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Solvatochromic Shift of Aromatic Ketyl Anions due to Hydrogen Bonding

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The electronic spectra of fluorenone radical anions generated by γ-irradiation at 77 K in glassy matrices of ethanol and ethanol–2-methyltetrahydrofuran mixtures have been measured for elucidating the mechanism of the spectral change due to solvation of the radical anions by alcohols. Three kinds of the radical anions are generated in the mixed solvent: the radical anions without hydrogen bond ($\varepsilon = 1.05\times10^4$ dm^3 mol^{-1} cm^{-1} at λ_{max}=568 nm), with one ethanol molecule ($\varepsilon = 0.67\times10^4$ dm^3 mol^{-1} cm^{-1} at λ_{max}=529 nm) and two ethanol molecules ($\varepsilon = 0.37\times10^4$ dm^3 mol^{-1} cm^{-1} at λ_{max}=448 nm) hydrogen-bonded through the π electron on the carbonyl oxygen. The spectral shift and the decrease of the molar extinction coefficient of aromatic ketyl radical anions are explained as due to the stabilization of a carbonyl antibonding π orbital by hydrogen bonding.

One of the powerful methods for studying solvation dynamics is the pulse radiolysis technique. In this method solute molecules are first generated by irradiation of a solution with a pulsed ionizing radiation, and the spectral change of the solute due to solvation are detected using a fast optical detection system.[1) However the technique is not always suitable for studying the solvation structure, because the spectral resolution of the detection system is not necessarily high enough for discriminating the solutes with different solvation structures.

The solvation dynamics of benzophenone radical anions in alcohols have been extensively studied by using the pulse radiolysis technique,[2–6) since solvation of the radical anions entails exceptionally large spectral shift. In these studies the spectral shift was attributed to electrostatic effects induced by the reorientation of solvent dipoles. On the other hand, Shida et al. attributed the spectral shift to hydrogen bonding between the anion radical and alcohol. They measured absorption spectra of benzophenone radical anions in γ-irradiated matrices at 77 K, and found the absorption maximum at 630 nm in ethanol matrix but at 800 nm in aprotic matrices.[7,8) Hoshino et al. measured transient absorption spectra of several aromatic ketyl radical anions in alcohols and found a gradual blue shift of the absorption maxima except for the fluorenone radical anion.[9) They claimed that the spectral shift was not due to hydrogen bonding but to reorientation of solvent dipoles. They considered that the neutral aromatic ketones had already been hydrogen-bonded to alcohols.[10) However, it was suggested later that the hydrogen bond could be formed through the out-of-plane π electron of the radical anion.[11,12) We recently studied in detail the solvation of benzophenone radical anion in γ-irradiated ethanol–2-methyltetrahydrofuran mixtures at cryogenic temperatures and concluded that the spectral shift is due to hydrogen bonding between the radical anion and ethanol.[13) The out-of-plane π electron localized mainly on the carbonyl oxygen is invoked for the bond. The preexisting in-plane hydrogen bond between the neutral aromatic ketone and alcohol is considered not to affect the absorption spectrum due to π–π transitions.

Although the molecular structure of fluorenone is similar to that of benzophenone, Hoshino et al. failed to detect the spectral shift of the former radical anion by solvation. On the other hand, Shida et al. observed the solvent dependency of the absorption spectrum and proposed that the hydrogen bonding with one and two alcohol molecules is responsible for the apparently complex spectra of the fluorenone radical anion in alcoholic matrices.[11,12,14)

In the present study the electronic spectra of the fluorenone radical anion in γ-irradiated ethanol–2-methyltetrahydrofuran mixtures have been measured at 77 K to elucidate the nature of the solvation process. A molecular orbital explanation is given for the spectra change of aromatic ketyl radical anions due to the formation of hydrogen bond.

