Determination of the Acidity Constants of some Phenol Radical Cations by means of Electron Spin Resonance

BY WILLIAM T. DIXON * AND DAVID MURPHY

Bedford College, Regent's Park, London NW1 4NS

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Phenoxyl radicals were generated in solutions containing from 0 to 75 % sulphuric acid. The changes observed in the e.s.r. spectra over this range are shown to be due to progressive formation of phenol radical cations. In favourable cases plots of the e.s.r. parameters against acidity enabled us to determine the pK_a of the radical cations, which varied from -2.0 (phenol radical cation) to -0.8 (hydroquinone radical cation). Changes in the coupling constants in going from a phenoxyl radical to the corresponding phenol radical cation are usually relatively small, but the *g*-values change from 2.004 ± 0.0004 to 2.003 2 ± 0.0004 . The free energy changes involved in competing oxidative processes are discussed and the data support the view that the C—O group in phenoxyl resembles that in ketones.

In studying phenoxyl-type radicals ^{1, 2} we have noticed that many of the e.s.r. spectra are pH dependent. It is well known that as solutions change from being alkaline (pH 10) to acid (pH 2), changes occur in the e.s.r. spectra ¹⁻⁵ of semiquinones owing to protonation of the anionic forms. We have found that as the acidity is increased still more (pH < 0), further changes are observed indicating progressive formation of positive ions,^{4, 6} which in some cases have already been observed in non-aqueous solvents.^{7, 8}

Systematic observation of phenoxyl radicals, generated by flash photolysis in strong sulphuric acid solutions, has enabled the pK_a of various substituted phenol radical cations⁹ to be determined, although no evidence for the protonation of the parent radical, phenoxyl, was obtained even when it was generated in 12 mol dm⁻³ sulphuric acid.

Following previous workers, we have used e.s.r. as a tool, generating the phenoxyl radicals by cerium (IV) oxidation in a flow system.^{1, 2} By varying the acidity of the solutions we have followed the equilibrium (1)

$$ArO \cdot \stackrel{^{+H^{+}}}{\underset{^{-H^{+}}}{\Rightarrow}} \dot{Ar}^{+}OH$$
(1)

and determined the pK_a of a number of radicals including the phenol radical cation itself.

EXPERIMENTAL

E.s.r. spectra were obtained by flowing 10^{-2} mol dm⁻³ solutions of the phenols in aqueous sulphuric acid against 10^{-2} mol dm⁻³ cerium(1v) sulphate ¹⁰ in the flow system described previously.² The sulphuric acid+water solutions were made up by weight fraction using commercial 97 % H₂SO₄. The quality of the spectra varied considerably over the range studied and resolution was at its optimum when the solvent corresponded to the compound H₂SO₄.4H₂O. The flow rates, which were the maximum obtainable, varied from 16 cm³ s⁻¹ (pure water) to 2 cm³ s⁻¹ (75 % H₂SO₄).

The phenols were commercial materials, purified by the usual methods; all had physical constants which agreed well with those of the literature.

g-Values were measured using Fremy's salt (g = 2.0055)¹¹ which itself was standardised against the *p*-semiquinone anion,¹² and the temperature of the solutions was $22.5\pm0.5^{\circ}$ C.

RESULTS

Once the practical difficulties associated with using strong sulphuric acid solutions had been overcome, the procedure was conceptually very simple, *i.e.*, e.s.r. spectra



FIG. 1.-E.s.r. parameters for the radical from catechol as a function of acidity. A: g-shift relative to Fremy's salt, B: $a_4+a_5-7.0$, C: $a_3+a_6+2.0$, D: difference curve for curve A.

had to be obtained for each radical species over a wide range of acidities. Proton exchange was always fast ⁶ (pH < 2) so the spectra obtained were completely averaged and no hyperfine interactions with hydroxylic protons could be observed. Each



FIG. 2.—g-shifts, relative to Fremy's salt, of radicals as functions of acidity. A: from hydroquinone, B: from resorcinol, C: from *m*-cresol, D: from phenol, E: difference curve for phenol.

