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ESR Studies of Nitrobenzene Ion-Pair Equilibria in *N,N*-Dimethylformamide

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The hyperfine splitting constants of the nitrobenzene radical anion in DMF vary with the type of the counter cations and the concentrations. The tendency of these variations is related to the shift of the half-wave reduction potential of nitrobenzene. The variation of the nitrogen ^{14}N hyperfine splitting constant is attributable to the formation of ion pairs involving the nitrobenzene radical anion and its counter cation. The ion-pair formation constants were evaluated from the changes in the hyperfine splitting and are completely consistent with those obtained from polarographic studies.

In recent years, ESR techniques have been extensively applied to studies of radical ions and ion pairs in the liquid phase, revealing detailed structure and kinetic information of the ion-pair systems.[1-3] In particular, discussions treating the equilibrium between a tight ion pair and a loose ion pair have been reported by a few workers[4,5] and the migrations of the cation in ion-pair systems have also been examined by many workers.[6-8] A large part of these investigations were carried out in solvents such as tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME), in which alkali metal hyperfine splitting (hfs) might arise from ion-pair systems of alkali metal ions and hydrocarbon radical anions. In these solvents, the observed hfs under normal conditions ($\sim 10^{-4}$ M) should be equal to that of the ion-pair system because large numbers of radical ions exist in the form of ion pairs due to the large value of the ion-pair formation constant, thus the existence of a free ion was not confirmed by ESR techniques.

On the other hand, in the solvents having a high dielectric constant, such as *N,N*-dimethylformamide (DMF) and acetonitrile, generally no alkali metal hfs has been observed in the ion-pair systems composed of hydrocarbon radical anions and alkali metal cations. This suggests that the studies on pairing in these solvents based on the hfs due to alkali metal cations are invalid. Furthermore, the observed hfs of the radical ions in these solvents is very close to that for free ions, which may be due to the small value of the ion-pair formation constant. For these reasons, the ion-pairing phenomena in solvents, such as DMF, are very difficult to discuss.

Since the variation in the nitrogen ^{14}N hfs of the nitrobenzene radical anion and its derivatives is very sensitive to the type of alkali metal cation and the concentration,[9-12] many workers have attempted to discuss ion pairing and solvent effects on the basis of the variation of the nitrogen hfs. Kitagawa *et al.* have reported qualitatively on the variation of the hfs of *p*-chloronitrobenzene radical anions with various counter cations and the concentrations of these in DMF.[27] However, the authors were unable to obtain quantitative results concerning the ion-pair equilibrium from their experimental results. Therefore, we discuss more quantitatively the variation of the hfs and obtain interesting quantities such as the ion-pair formation constant, the hfs of the free ion, and that of the ion pair.

The polarographic reduction waves of nitrobenzene are also highly affected by the type of supporting electrolytes as is shown in the paper of Holleck and Becher.[13] The polarographic techniques not only offer some information concerning the ion pair but also allow the present authors to determine the ion-pair formation constant and the coordination number in such solvents.

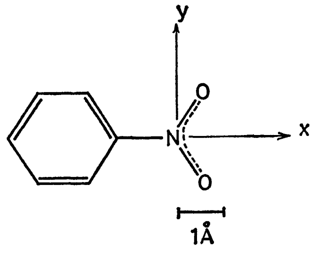

Fig. 1.

In this paper, the influence of alkali metal cations on the ESR spectra is dealt with and the structures of the ion-pair systems and the equilibrium between the free nitrobenzene radical anion and the ion pair composed of alkali metal cations is discussed. Quantitative correlations are drawn between the results obtained from the polarographic studies and those from the ESR studies.

Experimental

Materials. DMF was pre-dried with CaH_2 and was further dried over 4A and 5A molecular sieves in a vacuum. All salts, which were purified by recrystallization from aqueous solutions, were well dried in a vacuum (of less than 5×10^{-5} mmHg) for more than 24 h.

Nitrobenzene was used after additional degassing in a vacuum line and was stored in a graduated 0.5 ml pipet.

Tetrahydrofuran, which was used for the metal reduction of nitrobenzene, was refluxed over potassium metal and then distilled. The distillate was degassed five times in a vacuum and rigorously dried with the addition of sodium anthracenide to absorb trace amounts of moisture and oxygen.

The ESR spectra were measured with a Hitachi X-band ESR spectrometer model 771, employing field modulation at 100 kHz, while maintaining the room temperature at 21—23 °C.

Preparations of the Radical Anion. Electrolytic Reduction: In a solution containing 0.1 M of the supporting electrolytes, nitrobenzene radical anions were prepared by electrolytic reduction in a vacuum electrolytic cell with two Pt electrodes. The concentration of nitrobenzene was about 5×10^{-4} M in the present series of measurements, and a sample solution was electrolyzed carefully for more than 24 h to convert all nitrobenzene to its radical anion in the cavity of the ESR spectrometer. When the electrolyte was lithium perchlorate, the selective production of the radical anion was so difficult due to the small difference between the first and the second waves in the polarogram that the preparation of the radical anions was carried out by the lithium metal reduction procedure.

Alkali-metal Reduction. Alkali-metal reduction in THF was carried out by the conventional method.[14] Sodium and potassium metals were purified in a vacuum (see Fig. 2) and the surface of the lithium metal was etched by treatment with a THF–nitrobenzene solution. The pieces were stored in a tube with a break-seal.

