Electron Spin Resonance Spectra of Hydroxyl Adducts of Some Aromatic Acids

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The first e.s.r. spectra of hydroxyl adducts of some naphthalene derivatives are reported. The spin distribution in these radicals resembles those in corresponding naphthoxyl radicals. Further examples of cyclohexadienyl-type radicals are also given and the detailed mechanism of the formation of benzyl and phenoxyl radicals in the Ti^{III}–H_2O_2 system is further clarified.

RADICALS of the cyclohexadienyl type are important intermediates in many homolytic reactions of aromatic compounds and a number have been directly observed by means of e.s.r. spectroscopy.[1-4] Though heterocyclic analogues of these radicals have been studied relatively extensively,[5-7] only one example has been reported of an adduct radical in the naphthalene system, and that was in a single crystal.[8] We have extended the range of hydroxyl adduct radicals by using sulphonic acids which are water soluble, and have also obtained spectra arising from both α- and β-addition to the naphthalene skeleton.

Some of the results obtained with sulphonic acids were rather unexpected but not inconsistent with the ideas developed by Norman *et al.*[2,3] for the mechanism of formation of benzyl[2] and of phenoxyl[3] radicals in the Ti^{III}–H_2O_2 system.

RESULTS

Spectra from Naphthalenesulphonic Acids.—Naphthalene compounds are generally much less soluble in water than corresponding benzenoid compounds and this, together with the increased number of sites for possible attack, makes

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[8] V. R. Bohme and H. C. Wolf, *Chem. Phys. Letters*, 1972, **17**, 582.

them poor substrates in the Ti^{III}-H_2O_2 system. The naphthalenemonosulphonic acids, however, are soluble in water, but give at best, weak signals due to mixtures of radicals in the flow system. In contrast to this, the symmetrical disulphonic acids gave relatively intense spectra in which one component was much stronger than the others and could be picked out with ease. In these cases the signal ascribed to a Ti^{II}-HO_2· complex [3,9] was entirely quenched, in contrast to the situation with monosulphonic acids, showing the relatively unreactive nature of the latter species.

The coupling constants were assigned by comparison with the corresponding naphthoxyl radicals,[10] implying that the

hydroxy-group is pushed further from the plane of the ring, moving the methylene proton nearer to that plane and hence decreasing hyperconjugation. The electrophilic nature of the hydroxyl radical is shown by a preponderance of addition ' meta ' to a sulpho-group.

Toluene-p-sulphonic Acid.—The results using this substrate seemed to be anomalous because at the high acidity of our solutions one would have expected to observe only the substituted benzyl radical.[2,4] Benzyl radicals arise from initial addition of ·OH followed by acid catalysed loss of water.[2] The presence of the

TABLE 1

Coupling constants (10^{-4} T) in hydroxyl adduct radicals of some naphthalenedisulphonic acids (corresponding naphthoxyl coupling constants in parentheses)

Substituent	Position of OH attack	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
3,6-(SO$_3$H)$_2$	1	a_β 24·4	9·4 (8·3)		13·3 (10·8)	3·0 (2·5)		3·5 (2·5)	1·0 (0)
3,7-(SO$_3$H)$_2$	1	a_β 22·0	10·4 (8·3)		13·4 (10·8)	3·0 (2·5)	1·1 (0·7)		1·1 (0)
4,8-(SO$_3$H)$_2$	2	11·75 (10·8)	a_β 32·75	2·5 (1·5)		1·9 (1·5)	6·25 (5·4)	1·9 (1·2)	

TABLE 2

Coupling constants (10^{-4} T) in radicals from attack by ·OH on some benzene acids

Substituents	Position of ·OH attack	a_1	a_2	a_3	a_4	a_5	a_6
3-SO$_3$H	1	35·0	8·75		13·25	2·75	9·5
3,5-(SO$_3$H)$_2$	1	35·5	9·0		13·5		9·0
4,6-(SO$_3$H)	1	30·75	8·75	2·25		2·25	
3-CO$_2$H-4-SO$_3$H	1	36·6	8·5			2·8	9·0
3-SO$_3$H-4-CO$_2$H	1	36·0	9·0			2·8	9·5
2,6-(CO$_2$H)$_2$-4-SO$_3$H	1	24·5		2·75		2·75	
4,5,6-(CO$_2$H)$_3$	1	32·0	8·25	2·5			
3,4,5-(CO$_2$H)$_3$	1	36·25	8·6				
2,3,5,6-(CO$_2$H)$_4$	1	28·75			12·4		
2-CH$_3$-5-SO$_3$H	1	32·5	a_{Me} 9·5	2·75	13·0		8·5
2-CH$_3$-4-SO$_3$H-5-EtO$_2$CO	1	32·75	a_{Me} 9·75	2·25			7·75
1-OH-2-CO$_2$H-4-SO$_3$H	2			8·5		12·25	2·25
1-OH-2-CO$_2$H-4-SO$_3$H	1 *			1·6		2·2	7·1
1-OH-4-SO$_3$H	1 *		7·25	2·1		2·1	7·25
1-OH-2,4-(SO$_3$H)$_2$	1 *			1·75		2·25	6·3
1-OH-2,4,6-(SO$_3$H)$_3$	1 *			2·0		2·0	
1-CH$_3$-4-SO$_3$H	1 †	a_{CH_3} 16·25	5·25	1·75		1·75	5·25

a_1 = Methylene proton splitting.

