Oxygen-17 and Carbon-13 Hyperfine Interactions in the Electron Paramagnetic Resonance Spectrum of the Hydroquinone Cation Radical

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Abstract: The ^{17}O and ^{13}C esr hyperfine splitting constants have been measured for the hydroquinone ($HQ^{\cdot +}$) cation radical. For naturally occurring ^{13}C, three splitting constants were observed and were assigned magnitudes and signs of +4.23, −1.65, and −1.20 G; for an enriched ^{17}O sample a splitting constant of −7.83 G was assigned. These values have been compared with similar results for the *p*-benzosemiquinone ($PBSQ^{\cdot -}$) anion radical. Evaluation of the spin density distributions from the available data shows that within the series $PSBQ^{\cdot -}$ in DMSO, $PBSQ^{\cdot -}$ in H_2O, and $HQ^{\cdot +}$ there is decreasing spin density on oxygen caused by the increasing environmental perturbations. The data show that there is a close relationship between the $HQ^{\cdot +}$ and the $PBSQ^{\cdot -}$. Molecular orbital calculations were performed to reproduce the spin density distributions at all positions as estimated from the hyperfine splitting data. In the light of these additional data the σ–π parameters for oxygen and carbon have also been reevaluated for these systems. The measured g values for the three systems are also found to correlate well with the spin density on oxygen and the energy of the orbital containing the unpaired electron.

Solvent perturbations of the *p*-benzosemiquinone ($PBSQ^{\cdot -}$) anion radical are well documented,[2a] the effect being greatest for hydroxylic solvents which presumably hydrogen bond to the carbonyl oxygen atom. It therefore seems logical to consider the hydroquinone cation radical ($HQ^{\cdot +}$) as an extreme case of this type of perturbation. This suggestion has been made previously with regard to the dimethyl derivatives[2b] but has not been tested in detail.

The major effect of such perturbations is to change the spin density distribution in the carbonyl groups. These spin density changes have previously been inferred from changes in g values, which are predicted to depend primarily on the spin density on the oxygen atom. The change of approximately a factor of 2 in the difference from the free spin g value between the $PBSQ^{\cdot -}$ and $HQ^{\cdot +}$ is assumed to result from a corresponding spin density change. The effects on the ring positions are small, and therefore, measurements of the proton hyperfine splitting constants give no information on the spin distribution in the carbonyl groups. However, more direct information on the spin density changes in the carbonyl group can be obtained from the measurement of oxygen-17 and carbon-13 interactions. These measurements have already been made[2a,3,4] for the $PBSQ^{\cdot -}$ radicals in a variety of solvents, but have not been measured for the $HQ^{\cdot +}$ radicals, and the purpose of this paper is to report on the measurement of the ^{17}O and ^{13}C splitting constants for this radical. These results are then used to examine our contentions regarding the similarity of the $HQ^{\cdot +}$ and $PBSQ^{\cdot -}$ radicals by means of a comparison between $PBSQ^{\cdot -}$ radicals in dimethyl sulfoxide (DMSO) and in water and the $HQ^{\cdot +}$ radical in nitromethane.

Experimental Section

Oxygen-17-enriched hydroquinone was prepared from enriched *p*-benzoquinone-^{17}O (prepared according to the procedures of Gulick and Geske[2a]). Approximately 48 mg of the benzoquinone was dissolved in water and treated with anhydrous sulfur dioxide. The resulting hydroquinone was isolated by ether extraction: yield 30 mg, mp 171–173°. No further purification was needed. The ^{17}O content of the hydroquinone was about 10 atom % as observed from the intensity of the ^{17}O satellite lines in the esr spectrum.

The cation radical was produced from hydroquinone by reaction with $AlCl_3$–CH_3NO_2.[5] The esr spectra were observed on a Varian E-3 spectrometer, the field calibration being checked against a standard perylene radical anion spectrum.[6] Computer simulations and molecular orbital calculations were carried out on previously described programs.[7]

Results

^{13}C Spectra. The $HQ^{\cdot +}$ radical exhibits an esr spectrum[5] consistent with *cis* and *trans* isomers (Figure 1) at temperatures below about −20°, with splitting constants as shown in Table I. Further examination of the

Table I. Splitting Constants and g Factors for PBSQ Anion and HQ Cation Radicals

	PBSQ in DMSO[a]	PBSQ in H_2O[a]		HQ in CH_3NO_2
a_{CH}^H	−2.417	−2.357	*cis* −2.356, −2.147 *trans* −2.456, −2.055	−2.253 (av)[b]
a_{OH}^H				−3.294[b]
a_1^C	−2.13	+0.24		+4.23[c]
a_2^C	−0.123[d]	−0.713		−1.2, −1.65[c]
a^O	−9.46	−8.70		−7.83[c]
g	2.00541[e]	2.00469[e]		2.00350[c]

[a] Data from ref 2a. [b] Data from ref 5. [c] This work. [d] Estimated by M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 1350 (1965). [e] Data from P. J. Zandstra, *ibid.*, **41**, 3655 (1964).