Experimental

Ethanol (Wako Pure Chemical Co.; >99.5%) was used without further purification. 2-Methyltetrahydrofuran (MTHF) was used after purification with usual procedures.[3) The volume fractions of ethanol in the ethanol–MTHF mixture were 0, 0.25, 0.5, and 1 at 293 K. The solutions containing 0.04 mol dm^{-3} of fluorenone were degassed by several freeze-pump-thaw cycles and then sealed in high-purity quartz cells with an optical path length of 0.2 cm. The samples were then immersed in liquid nitrogen to produce crack-free glass matrices.

The samples were irradiated at 77 K with ^{60}Co γ-rays to a dose of 2.2 kGy to generate the fluorenone radical anion by the following reactions,

$$S \rightsquigarrow S^+ + e^-,\quad e^- + Fl \longrightarrow Fl^-,$$

where S and Fl denote the solvent and fluorenone molecules, respectively. The absorption spectra were measured at 77 K on a Shimadzu MPS-5000 spectrophotometer equipped with a cryostat for optical measurements. The concentration of the radical anion was calculated from the absorbed dose using the yields of 2.35 and 2.55 scavengeable electrons per 100 eV absorbed by ethanol and MTHF, respectively.[8) The yield for the mixed matrices was assumed to be proportional to the composition of the solvent molecules.

Results

Figure 1 shows the absorption spectra of fluorenone radical anion in neat MTHF, neat ethanol, and in the equivolume mixture of MTHF and ethanol. The radical anion in neat MTHF showed an absorption maximum at 568 nm with the molar extinction coefficient of 1.05×10^4 dm^3 mol^{-1} cm^{-1}. In neat ethanol, the absorption maximum was shifted to 448 nm. The hatched part of the spectrum in Fig. 1 is due to the neutral fluorenone ketyl radical generated by proton transfer to the radical anion.[8,14] The yield of the ketyl radical was estimated to be 16% of the electron yield. After the correction for the conversion into the neutral radical, the extinction coefficient of the radical anion in ethanol was determined to be 0.37×10^4 dm^3 mol^{-1} cm^{-1}. The radical anion in the mixed matrix showed a new peak in addition to the peaks corresponding to those in neat MTHF and ethanol. The appearance of the three peaks clearly indicates that the radical anion exists in three forms, i.e., without and with one and two ethanol molecules hydrogen-bonded to the radical anion.

The absorption spectrum of the radical anion with one hydrogen-bonded ethanol molecule was obtained by substracting the spectra for neat MTHF and ethanol from the spectrum for the mixed matrix. The absorption of the overlapping neutral ketyl radical was corrected by assuming that the ratio of the radical against the radical anion with two hydrogen-bonded ethanols is independent of the composition of the mixed solvent. Fig. 2 shows the normalized spectra of the three components, $I_0(\lambda)$, $I_1(\lambda)$, and $I_2(\lambda)$, corresponding to the fluorenone radical anion with zero, one, and two

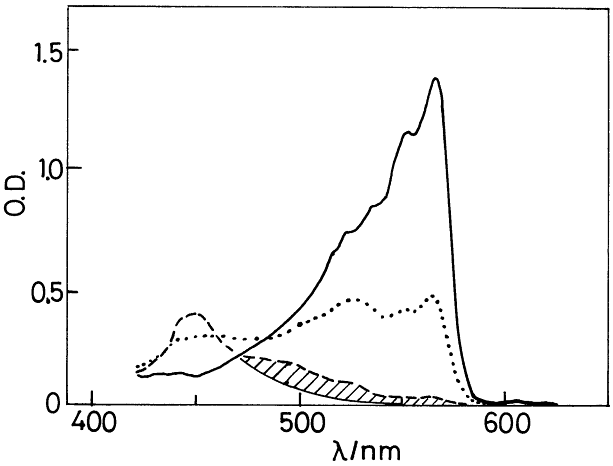

Fig. 1. Absorption spectra of fluorenone radical anions in glassy matrices of (—) neat MTHF, (---) neat ethanol, and (···) 1:1 mixture of MTHF and ethanol.

