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Electron Spin Resonance during Photolysis of *p*-Benzoquinone and Its Derivatives in Ethanol

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Electron spin resonance measurements were carried out at room temperature during photolysis of solutions containing *p*-benzoquinone, 2-methyl-*p*-benzoquinone, 2,5-dimethyl-*p*-benzoquinone and 1,4-naphthoquinone in ethanol. From all quinones, the semiquinone radicals and semiquinone anions are found to form simultaneously. When the solution is made acidic, the semiquinone anion transforms into the semiquinone radical, so that the spectrum of the latter is easily determined. For benzoquinone, the semiquinone radical is formed efficiently by light of $\lambda \approx 300$ nm, and has a life of about 0.05 sec. The semiquinone anion is formed by light of $\lambda \approx 460$ nm and is rather long-lived (about 0.5 sec). These results suggest that the semiquinone anion may be formed mostly by photodissociation of charge-transfer complex between benzoquinone and alcohols. Observed proton hyperfine coupling constants were subjected to the molecular orbital treatment. The coupling constants in all the semiquinone anions examined are well interpreted by McLachlan's approximate SCF-MO method and Colpa-Bolton's relation with $Q=27$ G and $K=12.8$ G. However, good agreement is not attained between the observed coupling constants and the calculated ones for the semiquinone radicals.

Semiquinone anions and semiquinone radicals are well known to be involved in both reduction and oxidation processes between quinones and hydroquinones. Since Venkataraman and Fraenkel's pioneering work of detecting electron spin resonance (ESR) spectra of semiquinone anions by oxidizing hydroquinone and durohydroquinone in alkaline solution with oxygen,[1] ESR studies have been extensively made on semiquinone anions formed by oxidizing hydroquiones,[2,3] and by reducing quinones with glucose or sodium dithionite,[3] or electrochemically[4,5] in alkaline solutions. Semiquinone anion was also observed by photolysing duroquinone in the presence of excess alkoxide ion in the solution.[6]

Observed hyperfine structure due to protons in semiquinone anions were first examined with reference to the spin densities calculated from the simple Hückel molecular orbital treatment combined with the McConnell relation.[7] Their observed values agreed rather well with the theoretically expected ones, except for methyl-substituted benzosemiquinone anions.[3,8] The hyperfine coupling constants were found to be affected, more or less depending on the position of proton, by solvent,[4] which was interpreted as due to the complexing between the oxygen atoms in the semiquinone anion and the solvent molecules, using the approximate SCF-MO method developed by McLachlan[9] to estimate the spin densities with the Coulomb integral of oxygen atoms and the resonance integral of C–O bond as adjustable parameters.[5,10] Later, this solvent effect was elucidated from the hyperfine structure due to ^{13}C nuclei.[11,12]

By means of flash photolysis, Bridge and Porter first observed semiquinone anions and radicals as intermediate entities formed in the solutions of many quinones.[13] Photolysis was found to be a convenient and useful way to form semiquinone radicals for ESR studies. Gough and Symons detected ESR spectra of *p*-benzosemiquinone[14] and durosemiquinone radicals[6,15] and described the dependence of their hyperfine structure upon the nature of the solvent by the valence-bond treatment. They reported that the semiquinone radicals or anions were observable depending on pH of the solutions. Recently, Wilson[16] examined the hyperfine structure of his spectrum of *p*-benzosemiquinone radical in photolyzed dimethoxyethane solution in reference with the McLachlan's SCF-MO calculation of spin densities and excess charges and Colpa and Bolton's relation[17] instead of the McConnell's.

The present authors studied the kinetical behavior of free radicals formed during photolysis of benzophenone solution in alcohols by using a flow-technique combined with ESR.[18] Here, this study is extended to solutions of *p*-benzoquinone and its derivatives in alcohols, mainly ethanol, and it is found that both semiquinone radicals and anions are formed simultaneously in neutral solution. The mechanism of

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[1] B. Venkataraman and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **77**, 2707 (1955); *J. Chem. Phys.*, **23**, 588 (1955).

[2] B. Venkataraman, B. G. Segel, and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959).

[3] G. Vincow, G. K. Fraenkel, *ibid.*, **34**, 1333 (1961).

[4] E. W. Stone and A. H. Maki, *ibid.*, **36**, 1944 (1962).