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(2) (a) W. M. Gulick and D. H. Geske, *J. Amer. Chem. Soc.*, **88**, 4119 (1966), and references therein; (b) P. D. Sullivan and J. R. Bolton, *ibid.*, **90**, 5366, (1968).

(3) E. W. Stone and A. H. Maki, *ibid.*, **87**, 454, (1965).

(4) M. Broze, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, **46**, 4891 (1967).

(5) A. B. Barabas, W. F. Forbes and P. D. Sullivan, *Can. J. Chem.*, **45**, 267 (1967).

(6) J. R. Bolton, *J. Phys. Chem.*, 71, 3702 (1967).

(7) W. F. Forbes, P. D. Sullivan, and H. M. Wang, *J. Amer. Chem. Soc.*, **89**, 2705, (1967).

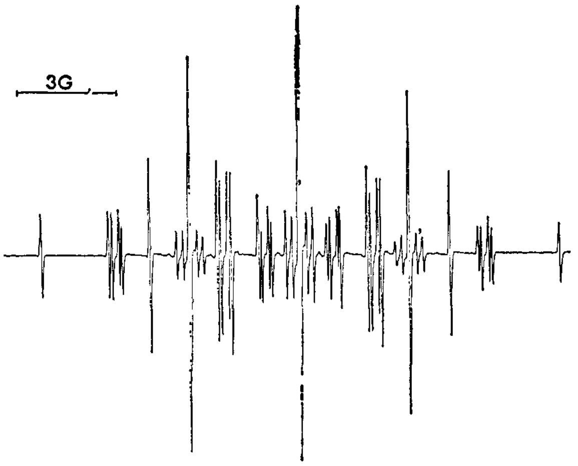

Figure 1. A fully resolved spectrum of the hydroquinone cation radical in $AlCl_3$–CH_3NO_2.

regions beyond the outermost lines of the spectrum under high gain conditions revealed the presence of several additional lines as shown in Figure 2. These lines are of the approximately correct intensities to arise from naturally occurring carbon-13 hyperfine interactions and are so assigned. The three lines observed correspond to splitting constants of 4.23, 1.20, and 1.65 G. Satellite lines of similar origin are found in the central portion of the spectrum and are also consistent with these three splitting constants. It was not possible to draw any conclusions regarding the signs of these ^{13}C splitting constants since an insufficient number of lines are completely resolved to allow intensity comparisons. The assignment of the ^{13}C splitting will be discussed further in the next section.

^{17}O Spectra. Under high gain conditions, the regions beyond the outer line of the main spectrum of ^{17}O-enriched $HQ^{\cdot +}$ displayed considerable additional structure (see Figure 3a) which was attributed to interaction with HQ molecules containing one oxygen-17 atom. Since ^{17}O has a nuclear spin of $^5/_2$, the original spectrum should be repeated six times. This was found to be the case and the experimental spectrum could be simulated (Figure 3b) assuming an ^{17}O splitting constant of 7.83 G. The line width of the lines associated with the ^{17}O interactions was also found to have increased to around 200 mG compared with line widths of around 100 mG for the unlabeled spectrum. A determination of the sign of the oxygen splitting was precluded by the slow decay of the signal during the measurement of the spectra, but it is almost surely negative.[8]

