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ESR Spectra of Monoprotonated Semiquinone Radicals Formed during Photolysis of *p*-Benzoquinone and Its Methyl Derivatives

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Proton hyperfine coupling constants of monoprotonated *p*-benzosemiquinone, durosemiquinone, 2,6-dimethyl-*p*-benzosemiquinone, 2,5-dimethyl-*p*-benzosemiquinone and methyl-*p*-benzosemiquinone radicals were determined from ESR spectra during photolysis of the corresponding quinones under identical conditions, *i.e.*, in ethanol and at about 20 °C. By considering all these constants together, the ESR spectra were assigned and following results obtained: (1) the hydroxyl groups were at the oxygen atom further from the methyl substituents, (2) the coupling constant was generally -1.86—-1.65 G for the hydroxylic protons, (3) the absolute value of the coupling constant for both ring and methyl protons was in the range 0—0.7 G for *ortho*-positions and 4.3—5.2 G for *meta*-positions relative to the hydroxyl group, and (4) the hydroxylic proton of durosemiquinone had an exceptionally small coupling constant because of steric hindrance of the methyl groups. The temperature dependence of the coupling constants in *p*-benzosemiquinone revealed an asymmetry of the meta-ring protons at low temperature due to the hindrance of hydroxyl group rotation. The coupling constants for *p*-benzosemiquinone were calculated with the INDO method. However, the results were not satisfactory because the calculated coupling constant was too large for the ortho-protons and the asymmetry calculated for the conformation with the hydroxylic proton fixed at one of the stationary sites was too small to interpret the observations.

Ultra-violet photolysis of quinones in a hydrogen-donating solvent results in the formation of monoprotonated semiquinone radicals, which have been characterized by flash photolysis studies[1] and by electron spin resonance (ESR) studies during photolysis. ESR spectra of the semiquinone radicals have been observed under various conditions as listed below:

quinone	solvent
p-benzoquinone	alcohols,[2,3,8,9] acetone,[2] tri-*n*-butyl phosphate,[2,3] 1,2-dimethoxyethane,[2,5] tetrahydrofuran,[2,3,4] 1,4-dioxane,[2,8]
duroquinone	alcohols,[3,6,8] acetone,[4,6] tri-*n*-butyl phosphate,[3,6] sulpholane,[6] tetrahydrofuran,[3,4,6] 1,4-dioxane,[6,8] benzene,[6]
2,3-dimethyl-*p*-benzoquinone	1,2-dimethoxyethane,[4]
2,5-dimethyl-*p*-benzoquinone	1,2-dimethoxyethane,[4]
2,6-dimethyl-*p*-benzoquinone	alcohols,[7] acetone,[7] tri-*n*-butyl phosphate,[7] 1,2-dimethoxyethane,[7] tetrahydrofuran,[4,7] 1,4-dioxane,[7]
1,4-naphthoquinone	alcohols,[8,9] 1,4-dioxane,[8]
anthraquinone	2-propanol,[8] 1,4-dioxane.[8]

One of the principal aims of the present investigation is the comparison of the ESR spectra of the *p*-benzosemiquinone radical and its methyl derivatives in a particular solvent, ethanol, because hyperfine coupling constants of semiquinone radicals depend on the nature of solvent[3,6,7] and on the temperature as well.[3,5]

The ESR spectra during photolysis of *p*-benzoquinone and its derivatives in alcohols have been studied:[10,11] it was found that the spectra of both semiquinone radicals and semiquinone anions were recorded simultaneously even in neutral solution. The mechanism of formation of these radicals has also been discussed.[10,11] The present investigation is an extension of our previous ones and concerns only the semiquinone radical spectra observed during steady-state photolysis. The observed hyperfine coupling constants of the *p*-benzosemiquinone[2] and durosemiquinone radicals[6] were compared with those calculated using a valence-bond treatment with variable parameters in an attempt to understand the dependence of the hyperfine coupling constants on the nature of solvent. Later, the spectrum of *p*-benzosemiquinone was reproduced with McLachlan's simple SCF molecular orbital treatment,[5] but the agreement seems to be fortuitous because this treatment included many adjustable parameters and, in addition, it is valid only for alternant hydrocarbon radicals.[12] In the present investigation, the *p*-benzosemiquinone radical spectrum was calculated in the INDO approximation, which has been successful in reproducing ESR spectra of a fairly large number of free radicals.[13] Unfortunately, the INDO treatment did not give satisfactory results for the *p*-benzosemiquinone radical. To demonstrate the failure of the INDO method for this particular radical is another aim of this report.

