two-photon matrix photoionization techniques and trapped in solid argon. Five absorptions in the visible and ultraviolet regions have been assigned to the radical cations. The argon matrix absorption spectra for the naphthalene cation are in agreement with photoelectron and photodissociation spectra, absorption spectra of the ions in Freon glasses, and simple HMO calculations. Substituent effects were noted for the origins of the five transitions and the vibronic spacings. The C(9)–C(10) stretching vibrational interval in the red cation transitions are 40–50 cm^{-1} above Raman bands of the precursors and the ring deformation intervals are up to 30 cm^{-1} below precursor values. The 2-substituted naphthalene cations gave sharper and stronger absorption bands than the 1-substituted species.

Acknowledgment. The authors gratefully acknowledge support from the National Science Foundation under Grant CHE 79-10966.

Carbon-13 Hyperfine Constants, *g* Factors, and Electronic Structure of *m*-Benzosemiquinone Radical Anions[1]

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The ^{13}C ESR spectra of the carboxylated *m*-benzosemiquinone radical anions produced in aqueous solution by in situ radiolysis techniques have been observed. Carboxyl substitution does not perturb the spin distribution appreciably so that ^{13}C hyperfine constants can be readily assigned to *m*-benzosemiquinone. This radical is an odd-alternant species with appreciable spin density at the 4 and 6 positions of the ring system but very little at the 2 position. The large proton and ^{13}C hyperfine constants and relatively low *g* factors of these radicals show that there is very little spin density on the oxygen atoms.

Introduction

Oxidation of resorcinol in basic aqueous solution is known to produce the *m*-benzosemiquinone radical anion (I).[2] On the time scale of ESR experiments the protons on the 4 and 6 positions are equivalent so that the unpaired spin density appears to be equally distributed between the two oxygen atoms in much the same way as in the ortho and para isomers. These two protons, however, have relatively large hyperfine constants (11.4 G) indicating that in contrast to its isomers a major fraction of the spin density is located on the ring. Electronically the two types of radicals are quite different; only in *m*-semiquinone do the oxygen atoms and the ring carbon atoms form an odd-alternant system. It is expected that the unpaired spin density will be located primarily on the oxygen atoms and on positions 2, 4, and 6 while the spin density at the 1, 3, and 5 positions will be small or negative. Chemically *m*-semiquinone is relatively reactive and behaves more like a substituted phenoxyl radical than like the other semiquinones. For example, in contrast to the latter it disappears rapidly in second-order processes and oxidizes ascorbic acid quite readily.[3] However, the g factor (2.00383; see below) is considerably smaller than that of phenoxyl radical (2.00461)[4] so that there is clearly destructive interference between the contributions from the two oxygen atoms. It is useful to have ^{13}C hyperfine data to provide further information on the electronic structure of this important radical. Attempts to examine it directly at natural abundance levels (1.1% ^{13}C) with in situ irradiation techniques[5,6] were unsuccessful because only relatively low concentrations were available as the result of its high reactivity. Because the rate constants for disappearance of the carboxyl derivatives are lower by 2 orders of magnitude,[7] we have been able to produce a sufficiently high steady-state concentration to observe the ^{13}C satellites of all the ring carbon atoms in the 2-carboxy, 4-carboxy-, and 5-carboxy-*m*-semiquinone and report the ESR parameters here. These data show that the electron distribution is perturbed by carboxyl substitution only to a minor extent. Assignments can be made to the individual carbon atoms and realistic estimates given for the ^{13}C hyperfine constants in the unsubstituted radical. Of particular importance is the low spin density at the C_2 position as manifested by both the proton and ^{13}C hyperfine constants. These data are particularly valuable in providing information on the contributions of local and remote spin density to the ^{13}C hyperfine interactions in a well-defined system.

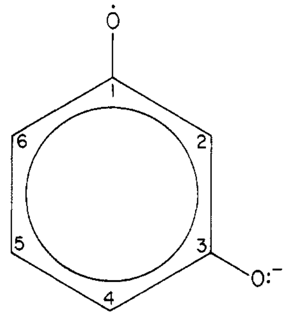

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TABLE I: Proton Hyperfine Constants and *g* Factors for *m*-Benzosemiquinones[a]

		a^{H},[d-f] G			
species[b]	*g* factor[c]	H(2)	H(4)	H(5)	H(6)
m-BSQ	2.00383	0.68	11.44	2.43	11.44
2-COO^--*m*-BSQ	2.00386		11.34	2.41	11.34
4-COO^--*m*-BSQ	2.00389	0.68		2.31	10.99
5-COO^--*m*-BSQ	2.00385	0.68	11.41		11.41