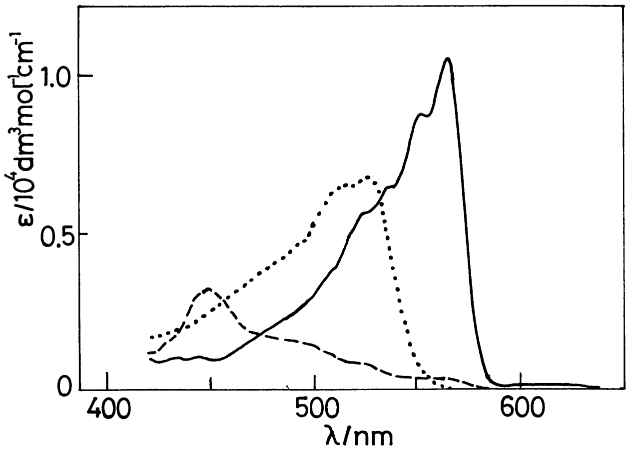

Fig. 2. Spectral components of the absorption spectra of fluorenone radical anions in ethanol–MTHF mixed matrices.

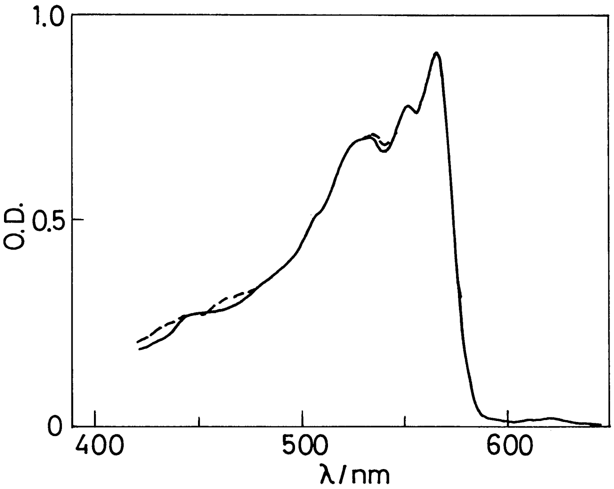

Fig. 3. Comparison of the (—) observed and (---) calculated spectra of fluorenone radical anions in 25% ethanol matrix.

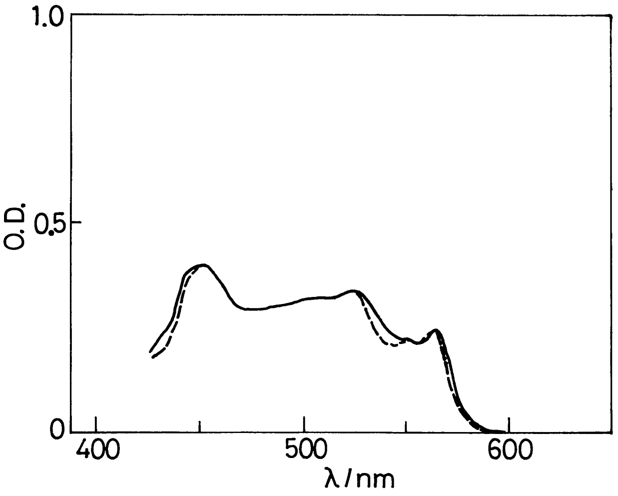

Fig. 4. Comparison of the (—) observed and (---) calculated spectra of fluorenone radical anions in 75% ethanol matrix.

