(39) P. C. Dmivedi and C. N. Rao, *Spectrochim. Acta, Part A*, **26**, 1535 (1970).

(40) J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1795 (1962).

(41) P.G. Sears, E. D. Wilhoit, and L. R. Dawson, *J. Phys. Chem.*, **59**, 373 (1955); E. G. Taylor and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1731 (1947); M. J. McDowell and C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

(42) M. L. Jansen and H. L. Yeager, *J. Phys. Chem.*, **77**, 3081 (1973).

(43) Absorption bands have been numbered from high to low frequency. In a few cases, there are sufficiently large frequency shifts so that some band positions are out of normal order. These occasions will be noted as they arise.

(44) Writing out explicit expressions for K_s: K_s = [SW]/[S][W]; [SW] = [CW] + [AW]; [CW] = K_c[C][W]; [AW] = K_a[A][W]. Substituting these quantities into the expression for K_s, we find $K_s = K_cC_0/[S] + K_aA_0/[S]$, where C_0 and A_0 are the stoichiometric concentrations of the ions. Consider the limiting case of a small degree of hydration of the salt. Then [S] → S_0, the stoichiometric salt concentration, and $K_s = nK_c + mK_a$, where n and m are the moles of cations and anions per mole of salt. Thus, under the special conditions of low water concentration (e.g., only monohydrate formation) and low salt concentration, we expected K_s to be the weighted sum of the independent ion equilibrium quotients.

(45) This assumption is not unreasonable for weakly perturbed systems.[17]

(46) One can rationalize the difference in sensitivity to counter-ion since anions, in general, are much more polarizable than are cations. The OH stretching frequency is presumably responsive to the (small) changes in electron distribution induced via such polarization effects.

(47) In our experiment, these species would be more correctly designated "solute shared".

(48) We note in passing that these bands move to lower frequency as the cation polarizing ability increases. Bands arising from water molecules associated with anions in *contact ion pairs* would be expected to show an increasing frequency because the cations would remove electron density from the vicinity of the protons of the water/methanol molecules. This behavior has not been observed in our experiments. Nor is the concentration of contact ion pairs expected to be significant in the aprotic solvents we used.

Equilibrium Studies by Electron Spin Resonance. XII. The Relationship between Charge Density and Ion Pair Dissociation Determined by the Use of *g* Values

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Received November 27, 1974

Abstract: The addition of salt (KI) to solutions of the free anion radical of 2,6-di-*tert*-butylbenzoquinone, anthraquinone, or naphthaquinone results in a decrease in the observed g value due to the formation of ion pairs. The observed g value for the anion radical in solution containing a given amount of KI has been found to be a weighted average between that for the ion pair and that for the free ion in pure hexamethylphosphoramide. The equilibrium constant for the dissociation of the ion pair to form the free anion radical has been algebraically related to the observed g value leading to the first determination of ion pair dissociation constants by the use of g values. Further, the enthalpy of ion pair dissociation has been related to the rate of change of the g value with respect to temperature (dg/dT). To use the time averaged g values the rate of ion pair dissociation and formation must be fast on the ESR time scale. This has been found for semiquinones, for which the INDO calculated electron density on the oxygen atoms available for ion pair formation is less than 6.459. When the oxygen electron density is larger than this value the free ion and ion pair are observed simultaneously. Not only are the kinetics of ion pair dissociation affected by the INDO calculated charge densities, but the K_{eq} decreases with increasing charge density. However, the anthrasemiquinone system yields a K_{eq} that is too small according to this trend. This suggests a greater polarizability of this system.