[a] In aqueous solution (pH ~11) at ~20 °C. [b] *m*-BSQ is *m*-benzosemiquinone. [c] ±0.00002 (standard deviation). [d] ±0.02 G (standard deviation). [e] Stone and Waters (ref 2) have reported values of 0.7, 11.2, 2.4, and 11.2 G for protons at the 2, 4, 5, and 6 positions of *m*-benzosemiquinone and similar values for the carboxyl derivatives. [f] Dixon, Moghimi, and Murphy (ref 10) have reported values of 0.7, 11.2, 2.8, and 11.2 G for protons at the 2, 4, 5, and 6 positions of *m*-benzosemiquinones.

Experimental Section

ESR spectra were observed at X-band (9200 MHz) during continuous electron irradiation of N_2O-saturated 10^{-3} M aqueous solutions of resorcinol (Mallinkrodt) and its monocarboxylates (Aldrich) at pH ~11 as previously described.[6,8] The signal-to-noise ratio of the spectrometer has now been improved by about a factor of two by including a low noise microwave amplifier in the detector arm. Computer control of the scan combined with magnetic field/microwave frequency locking gives a linear presentation of the spectra at scan rates as low as 0.05 G/min and makes it possible to employ relatively long time constants. These improvements have allowed us to develop the ^{13}C features of the spectra quite well. Spectra were recorded in second derivative format with 100-kHz and 200-Hz field modulation with phase-sensitive detection at these same frequencies. Magnetic field measurements were made by NMR methods[5] and *g* factors were determined by reference to $g = 2.00306$ for $\cdot SO_3^-$.[9]

Results and Discussion

Proton Hyperfine Constants and g Factors. The *g* factors and proton hyperfine constants observed in the present studies for *m*-semiquinone and its monocarboxylic derivatives are reported in Table I. At the pH of these experiments (~11) these radicals exist as the anion and dianions, respectively. It is clear from the hyperfine data, which are in good agreement with previously reported values,[2,10] that carboxyl substitution does not perturb the electronic configuration to any major extent. There is no evidence from the proton data that carboxyl substitution drains any appreciable spin density from the ring system as it does in the case of the hydroxylcyclohexadienyl radicals.[8] The individual values can be assigned to the positions as indicated with certainty. Taking *Q* in the McConnell relationship as 25 G one estimates unpaired spin densities of 0.03, 0.46, and 0.46 at the odd-alternant positions (C_2, C_4, and C_6, respectively). Presumably the value of 2.4 G observed for $a(H_5)$ corresponds to a negative spin density (−0.10) at C_5. The unpaired spin density on each of the oxygen atoms cannot be significantly greater than ~0.1 unless there is compensating negative spin density on the C_1 and C_3 carbon atoms.

The *g* factors are reported here for the first time. They are considerably lower than for *o*- and *p*-semiquinone (2.00455 and 2.00456, respectively)[4,11] and indicate that the spin–orbit interaction with oxygen is only about one-half of that in the latter radicals where the spin density on each of the oxygen atoms is estimated as ~0.3. From the *g* factors we estimate an unpaired spin density ~0.20 ± 0.05 on each of the oxygen atoms in *m*-semiquinone which implies a spin density of −0.10 ± 0.05 on the C_1 and C_3 atoms. Carboxyl substitution affects the *g* factor very little even when at a position of appreciable spin density (by 0.00006 in 4-carboxy-*m*-semiquinone). This increase is only-about one-sixth the increase of 0.00034 noted for carboxyl substitution at the 3 position of the hydroxycyclohexadienyl radical[8] where the spin density is comparable. Obviously the contributions of the carboxyl group to the *g* factor are fairly subtle.

^{13}C Hyperfine Data. The spectra recorded at a 100-fold increased gain at fields below that of the lowest lines of the proton patterns are illustrated in Figure 1. As indicated by the stick spectra all of the observed structure corresponds to splitting of the proton patterns by one additional ^{13}C hyperfine interaction. There is no evidence for any significant contribution by impurity radicals. The ^{13}C hyperfine constants determined from these spectra are given in Table II. In the case of the 4-carboxy- and 5-carboxy-*m*-semiquinones, splitting by seven carbon atoms is apparent. The 4-carboxy derivative is especially valuable in that all seven carbon atoms exhibit different hyperfine interactions so that we are assured of properly counting them. Broadening of the outer lines in the other two radicals as the result of incomplete averaging of the anisotropies makes their intensities appear to be somewhat low but careful comparison of the integrated absorbances shows that, in fact, they correspond to two equivalent carbon atoms. In the case of the 2-carboxy derivative splitting by only six carbon atoms is seen, presumably because the carboxyl carbon atom has a hyperfine interaction too small to be observable.

