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Solvent Induced Structural Change of 18-Crown-6 Complexed Ion Pair with 9-Fluorenone Anion Radical as Studied by ESR Spectroscopy

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ESR spectra of the ion pairs of the 9-fluorenone anion radical with 18-crown-6 complexed sodium and potassium ions were examined. From the dependence of the carbonyl ^{13}C hyperfine splitting of the fluorenone anion on temperature and solvent, it was conclude that an ethereal solvent molecule can solvate the crown complexed cation on the opposite side of the anion with respect to the plane of the crown ether ring, equilibrium taking place between the solvated and unsolvated ion pairs in ethereal solution. The unsolvated species of both the potassium and the sodium ion pairs and the solvated species of the sodium ion pair are classified as contact ion pairs, the solvated species of the potassium ion pair a crown separated one. The equilibrium constant between the solvated and unsolvated ion pairs changes with temperature and solvent. From this change the enthalpy changes of solvation process were estimated for several solvents.

Recently interest has been focused on the high complexing ability of macrocyclic polyethers (crown ethers) with respect to the alkali metal ions. Since crown ethers form two dimensional complexes with cations in most cases, a counteranion and other donor molecules are capable of interacting with the cation on either or both sides of the plane of the crown ether ring, as demonstrated by X-ray crystallographic studies of a number of crown complexed inorganic salts.[1,2] This behavior of the complexes will be observed in solution.

Crown complexes alkali metal ions exist as ion pairs in ethereal solvents.[3–6] In these ion pairs it is possible that ethereal molecules can participate in coordination of the cation, since ethereal molecules are very strong cation-complexing agents[7] and one side of the two dimensional crown complex is occupied by a counteranion but the other is vacant. If this is the case, the structure of the ion pair in ethereal solvents would differ to some extent from those in solvents incapable of participating in coordination.

This paper deals with the solvation phenomena of the crown complexed ion pairs, on the basis of ESR studies of the 9-fluorenone anion radical forming an ion pair with 18-crown-6 complexed sodium and potassium ions. The carbonyl ^{13}C hyperfine splitting of the fluorenone anion is sensitive to environmental conditions, reflecting the structural changes of the ion pairs caused by cation solvation.

Experimental

Solvents. Ethereal solvents and toluene were used after being dried with sodium hydride or Na–K alloy.

Material. 15-Crown-5 and 18-crown-6 ethers (M. E. Merck) were used without further purification.

Preparation of the Anion Radical. The anion was prepared by reduction of 9-fluorenone with sodium or potassium mirror in a solution containing excess crown ether. All the operations were carried out in a high vacuum.

Measurements of ESR Spectra. A JES-PE ESR spectrometer, equipped with a magnet of a 10 in diameter pole piece and with a JES-VT-3A2 variable temperature controller was used.

Results and Discussion

Solvent Effect on the 18-Crown-6 Complexed Ion Pair. The carbonyl ^{13}C hyperfine splitting (a_C) of the fluorenone anion radical forming the ion pair with 18-crown-6 (C-6) complexed sodium ion shows an appreciable solvent dependence, ranging from 4.21 G in tetrahydrofuran (THF) to 5.00 G in toluene, diethyl ether and diisopropyl ether (Table 1). Since ethereal solvents solvate anions weakly and cations strongly, it is reasonable to assume that the solvent effect can be attributed to the difference of solvent in cation solvating power. It has been found that a_C increase with increasing cationic field acting on the carbonyl group,[8–10] the cationic field decreasing with increase in the separation between the cation and the anion. The observed decrease of a_C from toluene to THF certainly arises from the increase in the cation-anion separation caused by enhancement of cation solvation. Thus, the solvent order of decreasing a_C corresponds to that of increasing cation solvation. The solvent order of cation solvation (Table 1) differs somewhat from that observed in most cases. Polydentate solvents such as 1,2-dimethoxyethane and diglyme usually show stronger cation solvation than monodentate solvents such as THF and tetrahydropyran.[11,12] In the present system, however, the order is reversed. This suggests that the polydentate

TABLE 1. SOLVENT DATA ON ^{13}C hfs (a_c) AND RATIO OF SOLVATED TO UNSOLVATED SPECIES (K) FOR SODIUM ION PAIR AT 20 °C

Solvent	a_c(G)	K
Tetrahydrofuran	4.21	2.93
Tetrahydropyran	4.48	0.96
2-Methyltetrahydrofuran	4.51	0.86
Dioxane	4.58	0.66
1,2-Dimethoxyethane	4.58	0.66
Diglyme	4.59	0.63
1,2-Diethoxyethane	4.78	0.26
2,5-Dimethyltetrahydrofuran	4.85	0.16
Diisopropyl ether	5.00	0
Diethyl ether	5.00	0
Toluene	5.00	0

character of solvent does not work effectively, probably because most part of the coordination sphere around the cation is already occupied by the carbonyl and 18-crown-6 oxygen atoms, and the residual part can not allow more than one oxygen atom of solvent to coordinate the cation. This also indicates that only one solvent molecule can solvate the crown complexed cation forming the ion pair.

