Substituent Effects in the E.s.r. Spectra of Phenoxyl Radicals

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Regularities observed in the e.s.r. spectra of many *o*-, *m*- and *p*-substituted phenoxyl radicals allow unambiguous assignments of the coupling constants as well as the determination of their relative signs. It is shown that semiquinone anions can be classed as phenoxyl radicals and similarly for radicals from the oxidation of trihydroxybenzene derivatives.

With suitable parameters, the patterns of splittings in these radicals can be rationalised by means of McLachlan's SCF theory; a heteroatom model and an inductive model both explain most of the observed trends. INDO calculations gave a rather poor account of the splittings in phenoxyl.

The e.s.r. of *para*-benzosemiquinones ¹ and of phenoxyl ² have long since been available, yet although systematic investigations of substituent effects in semiquinones have been undertaken at various times, little has been added to the original work of Stone and Waters on short-lived phenoxyl radicals.³ These authors made the



FIG. 1.-Spectrum from oxidation of m-methoxyphenol.

important observation that the algebraic sum of the *ortho* and *meta* coupling constants in a *para*-substituted aryloxyl radical is approximately independent of the substituent. (See table 1). This simple rule enabled them to deduce empirically that these two coupling constants must generally have opposite signs. In fact, the relationship also holds good for *p*-benzosemiquinone where the two splittings are equal and of the same sign. We have investigated the origin and limitations of this intriguing rule and have also discovered analogous relationships among the *ortho*- and *meta*-substituted isomers.

The first necessity was to obtain more experimental data, for there were many gaps to be filled in the list of e.s.r. spectra of mono-substituted phenoxyl radicals and it was

also necessary to find substituents which had relatively large effects on the spin distribution. We have remeasured spectra previously reported because our equipment seems to give improved spectra for this class of transient radical ⁴ (see fig. 1).

The relatively complete set of spectra which we have now obtained has enabled us to assign the splittings, from more or less obvious trends, and also to deduce their relative signs.

EXPERIMENTAL

Most of the radicals were produced by flowing 10^{-2} M solutions in 0.5 M sulphuric acid against 10^{-4} M Ce^{iv} solutions. The alkaline solution spectra were at pH = 7-9. Spectra from o- and p-semiquinone anions were obtained in a static system which gave much better line widths. Coupling constants were measured to within ± 0.01 mT.

PARA-SUBSTITUTED PHENOXYL RADICALS

The results for this class of radicals are given in table 1. In order to obtain a " smooth " change in relative splittings in going from $X \equiv NO_2$, through $X \equiv OMe$ to $X \equiv O^-$ (semiquinone) the ortho and meta splittings have to have opposite signs in

TABLE 1,—COUPLING CONSTANTS (IN -10^{-4} T) of protons in *para*-substituted phenoxyl RADICALS

substituents	<i>a</i> ₂	<i>a</i> ₃	<i>a</i> ₄	a_5	<i>a</i> ₆
NO ₂	7.0	-2.4	$ a_{\rm N} = 2.4$	-2.4	7.0
СООН	6.75(7.1)	-2.2(-2.3)		-2.2	6.75
СНО	6.8	-2.2	$ a_{\rm H} = 0.3$	-2.2	6.8
COCH ₃	6.75	-2.1		-2.1	6.75
Н	6.6[6.6]	-1.8[-1.8]	10.2[10.2]	-1.8	6.6
CH ₃	6.1[6.2]	-1.4[-1.6]	$ a_{\rm CH_3} = 12.5$	-1.4	6.1
CHMe ₂	6.0	-1.2	$ a_{\rm CHi3} = 0.4$		
_			$ a_{\rm H} = 4.5$	-1.2	6.0
Cl	6.4	-1.9	$ a_{\rm CI} = 1.9$	-1.9	6.4
F	6.25	- 1.45	$ a_{\rm F} = 27.5$	-1.45	6.25
OCH ₃	4.9[5.2]	0.0[-0.7]	$ a_{\rm OMe} = 2.1$	0.0	4.9
NH ₂	4.0	0.5	$ a_{\rm N} = 6.6$	0.5	4.0
			$ a_{\rm NH} = 8.0$		
O ⁻ (alkali)	2.37[2.5]	2.37		2.37	2.37
OH (acid)	$2.4\{2.45\}$	2.4		2.4	2.4

[] value calculated using heteroatom model, () value calculated using inductive model, {} mean value of results from OMe derivative.

the majority of cases since then $|a_0 + a_m| = 4.7 \pm 0.2$ G. Presumably the large coupling constants correspond to positive spin densities so that the small splittings usually correspond to negative spin densities. From the results for meta substituted phenoxyl radicals, it is clear that the smaller proton splitting must be ascribed to the meta position and, therefore, that is the site of the negative spin densities observed. The coupling constant in semiquinone must be negative to maintain continuity.