Since one expects a carboxyl carbon atom to exhibit a hyperfine interaction ~50% of that of the protons in the unsubstituted radical,[8] one can assign the ^{13}C values of 5.38 and 1.20 G (1.29 G) observed, respectively, to the carbonyl positions in the 4-carboxy- and 5-carboxy-*m*-semiquinones. In the case of the 4-carboxy derivative, the alternative assignment of the 5.69-G value to the carboxyl group is possible but would seem to leave much too small a value for $a(C_1)$ to be consistent with the other values observed for the ring carbon atoms. The proportionality constant ($Q(CO_2^-)$) relating the ^{13}C carboxyl hyperfne interaction to the spin density appears to be only ~12 G in this type of radical. This value is substantially lower than $Q(CO_2^-)$ = 15.8 G given for the substituted hydroxylcyclohexadienyls.[8] The interactions between the CO_2^- group and the π systems must be rather different.

The 2-carboxy- and 5-carboxy-substituted radicals exhibit two pairs of equivalent ring carbon atoms with hyperfine constants of 15 and 6 G. Using arguments based on the calculations of Karplus and Fraenkel[12] and spin densities as given by the proton hyperfine constants one can assign the larger value to the C_4 and C_6 carbon atoms with virtual certainty. This assignment leaves the smaller values for the C_1 and C_3 positions. As indicated in Table II the 15.86- and 14.36-G hyperfine constants of 4-carboxy-*m*-semiquinone are similarly assigned, respectively, to C_4 and C_6 and its 6.20- and 5.69-G values to C_3 and C_1. The larger values for each pair are attributed to the carboxylated side of the ring based on the shift of spin density in that direction as indicated by the decrease ob-

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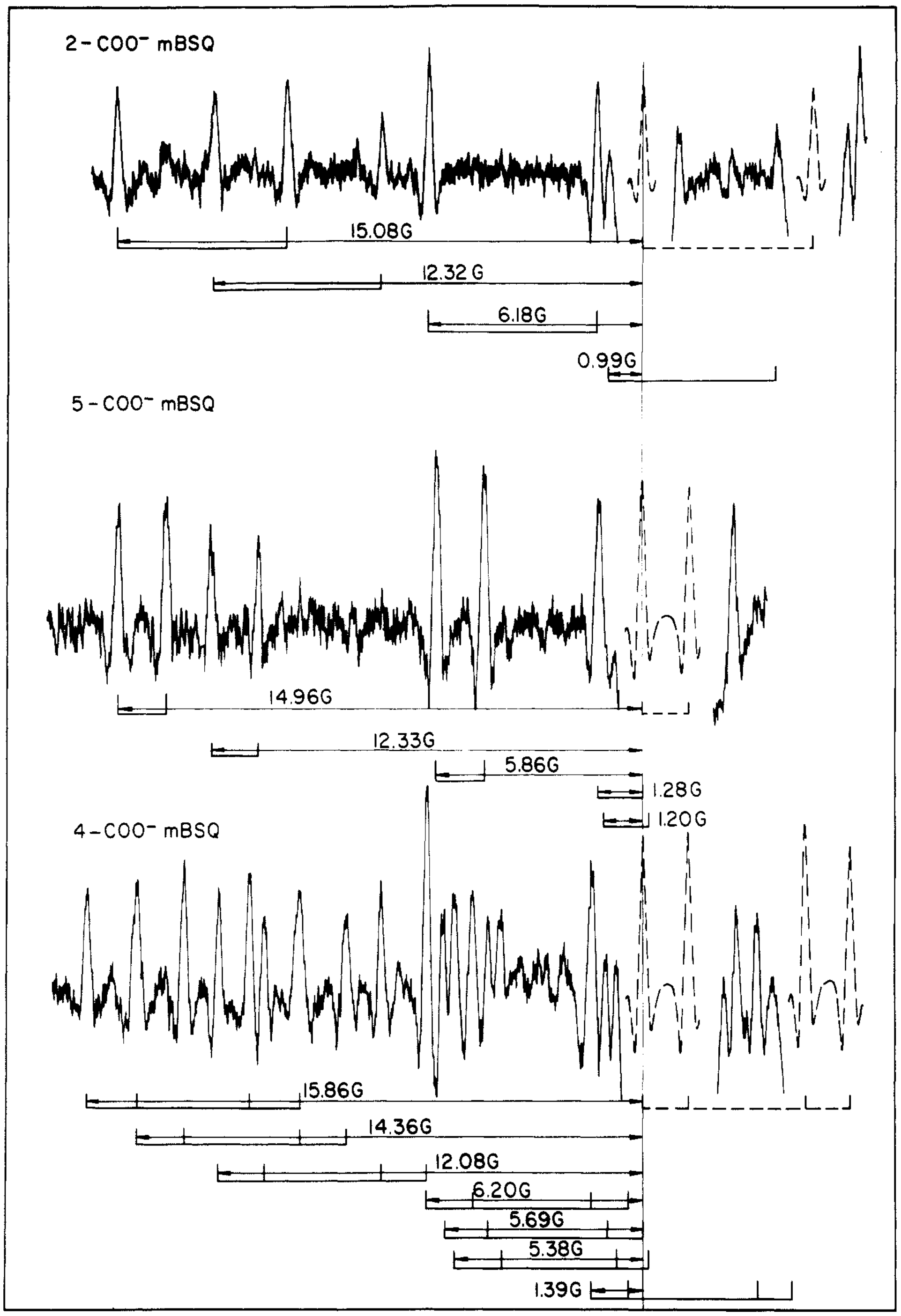