The thermodynamic parameters controlling the dissociation of ion pairs have been determined by the use of three basically different ESR techniques. These include methods based upon ESR coupling constants,[2] line widths (relaxation times),[3] and line intensities (spin concentrations).[4,5] Here we describe a new technique that can be used for the determination of the thermodynamic parameters controlling the dissociation of ion pair (β) to form free ion (α) and the solvated cation, eq 1. This technique is based upon the use of g values.

$$\beta \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \alpha + M^+ \qquad (1)$$

Since the first accurate measurements of g values for organic anion radicals in solution, several workers have noticed changes in g values with temperature.[6-8] Recently it has been reported that the g value dependence upon temperature is at least partially due to ion pairing.[9] The g values for the ion pair and free ion of durosemiquinone in dimethoxyethane have been accurately determined for a series of counterions, and for all cases the g value for the free ion is larger than that for the ion pair.[4]

It has been shown for a series of substituted nitrobenzene anion radicals[3,5a] and for benzosemiquinones[5b,2c] that the free ions exist simultaneously with the ion pairs in hexamethylphosphoramide (HMPA) containing a small amount of alkali metal salt. Further, the equilibrium between the ion pair and the free ion can be described by the two-site model expressed in eq 1. In the absence of the alkali metal salt many of these anion radicals are free of ion pairing in HMPA.[2c,3,5,10] For the substituted nitrobenzene systems the equilibrium constant for eq 1 increases with the σ value of the para substituent.[5a] This indicates that the ability of the ion pair to dissociate is inversely proportional to the charge density on the NO_2 group. For the semiquinone anion radicals ion pairing takes place at the site of the oxygen atoms.[2c,5b,7,11] Here we wish to report upon the relationship between the charge density on the oxygen atoms determined by INDO open shell calculations and the thermodynamic parameters of ion pair dissociation. This work should allow new insight as to the importance of coulombic attraction between the anion radical and the cation in ion pairing. Other factors, such as solvation and polarization of the anion, will also be discussed.

The appearance of the ion pair in solution with the free ion can result in two completely different effects upon the observed ESR pattern. If the time between ion association and dissociation events is short on the ESR time scale, the resulting spectrum is that for the time averaged species. This is the case for the *p*-dinitrobenzene anion radical in HMPA.[3a] However, if the time between ion association and dissociation events is long on the ESR time scale, both the ion pair and the free ion are observed simultaneously. In HMPA this seems to be the case for the majority of the anion radicals, and it is the case for the *p*-benzoquinone anion radical.[5b] A qualitative relationship between the rate of ion pair formation and dissociation and the INDO calculated oxygen charge densities will also be discussed.

For the formation of any weak molecular complex (x′), eq 2, a most useful expression has been developed for the case when only the spectroscopic parameters for the time averaged species can be observed. After the determination

$$x + y \rightleftarrows x' \qquad (2)$$

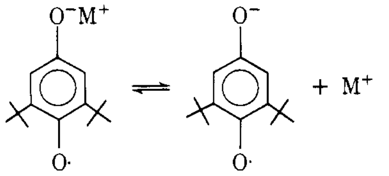
of the spectroscopic parameter (Γ^0) for uncomplexed x in the absence of y, a small amount of y can be added to the solution and the time averaged spectroscopic parameter ($\bar{\Gamma}$) will be observed. The equilibrium constant for eq 2 can then be determined by the use of eq 3 without direct measurement of the spectroscopic parameter for the complex (Γ')[2c,3,12,13]

$$1/(\Gamma - \Gamma^0) = 1/\{K_{eq}(\Gamma' - \Gamma^0)C_y^0\} + 1/(\Gamma' - \Gamma^0) \quad (3)$$

where C_y^0 represents the initial concentration of y. K_{eq} can be determined from the slope of a plot of $1/(\Gamma - \Gamma^0)$ vs. $1/C_y^0$. The intercept is $1/(\Gamma' - \Gamma^0)$. The only experimental condition is that the concentration of y is large in comparison with that for x. In this report the spectroscopic parameter to be inserted into eq 3 is the *g* value determined by ESR spectroscopy.

Results and Discussion

The equilibrium constant for the dissociation of 2,6-di-*tert*-butylbenzosemiquinone ion pair in HMPA (eq 4) has been previously determined by the use of time averaged coupling constants.[2c] For this reason the use of time averaged *g* values was first applied to this system in order to test the use of *g* values on a known system.

