Electron Spin Resonance Studies on Ion Pair Association and ^{13}C Hyperfine Splittings in Potassium *p*-Benzosemiquinone

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Abstract: Esr studies on the temperature dependence of the proton and ^{13}C hyperfine splittings in *p*-benzosemiquinone anion produced by alkali metal reduction have been carried out in detail. Tight or contact ion pairs and unassociated radical ions have been found to exist simultaneously in samples of *p*-benzosemiquinone^{-}K^{+} in 1,2-dimethoxyethane at low temperatures. The proton and ^{13}C splittings from unassociated and tight ion pairs were measured and the spin densities in the two types of radical species were evaluated using the experimental data. MO calculations were performed to fit the spin densities at all the positions in a given radical species. The spin density redistribution that takes place as a consequence to the formation of a tight ion pair has been discussed in the light of the MO results. There is also evidence from a study of the ^{13}C splittings that there is an intramolecular migration of the counterion in the tight ion pair at higher temperatures. The tight ion pairs have lower *g* values compared to the unassociated radical species.

The consequences of ion pairing on the electron spin resonance (esr) spectra of semiquinone–alkali metal systems have attracted the attention of several investigators.[2-7] It has also been pointed out from esr results that tight or contact ion pairs are formed under suitable conditions.[2,4] Although large variations in proton splittings have been observed in the ion paired species, a detailed understanding of the spin density redistribution resulting from ion pair formation is not possible from studying the variations in proton splittings alone.[8] Consequently, we have examined the variations in carbonyl-^{13}C splittings in *p*-benzosemiquinone-1-^{13}C anion, which is known to be very sensitive to interactions[8-11] that take place in the vicinity of the carbonyl oxygen atoms.

From *p*-benzosemiquinone anion (PBSQ) obtained by alkali metal reduction of *p*-benzoquinone (1,4-benzoquinone) we have been able to obtain strong esr signals with narrower lines, as compared to the signals obtained earlier,[2b,4] by adjusting the conditions of preparing the radicals. It has been possible to obtain spectra from ion paired species and unassociated species which are simultaneously present in the sample at low temperatures. The carbonyl-^{13}C splittings from the different species have also been examined in detail. The results are presented in section II and the assignments of the splittings discussed in section III. In section IV the analysis of the results in terms of spin density redistribution that takes place as a result of ion pairing is presented and in section V we discuss the results on molecular orbital calculations that were carried out with a view to reproduce the spin densities obtained from experimental data. In section VI we present the results on the structure of the ion pairs obtained from a study of the ^{13}C hyperfine components. The variations in *g* values resulting from ion pair association which has been observed are reported in section VII.

I. Experimental Section

The X-band esr spectrometer used and the temperature control unit employed for the investigations have been described elsewhere.[2b,4]

Unlabeled *p*-benzoquinone was prepared from hydroquinone (May and Baker Ltd.) according to the method of Gilman and Blatt.[12] The product was purified by sublimation (mp 116°). *p*-Benzohydroquinone-1-^{13}C was obtained by the method described by Das[13] and was the same material used in an earlier investigation.[14] The labeled hydroquinone was converted to the quinone using the same procedure employed for the unlabeled material. The enrichment of the ^{13}C at the 1 position is 50%.

The semiquinone anion radical from *p*-benzoquinone was made *in vacuo* by potassium reduction in 1,2-dimethoxyethane (DME) using well-known techniques.[15-18] The semiquinone radicals produced by this method are much less stable compared to hydrocarbon radicals produced by the same method. However, we have observed that the radical remains stable for longer periods of time if the purified quinone is freshly sublimed into the esr sample tubes for each individual preparation of the sample. This is easily done by providing an extra arm to the sample tube[18] into which the quinone can be introduced in the beginning of each sample preparation, without contaminating the rest of the sample tube. It was also observed that better esr signals were obtained from samples that were left at room temperature for about 24 hr after reduction. Presumably, the reduction reaction is slow and after 24 hr the amount of unreduced material that can cause line broadening by electron exchange with the semiquinone is minimized. The MO calculations were done using a CDC 3600 computer.

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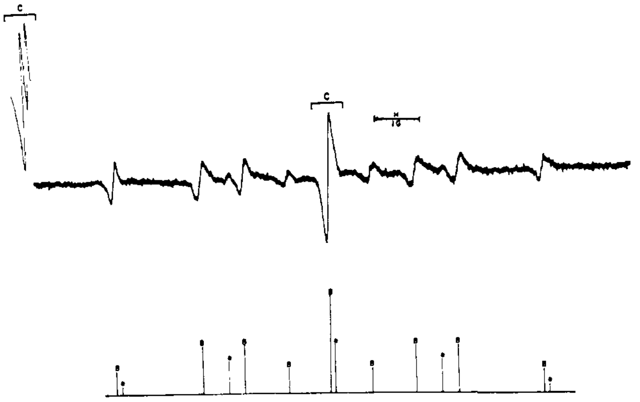

Figure 1. First derivative of the esr spectrum of *p*-benzosemiquinone ion in DME with potassium as counterion at −75°, together with the "stick plot." The stick plot assumes the concentration of the A and B species in the proportion 1:3. The portion marked "C" is the central region of the spectrum and this portion is shown separately under high resolution at the left-hand top portion of the figure.

