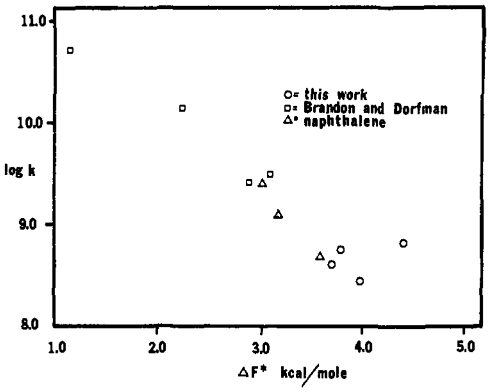

Figure 11. Plot of rate constant *vs.* Marcus free energy for several electron-transfer reactions.

and ethanol. Their work is different from ours in several respects.

The electron-transfer reaction between benzonitrile and its anion radical has a standard free energy of zero since the reactants and products are identical. This is not the case for the cross reaction they studied which has a standard free energy of activation of -2.01 kcal/mol. This nonzero free energy as well as the solvation term involving the dielectric constant and index of refraction contributes to the free energy of activation. Figure 11 plots log *k* *vs.* ΔF^* for their data and ours.

It should be noted that one of their solvents, diethylamine, has a dielectric constant of 3.8 but fits the correlation. This is because their solutions contain only reactants and solvents; there is no supporting electrolyte present to take part in ion pairing. Also included in Figure 11 are three points for the electron-transfer reaction between the naphthalene free anion radical and its parent determined by esr. The information is taken from Table V of the work of Szwarc, *et al.*,[69] where references to the original literature are given.

As can be seen in Figure 11 the overall agreement is quite good and the Marcus theory appears to give a reasonable description of the electron-transfer reactions of this group of organic radicals where ion pairing is not thought to play a significant role.

Acknowledgment. The support of the Robert A. Welch Foundation and the National Science Foundation (GP 6688X) and an award of a NASA and NIH fellowship to B. K. are gratefully acknowledged. The esr instrument was purchased with funds provided by the National Science Foundation (Grant No. GP-2090). We are grateful to Miss Alice Shen for preparation of pyromellitonitrile.

[69] M. Szwarc, J. Jagur-Grodzinski, and K. Hofelman, *J. Amer. Chem. Soc.*, 91, 4645 (1969).

Electron Paramagnetic Resonance Studies of Triple Ions and Alcohol-Solvated Ion Pairs of Anthraquinone[1]

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Abstract: Comprehensive epr studies of triple ions ($M^+A^-M^+$) and alcohol-solvated ion pairs (M^+A^+HOR) of anthraquinone are reported. The process of the formation of Li, Na, and K triple ions and the kinetics of the formation and dissociation of triple ions were studied. The role of triple ion formation in the intermolecular cation-transfer reaction was clarified. The structures of triple ions and the spin distributions in triple ions are studied and compared with those of ion pairs. The improved MO calculations of the spin distributions in ion pairs and triple ions are reported. The structures of solvated ion pairs were determined from the direction of the changes of spin densities upon solvation. The changes of alkali metal splittings upon solvation were also studied and discussed in terms of the structures of solvated ion pairs and triple ions.

The presence of triple ion, $R^-(M^+)_2$, and ion quadruplet, $R^-(M^+)_2X^-$, in dilute ethereal solutions of radical ions having two polar groups in symmetric positions has been reported on several occasions.[2-7] The structures of such species[3,5-7] and the possible roles of these species in intermolecular cation-transfer reactions[4,8-10] have been discussed recently. However, the properties of the triple ions and ion quadruplets have been investigated far less than those of ion pairs, R^-M^+, and there are many unknown aspects about their structural and kinetic properties. Their kinetic properties, in particular, are not yet well understood.

The present paper describes our attempts to obtain a comprehensive understanding of the properties of triple ions and ion quadruplets. We first investigated the

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[1] This research was supported by the grant from the National Science Foundation.

[2] (a) J. V. Acrivos, *J. Chem. Phys.*, 47, 5389 (1967); (b) T. E. Gough and P. R. Hindle, *Can. J. Chem.*, 47, 1698 (1969).

[3] T. E. Gough and P. R. Hindle, *ibid.*, 47, 3393 (1969).

[4] A. W. Rutter and E. Warhurst, *Trans. Faraday Soc.*, 66, 1866 (1970).

[5] T. E. Gough and P. R. Hindle, *ibid.*, 66, 2420 (1970).

[6] S. A. Al-Baldawi and T. E. Gough, *Can. J. Chem.*, 48, 2798 (1970).

[7] S. A. Al-Baldawi and T. E. Gough, *ibid.*, 49, 2059 (1971).

[8] R. F. Adams and N. M. Atherton, *Trans. Faraday Soc.*, **64**, 7 (1968).

[9] A. W. Rutter and E. Warhurst, *ibid.*, 64, 2338 (1968).

[10] T. E. Gough and P. R. Hindle, *Can. J. Chem.*, **48**, 3959 (1970).

process of triple ion formation of the anthraquinone anion with Li, Na, and K cations. We investigated their structures, spin distributions in anions, and kinetic properties for formation and dissociation of triple ions. We then demonstrated that intermediate triple ions or ion quadruplets are formed in the course of cation-transfer reactions. Second we investigated the formation of alcohol-solvated anthraquinone ion pairs. In view of the great stability of the triple ion, it may be anticipated that the alcohol solvates the oxygen not occupied by a metal ion, forming a triple ion-like solvated complex, ROHA$^-$M$^+$, although alcohol solvates easily the carbonyl oxygen associated with metal ion in other ketyls.[11,12] Our epr studies confirm the formation of a triple ion-like solvated complex in the present systems.

Experimental Section

Solutions of triple ions were prepared by adding carefully weighed dry alkali metal tetraphenyl boride ($MBPh_4$) through break seals into the solutions of anthraquinone ion pair (M^+A^-). Commercial $NaBPh_4$ was purified by successive recrystallization. $LiBPh_4$ and $KBPh_4$ were prepared according to the method described by Bhattacharyya, Lee, Smid, and Szwarc.[13]

Preparations of radical anions, addition of alcohol, and epr measurements were made according to the procedures already described elsewhere.[14]

Results and Discussions

Formation of Triple Ion. Upon addition of very small amounts of $MBPh_4$ ($10^{-4} \sim 10^{-3}$ *M*), epr spectra of ion pairs (A^-M^+) change to those of triple ions ($M^+A^-M^+$). The identification of the triple ion epr spectra in the case of Li is made directly by the observation of the septet lithium splittings with 1:2:3:4:3:2:1 intensity ratios (Figure 1a). In the case of Na–anthraquinone in MTHF the observed spectrum agrees very well with the computer simulated spectrum obtained by assuming that the anion interacts with two sodium ions (Figure 1b,c). The excellent agreement of the simulated spectrum with the observed spectrum leaves little doubt about this assignment. In other cases no clear-cut observations of alkali metal splittings due to two cations were made, but indirect evidences, such as the changes in proton hyperfine splittings, indicate that triple ions are formed after the addition of $MBPh_4$. These changes in proton splittings in triple ions were rationalized by the MO calculations described in the latter part of the paper. Epr spectra of these triple ions are shown in Figure 1d–f.