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of the e.s.r. parameters was therefore made up of contributions proportional to the concentrations of the participating species, so that on plotting the values of the parameters against the molarity of acid, a series of equivalent titration-type curves was obtained (see fig. 1).

starting	substituents in radical cation	coupling constants a (±0.05) /10 ⁻⁴ T						n 44
material		± 0.00015	<i>a</i> ₂	<i>a</i> 3	a4	<i>a</i> 5	a6	(±5 %)
phenol	О- ОН	2.004 61 2.002 91	6.65 5.3	(-)1.85 (-)0.8	10.2 10.7	(-)1.85 (-)0.8	6.65 5.3	-4.75
o-cresol	1-O ⁻ 2-Me 1-OH 2-Me	2.004 29 2.003 31	7.5(Me) 7.5(Me)	(-)2.0 (-)1.6	9.8 9.8	()1.5 ()0.1	6.0 4.0	-3.85
<i>m</i> -cresol	1-O ⁻ 3-Me 1-OH 3-Me	2.004 47 2.003 12	5.9 4.0	(-)1.5(Me) (-)0.2(Me)	10.5 11.0	(-)1.9 (-)1.2	7.1 6.4	- 3.70
p-cresol	1-O⁻ 4-Me 1-OH 4-Me	2.004 32 2.003 17	6.1 4.5	(~)1.4 (~)0.05	12.7(Me) 15.1(Me)	(-)1.4 (-)0.05	6.1 4.5	-3.25
o-amino- phenol	1-0- 2-NH2*	2.003 72	${a_{N} 4.8 \atop a_{NH_2} 5.25}$	0.1	4.25	2.95	1.0	
	1-OH 2-NH2	2.003 13	$a_{NH_{2}}^{a_{N}} $ 8.1	2.6	1.6	6.6	(-) 0.9	~0.2
<i>m</i> -amino- phenol	1-0- 3-NH ₂		_		_			
	1-OH 3-NH ₂	2.002 77	3.05	$a_{\rm NH2}^{a_{\rm N}7.0}$	8.6	(-)2.05	10. 45	≳1
p -amino- phenol	1-0- 4-NH2*	2.003 77	2.75	1.75	${a_{\rm N} 5.25 \atop a_{\rm NH2} 5.5}$	1.75	2.75	-
	1-OH 4-NH ₂	2.003 15	0.4	4.0	$a_{\rm NH_2} 8.0$	4.0	0.4	~1.5
o-methoxy- phenol	1-O ⁻ 2-OMe 1-OH 2-OMe	2.004 35 2.003 62	1.8(OMe) 2.9(OMe)	(-)1.9 (-)1.1	8.5 6.8	0.0 2.9	4.3 1.45	_
nmethoxy- phenol	1-O- 3-OMe 1-OH 3-OMe	2.004 29 2,003 15	3.5 0.3	0.6(OMe) 2.6(OMe)	11.4 10.25	(-)2.3 (-)2.25	9.0 11.25	_
<i>p</i> -methoxy- phenol	1-O ⁻ 4-OMe 1-OH 4-OMe	2.004 45 2.003 58	5.05 1.9	(-)0.2 2.2	2.1(OMe) 3.2(OMe)	(-)0.2 3.0	5.05 1.9	-
catechol	1-О- 2-О- 1-О- 2-ОН » 1-ОН 2-ОН	2.004 47 2.004 28 2.003 55		0.75 (-)1.2 (-)0.25	3.7 7.0 4.85	3.7 1.2 4.85	0.75 3.0 (-)0.25	-3.05
resorcinol	1-O- 3-O- 1-O- 3-OH ^b 1-OH 3-OH	2.003 92 2.004 35 2.003 12	(-)0.7 3.9 0.4	_	11.5 11.3 10.9	(-)2.4 (-)2.3 (-)2.1	11.5 8.7 10.9	-2.2
hydro- quinone	1-O⁻ 4-O⁻ 1-O⁻ 4-OH ⁰ 1-OH 4-OH	2.004 55 2.004 27 2.003 52	2.37 5.1 2.25	2.37 (-)0.3 2.25		2.37 (-)0.3 2.25	2.37 5.1 2.25	-1.15

TABLE 1

^a Negative spin density on ring carbon given in brackets when inferred from trends in experimental data; ^b average values only seen, values given calculated from trends in ref. (1); ^c coupling constants from H. Yoshida, K. Hayashi and T. Warashima, *Bull. Chem. Soc. Japan*, 1972, **45**, 3515; ^d pA = value of H_0 function where the concentrations of the phenoxyl and its corresponding radical cation were equal; ^e values from ref. (16).

In most cases the largest change in going from the neutral to the protonated species was that due to the change in the g-value, making this the most useful quantity for determining the pK_a , especially since the centres of spectra could usually be pinpointed even when resolution was poor.