Figure 1. Second-derivative ESR spectra of the low-field ^{13}C satellites for 2-carboxy-, 5-carboxy-, and 4-carboxy-*m*-benzosemiquinone radicals. All spectra were recorded at 9.2 GHz and 20 °C and are presented in direction of increasing field. The low-field lines of the proton hyperfine patterns are indicated as dashed peaks and are recorded at one-hundredth the gain of the satellite lines. They are aligned so that one can directly compare the relative splittings by ^{13}C. The stick spectra are for the low-field ^{13}C satellites as they repeat according to the small proton splittings. The additional lines observed correspond to the structure expected from the mirror symmetry about the center of these proton patterns. The arrows correspond to one-half of the ^{13}C splittings and are labeled with the corresponding $a(^{13}C)$ values.

served in $a(H_6)$. The assignment of the 14.36-G value to $a(C_6)$ and 5.69-G value to $a(C_1)$ is corroborated by the estimates of 14.41 and 5.64 G obtained by correcting the values observed in the 5-carboxy derivative by the ratio of the C_6 proton hyperfine constants (10.99/11.41; both $a(C_6)$ and $a(C_1)$ should primarily reflect the spin density at C_6; see below).

Each of these three radicals also has a unique carbon atom with a hyperfine constant of ~1 and ~12 G. The larger of these values almost certainly reflects the high spin density at the C_4 and C_6 positions and can, therefore, be reasonably assigned to the C_5 ring atom, in which case it must be of negative sign. Using the Karplus–Fraenkel relationship one estimates that $a(C_5)$ should be ~ -0.9 $a(C_4)$ or 13.5 G so it seems clear that the smaller of the two unique hyperfine constants cannot be assigned to the C_5 atom. By default it must be assigned to C_2 in accord with the low spin density at that position manifested by the proton hyperfine constants.

^{13}C Hyperfine Constants for m-Benzosemiquinone. Because the effects of carboxyl substituents are small, it is clear that the ^{13}C hyperfine constants in the unsubstituted radical cannot be far different from those in the carboxylates. The values are taken as those observed in the 5-carboxy radical, where the spin density is low, and substitution should have very little effect, except possibly

TABLE II: ^{13}C Hyperfine Constants in Carboxylated *m*-Benzosemiquinones[a]

species[b]	a^{13C},[e] G C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	COO^-
m-BSQ[d]	(5.9)	(1.3)	(5.9)	(15.0)	(12.3)	(15.0)	
2-COO^--*m*-BSQ	6.18	0.99	6.18	15.08	12.32	15.08	
4-COO^--*m*-BSQ[e]	5.69[f]	1.39	6.20	15.86	12.08	14.36	5.38[f]
5-COO^--*m*-BSQ	5.86	1.28[g]	5.86	14.96	12.33	14.96	1.20[g]

[a] In aqueous solution (pH ~11) at 20 °C. [b] *m*-BSQ is *m*-benzosemiquinone. [c] Accuracy is, in general, estimated as ±0.03 G (standard deviation). Hyperfine constants >10 G have been corrected for second-order shifts. [d] Values for *m*-benzosemiquinone estimated from observations on the carboxylated derivatives as described in text. [e] Specific assignments are based on a shift in spin density toward the carboxylated side as manifested by a decrease in $a(H_6)$; see text. [f] Assignment of $a(C_1)$ and $a(C_{CO_2})$ atoms can be interchanged; see text. [g] Appear in Figure 1 as a single line. Difference of 0.08 G determined by comparison of observed intensity with simulated spectra. Assignment of $a(C_2)$ and $a(C_{CO_2})$ can be interchanged.