ORTHO-SUBSTITUTED PHENOXYL RADICALS

Two important conclusions arise from inspection of table 1. First, it is clear that substituents lead to a change in the spin distribution in these radicals but that these changes can be arranged in a regular series and depend roughly on the electrondonating power of the substituent. Secondly, using this regularity, semiquinone

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anions can be regarded not as totally different species but rather as a phenoxyl radical with a particular substituent, i.e., $X \equiv O^-$. From the results given in table 2 it is clear that there are also trends in the splitting patterns when the substituents are in the *otrho*

TABLE 2	COUPLING	CONSTANTS	(-10-4	11 (T	N ORTHO-SUBSTITUTED	PHENOXYL I	RADICALS
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substituents	<i>a</i> ₂	<i>a</i> ₃	<i>a</i> ₄	<i>a</i> 5	<i>a</i> ₆
NO ₂	$ a_{\rm N} = 2.1$	-1.2	10.25	-2.4	7.25
COOH		-1.25(-0.6)	10.2(10.3)	-2.1(-2.4)	7.15(7.8)
СНО		-1.7	10.0	-2.0	7.1
COCH ₃		-1.5	10.25	-2.0	7.0
Н	6,6	-1.8	10.2	-1.8	6.6
CH3	$ a_{\rm CH_3} = 7.5$	-2.0[-2.3]	9.7[9.6]	-1.5[-1.6]	6.0[5.9]
CHMe₂	$ a_{\rm H} = 4.0$	-2.0	9.6	-1.5	6.0
Cl	$ a_{\rm Cl} = 1.05$	-2.0	9.8	-1.6	6.0
F	$ a_{\rm F} = 16.8$	-2.1	10.0	-1.4	5.5
OCH3	$ a_{\rm OCH_3} = 1.8$	-1.9[-2.6]	8.5[8.1]	0.0[-0.3]	4.3[4.0]
NH2	$ a_{\rm N} = 6.62$	-0.9	6.62	1.5	2.6
	$ a_{\rm NH} = 8.13$				
O [–] (alkali)		0.75[0.6]	3.75[3.5]	3.75	0.75
OH (acid)		1.0{1.2}	4.1{4.25}	4.1	1.0

for figures in brackets refer to table 1.

position. However, there is the initial problem of assignment and we have had to arrive at those given in the table by finding consistent regularities. The ambiguities could not be resolved convincingly by any simple arithmetic relationship and we had to resort to a graphical procedure (see fig. 2). What we have done is to plot the algebraic sum (or the difference) of pairs of splitting constants against each of the remaining



FIG. 2.—Graph for coupling constants for *ortho*-substituted phenoxyl radicals. A, $a_m = a_3$; B, $a_m = a_5$.

two. This gives rise to graphs containing series of points and those which fall on the same smooth curve must correspond to each other, remembering that only one point on each curve can arise from one particular substituent. Since the parent radical phenoxyl, and o-benzosemiquinone both give points lying on the curves we can assign all four splittings for each radical. We also deduce that the two splittings in *ortho*-semiquinone have the same sign and that in the radical with X = NH_2 , the two small coupling constants have opposite signs. For clarity in fig. 2 we have used the final assignments which were the outcome of the investigation of all the obvious possibilities.

META-SUBSTITUTED PHENOXYL RADICALS

The results for these are given in table 3 and the assignments were made by an analogous method to those considered above, one of the resulting graphs being given in fig. 3. As expected, the radical from resorcinol can be treated as a *meta*-substituted phenoxyl radical and the smallest splitting observed in its spectrum would appear to

TABLE 3.—COUPLING CONSTANTS (IN -10^{-4} T) IN *meta*-substituted phenoxyl radicals

substituents	<i>G</i> 2	<i>a</i> ₃	<i>a</i> 4	a_5	<i>a</i> ₆
NO_2	7.35	$ a_{\rm N} = 0.5$	9.8	-2.1	6.75
COOH	7.25(7.4)		9.9(9.8)	-1.9(-1.6)	6.5(5.9)
CHO	7.1		9.8	-2.0	6.75
COCH ₃	7.1		9.9	-1.9	6.5
Н	6.6	-1.8	10.2	-1.8	6.6
CH3	5.9[6.2]	$ a_{\rm CH_3} = 1.5$	10.5[10,2]	-1.9[-2.0]	7.1[6.7]
CHMe ₂	5.9	$ a_{\rm H} = 0.8$	10.3	-1.9	7.0
Cl	6.2	$ a_{\rm CI} = 0.25$	10.5	-2.1	7.5
F	5	$ a_{\rm F} = 5.8$	10.75	-2.25	8
OCH ₃	3.5[4.6]	$ a_{\rm OCH_3} = 0.6$	11.4[10.8]	-2.3[-2.4]	9.0[8.0]
NH2	3.1	$ a_{\rm N} = 6.9$	10.9	-2.0	8.6
		$ a_{\rm NH} = 8.1$			
O ⁻ (alkali)	-0.7[-0.8]		11.2[12.8]	-2.8[-3.4]	11.2
OH (acid)	3.75{3.5}		10.0{10.2}	$-2.3\{-2.3\}$	10.0

for figures in brackets refer to table 1.



