unimolecular rearrangement of the electronically excited molecule. This unimolecular reaction must compete with the spontaneous (radiative and nonradiative) decay of the excited state and with its quenching by oxygen. Measurements, made by M. Walker of this department with a phase shift apparatus[11] using a deaerated 5×10^{-5} M solution of I in cyclohexane, indicate a mean lifetime of fluorescence of 2.5×10^{-9} sec. The rate constants for the spontaneous decay of the triplet and for the oxygen quenching of the first excited singlet and the lowest triplet have not been determined for I. It is plausible that they are in general similar to the corresponding values for anthracene, which are as follows: first-order decay of the triplet, 30 sec^{-1};[12] second-order (oxygen) quenching of the excited singlet,[8] 2.3×10^{10} l./mole sec; second-order quenching of the triplet,[12] 2.3×10^{9} l./mole sec. Values of these orders of magnitude preclude the possibility that the active intermediate for isomerization is exclusively the triplet state. The postulate that the observed reaction is the result of a spontaneous rearrangement of the fluorescent state is consistent with the observed values for air- and oxygen-saturated solutions. However, the relatively high value obtained for deoxygenated solutions is incompatible with this mechanism. This value, if correct, suggests that both the excited singlet and the triplet states can isomerize, but that the triplet state contributes significantly to the reaction only in deoxygenated solutions.

Acknowledgment. We wish to express our gratitude to Dr. S. Fenton (Minnesota) for suggesting this problem and providing the sample of 1,2-bis(9-anthryl)-ethane, and to Dr. R. Lumry (Minnesota) and his colleagues, Dr. T. Bednar and Dr. M. Walker, for determining the fluorescence spectrum and mean lifetime.

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Electron Spin Resonance Studies on Ion Pairing in Semiquinone–Alkali Metal Systems

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Abstract: Esr spectra from semiquinone anion radicals produced by alkali metal reduction of parent quinones in ether solvents have been investigated. The results reveal large changes in the spin density distribution in the semiquinone rings as a consequence of association of the anion with alkali metal cations. Ion pairs with different amounts of solvation have been detected, and the results have been interpreted in terms of an ion-pair equilibrium model. Alternating line-width effects have also been observed in the semiquinone–alkali metal system. This arises from the time-dependent modulations of the isotropic ring proton splitting constants resulting from an equilibrium between "solvated" and "intimate" ion pairs in which the metal cation does not drift away from the radical anion.

There has been considerable interest in the experimental and theoretical investigations of the electron spin resonance (esr) of semiquinones in the recent past. The semiquinones form a convenient system for such investigations for various reasons, like ease of producing radicals using different methods and the simplicity of their esr spectra. *p*-Benzosemiquinone (PBSQ), which forms the simplest member of the semiquinone type of radicals, has been investigated extensively, and accurate data are available for hyperfine splittings from protons[1–12] and carbon-13[13–20] and oxygen-17[21,22] nuclei. From these data a good deal of information is available[14,19,20,22] as regards the unpaired electron density distribution in the molecule and the solvent-induced perturbations on the distribution of the π density.

In the past, semiquinone ion radicals have been produced by air oxidation of the hydroquinone in alkaline solvents,[1–11,13–17] by electrolytic methods[18–22] and by ultraviolet irradiation methods.[23] However, a very

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Table I. Hyperfine Splitting Constants (gauss) in *p*-Benzosemiquinone Anion in DME[a]

Temp, °C	Na				K		
	A species[b]	B species			A species[b]	B species[b]	
	a^{H}	a_1^{H}	a_2^{H}	a^{Na}	a^{H}	a_1^{H}	a_2^{H}
60	...	...	...	...	2.35 ± 0.03	...	...
25	2.40 ± 0.02	2.06 ± 0.02	2.74 ± 0.02	1.09	2.41 ± 0.01	...	...
10	2.36 ± 0.02	2.05 ± 0.04	2.66 ± 0.04	1.07	...	...	...
−20	2.42 ± 0.01	...	...	...	2.38 ± 0.01	...	...
−60	2.32 ± 0.09	...	...	...	...	2.16 ± 0.01	2.66 ± 0.01

[a] See text for definition of "A" and "B" species. [b] No metal splitting observed in the spectra.

successful technique in producing aromatic radicals has been the reduction of the parent material in a polyether using alkali metals; the method has been described previously.[24–27] A variety of interesting results have been obtained on the alkali metal–aromatic radical ion pairs obtained in this manner. The interest centered mainly around the structure of ion pairs,[28–39] the different types of ionic equilibria existing in the radical–alkali metal system,[28,30,39–43] and the effect of intramolecular and intermolecular interactions on the esr spectra.[30,34,39–42] The observation of an alternation in line broadening in the esr spectra resulting from an intramolecular exchange of a cation first observed by de Boer and Mackor[41,42] and supported by later workers[23,34] has been of particular interest.