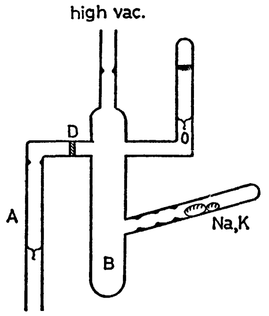

Fig. 2. The apparatus used for preparation of the radical anion.

After the preparation of the radical anion-THF solution, the solution was introduced into A through sintered glass D. The solvent was removed by distillation into a tube B using liquid nitrogen and tube B was sealed off. The solid metal nitrobenzenide was dissolved in DMF containing a given amount of salts. All experiments were carried out in a high vacuum line using break-seals.

Results

Hyperfine Splitting Constants Obtained in a Solution of 0.1 M Salt Concentration. Figure 3 shows the ESR spectra obtained in a solution of 0.1 M salt concentration. The sample solutions were prepared by the electrolytic reduction method excepting the 0.1 M lithium perchlorate solution. Lithium nitrobenzenide was prepared by the metal reduction method and was dissolved in a 0.1 M lithium perchlorate solution. A well-resolved ESR spectrum was obtained in a solution of 0.1 M TEAP, while those obtained in cesium and rubidium salts were extraordinarily broad. Table 1 shows the hfs obtained from an analysis of these spectra, which were confirmed by simulation using a JEOL spectrum computer, model JRA-5. The approximate line-widths ($\Delta H_{1/2}$) are also shown in the table. It was not possible to confirm the spectrum obtained in the solutions of cesium perchlorate and rubidium perchlorate with simulation owing to the broadening of the line-width.

In general, hfs due to the nucleus varies with the kind of salt. The variations of the nitrogen hfs ($\mathbf{a}_N$) and the proton hfs at the *para*-position ($\mathbf{a}_p$) were remarkably large. The values of $\mathbf{a}_N$ and $1/\mathbf{a}_p$ increased with decreasing radius of the cation. Thus, it is possible to compare the nitrogen hfs in the solutions of Li^+, Na^+, K^+, Cs^+ and Rb^+ in descending order (with the value for Cs^+ about the same as that for Rb^+), which is essentially the same as that obtained from the polarographic studies.

Variation of ^{14}N hfs with the Concentration of Counter Cations. Figure 4 shows the variations of the nitrogen hfs as a function of the concentration of the added salt, while maintaining the total ionic strength at 0.1 M with TEAP. The nitrobenzene radical anions were obtained by the metal reduction procedure, and were dissolved in a solution of arbitrary concentration of the added salt. The total concentration of the radical anions was less than 5×10^{-4} M for these experiments.

The variations of the nitrogen hfs show a regular shift in the concentration range of 10^{-3}—10^{-1} M for both sodium perchlorate and potassium nitrate. This behavior is the same as that for the *p*-chloronitrobenzene radical anion in DMF reported by Kitagawa *et al.*[27] However, no reports on the quantitative explanations to the change of the ^{14}N hfs, have apparently been published to date.

The origins of the curves indicate the hfs in a 0.1 M TEAP-solution containing about 5×10^{-4} M of the alkali metal cations. The values of the origins of the two curves are identical and equal to the hfs obtained in a 0.1 M TEAP-solution by the electrolytic reduction method without alkali metal cations. These results show that nitrobenzene radical ion pairs composed of sodium and potassium cations are almost dissociated in a solution of TEAP. We must also mention that the hfs in a 0.1 M TEAP-solution is completely consistent with the hfs obtained in a solution of alkali metal nitrobenzenide ($\sim5\times10^{-4}$ M) in the absence of TEAP. This result seems to indicate that the nitrobenzene radical anions are almost free in a solution of TEAP.

The variation of the nitrogen hfs is shown in Fig. 5 as a function of the concentration of lithium perchlorate.

TABLE 1. PROTON AND NITROGEN HYPERFINE SPLITTING CONSTANTS OF NITROBENZENE RADICAL ANIONS IN A SOLUTION WITH A 0.1 M SALT CONCENTRATION (IN GAUSS)

Position[a]	$LiClO_4$	$NaClO_4$	KNO_3	$RbClO_4$[d]	$CsClO_4$[d]	TEAP
$\mathbf{a}_N$	11.36	11.12	10.50	10.0	$\approx$10.0	9.62
$\mathbf{a}_p$	3.86	3.88	3.95	—	—	4.01
$\mathbf{a}_o$	3.40	3.38	3.35	—	—	3.36
$\mathbf{a}_m$	1.11	1.09_5	1.06	—	—	1.06
$H_{1/2}$[b]	0.68	1.10	0.45	2.5	$>$ 2.5	0.45
r_c[c]	0.60	0.95	1.33	1.48	1.69	—

a) $\mathbf{a}_N$; nitrogen hyperfine splitting constant. $\mathbf{a}_p$, $\mathbf{a}_o$, $\mathbf{a}_m$; *para*-proton hyperfine splitting constant, *etc.* b) Line-width (in gauss). c) Pauling's cationic radius (in Å). d) Still not completely confirmed by simulation.