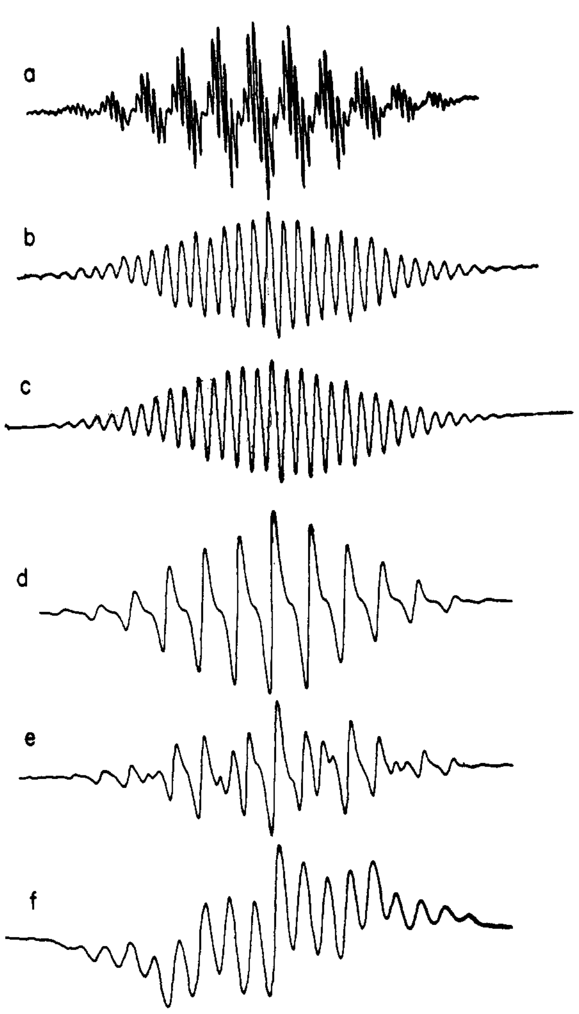

Figure 1. Epr spectra of triple ions of anthraquinone: (a) Li triple ion in MTHF at 10.2° obtained by the addition of 2.6×10^{-3} *M* $LiBPh_4$; (b) Na triple ion in MTHF at −10.4° obtained by the addition of 2.2×10^{-3} *M* $NaBPh_4$; (c) computer simultated spectrum of (b) with the assumption $a_1 = a_1' = a_4 = a_4' = 0.384$ G, $a_2 = a_2' = a_3 = a_3' = 0.992$ G, and $a_{Na} = 0.2$ G with the intensity ratio, 1:2:3:4:3:2:1; (d) Li triple ion in THF at 21.5° obtained by the addition of 4.6×10^{-4} *M* $LiBPh_4$; (e) Na triple ion in THF at −46.8° obtained by the addition of 7.3×10^{-4} *M* $NaBPh_4$; (f) K triple ion in THF at 19.6° obtained by the addition of 4.9×10^{-4} *M* $KBPh_4$.

Table I. Formation of Triple Ions in THF at Room Temperature[a]

Ion pair	$KBPh_4$	$NaBPh_4$	$LiBPh_4$
A^-Li^+	$Li^+A^-Li^+$ (5.58×10^{-4} *M*)	$Li^+A^-Li^+$ (4.17×10^{-4} *M*)	$Li^+A^-Li^+$ (4.60×10^{-4} *M*)
A^-Na^+	$K^+A^-K^+$[b] (1.12×10^{-3} *M*)	$Na^+A^-Na^+$ (7.31×10^{-4} *M*)	
A^-K^+	$K^+A^-K^+$ (4.88×10^{-4} *M*)		

[a] The numbers in parentheses are the concentrations of $MBPh_4$ salts. [b] At −95°, the spectrum is identified as the A^-K^+ ion pair.

The triple ions produced by the addition of small amounts of $MBPh_4$ to the solutions of anthraquinone ion pairs with different alkali metals are tabulated in the Table I. When the amount of added $MBPh_4$[15] is low the triple ion formed often does not contain the added cation as shown in Table I. For example, Li triple ion was always found regardless of the type of the ion added. This observation appears to be rather puzzling but can be understood in the following way. In the solution of alkali metal anthraquinone, presumably there are many different types of ionic species such as dinegative ion, $A^{2-}M^+_2$, paramagnetic and diamagnetic ion clusters, $(A^-M^+)_n$, as well as ion pair. By the addition of alkali metal ions, new equilibria among different ionic species are established and the most

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(11) K. Nakamura and N. Hirota, *Chem. Phys. Lett.*, **3**, 137 (1969).

(12) K. Nakamura, B. F. Wong, and N. Hirota, to be published.

(13) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, 69, 608 (1965).

(14) N. Hirota, *J. Amer. Chem. Soc.*, **89**, 32 (1967).

(15) For example, the addition of 1.12×10^{-3} *M* $KBPh_4$ into A^-Na^+ ion pair solution forms $K^+A^-K^+$ triple ion.

stable triple ion under the given condition appears. Thus, the cation forming the triple ion may not be the cation added to the solution. Attempts were made to make unsymmetric triple ions such as $Li^+A^-Na^+$. In our studies, however, no such species were observed.

The results given in the Table I together with other observations lead us to the following conclusions about the stabilities of the triple ions. (1) Symmetric triple ions are far more stable than unsymmetric triple ions (such as $Na^+A^-Li^+$). (2) The dissociation of triple ions into ion pairs and free cations (M^+) takes place at very low temperature. For example, K-anthraquinone with 1.12×10^{-3} M $KBPh_4$ gives a triple ion spectrum at 25° but an ion pair spectrum at $-95°$. Thus the dissociation constant of the triple ion increases with the decrease of temperature.

The equilibrium constants for the formation of triple ion cannot be determined accurately but, from relative intensities of the epr spectra, they were estimated to be approximately $10^3 \sim 10^4$ M^{-1} for the Na triple ion in THF at 25°.

The triple ions or ion quadruplets can be formed by the addition of other salts such as NaI,[9] but usually higher concentrations of salts are needed in order to obtain these species. These alkali metal salts generally form ion pairs in ethereal solutions. Therefore, the formation of triple ion strongly depends on the dissociation constant (K_D) of the added salts as well as the equilibrium constant (K_T) for the formation of triplet ion. The general scheme for the formation of triple ions and ion quadruplets by the addition of alkali metal salts is probably given by

$$R^-M^+ + M^+ \rightleftarrows M^+R^-M^+ \tag{A}$$

$$R^-M^+ + MX \rightleftarrows M^+R^-M^+ + X^- \tag{B}$$

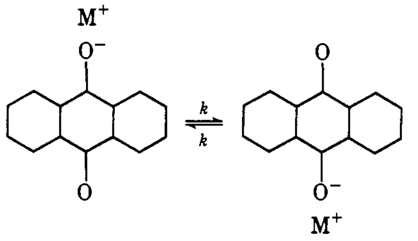
$$R^-M^+ + MX \rightleftarrows M^+R^-M^+X^- \tag{C}$$

The formation of triple ion by process A obviously depends on the availability of free cation and strongly depends on the dissociation constants of the added salts. With the salts with very small dissociation constants process A is probably negligible. The equilibrium constant for the formation of triple ions by process B is given by $K_T \cdot K_D$, where K_T is the equilibrium constant for the formation of triple ion and K_D is the dissociation constant of the added salt. When K_D is small the triple ion formation by this process is also small. If that is the case, the major process is probably the formation of ion quadruplets (C). Seemingly conflicting observations concerning the formation of triple ions obtained using different salts could be understood easily by considering both K_D and K_T.

Dynamic Processes Involving Triple Ions and Ion Quadruplets. (1) Rate of Formation of Triple Ion. In order to obtain information about the process of forming triple ion, we have investigated the line-width broadening of the epr spectra of Na^+A^- produced by the addition of small amount of $NaBPh_4$. As discussed in a separate paper,[16] many of the lines in the epr spectra of Na^+A^- in THF at 25° are in the slow limit of cation migration, although some lines are in the rapid migration limit. The results of the addition of small amounts of $NaBPh_4$ are shown in Figure 2. It is seen that all the lines are broadened substantially after the addition of $NaBPh_4$, but the main characteristics of spectrum are unmistakably those of an ion pair.

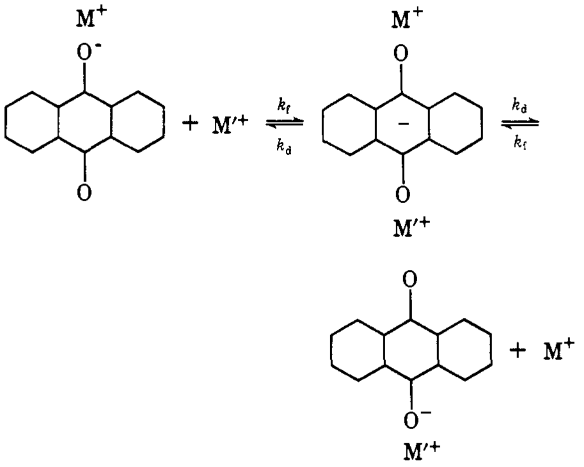
The possible dynamic processes taking place in the presence of excess $NaBPh_4$ are the following.