Discussion

1. Spin Density Distributions. The esr results for the $PBSQ^{\cdot -}$ radical in dimethyl sulfoxide (DMSO), an aprotic solvent, in water, a strong hydroxylic solvent, and for the $HQ^{\cdot +}$ radical in nitromethane are shown in Table I. In order to evaluate the spin density distributions in these systems the methods of Gulick and Geske[2a] and Das and Fraenkel[9] will be followed. A number of assumptions are inherent to this model. First, the proton splitting constants are related *via* McConnell's equation (eq 1) to the spin density on the adjacent carbon atom. The constant of proportionality Q_{CH}^H is assigned a value of -27 G. Second, the

$$a_{CH}^{H} = Q_{CH}^{H}\rho_{C}^{\pi} \qquad (1)$$

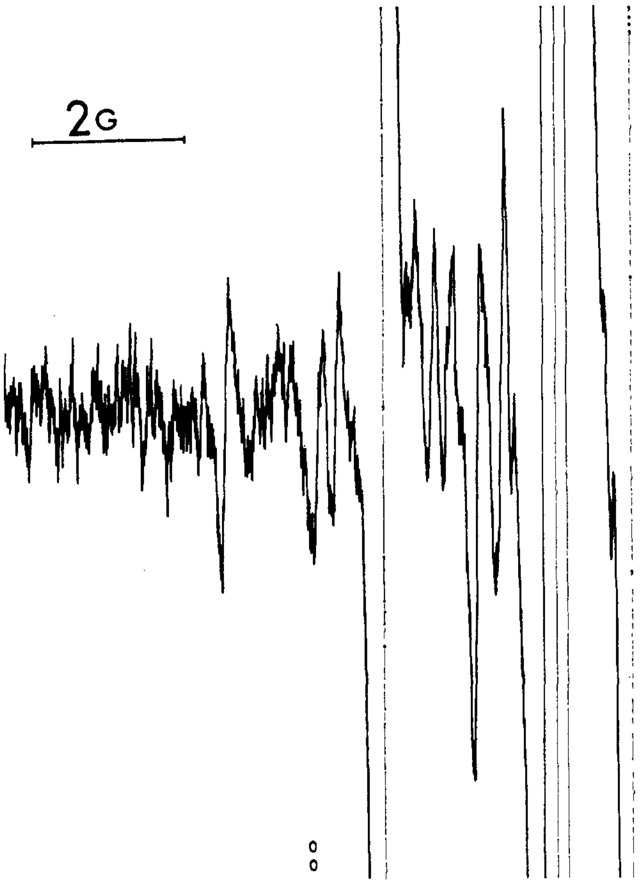

Figure 2. The region beyond the outermost line of the $HQ^{\cdot +}$ spectrum showing the three naturally occurring carbon-13 splittings.

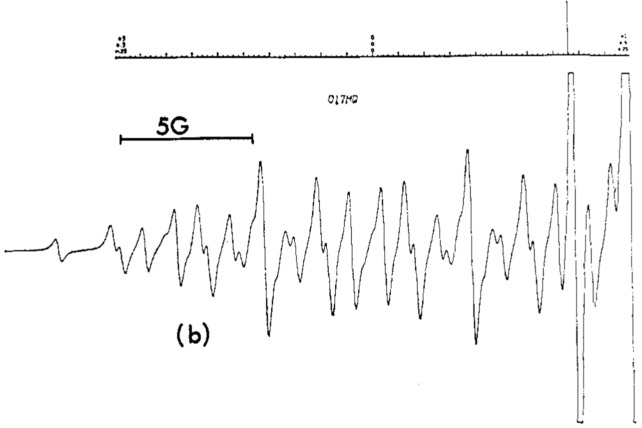

Figure 3. (a) The experimental O-17-enriched $HQ^{\cdot +}$ esr spectrum beyond the outermost line (×) of the unlabeled species. (b) A computer simulation of the O-17-enriched spectrum with opposite phase and slightly different scale.

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(8) M. Broze and Z. Luz, *J. Chem. Phys.*, **51**, 738, (1969).
(9) M. R. Das and G. K. Fraenkel, *ibid.*, **42**, 1350 (1965).

carbon-13 splitting constants at the 1 and 2 position may be expressed according to the equations developed by Karplus and Fraenkel[10] (eq 2 and 3). The constants

$$a_1^{\mathrm{C}} = 16.2\rho_1^{\pi} - 13.9(\rho_2^{\pi} + \rho_6^{\pi}) + Q_{\mathrm{CO}}^{\mathrm{C}}\rho_1^{\pi} + Q_{\mathrm{OC}}^{\mathrm{C}}\rho_{\mathrm{O}}^{\pi} \quad (2)$$

$$a_2^{\mathrm{C}} = 35.6\rho_2^{\pi} - 13.9(\rho_1^{\pi} + \rho_3^{\pi}) \quad (3)$$