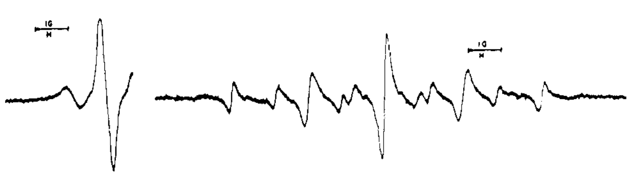

Figure 2. First derivative of the esr spectrum of *p*-benzosemiquinone-1-^{13}C ion in DME with potassium as counterion at room temperature. On the left of the main spectrum is shown under high modulation the end proton line on the high-field side together with the ^{13}C satellite.

II. Results

Unlabeled *p*-Benzosemiquinone Anion (PBSQ). Investigations were carried out on samples of PBSQ-K in DME at various temperatures ranging from −100° to room temperature. The spectrum obtained from unlabeled PBSQ at −75° is shown in Figure 1. Although in the full spectrum the central lines are not resolved, they do get resolved when low modulations are used and the region marked "C" in the main spectrum is shown separately under high resolution at the left end of the spectrum. The spectrum can be interpreted in terms of two distinct species, an intimate ion pair (B species)[2b,4] in which there are two groups of two equivalent protons as one of the oxygen atoms is complexed with the metal ion, and another with equally separated hyperfine components ("A" species)[2b,4] in which all four protons are equivalent. This can be an unassociated species.[7] A stick plot for a mixture of A and B species in the proportion 1:3 with splitting constant obtained from the experimental spectrum at −75° is also shown Figure 1. The room temperature spectrum is similar to the one reported by Chen, Warhurst, and Wilde.[7] The values of the splitting constants obtained from PBSQ prepared from a freshly made sample of the quinone are reported in Table I. It may be noticed that these values are slightly different from the values reported earlier.[4] This results from the fact that spectra obtained in the present experiments are better resolved and they have hyperfine lines with smaller widths. Consequently better measurements were possible with these spectra.

It can also be noticed from Figure 1 that the centers of the spectra from A and B species occur at different *g* values. The *g* value of the A species is 2.00551 ± 0.00002 and for the B species is 2.00543 ± 0.00002. The measurements of the *g* values were made using the same procedure described elsewhere.[19]

***p*-Benzosemiquinone-1-^{13}C Ion (PBSQ*).** Samples of PBSQ* prepared by reducing *p*-benzoquinone-1-^{13}C in DME using potassium metal were also examined in the same temperature range as for PBSQ. Figure 2 shows the esr spectrum obtained from PBSQ* at room temperature. The spectrum is *A type*,[20] and only one averaged proton splitting is observed as in the case of the unlabeled compound. All the ^{13}C lines from the main proton lines can be seen in this spectrum. The end proton line on the high-field end of the main spectrum together with its high-field satellite recorded under high modulation is shown on the left end of the main spectrum in order to indicate clearly the position of the ^{13}C satellite. Analysis of the spectrum yields a value of 2.04 G for the ^{13}C splitting. Examination of the ^{13}C satellites from spectra obtained with slow scan rates indicates that the high-field components are sharper compared to their low-field analogs. Consequently, this splitting is negative[8,21–23] since it is also known[8,10] that the spin densities at the 1 and 4 positions are positive.

Table I. Hyperfine Splitting Constants in *p*-Benzosemiquinone$^-$K$^+$ in DME

Temp, °C	Nucleus[a]	Hyperfine splittings, G A species[b] Exptl[c]	 Calcd[d] (McLachlan)	 B species[b] Exptl[c]	 Calcd[d] (McLachlan)
25[e]	a^H	...	...	−2.395 ± 0.008	−2.384
	a_{CO}^C	...	...	−2.04 ± 0.02	−1.940
−75	a_2^H	−2.410 ± 0.005	−2.406	−1.935 ± 0.005	−1.944
	a_3^H	−2.410 ± 0.005	−2.406	−2.885 ± 0.005	−2.800
	a_1^C	−2.45 ± 0.02	−2.445	−0.79 ± 0.02	−0.792
	a_4^C	−2.45 ± 0.02	−2.445	−3.50 ± 0.02[f]	−3.288

[a] See Figure 4 for the numbering of atom positions. [b] See text for definitions of A and B species. [c] The errors quoted are for a given sample preparation. [d] Evaluated using the spin densities obtained by MO calculation, and reported in Table II. [e] The spectrum at 25° is A type, although it is from B species radicals (see text). [f] Sign of the splitting assigned on the basis of MO results (see text).