(1) Intramolecular cation exchange

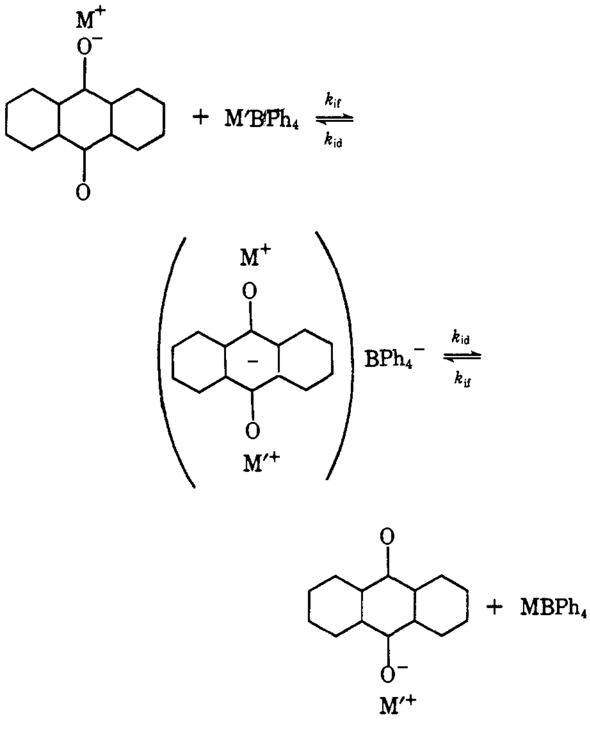


(D)

(2) Intermolecular cation-transfer reaction through triple ion and ion quadruplet



(E)



(F)

(3) Intermolecular cation-transfer reaction without

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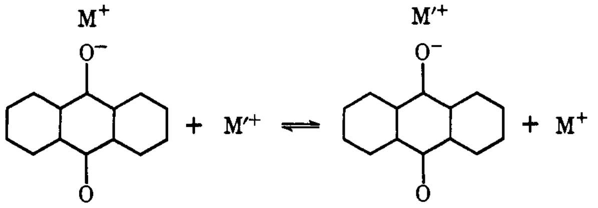
(16) K. S. Chen and N. Hirota, to be published.

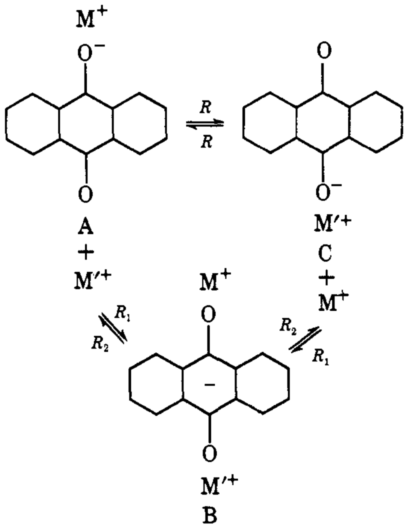
involving triple ion



(G)

In view of the similarity of the ion pair structure of the anthraquinone ion pair[16] to those of fluorenone and xanthone ketyls,[17] it seems reasonable to assume that the rate constants of process G are on the order of ~5 × 10^8 M^{-1} $\sec^{-1}$ at 25° in THF.[18,19] If we assume this rate constant it is not possible to explain the line broadening observed on the addition of ~1 × 10^{-4} *M* $NaBPh_4$. (The increase in the line width expected from process G is less than $^1/_{10}$ of the observed broadening.) In the solutions of low $NaBPh_4$ concentration, reactions with ion-paired salt, process F, are much slower than those with free cation, process E.[20] We thus neglect process F.

Thus the dynamic processes taking place in solution are approximated by the following process.



(H)

Here *R*, R_1, and R_2 are the intramolecular cation exchange rate, the rate for formation of triple ion, and the rate for dissociation of triple ion, respectively. As Figure 2b shows, the addition of a small amount of $NaBPh_4$ appears to broaden all the lines almost equally. Although the lines indicated by arrows are particularly sensitive to the rate of intramolecular cation transfer, there are no specific broadenings or sharpenings of these peaks. By the addition of more excess $NaBPh_4$ the spectrum is further broadened and changed to a different spectrum (Figure 2c).

In order to see if the observed changes in spectrum can be explained by scheme H we have computer simulated the spectra using the steady-state solution of the modified Bloch equation[21] for scheme H with the appropriate hyperfine splittings and rates. Using the standard notation,[22] the steady-state solution of the modified Bloch equation for process H is given in eq 1.

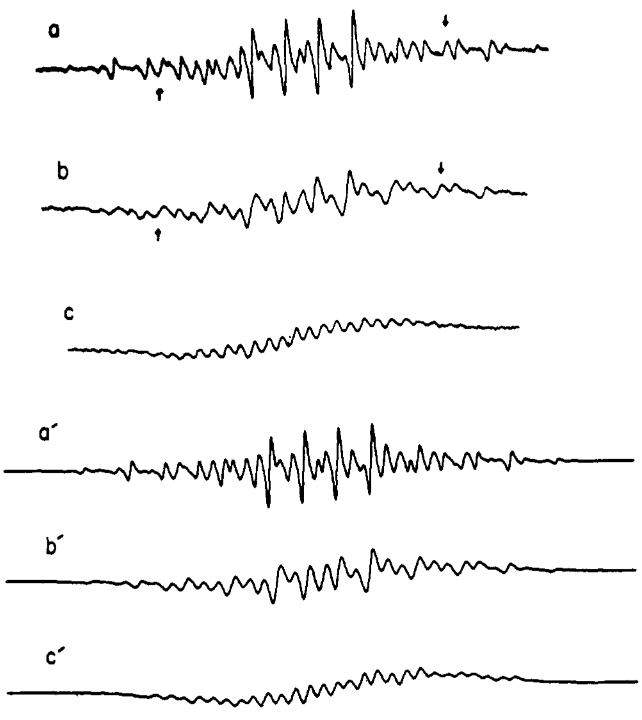


Figure 2. Epr spectra of anthraquinone: (a) Na ion pair in THF at 26.5°; (b) Na ion pair in THF at 26.5° after the addition of 3.6 × 10^{-4} *M* $NaBPh_4$; (c) Na triple ion in THF at 7.1° obtained by the addition of 7.3 × 10^{-4} *M* $NaBPh_4$; (a') computer simulated spectrum of (a), obtained by assuming pure intramolecular cation transfer with rate 1.20 × 10^6 $\sec^{-1}$; (b') computer simulated spectrum of (b), obtained by eq 1 with $R = 1.20 \times 10^6\ \sec^{-1}$, $R_1 = 1.0 \times 10^6\ \sec^{-1}$, and $R_2 = 1.6 \times 10^6\ \sec^{-1}$; (c') computer simulated spectrum of (c), obtained by eq 1 with $R = 0.9 \times 10^6\ \sec^{-1}$, $R_1 = 4.8 \times 10^6\ \sec^{-1}$, and $R_2 = 1.6 \times 10^6\ \sec^{-1}$.

$$G = -\frac{i\gamma_e H_1 M_0}{R_1 + 2R_2} \times \left\{ \frac{R_2[(\alpha_A + R_1 + 2R)^{-1} + (\alpha_C + R_1 + 2R)^{-1}] + R_1(\alpha_B + 2R_2)^{-1} + (2R_2 - R)R_1(\alpha_B + 2R_2)^{-1} \times [(\alpha_A + R_1 + 2R)^{-1} + (\alpha_C + R_1 + 2R)^{-1}]}{1 - R[(\alpha_A + R_1 + 2R)^{-1} + (\alpha_C + R_1 + 2R)^{-1}] - R_2R_1(\alpha_B + 2R_2)^{-1}[(\alpha_A + R_1 + 2R)^{-1} + (\alpha_C + R_1 + 2R)^{-1}]} \right\} \quad (1)$$

where

$$\alpha_A = \frac{1}{T_{2A}} + i(W - W_A)$$

$$\alpha_B = \frac{1}{T_{2B}} + i(W - W_B)$$

$$\alpha_C = \frac{1}{T_{2C}} + i(W - W_C)$$

The values of $1/T_{2A}$, $1/T_{2B}$, and $1/T_{2C}$ which fit the ion pair and triple ion spectra were used for the simulation. As shown in Figure 2, excellent fits to the observed spectra were obtained by adjusting the rates. The simulated spectra are rather sensitive to the choices

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[17] K. S. Chen, S. W. Mao, K. Nakamura, and N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6004 (1971).