The present work was undertaken with a view to investigate the ion-pairing phenomenon in the semiquinone–alkali metal system in detail using the alkali metal reduction technique in ether solvents. From earlier experimental observations[10–12,18–20,23] one expects large perturbations in the unpaired electron density in the semiquinone ring systems as a consequence of ion pairing. The expectations have been substantiated by esr results. The results obtained on the semiquinones with different alkali metals using 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) as solvents together with the temperature dependence of the splittings are reported in section III. These results and the mechanism of the alternation in line broadening that we have observed in the present system are discussed on the basis of an ion-pair equilibrium model in section V.

II. Experimental Section

p-Benzoquinone was prepared from hydroquinone (May & Baker Ltd.) according to the method of Gilman and Blatt[44] and was purified by sublimation (mp 116°). Duroquinone was synthesized starting from durene (Fluka, Switzerland) using known methods.[45] The product was crystallized from ethanol and purified by vacuum sublimation (mp 111°). 2,6-Dichloroquinone was obtained from Eastman Organic Chemicals and was purified by vacuum sublimation before use. DME and THF were obtained commercially. The solvents were purified according to methods described previously.[27,46]

The semiquinone radicals were made *in vacuo* by reducing the corresponding quinones with alkali metals using known techniques.[24–27]

The X-band esr spectrometer used has been described previously.[12] The temperature studies were made using a Varian V-4540 temperature-control unit. The details of field calibration have been described elsewhere.[47]

III. Experimental Results

***p*-Benzosemiquinone Ion (PBSQ).** The results obtained on PBSQ with sodium and potassium as gegenions using DME as solvent are given in Table I.

The PBSQ–K sample in DME was bluish green in color and was stable for 36–48 hr. Afterwards the radicals gradually decayed. At room temperature the esr spectrum from this sample was qualitatively similar to those observed for PBSQ by air oxidation of hydroquinone or by the electrolytic reduction of *p*-benzoquinone, and the hyperfine splitting arises from the interaction of the unpaired electron with four equivalent protons. However, on cooling the sample, the spectrum gradually changed its shape. At −20°, lines with total z component of the proton nuclear spin angular momentum $M_{H} = \pm 1$ were broadened and were comparable in intensity to lines with $M_{H} = \pm 2$. At −60°, a nine-line esr spectrum was observed, and it has been reported in a preliminary communication.[12] This spectrum has been attributed to a radical species which has two sets of two equivalent protons.

In Table I, the radical species in which the four ring protons are equivalent is referred to as the "A" species, and the one in which they form two sets of equivalent groups is referred to as the "B" species. The same terminology will be used in discussing the results from durosemiquinone (2,3,5,6-tetramethyl-*p*-benzosemiquinone) also. Radical species in which all the four

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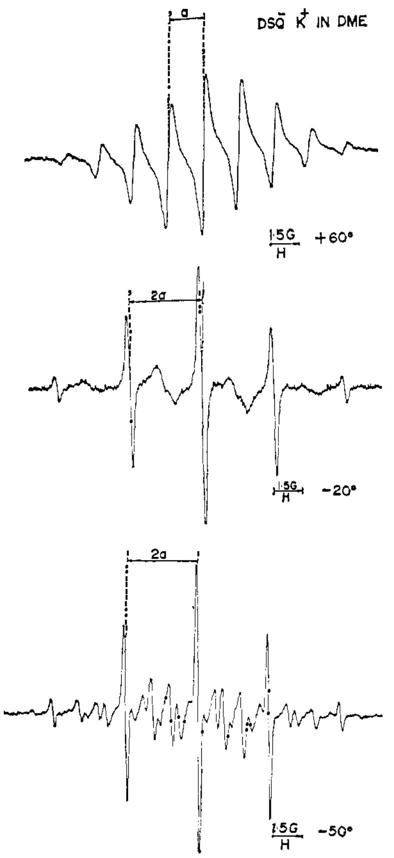

Figure 1. First derivatives of the esr spectra from durosemiquinone ion in DME with potassium as counterion.

methyl groups are equivalent will be designated as the "A" species, and the one in which they fall into two groups of equivalent protons will be referred to as the "B" species.