Experimental

The apparatus used has been described in detail elsewhere.[14] A solution of the quinones in ethanol was first bubbled with helium and then photolyzed with unfiltered light from a super-high pressure mercury arc while flowing at a rate of about 4 ml/min. All chemicals were analytical grade and were used without further purification.

When the intense spectrum of the semiquinone anion interfered the recording of that of the semiquinone radical, the anion was suppressed by adding a small amount of acetic acid to the solution.[10]

Results and Discussion

Assignment of Hyperfine Coupling Constants. The ESR spectrum recorded during the photolysis of durosemiquinone in ethanol with a small amount of acetic acid is shown in Fig. 1A. It clearly shows a hyperfine structure attributable to two sets of six equivalent protons and a proton (as shown by the stick spectrum in the figure), though the outmost hyperfine lines were too weak to be recorded with our conditions. The spectrum is attributed to a monoprotonated durosemiquinone radical and is essentially the same as those previously reported.[3,6] Although the hyperfine coupling constants are temperature dependent, their values at 22 °C are given in Table 1 for comparison with those of other semiquinone radicals.

Figure 1B shows an ESR spectrum (indicated by the sticks) of 2,6-dimethylbenzosemiquinone radical recorded during the photolysis. Some weak lines are observed in the central part, which are thought to be due to 2,6-dimethyl-*p*-benzosemiquinone anion, because they disappeared when a small amount of acetic acid was added to the solution. A large hyper-

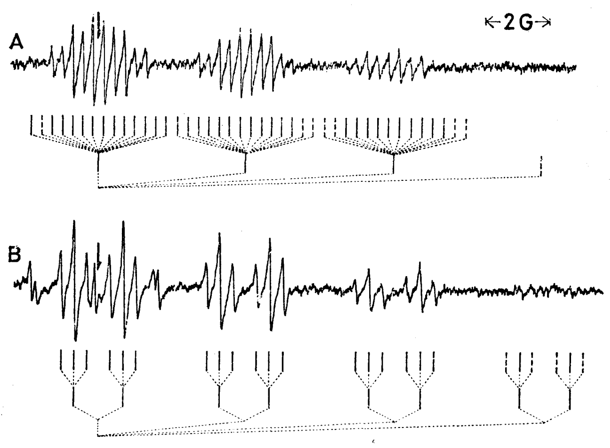
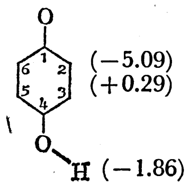
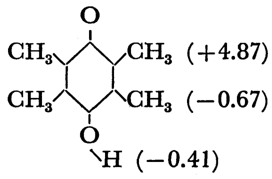
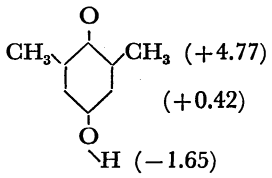
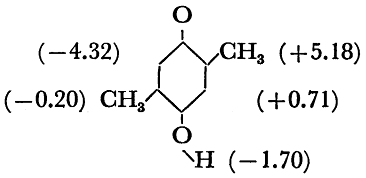
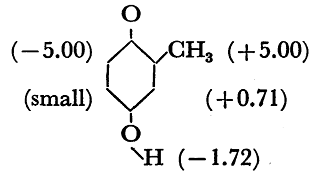


Fig. 1. ESR spectra of monoprotonated (A) durosemiquinone radical observed during photolysis of ethanol solution of duroquinone (5 mM) in the presence of a small amount of acetic acid at 31 °C and (B) 2,6-dimethylbenzosemiquinone radical observed during photolysis of ethanol solution of 2,6-dimethyl-*p*-benzoquinone (5 mM) at 32 °C. A high-field half of the spectra is shown. Arrows indicate the center of the spectra.