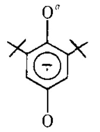
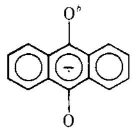
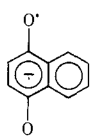


(4)

The reduction of 2,6-di-*tert*-butylbenzoquinone in HMPA by potassium metal yields the free anion radical,[2c] which is characterized by the coupling constant given in Table I and a *g* value[14] of 2.004814 ± 0.000008. Successive additions of potassium iodide, which is essentially fully dissociated in HMPA,[15,16] to this solution result in a decrease in the observed *g* value, Figure 1. This decrease must be due to an interaction between the anion radical and the added salt, most likely the formation of the ion pair, which exists in rapid equilibrium with the free ion.

Utilizing the free anion radical as a standard, the difference in the observed *g* value for a sample containing a known concentration of KI and that of the standard is $\Delta\bar{g}$. Δg^0 is the difference in the *g* value for the free ion and that of the standard, which is clearly equal to zero. $\Delta g'$, the difference in the *g* value for the free ion and ion pair, can only be obtained by extrapolation. Substituting these parameters in for Γ, Γ', and Γ^0 in eq 3 and writing it in terms of a weak complex dissociation yields

Table I. ESR Parameters for the Semiquinones in HMPA with Added KI

Semiquinone	Concentration of K^+, *M*	$\Delta\bar{g} \times 10^5$	A_H, G
	0	0	2.346
	0.051	3.18	2.260
	0.080	3.95	2.223
	0.150	5.29	2.182
	0.328	6.94	2.122
	0	0	0.97, 0.22[d]
	0.020	0.68	
	0.060	1.82	
	0.104	2.36	
	0.225	3.31	0.97, 0.22
	0	0	3.28, 0.64,[d] 0.23
	0.050	1.64	
	0.075	2.57	
	0.121	3.25	
	0.357	6.30	3.28, 0.64, 0.23

[a] The data given for this compound were taken at 28°. [b] The data given for this compound were taken at 25°. [c] The data given for this compound were taken at 20°. [d] These coupling constants remain constant with changing K^+ concentration.

$$1/\Delta\bar{g} = K_{eq}/\Delta g'[K^+] + 1/\Delta g' \qquad (5)$$

From eq 5 a plot of $1/\Delta\bar{g}$ vs. $1/[K^+]$ should be linear and have a slope of $K_{eq}/\Delta g'$ and an intercept of $1/\Delta g'$. Treated in this manner our data did yield a straight line, Figure 2. Table I shows a representative set of ESR parameters for various concentrations of potassium ion.

At 28° the equilibrium constant determined from Figure 2 is 0.076 ± 0.009. The equilibrium constant previously determined for this reaction by the use of ESR coupling constants is 0.094 ± 0.01 at 28°.[2c,17] The equilibrium constant obtained here by the use of *g* values and eq 5 is clearly equal to that previously obtained within experimental error.

Anthraquinone (10^{-2} to 10^{-4} *M*) in HMPA will dissolve small amounts of potassium metal to form the free anion radical, which exhibits an ESR spectrum consistent with proton coupling constants of 0.97 G (2 H's) and 0.22 G (2 H's). Addition of potassium iodide to this solution results in some line broadening but does not result in a detectable change in the coupling constants up to 0.4 *M* in K^+. Based solely on coupling constants there does not appear to be any ion pair formation. However, utilizing the anthrasemiquinone free ion as a standard, $\Delta\bar{g}$ smoothly increases with increasing potassium ion concentration. Clearly an ion pair is formed. A representative set of *g* value changes is given in Table I.

