Qualitative Analysis of Some Substituted Naphthols and 8-Hydroxyquinolines using Electron Spin Resonance Spectroscopy

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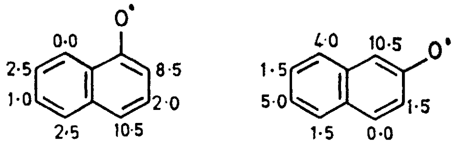
From the proton hyperfine splittings observed in the e.s.r. spectra of radicals generated in a flow system by oxidising naphthols or 8-hydroxyquinolines, the position of substituents can often be inferred.

DURING the course of our investigations of naphthoxyl radicals[1] we came across a number of naphthoic and naphthalenesulphonic acids which were available because of their use in the dye industry near the turn of the century. The identification of these compounds[2] was no easy matter by classical chemical techniques, because some of these carboxylic acids have a marked tendency towards decarboxylation, and the sulphonic acids are liable to undergo intramolecular rearrangement.

Our interests have been with those acids which have a hydroxy substituent since we can then generate the corresponding naphthoxyl radicals by oxidation with Ce^{IV} in a flow system.[1,3] In principle the set of parameters obtained from the e.s.r. spectra of these radicals leads to their characterisation since the proton coupling constants (in 10^{-4}T) fall into the following two definite patterns (Scheme).



SCHEME

The significance of these results is that the position of a substituent can be deduced, in favourable cases, from the coupling constant which is 'missing' from whichever set is applicable. We can justify this assumption because previous work[1,4,5] has shown, that in radicals of this type, substituents such as CO_2H and SO_3H do not alter the general odd electron density very much.

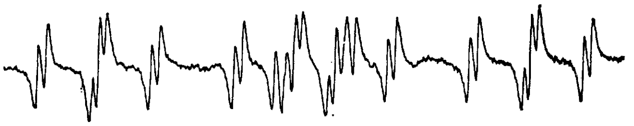
TABLE 1

E.s.r. parameters ($a/10^{-4}$ T) of radicals from the oxidation of naphthols

Positions of substituents in naphthalene	1-OH 3-SO_3H	1-OH 5-SO_3H	1-OH 6-CO_2H	1-OH 3-SO_3H 6-SO_3H	1-OH 3-SO_3H 8-SO_3H	2-OH 1-Cl	2-OH 5-CO_2H	2-OH 7-CO_2H	2-OH 8-CO_2H
a_1						a_{Cl} 1.4 †	10.6	10.75	10.75
a_2	8.65	8.3	8.1	8.8	9.0				
a_3		2.1	2.25			1.4	1.6	1.5	1.5
a_4	10.65	10.6	10.6	10.6	10.75	0	0	0	0
a_5	2.6		2.25	2.4	2.2	1.4		1.25	1.5
a_6	0.75	0.85			0.7	4.7	4.9	5.5	4.25
a_7	2.6	2.65	2.5	2.7	2.2	1.4	1.6		1.5
a_8	0	0.6	0	0.4	0	4.2	4.25	4.25	

† Chlorine coupling similar to that in *p*-chlorophenoxyl whose e.s.r. parameters are: a_o 0.63, a_m 0.175, a_{Cl} 0.2 (measured in this laboratory) mT.

Characterisation of Some Naphthoxyl Radicals.—Polymorphism is particularly troublesome in naphthalene chemistry, and has led us to some useful applications of the above ideas.



E.s.r. spectrum of 3,6-disulphonato-1-naphthoxyl

In fact we were led to appreciate the value of e.s.r. as an analytical tool when we attempted to prepare a complete series of hydroxynaphthoic acids for use in our studies of autoxidation of naphthalene derivatives.[5,6] It was very difficult to characterise some of these compounds from the literature; for example, from 2-naphthoic acid we were able to prepare pure, sharp melting crystals of 7-hydroxy-2-naphthoic acid, m.p. 259, 275, and 269°, all of which are quoted in the literature[2] by different authors. Each gave the same acetyl derivative, m.p. 209°, and had the same e.s.r. spectrum in our flow system. In this exercise we were able, using e.s.r., to directly pinpoint the position of a substituent in a number of cases (see Table 1).