Table 1. Observed hyperfine coupling constants of protons in monoprotonated semiquinone radicals formed during photolysis of ethanol solutions

Parent molecule	Temperature	Radicals and hyperfine coupling constants (in G)
p-Benzoquinone	19 °C	
Duroquinone	22 °C	
2,6-Dimethyl-*p*-Benzoquinone	23 °C	
2,5-Dimethyl-*p*-Benzoquinone	18 °C	
Methyl-*p*-Benzoquinone	24 °C	

fine splitting of 4.77 G, due to six equivalent protons, indicates that hydrogen addition occurs exclusively on the oxygen atom attached to the carbon at the 4-position, remote from the two methyl groups. The observed hyperfine coupling constants are essentially the same as those reported previously[7] and are listed in Table 1.

In addition to the coupling constants of the two semiquinone radicals, hyperfine coupling constants previously determined[10] at about 20 °C for *p*-benzosemiquinone radical, 2,5-dimethylbenzosemiquinone radical and methyl-*p*-benzosemiquinone radical are shown in Table 1 for comparison. The ESR spectra of 2,5-dimethylbenzosemiquinone radical in alcohols and of methyl-*p*-benzosemiquinone radical have not been assigned before.

Based on a molecular orbital[3,4] and a valence-bond[2,6] treatment, the spin density has a large positive value on carbon atoms at the *meta*-position (relative to the hydroxyl group) and a small negative value on the carbon atom at the *ortho*-position. Therefore, if one considers the induction of a negative spin on the orbital of the ring-hydrogen and a positive spin on the orbital of the methyl-hydrogen, the observed hyperfine coupling constants as well as their sign may be assigned as shown in the third column in Table 1, except for the monoprotonated methyl-*p*-benzosemiquinone radical. The ESR spectrum observed during photolysis of the methyl-*p*-benzoquinone in acidic ethanol had a hyperfine structure due to six protons, four of which are equivalent (see Fig. 6b in Ref. 10). Although one proton is missing, the spectrum is tentatively assigned to methyl-*p*-benzosemiquinone radical as shown in Table 1 by comparing hyperfine coupling constants of other semiquinone radicals and by analogy with photochemical reactions of other quinones. The hyperfine coupling constants of the ring proton and that of the methyl protons at the *meta*-positions are probably accidentally the same, and the hyperfine coupling constant of one of the *ortho*-ring protons was too small relative to the line-width (150 mG) to be observed. The hyperfine coupling constant of the hydroxylic proton was in the range $-1.7\sim-1.9$ G for all semiquinone radicals except for durosemiquinone radical where a large steric hindrance of the methyl groups may exist (see below).

The Temperature Dependence of the Hyperfine Coupling Constants. The absolute value of the hyperfine coupling constant of the ring protons and methyl protons decreases slightly with decreasing temperature, whereas the hyperfine coupling constant of the hydroxylic proton increases rather remarkably, as shown in Fig. 2 for the *p*-benzosemiquinone radical. Although such a tendency has already been reported,[3] it should be stressed that the protons at 2- and 6-positions become inequivalent at low temperature because of hindrance to rapid rotation of the hydroxyl group.

The spectrum of *p*-benzosemiquinone radical consists of three pairs of triplets at high temperature. The third and fourth triplet patterns from the low-field end of the spectrum change of five-line patterns at low temperature. Using the modified Bloch equation,[15] the change of the patterns could be reproduced well from the hyperfine coupling constants and the linewidth estimated from the outer triplets, as shown in Fig. 3. The good agreement between observed and simulated patterns shows unambiguously that the difference in hyperfine coupling constant between protons at 2- and 6-positions is equal to 7.5%. The difference was found to be 6.3% in tetrahydrofuran[4]