The PBSQ–Na sample in DME was also bluish green in color, but it was less stable, and it was necessary to complete the esr measurements within 10–12 hr after the sample was prepared. The room-temperature spectrum was a superposition of two spectra, one from the A species with one proton splitting constant and another from the B species with two proton splitting constants. The spectrum from the B species shows additional structure due to ^{23}Na ($I = {}^3/_2$) hyperfine interaction (see Table I). However, the relative concentration of the two species could not be correctly determined as a result of the highly overlapped nature of the experimental spectrum. At −20° the lines were considerably broadened, and it was not possible to obtain accurate data from the spectrum. The sample showed the same behavior even on further cooling.

Attempts to record esr spectra from PBSQ–Li in DME and PBSQ–M (M = Li, Na, K) in THF were not successful as the radicals were found to be unstable.

Durosemiquinone Ion (DSQ). Unlike PBSQ, samples of DSQ with lithium, sodium, and potassium as counterions were quite stable in both DME and THF. The results obtained from these samples are reported in Tables II and III.

DSQ–K Samples. When the radical was prepared with potassium metal in DME, the sample exhibited esr spectra with equally spaced components at room temperature and at 60°. These could readily be interpreted as arising from 12 equivalent methyl protons (A species). However, the room-temperature spectrum showed dormant alternating line-width effects. At − 20° the alternating line-width effect was considerably enhanced (Figure 1), and as the temperature was further lowered lines arising from the B species started appearing. At −80°, the spectrum could be interpreted in terms of two groups of equivalent protons, each consisting of six protons and arising from pure B species. A sample of DSQ–K in THF solution behaved essentially in the same manner. However, at room temperature there was larger alternation in the width of the lines in the esr spectrum from this sample as compared to the spectrum from DSQ–K in DME. No potassium splittings were observed in either case.

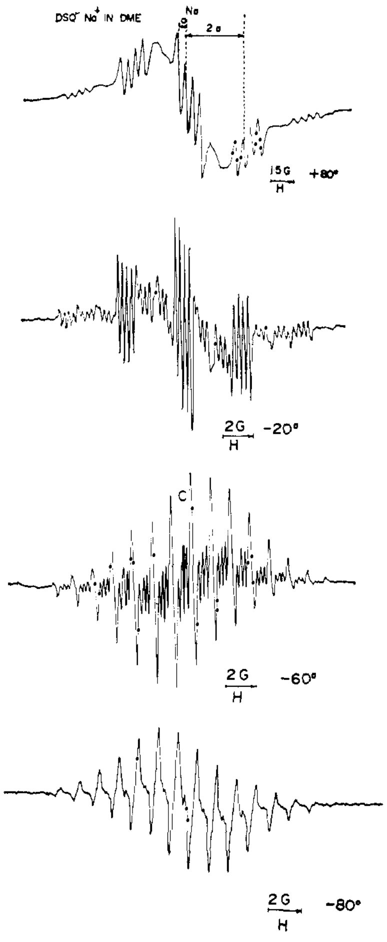

Figure 2. First derivatives of the esr spectra from durosemiquinone ion in DME with sodium as counterion.

DSQ–Na Samples. The spectra from this sample in DME at different temperatures are shown in Figure 2. Except at −80°, at all other temperatures reported in Table II, the individual figures arise from both A and B species of DSQ. Both species show hyperfine splittings arising from ^{23}Na hyperfine interaction (see assignments of splitting constants below). A different extent of alternation in the line broadening at different temperatures is also evident in Figure 2.