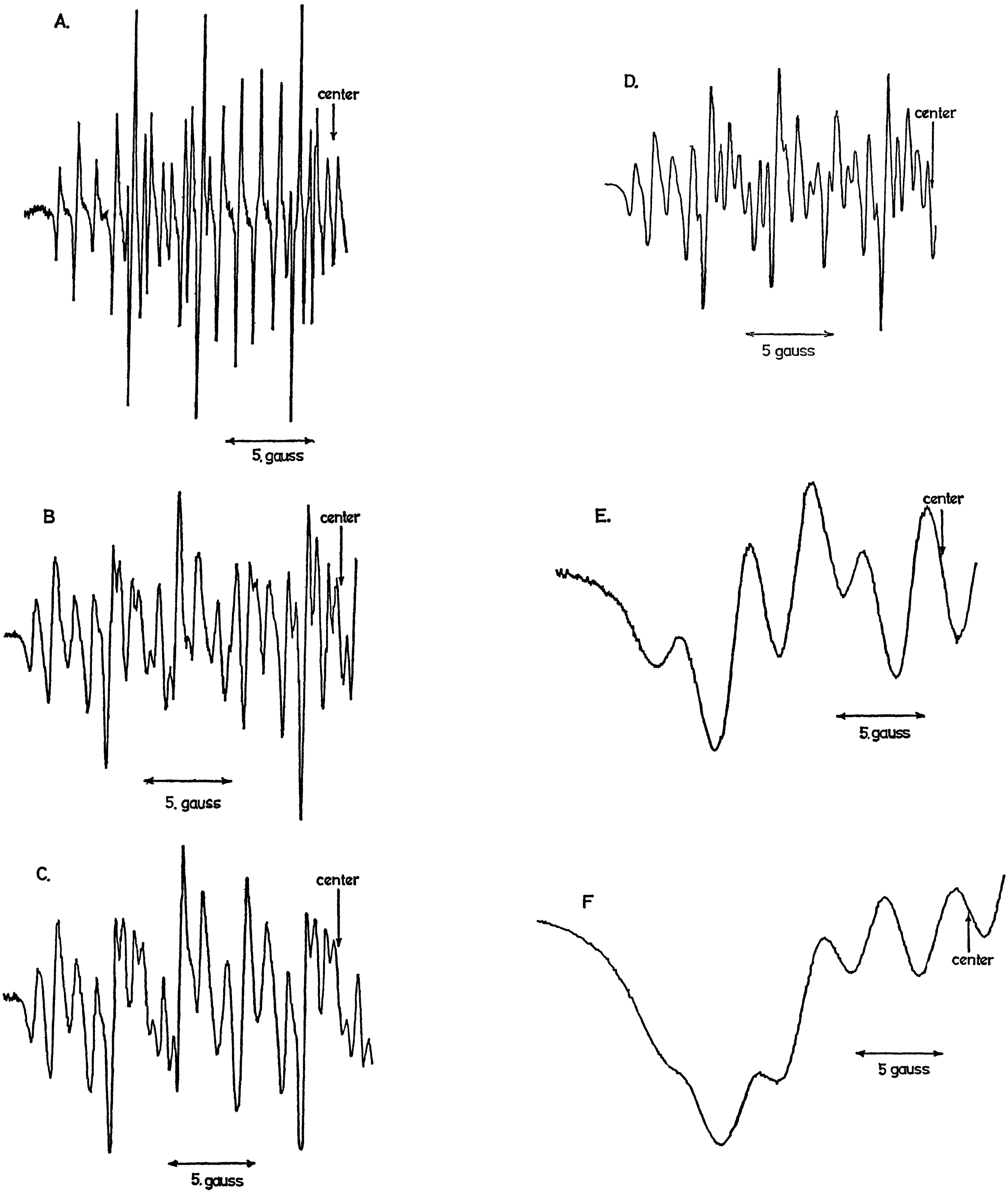

Fig. 3. The ESR spectra obtained in the solution of 0.1 M salt concentration.
A: 0.1 M TEAP, B: 0.1 M $LiClO_4$, C: 0.1 M $NaClO_4$,
D: ≈0.1 M (saturation) KNO_3, E: 0.1 M $RbClO_4$, F: 0.1 M $CsClO_4$.

ESR spectra obtained in the region of lower concentration of lithium perchlorate are shown in Fig. 6 and the outlined spectrum simulations are also displayed as stick diagrams. Obviously, the spectra due to two different species are superimposed in these spectra, that is, the two different species are the ion pairs and the free ions, respectively. The relative intensities due to the free ions decrease with increasing concentration of lithium perchlorate. In the region of lower concentration of the salt, the nitrogen hfs due to the ion pair decreases with increasing concentration of the salt. On the other hand, the hfs due to the free ions increases with an increase of the concentration of the salt, as shown in Fig. 5. Thereafter, the hfs increases monotonically with the concentration of sodium and potassium ion pairs, as shown in Fig. 4.

In an infinitely-dilute solution (of less than 5×10^{-4}M), the ESR spectrum consisted of the free ion and the nitrogen hfs coincided with that obtained in a solution of TEAP, as in the studies of the sodium and potassium

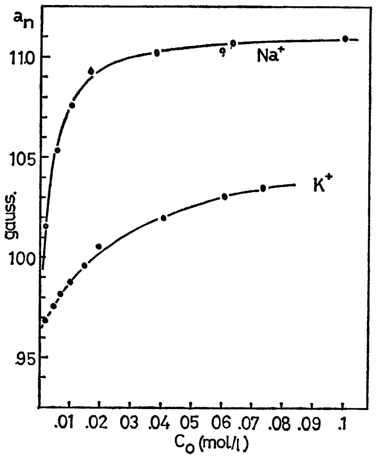

Fig. 4. Variation of the nitrogen hfs with the concentration of the metal cations. Total ionic strength kept formally at 0.1 M.
Na^+, added sodium perchlorate.
K^+, added potassium nitrate.