Figure 3 shows the spectrum obtained from the sample at −75°. On the left end of the main spectrum is shown the end proton line with its satellites recorded under high modulation. Three different sets of ^{13}C

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(20) We use *A type* to indicate the fact that although the spectrum resembles the one obtained from *A species*, an A-type spectrum need not arise from A species. B species radicals at high temperature will give an A-type spectrum with averaged splittings, and in fact it is the B species that give rise to the room temperature spectrum (see section VI).

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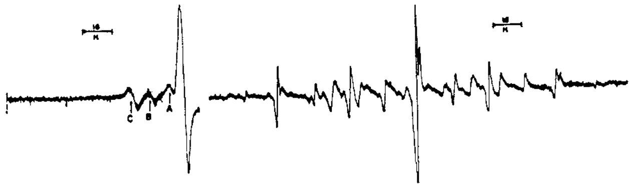

Figure 3. First derivative of the esr spectrum of *p*-benzosemiquinone-1-^{13}C ion in DME with potassium as counterion, at −75°. On the left of the main spectrum is shown under high modulation the end proton line on the high-field side together with the ^{13}C satellites. The satellites marked A and C arise from the B species and the satellite marked B arises from the A species (see text).

satellites are discernible from the low-temperature spectrum. The magnitudes of the different splittings are 3.50, 2.45, and 0.79 G. From a comparison of the spectrum obtained from unlabeled PBSQ at −75°, it can be seen (see also section III) that the 2.45-G splitting arises from the A species. This is also a negative splitting from observations on the intensities of the ^{13}C satellites. However, it is necessary to look at specific regions in the spectrum at different temperatures in order to make this out, and the intensity variations are not so much evident as in the case of the room-temperature spectrum. At low temperatures, owing to the presence of larger number of lines arising from both the A and B species, the problem of finding unoverlapped pairs of satellites is more severe.

The other two carbon-13 splittings (3.50 and 0.79 G) can be attributed to the B species radicals. Despite the problem of overlap of different satellites, by studying the end regions of the spectrum it is possible to determine the sign of the 0.79-G splitting with confidence. This splitting is found to be negative. On the other hand it is not possible to determine the sign of the 3.50-G splitting experimentally with the same confidence. It is difficult to locate any unoverlapped pair of satellites corresponding to the 3.50-G splitting and arising from the same proton line. Even for the extreme proton lines, as a result of the larger magnitude of the ^{13}C splitting the satellites in the inner portion of the spectrum lie well inside so that they are overlapped by other lines. However, by looking at the satellites corresponding to this splitting at different temperatures at which they are observable, it can be concluded that the splitting is likely to be negative. We also note, *a posteriori*, from the results in section V that the negative sign is in better accord with spin densities obtained from MO calculations.

The g values from the different species from the labeled compound do not differ from the values of the corresponding radical species derived from the unlabeled material.

III. Assignment of Splitting Constants

The assignment of the proton splittings from the A species can be done in a straightforward manner as there is only one proton splitting for this species. For the B species, from MO arguments and also based on esr observations on 2,6-dichlorosemiquinone ion, it has been pointed out[2,4] that the smaller proton splitting can be assigned to the group of protons nearer to the complexed oxygen atom and the larger proton splitting can be assigned to the group away from the complexed oxygen.

As regards ^{13}C splittings, the assignment for the high-temperature spectra is again straightforward as the spectra are A type and hence only a single ^{13}C splitting is expected from the labeled carbon atom at the carbonyl position.

At low temperatures both A and B species occur in comparable amounts. The problem of assigning one of the three observed ^{13}C splittings to the A species is simple and it can be readily done by looking for the pairs of satellites that lie symmetric with respect to the proton lines from the A species. However, this is not so simple as there is considerable overlap of the satellite lines in the central region of the spectrum. Analysis of the satellites from the end proton lines of the different species indicates that the 2.45-G satellites occur symmetrically on either side of the proton lines from the A species and the 3.50- and 0.79-G splittings occur symmetrically with respect to the proton lines from the B species.

The next step is to assign the two other splittings to the tight ion pair. Once ion pairing takes place, the two carbonyl carbon atoms are no longer equivalent and, depending upon whether the metal remains in the vicinity of the labeled carbonyl group or the unlabeled group, one should expect two sets of ^{13}C splittings from the intimate ion pair. The probability of the metal atom's remaining at either end of the monolabeled molecule is the same and hence the intensities of the two sets of satellites are expected to be the same. Also the intensity of these sets of satellites for the end proton lines is expected to be one-half the intensity of the satellites from the A species if both the A and B species are present in equal amounts. However, it can be seen from the spectrum obtained from PBSQ* that the proportion in which the A and B species are present at −75° is roughly 1:3. In the absence of line-width contributions resulting from the difference in spin densities at the carbonyl carbon positions in the three different cases, the intensities of the satellites arising from the A and B species should be in the ratio 2:3. In principle it should be possible to distinguish between the ^{13}C lines arising from A and B species using this criterion for intensity ratio also. However, it is well known that there are larger line-width contributions to the ^{13}C satellites from high spin density positions and that this broadening resulting from the local contribution is larger at lower temperatures.[24,25] As a result of all these complications the evidence for the assignment of the splittings from intensity considerations is not quite categorical.