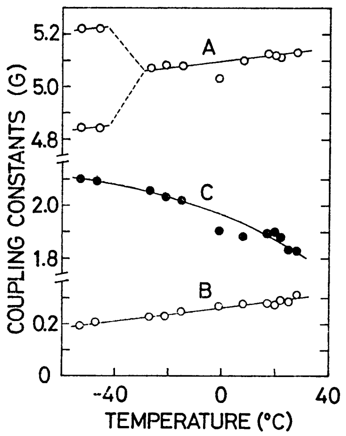


Fig. 2. Temperature dependence of the hyperfine coupling constants of the ring proton at (A) 2- and 6-positions (negative in sign) and (B) 3- and 5-positions and (C) of hydroxylic proton (negative in sign) in monoprotonated *p*-benzosemiquinone radical in ethanol.

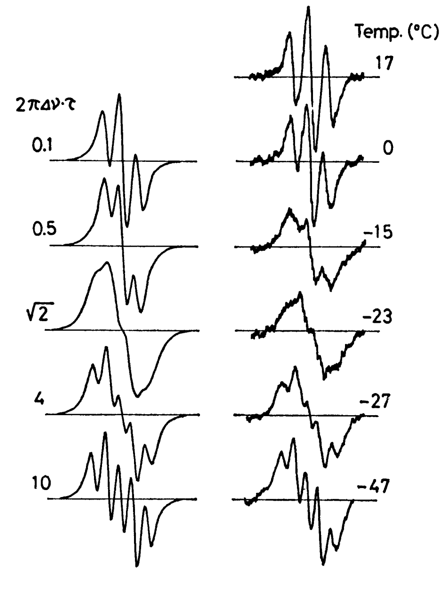


Fig. 3. Change of the ESR spectrum of *p*-benzosemiquinone radical due to the conformational exchange of the hydroxylic proton between two stationary sites in the nodal plane of ring π-system in the intermediate range of exchanging rate. Left spectra: simulated from the modified Bloch equations and the hyperfine coupling constants in Fig. 2 for each value of $2\pi\Delta\nu\cdot\tau$ shown in the figure (see also the text). Right spectra: observed at each temperature shown in the figure. Only the third triplet component (at room temperature) from the low field is shown.

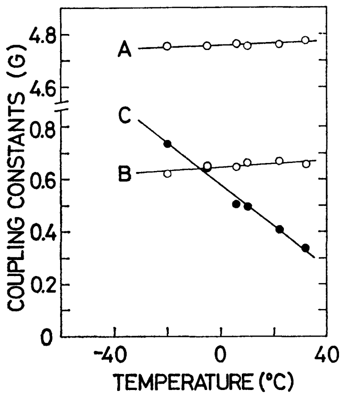


Fig. 4. Temperature dependence of hyperfine coupling constant of methyl protons at (A) 2- and 6-positions (negative in sign) and (B) 3- and 5-positions and (C) of hydroxylic proton (negative in sign) in monoprotonated durosemiquinone radical in ethanol.

and 5.4% in 1,2-dimethoxyethane.[5)]

The temperature dependence of the hyperfine coupling constants in durosemiquinone radical is shown in Fig. 4. The absolute value of the hyperfine coupling constant of the hydroxylic proton increases greatly with decreasing temperature, consistent with the previous observation for durosemiquinone radical in 2-propanol, tetrahydrofuran and tri-*n*-butyl phosphate.[3)] In addition, it was found in the present study that the hyperfine coupling constants of the methyl protons decrease slightly in absolute value, with decreasing temperature, as do those of the ring protons in the *p*-benzosemiquinone radical. The magnitude and sign of the hyperfine coupling constant of the hydroxylic proton is determined by two opposing contributions: one is a negative contribution from conjugation between the oxygen and the aromatic π-system and the other is a positive contribution from the direct overlap between the aromatic π-system and the proton.[3,16)] If the hydroxylic proton is in the nodal plane of the π-system, its hyperfine coupling constant is determined exclusively by the former contribution and therefore has a negative sign. When rotation about the C–O bond brings the proton out of the nodal plane, the coupling constant approaches zero and then increases. The observed magnitude and temperature dependence of the hyperfine coupling constant of the hydroxylic proton indicate that it is negative in ethanol as in 2-propanol and tetrahydrofuran,[3)] although the proton is located more out of the nodal plane in the durosemiquinone radical than in the other semiquinone radicals because bulky methyl groups are closer to the hydroxyl group in the durosemiquinone radical. At low temperatures, the position of the hydroxylic proton is closer to the nodal plane, giving a hyperfine coupling with a large negative value.