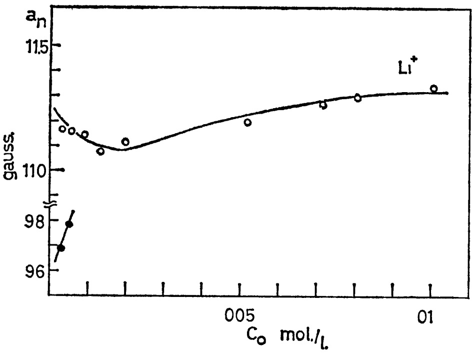

Fig. 5. Variation of the nitrogen hfs with the concentration of lithium perchlorate.
○: Nitrogen owing to ion pair.
●: That of free ion.

nitrobenzenide systems.

In the region of high concentration of lithium perchlorate, the ESR spectra also consisted of a single species, the ion pair.

Discussion

Perturbation of the Distribution of Unpaired Spin Densities. As stated above, it is possible to compare the nitrogen hfs in the solutions of Li^+, Na^+, K^+, Cs^+ and Rb^+ in descending order. It seems that the radius of the alkali metal cation may be responsible for this order.

The interactions between the radical anions and the counter cations have been formulated by Huch and Rowland,[15] and McClelland.[16] Since the McClelland theory based on the Hückel approximation is of a simple form, its application to aromatic radical anions and their derivatives has been carried out by many workers.[17–20] Takeshita and Hirota[21] modified the cationic field effects to the following effective Hamiltonian ($H'_{\rm eff}$):

$$H'_{\rm eff} = H^0_{\rm eff} - \frac{Ze^2}{\varepsilon(r)r} \qquad (1)$$

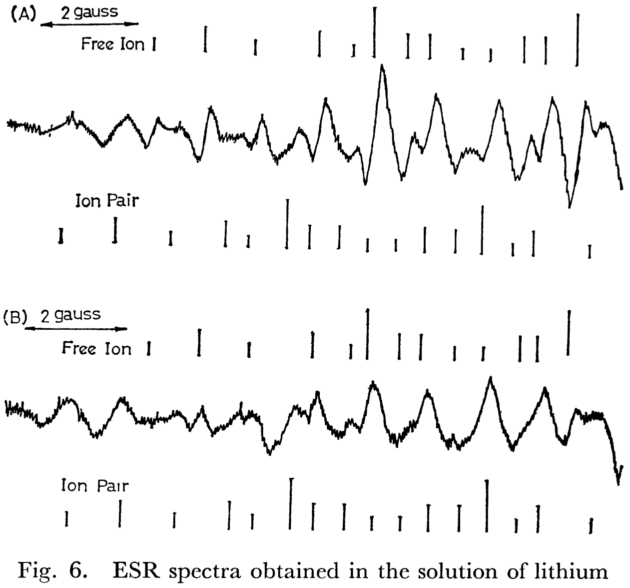

Fig. 6. ESR spectra obtained in the solution of lithium perchlorate.
The stick diagrams indicate the splittings of the ion pair and free ion.
A) In a solution of 5.1 mM lithium perchlorate.
B) In that of 8.8 mM lithium perchlorate.

where $\varepsilon(r)$ is a screening factor which accounts for the screening effects of the solvent in the cationic fields. The solvent effect on the hfs can be taken into account with this screening parameter. In the present calculations of the perturbation energy and the variations of the spin density, some values of the screening parameter have been applied.

The dimensions of the radical anion and the parameters of the Coulomb and exchange integrals were choosen to be as follows:[22]

aromatic C-C$=1.39$ Å
aromatic angle$=120°$
C-N$=1.49$ Å
N-O$=1.21$ Å
O-N-O$=117°$

$\delta\alpha_{\rm O}=1.4\beta$
$\delta\alpha_{\rm N}=2.2\beta$
$\beta_{\rm NO}=1.67\beta$
$\beta_{\rm NC}=1.2\beta$

All overlap integrals were neglected in the sense of simple Hückel approximation. From the extensive calculations of the interaction energy, the time averaged position of the cation is determined on the X-axis of the coordination system as shown in Fig. 1. This conclusion agrees with the case of 4-nitropyridine *N*-oxide anion radicals in DME reported by Kawamura *et al.*[23] The interaction energy, when the dielectric constant of DMF is used as the screening factor, is less than that when the factor is equal to 1. However, the minimum points of the potential surfaces are consistent with each other.

The unpaired spin densities of each position were calculated using the method of McClelland with the McLachlan approximate configurational interaction treatment,[24] assuming the cations approach the nitrobenzene radical anions along X-axis.

The calculations of the hfs of ring protons ($\mathbf{a}_{\rm H}$) were carried out using the following generally applied equation:[25]

$$\mathbf{a}_{\mathrm{H}} = -Q \cdot \rho_{\mathrm{C}}^{\pi} \qquad (2)$$

where Q is taken to be 27.3

On the other hand, the nitrogen hfs were theoretically calculated using the following equation, which was given by Rieger and Fraenkel:26)

$$\mathbf{a}_{\mathrm{N}} = 99.0 \cdot \rho_{\mathrm{N}}^{\pi} - 2 \times 35.8 \cdot \rho_{\mathrm{O}}^{\pi} + 17 \cdot \rho_{\mathrm{C}}^{\pi} \qquad (3)$$

in which ρ_{N}^{π}, ρ_{O}^{π}, and ρ_{C}^{π} are the π-electron spin densities at the nitrogen, oxygen and adjacent carbon atoms, respectively. In the present calculations of the spin densities, the parameter λ in the procedure of McLachlan was set at 1.2.