It should also be noticed that the intensity of the ^{13}C satellites is much less compared to the expected intensity which is one-half the intensity of the proton lines. This observation is also a consequence of the additional line-width contributions to the width of the ^{13}C lines and has been observed by other workers also.[24] In addition an intramolecular alkali metal migration or interconversion of the radical species also can broaden the ^{13}C satellites.

Finally, there remains the problem of assigning the two ^{13}C splittings to specific positions in the B species. This can be done only with the help of the results on MO calculations. From considerations that we will

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[25] J. H. Freed and G. K. Fraenkel, *ibid.*, **32**, 1433 (1960).

take up later in section V, we simply state here that the −0.79-G splitting can be assigned to the carbon atom at position 1 of the B species (adjacent to the proton positions corresponding to the smaller splittings) and the −3.50-G splitting can be assigned to position 4.

IV. Evaluation of Spin Densities from Experimental Splittings

In evaluating spin densities from experimental data we adopt essentially the method used by Das and Fraenkel[8] and followed by Gulick and Geske.[26] In the A species and also for A-type spectra with one proton splitting constant the procedure is simple. The four proton positions are equivalent and the spin densities at these positions are evaluated from proton splittings by using McConnell's relationship[27]

$$a_i^{\mathrm{H}} = Q_{\mathrm{CH}}^{\mathrm{H}}\rho_i^{\pi} \qquad (1)$$

We use a value of −27 G for $Q_{\mathrm{CH}}^{\mathrm{H}}$ [8,26]

The carbonyl carbon-13 splittings, $a_{\mathrm{CO}}^{\mathrm{C}}$, can be expressed in terms of the Karplus–Fraenkel relationship[28] and using the values of the carbonyl-^{13}C parameters obtained by Das and Fraenkel,[8] it is given by

$$a_{\mathrm{CO}}^{\mathrm{C}} = 33.8\rho_{\mathrm{C}}^{\pi} - 13.9(\rho_{\mathrm{C'}}^{\pi} + \rho_{\mathrm{C''}}^{\pi}) - 27.1\rho_{\mathrm{O}}^{\pi} \qquad (2)$$

where C, the carbonyl carbon atom, is bonded to an oxygen atom, O, and two other carbon atoms, C′ and C″. In PBSQ, carbon atoms C′ and C″ are equivalent for any carbonyl-^{13}C splitting for both A and B species and hence $a_{\mathrm{CO}}^{\mathrm{C}}$ can be conveniently written in the form

$$a_{\mathrm{CO}}^{\mathrm{C}} = 33.8\rho_{\mathrm{CO}}^{\pi} - 27.8\rho_{\mathrm{CH}}^{\pi} - 27.1\rho_{\mathrm{O}}^{\pi} \qquad (3)$$

where ρ_{CO}^{π} is the π-electron density on the carbonyl carbon, ρ_{CH}^{π} the spin density on the CH carbon atoms adjacent to the carbonyl carbon, and ρ_{O}^{π} the spin density on the oxygen atom. In addition to eq 1 and 3 there is the relation of the conservation of spin density

$$\sum_{\mathrm{all\ i}} \rho_i^{\pi} = 1 \qquad (4)$$

Using eq 1, 3, and 4 one can map out the spin densities in the A-type radicals, and these values are given in Table II.

However, the problem of finding the spin densities for the B species is not so simple. In this case there are six different spin densities for the eight atoms constituting the molecule as the only positions that are equivalent are 2 and 6 forming one group and 3 and 5 forming another group. In order to map out the spin densities one can set up only five different equations, two for the proton splittings from positions 2 and 3, two for the ^{13}C splittings from positions 1 and 4, and a fifth equation for the spin density conservation. This procedure is clearly inadequate for mapping the spin densities in the B species. One can circumvent this difficulty if it is possible to find out any specific relationship between any two of the spin densities at positions that are not equivalent in the B species. Such a relation has been found to exist between the spin densities at the carbonyl carbon and the carbonyl oxygen of a given CO group in electrolytically generated PBSQ samples. For this we make use of the data obtained by Das and Fraenkel.[8] They have obtained seven different sets of values for the spin densities at various positions in PBSQ for different solvent compositions, making use of experimental splittings (see Table III of ref 8). A least-squares analysis of the seven different sets of values for the spin densities at the carbonyl carbon position, ρ_{CO}^{π}, and the corresponding spin density on the carbonyl oxygen, ρ_{O}^{π}, shows that there is a straight-line relationship between ρ_{CO}^{π} and ρ_{O}^{π}. It can be expressed in the form

$$\rho_{\mathrm{CO}}^{\pi} = -1.115\rho_{\mathrm{O}}^{\pi} + 0.3406 \qquad (5)$$

The slope has a standard deviation of 1.2% and the intercept has a standard deviation of 0.7%. The linearity between ρ_{CO}^{π} and ρ_{O}^{π} can also be observed if one uses an alternative set of experimental spin densities, *viz.*, the spin densities in different pure solvents like DMSO,[9,11] DME,[8,10] acetonitrile,[11,26] ethanol,[8] and water.[11,26]