in these were calculated[10] for carbon atoms with equivalent sp^2 hybrid bonds and with standard bond lengths. Changes in these conditions will result in changes in the numerical values of the constants. Since the hybridization and the bond lengths are not standard for the PBSQ$\cdot^-$ and HQ$\cdot^+$ radicals, we would expect that to be completely accurate a different set of constants should be assigned to each molecule. Since we have no detailed information on how changes in hybridization and bond length would affect these constants, and since in fact we do not know the hybridization or bond lengths in these molecules, we must use the best available numbers, which are those given above. It should be borne in mind, however, that the spin densities are evaluated using this model and are not necessarily the absolute values. Third, the values of the constants $Q_{\mathrm{CO}}^{\mathrm{C}}$ and $Q_{\mathrm{OC}}^{\mathrm{C}}$ were evaluated from carbon-13 data of the PBSQ$\cdot^-$ in water and the 2,5-dioxy-1,4-benzosemiquinone radical anion, to give $Q_{\mathrm{CO}}^{\mathrm{C}} = 16.57$ and $Q_{\mathrm{OC}}^{\mathrm{C}} = -25.12$ G.[2a,9]

With the above assumptions the spin-density distributions for the PBSQ$\cdot^-$ radical were evaluated from the available C-13 and proton splitting constants.[2a] The spin densities were then substituted into the expression proposed for the oxygen-17 hyperfine interaction (eq 4), giving $Q_{\mathrm{OC}}^{\mathrm{O}} = -40.41$ G and $Q_{\mathrm{CO}}^{\mathrm{O}} = -16.69$ G.

$$a^{\mathrm{O}} = Q_{\mathrm{OC}}^{\mathrm{O}}\rho_{\mathrm{O}}^{\pi} + Q_{\mathrm{CO}}^{\mathrm{O}}\rho_1^{\pi} \quad (4)$$

It is possible, in principle, to treat the results for the HQ$\cdot^+$ radical in the same manner, so that the spin density distribution could be obtained from the experimental proton and ^{13}C splitting constants and the value of the ^{17}O splitting constant cross-checked by eq 4. However, since the assignments and the signs of the ^{13}C interactions are uncertain and can only be guessed, we proceeded in the reverse order. That is, assuming eq 4 to be correct (using the values of $Q_{\mathrm{OC}}^{\mathrm{O}}$ and $Q_{\mathrm{CO}}^{\mathrm{O}}$ evaluated above) the spin density distribution was obtained from the proton and ^{17}O splitting constants. Thus for HQ$\cdot^+$, $a_{\mathrm{CH}}^{\mathrm{H}} = -2.253$ G (average); $\rho_2^{\pi} = 0.0834$, therefore $\rho_1^{\pi} + \rho_{\mathrm{O}}^{\pi} = 0.334$ and since $a^{\mathrm{O}} = -7.83$ G this gives $\rho_1^{\pi} = 0.2372$ and $\rho_{\mathrm{O}}^{\pi} = 0.0958$. Having obtained a spin distribution the ^{13}C splitting constants can be evaluated from eq 2 and 3 and compared with the experimental values. The evaluation of the C-1 splitting constant is straightforward.

$$a_1^{\mathrm{C}} = 16.2(0.2372) - 13.9(0.0873 + 0.0795) + 16.6(0.2372) - 25.1(0.0958) = +3.06\ \mathrm{G} \quad (5)$$

For the C-2 splitting constants the fact that HQ$\cdot^+$ exists as *cis* and *trans* isomers must be taken into account. This leads us to expect four different ^{13}C splitting constants for the 2 position. The ring proton splitting constants have previously been assigned to the *cis* and *trans* isomers by means of molecular orbital calculations[5] and by investigation of the dimethyl-substituted compounds.[2b] These two methods lead to the following assignments of the splitting constants.

trans

$$a_{\mathrm{CH}}^{\mathrm{H}}(2,5) = 2.476 \qquad \rho_{\mathrm{C}}^{\pi}(2,5) = 0.0910 \quad (6)$$

$$a_{\mathrm{CH}}^{\mathrm{H}}(3,6) = 2.055 \qquad \rho_{\mathrm{C}}^{\pi}(3,6) = 0.0761 \quad (7)$$

cis

$$a_{\mathrm{CH}}^{\mathrm{H}}(2,3) = 2.356 \qquad \rho_{\mathrm{C}}^{\pi}(2,3) = 0.0873 \quad (8)$$

$$a_{\mathrm{CH}}^{\mathrm{H}}(5,6) = 2.147 \qquad \rho_{\mathrm{C}}^{\pi}(5,6) = 0.0795 \quad (9)$$

