ESR Studies of Naphthalene-alkali Metal Ion Pairs. The Effect of Alkali Ions on the Proton-coupling Constants and the Structure of the Ion Pairs

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Following the work of Adam and Weissman⁽¹⁾ and Atherton and Weissman,⁽²⁾ a number of ESR investigations of radical anion-alkali metal ion pairs have been reported. In the pioneering work of Atherton and Weissman, they suggested that in naphthalene-alkali metal ion pairs the equilibrium position of the alkali ion was situated above the nodal plane of the lowest antibonding molecular orbital of naphthalene, *i. e.*, above the 9—10 bond; they suggested this on the basis of an examination of the temperature dependence of the alkali metal hyperfine splittings. Although they found no variation in the proton-coupling constants on the formation of the ion pair, thereafter a few examples showing a variation in the proton coupling

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1) F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 1518 (1958).
2) N. M. Atherton and S. I. Weissman, *ibid.*, **83**, 1330 (1961).

TABLE 1. THE COUPLING CONSTANTS OF THE NAPHTHALENE RADICAL ANION*

Solvent	Cation	Proton coupling constant (in gauss) a_α	Proton coupling constant (in gauss) a_β	Metal coupling constant (in gauss) a_M
Dioxane	Li	4.792	1.788	1.213
Dioxane	Na	4.871	1.857	1.295
Dioxane	K	4.861	1.837	—
DMF	Li, Na, K	4.906	1.812	—

* the values at 24°C.

TABLE 2. THE EFFECT OF CATIONS ON THE PROTON COUPLING CONSTANTS

	Observation (in gauss)*1			Calculation (in gauss)	
	Naph$^-$-Li$^+$	Naph$^-$-Na$^+$	Naph$^-$-K$^+$	Model A*2	Model B*3
a_α	−0.114	−0.035	−0.045	−0.176	−0.349
a_β	−0.024	+0.045	+0.025	+0.205	+0.003

*1 The values were obtained by taking the difference between the proton coupling constants observed in dioxane and in DMF; $a_{\text{diox.}} - a_{\text{DMF}}$.

*2 The cation was assumed to be above the center of the molecular plane of the radical anion and at a distance of 3.5 Å from it.

*3 The cation was assumed to be hopping rapidly from the position above the center of the one benzene ring to that of the other benzene ring. The distance between the two ions was taken to be 2.8 Å.

constants with alkali ions have been reported.[3] In this paper we wish to report the effect of the ion pair formation on the proton-coupling constants observed for the naphthalene-alkali ion system in dioxane. As is well known, dioxane is a good solvent for the formation of ion pairs; we could observe significant changes in the proton-coupling constants, changes attributable to the effect of the alkali ion in the solvent. Through an examination of these data in terms of the MO method, we will estimate the structure of the ion pairs.

Table 1 gives the observed proton-coupling constants of the naphthalene radical anion in dioxane, together with the data observed in dimethylformamide (DMF). As the table shows, in dioxane the proton-coupling constants varied significantly with the alkali ions, while no variation was observed in DMF. In DMF, the radical anions showed no alkali metal hyperfine splittings, either. The negligible cation effect on the proton-coupling constants and the lack of the alkali metal coupling constant suggest that the radical anion may exist as a "free" anion, or as "a weak ion pair" (a solvent-separated ion pair) in which the radical anion is scarcely perturbed at all by the cation. Hence, one may estimate the effect of the formation of the ion pair on the proton-coupling constants by taking the difference between the proton-coupling constants observed in dioxane and in DMF. Table 2 shows the difference between the coupling constants observed in these two solvents. It shows that the proton-coupling constant at the α position may decrease on the formation of the ion pair with a sodium or potassium ion, while that at the β position may increase. Interestingly, however, on the formation of the ion pair with a lithium ion, the proton-coupling constants at both the α and β positions decrease, the coupling constant at the α position more extensively than is the case for the ion pair with sodium or potassium ion, while that at the β position does so only slightly.

To account for these observations and to obtain information on the structure of the ion pairs, we examined the interaction between the two ions in terms of the MO method. The details of the method used for the calculations have been described in a previous paper.[3b] For the present paper the proton-coupling constants were calculated from the spin densities using Colpa and Bolton's relation.[4]

In the naphthalene-alkali metal ion pairs, the most plausible structure for the ion pairs may be that in which the equilibrium position of the alkali ion is just above the center of the molecular plane of the radical anion. As is shown in Fig. 1, the MO calculation admittedly suggests that such an ion-pair structure may be most likely when the distance between the two ions is larger than about 3.5 Å.