Table II. Experimental and Calculated Spin Densities, *p*-Benzosemiquinone^{-}K^{+} in DME

Type of spectrum	Position[a]	Spin densities Exptl[b]	Calcd[d] (McLachlan)
A type[c] (25°)	1	0.1512	0.1523
	2	0.0885	0.0883
	7	0.1718	0.1709
A type[c] (A species, −75°)	1	0.1435	0.1436
	2	0.0893	0.0891
	7	0.1779	0.1783
B type[c] (B species, −75°)	1	0.1631	0.1615
	2	0.0717	0.0720
	3	0.1068	0.1043
	4	0.1334	0.1401
	7	0.1591	0.1570
	8	0.1858	0.1890

[a] See Figure 4 for numbering of positions. [b] See text for evaluation of spin densities from observed splittings. [c] See text for the definition of A and B species. [d] See text for the carbonyl group parameters that predict the calculated spin densities.

If it is assumed that eq 5.5 holds good separately for both the carbonyl groups in the B species, we can map out the spin densities at various positions in the molecule. As an illustration we will take up the following assignments for the splittings: $a_2^{\mathrm{H}} = -1.935$ G, $a_3^{\mathrm{H}} = -2.885$ G, $a_1^{\mathrm{C}} = -0.79$ G, and $a_4^{\mathrm{C}} = -3.50$ G. Using the value of a_2^{H} in eq 5.1 and taking $Q_{\mathrm{CH}}^{\mathrm{H}} = -27$ G, $\rho_2^{\pi} = 0.0717$. Using this value of ρ_{CH}^{π}, and substituting the value of ρ_{CO}^{π} in terms of ρ_{O}^{π} from eq 5.5, we can obtain the value of ρ_1^{π} and ρ_7^{π} from eq 5.3. The values obtained using $a_1^{\mathrm{C}} = -0.79$ G are $\rho_1^{\pi} = 0.1631$ and $\rho_7^{\pi} = 0.1591$. In an exactly similar manner, using $a_3^{\mathrm{H}} = -2.885$ G and $a_4^{\mathrm{C}} = -3.50$ G, we obtain $\rho_3^{\pi} = 0.1068$, $\rho_4^{\pi} = 0.1334$, and $\rho_8^{\pi} = 0.1858$. The values of the spin densities obtained as above are shown as experimental spin densities in Table II.

The spin densities in the B species can be mapped out in a slightly different manner also. Instead of assuming the linearity between ρ_{CO}^{π} and ρ_{O}^{π} at *both* ends of the molecule, one can calculate the spin densities assuming the linearity at only *one* end and then make use of eq 5.4. Two such sets of spin densities can be obtained by assuming the linearity between ρ_1^{π} and ρ_7^{π}, and ρ_4^{π}

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(26) W. M. Gulick, Jr., and D. H. Geske, *J. Amer. Chem. Soc.*, **88**, 4119 (1966).

(27) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956); H. M. McConnell and H. H. Dearman, *ibid.*, **28**, 51 (1958); H. M. McConnell and D. B. Chestnut, *ibid.*, **28**, 107 (1958).

(28) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

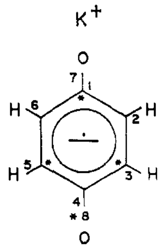

Figure 4. Numbering of atom positions in the tight ion pair of *p*-benzosemiquinone anion with potassium.

and ρ_8^π in turn. These sets of spin densities do not differ appreciably among themselves, nor do they differ in any appreciable extent from the spin densities in Table II. The average difference between the different sets is only 0.0003.

In Table II the spin densities obtained from the A-type spectra are different for room temperature and $-75°$. The difference arises mainly as a result of the difference in the value of a_1^{C} at the two temperatures. Although similar temperature dependence of ^{13}C and ^{14}N splittings have been observed earlier,[29,30] in the present case the observed variation in the splitting is quite large. This may arise from the fact that at room temperature the migration of the alkali metal between the two oxygen atoms is fast and the ^{13}C splitting that one observes is an averaged ^{13}C splitting from the B species. Consequently, the average values of the spin densities obtained using the room temperature spectrum are not strictly comparable to the values obtained from the A species radical at $-75°$.

V. Molecular Orbital Calculations

There are several MO calculations available for the symmetric *p*-benzosemiquinone anion radical.[8,10,31,32] However, there are no published data available for the molecular orbital calculations for the unsymmetrically complexed species. Sufficient data now exist for the unsymmetrically complexed PBSQ to determine the complete π-electron spin density distribution in a semiempirical manner. We have therefore performed molecular orbital calculations in an attempt to reproduce these semiempirical spin densities.