In interpreting the spectra from DSQ–Na samples, the equally spaced four-line pattern arising from the A species could be easily picked out. The problem was then reduced to assigning the rest of the lines to B species. In order to do this, spectra were reconstructed

Table II. Hyperfine Splitting Constants (gauss) in Durosemiquinone Anion in DME[a]

Temp, °C	Li[c]		Na					K		
	B species[b]		A species		B species			A species[b]	B species[b]	
	a_1^{H}	a_2^{H}	a^{H}	a^{Na}	a_1^{H}	a_2^{H}	a^{Na}	a^{H}	a_1^{H}	a_2^{H}
80	...	...	1.920 ± 0.004	0.504 ± 0.011	...	...	...	...	...	...
60	0.768 ± 0.094	3.125 ± 0.009	...	...	...	...	...	1.901 ± 0.005	...	...
25	0.863 ± 0.005	2.981 ± 0.004	1.926 ± 0.003	0.387 ± 0.008	...	...	...	1.916 ± 0.008	...	...
−20	0.964 ± 0.003	2.887 ± 0.003	1.898 ± 0.006	0.299 ± 0.014	1.280 ± 0.007	2.565 ± 0.006	2.331 ± 0.008	...	...	...
−50	1.017 ± 0.005	2.825 ± 0.005	...	...	...	...	...	1.915 ± 0.002	1.415 ± 0.008	2.413 ± 0.006
−60	...	...	1.940 ± 0.007	0.264 ± 0.015	1.280 ± 0.002	2.562 ± 0.003	1.789 ± 0.003	...	...	...
−70	1.033 ± 0.012	2.796 ± 0.013	...	...	...	...	...	...	1.434 ± 0.009	2.407 ± 0.009
−80	...	...	...	...	...	...	...	...	1.434 ± 0.009	2.402 ± 0.012

[a] See text for definition of "A" and "B" species. [b] No metal splitting observed in the spectra. [c] No A species observed for the sample.

Table III. Hyperfine Splitting Constants (gauss) in Durosemiquinone Anion in THF[a]

Temp, °C	Li[c]		Na[c]			K		
	B species[b]		B species			A species[b]	B species[b]	
	a_1^{H}	a_2^{H}	a_1^{H}	a_2^{H}	a^{Na}	a^{H}	a_1^{H}	a_2^{H}
25	0.815 ± 0.004	3.039 ± 0.003	1.056 ± 0.017	2.739 ± 0.006	0.346 ± 0.007	1.913 ± 0.003	...	...
−20	0.860 ± 0.007	2.955 ± 0.008	1.198 ± 0.002	2.653 ± 0.001	0.257 ± 0.002	...	1.313 ± 0.014	2.534 ± 0.010
−40	0.892 ± 0.009	2.952 ± 0.008	1.208 ± 0.002	2.623 ± 0.001	0.208 ± 0.002	...	1.312 ± 0.006	2.485 ± 0.004
−60	0.955 ± 0.016	2.936 ± 0.013	...	...	...	...	1.350 ± 0.004	2.458 ± 0.002
−80	...	...	...	...	...	...	1.381 ± 0.004	2.505 ± 0.002

[a] See text for definition of "A" and "B" species. [b] No metal splitting observed in the spectra. [c] No A species observed for the sample.

and compared with the experimental one. In doing so, it was assumed that the sum of the two proton splitting constants, a_1^{H} and a_2^{H}, for the B species is twice the proton splitting constant, a^{H}, for the A species. This is justifiable as it holds true for all other spectra from B species. Consequently, the individual values of a_1^{H} and a_2^{H} were varied keeping their sum constant. Different values of a^{Na} were then used for computing each spectrum.

Taking the −60° case as a typical representative of the group, stick plots were constructed and were compared with the experimental spectrum. After successfully interpreting the −60° spectrum, it was possible to pick out typical patterns arising from the B species in the overlapped spectra at other temperatures, and an intelligent guess regarding the splitting constants from the B species could be made. Stick diagrams were then reconstructed which explained all the observed lines in the experimental spectrum.

The splitting constants for the B species at 80° and at room temperature could not be calculated because of the broadening of the lines in the region where lines from the B species were expected. Consequently, no assignments of proton splitting constants for the B species could be made at these temperatures. The values of the splitting constants in DME are reported in Table II.

The DSQ–Na sample in THF behaved in a slightly different fashion. At all the temperatures at which investigations were carried out, only the B-type of spectra were observed. They exhibited ^{23}Na hyperfine splittings. No alternation in the widths of hyperfine components were observed in this case. The splitting constants are reported in Table III.