Since it is unreasonable to assume any specific interaction between an alkali metal ion and a toluene molecule, the crown complexed ion pair in toluene would exist in unsolvated state. The fact that a_C in diethyl ether and diisopropyl ether is identical with a_C in toluene indicate that these solvents can not solvate the crown complexed cation in the present system.

Hyperfine splittings due to sodium were observed, irrespective of solvent. Addition of C-6 led to the increase of the sodium hyperfine splitting (a_{Na}) in a solvent, in contrast to the decrease of a_C (for example, in the THF solution, $a_{Na}=0.49$ G in the presence of C-6, while $a_{Na}=0.41$ G in the absence of C-6 at 20 °C).[13] Since the complex formation of a crown ether with a cation causes increase in the separation of the cation and the counteranion, the increase of a_{Na} observed suggests that factors other than the cation-anion separation play an important role for deciding the magnitude of a_{Na}.[10,13]

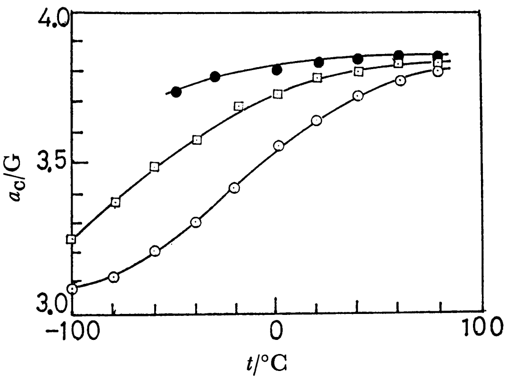

Fig. 1. Temperature dependence of the ^{13}C hfs in the fluorenone anion radical for potassium ion pair.
○: THF, □: MTHF, ●: DMTHF.

Temperature Dependence of a_C. The a_C values of both the potassium and the sodium ion pairs decrease with lowering in temperature, the magnitude of decrease varying with solvent. In a solvent with stronger cation solvation power a_C shows a larger temperature dependence. The change of a_C with temperature is significant in THF, but almost independent of temperature in diethyl ether. Figure 1 shows temperature *vs.* a_C curves of the C-6 complexed potassium ion pair in THF, 2-methyltetrahydrofuran (MTHF), and 2,5-dimethyltetrahydrofuran (DMTHF) in the temperature range -100 °C—$+80$ °C. At high temperature a_C of these three solutions approach each other, converging to the value nearly equal to a_C in diethyl ether ($a_C=3.90$ G); at low temperatures a_C in THF shows a value of lower limit ($a_C=3.05$ G). Similar features can be observed in the temperature *vs.* a_C curves of the C-6 complexed sodium ion pair (Fig. 2).

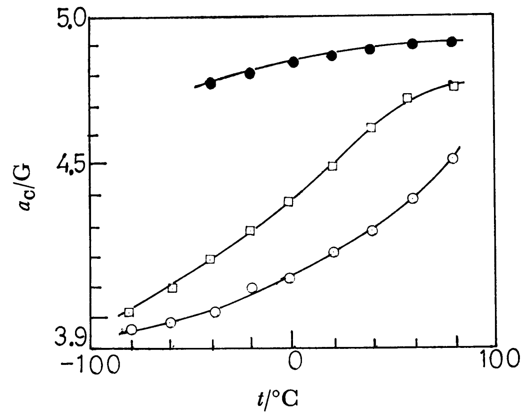

Fig. 2. Temperature dependence of the ^{13}C hfs in the fluorenone anion radical for sodium ion pair.
○: THF, □: MTHF, ●: DMTHF.

