Reorganization Energy Induced by Noncovalent Bonding Interaction in Electron Transfer Reactions

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A simple model is proposed to calculate a component of the electron-transfer reorganization energy derived from the reversible process of noncovalnt bond formation/dissociation between the reactant and hydrogen bonding donor or ligand. In the model, the reorganization of the formation/dissociation of the noncovalent-bonded complex is estimated by considering the chemical equilibrium change during the electron-transfer reaction. The effects of the hydrogen bonding and the ligand binding on the reorganization energies are calculated for the one-electron reduction processes of quinones, flavin, and the hem-fragment of cytochrome *c* based on the formation/dissociation constants of the noncovalent-bonded complexes in the liquid phase.

Introduction

Noncovalent interactions such as hydrogen bonding and ligand binding play a crucial role in determining the structures and functions of biological electron transfer (ET) systems. Thus, the effects of the noncovalent bonding on the ET reactions have been widely investigated in order to understand the ET mechanism and to determine the factors for the efficient energy conversion.[1−17] So far, it has been suggested that noncovalent bonding regulates the ET parameters of the electronic coupling matrix element (V) and the reaction free energy ($-\Delta G$), fixing the ET cofactors to their appropriate positions in the biological systems. Although the reorganization energy (λ) is also a fundamental parameter of the ET reactions,[18,19] there has been only a few studies on the reorganization process of ET through the specific interaction of noncovalent bonding.[20−22]

Recently, we have developed a novel method to investigate the λ for photoinduced ET systems using time-resolved EPR (TREPR) spectroscopy in polar solvents.[21,23,24] In our previous papers, the λ values for the charge recombination reactions were determined with the good accuracy from the observation of the chemically induced dynamic electron polarization (CIDEP)[25] generated in nanometer-separated radical ion pairs (RIPs). It was found that the solvent reorganization energies are larger by ca. 0.2 eV than the predictions of the Marcus continuum dielectric model[18] when the RIP systems involve the hydrogen-bonded complexes formed by the electron acceptor of quinone and alcohols.[21]

In this letter, we propose a simple model to calculate the component of λ derived from the reversible process of noncovalent bond formation/dissociation between the ET cofactor and the hydrogen bonding donor or ligand molecule. Considering the chemical equilibrium change during the ET reactions, the effects of the hydrogen bonding and ligand binding on the λ are calculated from the formation/dissociation constants of the noncovalent-bonded complexes in solutions.

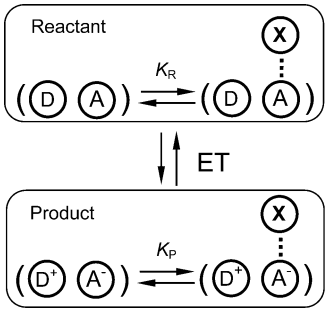

Figure 1. Schematic representation of the electron donor−acceptor (D−A) systems involving the noncovalent-bonded complex formed by A and the hydrogen bonding donor or ligand molecule (X).

Model

An example of the electron donor−acceptor (D−A) systems involving the noncovalent-bonded complexes is shown in Figure 1. Here the structures of the complexes in which A and A^- form the noncovalent bonding with the hydrogen bonding donor or ligand (X) are the same in the reactant and product states. The chemical equilibria between the nocovalent-bonded and free A are represented by the equilibrium constants of K_R and K_P in the reactant and the product states, respectively, as follows:[12−15]

$$A + mX \overset{K_R}{\rightleftharpoons} A - X_m \qquad K_R = \frac{[A - X_m]}{[A][X]^m} \tag{1}$$

$$A^- + mX \overset{K_P}{\rightleftharpoons} A^- - X_m \qquad K_P = \frac{[A^- - X_m]}{[A^-][X]^m} \tag{2}$$

The m term is the number of X attached to A and A^-. We can rewrite the equilibrium constants as follows:

$$K'_R = K_R[X]^m, \quad K'_P = K_P[X]^m \tag{3}$$

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TABLE 1: Maximum Values of the Reorganization Energies (λ_{CEC}) Due To the Formation/Dissociation of the Noncovalent-Bonded Complexes Calculated from Equation 5 in One-Electron Reduction Processes of Quinones, Flavin, and Heme-Fragment of Cytochrome *c* with the Hydrogen Bonding Donor or Ligand