A plot of $1/\Delta\bar{g}$ vs. $1/[K^+]$ for this system is linear, Figure 2, and the calculated equilibrium constant is 0.14 at 25°. Since the enthalpy can be obtained from the rate of change of the equilibrium constant with temperature, there must exist a relationship between the enthalpy of dissociation of the ion pair and the rate of change of $\Delta\bar{g}$ with temperature ($d\Delta\bar{g}/dT$). Since $\Delta\bar{g}$ is a weighted average between $\Delta g'$ and zero

$$\Delta\bar{g} = \Delta g'(\beta)/\{(\alpha) + (\beta)\} \qquad (6)$$

and

$$K_{eq} = [K^+](\Delta g' - \Delta\bar{g})/\Delta\bar{g} \qquad (7)$$

thus

$$\Delta\bar{g} = \Delta g'/\{1 + K_{eq}/[K^+]\} \qquad (8)$$

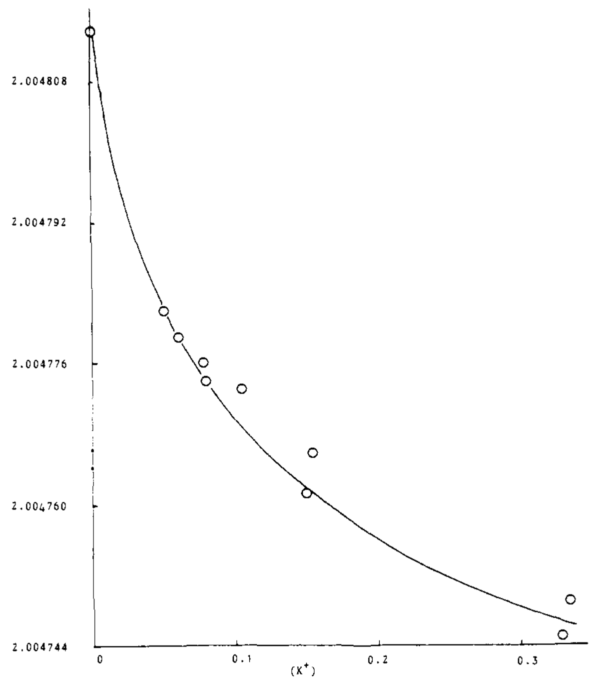


Figure 1. Plot of the observed g value for the system 2,6-di-*tert*-butylbenzoquinone-HMPA-K with added KI vs. the potassium ion concentration (M).

Taking the ln of both sides of eq 8 and differentiating with respect to $1/RT$ yields

$$d(\ln \Delta\bar{g})/d(1/RT) = \Delta H^0/\{1 + [K^+]/K_{eq}\} \qquad (9)$$

From this a plot of ln $\Delta\bar{g}$ vs. $1/RT$ should yield a curve, and the slope of the curve at $T = 25°$ is equal to $\Delta H^0/\{1 + [K^+]/K_{eq}\}$. The slope of the curve at this point was obtained graphically,[18] and knowing K_{eq} at 25°, ΔH^0 was found to be about -1.1 kcal/mol.

Naphthasemiquinone was treated in a similar manner. The equilibrium constant for the dissociation of the naphthasemiquinone ion pair was found to be 0.28 at 20°, Figure 2. Representative data for this system can be found in Table I. ΔH^0 was determined in the same manner and found to be about -1.8 kcal/mol. Since the enthalpies determined in this manner are taken from only one point on a curve, they are subject to large error. However, the values obtained for ΔH^0 can be checked using the integrated form of eq 9.

Integrating both sides of eq 9 yields

$$C + \ln \Delta\bar{g} = \Delta H^0/RT - \ln \{1 + [K^+] \exp(\Delta H^0/RT - \Delta S^0/R)\} \qquad (10)$$

where C is a constant of integration. Now knowing K_{eq} and ΔH^0 at 20°, C can be calculated from eq 10. Once C is determined the temperature can be varied, and a plot of ln $\Delta\bar{g}$ vs. $1/RT$ can be made from eq 10. We can now compare this expected plot for any value of ΔH^0 with the experimental plot. Utilizing -2.0 kcal/mol for the naphthasemiquinone system a resonable fit was obtained, Figure 3. The thermodynamic parameters for all of the semiquinones studied are given in Table II. It should be noted here that the parameters obtained for p-benzosemiquinone were obtained by simultaneous observation of the free ion and ion pair. That is, for this system the time between ion pair dissociation and association events is long on the ESR time scale, and the ESR line intensities were used.[5b] This is in contrast with the 2,6-di-*tert*-butylsemiquinone, naphthasemiquinone, and anthrasemiquinone systems where only the time averaged spectra were obtained.