The MO calculations have been performed using the simple Hückel method and also using the McLachlan method[33] of including configuration interaction in an approximate way. The parameter λ introduced in this procedure has been given the value 1.2. The Coulomb integral for the oxygen atom (α_{O}) and the resonance integral for the carbon–oxygen bond (β_{CO}) were adjusted by varying the parameters δ_{O} and γ_{CO} in the defining expressions, $\alpha_{\mathrm{O}} = \alpha + \delta_{\mathrm{O}}\beta$ and $\beta_{\mathrm{CO}} = \gamma_{\mathrm{CO}}\beta$, where α and β are the Coulomb and resonance integrals for an aromatic carbon atom. An inductive parameter for the carbon atom of the carbonyl group was not included in the calculations. Since the results of both the Hückel and McLachlan methods are similar we will be reporting the results from the McLachlan method only in the following discussion.

In the present calculation our essential interest was to examine the effect of varying the δ_{O} and γ_{CO} values for one of the CO groups, keeping the values of δ_{O} and γ_{CO} unchanged for the other group. We were also interested in finding out the difference between the A and B species at a given temperature from a molecular orbital viewpoint.

For the A species radicals the δ_{O} and γ_{CO} values are the same for both the CO groups and initial calculations were done over a range of values ($1.0 \leq \delta_{\mathrm{O}} \leq 1.75$ and $1.0 \leq \gamma_{\mathrm{CO}} \leq 1.6$) with intervals of 0.05 unit for δ_{O} and 0.02 unit for γ_{CO}. In the case of A-type radicals the best fit[34] was obtained using the following values for the parameters in the McLachlan method: $\delta_{\mathrm{O}} = 1.50$, $\gamma_{\mathrm{CO}} = 1.28$ at room temperature and $\delta_{\mathrm{O}} = 1.451$, $\gamma_{\mathrm{CO}} = 1.30$ at $-75°$. The experimental spin densities and the calculated spin densities using the above parameters are shown in Table II.

For the B-type radicals, the two CO groups are no longer equivalent. Let us assume that the complexing takes place at oxygen atom 7 (see Figure 4). We can now define $\delta_{\mathrm{O}}(7) = \delta_1$, $\gamma_{\mathrm{CO}}(1,7) = \gamma_1$, $\delta_{\mathrm{O}}(8) = \delta_2$, and $\gamma_{\mathrm{CO}}(4,8) = \gamma_2$. Initial calculations were done using the following range of parameters: $1.0 \leq \delta_1 \leq 1.75$, and $1.30 \leq \gamma_1 \leq 1.36$, keeping $\delta_2 = 1.45$ and $\gamma_2 = 1.30$. The δ value was varied with increments of 0.05 unit and the γ values were varied with increments of 0.02 unit. After looking for an over-all fit at all positions by comparison with experimental spin densities at $-75°$, calculations were performed using finer intervals, with $1.45 \leq \delta_1 \leq 1.65$ and $1.23 \leq \gamma_1 \leq 1.30$ with intervals of 0.01 unit. The parameters that gave the best fit[34,35] were $\delta_1 = 1.50$ and $\gamma_1 = 1.23$, with $\delta_2 = 1.45$ and $\gamma_2 = 1.30$.

There are some trends that can be noticed in the values for the MO parameters for the A and B types of radicals. It can be seen that a larger δ_1 value is required for the B species for a good fit. Since β is negative, this larger value of δ_1 corresponds to a more negative value of the Coulomb integral, α_{O}, for the complexed oxygen atom and is therefore in the anticipated direction. On the other hand, it is difficult to speculate on the significance in the change in the value of γ, as the present type of calculations are only approximate in nature.

The present calculations also show some trends in the values of the spin densities at any given position in the ring when either the Coulomb integral or the resonance integral parameter is varied in a systematic way. The sign of the change in calculated spin density with increase in the value of the given parameter, in general, alternates at adjacent ring sites (see the starred and unstarred positions in Figure 4). Similar effects have been observed by Claxton, Gough, and Symons[36] in

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(29) M. R. Das and G. K. Fraenkel, *J. Chem. Phys.*, 42, 792 (1965).

(30) M. R. Das, unpublished results.

(31) G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, 34, 1333 (1961).

(32) M. Broze, Z. Luz, and B. L. Silver, *ibid.*, 46, 4891 (1967).

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

(34) Nowhere in the range of parameter values covered is the agreement as good and the trend of the data indicates that outside this range the agreement would be poorer.

(35) In the case of the B species finding the best fit for the experimental spin densities involves comparison with calculated spin densities at six different positions. Consequently the following criterion was adopted to find the best fit. After finding out different sets of calculated numbers close to the experimental spin densities, the calculated values were used to predict ^{13}C splittings at positions 1 and 4 using eq 5.3. The set which predicted the closest values for experimental splittings was chosen as the best calculated spin densities. For the A species radicals the best parameters obtained by a comparison of spin densities alone predict the closest ^{13}C splittings also.