Figure 7 shows the calculated hfs of the *para*-proton and nitrogen which are greatly affected by the distance of closest approach of the cations, assuming the screening parameter to be 37.0. The hfs of the *meta*- and *ortho*-protons are apparently not changed by the distance of closest approach of the cations. The nitrogen hfs increases with the decrease in the distance of closest approach of the cations. On the other hand, the *para*-proton hfs shows the opposite tendency. The same observations were made for the cations when the screening parameter was nearly equal to the dielectric constant of DMF. However, when the screening parameter was chosen to be 1, as has often been done by other workers,3,20) the variations of the nitrogen hfs became extraordinarily large.

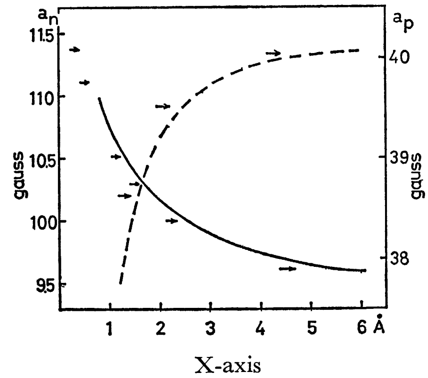

Fig. 7. The calculated hfs of the *para*-proton and nitrogen assuming $\varepsilon(r)=37.0$. The cation is on the X-axis. The arrows indicate the observed value in the solution of 0.1 M salt concentration (Table 1).

Takeshita and Hirota have concluded that the screening parameters in contact ion-pair systems are closer to the macroscopic dielectric constant than to 1.21) Although detailed information about the ion-pair structures has not been obtained at the present stage of these investigations, it seems to be a reasonable approximation to set the value of the screening parameter in the vicinity of the dielectric constant of DMF. More detailed discussions of the structure of ion pairs will now be presented on the basis of the present research.

It can be semi-quantitatively explained from the above calculations that nitrogen hfs in solutions of Li^+, Na^+, K^+, Cs^+, Rb^+, and $\mathrm{Et_4N}^+$ can be arranged in this descending order. That is, the smaller the radius of the cation, the closer the cation can approach the radical anion of nitrobenzene.

Discussion of Ion-Pair Equilibria. *Sodium and Potassium Ion-Pair Equilibria*: The above discussion was limited to the observed hfs obtained in solutions with a constant salt concentration (0.1 M). However, the ion-pair formations must be rigorously discussed on the basis of equilibrium considerations.

The regular shifts of the nitrogen hfs as a function of the concentration of the added salts, as shown in Fig. 4, are discussed considering the next equilibrium between the free ions and ion pairs:

$$(\mathrm{A}^{\overline{\cdot}}, \mathrm{M}^+)_{\mathrm{IP}} \rightleftharpoons \mathrm{A}_{\mathrm{f}}^{\overline{\cdot}} + \mathrm{M}^+, \qquad (4)$$

where $\mathrm{A}_{\mathrm{f}}^{\overline{\cdot}}$ is the free nitrobenzene radical anion, $(\mathrm{A}^{\overline{\cdot}}, \mathrm{M}^+)_{\mathrm{IP}}$ the ion pair and M^+ the counter cation.

The coordination number in the sodium nitrobenzenide ion ion-pair system has been proved to be 1 from polarographic studies. Although the number in the potassium nitrobenzenide ion-pair system was not determined exactly by means of polarography, the discussion of this system is continued assuming the coordination number to be 1.

One can expect that the ion pairs and free ions have different hfs and that the variations of the ring proton hfs are less than those for nitrogen. It is possible to interpret the regular shift of the nitrogen hfs as a function of the concentration of the added salt, based on the rapid equilibrium of reaction (4), assuming that the ring proton hfs does not change for the two different states, *the ion pair* and *the free ion*.

In general, if the forward and backward reaction rates of reaction (4) are slow, the spectrum will consist of two separate signals which are obtained in a solution of lithium perchlorate as described above. If they are rapid, only one signal will appear at an approximately averaged position. In the case of the sodium and potassium nitrobenzenides, the nitrogen hfs showed a regular increase with an increase of the concentration of the counter cation and all ESR spectra could be simulated by one species. These results indicate that the equilibrium of reaction (4) in these cases are in the limit of the rapid exchange region.