[5] R. Dehl and G. K. Fraenkel, *ibid.*, **39**, 1793 (1963).

[6] T. E. Gough and M. C. R. Symons, *Trans Faraday Soc.*, **62**, 269 (1966).

[7] H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956); H. M. McConnell and D. B. Chesnutt, *ibid.*, **28**, 107 (1958).

[8] R. W. Brandon and E. A. C. Lucken, *J. Chem. Soc.* **1961**, 4273.

[9] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

[10] J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

[11] E. W. Stone and A. H. Maki, *J. Amer Chem. Soc.* **87**, 454 (1965).

[12] M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965).

[13] N. K. Bridge and G. Porter, *Proc. Roy. Soc., Ser. A*, **244**, 259, 276 (1958).

[14] T. E. Gough, *Trans Faraday Soc.*, **62**, 2321 (1966).

[15] T. A. Claxton, T. E. Gough, and M. C. R. Symons, *ibid.*, **62**, 279 (1966).

[16] R. Wilson, *J. Chem. Soc., B*, **1968**, 1581.

[17] J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

[18] H. Yoshida and T. Warashina, This Bulletin, **44**, 2950 (1971).

their formation is examined in detail for *p*-benzoquinone. The observed hyperfine structure due to protons is discussed for all quinones examined in terms of the McLachlan's MO treatment and the Colpa and Bolton's relation.

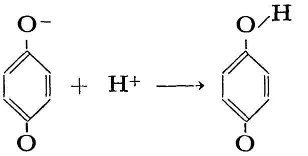
Experimental

The apparatus used has been described in detail previously.18) ESR measurements were carried out with a conventional X-band spectrometer (Varian, E-3) during photolysis with a super-high pressure mercury arc (Philips, SP 500) of solutions from which dissolved oxygen was removed by bubling helium gas beforehand. The effective volume of a quartz flat cell was 7×0.2×32 mm.

All chemicals were analytical grade and used as received without further purification, except where otherwise stated.

Results and Discussion

Formation and Decay of p-*Benzosemiquinone Anions and Radicals.* When the solution of *p*-benzoquinone in ethanol is photolyzed, the ESR signal as shown in Fig. 1a is observed. Apparently, the signal is composed of an quintet spectrum and that of triple double-triplet. The former is attributed to *p*-benzosemiquinone anion with four equivalent protons, while the latter is due to *p*-benzosemiquinone radical (monoprotonated benzosemiquinone). If the solution is made acidic by adding a small amount of acetic acid, almost all of the semiquinone anion transforms into the semiquinone radicals as expected from the observation in the flash photolysis study,13) through the protonation reaction,



(1)

though a weak spectrum of the semiquinone anion is still observable (see Fig. 1b). The observed concentration of the semiquinones is of the order of 10^{-6} M. The half-life is found, by shutting off and flashing the photolyzing light rapidly, to be a few hundreds milliseconds for the semiquinone anion and less than one hundred milliseconds (the response time of the spectrometer) for the semiquinone radicals in the absence of acetic acid.

The temperature dependence of the yield was examined for both anion and radical at a fixed flow rate of solution, and the results are shown in Fig. 2 for methanol and in Fig. 3 for ethanol as solvent. The yield of anion decreases with increasing temperature, while that of radical remains almost unchanged. The dependence of yield upon the resident time of solution in the cell (the effective volume of the cell/the flow rate) is examined for the solution in methanol, as shown in Fig. 4. As the solution is heated during photolysis, its temperature varys depending on the flow rate. In Fig. 4, the observed values are plotted after correcting the temperature effect by using the relationship between the yield and the temperature shown in Fig. 2. The observed yield of anion increases remarkably with increasing the resident time of solution, reaching at a plateau value. This suggests that the life time of