In a few cases we could obtain " pure " spectra of the radical cations but in others, such as phenol and the cresols, we had to be content with locating the point corresponding to a 50:50 mixture of aryloxyl radical and its protonated counterpart. It is at this point, which ultimately leads to the pK_a of the radical cation, 1^{3-15} that

the rate of change of the e.s.r. parameters with respect to acid strength (H_0) is at a maximum (see fig. 1 and 2).

The spectra from the methoxyphenols and the aminophenols were too poorly resolved at most points in the range to draw curves such as those in fig. 1 and 2, though in the latter case we could bracket a limited range containing the pK_a of the positive ions. Electron-withdrawing substituents, such as fluorine or carboxyl, pushed the pK_a of the phenol radical cation outside the range we could measure.

The results of observations and extrapolations for the radicals whose acidity constants we were able to measure are given in table 1.



FIG. 3.—Graphical relationship between corresponding coupling constants in phenoxyl radicals and in phenol radical cations. Curve A, meta splittings, Curve B, ortho splittings, Curve B', para splittings.

The fact that for each radical the changes in all the parameters follow the same pattern to give curves as in fig. 1, is good evidence that we have indeed been observing simple equilibria between protonated and neutral species.

The changes in g-value are of the expected order (from what we already know of p-benzosemiquinone),⁷ and the patterns of coupling constants in the "radical cations" are those expected from previous work, which indicates that -OH has effects on the spin distribution about half way between those of ---H and ---O--.

We might expect a series of simple relationships between corresponding splittings in phenoxyl radicals and phenol radical cations,¹ and indeed a plot of corresponding coupling constants yields two curves, one for *m*- and the other for *o*- or *p*-positions (see fig. 3).

These curves have enabled us to assign coupling constants in ambiguous cases where we were unable to follow the usual smooth transition to the protonated form.

It is worthwhile noticing here that the *p*-methoxyphenol radical cation had an unsymmetrical splitting pattern. We can attribute this to the effects of restricted rotation of the methoxyl group.17



The previous assignments 1 for aminophenoxyl radicals appear to be incorrect in the light of the new results.

DISCUSSION OF ACIDITY CONSTANTS

Substituents change the spin distribution in the phenoxyl radical, the order of potency being

 $NO_2 < CO_2H < Me < OH \approx OMe < NH_2 < O^-$.

This order was deduced from a detailed investigation of trends in aryloxyl radicals ¹ and corresponds within any one series of o-, m- or p-substituted radicals to the reverse order of the pA of the radical cations (see table 2). There is also a loose correlation

		TABLE 2		
substituents	<i>a</i> ₆	<i>a6</i> ′	Δg	pA(HO+·Ar)
Н	6.65	5.3	0.001 70	-4.75
<i>p</i> -Me	6.1	4.5	0.001 15	-3.25
p-OH	5.1	2.25	0.000 75	-1.15
p-OMe	5.05	1.9	0.000 87	
$p-NH_2$	2.75	0.4	0.000 62	$\sim +1.5$
<i>p</i> -O ⁻	2.37	-0.3	0.000 28	> + 3.0*
substituents	$a_4 - a_6$	$a_4'-a_5$	Δg	₄(HO+•Ar)
Н	3.55	5.4	0.001 70	-4.75
<i>m</i> -Me	3.4	4.6	0.001 35	- 3.70
m-OH	2.6	0.0	0.001 23	-2.20
<i>m</i> -OMe	2.4	-1.0	0.001 14	—
m-NH ₂		-1.85		>+1
<i>m</i> -O ⁻	0.0	-2.6	0.000 43	>+1
substituents	$a_4 + a_6$	$a'_4 + a'_6$	Δg	pA(HO+·Ar)
Н	16.85	16.0	0.001 70	-4.75
o-Me	15.8	13.8	0.000 98	- 3.85
o-OMe	12.8	8.25	0.000 73	
o-OH	10.0	4.6	0.000 73	-3.05
o-NH2	5.25	0.7	0.000 59	$\sim +0.2$
<i>o</i> -O ⁻	4.45	0.0	0.000 19	>+1.0*

 a_r = coupling constant in ArO. $\Delta g = g(\text{ArO.}) - g(\text{Arr.OH})$. $a_{r'}$ = coupling constant in Ar⁺·OH. * from ref. (4), coupling constants in 10⁻⁴T.