FIG. 3.—Graph for coupling constants for *meta*-substituted phenoxyl radicals. \bigcirc', \times' points if $a_2 = -0.07 \text{ mT}$ in "semiquinone" from resorcinol. A, $a'_0 = a_2$; B, $a'_0 = a_6$.

be due to negative spin density on the 2 position, which differs from previous conclusions.⁵ In simple m.o. terms it is clear that the odd electron goes into an antisymmetrical orbital when $X = O^-$ so that a_6 , a_5 , and a_4 all maintain the same sign along the series whereas a_2 has to change rather drastically.

Once again the effects of substituents are in a similar order to their electron donating power and we can arrange them in the following series :

$$NO_2$$
; CO_2H ; H; Me; Cl; F; OMe; NH_2 ; O⁻

A worthwhile point to remember here is that, as implied by Stone and Waters,³ these results and inferences are self-contained and do not depend on any parallels drawn between these radicals and those of other types.

RADICALS FROM DI- AND TRI-HYDROXY BENZENE DERIVATIVES

Attempts to make assignments in p-semiquinones have centred around "addition" rules ⁶⁻⁸ which state that the effects of substituents are additive. These rules have been developed extensively only for substituents which have relatively little effect on the overall spin distribution, such as alkyl groups and halogen. We now prefer to follow graphical procedures analogous to those used above.

TABLE 4.—COUPLING CONSTANTS (IN 10^{-4} T) IN RADICALS FROM DI-SUBSTITUTED PHENOXYL RADICALS

	<i>a</i> ₂	<i>a</i> ₃	<i>a</i> ₄	<i>a</i> ₅	a_6
20 ⁻ , 3Me	_	$a_{\rm Me} = 0.65$	2.9[3.0]	4.15[3.6]	0.3[0.3]
20 ⁻ , 4Me		0.15[0.24]	$a_{\rm Me} = 4.85$	3.8[3.6]	0.95[0.7]
20 ⁻ , 30Me		$a_{\rm OMe} = 0.65$	1.3[1.8]	4.75[4.0]	0.55[0.4]
20 ⁻ , 40Me	—	0.0[-0.6]	$a_{\rm OMe} = 1.1$	3.7[4.1]	0.75[0.8]
20 ⁻ , 3CO₂H			5.15(5.2)	2.9(3.5)	1.7(2.4)
20 , 4CO₂H	<u></u>	1.25(2.8)		3.25(3.6)	0.75(1.3)
20-, 30-			-0.95[-1.6]	5.5[4.3]	0.95
20~, 40-	—	-0.6[-1.4]		4.98[6.1]	1.35[1.0]
40~, 2Me		1.75[2.1]		2.6[2.8]	2.4[2.4]
40~, 20Me		0.57[0.9]		3.66[3.5]	2.01[2.2]
40 , 2CO ₂ H		2.6(4.8)		2.0(2.5)	2.25(3.3)
2OH 6OH*	$a_{\rm OH} = 0.75$	-1.5[-2.0]	7.6[7.6]	-2.0	$a_{\rm OH} = 0.75$

* In flow system using ceric ammonium nitrate as oxidant under near-neutral conditions; for figures in brackets refer to table 1.



FIG. 4.—Graph for coupling constants in 3-substituted o-semiquinones. A, $a'' = a_4$; B, $a'' = a_5$; C, $a'' = a_6$.

Once again, regularities can be found by plotting for example the sum of two splittings against the third and there are smooth transitions to the semiquinones of 1,2,4-trihydroxybenzene and of pyrogallol ⁹ from those of quinol or catechol (e.g., see fig. 4). The smallest splitting in the semiquinone of 1,2,4-trihydroxybenzene turns out to be negative. In the radical from phloroglucinol the expected Jahn-Teller distortions are evidently being rapidly averaged out and the sum of the three coupling constants (23.4 G) is much the same as it is in all *meta*-substituted phenoxyl radicals.