DSQ–Li Samples. Samples of DSQ–Li in both DME and THF behaved essentially in the same manner. The spectra at different temperatures could be explained in terms of B species spectra with two splitting constants, each arising from six equivalent protons. There was no observable Li metal splitting unlike the experiments in *t*-pentyl alcohol,[23] and no alternating line-width effects were present. A typical spectrum from the DSQ–Li sample is given in Figure 3. The splitting constants are reported in Tables II and III.

In all instances where the presence of a B species with two splitting constants could be detected, the larger splitting constant, a_2^{H}, increases with temperature and the smaller one, a_1^{H}, decreases with temperature. The variation depends on the solvent and the counterion used, and this will be discussed later. The proton splitting constant, a^{H}, for the A species does not show any measurable temperature variation, although the ^{23}Na splittings in both the A and B species increase with temperature (Tables II and III).

2,6-Dichlorosemiquinone Ion (2,6-DCSQ). Solutions of 2,6-DCSQ in DME and THF were green in color. The radicals were unstable and they decayed completely in 1–1.5 hr. The expected[5] three-line spec-

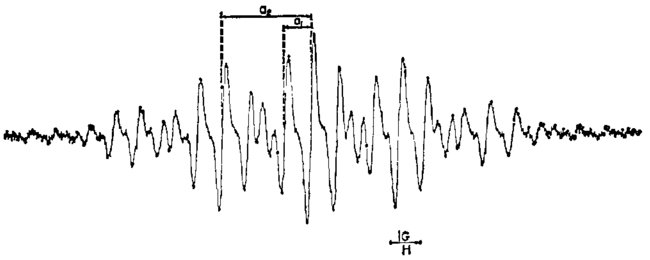

Figure 3. First derivative of the esr spectrum from durosemiquinone ion in DME with lithium as counterion.

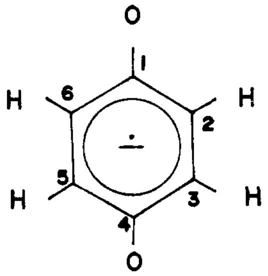

Figure 4. *p*-Benzosemiquinone anion.

trum, with approximate intensity distribution 1:2:1, arising from two equivalent protons was observed from all the samples from which signals could be recorded. However, except for 2,6-DCSQ-K in DME, all the other samples in DME as well as in THF gave spurious esr signals which could not be attributed to any simple radical species arising from 2,6-dichloroquinone. The correct lines from 2,6-DCSQ could be easily identified from intensity considerations and spacings of the hyperfine components. There was no change in the number of lines with temperature, and no alkali metal splittings were present either. Consequently, little information could be obtained by making extensive temperature studies. The results obtained at room temperature and at −75° are given in Table IV. For all the samples, careful measurements have shown a difference in the proton hyperfine splitting with temperature, contrary to a preliminary report.[12] The proton splitting constant increases with temperature for all samples, and at the same temperature the DME samples show a larger splitting as compared to THF samples.

Table IV. Proton Splitting Constants (gauss) for 2,6-Dichlorosemiquinone Anion

Temp, °C	DME[a]		THF[a]	
	Na	K	Li	K
25	2.869	2.989	1.471	...
−75	2.139	2.943	...	3.124

[a] No metal splitting observed in the spectra.

IV. Assignments of Splitting Constants

1. Assignments of Proton Splittings in B Species. There is no ambiguity in the assignment of proton splittings for the A species radicals. Once the proton splittings are assigned, it is not difficult to make assignments for the alkali metal splittings also. However, the spectra from the B species result from two equivalent groups of protons as a consequence of ion-pair association. The positions 2, 3, 5, and 6 (see Figure 4) in a *p*-benzosemiquinone ring can be divided into two equivalent groups in any one of three ways, (a) 2,5 and 3,6; (b) 2,3 and 5,6; or (c) 2,6 and 3,5. However, it is possible to make a satisfactory choice in the following manner. Previous experimental investigations[10–12,18–20] on the semiquinone radicals indicate that most interactions with the surroundings take place through the oxygen atoms in the semiquinone ring. Consequently, the most probable position of the alkali metal counterion also is near one of the oxygens which has maximum charge density.[20] If this assumption is made, the best possible division will be to have the 2 and 6 positions in one group and the 3 and 5 positions in the other. There is experimental evidence to support this view. For 2,6-DCSQ one expects association with the counterion at least to the same extent as in the case of either PBSQ or DSQ owing to the presence of two electronegative chlorine atoms in the ring. When there is strong association, one expects a four-line spectrum from 2,6-DCSQ if either of the groupings a or b were correct. On the other hand, the spectra from 2,6-DCSQ showed only three hyperfine components at all conditions, irrespective of the difference in the temperature of the experiment, the metal cations, and the solvents used, although the magnitude of the splittings changed considerably under different experimental conditions.