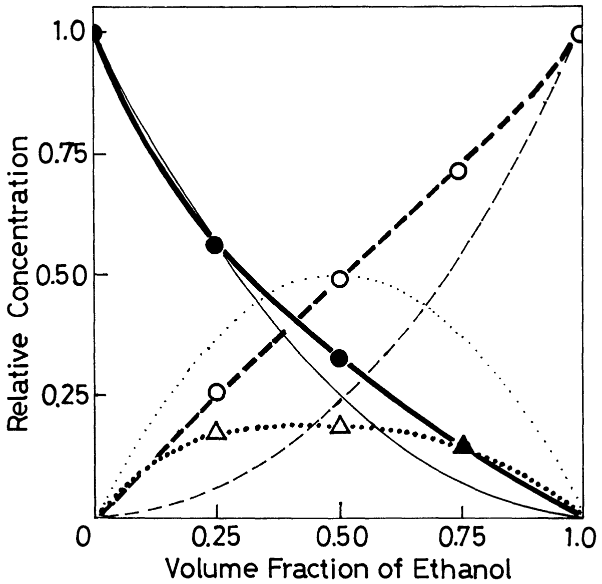

Fig. 5. Dependence of ethanol concentration on the relative concentration of three types of fluorenone radical anions in ethanol–MTHF mixed matrix: the radical anion (●, —) without ethanol, (△, ···) with one, and (○, ---) two hydrogen-bonded ethanol molecules. Thinner curves show the relative concentrations calculated under the assumption of random spatial distribution of ethanol (see Eq. 2 in the text).

hydrogen-bonded ethanol molecules, respectively. The absorption spectrum, $S(\lambda)$, for the mixed matrix of volume fraction x of ethanol is expressed as a sum of the three spectral components,

$$S(\lambda)=[W_0(x)I_0(\lambda)+W_1(x)I_1(\lambda)+W_2(x)I_2(\lambda)]C(x), \qquad (1)$$

where $W_i(x)$ is the mole fraction of the three types of the radical anion with respect to the total radical anions, and $C(x)$ is the yield of the scavengeable electrons. Figs. 3 and 4 compare the observed and calculated spectra for the mixed matrices of x=0.25 and 0.75, respectively. The value of $W_i(x)$ was determined by best-fitting the calculated spectrum with the observed one. The fair agreement of the spectra indicates that only three types of the radical anion exist in the mixed matrices. The mole fractions determined from the observed spectra are shown in Fig. 5.

Discussion

Since the observed absorption spectra of the fluorenone radical anion in the mixed matrices of ethanol and MTHF can be reconstructed from the three components, the solvation process for the fluorenone radical anion is considered to be essentially the same as that for benzophenone and other aromatic ketyl radical anions; the radical anion is viewed as hydrogen-bonded with one and two ethanol molecules through the out-of-plane π electron on the carbonyl oxygen.

If there is no specific interaction between the neutral fluorenone and ethanol, and if the ethanol molecules are randomly distributed around fluorenone, the probability that a fluorenone radical anion finds an ethanol molecule at the site for hydrogen bonding is given by x. The probability of the hydrogen bond formation is then given by

$$W_0(x)=(1-x)^2,\ W_1(x)=2x(1-x),\ W_2(x)=x^2. \qquad (2)$$

The shapes of $W_i(x)$ in Eq. 2 are also shown with thinner curves in Fig. 5. Although $W_0(x)$ is close to the observed curve, $W_1(x)$ is much higher while $W_2(x)$ is lower than the observed $W_i(x)$. This suggests that a considerable part of the radical anion with one hydrogen-bonded ethanol molecule is converted into the radical anion with two hydrogen-bonded ethanol molecules. A candidate for the second hydrogen bond might be an in-plane ethanol molecule which has been hydrogen-bonded to neutral fluorenone.

Now the reason why Hoshino et al. failed to detect the spectral shift of the fluorenone radical anion is clear. The absorption of the radical anion with one hydrogen-bonded alcohol molecule is very weak due to the first conversion of the radical anion into that with two hydrogen-bonded alcohol molecules. The absorption of the latter radical anion is also weak due to the small extinction coefficient. The low spectral resolution in their pulse radiolysis study allowed them to detect only the wavelength-independent decrease of the absorption band of the radical anion without hydrogen bond.