According to the two-jump model, the observed nitrogen hfs ($\mathbf{a}_{\mathrm{ob}}$) in the limit of rapid exchange between two states is given by:28,29)

$$\mathbf{a}_{\mathrm{ob}} = \frac{\tau_{\mathrm{f}}}{\tau_{\mathrm{f}}+\tau_{\mathrm{IP}}} \cdot \mathbf{a}_{\mathrm{f}} + \frac{\tau_{\mathrm{IP}}}{\tau_{\mathrm{f}}+\tau_{\mathrm{IP}}} \cdot \mathbf{a}_{\mathrm{IP}}, \qquad (5)$$

where τ_{f} and τ_{IP} are the lifetimes of the free ions and ion pairs, respectively. Using the rate constants of the forward and backward reactions, the reaction rates are given by the following equations:

for the forward reaction:

$$v_{\mathrm{f}} = \frac{[(\mathrm{A}^{\overline{\cdot}}, \mathrm{M}^+)_{\mathrm{IP}}]}{\tau_{\mathrm{IP}}} = k_1 \cdot [(\mathrm{A}^{\overline{\cdot}}, \mathrm{M}^+)_{\mathrm{IP}}], \qquad (6)$$

for the backward reaction:

$$v_{\mathrm{b}} = \frac{[\mathrm{A}_{\mathrm{f}}^{\overline{\cdot}}]}{\tau_{\mathrm{f}}} = k_{-1} \cdot C_{\mathrm{M}^+} \cdot [\mathrm{A}_{\mathrm{f}}^{\overline{\cdot}}], \qquad (7)$$

where $[\mathrm{A}_{\mathrm{f}}^{\overline{\cdot}}]$, C_{M^+} and $[(\mathrm{A}^{\overline{\cdot}}, \mathrm{M}^+)_{\mathrm{IP}}]$ are the concentrations of these species. The ion-pair formation constant for reaction (4) is given by

$$K_{\mathrm{f}} = \frac{k_{-1}}{k_1} = \frac{\tau_{\mathrm{IP}}}{\tau_{\mathrm{f}} \cdot C_{\mathrm{M}^+}}. \qquad (8)$$

When Eq. 8 is substituted into Eq. 5, Eq. 5 can be rewritten as

$$\mathbf{a}_{\mathrm{ob}}=\frac{1}{1+K_{\mathrm{f}}\cdot C_{\mathrm{M}^+}}\cdot\mathbf{a}_{\mathrm{f}}+\frac{K_{\mathrm{f}}\cdot C_{\mathrm{M}^+}}{1+K_{\mathrm{f}}\cdot C_{\mathrm{M}^+}}\cdot\mathbf{a}_{\mathrm{IP}}. \tag{9}$$

If $\mathbf{a}_{\mathrm{ob}}$ is normalized as follows:

$$\mathbf{a}_{\mathrm{ob}}=\frac{\mathbf{a}_{\mathrm{ob}}-\mathbf{a}_{\mathrm{f}}}{\mathbf{a}_{\mathrm{IP}}-\mathbf{a}_{\mathrm{f}}}, \tag{10}$$

Eq. 10 can be expressed in the simple form

$$\bar{\mathbf{a}}_{\mathrm{ob}}=\frac{K_{\mathrm{f}}\cdot C_{\mathrm{M}^+}}{1+K_{\mathrm{f}}\cdot C_{\mathrm{M}^+}}. \tag{11}$$

On the other hand, Eq. 9 can also be transformed into:

$$\frac{1}{\mathbf{a}_{\mathrm{ob}}}=\frac{1}{K_{\mathrm{f}}\cdot\mathbf{a}_{\mathrm{IP}}}\cdot\frac{1}{C_{\mathrm{M}^+}}\left(1-\frac{\mathbf{a}_{\mathrm{f}}}{\mathbf{a}_{\mathrm{ob}}}\right)+\frac{1}{\mathbf{a}_{\mathrm{IP}}}. \tag{12}$$

For exact arguments concerning the regular increase of the nitrogen hfs from Eq. 12, it is necessary to assume the following approximations.

1. The concentrations of the cation are equal to that of the salt, if the dissociation constant of the salt is large, *i.e.*, $C_{\mathrm{M}^+}=C_{\mathrm{o}}$, where C_{o} is concentration of the salt.
2. Nitrogen hfs of the free nitrobenzene radical anion is equal to that obtained in a 0.1 M solution of TEAP, *i.e.*, $\mathbf{a}_{\mathrm{f}}=9.62$ (± 0.01) gauss.

The second approximation seems to be almost correct as was discussed above.

From a plot of the inverse of the observed nitrogen hfs ($1/\mathbf{a}_{\mathrm{ob}}$) *vs.* $1/C_{\mathrm{M}^+}\cdot(1-\mathbf{a}_{\mathrm{f}}/\mathbf{a}_{\mathrm{ob}})$, the hfs of the ion pairs and the ion-pair formation constants can be obtained by determining the intercept and the slope of the straight-line, respectively.

Figure 8 shows the plot for the solutions of sodium perchlorate. A straight-line is found over the wide concentration range of $1\times 10^{-3}-10^{-1}$ M. The hfs of the ion pairs and the formation constant were determined from the intercept and the slope by least-squares calculations, respectively. The nitrogen hfs of the ion pair is equal to $\mathbf{a}_{\mathrm{IP}}=11.23$ (± 0.03) gauss, and the formation constant was calculated to be $K_{\mathrm{f}}=220$ (± 5) 1/M from the slope with $\mathbf{a}_{\mathrm{IP}}$ obtained from the intercept. It is particularly noteworthy that the formation constant of the sodium nitrobenzenide system, as determined from the variation of the nitrogen hfs is completely compatible with that obtained from polarographic studies (200 $\pm$20 1/M) to within the experimental error. (Detailed discussions of the polarographic studies will be published elsewhere.) This coincidence seems to be most important argument in this paper. It strongly supports the approximate correctness of the present treatment of the regular increase of the nitrogen hfs. Figure 9 shows the normalized hfs $\mathbf{a}_{\mathrm{ob}}$ as a function of the concentration of the counter cation (C_{M^+}) for the various formation constants. The curves in Fig. 9 are in qualitative accordance with the regular shifts of the nitrogen hfs as shown in Fig. 4. The experimental points obtained for the sodium nitrobenzenide system are also plotted in the same figure.