2. Position of Counterion and Magnitude of Ring Proton Splittings. From the experimental data alone it is difficult to assign the splittings, a_1^{H} and a_2^{H}, in PBSQ and DSQ to specific positions in the molecule. The problem arises, in the case of the B species, whether the larger splitting constant, a_2^{H}, should be assigned to the group of protons that are nearer to the oxygen atom complexed with the alkali metal or to those farther away from it. A satisfactory assignment is, however, possible by comparing the temperature dependence of the splittings in PBSQ and DSQ with that of 2,6-DCSQ (see section V2).

It is reasonable to assume that in the "intimate" species of 2,6-DCSQ the metal cation is near the oxygen atom having two chlorine atoms as neighbors because of the higher electronegativity of the chlorines as compared to protons.[48] It is experimentally observed that the proton splitting constant for 2,6-DCSQ increases with temperature. It may therefore be assumed that the splitting from protons away from the metal cation increases with temperature. On this basis the larger splitting constant, a_2^{H}, in *p*-benzo- and durosemiquinones, which shows a positive temperature coefficient, can be assigned to protons farther away from the metal cation and the smaller splitting constant, which decreases with temperature, to protons nearer to the metal cation. It may also be noticed that the effect of association at an oxygen site in the semiquinone is to increase the electronegativity of the oxygen atom, which results in the use of a larger numerical value for the Coulomb integral parameter for the complexed oxygen.[20]

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(48) It may be noticed that Lücken[11] has reported the existence of two types of "intimate" ion pairs for 2,6-DCSQ in anhydrous *t*-butyl alcohol, the major fraction having the alkali metal complexed to the oxygen atom flanked by the chlorine atoms and a small fraction with the alkali metal complexed to the oxygen flanked by protons. It has also been observed that simple MO theory predicts larger association at the oxygen flanked by chlorine atoms.

Lücken[11] has shown that simple MO theory predicts an increase in the splitting constant of one pair of protons with a simultaneous decrease in the splitting constant of the other pair as a result of complex formation involving one of the oxygen atoms. Lücken[11] has noticed further that the pair *ortho* to the complexed oxygen atom has a lower coupling constant.

V. Discussion

1. The Ion-Pair Equilibrium Model. The additional hyperfine structure arising from ^{23}Na nuclei in the esr spectra from PBSQ–Na and DSQ–Na in DME and THF suggests the formation of ion pairs in these systems. Even in the absence of alkali metal hyperfine splitting, the observation of esr spectra from the B species, when potassium and lithium are used as counterions, supports ion-pair formation. Further, experimental evidence from both PBSQ and DSQ reveals the presence of more than one type of ion pair which are interconvertible. The best evidence for the simultaneous existence of two types of ion pairs is obtained from DSQ–Na in DME. Esr lines from both A and B types of radical with different ^{23}Na splittings have been observed in this case. Presumably, the ion pairs differ from each other in their different extents of solvation. The formation of ion pairs with different amounts of solvation has been observed by other workers also.[39,49–54] Hirota[39] has observed different distinct solvated species in the naphthalene negative ion, where the radical species have different ^{23}Na splittings, although the magnitude of the proton splittings remains unchanged. In the present instance, as a consequence of stronger association between the alkali metal and the radical, we do observe changes in both proton splittings and alkali metal splittings in species that are solvated to different extents. In fact, the results reported in section IV can be satisfactorily explained on the basis of an ion-pair equilibrium model in which an "intimate" or "contact" ion pair is in equilibrium with a "loose" or "solvated" ion pair. The different possible equilibria for a species with a given nuclear spin state are indicated below (Figure 5). Species of the type $M^+\|R^-$ represent the solvated ion pair, and the ones of the type M^+R^- represent the intimate pairs.