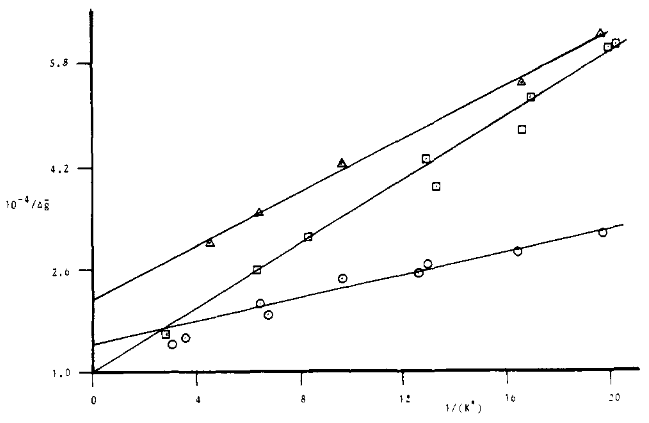


Figure 2. Plots of $1/\Delta\bar{g}$ vs. the reciprocal of the potassium ion concentration in moles/liter. The 2,6-di-*tert*-butylbenzoquinone system is represented by ⊙, the naphthaquinone system by ⊡, and anthraquinone system by ▲.

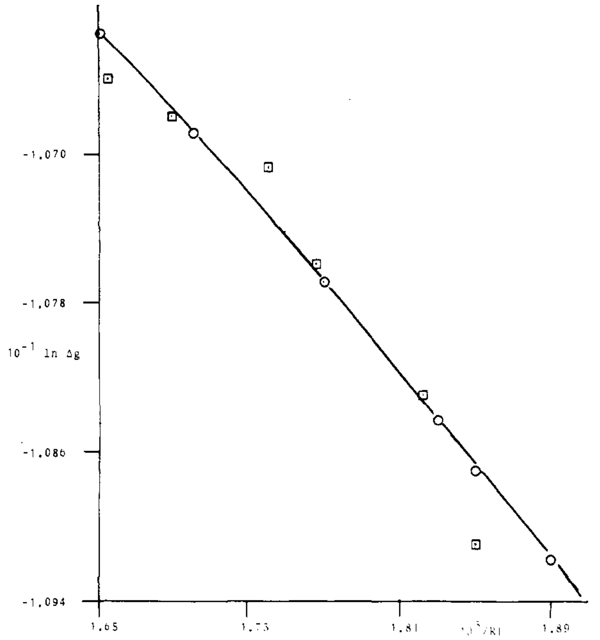


Figure 3. Plot of ln Δg vs. $10^3/RT$ for the naphthaquinone-HMPA-K system with added KI. The plot represented by the circles is calculated from eq 10 using -2.0 kcal/mol for ΔH^0. The squares represent real experimental points.

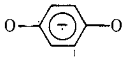
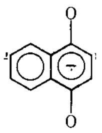
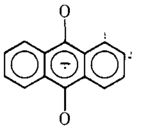
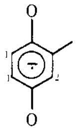
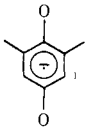
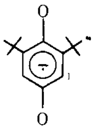
Table II. Thermodynamic Parameters Controlling the Ion Pair Dissociation and $\Delta g'$ for the Potassium Salt of the Following Quinones