If these assignments are correct four ^{13}C splitting constants are calculated from eq 2, two each for the *cis* and *trans* isomers. They are $a^{\mathrm{C}}(2,5) = -1.11$ G, $a^{\mathrm{C}}(3,6) = -1.85$ G for the *trans* isomer and $a^{\mathrm{C}}(2,3) = -1.40$ G, $a^{\mathrm{C}}(5,6) = -1.57$ G for the *cis* isomer. Alternatively if the assignment of the proton splitting constants were reversed, *i.e.*, the *cis* splitting constants are assigned to the *trans* isomer and *vice versa*, then four ^{13}C splitting constants are calculated which are different from above; $a^{\mathrm{C}}(2,5) = -1.29$ G, $a^{\mathrm{C}}(3,6) = -1.68$ G for the *trans* isomer and $a^{\mathrm{C}}(2,3) = -1.32$ G, $a^{\mathrm{C}}(5,6) = -1.65$ G for the *cis* isomer. A comparison with the experimental values of 4.23, 1.20, and 1.65 G indicates that the largest value should be assigned to the ^{13}C at the 1 position with, in all probability, a positive sign. The two smaller splittings are then assigned to ^{13}C splittings from the 2 position and the calculations lead us to expect that the sign of these interactions is negative. It should be noted that the experimental values are very close to those predicted for the latter assignment of isomers. This does not support our previous assignments for the *cis* and *trans* isomers but in view of the small differences between the two possibilities, the calculated ^{13}C splittings are not considered to be sufficiently reliable to warrant the rejection of our previous assignment.

The above discussion assigns the ^{13}C splittings of the HQ$\cdot^+$ radical starting from the ^{17}O and proton splittings. It is perhaps now instructive to retrace our steps and recalculate the spin density distribution for the HQ$\cdot^+$ radical from these newly assigned ^{13}C splittings, and from one further assumption, which is that the average ^{13}C splitting at the 2 position is $(-1.65 + -1.20)/2 = -1.425$ G. Using this averaged value together with $\rho_2^{\pi}(\mathrm{av}) = 0.0834$ an expression can be written

$$a_2^{\mathrm{C}} = -1.425 = 21.7(0.08344) - 13.9(\rho_1^{\pi}) \quad (10)$$

which gives $\rho_1^{\pi} = 0.2327$ and therefore $\rho_{\mathrm{O}}^{\pi} = 0.1010$. The value of a_1^{C} should now also be made consistent. We can write

$$a_1^{\mathrm{C}} = +4.23 = 16.1(0.2327) - 27.8(0.08344) + Q_{\mathrm{CO}}^{\mathrm{C}}(0.2327) + Q_{\mathrm{OC}}^{\mathrm{C}}(0.1010) \quad (11)$$

Simplifying, we get eq 12, which can be compared with the similar expression[2a] found for PBSQ$\cdot^-$ anion in H_2O (eq 13). Solving between eq 12 and 13 gives

$$2.803 = 0.2327Q_{\mathrm{CO}}^{\mathrm{C}} + 0.1010Q_{\mathrm{OC}}^{\mathrm{C}} \quad (12)$$

$$-0.353 = 0.1876Q_{\mathrm{CO}}^{\mathrm{C}} + 0.1378Q_{\mathrm{OC}}^{\mathrm{C}} \quad (13)$$

$Q_{\mathrm{OC}}^{\mathrm{C}} = -46.37$ G, $Q_{\mathrm{CO}}^{\mathrm{C}} = 32.13$ G, as compared to $Q_{\mathrm{OC}}^{\mathrm{C}} = -25.12$ G and $Q_{\mathrm{CO}}^{\mathrm{C}} = 16.57$ G, obtained from PBSQ$\cdot^-$ anion in H_2O and 2,5-dioxy-1,4-benzosemiquinone.[2a] The ratio $-Q_{\mathrm{OC}}^{\mathrm{C}}/Q_{\mathrm{CO}}^{\mathrm{C}}$ is similar in the

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(10) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, 35, 1312, (1961).

two cases, 1.44 and 1.51, respectively, suggesting perhaps that the ratio is more important than the absolute values. Since our new values have been obtained for the same molecule under different conditions rather than from different molecules they might, in this respect, be considered more appropriate. The only apparent effect of the new parameters is to change the spin-density distribution in the PBSQ$\cdot^-$ in DMSO; with $a_1^c = -2{,}13$ G, ρ_O^π and ρ_1^π are found to be 0.1586 and 0.1622, respectively (see Table II).