Molecular Orbital Calculations. Hyperfine coupling constants of semiquinone radicals were first examined theoretically with a valence-bond treatment with parameters adjusted to fit the calculated spin densities to those observed and to account for the dependence of the coupling constants upon the solvent polarity.[2,6)] Later, McLachlan's approximate self-consistent treatment was used to reproduce the observed hyperfine coupling constants.[3–5)] However, agreement between the observed and calculated coupling constants obtained by this molecular orbital treatment seem to be fortuitous,[5)] because the calculation involved many adjustable parameters.

In the present investigation, we tried to calculate the hyperfine coupling constants of the protons in a semiquinone radical using the INDO approximation. However, though this molecular orbital treatment developed by Pople and Beveridge has been shown to be promising in predicting the value of the hyperfine coupling constants for several kinds of free radicals without any parametrization other than the conformation of the free radicals,[12)] we could not get satisfactory results.

TABLE 2. PROTON HYPERFINE COUPLING CONSTANTS OF MONOPROTONATED *p*-BENZOSEMIQUINONE RADICAL CALCULATED BY THE INDO METHOD AND THOSE OBSERVED IN ETHANOL SOLUTION

Hyperfine coupling constants (G)	
Calculated	Observed
Planar	At −53 °C
$a_2 = -6.0218$	-5.22
$a_6 = -6.0041$	-4.84
$a_3 = 3.3539$ $a_5 = 3.4095$	$\left.\right\}$ 0.20
$a_{OH} = -0.7276$	-2.10
Non-planar	At 19 °C
$\left.\begin{matrix}a_2=\\a_6=\end{matrix}\right\}$ -6.0747	$\left.\right\}$ -5.09
$\left.\begin{matrix}a_3=\\a_5=\end{matrix}\right\}$ 3.4945	$\left.\right\}$ 0.29
$\alpha_{OH} = 15.7278$	-1.86

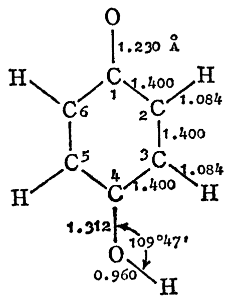


Table 2 shows representative results obtained from the INDO calculations of the proton hyperfine coupling constants in *p*-benzosemiquinone radical for the conformation with normal bond lengths and bond angles also shown in the same table. The isotropic hyperfine coupling for all the protons was derived from the 1s spin density on the corresponding hydrogen atoms obtained from the INDO approximation by using the proportionality constant relating the spin density to the coupling constant, 539.86 G.[13)]

The calculated hyperfine coupling constants of the protons do not agree with the observed ones. The hyperfine coupling constants of the hydroxylic proton depend very much on the conformation of the radical, *i.e.*, whether the proton is in the nodal plane or out of it. However, the coupling constants of the ring protons are not affected by the conformation. Both of two extreme conformations (one was planar with the hydroxylic proton in the nodal plane and the other was non-planar with the hydroxylic proton in the symmetry plane perpendicular to the ring) gave hyperfine coupling constants of 3.4~3.5 G for protons at 3- and 5-positions (*ortho*-position relative to the hydroxyl group) and about −6.0 G for 2- and 6-positions (*meta*-positions relative to the hydroxyl group). Although the values for the *meta*-positions are rather close to the observed ones, the values for the ortho-positions are ten times as large as the observed values. In addition, the calculated difference in hyperfine coupling between the two protons at the *meta*-position is 0.29% for the planar conformation, which is very much smaller than the observed difference of 7.5%.