[18] N. Hirota and S. I. Weissman, *ibid.*, **86**, 2537 (1964).

[19] B. F. Wong and N. Hirota, *ibid.*, in press.

[20] In the sodium fluorenone (in THF) system, the rate constant of intermolecular cation exchange with Na^+ is 10^2 times larger than with $NaBPh_4$.[19] Accordingly we made this assumption.

[21] (a) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); (b) H. M. McConnell, *ibid.*, **28**, 430 (1958).

[22] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

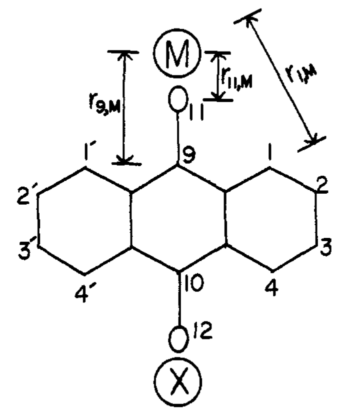


Figure 3. Numbering of the atoms and the definition of $r_{i,M}$ of the anthraquinone system.

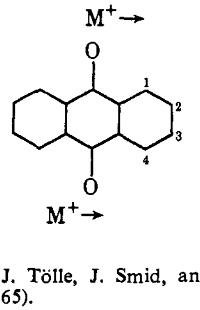
of R_1 and R_2. Thus one can make relatively accurate estimates of R_1 and R_2.

The best fits to the observed spectra given in Figure 2 were obtained with $R = 1.2 \times 10^6$ sec^{-1}, $R_1 = k_1[\mathrm{Na}^+] = 1.0 \times 10^6$ sec^{-1}, $R_2 = 1.6 \times 10^6$ sec^{-1} at 26.5°; $R = 0.9 \times 10^6$ sec^{-1}, $R_1 = 4.8 \times 10^6$ sec^{-1}, and $R_2 = 1.6 \times 10^6$ sec^{-1} at 7°. Using the known dissociation constant for $NaBPh_4$[23] the amount of Na^+ in the solution of 7.3×10^{-4} M $NaBPh_4$ is estimated to be 2.4×10^{-4} M at 7°. This gives the estimate of k_1 to be 2×10^{10} M^{-1} sec^{-1}. This rate constant is considered to be a diffusion-controlled rate constant and is about 40 times larger than cation-transfer reaction rates for ketyls. The lifetime of the triple ion is given by $\tau_T = 1/R_2$. In the case of Na–anthraquinone in THF this is estimated to be $\sim 10^{-6}$ sec. The epr spectrum of Na triple ion in THF is notably broader than that of the Na triple ion in MTHF and Li triple ion in MTHF and THF. The broader line width of the Na triple ion in THF is most likely due to the short lifetime of the triple ion in THF

The equilibrium constant ($K_T = k_f/k_d$) for $Na^+A^-Na^+$ is estimated to be $\sim 2 \times 10^4$ M^{-1}. This value is in good agreement with that estimated from the intensity ratios of the epr spectra of A^-M^+ and $M^+A^-M^+$ at lower temperature.[24]

It should be also mentioned that a scheme similar to H was recently used by Gough and Hindle to explain the spectrum of potassium durosemiquinone in the presence of $KBPh_4$.[25]

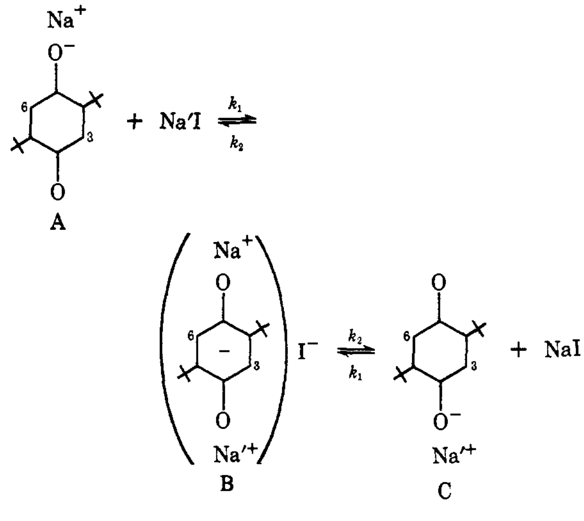
(2) Intermolecular Cation-Transfer Reaction and the Formation of Triple Ions and Ion Quadruplets. Rutter and Warhurst previously suggested[9] that intermolecular cation-transfer reactions proceed through a concerted mechanism described below.



Such a mechanism was suggested also for several other systems.[8] In the case of anthraquinone, this suggestion was made based on the disappearance of the line-width alternation after the addition of very large excess of NaI. However, this evidence is considered to be rather dubious, since under their experimental conditions the major species existing in solution is identified as a triple ion. This identification is made from the fact that the a_1 ($=a_4$) splitting of the epr spectrum of Na^+A^- in the presence of 4×10^{-1} M NaI is 0.4 G which is in reasonable agreement with the a_1 ($=a_4$) splitting of the Na triple ion determined in the present study (0.39 G), but $^1/_2(a_1 + a_4)$ for the ion pair is quite different from this value, being 0.33 G. The number of the atoms is shown in Figure 3. Therefore, their observations show that in the presence of 4×10^{-1} M of NaI the major species in solution is triple ion or ion quadruplet and the rapid cation exchange takes place between the associated cations and others in solution.

In Na–anthraquinone in THF the rate constant for the triple ion formation is 2×10^{10} M^{-1} sec^{-1} and is more than one order of magnitude higher than the rate constants for ordinary cation-transfer reactions. The lifetime of the triple ion is $\sim 10^{-6}$ sec. When a triple ion dissociates into an ion pair and a free cation, there is a probability of $^1/_2$ that the original cation is transferred. Therefore, when the concentration of cation is low ($[M^+] \ll 10^{-3}$ M), the effective pathway for intermolecular cation exchange in the present system is through the formation of triple ion. However, when $[M^+]$ and [MX] become higher, the major species in solution becomes triple ion or ion quadruplet and the main reactions are the processes A, B, and C and intermolecular cation-exchange reaction between cations associated with the triple ion and others in solution. Although the applicability of this conclusion to the other systems should be examined carefully depending on the systems, we think that this conclusion has wide applicability to the intermolecular cation-transfer reactions in similar systems.[4,9]

The mechanism involving triple ion intermediate in intermolecular cation transfer reaction was first suggested by Rutter and Warhurst.[4] They suggested that the triple ion formation is most likely involved in the cation exchange reaction between 2,5-di-*tert*-butylbenzosemiquinone and NaI. In order to confirm their



(I)

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[23] C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, 87, 5548 (1965).

[24] K_T is estimated to be $\sim 10^4$ M^{-1} from the intensity ratios of epr spectra of A^-M^+ and $M^+A^-M^+$. In this estimate the contribution to the formation of triple ion by process B may give a large value of K_T.

[25] T. E. Gough and P. R. Hindle, *Can. J. Chem.*, 49, 1529 (1971).