E.S.R. SPECTRA OF SEMIQUINONES IN ACID SOLUTION

In acid solution the semiquinones from quinol catechol⁹ and resorcinol⁵ are protonated and, provided the rate of proton exchange is fast enough, an averaged spectrum is observed.^{10, 11}



The results we have obtained in acid solution are shown in the tables. From the coupling constant of the proton on position 2 in resorcinol, it is clear that OH has approximately the same effect as OMe, as suggested by Carrington and Smith.¹⁰ In the table the empirical predictions are made using the results for corresponding methoxy-substituted derivatives. The agreement between the empirical estimate and experiment is very good.

THEORY OF SPIN DENSITIES IN PHENOXYL-TYPE RADICALS

The results of INDO calculations¹² were disappointing for, as in similar radicals,¹³ calculated negative spin densities are much too high and the coupling constants are highly sensitive to bond lengths, e.g.,

$$C-O = 1.3 \text{ Å}, C-C = 1.40 \text{ Å}, C-H = 1.08 \text{ Å}$$

$$a_o = -0.50, a_m = +0.28$$
, and $a_p = -0.44$ (in mT)

with carbon-carbon bond lengths of 1.46, 1.34A (alternating) the predictions become

$$a_{o} = -0.58$$
; $a_{m} = 0.38$; $a_{p} = -0.73$.

EMPIRICAL SCF THEORY

Because of the occurrence of appreciable negative spin densities in many of the radicals observed, simple m.o. theory ¹⁴ could not be applied satisfactorily, so McLachlan's approach ¹⁵ was used to include such a possibility. The familar problem of parameterisation appears here for it was discovered that none of the existing sets of parameters given for oxygen ^{14, 16} gave good predictions for phenoxyl. Taking the only variable parameters for atom X as being the coulomb integral $\alpha_{\rm X} = \alpha + h_{\rm X}\beta$, and the resonance integral to a neighbouring carbon atoms $\beta_{\rm CX} = k_{\rm X}\beta$, we found a family of values of $h_{\rm X}$, $k_{\rm X}$ which gave exact predictions for phenoxyl and good predictions for oxygenated derivatives such as *o*- and *p*-benzosemiquinone and the semiquinones from 1,2,4- and 1,2,3-trihydroxybenzenes. One such pair was heteroatoms, each can be assigned two parameters as above for oxygen. With $h_{\rm X} = 1.5$, values for methyl, $k_{\rm CH_3} = 0.3$ and methoxyl $k_{\rm OMe} = 0.6$ lead to good

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predictions confirming the signs and relative magnitudes of the observed coupling These results imply that the McLachlan approach using this parameterconstants. isation can be used with a fair degree of confidence to assist in the assignment of coupling constants and to confirm the nature of radicals. No satisfactory parameters could be found for electron-attracting substituents. An even more simple theoretical model for phenoxyl is to regard it as a benzene positive ion on which is attached an O⁻ substituent.^{18, 19} We consider only a change in Coulomb integral of the adjacent carbon atom so there is one "inductive" parameter for each substituent, i.e., the coulomb integral $\alpha' = \alpha + \delta_{\mathbf{x}} \beta$.

The best agreement over the range of radicals studied was with a Q value of -2.4 mT and $\delta_{\bar{0}} = -1.5$, $\delta_{Me} = -0.2$, $\delta_{CO_2H} = +0.2$, $\delta_{OMe} = -0.6$. Though the results with this simple model were not so good when there were two electron-donating groups *para* with respect to each other, the calculations for $X = CO_2H$ did confirm the assignments given in the tables.

CONCLUSIONS

The inference which can be drawn from this investigation is that the splitting patterns observed in a given class of radicals can be expected to change in a smooth way with substitution. This variation with substituents, however, is not necessarily as simple as implied by attempts to impose addition 6 or superposition rules 20 which could lead, perhaps, to false conclusions if pushed too far.

The trends deduced from the spectra have been confirmed by simple m.o. theory in conjunction with McLachlan's refinement. These trends do not themselves depend critically on the parameterisation and so add to our confidence that the theoretical models proposed will be useful as aids in the assignment of coupling constants in related radicals.

It is interesting that recent work on the radiolysis of alkaline solutions of phenols has led to the production of aminophenoxyl radicals ²¹ which have different e.s.r. parameters to those given above. We tentatively suggest that these differences arise from rapid proton exchange on the oxygen in our acidic solutions. However, the reported assignments must be wrong according to our work, for the data fit our curves. The splittings in *ortho*-aminophenoxyl have to be assigned as follows:

$$a_3 = 0.0, a_4 = 0.431, a_5 = 0.294, a_6 = 0.101$$
 mT.

In ref. (21) a_5 and a_6 were assigned the other way around. This illustrates how useful this approach can be. In the absence of a sufficiently complete series of results on related compounds we would have to resort to the empirical theories.

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