(36) T. A. Claxton, T. E. Gough, and M. C. R. Symons, *Trans. Faraday Soc.*, 62, 279 (1966).

the calculation of spin densities in monoprotonated durosemiquinone using valence bond methods. The effect of varying the value of δ_1, keeping the other values constant, is illustrated in Figure 5. Two cases have been shown, one in which $\gamma_1 = \gamma_2 = 1.30$ with $\delta_2 = 1.45$, and another in which $\gamma_1 = 1.28, \gamma_2 = 1.34$, and $\delta_2 = 1.45$. The effect of varying the value of γ_{CO} is essentially similar to that of varying δ_O. However, the sign of the change in spin densities at the different positions corresponding to an increase in δ_1 is just the opposite of the sign corresponding to an increase in γ_1. Thus, increase in the value of γ_1 results in increase in the spin densities at positions 2, 4, and 7 and decrease in the spin densities at positions 1, 3, and 8. ρ_4 is the least sensitive with respect to change in γ_1, and ρ_2 is more sensitive compared to ρ_3.

Molecular Orbital Calculations and Spin Densities Predicted from ^{13}C Splittings. It has been mentioned in section III that it is difficult to assign the two different ^{13}C splittings from the B species to specific positions in the ring from experimental data alone. Furthermore, the sign of the larger ^{13}C splitting was also uncertain. In choosing between the different possibilities we will make use of MO arguments in conjunction with arguments based on experimental findings by Das and Fraenkel[3] on the behavior of carbonyl-^{13}C splittings. It was observed by these investigators that an increased ionic interaction at the carbonyl oxygen results in a decrease in the spin density at the oxygen position and an increase in the spin density at the carbonyl carbon position. The same trend in the spin density redistribution is predicted by an increase in the value of the Coulomb integral parameter for the carbonyl oxygen in a MO calculation.

Our results show that if the Coulomb integral parameter δ_1 is given a larger numerical value corresponding to an increased interaction at the oxygen position 7, the MO results predict a more *positive* value for the ^{13}C splitting at position 1 as compared to the carbonyl-^{13}C splitting in the A species and a more *negative* value at position 4. This trend indicates that the -0.79-G splitting can be attributed to carbon atom 1 of the B species (Figure 4). Consequently the other splitting is from the carbon atom at position 4 and it can be assigned a negative sign since one expects this splitting to be more negative compared to the splitting from the A species radicals on the basis of MO arguments.

VI. Structure of Ion Pairs and Alternating Line Widths

The present experiments reveal some interesting aspects regarding the structure of ion pairs in semiquinone–alkali metal systems. The low-temperature experiments on PBSQ clearly show that there are at least two different types of radicals (A and B species) that are present in equilibrium with each other. The B species radicals are contact ion pairs in all likelihood and the A species observed at low temperatures are unassociated or "free" species. Experiments at different temperatures also indicate that these species do undergo interconversion among themselves. By looking at the spectra at −75° (Figure 3) and at room temperature (Figure 2) two points are obvious. At room temperature the spectrum is A type. Further, the room temperature spectrum shows alternating line-width effects with $M_H = \pm 1$ lines being broad, although the A species radicals at −75° show little alternating line-width effects. Several investigators have attributed[3,6,37] the alternating line-width effects observed in semiquinone–alkali metal systems to an intramolecular migration of the counterion between the two oxygen atoms. In fact, a careful examination of the ^{13}C satellites from the room-temperature spectrum provides direct experimental support to this mechanism. It can be seen from Figure 2 that the ^{13}C satellites for the $M_H = 0$ line are slightly smaller in intensity compared to the satellites arising from the proton lines having $M_H = \pm 1$. Such a broadening of the satellites from the $M_H = 0$ line cannot be satisfactorily explained by an ion pair equilibrium model as one expects equal broadening of the satellites arising from the $M_H = 0$ line and $M_H = \pm 1$ lines, if the interconversion reaction is between a B species radical, with averaged out splittings resulting from a fast migration of the counterion, and a free ion. It is also clear that the spectrum at room temperature is not arising from a fast interconversion of unsymmetrically complexed B species with two distinct unaveraged ^{13}C splittings and A species radicals. If this were the case one expects two ^{13}C satellites for the end lines in the room-temperature spectrum whereas we observe only one satellite. On the other hand, the relative broadening of the satellites is easily understandable if we assume a migration of the alkali metal. When the alkali metal migrates from the labeled group to the unlabeled group the magnitude of the ^{13}C splitting changes from -0.79 to -3.50 G[38] and the proton splittings from the protons closer to the labeled carbon changes from -1.935 to -2.885 G. When averaging takes place the ^{13}C lines from the central proton line are expected to be broader since the satellite line positions are separated by 1.355 G corresponding to the alkali metal being present at the two different ends of the molecule as compared to a separa-