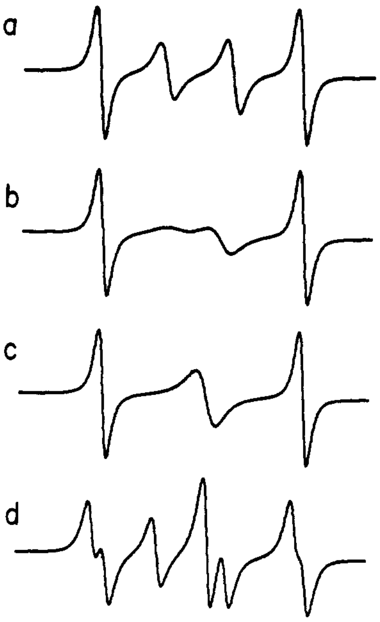

Figure 4. Computer simulated spectra for 2,5-di-*tert*-butylbenzoquinone undergoing intermolecular cation-transfer reaction. Simulations were made by assuming the mechanism I with the rates indicated below. The spectra a–c should be compared with the experimental spectra obtained by Rutter and Warhurst (see ref 4, Figure 2, and ref 9, Figure 2): (a) $R_1 = 1.9 \times 10^6$ sec^{-1}, $R_2 = 1.0 \times 10^7$ sec^{-1}; (b) $R_1 = 1.0 \times 10^7$ sec^{-1}, $R_2 = 1.0 \times 10^7$ sec^{-1}; (c) $R_1 = 2.0 \times 10^7$ sec^{-1}, $R_2 = 1.0 \times 10^7$ sec^{-1}; (d) $R_1 = 1.0 \times 10^6$ sec^{-1}, $R_2 = 5.0 \times 10^5$ sec^{-1}. The following assignments of the splittings were made: ion pair $a_6(\mathrm{A}) = a_3(\mathrm{C}) = 1.5$ G; $a_3(\mathrm{A}) = a_6(\mathrm{C}) = 3.1$ G; triple ion $a_3(\mathrm{B}) = a_6(\mathrm{B}) = 2.27$ G. The g values of the ion pair and the triple ion were assumed to be different by 2×10^{-4}.

suggestion and to obtain the quantitative information about the stability of the intermediate, we made an analysis of the line width variations of the spectrum of 2,5-di-*tert*-butylbenzosemiquinone caused by the addition of NaI. The intermolecular cation-transfer process involving this system has been studied experimentally by Rutter and Warhurst using NaI.[4,9] Since the intramolecular cation exchange is slow in this system, the dynamic processes taking place in the presence of excess NaI are given as shown in (I). Here k_1 and k_2 are the rate constants. R_1 and R_2 are the rates for the formation and dissociation of the intermediate ion quadruplet and are given by $R_1 = k_1[\mathrm{NaI}]$ and $R_2 = k_2$. The steady-state solution of the above process is given as shown in eq 2.

$$G = G_\mathrm{A} + G_\mathrm{B} + G_\mathrm{C} = \frac{-i\gamma_\mathrm{e}H_1M_0}{R_1 + 2R_2} \times \frac{R_2[(\alpha_\mathrm{A} + R_1)^{-1} + (\alpha_\mathrm{C} + R_1)^{-1}] + R_1(\alpha_\mathrm{B} + 2R_2)^{-1} + 2R_1R_2(\alpha_\mathrm{B} + 2R_2)^{-1}[(\alpha_\mathrm{A} + R_1)^{-1} + (\alpha_\mathrm{C} + R_1)^{-1}]}{1 - R_2R_1(\alpha_\mathrm{B} + 2R_2)^{-1}[(\alpha_\mathrm{A} + R_1)^{-1} + (\alpha_\mathrm{C} + R_1)^{-1}]} \tag{2}$$

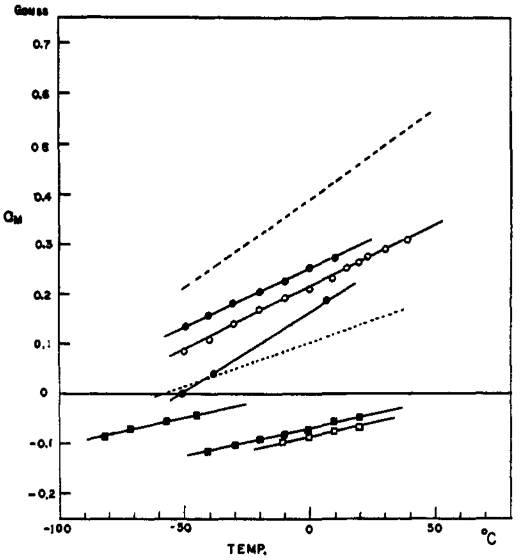

Figure 5. Temperature dependences of the alkali metal splittings of triple ions and ion pairs of anthraquinone: triple ions (□) Li in MTHF, (⊡) Li in 6.1 mol % of 2-PrOH in MTHF, (■) Li in THF, (●) Na in THF, (○) Na in MTHF, (⊙) Na in 6.1 mol % of 2-PrOH in MTHF; ion pairs (·····) Li in THF, (-----) Na in THF.

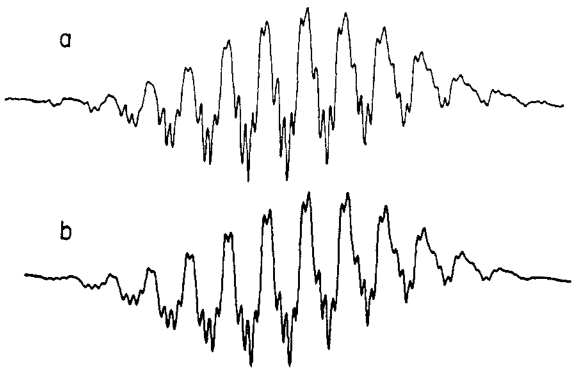

Figure 6. Epr spectra of Li triple ion of anthraquinone in THF at −81.2°: (a) experimental spectrum; (b) computer simulated spectrum with $A = 0.095$ G, $B = -0.006$ G, and $C = 0.0$ G. (The Li splitting is negative at this temperature.)

The computer simulated spectra with various rates, R_1 and R_2, are shown in Figure 4. These computed spectra reproduce the Rutter and Warhurst's observed spectra[4,9] quite well, confirming that the ion quadruplets are involved in the exchange process. The model without including stable intermediates can also predict the changes in line-width variation. However, the observed spectra show asymmetric broadenings of the two inner peaks. These asymmetric broadenings cannot be explained without including intermediates. In the present model this broadening can be explained quite easily by considering the g value differences between the ion pair and the triple ion.

Alkali Metal Splittings and the Structures of Triple Ions. As shown in Figure 5 temperature dependence of the alkali metal splittings of the triple ions is very similar to those of ion pairs, but the values of alkali metal splittings for triple ions are always smaller. In the case of $\mathrm{Li^+A^-Li^+}$, splittings are negative as shown in Figure 5. Solvent dependence of the splittings is also similar to that found in ion pairs. The observations indicate that the relative positions of the cations with respect to >C=O in the triplet ions are rather similar to those in the ion pairs. Structures of ion pairs have been discussed in the previous paper.[16] The smaller values of the splittings in triple ions indicate that the cations are closer to the nodal planes of the 2pπ orbitals of oxygens (in plane position) in the triple ions. Particularly, the negative splittings in the Li system indicate that cations are very close to the "in plane" position. The Li spectra show asymmetric broadenings of seven lithium splittings as shown in Figure 6.