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3) a) A. H. Reddoch, *J. Chem. Phys.*, **43**, 3411 (1965). b) M. Iwaizumi, M. Suzuki, T. Isobe and H. Azumi, This Bulletin, **40**, 1325 (1967).

4) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

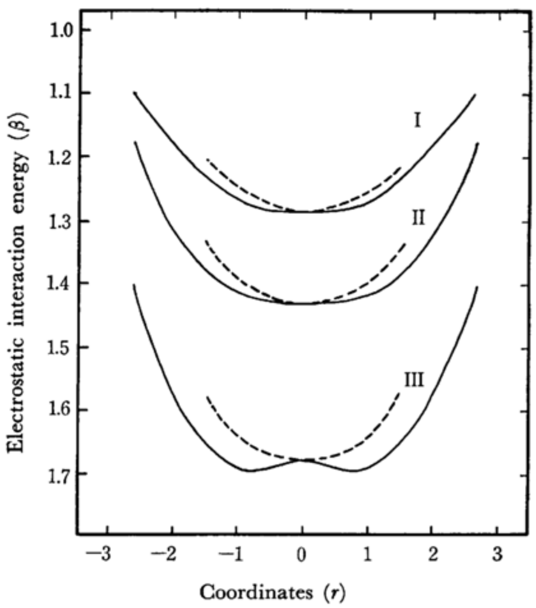

Fig. 1. Electrostatic interaction within Naphthalene-alkali metal ion-pair.
The origin of the coordinates is taken at the center of the anion molecule. Solid lines correspond to x coordinate (long axis) and dotted lines to y coordinate (short axis). The coordinates are in unit of r, a C–C bond length (1.39 Å). The distance between the two ions is taken as I: 4.0 Å, II: 3.5 Å and III: 2.8 Å, respectively.

Then, we attempted to calculate the proton-coupling constants in the presence of the cation, assuming that the alkali ion is placed just above the center of the molecular plane and at a distance of 3.5 Å from it. The results are shown in Table 2 (model A). As the table shows, the qualitative behavior of the calculations is in good agreement with the observation for the ion pairs with sodium and potassium ions rather than for the ion pair with a lithium ion; *i. e.,* the calculation predicts well the decrease in the α proton-coupling constant and the increase in the β proton-coupling constant.

As has been noticed above, the ion pair with a lithium ion shows a different behavior in the proton-coupling constants from in the cases of the ion pairs with sodium and potassium ions. This fact may imply that the structure of the ion pair is somewhat different from those of the ion pairs with a sodium or potassium ion. As it is, one may notice that in Fig. 1 the double minima occur well in the potential as the distance between the two ions becomes shorter. Since the lithium ion can approach the molecular plane more closely, it may be expected that with the lithium ion we can see a potential with double minima. Therefore, the calculation for the proton-coupling constant was attempted on the assumptions that the equilibrium position of the alkali ion is above the center of the benzene ring and that the alkali ion migrates rapidly back and forth between the two equilibrium positions above the anion molecule, so as to average the coupling constants of the protons at positions symmetrical to the short axis of the molecule. As Table 2 (model B) shows, the calculation predicts well the qualitative change in the effect of the cation upon going from the ion pair with a sodium or potassium ion to that with a lithium ion. Although the changes in the proton-coupling constants calculated are rather large compared to the observed ones, considering the nature of the calculation the results of the calculation are rather satisfactory. Therefore, one may conclude that the most likely structure of the naphthalene-sodium or -potassium ion pair in dioxane is that in which the equilibrium position of the alkali ion is situated above the center of the molecular plane of the naphthalene radical anion, while in the case of the ion pair with a lithium ion in dioxane the equilibrium position of the lithium ion may be rather above the benzene ring and the lithium ion may migrate between the two equilibrium positions.

In the case of the naphthalene-potassium system in dioxane, no potassium hyperfine splitting was observed. However, in view of the fact that the proton-coupling constants are affected by the potassium ion in a way similar to the case of the sodium ion, an ion pair must be formed. The lack of a splitting from the potassium ion is probably due to the small magnetogyric ratio of ^{39}K.

Recently, Smid *et al.*[5] reported that the naphthalene sodium metal ion pair in dioxane must be a contact ion pair. Our conclusion regarding the ion pair with a lithium ion may suggest that the naphthalene-lithium metal ion pair is also a contact ion pair in dioxane.

The numerical calculations were carried out on the NEAC 2230 at the Computer Center, Tohoku University.

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[5] T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.,* **88**, 307 (1966).