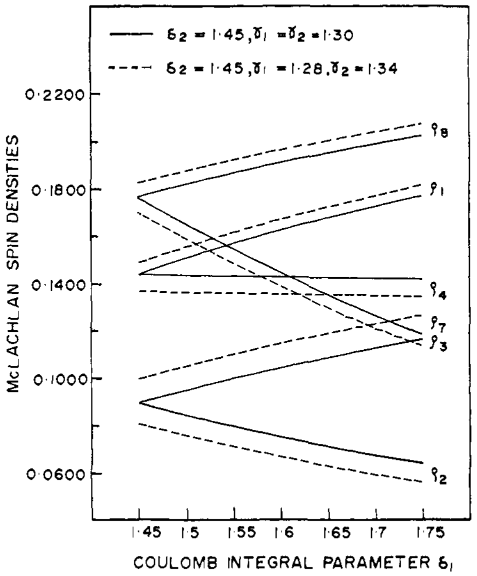

Figure 5. Calculated spin densities at the different atom positions in the tight ion pair of *p*-benzosemiquinone ion as a function of the Coulomb integral parameter δ_1 for the oxygen atom at position 7.

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(37) P. S. Gill and T. E. Gough, *Can. J. Chem.*, 45, 2112 (1967).

(38) For the purpose of illustration we are using the values of the splitting constants at −75°, and any temperature dependence of the splitting constants have not been taken into account.

tion of 0.41 G for the pair of satellite line positions under consideration for the $M_H = \pm 1$ lines.

It may be pointed out that detailed investigations in our laboratory on the durosemiquinone (DSQ)–K and DSQ–Na systems in both DME and tetrahydrofuran also point to the fact that the alkali metal migration is responsible for the alternation in the widths of the hyperfine components in the esr spectra in agreement with observations made by other investigators.[3,6,7]

VII. *g* Shifts and Ion Pairing

One of the interesting features in the present results is the difference in the *g* values observed for the A and B species. At $-75°$ the *g* value for the A species is 2.00551 ± 0.00002 and for the B species is 2.00543 ± 0.00002. It is not possible to obtain accurate *g* values from our spectra for the A and B species at higher temperatures. Consequently, any temperature dependence in the *g* values of these species could not be determined at the present stage.

Zandstra[39] has reported *g* value variations in PBSQ resulting from solvent interactions, and it has been observed that the *g* value is higher in dimethyl sulfoxide as compared to ethanol–water solutions where the solvent interaction is greater. Similar effects have been reported for benzophenone anions[40] in which there is a decrease in the *g* value resulting from an increase in cationic perturbation. The decrease has been attributed to a shift in the spin density from the carbonyl group into the ring[40] which results in a reduction in the orbital contribution to the *g* value. In the present case also the intimate ion pair has a smaller *g* value and the lowering of the *g* value can be attributed to increased cationic perturbation. There is also evidence for a shift in the spin density from the oxygen atoms to the ring that results from ion pairing. Further work on the *g* value variations with difference in cations and also from variations resulting from a change in temperature is under progress.

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Magnetic Resonance Study of Conformational Inversion In Some Substituted 10,10-Dimethyl-9,10-dihydroanthracenes[1,2]

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Abstract: The ring inversion in 10,10-dimethyl-9-methylene-1,8-dichloro-9,10-dihydroanthracene (I), 9-(dichloromethylene)-10,10-dimethyl-9,10-dihydroanthracene (II), and 9-(dibromomethylene)-10,10-dimethyl-9,10-dihydroanthracene (III) in 1,1,2,2-tetrachloroethane solution has been studied using nmr complete line-shape analysis methods. Exchange rates were calculated from the nmr spectrum of methyl group protons by treating them as uncoupled exchanging AB systems with equal population. The low-field methyl peak in the spectra of compounds studied was assigned to the equatorial methyl and the high-field peak to the axial methyl. The $\Delta F^{\ddagger}$ for ring inversion was found to be 15.9, 17.4, and 19.0 kcal/mol in compounds I, II, and III and qualitative interpretation was proposed in terms of nonbonded interactions between the exocyclic methylene substituents and the *o*-aryl substituents in the assumed planar transition state. The changes in the activation parameters obtained by using different $1/T_2$ values for line-shape calculations were also studied.

Considerable attention has recently been devoted to the question of conformational stability in 9,10-dihydroanthracene systems.[5] From these studies it appears that the preferred conformation of the center ring in substituted 9,10-dihydroanthracenes is influenced to largest degree by the nature and bulk of the substituent in either the *o*-aryl or *meso* positions. Curtin and coworkers[6] have synthetized a series of substituted 10,10-dimethyl-9-methylene-9,10-dihydroanthracenes and measured their nmr spectra. The nmr spectra of the methyl resonance region in these compounds showed varying degrees of equivalence depending upon the substituents on the methylene carbon. These observations were consistent with a hindered boat–boat

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(4) Alfred P. Sloan Fellow.

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