for $a(C_5)$. This latter value is expected to be represented very well by the splitting observed in 2-carboxy-*m*-semiquinone, where the substituent is remote. This value is, in fact, unchanged from that observed in the 5-carboxy radical. ^{13}C hyperfine constants estimated for the unsubstituted radical, based on these arguments, are given parenthetically in Table II and should be accurate to ~0.1 G.

Using the proton data estimates of the spin density distribution one can solve the Karplus–Fraenkel equations describing $a(C_4)$ and $a(C_5)$

$$a(C_n) = Q_\alpha \rho_\alpha + Q_\beta(\rho_{\beta 1} + \rho_{\beta 2})$$

in terms of the local and adjacent carbon π spin densities (ρ_α, $\rho_{\beta 1}$, and $\rho_{\beta 2}$) where Q_α and Q_β are proportionality constants ($S_c + Q^C_{CH} + 2Q^C_{C-C_\beta}$) and $Q^C_{C_\beta-C}$ in the Karplus–Fraenkel notation). Taking $\rho(C_3) = -0.1$ the data in Table II give $Q_\alpha = 28.2$ G and $Q_\beta = -10.1$ G. These values are slightly smaller than the 36 and −14 G given by Karplus and Fraenkel.[12] If we accept the magnitude of the spin density on C_2 to be ~0.03 then it must, in fact, be of negative sign for the small value of $a(C_2)$ to be consistent with the Karplus–Fraenkel relationship, i.e., the effect of spin density on C_2 must cancel that on C_1 and C_3. If this conclusion is correct then $a(C_2) = 1.3$ G indicates a spin density of −0.1 on C_1 and C_3. The contribution to $a(C_1)$ and $a(C_3)$ from spin on the oxygen atoms must be small, in agreement with the estimates of Strauss and Fraenkel[13] that $Q^C_{OC} < 5$ G. Ab initio calculations on this very interesting system are currently being carried out by D. Chipman to provide further insight on the electron distribution and particularly on the low values observed for $a(H_2)$ and $a(C_2)$. We are also carrying out a detailed study of ^{13}C hyperfine interactions in a number of ortho- and para-substituted semiquinones for further comparisons.[11]

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H Atom Yields in the Pulse Radiolysis of H_2: Reactions with O_2, ClNO, and HI

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The hydrogen atom yield in the pulse radiolysis of H_2 at high dose rates was measured by four independent calibration techniques, using reactions of H with O_2, ClNO, and HI. Spectrophotometrical detection of HO_2 in the reaction $H + O_2 + H_2 \rightarrow HO_2 + H_2$ (1), of ClNO in $H + ClNO \rightarrow HCl + NO$ (2), of HI in $H + HI \rightarrow H_2 + I$ (3), and of I_2 in (3) followed by $I + I + NO + H_2 \rightarrow I_2 + NO + H_2$ allowed determination of the hydrogen yield in 1 bar of H_2. The H atom yield was compared with the O_3 yields in pure O_2 and in O_2/SF_6 mixtures under identical irradiation conditions, which lead to relative G(H) values: $G(H)_{H_2} = 1.38G(O_3)_{O_2}$ and $G(h)_{H_2} = 2.07G(O_3)_{O_2/SF_6}$. On the basis of $G(O_3)_{O_2} = 12.8$ a value $G(H) = 17.6$ is obtained. The rate constants of reactions 1, 2, and $I + NO + H_2 \rightarrow INO + H_2$ (4) were measured as $k_1 = 2.17 \times 10^{16}$ cm^6 mol^{-2} s^{-1}, $k_2 = 9.24 \times 10^{12}$ cm^3 mol^{-1} s^{-1}, and $k_4 = 2.7 \times 10^{15}$ cm^6 mol^{-2} s^{-1}.

Introduction

The pulse radiolysis of hydrogen provides a well-defined source of hydrogen atoms in the gas phase. It has been used to study a series of hydrogen atom reactions with added molecules[1-3] like O_2, C_6H_6, and $C_6H_5CH_3$; the spectra of the radicals produced, like HO_2, C_6H_7, and $C_6H_6CH_3$, were recorded[2,3,4] and radical–radical reactions investigated.[3,5-7] The absolute values of the rate constants for

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