Commercial samples of a number of sulphonated naphthols were obtained also and we have been able to show, from the remarkable pure e.s.r. spectra obtained (see Figure) that no appreciable † quantities of other naphthols were present.

From the general pattern of coupling constants in naphthoxyl radicals we could extrapolate to radicals

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† In many cases[1] 1—2% of other isomeric sulphonic acids gave rise to weak, but analysable spectra.

[1] W. T. Dixon, W. E. J. Foster, and D. Murphy, *J.C.S. Perkin II*, 1973, 2124.

[2] 'Encyclopaedia of Organic Chemistry,' Series C, Vol. 12B, Elsevier, Amsterdam, 1953 and references therein.

[3] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 213.

[4] L. H. Piette, M. Okamura, G. P. Rabold, R. T. Ogata, R. E. Moore, and P. J. Scheuer, *J. Phys. Chem.*, 1967, **71**, 29.

[5] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1974, 739.

[6] W. T. Dixon, P. M. Kok, and D. Murphy, *Tetrahedron Letters*, 1976, 623.

from hydroxyquinolines. The presence of nitrogen in these radicals would, in general, increase the complexity of their e.s.r. spectra and decrease their definition. This is what we found, for example with 5-hydroxyquinoline whose e.s.r. spectrum was too poor for analysis. In the case of 8-hydroxyquinolines, however, we predicted [7,8] zero spin density on the nitrogen and this is what we found, for the absence of nitrogen splitting made it possible to analyse the corresponding spectrum as well as those from some derivatives.

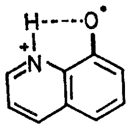
TABLE 2

Coupling constants ($a/10^{-4}$T) of radicals from oxidation of 8-hydroxyquinolines

Positions of substituents in quinoline	8-OH	5-SO_3H 8-OH	7-CO_2H 8-OH
a_N	0	0	0
a_2	1.25	1.2	1.3
a_3	0	0.7	0.8
a_4	3.5	3.2	2.2
a_5	11.0		11.2
a_6	1.25	1.4	1.9
a_7	8.75	9.3	
a_8		a_{peri} 0.4	a_{peri} 0.4

Nitrogen seems to have a greater perturbing effect on the spin densities than do the other substituents in the naphthoxyl radicals but nevertheless, the spectra do fall in with the general pattern.

In the better resolved spectra from 8-hydroxyquinoline derivatives, an extra proton splitting could be detected, and we ascribe it to a *peri*-proton on the nitrogen, by analogy with the radicals from 1,8-dihydroxynaphthalene [1,4,5] and its derivatives.



Conclusions.—What we have reported here does illustrate a possible use of e.s.r. as an analytical tool, for effectively we actually diagnosed the substitution patterns of naphthols when previously we had expected different isomers. This was possible because we have already studied [1] a sufficiently large number of reference compounds. This cannot be said of any of the more usual spectroscopic techniques such as i.r. or n.m.r., both of which gave rather poorly resolved spectra. Analysis in these two cases would require spectra of authentic samples, otherwise little value could be gleaned from them. Spin labelling and spin trapping techniques are already used for the identification of various types of compound, but it seems that the applications of e.s.r. could become broader in scope. We do not envisage that it will ever replace any other standard analytical technique, but it could become more used in areas where there is insufficient reference data, or where the material possesses undesirable properties which make interpretation by other methods intractable or ambiguous.

EXPERIMENTAL

The spectra were observed using a Varian E4 spectrometer. The naphthoxyl radicals were obtained using a flow system as described previously.[1,3,9] Substrates were dissolved in water or in the minimum amount of ethanol, and the solutions diluted to 2×10^{-3} mol dm^{-3}. These solutions were oxidised in the flow system using cerium(IV) sulphate (2×10^{-3} mol dm^{-3}) in aqueous sulphuric acid (0.2 mol dm^{-3}).

Many of the naphthols were commercial materials; those which were not were prepared by standard methods given in ref. 2.

[7/1971 *Received, 9th August,* 1977]

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[7] W. T. Dixon and D. Murphy, *J.C.S. Perkin II*, 1975, 850.

[8] P. Ashworth, *Tetrahedron*, 1976, 261.

[9] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119