Quinone	K_{eq}[a]	$\Delta H°$, kcal/mol	$\Delta g' \times 10^5$
2,6-Di-*tert*-butylbenzoquinone	0.076 ± 0.009[a] (28°)	−1.52 ± 0.1[b]	7.75
Naphthaquinone	0.28 ± 0.05 (20°)	−2.0 ± 0.4[c]	11.1
Anthraquinone	0.14 ± 0.03 (25°)	−1.1 ± 0.4[c]	5.50

[a] The errors in K_{eq} were calculated from propagating the errors in the slopes and intercepts in Figure 2. The enthalpy for the 2,6-di-*tert*-butylbenzoquinone system has been determined by the use of time averaged coupling constants.[16] [c] These errors are estimated.

The reason for the longer time between ion association and dissociation events for the p-benzoquinone system is probably due to a larger charge density on the oxygen atoms in this anion radical. Apparently the effect of the two *tert*-butyl groups in the 2,6-di-*tert*-butylsemiquinone is to lower the charge density on the carbonyl oxygen that is available to participate in ion pairing. It has been shown

Table III. Calculated and Experimental Coupling Constants for the Following Semiquinone Free Ions

Semiquinone	A_H, G	Position	A_H, cal	1.54 × A_H, cal
	2.42	1	−1.59	−2.45
	3.28	1	−2.13	−3.28
	0.64	2	−0.38	−0.59
	0.23	3	+0.29	
	0.97	1	−0.635	−0.98
	0.22	2	+0.415	
	1.75	(CH_3)	+2.68	
	2.14	1	−1.536	−2.37
	2.05	2	−1.320	−2.03
	2.39	3	−1.658	−2.55
	2.35	1	−1.77	−2.73
	1.71	(CH_3)	+1.36	
	2.35	1	−1.92	−2.96

[a] Calculations on this semiquinone were carried out as described in the Experimental Section.

previously that the oxygen atom that is sandwiched between the two *tert*-butyl groups is too sterically hindered to participate in ion pairing with the potassium ion.[2c] In order to see if methyl groups would cause a similar effect upon the oxygen charge density and thus upon the ion pairing kinetics the anion radicals of 2,6-dimethylbenzoquinone and methylbenzoquinone were investigated.

Reduction of 2,6-dimethylbenzoquinone in HMPA with potassium results in a solution of the free anion radical characterized by coupling constants of 2.35 G (2 H's) and 1.71 G (6 H's). Addition of KI to this solution results in the formation of the ion pair that is further split by the potassium nucleus by 0.29 G. This ion pair is observed simultaneously with the free ion.

The free anion radical of methylbenzoquinone in HMPA is characterized by coupling constants of 1.75 G (3 H's), 2.14 G (1 H), 2.05 G (1 H), and 2.39 G (1 H). Addition of KI to this solution also results in the formation of an ion pair that is observed simultaneously with the free ion. The ion pair is further split by the potassium nucleus by 0.33 G.

From the fact that the rate of ion pair formation and dissociation is slow on the ESR time scale it appears that the charge density on the oxygen involved in ion pairing may be larger for the methylbenzoquinone and 2,6-dimethylbenzoquinone anion radicals than it is for the anion radicals of 2,6-di-*tert*-butylbenzoquinone or the polyaromatic quinones.

In order to obtain a context for comparison of the relative charge densities on these oxygen atoms, INDO open shell calculations were carried out on each of the anion radicals studied. The bond lengths were adjusted to optimize agreement with the observed ESR coupling constants for the benzosemiquinone free anion radical. These bond lengths were then kept constant for the entire series of compounds. It is noted in Table III that if the negative calculated coupling constants are multiplied by a factor of 1.54 they give excellent agreement with the empirical values.