In the intimate pairs, the alkali metal cation is close to one of the oxygens, and this perturbs the unpaired electron distribution in the semiquinone ring. Two sets of equivalent ring positions are formed resulting in the B type of radical exhibiting two proton splitting constants, a_1^H and a_2^H. In the solvated pair, which corresponds to the A type of radicals, the equivalence of the four ring proton positions is retained as the alkali metal is farther separated from the oxygen atom by the solvent layer.

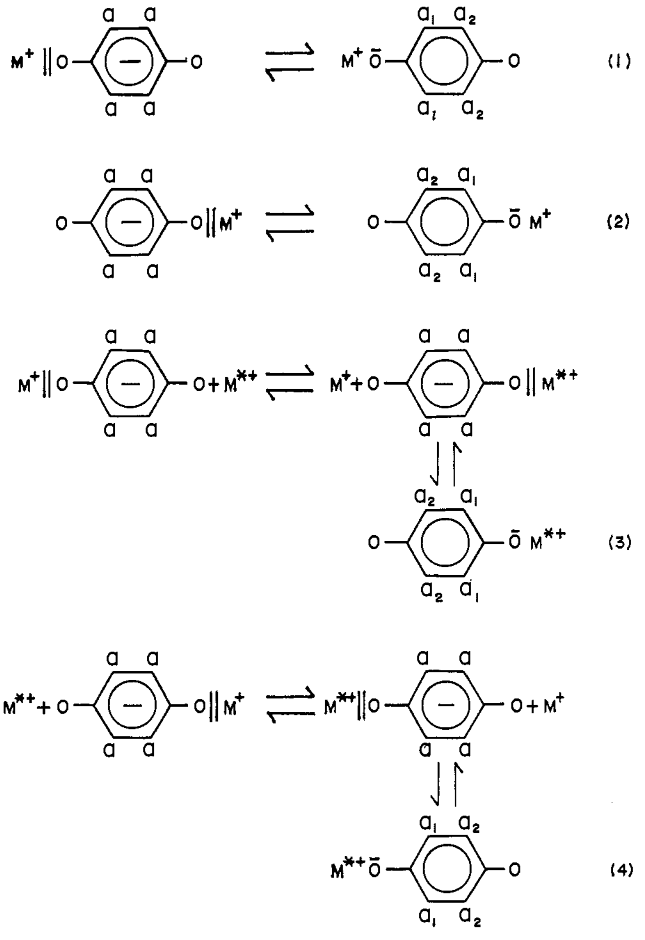

Figure 5. Different possible ion-pair equilibria for *p*-benzosemiquinone ion with a given nuclear spin state.

If the metal ion does not leave the vicinity of the radical anion, equilibria 1 and 2 (Figure 5) can be considered to be intramolecular processes insofar as the preservation of the spin state of the metal nucleus during the conversion is concerned. Equilibria 3 and 4 are intermolecular processes in which the metal cation from the oxygen at one end of the molecule gets detached from the anion, and another cation from the surroundings gets associated with the anion at the other end. However, owing to the presence of sharp alkali metal lines even in spectra exhibiting alternating line widths, it may be argued[42] that intermolecular processes are absent in the system. The preservation of the spin state of the alkali nucleus during the exchange process, which is fulfilled by the intramolecular processes 1 and 2, can then explain all the observed effects satisfactorily. Thus equilibria 1 and 2 which can be simply represented by

$$R^-\|M^+ \rightleftharpoons R^-M^+ \qquad (5)$$

need only be considered. This assumes that each alkali metal, to begin with, is associated with a radical ion in the form of either a solvated or an intimate ion pair.

2. Temperature Dependence of Splitting Constants and Structure of Ion Pairs. de Boer[55] has noticed that, although two splitting constants are observed for the aliphatic protons (which are equivalent in the absence of association) in pyracene anion, their values remain unchanged with any variation in temperature. However, in the durosemiquinone–alkli metal system (Tables II and III), it has been observed that the smaller splitting constant, a_1^H, decreases with temperature and the larger splitting, a_2^H, increases with temperature. Table V gives the difference in the two splitting constants ($a_2^H - a_1^H$) at various temperatures for durosemi-

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quinone with different counterions in DME and THF. Table V shows several interesting features. The values of ($a_2^H - a_1^H$) increase as the temperature of a given sample is increased. The increase is more for a THF solution as compared to a DME sample at a given temperature, and for different alkali metals the value increases in the order Li > Na > K. From Tables II and III it is also clear that just like ($a_2^H - a_1^H$), the sodium splitting, a^{Na}, also has a positive temperature coefficient.

