symons,[11] supposes that the phenoxy-radical can be regarded as a derivative (V) of a benzene cation in which only 5 electrons are associated with the aromatic ring, but for this model the *ortho-* and *meta*-coupling constants should be identical. A more complicated superposition model due to Schug, Brown, and Karplus[12] gives, for phenoxy, ρ_o 0·32, ρ_m —0·21, and ρ_p 0·28, which differ notably from our findings in regard to the size of the negative spin density at the *meta*-position and in regard to the $\rho_o : \rho_p$ ratio. Far better is the approach of Atherton, Land, and Porter[13] who stress the point that the electronegativity of the oxygen atom should be taken into account in calculations of spin densities. By including contributions from excited doublet states having three singly occupied orbitals they compute ρ_o 0·154, ρ_m —0·022, and ρ_p, 0·338. These, though all smaller than our figures, correctly assess ρ_m as having a very small negative value and give $\rho_p > \rho_o$. In principle this treatment, which takes into account the dipolar character of the C–O bond in phenoxyl, could be extended to substituted radicals $\mathrm{R{-}C_6H_4{-}O\cdot}$ in which electrical dipole interactions between the R–C bond and the remainder of the radical should systematically modify the nuclear spin distributions ρ^{π}.

At present, however, we offer only qualitative comments concerning implications of the numerical values in Tables 1 and 2. Our experimental results indicate that the major portion of the unpaired electron spin in the radicals of alkylated phenols must be associated with carbon atoms C_2–C_6, only 20—25% remaining associated with both the oxygen centre and the carbon atom to which it is directly attached. In accordance with modern views we have assigned a negative spin density to the *meta*-carbon centres C_3, C_5; it may be that at C_1 there is a negative spin density of similar magnitude. Direct support for the concept of negative spin densities comes from Table 1 from which we can see that for *para*-substituted phenoxy-radicals, neglecting signs, we have

$$a_o^{\mathrm{H}} - a^{\mathrm{H}} = 4{\cdot}5 \pm 0{\cdot}2.$$

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[9] McConnell, *J. Chem. Phys.*, 1956, **24**, 633, 764; McConnell and Dearman, *ibid.*, 1958, **28**, 51; McConnell and Chesnut, *ibid.*, p. 107; McLachlan, *Mol. Phys.*, 1958, **1**, 233.

[10] Chesnut, *J. Chem. Phys.*, 1958, **29**, 43; Fesenden and Schuler, *ibid.*, 1960, **33**, 936; Karplus and Fraenkel, *ibid.*, 1961, **35**, 1312.

[11] Symons, *Adv. Phys. Org. Chem.*, 1963, **1**, 283.

[12] Schug, Brown, and Karplus, *J. Chem. Phys.*, 1962, **37**, 330.

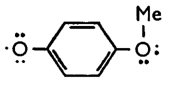
[13] Atherton, Land, and Porter, *Trans. Faraday Soc.*, 1963, **59**, 818.

A similar relation holds for the radical-anions produced by reduction of compounds *p*-$R{\cdot}C_6H_4{\cdot}NO_2$,[6] and it is consistent only with the view that the coupling constants at *ortho*- and *meta*-positions have opposite signs.

Both for *o*- and for *p*-alkyl substituents the coupling constants decrease in the sequence Me > Et > $Pr^n \approx$ Bz > Pr^i > Bu^s. This can only be in part due to change in the local spin densities ρ^π, for, as Table **3** shows, the main change is probably to be associated with the magnitudes of the constants $Q^H_{C\text{-Alkyl}}$. These constants are a measure of the interaction of a hydrogen nucleus in a C–H bond in proximity to the π-electron system of a benzene ring. With α-CH groups the value of $Q_{C\text{-}H}$ depends on the orientation of the C–H bond with respect to the electron symmetry axis. $Q^H_{C\text{-Alkyl}}$ thus depends to a large extent on the mean conformations of substituent groups CH_2R or CHR_2 relative to the benzene ring, α-CH groups coplanar with nuclear CH groups making a greater contribution than CH groups at a large angle to it.

However, the coupling constants of nuclear-bound hydrogen atoms vary with electron spin densities at the corresponding carbon centres. Alkyl substituents which are electron-repelling lower the coupling constants in the *ortho*- and *para*-positions of aryloxy-radicals, whereas electron-attracting groups, *e.g.*, CO_2H, CHO, and NO_2, enhance them. These changes can well indicate variations of spin density, ρ^π, by inductive effects. It may be noted too that radicals with low total electron spin density in the aromatic ring, *viz.*, alkylated phenols, are formed from easily oxidised phenols, whilst those with high nuclear spin density are formed by less easily oxidised phenols. This is rational, since for electron transfer to an oxidant, $^-O{\cdot}C_6H_4R \longrightarrow {\cdot}O{\cdot}C_6H_4R + e$, an electrophilic substituent R should, by electron pull from the oxygen atom, both increase the electronic charge in the benzene ring and decrease the ease of formation of the aryloxy-radical from the corresponding anion.

The results in Table 2 show that methoxyl and similar groups decrease the ring coupling constants, especially in *ortho*-positions, very much more than do alkyl groups. This may indicate that much of the electron spin of such radicals is associated with the two oxygen atoms; the contributing canonical structures (VI) and (VII) are systems with 9 resonating electrons and so should not be analysed in the same way as the **7** electron systems (IV) of Table **1**.



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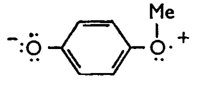

(VII)

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