with the change in g-value in going from the radical cation to the corresponding dhenoxyl radical, but no useful correlations with Hammett σ -constants were detected.¹⁸⁻²⁰

THERMODYNAMIC CONSIDERATIONS[†]

The point of balance between the protonated and unprotonated forms of a base is a measure of its basicity as compared with the indicators used to establish the acidity (H_0) scale. However, this point does not correspond directly to the value of the thermodynamic equilibrium constant because activities under these strongly acidic conditions do not correspond to concentrations. It is convenient to write the formula for the equilibrium constant K_a in the form of eqn (2)

$$\log K_{\rm a} = \log K_{\rm c} + \log \frac{f_{\rm H} + f_{\rm B}}{f_{\rm BH^+}} \tag{2}$$

where $K_c = [H^+][B]/[BH^+]$ and f_{H^+} is the activity coefficient for hydrogen ions, *etc.* K_c can be calculated at each acidity and so to determine K_a , we need to extrapolate to the point where the activity coefficient term disappears. Various ways of achieving this are suggested in the literature ²¹ and are more or less effective in particular cases. One method is to replace the term $\log a_{H^+}f_B/f_{BH^+}$ by a term proportional to the Hammett acidity function H_0 as in eqn (3)

$$pK_{a} = -\log K_{a} = \log \frac{[BH^{+}]}{[B]} + mH_{0}.$$
(3)

We found that a plot of H_0 against log $[BH^+]/[B]$ tended towards a straight line at low values of H_0 but not always over a large enough range to make the extrapolation to $H_0 = 0$ completely clear-cut (see fig. 4).



FIG. 4.—Extrapolations in case of o-cresol radical cation. \bigcirc , $y = H_0 + \log [BH^+]/[B]$, $x = H_0 + \log [H^+]$. \bigcirc , $y = \log [BH^+]/[B]$, $x = \frac{2}{5}H_0$. \bigcirc , $y = \log K_c$, $x = -\frac{1}{2}d(\log K_c)/d(\log[H^+])$.

A generally better series of straight lines was obtained using eqn (4) $^{22, 23}$ where the extrapolation is to $H_0 = -\log [H^+]$.

$$\log ([BH^+]/[B]) + H_0 = \phi(H_0 + \log [H^+]) + pK_a.$$
(4)

However, there still remains a doubt as to the exact relevance of the H_0 function ²⁴ to the acid-base equilibria we have been studying, and so we have used an independent

† We would like to thank a referee for helpful comments in this section.

method of extrapolating to infinite dilution (in water). It is clear that K_c should approach its limiting value asymptotically and since the activity coefficients depend on acid concentration, eqn (5) has the desired properties

$$\log K_a = y + A e^{-nx} \tag{5}$$

where $x = \log [H^+]$, $y = \log K_c$ and it is assumed that the activity coefficient term disappears at infinite dilution, an assumption which we cannot justify rigorously at this stage.

Differentiating eqn (5) we obtain eqn (6)

$$y = pK_a + \frac{1}{n}\frac{\mathrm{d}y}{\mathrm{d}x}.$$
 (6)

We use eqn (5) and (6) consecutively, *i.e.*, by first plotting y against x and then against the slope (dy/dx) of the resulting curve. This is conveniently done on the same graph.

A comparison of the three methods of extrapolation is given in fig. 4 for a case in which they lead to the same answer; in other cases the agreement is probably within the experimental error (see table 3).

FABLE 3.—ACIDITY	PARAMETERS FOR	RADICAL CATIONS
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norent			- K/- 4 (+ 10.9/)			
compound	pA(±5 %)	(1) (2)		(3)	(rounded)	
phenol	-4.75	-2.0	-2.0	- 1.9	0.4	
o-cresol	-3.85	-1.8	-1.8	-1.8	0.5	
m-cresol	-3.70	-1.9	-1. 9	- 1.9	0.5	
p-cresol	-3.25	-1.6		-1.7	0.5	
catechol	-3.05	-1.75	-1.6	- 1.65	0.5	
resorcinol	-2.2	-1.55	-1.4	-1.5	0.7	
hydroquinone	-1.15	-0.75	-0.75	-0.8	0.7	

(1) from plot $H_0 + \log [\text{H}^+]$ against $H_0 + \log [\text{BH}^+]/[\text{B}]$. (2) from plot H_0 against $\log [\text{BH}^+]/[\text{B}]$ (3) from plot $\log K_c$ against $d(\log K_c)/d(\log [\text{H}^+])$.