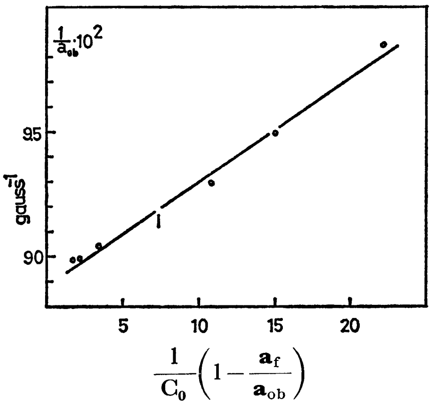

Fig. 8. Plot $1/\mathbf{a}_{\mathrm{ob}}$ *vs.* $1/C_0(1-\mathbf{a}_{\mathrm{f}}/\mathbf{a}_{\mathrm{ob}})$ for the sodium perchlorate addition.

Slope; $4.05(0.09)\times 10^{-4}$, Intercept; $8.90(0.02)\times 10^{-2}$. Standard deviations are shown in parentheses.

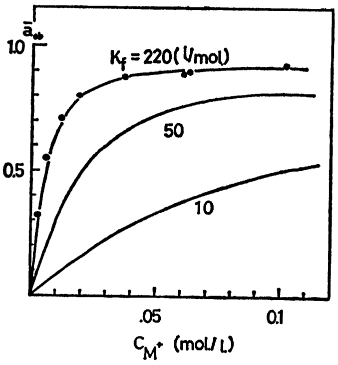

Fig. 9. Plot of Eq. 11 for the variation of the average nitrogen hfs with the concentration of the cation. The lines have been drawn for $K_{\mathrm{f}}=10$, 50, 220 (1/M).

●; Experimental points in the case of sodium nitrobenzenide.

It is also important that the hfs of the ion-pair itself can be evaluated from the above discussion in solvents having a high polarity, such as DMF, because this quantity is useful for discussions of the structure of the ion pairs. The present paper is the first report in which the hfs of the ion-pair itself was determined in a high polar solvent.

Since potassium nitrate does not have a large dissociation constant in DMF, the concentrations of the potassium ions must be calculated. Although there is some question as to the validity of using the dissociation constant ($K_{\mathrm{d}}=0.043$ 1/M) reported by Ames and Sears[30] for this purpose, the concentrations of the ion were calculated.

Figure 10 shows the plots of $1/\mathbf{a}_{\mathrm{ob}}$ *vs.* $1/C_{\mathrm{M}^+}\cdot(1-\mathbf{a}_{\mathrm{f}}/\mathbf{a}_{\mathrm{ob}})$ and $1/C_{\mathrm{o}}\cdot(1-\mathbf{a}_{\mathrm{f}}/\mathbf{a}_{\mathrm{ob}})$ which give straight lines. The difference in the linearity of the two lines is not significant. But the standard deviations of the slope and intercept of the plot with the potassium nitrate concentration are less than that of the plot as a function of the concentration of potassium ions. The hfs of the ion pair is equal to $\mathbf{a}_{\mathrm{IP}}=10.99$ (± 0.05) gauss, and the formation constant was determined to be $K_{\mathrm{f}}=30$ (± 6) 1/M, from the slope and intercept of the line with the concentration of potassium ions. On the other hand, the hfs and the formation constant can also be

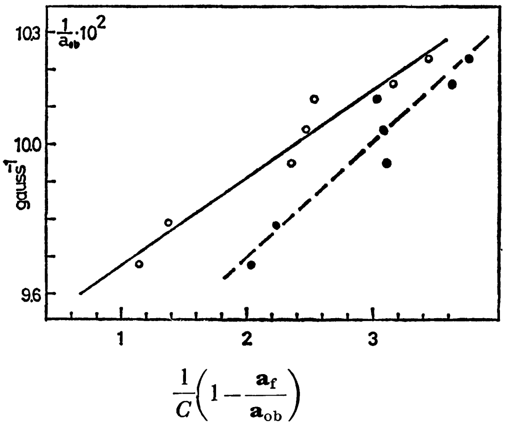

Fig. 10. Plot $1/\mathbf{a}_{ob}$ *vs.* $1/C_M{}^+(1-\mathbf{a}_f/\mathbf{a}_{ob})$ and $1/C_0\cdot(1-\mathbf{a}_f/\mathbf{a}_{ob})$ for the potassium nitrate addition.

○; Against the salt concentration.
Slope; $2.4(0.2)\times10^{-3}$, Intercept; $9.44(0.02)\times10^{-2}$

●; Against the cation concentration calculated from the dissociation constant of potassium nitrate in DMF.
Slope; $3.0(0.4)\times10^{-3}$, Intercept; $9.1(0.1)\times10^{-2}$

determined from the plot as a function of the potassium nitrate concentration, as summarized in Table 2.

Lithium Ion-Pair Equilibrium: As shown in Fig. 6, the ESR spectra obtained in the solutions of lower concentration of lithium ions (of less than 10^{-2} M) are a superposition of the two spectra due to the free ions and ion pairs. In this region, the exchange reaction (4) is a "*slow exchange*" reaction in the sense of magnetic resonance spectroscopy. In general, the spectrum consists of two separate signals when the reaction rates for reaction (4) are small, as stated above.