Table IV. Ion Pair Dissociation Equilibrium Constants, INDO Calculated Electron Densities, and Relative Rates of Ion Pair Formation and Dissociation for the Following Semiquinones

Semiquinone	$q_0 - 6$	$K_{eq}(25°)$	Rel rate
Benzosemiquinone	0.465	0.036	Slow
2,6-Di-*tert*-butylbenzosemiquinone	0.457	0.075	Fast
Naphthasemiquinone	0.449	0.29	Fast
Anthrasemiquinone	0.434	0.14	Fast
2,6-Dimethylbenzosemiquinone	0.459[a] 0.456		Slow[b]
Methylbenzosemiquinone	0.457[a] 0.474		Slow[b]

[a] This electron density is for the oxygen furthest from the methyl groups. [b] Spectra for these systems were too complex to allow the determination of K_{eq}.

This excellent agreement between the experimental and adjusted theoretical values for the negative ring proton coupling constants suggests that the trends characterizing other ground state electronic properties are also well elucidated by the INDO calculation for comparison of the charge distribution on these molecules. Accordingly, the capacity of the quinoid oxygen for ion pairing ought to be reflected in the relative charge density on the oxygens as calculated using the INDO technique. From Table IV we see that the calculated electron density in excess of the oxygen atom valence density on the oxygen available for ion pairing is generally greater in those cases where the rate of ion pair formation and dissociation is slow on the ESR time scale. Further, the smaller electron densities (q_0) found for the anthrasemiquinone, naphthasemiquinone, and 2,6-di-*tert*-butylsemiquinone correlate with rapid rates of ion pair formation and dissociation, Table IV.

It is noticed from Table IV that the difference in $q_0 - 6$ for the 2,6-di-*tert*-butylbenzoquinone and the 2,6-dimethylbenzoquinone anion radicals is only 0.002 with the system of lower charge density being, as expected, in the fast exchange limit and the system of higher charge density in the slow exchange limit. However, the INDO calculation is not reliable to such an accuracy as to make this difference meaningful. Further, it must be remembered that whether the ESR spectrum is in the fast or slow exchange limit depends not only upon the rates, but also on the differences in the ESR parameters (proton and alkali metal splitting and g values) of the free ions and ion pairs.

In order to be more specific as to the effect of charge density upon the rate constants of ion pair formation and dissociation, k_1 and k_2 are defined as the forward and reverse rate constants in eq 11.

$$K_{eq} = k_1/k_2 = [\alpha][K^+]/[\beta] \qquad (11)$$

The rate of ion pair formation is, and is expected to be, very close to a diffusion controlled process.[16] Thus k_2 is not expected to vary from one system to another. On the other hand, k_1 is the dissociation constant of the ion pair and is strongly affected by the coulombic interaction between the cation and anion. A relatively high charge density on the available oxygen should result in a stronger coulombic attraction with consequent tighter ion pairs and smaller values for k_1. Since k_2 should not vary appreciably from one system to another, K_{eq} is proportional to k_1 and should be a good measure of the strength of the coulombic interactions.

From the discussion above a correlation is expected between the equilibrium constants and the INDO calculated charge densities. It can be seen from Table IV that the equilibrium constant for the ion pair dissociation decreases with increasing charge density. This is consistent with the fact that the larger coulombic attraction favors ion pairing (lowers k_1). The anthraquinone system, however, seems to have a smaller equilibrium constant than would be predicted purely on the basis of free ion charge density. This deviation is due to the fact that we really should be comparing the charge densities in the ion pairs, but using the INDO program described here it is impossible to carry out calculations on ion pairs. Therefore, we are assuming that the charge density in the ion pair is proportional to the charge density in the free ion. The deviation of the anthraquinone system is evidently due to this assumption. Another way of stating this is that the anthrasemiquinone is more polarizable, which is not accounted for in the INDO calculations. Thus the cation induced polarization is probably of greater importance in controlling the dissociation of the anthrasemiquinone ion pair than it is in the other ion pairs of the series.