Table II. Summary of Spin Density Distributions

		ρ_1^π	ρ_2^π	ρ_O^π
PBSQ in	*a*	0.1457	0.0896	0.1753
DMSO	*b*	0.1622	0.0896	0.1586
PBSQ in	*a*	0.1876	0.0873	0.1378
H_2O	*b*	0.1876	0.0873	0.1378
HQ in	*a*	0.2373	0.0834	0.0958
CH_3NO_2	*b*	0.2327	0.0834	0.1010

[a] Evaluated by previous calculations[2a] and from the ^{17}O and proton splitting constants of HQ$\cdot^+$ radical. [b] Evaluated from ^{13}C and proton splittings only of HQ$\cdot^+$ and PBSQ$\cdot^+$ radical in H_2O.

In the light of our different spin densities (rows *b* in Table II) we can now reconsider the ^{17}O splitting constants using eq 4. For the three systems the best set of *Q* parameters is $Q_{OC}{}^O = -44.50$ G, $Q_{CO}{}^O = -14.30$ G. This is only slightly different from the previous set[2a] and give good agreement with the experimental results as shown in Table III.

Table III. Calculated[a] and Experimental Oxygen-17 Splitting Constants

	a^O (calcd)	a^O (exptl)
HQ	−7.82	−7.83
PBSQ in H_2O	−8.81	−8.70
PBSQ in DMSO	−9.43	−9.46

[a] Calculated from eq 3 with $Q_{OC}{}^O = -44.5$ G, $Q_{CO}{}^O = -14.3$ G, and using the *b* spin densities from Table II.

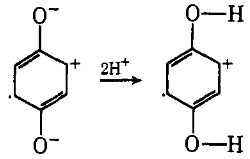
One fact which emerges rather strongly from this work concerns the value of the parameter $Q_{CO}{}^O$. Broze and Luz[8] have suggested from semiempirical correlations of a series of radicals that the relationship $a_O = Q_{OC}{}^O\rho_O{}^\pi$ is perfectly adequate to describe the O-17 splittings; that is, $Q_{CO}{}^O$ is considered to be zero. They suggested that the previous result of Gulick and Geske[2a] in which $Q_{CO}{}^O = -16.7$ G, was less reliable owing to its inconsistency with their theoretical calculations.[8] In this paper, from considerations of the carbon-13 splittings we are able to show that the spin density on oxygen increases by between 57 and 83% from HQ$\cdot^+$ in CH_3NO_2 to PBSQ$\cdot^-$ in DMSO, whereas the corresponding increase in the O-17 splitting constant is only 21%. This in itself indicates that the O-17 splitting constant cannot be directly proportional to the spin density on oxygen, and substantiates the original conclusions of Gulick and Geske regarding the magnitude of $Q_{CO}{}^O$. Because of the fact that Broze and Luz evaluated the spin densities on oxygen from molecular orbital calculations with little or no regard for the proton or carbon-13 splitting constants, we suggest that the simple relationship which they propose should be used with extreme caution until more experimental work (particularly with regard to ^{13}C splittings) has been obtained and the various relationships have been tested more fully.

Since the spin density on oxygen for the HQ$\cdot^+$ radical has been evaluated the constant relating the hydroxyl proton splitting constant and the spin density on oxygen (eq 14) can be calculated. From the spin densities in

$$a_{OH}{}^H = Q_{OH}{}^H\rho_O{}^\pi \qquad (14)$$

Table II $Q_{OH}{}^H = -32.6$ or -34.4 G. This value is somewhat higher than previously suggested values (5–24 G),[2,5,11] but since these previous values were obtained without the benefit of carbon-13 splittings our present value is probably less arbitrary.

2. Molecular Orbital Calculations. Our model for the MO calculations is one in which both PBSQ$\cdot^-$ and HQ$\cdot^+$ radicals are considered as perturbed benzene cation radicals (*i.e.*, compare I and II). It should