From the solution of the modified Bloch equation for the two-jump model, the ratio of the separation between the positions of the two maxima (Δ) to that when the exchange between the two states does not exist (Δ_0) is given by:[31]

$$\frac{\Delta}{\Delta_0}=\left[1-\frac{1}{2\cdot\pi^2\cdot\tau^2\cdot(\nu_{IP}-\nu_f)^2}\right]^{1/2}, \tag{13}$$

assuming that the lifetimes of ion pairs and of the free ions are equal to each other, *i.e.*, that $\tau_{IP}=\tau_f=2\cdot\tau$, and that the inverse of the transverse relaxation times are negligibly small. ν_{IP} and ν_f are the resonance frequencies of the two states, respectively.

Equation 13 means that the greater the difference between the resonance frequencies of the ion pair and the free ion, the greater the decrease in the critical lifetime at which the two signals merge into only one signal. In other words, when the difference of the resonance frequencies is large, the spectrum will consist of two separate signals, even if the exchange reaction rate is relatively large. As shown in Table 1, the nitrogen hfs is highest in the solution of lithium perchlorate. Therefore, the difference between the resonance frequencies of the ion pair composed of lithium cations and the free ions is largest in the present experiments. The exchange rates of reaction (4) are accelerated with increasing concentration of lithium perchlorate, and the resonance lines merge into a single line in the intermediate exchange region.

In the region showing a regular increase of the nitrogen hfs as in Fig. 5, the equilibrium reaction is in the range of the rapid exchange as mentioned above.

Equation 12 was examined in order to determine the ion-pair formation constant and the nitrogen hfs of the ion pair in the rapid exchange region. Figure 11 shows the plot of $1/\mathbf{a}_{ob}$ with $1/C_M{}^+\cdot(1-\mathbf{a}_f/\mathbf{a}_{ob})$. The variations of the nitrogen hfs in the region of rapid exchange are not so large, and the error of the hfs becomes of importance in the accuracy of the formation constant and the hfs of the ion pair. Analyzing the linear relation using the least-squares method, the hfs of the ion pair itself and the formation constant are $\mathbf{a}_{IP}=11.36$ (±0.03) gauss and $K_f=340$ (±40) 1/M, respectively. The formation constant determined here is somewhat larger than that determined by polarographic techniques, as shown in Table 2. The accuracy of the formation constant using ESR

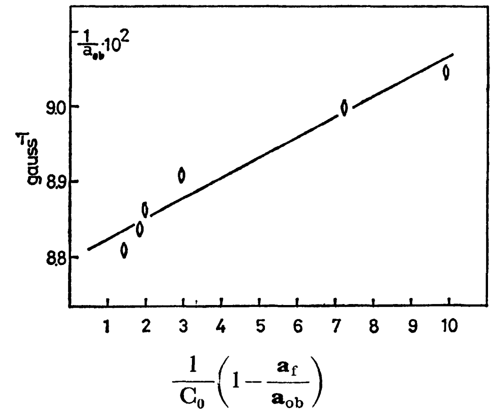

Fig. 11. Plot $1/\mathbf{a}_{ob}$ *vs.* $1/C_0(1-\mathbf{a}_f/\mathbf{a}_{ob})$ for the lithium perchlorate addition.
Slope; $2.5(0.3)\times10^{-4}$, Intercept; $8.80(0.02)\times10^{-2}$

Table 2. Summary of the formation constants, the hfs of the ion pair, and the coordination numbers obtained from the ESR and Polarographic studies in DMF

Cation	Formation Constant (1/M)		Nitrogen hfs (gauss)	Coordination number	
	ESR	Polarog.[c]		ESR	Polarog.[c]
Li^+	340($\pm$40)	150($\pm$10)	11.36($\pm$0.03)	1	1
Na^+	220($\pm$ 5)	200($\pm$20)	11.23($\pm$0.03)	1	1
K^+	41($\pm$ 3)[a] 30($\pm$ 6)[b]	— —	10.58($\pm$0.03) 10.99($\pm$0.05)	1	—

a) Using the concentration of potassium nitrate. b) Using the concentration of potassium ions. c) Details will be reported in the near feature.

techniques is not satisfactory because the change of the nitrogen hfs in the rapid exchange region is not large enough, as shown in Fig. 5. For this reason, the formation constant determined from the variations of the hfs appears to be approximately consistent with that obtained using polarographic techniques, which will be described in detail elsewhere.

The formation constants of the ion pairs between nitrobenzene radical anions and cesium and rubidium cations could not be determined because the line-width of the spectra in the solutions of these salts were extraordinarily large, as is seen in Fig. 3.

We found that the line-widths associated with the nitrogen nuclear spin quantum number $m_z=\pm 1$ were larger than that for $m_z=0$. The line-width broadening effects in the ESR spectra are now under study, a part of the results of which will be reported in the near future.

Summary

The ion pair formation constants, the nitrogen hfs of the ion-pair itself, and the coordination numbers are summarized in Table 2.

In the case of the lithium ion pair, the variations of the nitrogen hfs in the fast exchange region are so small that the formation constant obtained by polarographic techniques seems to be more correct than that obtained using ESR.

The formation constants of the sodium ion pair system obtained from both studies are completely consistent with each other.

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