Table II. Proton Splittings of Anthraquinone in Free Ion, Ion Pairs, and Triple Ions in THF

System	T, °C	a_1, G	a_2, G	a_3, G	a_4, G	$^1/_2(a_1 + a_4)$	$^1/_2(a_2 + a_3)$
A^-Na^+ free ion	−100	0.244	0.998	0.998	0.244	0.244	0.998
A^-K^+ ion pair	−100	0.552	0.678	1.320	0.060	0.306	0.999
A^-K^+ ion pair	20	0.672	0.565	1.435	−0.050	0.311	1.000
A^-Na^+ ion pair	−100	0.646	0.600	1.396	−0.010	0.318	0.998
A^-Na^+ ion pair	20	0.857	0.390	1.600	−0.197	0.330	0.995
A^-Li^+ ion pair	−100	0.996	0.278	1.694	−0.220	0.388	0.986
A^-Li^+ ion pair	20	1.093	0.170	1.804	−0.309	0.392	0.987
$K^+A^-K^+$ triple ion	19.8	0.334	0.989	0.989	0.334	0.334	0.989
$Na^+A^-Na^+$ triple ion	−46.8	0.384	0.985	0.985	0.384	0.384	0.985
$Li^+A^-Li^+$ triple ion	22	0.479	0.977	0.977	0.479	0.479	0.977

Table III. Coulomb and Resonance Integrals[a]

	Free ion	Ion pair	2-PrOH solvated	Triple ion
(1) Formula Used in MO Calculation				
$H'_{11.11}$ $(=\alpha + \delta_{11}\beta)$	$H_{11,11}$	$H_{11.11} + x$[b]	$H_{11.11} + x - cy$[c,d]	$H_{11.11} + x$
$H'_{9.9}$ $(=\alpha + \delta_0\beta)$	$H_{9.9}$	$H_{9.9} + dx$	$H_{9.9} + dx - cdy$	$H_{9.9} + dx$
$H'_{11,9}$ $(=\gamma_{11.9}\beta)$	$H_{11.9}$	$H_{11.9} + ax$	$H_{11.9} + ax - cay$	$H_{11.9} + ax$
$H'_{1.1}$ $(=\alpha + \delta_1\beta)$, $H'_{1'.1'}$ $(=\alpha + \delta_{1'}\beta)$	$H_{1,1}$	$H_{1.1} + bx$	$H_{1.1} + bx - cby$	$H_{1.1} + bx$
$H'_{12.12}$ $(=\alpha + \delta_{12}\beta)$	$H_{11.11}$	$H_{11.11} - cx$	$H_{11.11} - cx + y$	$H_{11.11} + x$
$H'_{10.10}$ $(=\alpha + \delta_{10}\beta)$	$H_{9.9}$	$H_{9.9} - cdx$	$H_{9.9} - cdx + dy$	$H_{9.9} + dx$
$H'_{12.10}$ $(=\gamma_{12.10}\beta)$	$H_{11,19}$	$H_{11.9} - cax$	$H_{11.9} - cax + ay$	$H_{11.9} + ax$
$H'_{4.4}$ $(=\alpha + \delta_4\beta)$, $H'_{4'.4'}$ $(=\alpha + \delta_{4'}\beta)$	$H_{1.1}$	$H_{1,1} - cbx$	$H_{1.1} - cbx + by$	$H_{1.1} + bx$
(2) Values of Parameters Used in the Calculation of the Curves in Figures 6, 7, and 9				
$H_{11.11}$	$\alpha + 1.15\beta$	$\alpha + 1.15\beta$	$\alpha + 1.15\beta$	$\alpha + 1.15\beta$
$H_{9.9}$	$\alpha + 0.11\beta$	$\alpha + 0.11\beta$	$\alpha + 0.11\beta$	$\alpha + 0.11\beta$
$H_{11.9}$	1.55β	1.55β	1.55β	1.55β
$H_{1.1}$	α	α	α	α
a	0.0	0.05	0.05	0.05
b	0.0	0.01	0.01	0.01
c	0.0	0.3	0.3	0.0
d	0.0	0.12	0.12	0.12
x	0.0	Variable	$0.57\ \beta$	Variable
y	0.0	0.0	Variable	0

[a] The notations used here are the same as the previous studies.[27] The coulomb and resonance integrals which do not appear in this table are α's and β's. [b] $x = \langle -e^2/\epsilon_{11}\gamma_{11.M}\rangle$. [c] $y = \langle -e^2/\epsilon_{12}\gamma_{12.PrOH}\rangle - \langle -e^2/\epsilon_{12}r_{12.THF}\rangle$. [d] c = solvation effect.

We have attempted to simulate the observed low-temperature spectrum of the Li triple ion by assuming that $1/T_2$ is given by

$$1/T_2 = A + BM_z + CM_z^2 \qquad (3)$$

Here M_z is the magnetic quantum number of Li nuclei. The simulated spectrum with $A = 0.095$ G, $B = -0.006$ G, and $C = 0$ is shown in Figure 6. Reasonably good agreement between the computed spectrum and the observed one was obtained showing that the major term which causes asymmetric broadening is the BM_z term.[26] Such a broadening is most likely due to the g anisotropy. Gough and Hindle previously observed similar asymmetric line broadenings in duroquinone systems.[3] They attributed the cause of such broadenings to the existence of a large difference between $g_{\|}$ and $g_{\perp}$ and concluded that the cations are in the plane of the carbonyls. We think their arguments are applicable to the present systems. Therefore the observed asymmetric broadenings also support the "in plane" structure of the triple ion.

Spin Distributions in Triple Ions. Comparison between Ion Pairs and Triple Ions. The perturbations of the spin densities by the associated cations in the ion pairs of anthraquinone have been discussed previously.[27] The values of the proton splittings of the triple ions are given in Table II together with those of the corresponding ion pairs. It is seen that the splittings at 1 and 4 positions are sensitive to the cation and are considerably larger than $^1/_2(a_1 + a_4)$ for the corresponding ion pairs, while the splittings at 2 and 3 positions change very little depending on the cation. In the previous studies of ion pairs McLachlan MO calculation,[28] combined with the McClelland treatment of the counter-ion effect,[29] has been used in order to explain the ion pair effects. We have made similar calculations on the triple ions as well as the ion pairs with some modifications in evaluating Coulomb and resonance integrals of the perturbed systems. Considerable improvements in the fits between the experimental spin densities and the calculated ones were obtained for ion pairs by these modifications. The Coulomb and resonance integrals used for these calculations are listed in Table III. The Coulomb and resonance integrals were changed in order to take into account the interactions between cation and electrons in anion. As in the previous

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(26) In doing simulation Lorentzian line shape was assumed. However, the actual line shape is perhaps not true Lorentzian because of the unresolved Li splittings. Small discrepancies between the observed and the simulated spectra are most likely due to this deviation.

(27) T. Takeshita and N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6421 (1971).

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

(29) B. J. McClelland, *Trans. Faraday Soc.*, **57**, 1458 (1961).

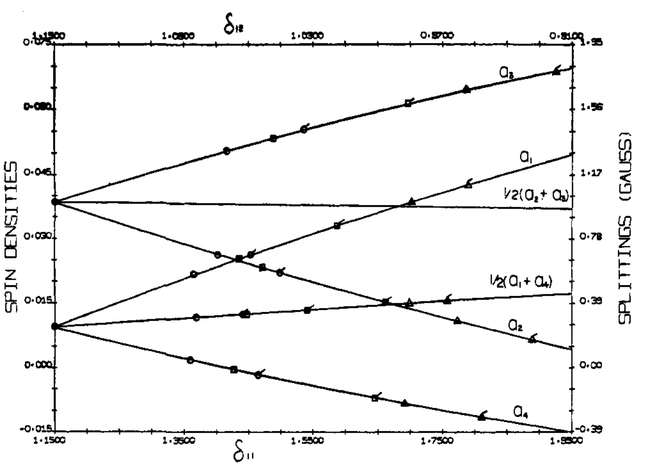


Figure 7. Calculated spin densities as functions of δ_{11} for ion pairs. For the conversion of spin densities into splittings $a_i = Q\rho_i$ with Q = 26 G was used. Points indicate the observed splittings in THF: (●) free ion at −100°, (Ó) K at 20°, (O) K at −100°, (□́) Na at 20°, (□) Na at −100°, (△́) Li at 20°, (△) Li at −100°.