The temperature and solvent dependence of a_C could be explained in terms of the equilibrium between the solvent and unsolvated species of the C-6 complexed ion pair:

$$\mathrm{A^-M^+C + S \rightleftarrows \underset{C}{A^-M^+S}}, \tag{1}$$

where $\mathrm{A^-}$ is the fluorenone anion, $\mathrm{M^+}$ an alkali metal ion, C a crown ether molecule, and S a solvent molecule. We always observe the average a_C of the solvated and unsolvated species, since the exchange rate between the both species is high in the ESR time scale. Since the solvation process is exothermic, the observed a_C approaches a_C of the unsolvated species at high temperature and a_C of the solvated species at low temperature. The equilibrium constant of Eq. 1 can be expressed by

$$K = (a_u - a_m)/(a_m - a_s), \tag{2}$$

where a_u and a_s are a_C of the unsolvated and solvated species respectively, and a_m is the observed splitting. a_u would be equal to a_C in toluene or diethyl ether, and a_s to or slightly smaller than the limiting value of a_C in THF at low temperatures. Therefore, substituting 5.00 G for a_u and 3.94 G for a_s in the sodium ion pair, and 3.90 G for a_u and 3.05 G for a_s in the potassium ion pair, we are able to calculate the equilibrium constant K of Eq. 1 by means of Eq. 2. The values of K at 20 °C for each solvent used are given in Table 1. The enthalpy change of the solvation process expressed by Eq. 1 can be estimated from the plots of ln K *vs.* $1/T$ for THF, MTHF, and DMTHF solutions of the sodium and potassium ion pairs (Table 2). The plots show that linearity holds between ln K and $1/T$ (Figs. 3 and 4).

A Possible Model. Possible models for solvation

Table 2. Enthalpy change (ΔH) of solvation process for sodium and potassium ion pairs

Solvent	ΔH (10^3 cal/mol)	
	Sodium	Potassium
Tetrahydrofuran	-3.4	-3.8
2-Methyltetrahydrofuran	-3.2	-2.6
2,5-Dimethyltetrahydrofuran	-1.4	-1.8

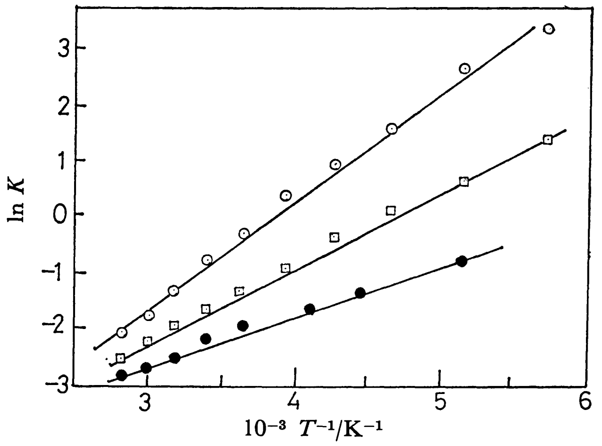

Fig. 3. Plots of ln K *vs.* $1/T$ for the potassium ion pair. The straight lines are obtained by the least squares method. ○: THF, □: MTHF, ●:DMTHF.

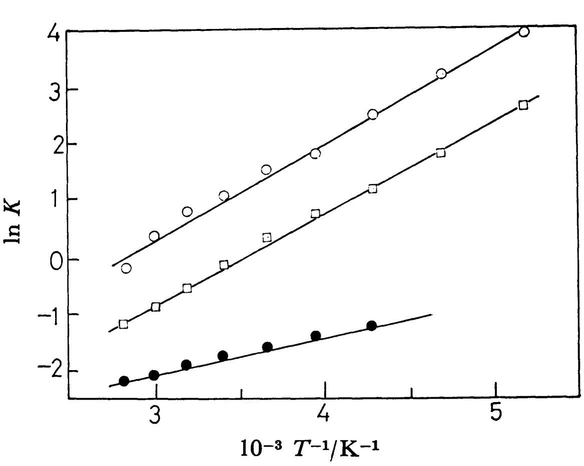

Fig. 4. Plots of ln K *vs.* $1/T$ for the sodium ion pair. The straight lines are obtained by the least squares method. ○: THF, □: MTHF, ●: DMTHF.