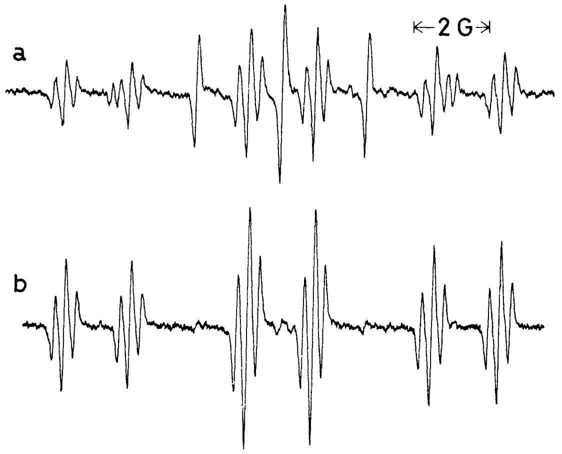


Fig. 1. ESR spectra observed during photolysis of *p*-benzoquinone solution in ethanol (5.5 mM). (a) Spectra due to benzosemiquinone radical (triple double-triplets) and due to benzosemiquinone anion (quintet) formed in neutral solution. (b) Spectrum due to benzosemiquinone radical in acidic solution containing 30 mM of acetic acid.

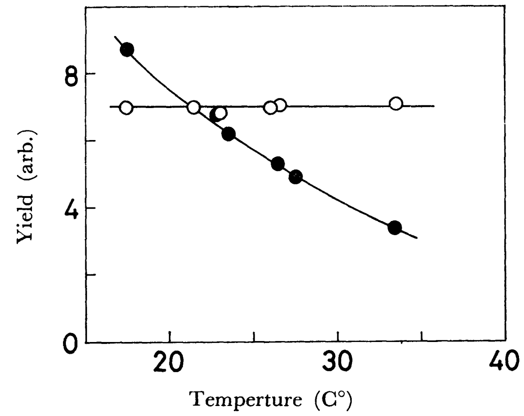


Fig. 2. Observed yield of benzosemiquinone radical (○) and benzosemiquinone anion (●) formed during photolysis of *p*-benzoquinone solution in methanol (5.5 mM) as a function of temperature. Resident time of flowing solution in the cell: 1.1 sec.

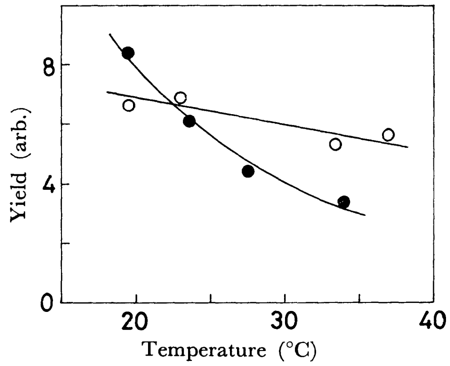


Fig. 3. Observed yield of benzosemiquinone radical (○) and benzosemiquinone anion (●) formed during photolysis of *p*-benzoquinone solution in ethanol (5.5 mM) as a function of temperature. Resident time of flowing solution in the cell: 1.5 sec.

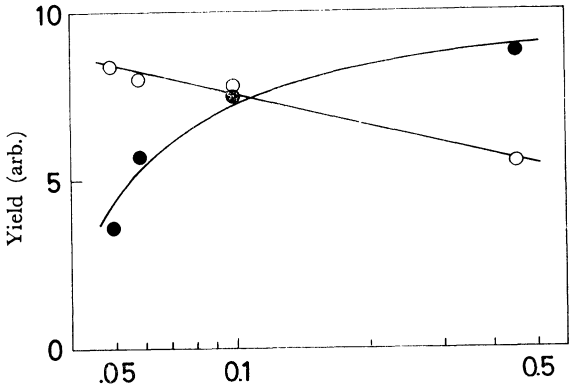
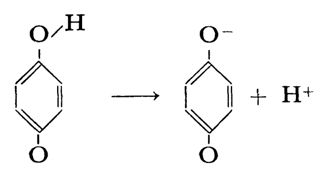


Fig. 4. Dependence of the yield of benzosemiquinone radical (○) and benzosemiquinone anion (●) formed during photolysis of *p*-benzoquinone solution in ethanol (5.5 mM) upon resident time of flowing solution in the cell. Observed values were plotted after the correction of temperature effect.

the anion is rather long (~0.5 sec) and that a fraction of the anions flow out of the cell before their chemical decay. On the other hand, the radical yield decreases with increasing resident time, and the reason is not known at the moment. This trend indicates, at least, that the radical formed disappears in the cell and that its life time is less than 0.05 sec. The above observation of the yields may indicate that the fate of anion, from its formation till disappearance, is independent of the radical in neutral solutions.