The characteristic features of the spectral change of aromatic ketone radical anions due to formation of the new hydrogen bond are the blue shift and the decrease in the molar extinction coefficients. These features can be qualitatively understood by a simple molecular orbital consideration. Shida et al. made molecular orbital calculations on the radical anions of aromatic ketones and found that the excess charge is located mainly on the carbonyl group in the ground state and on the aromatic group in the excited states.[8] They also assigned the visible absorption bands to intramolecular charge transfer bands. The ground and the excited states of the radical anion are therefore given by a linear combination of two structures; one is ψ_a with an excess negative charge on the carbonyl group (carbonyl antibonding π orbital) and the energy E_a, and the other is ψ_b with a negative charge on the benzene rings and the energy E_b. Neglecting the overlap integral between ψ_b and ψ_b, the transition energy $h\nu$ and the transition moment μ_{EG} for the charge transfer band are approximately given by

$$h\nu \simeq (E_b-E_a)[1+4H_{ab}^2/(E_b-E_a)^2]^{1/2}, \qquad (3)$$

$$\mu_{EG} \simeq -H_{ab}(\mu_{aa}-\mu_{bb})/h\nu-[(E_b-E_a)/h\nu]\mu_{ab}, \qquad (4)$$

where H_{ab} is the resonance integral between ψ_a and ψ_b, and μ_{jk} is a transition or an electric moment. The absolute value of μ_{ab} is much smaller than that of $\mu_{aa}-\mu_{bb}$. The value of (E_b-E_a) is close to $h\nu$. Therefore, the transition moment, square root of the transition probability, linearly decreases with increasing transition wavelength. The decrease in the transition probability arises from the decrease in the mixing of the ψ_a and ψ_b states due to the incease in the energy gap, E_b-E_a.

Due to the negative charge on the carbonyl oxygen, the radical anion in the ground state easily forms a hydrogen bond, which stabilizes the ψ_a and hence the ground states. Since the contribution of the ψ_a state is very low in the excited state, the excited state is not stabilized by hydrogen-bonding. The formation of the hydrogen bond therefore causes a blue shift of the absorption spectrum and the decrease in the transition probability. Since the transition probability is proportional to the product of the transition wavelength and the molar extinction coefficient, formation of the hydrogen bond also causes a decrease in the extinction coefficient. Figure 6 shows the relation between the wavelength at the absorption maximum, λ_{max}, and the extinction coefficient at λ_{max} for the fluorenone and the benzophenone radical anions. The extinction coefficient decreases with decreasing λ_{max}, which supports the validity of the above consideration. The extinction coefficient would increase with decreasing λ_{max}, if the transition probability were not decreased by formation of the hydrogen bond.

Provided the energy of the excited state is scarcely influenced by the formation of the hydrogen bond, the stabilization energy by hydrogen bonding is approximately the same as the energy of the spectral shift. The values of the stabilization energy are -0.22 and -0.20 eV for the first and the second hydrogen bonding to the benzophenone radical anion, respectively. For the fluorenone radical anion, the values are -0.16 and -0.42 eV, respectively. The large stabilization energy of -0.42 eV suggests that the formation of the second hydrogen bond is accelerated by the first hydrogen bond. The relative concentration of the fluorenone radical anion with one hydrogen-bonded ethanol is thus lower than the statistical one.

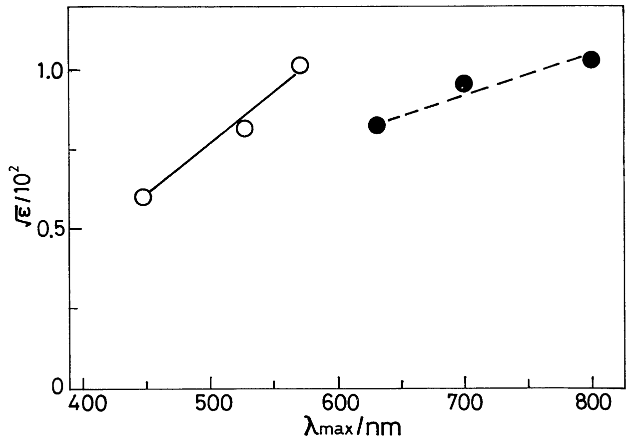

Fig. 6. Plot of the square root of molar extinction coefficients of (○) fluorenone and (●) benzophenone radical anions versus the wavelength at absorption maxima.