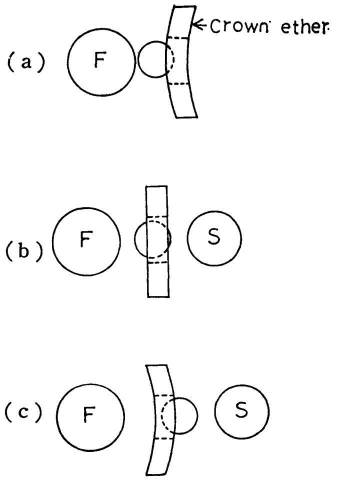

Fig. 5. Schematic representation for solvation process. Ⓕ: Fluorenone anion. Ⓢ: Solvent molecule. ○: Alkali metal cation.

process of the crown complexed cation are schematically shown in Fig. 5. In the unsolvated ion pairs the cation is pulled out of the plane of the crown oxygen atoms toward the fluorenone anion (Fig. 5 (a)). When a solvent molecule solvates the cation on the opposite side of the anion with respect to the plane of the crown ether ring, the location of the cation shifts toward the center of the ring plane (Fig. 5 (b)), the cation being located on the other side of the anion with respect to the crown ether (Fig. 5 (c)). For both cases of solvation, a conformational change of the crown ether molecule would take place and the separation between the anion and the cation would increase due to steric hinderance of the crown ether. When the ion pairs are classified in terms of a contact and crown-separated ion pair, the species for Fig. 5 (a) and (b) should be referred to a contact ion pair, and the species for Fig. 5 (c) to a crown-separated one. Since the lower limit of a_{C} for the crown complexed sodium ion in THF ($a_{\mathrm{C}}=3.94$ G) is close to the uncomplexed caesium ion pair in THF at 20 °C ($a_{\mathrm{C}}=3.90$ G),[13] the solvated sodium ion pair can be classified as a contact ion pair and would have the structure of Fig. 5 (b). On the other hand, the lower limit of a_{C} for the crown complexed potassium ion pair in THF ($a_{\mathrm{C}}=3.05$ G) is considerably small as compared with a_{C} of any uncomplexed contact ion pair observed so far, and even smaller than a_{C} of the free anion in dimethyl sulfoxide ($a_{\mathrm{C}}=3.20$ G). The a_{C} value of the free anion is dependent on the anion solvation power of solvent. a_{C} of the free anion in THF is estimated to be 1.34 G, using the relation between Gutmann's acceptor number and a_{C} obtained previously.[14] The potassium ion pair complexed by both a crown ether and solvent molecule would have a structure such as Fig. 5 (c) classified as a crown-separated ion pair. The model, in which the anion and a solvent molecule are located on each side of the plane of the crown ether ring, is supported by the result of ESR studies on the 15-crown-5 complexed potassium ion pair, a_{C} of the 15-crown-5 complexed ion pair ($a_{\mathrm{C}}=3.92$ G) being almost independent of solvent and temperature. This is probably due to the fact that, since the size of a potassium ion is too large to fit the cavity of 15-crown-5 ether, the solvent molecule can not solvate the crown complexed cation in such a manner as shown in Figs. 5 (b) and (c).[15]

The present conclusion is also supported by X-ray structures for dibenzo-18-crown-6 complexed NaNCS and $NaBr2H_2O$.[1,2] In the former the sodium ion is pulled out of the plane of the crown ether oxygen atoms toward the anion by 0.05 nm, while in the latter the sodium ion is sandwiched by a bromide ion and a water molecule and pulled out of the plane toward the bromide ion only by 0.027 nm.

The difference in a_{C} between the unsolvated and solvated species of the sodium ion pair is greater than that in a_{C} between the sodium ion pair ($a_{\mathrm{C}}=4.85$ G) and caesium ion pair ($a_{\mathrm{C}}=3.90$ G) in THF in the absence of C-6. This indicates that the increase of the cation-anion separation caused by the solvation of one ethereal molecule is of the same order of magnitude as the difference in ionic radius between a caesium ion and a sodium ion amounting to 0.07 nm. The reason why the interaction of one ethereal molecule with the sodium ion can induce such a large change in the separation might be considered as follows. On the basis of measurement of the electric dipole moment of the ion pair of *p*-toluenesulfonate with a dibenzo-18-crown-6 complexed potassium ion in octanoic acid, Ting-Po I and Grunwald[16) estimated the relative stabilities of several models for the ion pairs, ignoring the solvation energy of the cation, and shown that although the contact ion pair such as shown in Fig. 5 (a) is the most stable, the energy difference between models including crown-separated ion pairs are only few kilocalories per mole. The difference in energy is comparable to the solvation energy of a cation by one ethereal molecule. If the situation is similar to the present system, the solvation of the cation by one solvent molecule would be capable of inducing the observed structural changes of the ion pairs.

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