In order to elucidate the above argument, the effect of wavelength of the light on the formation of anion and radical was examined by inserting a cut-off filter in the light path. The results are shown in Fig. 5, where the abscissa indicates the wavelength of 50% transmission of filters used and the plots at 270 nm represent the observed yield for the photolysis without filter. The free radical is formed efficiently with light of $\lambda<300$ nm, whereas the anion is formed with light of $\lambda\approx460$ nm. The initial faint decrease in the yield of anion at $\lambda=270-310$ nm may be interpreted by the process,



(2)

However, the anion forms mostly for the wavelength appreciably longer than that for the formation of the radical.

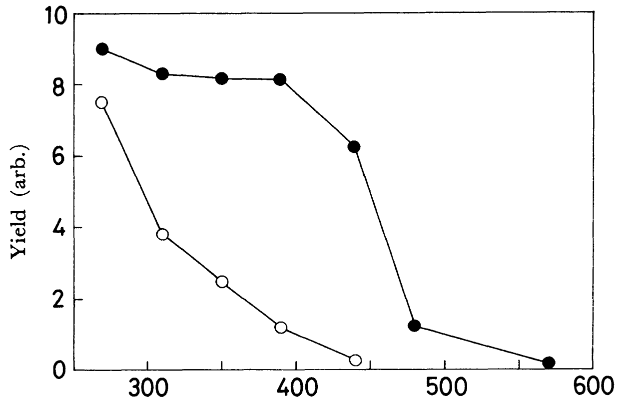


Fig. 5. Dependence of the yield of benzosemiquinone radical (○) and benzosemiquinone anion (●) formed during photolysis of *p*-benzoquinone solution in ethanol (5.5 mM) upon the wavelength of light.

The previous results of the flash photolysis study indicated that the primary process in the photolysis of duroquinone was the hydrogen abstraction of the singlet excited quinone to form semiquinone radical. However, in ethanol solution, formation of the semiquinone anion other than in process (2) was also suggested to occur.[13] In the present ESR study, the semiquinone anion is found not to form through the semiquinone radical, by using a selective wavelength of photolyzing light.

If electron transfer occurs directly from the solvent to *p*-benzoquinone under the light of $\lambda\approx460$ nm, the charge transfer interaction between *p*-benzoquinone and the solvent is necessarily involved so that the photo-excited electron donor and acceptor complex dissociates into ions. The efficiency of semiquinone anion formation did not change, though the ethanol was purified by distilling with concentrated sulfuric acid, refluxing with silver nitrate and sodium hydroxide and distilling again. Using dichloromethane as a solvent, the semiquinone radical is observed but the semiquinone anion is not. According to these results, the photo-excited quinone-alcohol complex probably dissociates to form the semiquinone anion, though the possibility cannot be excluded at this moment that some impurities in ethanol play an important role in the formation of the semiquinone anion.

An alternative interpretation is that the *p*-benzohydroquinone formed by disproportionation of the semiquinone radical[13] photo-dissociates to form the semiquinone anion. As a matter of fact, when the solution of *p*-benzohydroquinone in ethanol is photolyzed, an intense ESR spectrum of *p*-benzosemiquinone anion is observed, while the spectrum of semiquinone radical is so weak that it may be ignored. In this case, the question still remains as to why the hydroquinone dissociates to form the anion rather than to form the radical.

For all quinones examined, 2-methylbenzoquinone, 2,5-dimethylbenzoquinone and 1,5-naphthoquinone, corresponding semiquinone anions are observed in addition to semiquinone radicals.

Observed Hyperfine Coupling Constants. Proton hyperfine coupling constants in *p*-benzosemiquinone anion have been reported by several workers[1,2,19] in protic solvent, and the reported values are all very close to 2.368 determined by Venkataraman *et al.*[2] As it is independent of temperature in the range examined (18—36°C), this value was taken as a reference to determine hyperfine coupling constants in other semiquinones studied in the present investigation.

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[19] D. C. Reitz, F. Dravnieks, and J. E. Wetz, *J. Chem. Phys.*, **33**, 1880 (1960).