I II

therefore be possible to reproduce the spin density distributions in our three systems by systematic changes in the coulomb and resonance integrals of the oxygen atoms. The McLachlan perturbation corrections to the Hückel LCAO MO method[12] were employed and calculations made for a wide range of the coulomb (h_O) and resonance (k_{CO}) integral parameters. The first step was to find sets of h_O and k_{OC} values which would reproduce the spin densities at carbon atom 2. These values of h_O and k_{OC} were then plotted. The variation of $\rho_1{}^\pi$ and $\rho_O{}^\pi$ with these h_O and k_{OC} values was then found and the $\rho_1{}^\pi$ and $\rho_O{}^\pi$ values were plotted against h_O values. From the evaluated $\rho_1{}^\pi$ and $\rho_O{}^\pi$ spin densities (Table II) it was then possible to obtain the correct h_O and k_{OC} values. These values then completely reproduced the spin density distributions which have been evaluated. The values of the parameters are shown in Table IV. As can be seen the h_O parameter increases along the series as the perturbation of the oxygen atom increases. Concurrently the k_{OC} parameter decreases along the same series corresponding to an increase in bond length on going from >C=O to >C—O—H. As a further test of these parameters we have recalculated the spin densities in the dimethyl benzosemiquinones and hydroquinones using the pa-

Table IV. Coulomb and Resonance Integral Parameters for Oxygen which Completely Reproduce the Spin Densities in Table II

	$h_O{}^a$	$k_{OC}{}^a$	$h_O{}^b$	$k_{OC}{}^b$
PBSQ in DMSO	1.46	1.298	1.50	1.287
PBSQ in H_2O	1.72	1.22	1.72	1.22
HQ in CH_3NO_2	2.01	1.104	1.97	1.106

[a] Evaluated for the *a* spin densities in Table II. [b] Evaluated for the *b* spin densities in Table II.

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(11) J. Gendell, W. R. Miller, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 91, 4369, (1969).

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

Table V. Summary of MO Calculations for the Dimethyl Semiquinone and Hydroquinone Cation Radicals

Conditions	$a_{\mathrm{CH}}^{\mathrm{H}}$ (exptl)[a]	$a_{\mathrm{CH}}^{\mathrm{H}}$ (calcd)[b]	$a_{\mathrm{CH_3}}^{\mathrm{H}}$ (exptl)[a]	$a_{\mathrm{CH_3}}^{\mathrm{H}}$ (calcd)[c]	$Q_{\mathrm{CH_3}}^{\mathrm{H}}$[d]	ρ_{O}^{π}	$Q_{\mathrm{OH}}^{\mathrm{H}}$[e]
			2,3-Dimethyl				
Anion in DMSO	2.673	2.527	1.656	2.211	20.2	0.1725	
Anion in H_2O	2.592	2.457	1.702	2.130	21.6	0.1355	
Cation in CH_3NO_2	2.58	2.500	1.83	1.960	25.2	0.0957	32.60
			2,5-Dimethyl				
Anion in DMSO	1.971	1.884	1.978	2.834	18.8	0.1718	
Anion in H_2O	1.836	1.611	2.254	2.961	20.5	0.1346	
Cation in CH_3NO_2	0.95	0.982	3.81	3.442	29.9	0.0936	32.47
			2,6-Dimethyl				
Anion in DMSO	2.214	2.181	1.863	2.540	19.8	0.1723[f]	
Anion in H_2O	1.917	2.081	2.116	2.492	22.9	0.1353[f]	
Cation in CH_3NO_2	1.990	1.949	2.18	2.491	24.3	0.0945[f]	32.20[f]

[a] Taken from ref 2a and also from T. A. Claxton and D. McWilliams, *Trans. Faraday Soc.*, **64**, 2593 (1968). [b] Evaluated from the calculated spin densities with $|Q_{\mathrm{CH}}^{\mathrm{H}}| = 27$ G. [c] Evaluated from the calculated spin densities by $a_{\mathrm{CH_3}}^{\mathrm{H}} = \rho_{\mathrm{C}}^{\pi} Q_{\mathrm{CH_3}}^{\mathrm{H}}$ with $|Q_{\mathrm{CH_3}}^{\mathrm{H}}| = 27$ G. [d] Evaluated from $Q_{\mathrm{CH_3}}^{\mathrm{H}} = a_{\mathrm{CH_3}}^{\mathrm{H}}/\rho_{\mathrm{C}}^{\pi}$, where $a_{\mathrm{CH_3}}^{\mathrm{H}}$ are the experimental splitting constants and ρ_{C}^{π} are the calculated spin densities. [e] Evaluated from $Q_{\mathrm{OH}}^{\mathrm{H}} = a_{\mathrm{OH}}^{\mathrm{H}}/\rho_{\mathrm{O}}^{\pi}$ where $a_{\mathrm{OH}}^{\mathrm{H}}$ is the experimental hydroxyl proton splitting constant and ρ_{O}^{π} is the calculated spin density on oxygen. [f] Averaged values.