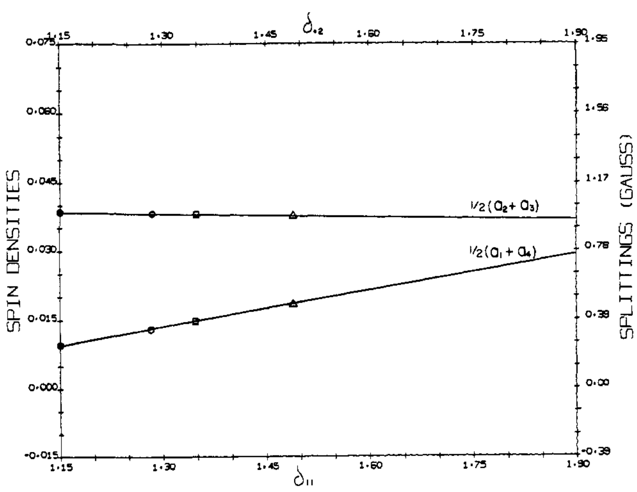


Figure 8. Calculated spin densities as functions of δ_{11} for triple ions. Points indicate the observed splittings in THF: (●) free ion at −100°, (O) K at 19.8°, (□) Na at −46.8°, (△) Li at 22°.

studies[27] spin densities were calculated as functions of carbonyl oxygen Coulomb parameters. The changes in the oxygen Coulomb parameters (x) represent the electrostatic interaction between cation and π electrons on the oxygen ($x = \langle -e^2/\epsilon_{11}r_{11,\mathrm{M}}\rangle$). Here ϵ_{11} is a screening constant and $r_{11,\mathrm{M}}$ is the oxygen–cation distance. In order to take into consideration the cation effects on the resonance integral between oxygen and carbonyl carbon, on the Coulomb integral of the carbonyl carbon, and on the Coulomb integrals of the carbons at 1 and 1′ positions, correcting parameters a, d, and b were introduced. These parameters are given as

$$\begin{aligned} a &= 2S_{11,9}/(1 + \epsilon_9 r_{9,\mathrm{M}}/\epsilon_{11}r_{11,\mathrm{M}}) \\ b &= \epsilon_{11}r_{11,\mathrm{M}}/\epsilon_1 r_{1,\mathrm{M}} \qquad (4) \\ d &= \epsilon_{11}r_{11,\mathrm{M}}/\epsilon_9 r_{9,\mathrm{M}} \end{aligned}$$

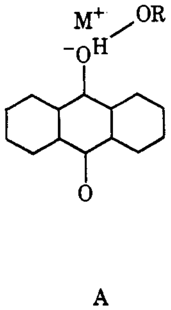
However, in the actual calculations they were largely treated as adjustable parameters. The carbonyl oxygen not associated with the cation has a considerably large charge density. It is, therefore, considered that ethereal solvents solvate considerably to this oxygen atom. The charge density and the degree of solvation change depend on the metal ion associated. In order to take into account this solvation effect another parameter c was introduced.

The spin densities at various carbon positions are calculated as functions of x (Figures 7 and 8). One can fit the experimental values of the splittings a_i (a_i are the four proton splittings in the case of ion pair and $^1/_2(a_2 + a_3)$ and $^1/_2(a_1 + a_4)$ in the case of triple ion) with various values of x. The fits were made so that the fluctuations among the values of x to fit the individual splittings become minimum. In general, better fits were obtained with small values of a, b, and d, but it was found that a relatively large value of c ($\sim$0.3) was necessary in order to obtain good fits to both $^1/_2(a_2 + a_3)$ and $^1/_2(a_1 + a_4)$. This perhaps indicates that the effect of solvation to the oxygen not associated with cation cannot be neglected in the case of anthraquinone. The values of parameters used to obtain the curves in Figures 7 and 8 are listed in Table III. Generally, satisfactory fits were obtained for ion pairs and triple ions.

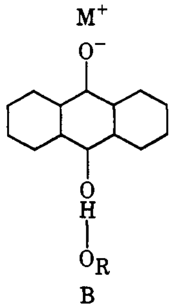
The required changes in the values of δ_{11} ($\Delta\delta_{11}$) to best fit the splittings in going from free ion to ion pair are 0.7 for Li, 0.5 for Na, and 0.35 for K using the room temperature values of splittings. On the other hand the triple ion data were best fitted with $\Delta\delta_{11}$ = 0.34 for Li, 0.2 for Na, and 0.14 for K. Although the calculation is a very approximate one the smaller values of $\Delta\delta_{11}$ for the triple ions seem to indicate that the cation anion interactions are significantly weaker in triple ions than in ion pairs. The solvation of cations is probably considerably stronger in triple ions.

The required δ_{11} to fit the splittings of the ion pairs of anthraquinone are somewhat larger than those required to fit the fluorenone data.[27] $\epsilon_{11}r_{11,\mathrm{M}}$ estimated from the best fit for anthraquinone ion pair are 8.2 for Li, 11.4 for Na, and 16.5 for K. If we assume $r_{11,\mathrm{M}}$ is 2 Å for Li, 2.5 Å for Na, and 3 Å for K, the screening constant becomes $\sim$4 for Li and Na ion pairs and 5.5 for K. Since $\Delta\delta_{11}$ for the triple ions are smaller, corresponding values of $\epsilon_{11}r_{11,\mathrm{M}}$ are much larger. Thus both larger ϵ_{11} and $r_{11,\mathrm{M}}$ appear to be necessary to explain the observed data of triple ions.

Solvation of Alcohol to Anthraquinone Ion Pairs. Triple Ion-Like Solvated Complexes. From our previous studies it is known that alcohol solvates to carbonyl oxygen atoms of ketyls.[11,12] In the case of the anthraquinone ion pair there are two possible solvated structures, A and B. Structure A is similar to the case of ketyls. In view of the great stability of the triple ions discussed in the earlier sections we might expect



A



B

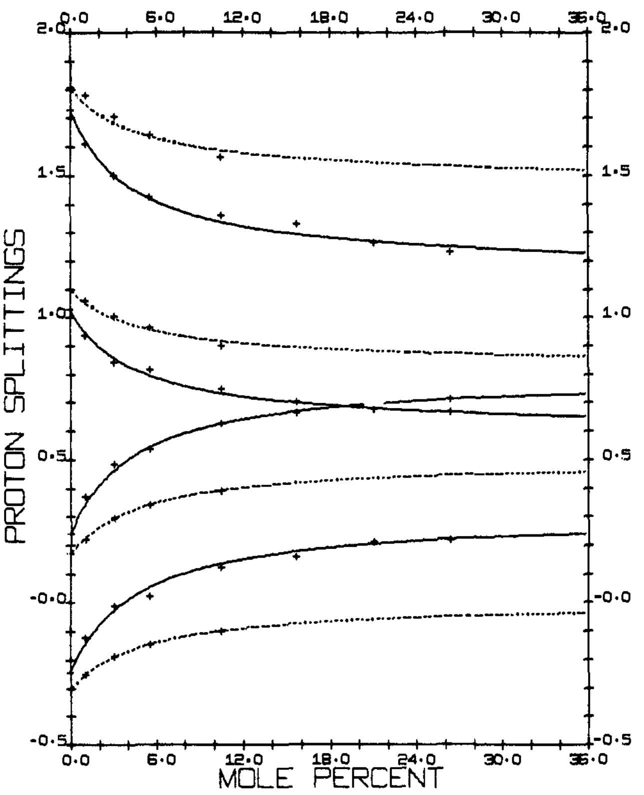


Figure 9. Changes of the proton splittings of the Li–anthraquinone ion pair by the addition of 2-PrOH: (–×–×–) at −70°, (·×·×·) at at 20°. The curves are computer fitted to the experimental points by using eq 5.

that the triple ion-like structure B is more favorable than A.

Epr studies can distinguish the difference between the solvation structures very easily, since the directions of the changes in proton splittings upon solvation are opposite. The changes of the splittings in each solvation structure are easily predicted by MO calculation. They are: structure A, a_1, a_3 increase and a_2, a_4 decrease as in the case of fluorenone ketyl;[12] structure B, a_1, a_3 decrease and a_2, a_4 increase. The observed changes of the splittings upon solvation are given in Figure 9 as functions of alcohol fraction. In the case of the Li ion pair it is clearly seen that the observed change agrees with the prediction based on structure B. The effect of solvation on the spin distribution was taken care of by increasing the Coulomb integral of the oxygen solvated by alcohol (y). When alcohol solvates to the oxygen it is expected that the redistribution of charge densities reduces the cation–anion interaction. Therefore the Coulomb integral of the oxygen atom attached to the cation was slightly reduced when the alcohol solvated. Figure 10 shows the spin density changes as a function of y which is the indication of the strength of solvation.