TABLE 1. OBSERVED PROTON HYPERFINE COUPLING CONSTANTS OF *p*-BENZOSEMIQUINONE RADICAL

Solvent	Temperature	Hyperfine coupling constant (G)		
		2 Ring protons	2 Ring protons	Hydroxy proton
Ethanol	19°C	0.29	5.09	1.86
	26°C	0.31	5.11	1.84
	36°C	0.34	5.21	1.81
Dichloromethane	34°C	0.85	5.64	1.40

Observed hyperfine coupling constants for the benzosemiquinone radical are summarized in Table 1. Their values in ethanol are compared with the values reported by Gough.[14)] They are found to be a little dependent on temperature; the coupling constants of ring protons increase with increasing temperature, whereas that of the hydroxy proton decreases. Such a trend agrees with what was observed by Wilson[16)] for the radical in dimethoxyethane as solvent.

Figure 6a and 6b show the ESR signals observed from neutral and acidic solution of 2-methylbenzosemiquinone in ethanol, respectively. Evidently, 2-methylbenzosemiquinone anion and some free radical are formed simultaneously in neutral solution, as in solution of *p*-benzoquinone. Venkataraman *et al.* reported hyperfine coupling constants of 2.462, 2.537 and 1.764 G for the ring protons and 2.045 G for the methyl protons, for 2-methylbenzosemiquinone anion.[2)] Although the signal in Fig. 6a is complex because of overlapping spectra, almost all hyperfine lines of the anion spectrum are seen at the position expected from the reported coupling constants. Separation between the outer most line (indicated by arrows) is measured to be 12.9 G, which agrees very well with 12.898 G, the sum of all hyperfine separation.

If the solution is made acidic, the signal becomes much simpler and only a spectrum of the quintet of double-doublet is observed. It may be ascribed to a neutral free radical. However, the number of protons involved is six, which indicates that the spectrum is not due to the semiquinone radical (monoprotonated 2-methylbenzosemiquinone). Although this interpretation has not yet been made, the observed hyperfine coupling constants are 5.00 (4 protons), 1.72 and 0.71 G at 24°C.

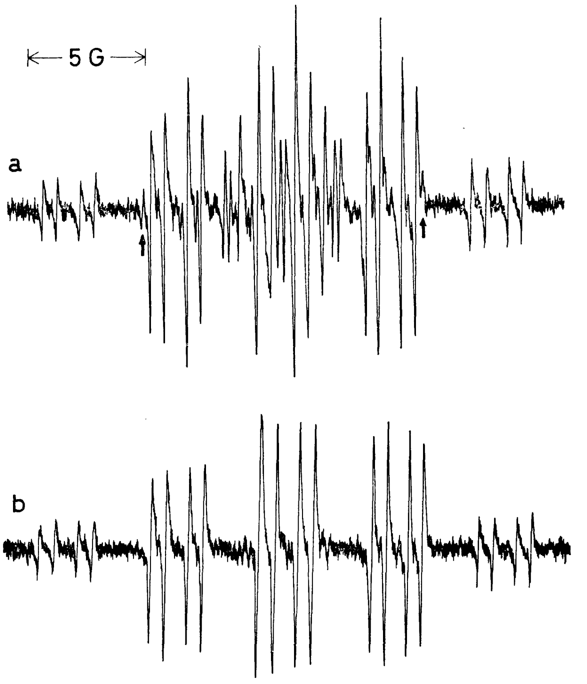


Fig. 6. ESR spectra observed during photolysis of 2-methyl-*p*-benzoquinone solution in ethanol (4.9 mM) (a) in the absence and (b) in the presence of 30 mM of acetic acid.

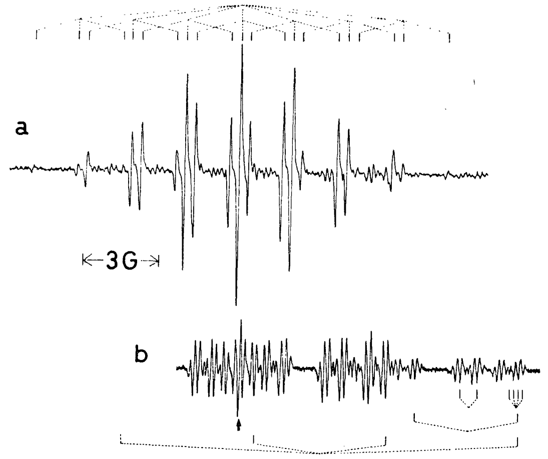


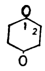
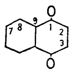
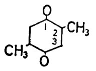
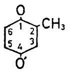
Fig. 7. ESR spectra observed during photolysis of 2,5-dimethyl-*p*-benzoquinone solution in ethanol (4.4 mM) (a) in the absence and (b) in the presence of 30 mM of acetic acid.