The agreement between calculation and observation for the hydroxylic proton could be obtained by arbitrarily adjusting the angle of rotation of the hydroxyl group around the C–O bond. However, the disagreement between calculation and observation in the magnitude of the hyperfine coupling constants of the protons at *ortho*-positions and that in the difference in hyperfine coupling of the protons at *meta*-positions indicate that INDO calculations produce very poor results for the monoprotonated *p*-benzosemiquinone radical. The reason for this is not known at this moment and is left to further theoretical investigation. We made several calculations for other bond lengths and bond angles in the acceptable range, but no appreciable improvement could be attained in the calculated results. We also examined unsuccessfully the effect of a hydrogen bond between the hydroxyl group of the radical and solvent ethanol. It may be interesting to note that the INDO method did not give satisfactory results for the hyperfine coupling constants of *p*-benzosemiquinone anion either.[13)]

Conclusions

The proton hyperfine coupling constants of shortlived monoprotonated semiquinone radicals (*p*-benzosemiquinone, durosemiquinone, 2,6-dimethylbenzosemiquinone, 2,5-dimethylbenzosemiquinone and methyl-*p*-benzosemiquinone radicals) have been compared with each other under identical conditions, namely, in ethanol solvent and at about 20 °C and assigned. Among them, 2,5-dimethylbenzosemiquinone and methyl-*p*-benzosemiquinone radicals, at least in ethanol, were first assigned in this investigation. The observed hyperfine coupling constants of the hydroxylic proton are all in the range $-1.86\sim-1.65$ G except for the durosemiquinone radical, where the hyperfine coupling constant is as small as −0.41 G, indicating that the hydroxylic proton is far out of the nodal plane of the ring π-system due to the bulky methyl groups located close to the hydroxyl group. The ESR spectrum of methyl-*p*-benzoquinone shows a hyperfine structure due to six protons, but it has been tentatively assigned to methyl-*p*-benzosemiquinone radical by comparing with the coupling constants in other semiquinone radicals.

The proton hyperfine coupling constants for *p*-benzosemiquinone radical were calculated in the INDO approximation. However, the results were unsatisfactory because the calculated hyperfine coupling constant of the protons in the *ortho*-positions relative to the hydroxyl group was much smaller in magnitude than the observed one. Furthermore, the calculated difference in hyperfine coupling between two protons in the *meta*-positions was too small to account for the hyperfine structure of the spectrum observed at low temperature where the hydroxylic proton is thought to be fixed at one of the stationary positions in the nodal plane of the ring π-system.

References

1) N. K. Bridge and G. Porter, *Proc. Roy. Soc. Ser. A.*, **244**, 259 (1958), **244**, 276 (1958). D. R. Kemp and G. Porter, *Proc. Roy. Soc. Ser. A*, **326**, 131 (1972); *Chem., Commun.* **1969**, 1029.

2) T. E. Gough, *Trans. Faraday Soc.*, **62**, 2321 (1966).

3) T. E. Gough and G. A. Taylor, *Can. J. Chem.*, **47**, 3717 (1969).

4) T. E. Gough, *ibid.*, **47**, 331 (1969).

5) R. Wilson, *J. Chem. Soc., B*, **1968**, 1581.

6) T. A. Claxton, T. E. Gough, and M. C. R. Symons, *Trans. Faraday Soc.*, **62**, 279 (1967).

7) T. A. Claxton, J. Oakes, and M. C. R. Symons, *ibid.*, **63**, 2125 (1967).

8) S. K. Wong, W. Sytnyk, and J. K. S. Wan, *Can. J. Chem.*, **50**, 3052 (1972).

9) P. B. Ayscough and R. C. Sealy, *J. Chem. Soc., B*, **1973**, 543.

10) H. Yoshida, K. Hayashi, and T. Warashina, This Bulletin, **45**, 3515 (1972).

11) H. Yoshida, J. Shoma, and T. Warashina, *ibid.*, **47**, 1396 (1974).

12) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

13) A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970).

14) H. Yoshida and T. Warashina, This Bulletin, **44**, 2950 (1971).

15) J. A. Pople, W. G. Schneider, H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw Hill, New York (1959).

16) A. B. Barabas, W. F. Farbes, and P. D. Sullivan, *Can. J. Chem.*, **45**, 224 (1967).