rameters in Table IV. The results of these calculations are shown in Table V. Good agreement for the ring proton splitting constants is found in each case using $Q_{\mathrm{CH}}^{\mathrm{H}} = -27$ G. Only poor agreement is found for methyl group splitting constants when a constant value of $Q_{\mathrm{CH_3}}^{\mathrm{H}}$ is used in the relation $a_{\mathrm{CH_3}}^{\mathrm{H}} = \rho_{\mathrm{C}}^{\pi} Q_{\mathrm{CH_3}}^{\mathrm{H}}$. However it is known that methyl group splittings are extremely charge dependent[13] and we find that increasing values of $Q_{\mathrm{CH_3}}^{\mathrm{H}}$ along the series shown gives better agreement with the calculations.[14]

3. *g* Value Correlations. It has been suggested that the deviation (Δg) of the *g* value from the free electron value of 2.0023 is equal to the sum of contributions from the atoms (X) in the molecule[15,16]

$$\Delta g = \sum_{\mathrm{X}} \rho_{\mathrm{x}}^{\pi} \gamma_{t}^{\pi} \qquad (15)$$

where ρ_{x}^{π} is the unpaired spin density on atom X and γ_t^{x} is a term which depends upon both the spin–orbit coupling constant and the energy (λ) of the orbital of the unpaired electron such that $\gamma_t^{\mathrm{x}} = (v + \lambda w)$, where v and w are constants. For the PBSQ$^{\cdot -}$ and HQ$^{\cdot +}$ radicals we must consider the summation of eq 15 over carbon and oxygen atoms. Since the spin–orbit coupling constant of oxygen is much greater than that of carbon we consider that the major contribution to Δg will be due to the oxygen atoms and that Δg will be given by eq 16 or 17. The values of λ for the three

$$\Delta g = 2\rho_{\mathrm{O}}^{\pi}\gamma_t^{\mathrm{O}} \qquad (16)$$

$$\Delta g = 2\rho_{\mathrm{O}}^{\pi}(v_{\mathrm{O}} + \lambda w_{\mathrm{O}}) \qquad (17)$$

systems are obtained from the molecular orbital calculations and are different (Table VI) for the two different spin density distributions (Table II, *a* and *b*). From the calculated values of λ and ρ_{O}^{π} and the experimental Δg values the constants v_{O} and w_{O} can be evaluated. For spin density distribution *a*, $v_{\mathrm{O}} = 118 \pm 27$, $w_{\mathrm{O}} = 99 \pm 70$, and the calculated Δg values from these values of v_{O} and w_{O} are shown in Table VI. For spin density distribution *b*, $v_{\mathrm{O}} = 142 \pm 12$, $w_{\mathrm{O}} = 156 \pm 35$, and the calculated Δg values are closer to the experimental values. In both cases, however, the agreement with the experimental Δg values is good and it is our contention that eq 17 should hold for PBSQ$^{\cdot -}$ and HQ$^{\cdot +}$ radicals and possibly for other semiquinone anions and hydroquinone cation radicals, provided that the spin density distributions are evaluated within the framework of our model. Further study of this hypothesis is presently underway.

Table VI. Δg Correlation

	Δg (exptl)	λ[a]	λ[b]	Δg (calcd)[a]	Δg (calcd)[b]
PBSQ in DMSO	31.1	−0.236	−0.280	33.2	31.2
PBSQ in H_2O	23.9	−0.366	−0.366	22.5	23.3
HQ in CH_3NO_2	12.0	−0.513	−0.510	12.9	12.6

[a] Calculated with spin density distribution *a*. [b] Calculated with spin density distribution.

Conclusion

We have shown within the framework of the model used to evaluate the spin density distributions that, along the series PBSQ$^{\cdot -}$ in DMSO, PBSQ$^{\cdot -}$ in H_2O, and HQ$^{\cdot +}$ in CH_3NO_2, there is a gradually increasing perturbation on the oxygen atoms leading to regular changes in the spin density distributions. It is believed that this constitutes a good example of the family relationship which exists between the semiquinone anion radicals and the hydroquinone cation radicals, a relationship which, incidentally has not received the attention it deserves.

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[13] J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

[14] Further discussion of this point will be made in a future publication.

[15] A. J. Stone, *ibid.*, **6**, 509 (1963).

[16] B. Lamotte and G. Berthier, *J. Chim. Phys.*, **63**, 369 (1966).