Very recently Murai et al. made a pulse radiolysis study on the spectral shift of benzophenone and fluorenone radical anions in MTHF due to ionic association with sodium cations.[15] They found stepwise shifts of the absorption spectra: 800 nm→720 nm→630 nm for the benzophenone radical anion and 570 nm→530 nm→450 nm for the fluorenone radical anion. The spectral shift is quite similar to that due to hydrogen bonding. They attributed the spectral shift to stepwise association of the ions: free ketyl anions→ketyl anion-sodium cation ion pairs→higher ion aggregates (dimer of the ion pair or the ketyl anion coordinating two sodium cations). The fair agreement of the absorption spectra between the higher ion aggregates and the radical anions with two hydrogen-bonded ethanol molecules strongly suggests that the higher ion aggregate corresponds to the radical anion coordinating two sodium cations instead of two alcohol molecules. The reaction rate for the formation of the higher ion aggregate was approximately the same as that for the ion pair formation, which also suggests that the higher ion aggregate corresponds to the ketyl anion coordinating two sodium cations. The reaction would be much slower if the aggregate were formed by a second-order reaction with the ion pairs. Luckhurst and Orgel measured ESR spectra of chemically-prepared fluorenone radical anions in the mixed solvent of *N,N*-dimethylformamide and methanol or ethanol.[16] They attributed the spectral shift by the alcohols to the formation of hydrogen bond between the fluorenone radical anion and the alcohol molecule. The ESR spectrum of the radical anion in pure alcohol was very similar to the spectrum of the radical anion coordinating a divalent metal cation,[17] this suggests that the electronic structure of the aromatic ketyl radical anion with two hydrogen-bonded alcohol molecules is very similar to that coordinating two monovalent cations or one divalent cation.

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References

1) M. A. Lewis and C. D. Jonah, *J. Phys. Chem.*, **90**, 5378 (1986), and the references therein.

2) M. Hoshino, S. Arai, and M. Imamura, *J. Phys. Chem.*, **78**, 1473 (1974).

3) M. Ogasawara, H. Yoshida, S. Karolczak, Cz. Stadovski, and J. Kroh, *Red. Phys. Chem.*, **23**, 711 (1984).

4) R. K. Huddleston and J. R. Miller, *Radiat. Phys. Chem.*, **17**, 383 (1981).

5) J. L. Marignier and B. Hickel, *Chem. Phys. Lett.*, **86**, 95 (1982).

6) J. L. Marignier and B. Hickel, *J. Phys. Chem.*, **88**, 5375 (1984).

7) T. Shida and W. J. Hamill, *J. Am. Chem. Soc.,* **88**, 3683 (1966).

8) T. Shida, S. Iwata, and M. Imamura, *J. Phys. Chem.,* **78**, 741 (1974).

9) M. Hoshino, S. Arai, M. Imamura, and A. Namiki, *Chem. Phys. Lett.,* **26**, 82 (1974).

10) R. S. Becker, *J. Mol. Spectrosc.,* **3**, 1 (1959).

11) T. Shida and H. Kubodera, Symposium on Molecular Structures, Tokyo, 1979, Abstr., p. 364.

12) T. Shida and H. Kubodera, VIth International Symposium on Solute–Solvent Interactions, Osaka, 1982, Abstr., p. 185.

13) T. Ichikawa, Y. Ishikawa, and H. Yoshida, *J. Phys. Chem.,* **92**, 508 (1988).

14) T. Shida, "Electronic Absorption Spectra of Radical Ions," Physical Science Data, Elsvier, Amsterdam (1988), Vol. 34, p. 15, 299.

15) H. Murai, K. Kotani, M. Ogasawara, and H. Yoshida, *Nippon Kagaku Kaishi,* **1989**, 1319.

16) G. R. Luckhurst and L. E. Orgel, *Mol. Phys.,* **8**, 117 (1964).

17) N. Hirota "Radical Ions," ed by E. T. Kaiser and L. Kevan, Interscience Publishers, New York (1968), p. 43.