The ESR signal observed from the neutral solution of 2,5-dimethylbenzoquinone is shown in Fig. 7a. In addition to a very weak spectrum, the spectrum of septet of triplet (indicated by sticks) is observed and reasonably attributed to 2,5-dimethylbenzosemiquinone anion. The observed hyperfine coupling constant of 1.83 G due to the ring protons and that of 2.25 G due to the methyl protons are in good agreement with the values reported previously.[2)] Figure 7b shows the spectrum observed from the acidic solution, which has hyperfine structure due to three unequivalent protons (4.32, 1.70 and 0.71 G) and two kinds of methyl protons (5.18 and 0.20 G at 18°C) attributable to the 2,5-dimethylbenzosemiquinone. The weak background spectrum in Fig. 7a looks like the spectrum due to the semiquinone radical. Therefore, both the semiquinone radical and anion are also formed simultaneously in the neutral solution of 2,5-dimethylbenzoquinone.

ESR signals observed from 1,4-naphthoquinone show a rather complex feature, because they are sometimes recorded as emission lines depending on the measuring conditions and will be reported in detail elsewhere.[20)] In this case, the 1,4-naphthosemiquinone radical and anion are also formed simultaneously in neutral solution, but their spectra are separable by referring to the spectrum from the acidic solution.

[20)] H. Yoshida, J. Sohma, and T. Warashina, to be published.

Table 2. Proton hyperfine coupling constant observed and calculated from molecular orbital treatment

Semiquinone Anion	Calculated				Observed
	Position	Spin density	Excess charge	a_H	$\lvert a_H \rvert$
	1	0.11026	0.16202		
	2	0.08806	−0.01697	−2.3586	2.368
	0	0.21361	−0.62808		
	1	0.12913	0.14981		
	2	0.12305	−0.04014	−3.2592	3.25
	7	0.02386	0.01275	−0.6482	0.64
	8	0.01822	0.04537	−0.5025	0.51
	9	0.02695	−0.02712		
	0	0.17878	−0.64066		
	1	0.11281	0.15870		
	2	0.09859	−0.00924		
	3	0.07289	−0.04003	−1.9341	1.83
	0	0.20752	−0.63146		
	1	0.11309	0.16310		
	2	0.09331	−0.00824		
	3	0.07466	−0.03805	−1.9796	1.764[2]
	4	0.10994	0.15784		
	5	0.09372	−0.01830	−2.5086	2.537[2]
	6	0.08615	−0.01886	−2.3052	2.462[2]
	0	0.21582	−0.62582		
	0′	0.20549	−0.63345		

Wertz and Vivo[21], and Adams *et al.*[22] reported poor resolved spectra of the nephthosemiquinone anion, and later Venkataraman *et al.* suceeded in observing its spectrum with well resolved hyperfine structure.[2] The present observation (see Table 2) is in good agreement with those previously reported. The observed hyperfine coupling constants for the naphthosemiquinone radical are 6.80, 1.63 (2 protons), 1.50, 0.34 and 0.17 G (2 protons) at 34°C.

Molecular Orbital Calculation. The observed spectra of semiquinone anions and semiquinone radicals indicate well resolved hyperfine structure and, therefore, may be compared to molecular orbital calculations. Vincow and Fraenkel examined the observed hyperfine coupling constants of semiquinone anions with reference to the simple Hückel MO calculations and obtained a good agreement between the observed coupling constants and expected ones.[3] However, Brandon and Lucken claimed that the agreement was obtained not only for a unique pair but also for several pairs of parameters, the Coulomb integral of the oxygen atom and the resonance integral of the carbon-oxygen bond, in the frame of the simple Hückel MO calculations.[23] In the present investigation, McLachlan's approximate SCF-MO method[9] with a value of 1.2 for λ was used to calculate spin densities, ρ_i, and excess charge densities, ε_i. Colpa and Bolton[17] suggested the dependence of isotropic hyperfine coupling constants in hydrocarbon radical anions and cations upon the excess charge density, and postulated the relation, $a_i^H=(Q+K\varepsilon_i)\rho_i$. According to the observed spectra of radical ions of anthracene, Bolton and Fraenkel suggested −27 and −12.8 G for Q and K,[24,25] which were used in the present investigation. Calculations were made with FACOM 230—60 computer of Hokkaido University Computing Center.