A significant factor is the ratio pK/pA which was always less than unity, as has been found with other oxygen bases.²³ This is related to the different demands of the acid and base forms for water of solvation.

We can use our newly acquired data to compare free energy changes of some of the reactions involved, for example, those in scheme 1.



Scheme 1

We shall use the numbers/letters by the arrows as labels for the reactions/equilibria, and instead of free energy changes we shall use pK, where for example

$$\Delta G(D^+) = 2.303 RT pK(D^+).$$

Since each compound in scheme 1 is at the same temperature and at low concentration, we can derive the following set of equations.

$$pK(I^{-}) - pK(D) = -pK_2$$
(i)

$$pK(I^{-}) - pK(I) = pK_a - pK_2$$
(ii)

$$pK(I) - pK(D) = -pK_a$$
(iii)

$$pK(D^+) - pK(D) = pK_1 - pK_a.$$
 (iv)

In the case of phenol itself,* $pK_a \approx -2.0$, $pK_1 \approx -6.75$, $pK_2 = 9.9$. Hence from the thermodynamic viewpoint :

from (i)-electron-loss from the phenoxide ion is favoured over hydrogen abstraction from phenol; from (ii)-electron-loss is much easier from the phenoxide ion than from phenol; from (iii)-hydrogen abstraction is easier than electron loss from phenol; and from (iv)-hydrogen abstraction from protonated phenol is slightly easier than from phenol.

Similar trends can be obtained for the cresols and when there is a hydroxyl substituent, but in the latter case further possibilities arise (see scheme 2).



Scheme 2

There are now some additional relationships (v)-(viii):

$$pK(I^{2-}) - pK(D^{-}) = -pK_3$$
 (v)

$$pK(I^{2-}) - pK(I^{-}) = pK_b - pK_3$$
 (vi)

$$pK(D^{-}) - pK(D) = pK_b - pK_2$$
 (vii)

$$pK(I^{-}) - pK(D^{-}) = pK_{b}.$$
 (viii)

In all three cases we expect $pK_b > 0$, since even at pH = 1, in our experiments, we could detect no sign of the radical anions. In contrast with the situation involving undissociated benzene diols, electron loss is favoured over hydrogen abstraction from the mono-anions [from (viii)] or from the neutral molecules [from (vii)]. This follows from the fact that $pK_2 \sim +10$, $pK_3 \sim +12$. A similar scheme can be written for the aminophenols where there is a choice between N-H and O-H bond fission (see scheme 3).



Scheme 3

* pK values of non-radicals are drawn from tables in ref. (25) and (26), given that the pK for phenol is doubtful but certainly negative.

For all three isomers the pK values are in the range

$$pK_1 = 4.3-5.5, \quad pK_2 = 8.5-10.00$$

 $pK_a > 0, \quad pK_b > 12.$

Thus it is easier for the neutral molecule to lose an electron than a hydrogen atom, which in turn is easier than losing a hydrogen atom from either the protonated aminophenol or the anion. This is analogous to the situation with the mono-anions of the dihydroxybenzenes, *i.e.*, loss of an electron from one of these latter anions is thermo-dynamically favoured over hydrogen abstraction either from the anion or from the parent dihydroxybenzene.

This illustrates a similarity between $-NH_2$ and $-O^-$ not only in their effects on the spin distribution in these radicals but also on the point of balance of the various equilibria.

These thermodynamic considerations cannot be used to predict the details of a reaction pathway since they only indicate overall energy changes and not free energies of activation, *i.e.*, not rate constants.

THE NATURE OF THE PHENOXYL RADICAL

From its pK_a , the hydroxyl group in the phenol radical cation bears little resemblance to that in phenol itself. However, its low *g*-value is close to the characteristic value for hydrocarbon radicals when there are hydroxyl or ether linkages present.^{12, 27} On the other hand, phenoxyl and semiquinone anions have abnormally high *g*-values which in aliphatic radicals are associated with a carbonyl group close to the radical centre,¹² e.g., for CH₂CH₂OH, g = 2.0025; for CHCHO, g = 2.0045.

This comparison, together with the obviously high spin density on the aromatic ring,¹⁰ suggests that the C—O linkage in phenoxyl resembles a carbonyl group.²⁸ This idea is supported by the similarity between the basicity parameters of phenoxyl (-4.75, 0.4) and those of acetophenone ²⁹ (-6.5, 0.5).

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