* Phenoxyl radicals confirmed by Ce^{IV} oxidation in the flow system. † Benzyl-type radical.

geometries of the naphthoxyls are simply related to those of the adduct radicals.

Radicals from Benzene Acids.—In some cases, such as for benzenesulphonic acid, mixtures of radicals were observed but lines due to meta-adducts could usually be picked out because their spectra were much wider than those from other isomers. The results for a variety of radicals are given in Table 2.

DISCUSSION

It is clear that carboxy- or sulpho-groups have little effect on the spin distribution in the adduct radicals although the coupling of the methylene proton does change markedly depending on the number of adjacent substituents, ranging from ca. 3·6 mT with no adjacent substituent, to ca. 2·5 mT when it has substituents on either side. The fused benzo-group can be regarded as a substituent and so the effect can be interpreted as being due only to steric forces. With increasing substitution the

[9] N. A. Vysotskaya, Russ. Chem. Rev., 1973, 42, 851.
[10] W. T. Dixon, W. E. J. Foster, and D. Murphy, J.C.S. Perkin II, 1973, 2124.

electron-withdrawing sulphonic acid group tends to favour loss of a proton from the methyl group but on the
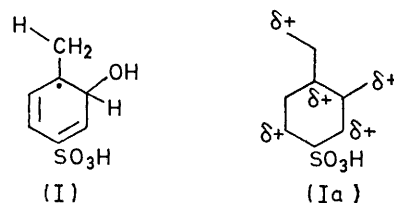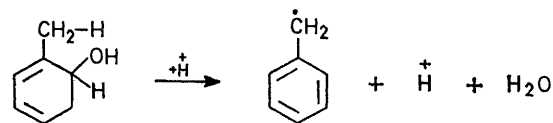
other hand would inhibit proton attack on the hydroxy-group, as we can see from the charge distribution in model (Ia). The observation of an adduct : benzyl

radical ratio of *ca.* 2 : 1 (from peak heights) at pH *ca.* 0, suggests that the rate determining step is the attack by a proton.[2] This was confirmed by varying the acidity of

pure spectrum (Figure) was obtained which could only be interpreted in terms of adduct (II). It seems that when the Ti^{III} complex reacts with H_2O_2 the hydroxyl radical


(a) ← 1·0 mT →   (b) ← 1·0 mT →
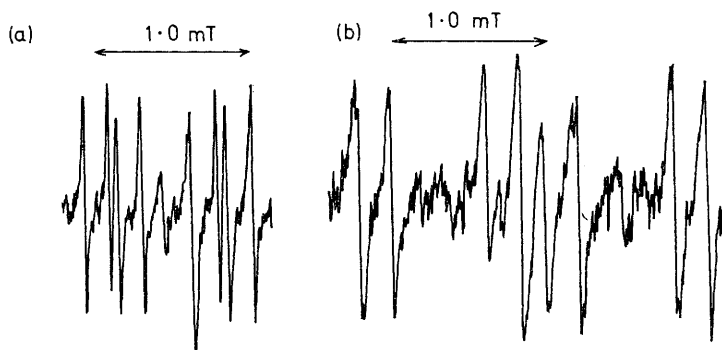
E.s.r. spectra from 5-sulphosalicylic acid (a) with Ce^{IV} and (b) with Ti^{III}–H_2O_2 and an excess of substrate

the solutions. In 5M-sulphuric acid a pure spectrum of the sulphonated benzyl radical was obtained, whereas at higher pH (zero sulphuric acid concentration) the benzyl radical could not be detected at all in the presence of a somewhat decreased signal from the adduct radical. It is interesting that the substituent on a *meta*-position is conjugated in the same sense as is the *para*-position of the ring, *i.e.* with the substituent in the 1-position.

Hydroxybenzenesulphonic Acids.—Having observed adduct radicals from toluene-*p*-sulphonic acid under strongly acidic conditions, we investigated the possibility of observing something similar with phenols. From the results it seems that the sulpho-group does not prevent loss of water from the initially formed adducts [3] so that we only observed phenoxyl radicals except in one special case, 5-sulphosalicylic acid. This compound evidently formed a complex with titanium(III) since when it was present in excess the solution became dark brown instead of purple. With high Ti^{III} concentrations a mixture of radicals was observed, the main one being the aryloxyl radical. When the Ti^{III} concentration was reduced with respect to the substrate concentration, a

formed attacks the nearest accessible site. This particular site would probably be favoured because it would initially carry a small negative charge [see (III)].
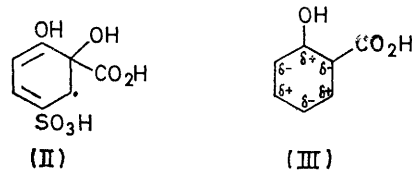
(II)   (III)

EXPERIMENTAL

The spectra were obtained using the flow system reported previously [10] and the signals were best obtained at the maximum flow rate we could achieve (*ca.* 15 ml s^{-1}). In the oxidations by Ti^{III}–H_2O_2 the substrates were in the range 0·1—0·3M. The experimental conditions were as in ref. 1, but the solutions were made strongly acidic with sulphuric acid (pH *ca.* 0). Attempts to purify the commercial samples of the sulphonic acids by recrystallization led to no improvement in the spectra obtained and sometimes led to worse results. We attribute this to the lability of the sulpho-group.