Finally it must be mentioned that the conductivity data in HMPA[15] do not necessarily imply that the KI is fully dissociated up to 0.3 *M*. An independent determination of the ion association constant (K_a) for potassium iodide was carried out in our laboratory, and K_a was found to be 4.3 ± 2.[16a] This small value for K_a indicates that KI is essentially fully dissociated, and corrections for this ion association between K^+ and I^- are small. All of the equilibrium constants reported in Table IV can now be corrected to include the association between the K^+ and I^-. The equilibrium constants for benzosemiquinone, 2,6-di-*tert*-butylbenzosemiquinone, naphthasemiquinone, and anthrasemiquinone are 0.034 ± 0.009, 0.087 ± 0.009, 0.67 ± 0.38, and 0.23 ± 0.08, respectively. These corrections are small (all of the corrected values are within experimental uncertainty of the values in Table IV). Also, the corrections introduce more error, making the numbers in Table IV more valuable for comparison.

Experimental Section

All of the organic compounds used were purchased from Aldrich Chemical Co. and recrystallized before use. The potassium iodide was purchased from Alfa Inorganics and was stored in a vacuum oven for 48 hr at 100° prior to use.

The method of reduction of the neutral molecule to form the anion radicals and the purification of the HMPA has been previously described.[10b]

The *g* values were measured on a Varian E-9 ESR spectrometer using the dual cavity technique.[19] All values for Δg were obtained by placing a sample of the free ion in one of the two cavities and a sample containing a known quantity of KI in the other. The *g* values reported for the 2,6-di-*tert*-butylbenzosemiquinone were obtained by the use of *p*-benzosemiquinone in *tert*-butyl alcohol as a *g* value standard.[6,7]

The temperature was controlled by a Varian temperature controller calibrated with an iron-constantan thermocouple. Values for dg/dT were obtained by taking two samples from the same solution and placing one in the variable temperature cell and the other in the remaining cavity.

Calculations using all-valence electron self-consistent Field (SCF) molecular orbital formalism[20,21] and the so-called "intermediate" neglect of differential overlap (INDO)[22] were performed on an IBM 370-145 computer using coordinates derived from geometrical considerations and a double precision version of the COORD[23] computer program.

Bond distances selected were consistent with crystallographic data,[24] though the C-O bond was deliberately assumed to be relatively short in order to optimize the coupling constants calculated for the semiquinones. All aromatic ring C-C bond distances were assumed to be 1.080 Å. All aryl-alkyl C-C bond distances and all alkyl-alkyl C-C bond distances were taken to be 1.520 Å. All alkyl C-H bond distances were assumed to be 1.090 Å. Aromatic ring angles were assumed 120° and normal tetrahedral bond angles (109.467°) were assumed where appropriate.

In the case of 2,6-di-*tert*-butylbenzosemiquinone, the INDO program used did not have sufficient orbital capacity to carry out the calculation. It was felt that an acceptable approximation to the charge and spin densities on this anion radical would be provided by 2,6-diisopropylbenzosemiquinone, and the calculations were carried out on this system. The methyl groups in the isopropyl substituents were positioned symmetrically out of the plane of the ring and directed toward the nearest oxygen.

Summary

A new technique has been developed for the determination of ion pair dissociation equilibrium constants. This technique is based upon the use of time averaged *g* values and has been used to investigate the thermodynamic parameters controlling the dissociation of several semiquinone ion pairs in HMPA. INDO calculated oxygen charge densities reveal that ion pair formation is thermodynamically hindered by low oxygen charge densities, but the rate of ion pair formation and dissociation is increased with decreasing oxygen charge density. For semiquinones containing extended π systems, such as anthrasemiquinone, ion polarizability must be considered.

Acknowledgment. The authors are grateful to the National Institutes of Health for support of this work, and to Research Corporation for a grant-in-aid making possible the purchase of the E-9 ESR spectrometer. This NIH support was from Grant No. RR-8102 from the Division of Research Resources. We are also grateful for the constant effort in our behalf displayed by Dr. Severino Ramos, director of the U.P.R. computer center, and members of his staff F. Verges, S. French, and V. Marqués. We also want to thank the reviewers for their very helpful comments.

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