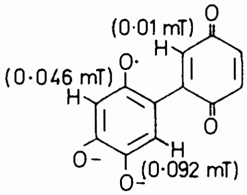
The Identification by Electron Spin Resonance Spectroscopy of Dimeric Species formed in the Autoxidation of Hydroquinone and Quinone

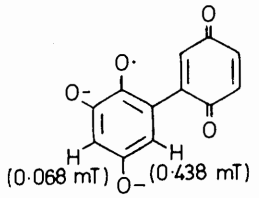
By **Paul Ashworth** and **William T. Dixon,*** Chemistry Department, Bedford College, Regents Park, London N.W.1

Some of the e.s.r. spectra observed during the autoxidation of hydroquinone and quinone appear to arise from the formation of dimeric products in the reaction since these spectra can be obtained from diquinone under similar conditions. The hyperfine splittings in these types of radicals can be explained in terms of the oxidation states of the two quinonoid rings.

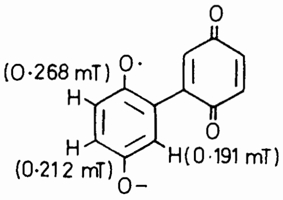
DURING our e.s.r. investigations of the autoxidation of hydroquinone and quinone,[1] we observed what we called ' tertiary radicals,' which, from their e.s.r. spectra, were identified as the dimeric species (IA) and (IB). Radical (IA) had apparently been observed before [2] during the reduction of diquinone by glucose in 10% NaOH, but had been identified as radical (II). We have previously advanced reasons [1] why such an assignment must be incorrect, for under the strongly alkaline conditions employed hydroxylation of the quinone ring invariably occurs giving rise to radicals of type (I). The three doublet splittings observed (0·092, 0·046, and 0·01 mT) are also consistent with (IA) rather than (II).



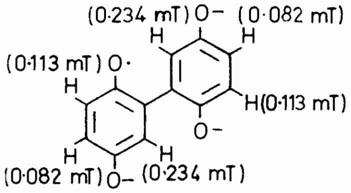
(IA)



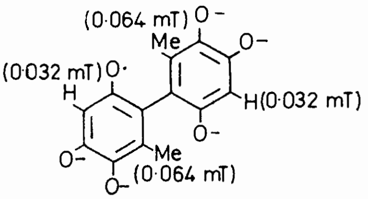
(IB)



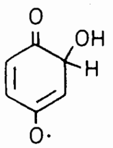
(II)



(IIIA)



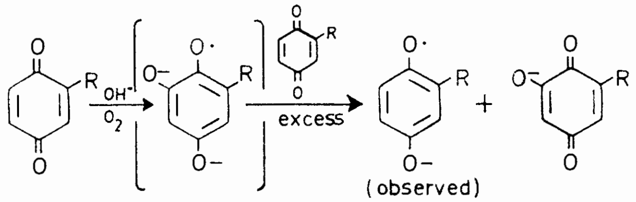
(IIIB)



(IV)

Radicals of type (IIIA) and (IIIB), containing a fully reduced second ring, have been observed [3,4] during the electro-reduction of certain quinones. It is found that the odd electron is shared equally between the two rings (fast spin exchange) even in radical (IIIB), where a high dihedral angle might be expected, and splitting from pairs of equivalent protons is observed in the spectra.

We have now obtained an authentic spectrum of radical (II), in which the e.s.r. coupling constants (0·268, 0·212, and 0·191 mT) are typical of a substituted semiquinone. This spectrum is identical to that obtained by Pedersen [5] during the autoxidation of *p*-benzoquinone, but which was ascribed by him to radical (IV), postulated as the chief intermediate in the hydroxylation process of quinones. However since our spectrum was obtained from diquinone in very dilute alkali, conditions under which only primary radicals are observed,[1] we can be certain that we are correct in our assignment.



Further, from the quinone under the usual conditions for obtaining secondary radicals (10% NaOH), we observed the spectra of (IA) and (IB), previously obtained by us from hydroquinone or quinone under the same conditions. The small doublet splitting of 0·01 mT in the spectrum of radical (IA) is apparently due to coupling with one proton in the quinone ring substituent, and from our knowledge of the relationship between the splittings in primary and secondary radicals we can estimate a small splitting of *ca.* 0·005 mT in radical (II). In fact a splitting of this order was observed in the spectrum obtained by Pedersen, but which we were unable to see due to the limitations of resolution.

We now feel that we have found the correct identity of the radicals associated with the various e.s.r. spectra obtained by us and by other workers during the autoxidations of hydroquinones and quinones. It is interesting that the quinone ring substituent leads to very little delocalisation of the odd electron, whereas the radicals of type (III), containing a fully reduced second ring, exhibit fast spin exchange between the two rings.

[3/1613 *Received*, 31*st July*, 1973]

---

[1] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.

[2] D. C. Reitz, J. R. Hollahan, F. Dravnieks, and J. E. Wertz, *J. Chem. Phys.*, 1961, **34**, 1457.

[3] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 1964, **41**, 284.

[4] J. Pilar, I. Buben, and J. Pospisil, *Coll. Czech. Chem. Comm.*, 1972, **37**, 3599.

[5] J. A. Pedersen, *J.C.S. Perkin II*, 1973, 424.