Table V. Temperature Variation of ($a_2^H - a_1^H$) in B Species of Durosemiquinone Anion (gauss)

Temp, °C	Li		Na		K	
	DME	THF	DME	THF	DME	THF
60	2.351	...	...	...	...	...
25	2.118	2.224	...	1.683	...	...
−20	1.923	2.095	1.285	1.455	...	1.221
−40	...	2.060	...	1.415	...	1.173
−50	1.808	...	...	...	0.998	...
−60	...	1.981	1.282	...	...	1.108
−70	1.763	...	...	...	0.973	...
−80	...	...	...	...	0.968	1.124

These results are understandable if we assume the position of the alkali metal ion to be near one of the oxygen atoms in the semiquinone and close to the plane containing the atoms in the ring, which forms a nodal plane for the π molecular orbital containing the unpaired electron.[37,42,55] The alkali metal may further be assumed to undergo oscillations[55] in a potential well at this position. In such a model, the effect of increasing the temperature or of decreasing the mass of the counterion will be to enhance the amplitude of the oscillations. Enhanced oscillation should result in the counterions spending more time away from the nodal plane, causing larger perturbation in the π molecular orbital. As the difference in ring proton splittings is caused by the perturbation induced by the counterion situated near one of the oxygen atoms, it is reasonable to expect the value of ($a_2^H - a_1^H$) to increase with a larger amount of perturbation (see also section IV2).

A change in ($a_2^H - a_1^H$) can also arise from a change in equilibrium constants.[56] However, in cases where only the B-type radical is present at all the temperatures, as in the case of Li–DSQ in DME and THF and Na–DSQ in THF, the variation in ($a_2^H - a_1^H$) may be arising from the oscillational mechanism.

3. **Alternating Line Widths in Semiquinone Anions.** Several instances of alternation in line broadening in the esr spectra of free radicals have been reported in the literature,[23,34,37,42,57–61] and this phenomenon is understood in a satisfactory fashion. However, it has been shown by de Boer and Mackor[41,42] that a novel mechanism, *viz.*, an intramolecular migration of the alkali metal cation between two equivalent sites in a radical, can give rise to alternation in line broadening. The alternation in the width of hyperfine components in the esr spectra from pyrazine[34] and durosemiquinone anions[23] has also been explained on the basis of this phenomenon. The alternating line-width effects observed in the present case can be satisfactorily explained on the basis of the ion-pair equilibrium model discussed in section VI. When either the lifetime τ_A of the A species or τ_B of the B species is large compared to the other, an esr spectrum corresponding to the species with the larger lifetime is observed, and in cases where both τ_A and τ_B are large compared to $1/\gamma(a_2^H - a_1^H)$, where γ is the gyromagnetic ratio of the electron, distinct lines from the two different species can be observed. In situation corresponding to $\tau_A \sim \tau_B = 1/\gamma(a_2^H - a_1^H)$ alternation in the widths of the lines can be observed.[62] Figures 1–3 show spectra corresponding to all these conditions. It is, in fact, possible to calculate the line shapes using this model, and this can be compared with experimental spectra. The result in kinetic data obtained on the system in this manner will be published later.[62]

Although most of our results also could be interpreted in terms of a jumping model, we favor the ion-pair equilibrium model in the present system. In the semiquinone system any intramolecular exchange of the cation should be less favored compared to hydrocarbon anions owing to the strong electrostatic attraction between the oxygen atom and the counterion. Further, our results show that the association between the ion pairs decreases in the order Li > Na > K for different cations. However, on the basis of an intramolecular exchange model, one should expect the association to be minimum for the lighter Li ion, and the association should increase in the order Li < Na < K. But it is not possible to lay too much emphasis on this argument to rule out the possibility of the jumping model as a decrease in ionic radius in going from K to Li favors association.

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