For *p*-benzosemiquinone and 1,4-naphthosemiquinone anions, computations were carried out with adjustable parameters γ_{CO} and δ_O ($\alpha_O=\alpha+\delta_O\beta$ and $\beta_{CO}=\gamma_{CO}\beta$ where α and β are the Coulomb and resonance integral for carbon atoms and carbon-carbon bond) for the carbonyl group. In the range of 0.3—3.0 and 0.3—2.0 for δ_O and γ_{CO} (with the interval of 0.05 units), respectively, the best agreement is obtained between the observed hyperfine coupling constants and calculated ones with the values of $\delta_O=1.2$ and $\gamma_O=1.3$, as shown in Table 2.

Gendell *et al.*[10] obtained the best agreement with $\delta_O=1.6$, $\gamma_{CO}=1.55$ and $\lambda=1.2$, using the simple McConell relation, $a_i^H=-23.7\rho_i$. Therefore, it is indicated that the smaller parameters are more suitable for the Colpa-Bolton's relationship than for McConell's. Das and Fraenkel examined the proton and ^{14}C splittings of *p*-benzosemiquinone and anthrasemiquinone anions with the McLachlan's method of calculating spin densities and the simple McConell's relationship, and found that unique pair of δ_O and γ_{CO} did not interpret well the hyperfine splittings of these semiquinone anions simultaneously.[12] The present results suggest that a unique pair of parameters may interpret the hyperfine splittings of *p*-benzosemiquinone derivatives.

For the methyl substituted benzosemiquinone anions, a conjugative model C–C′–H$_3$ was considered, and the previously used parameters,[26] $\delta_{H_3}=-0.5$, $\delta_{C'}=-0.1$,

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21) J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **24**, 479 (1956).

22) M. Adams, M. S. Bois Jr., and R. H. Sands, *ibid.*, **28**, 774 (1958).

23) R. W. Brandon and E. A. C. Lucken, *J. Chem. Soc.*, **1961**, 4273.

24) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964).

25) L. C. Snyder and T. Amos, *ibid.*, **42**, 3670 (1965).

26) R. Wilson, *Can. J. Chem.* **44**, 551 (1966).

$\gamma_{C'-H_3}=2.5$ and $\gamma_{C'-C}=0.9$, were used. The calculated coupling constants of the ring protons agree rather well with the observed ones for dimethyl-*p*-benzosemiquinone and methyl-*p*-benzosemiquinone anions.

For semiquinone radicals, the agreement between experimental results and the molecular orbital calculations has not been attained satisfactorily. Any combinations of the parameters for hydroxy group ($\delta_O=0.3$—3.0 and $\gamma_{CO}=0.3$—1.7) do not account for the observed proton hyperfine coupling constants in the *p*-benzosemiquinone radical and those in the naphthosemiquinone radical simultaneously, if the parameters for the carbonyl group are fixed to the values determined above for the semiquinone anions. The replacement of one of the carbonyl groups in the semiquinone anions with a hydroxy group may cause the decrease in the electronic charge on the other carbonyl group, which requires a set of parameters for the carbonyl group in the semiquinone radicals different from that in the semiquinone anions. This may be one of the possible reasons why the satisfactory resutls have not been obtained in the MO calculations for the semiquinone radicals.

Conclusion

Photolyzing the solutions of *p*-benzoquinone, 1,4-naphthoquinone, 2-methyl-*p*-benzoquinone and 2,5-dimethyl-*p*-benzoquinone in alcohol at room temperature, the short-lived semiquinone anions and radicals were observed simultaneously by ESR measurements, combined with a flow technique. Although a fraction of the semiquinone radicals possibly transforms into the semiquinone anion, the latter is mostly formed directly from the solute.

The proton hyperfine coupling constants were determined for the semiquinone anions and radicals except for those from 2-methyl-*p*-benzoquinone. For the semiquinone anions, the observed coupling constants agree well with those computed from the McLachlan's approximate SCF–MO method and the Colpa-Bolton's relationship between the coupling constants and the spin densities and excess charge densities.

The authors express their sincere thanks to Prof. T. Higashimura for giving the opportunity to use the experimental facilities.