The observed changes in the proton splittings by the successive additions of alcohol are shown in Figure 9. The changes of the splittings were well fitted by the one-step solvation equation

$$\underset{\text{A}}{M^+A^-(THF)_n} + \text{2-PrOH} \rightleftharpoons \underset{\text{B}}{M^+A^-(\text{2-PrOH})(THF)_{n-1}} + THF \qquad (J)$$

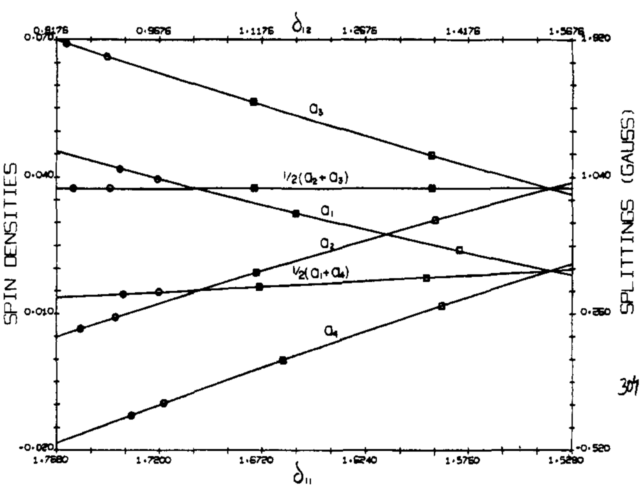


Figure 10. Calculated spin densities as functions of δ_{12} for alcohol-solvated ion pairs. Points indicate the observed splittings: (●) Li ion pair in pure THF at 20°, (○) Li ion pair in pure THF at −70°, (■) Li alcohol-solvated ion pair at 20°, (□) Li alcohol-solvated ion pair at −70°.

and the equilibrium constant K is given by

$$K = \frac{(a_A - a)[\text{THF}]}{(a - a_B)[\text{2-PrOH}]} \qquad (5)$$

Here we assumed that one THF solvent molecule in the first solvation sphere is replaced by a 2-PrOH molecule upon alcohol solvation. The values of K and a_B were determined by computer fitting and are given in Table IV. As shown in Figure 10 the determined values of a_B and the corresponding spin densities of the solvated ion pair are well fitted to the calculated values with $\Delta\delta y \simeq 0.45$ at −70° and $\Delta\delta y \simeq 0.25$ at 20°. These observations quite clearly indicate that the perturbation due to solvation of alcohol through hydrogen bonding formation is temperature dependent. The perturbation due to hydrogen bonding increases considerably at lower temperature indicating that alcohol is more tightly bound at lower temperature. The estimated K values at 20 and −70° are not much different indicating that ΔH for solvation is rather small.

Table IV. Estimated Equilibrium Constants K and the Limiting Splitting Constants a_B

$$\underbrace{AQ^-M^+(THF)_n}_{A} + \text{2-PrOH} \rightleftharpoons \underbrace{AQ^-M^+(THF)_{n-1}(\text{2-PrOH})}_{B} + THF$$

Positions	Proton splittings and equilibrium constants a_A	a_B	K
	M = Li at −70°		
1	1.026	0.603	21.7
2	0.239	0.793	21.8
3	1.727	1.165	21.7
4	−0.245	0.302	21.6
	M = Li at +20°		
1	1.093	0.830	19.6
2	0.170	0.496	20.0
3	1.804	1.460	19.7
4	−0.309	0.00	19.9
	M = Na at 20°		
$^1/_2(a_1 + a_4)$	0.329	0.422	13.7

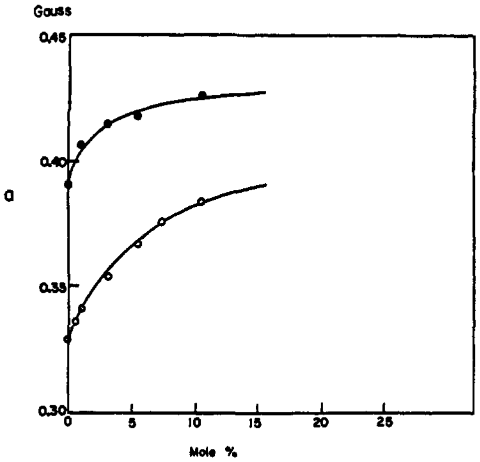


Figure 11. Changes of the proton splittings of $^1/_2(a_1 + a_4)$ for Li and Na ion pairs by the addition of 2-PrOH: (●) Li at −70°, (○) *Na at 20°*.

Solvation of alcohol to Na–anthraquinone cannot be studied in a similar way because of the complication due to the intramolecular cation migration. However, $^1/_2(a_1 + a_4)$ changes as the fraction of 2-PrOH increases (Figure 11). Therefore, it appears that similar solvation is taking place in Na system. However, this does not exclude the possibility of the solvation structure A. Other experimental evidence has to be given in order to decide the solvation structure.

From the previous studies of the solvation of 2-PrOH to fluorenone ketyls,[12] it is well established that the solvation of alcohol in structure A displaces cations making large changes in alkali metal splittings. If the solvation structure in anthraquinone is similar to the case of fluorenone ketyl, similar changes in alkali metal splittings are expected. On the other hand, if the solvation takes place to the carbonyl oxygen not attached to cation, this solvation has very little effects on the metal splittings. The differences in the solvation effects on the alkali metal splittings in two systems are quite evident from Figure 12. On the basis of these observations, it is concluded that alcohol solvates to the oxygen not associated with cation in both Li and Na systems.

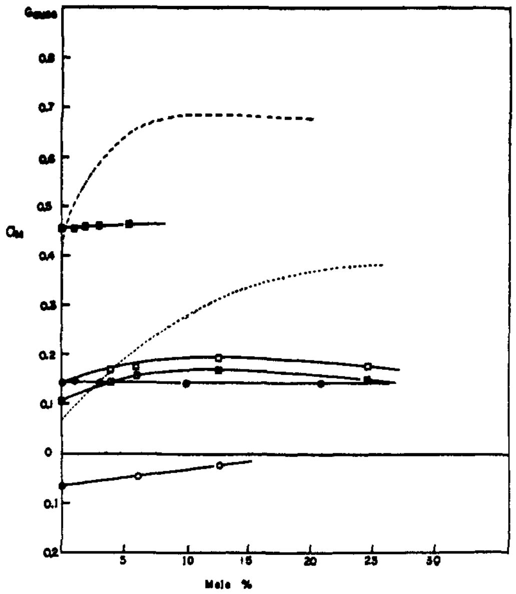


Figure 12. Changes of the alkali metal splittings of anthraquinone and fluorenone by the addition of 2-PrOH: anthraquinone (○) Li triple ion in MTHF at 20°, (●) Li ion pair in THF at 20°, (⊡) Na triple ion in MTHF at −40°, (□) Na triple ion in MTHF at −30°, (■) Na ion pair in THF at 20°; fluorenone (·····) Li ion pair in THF at 25°, (-----) Na ion pair in THF at 15°

It is interesting to compare the effects of alcohol solvation to the triple ions with those of ion pairs. The alkali metal splittings of triple ions are plotted against the mole fractions of 2-PrOH in Figure 12. Although small changes are observable upon addition of 2-PrOH, the changes are much smaller than in the case of ion pairs. Small changes in proton splittings were also found in the case of Li triple ion when 2-PrOH was added. Therefore, 2-PrOH is certainly solvating in the triple ions, but it is concluded that the effect of solvation to the triple ion structure is very small. The "in plane" position of cation is much more favorable in triple ion and the solvation of alcohol does not seem to change the relative position of cation with respect to anion.