system (oxidized species/hydrogen bonding donor or ligand)	equilibrium constants: oxidized	equilibrium constants: reduced	λ_{CEC}/eV	[X]/M[a]
1,4-benzoquinone/methanol in acetonitrile[b]	0.75/M^{-2}	25/M^{-2}	0.06	4.8×10^{-1}
1,4-benzoquinone anion/methanol in acetonitrile[b,c]	25/M^{-2}	1.77×10^4/M^{-2}	0.16	3.9×10^{-2}
9,10-phenantrenequinone/1,3-diphenylurea in dimethylformamide[d]	1/M^{-1}	905/M^{-1}	0.16	3.3×10^{-2}
10-isobutylflavin/diaminopyridine derivative in dichloromethane[e]	537/M^{-1}	2.5×10^5/M^{-1}	0.14	8.6×10^{-5}
Fe (III) AcMP8/*N*-acetylmethionine in water[f]	0.38/M	2.4×10^{-3}/M	0.11	3.0×10^{-2}
Ru (III) $(NH_3)_5$/*N*-acetylmethionine in water[g]	63/M	$\leq 1 \times 10^{-5}$/M	0.40	2.5×10^{-2}

[a] Concentration of hydrogen bonding donor or ligand that gives the maximum λ_{CEC} value. [b] Reference 12. [c] The effect of the 1:4 hydrogen-bonded complex of BQ with MeOH is omitted. [d] Reference 13. [e] Reference 14. [f] Reference 30. AcMP8 = *N*-terminal acetylated microperoxidase-8. [g] Reference 31.

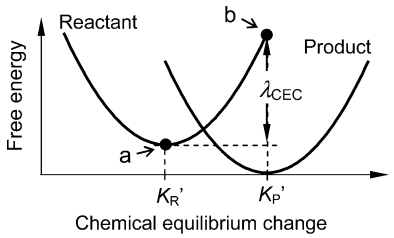

Figure 2. Schematic representation of the energy surfaces for the reactant and product states versus the reaction coordinate of the chemical equilibrium change. The energy difference between states a and b corresponds to the reorganization energy (λ_{CEC}) due to the chemical equilibrium change.

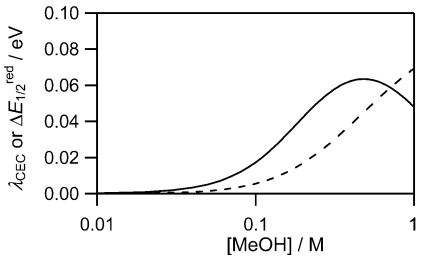

Figure 3. MeOH concentration dependences of λ_{CEC} (solid line) and $\Delta E_{1/2}^{red}$ (dashed line) calculated from eq 6 and the Nernst equation, respectively, with the formation constants of the hydrogen-bonded complexes of BQ in the neutral state ($K_R = 0.75\ M^{-2}$) and in the anion state ($K_P = 25\ M^{-2}$).

The dynamics of the formation/dissociation of the noncovalent bonding are assumed to be sufficiently fast to contribute to the reorganization of ET.[26] In the case that K_R' is different from K_P', the chemical equilibrium changes during the ET reaction.

Figure 2 is a schematic representation of the energy surfaces for the reactant and the product states versus the reaction coordinate of the chemical equilibrium change. We assumed that the energy surfaces are parabolic with respect to the coordinate of the chemical equilibrium change. K_R' determines the equilibrium reaction coordinate of the reactant state, whereas K_P' determines that of the product state. The difference in the chemical equilibria between the reactant and product states makes the reactant state nonequilibrium at the equilibrium reaction coordinate of the product state, resulting in a reorganization energy (λ_{CEC}) as shown in Figure 2. In the ET reaction systems accompanying the chemical equilibrium change, therefore, the outer-sphere reorganization energy of λ_O consists of λ_{CEC} and the reorganization (λ_{CDM}) due to the macroscopic dielectric relaxation represented with the continuum dielectric model

$$\lambda_O = \lambda_{CEC} + \lambda_{CDM} \tag{4}$$

To obtain the λ_{CEC} values, a change (dG) in the Gibbs energy on the reactant energy surface is calculated along the coordinate of the chemical equilibrium change. In the nonequilibrium state of b in Figure 2 where dn of A turns into A$-$X$_m$ from the equilibrium state of a, dG at a constant pressure and temperature is given by[27]

$$dG_{a\rightarrow b} = \lambda_{CEC} = (\mu_A - \mu_{A-X})\, dn \tag{5}$$

where μ_A and μ_{A-X} are the chemical potentials of A and A$-$X$_m$, respectively. The term ($\mu_A - \mu_{A-X}$) is expressed by K_R' and K_P' at the equilibrium reaction coordinate of the product state (see the Supporting Information). λ_{CEC} is thus represented by K_R' and K_P' as follows:

$$\lambda_{CEC} = \left\{ RT \ln\left(\frac{K_P'}{K_R'}\right)\right\} dn$$

$$dn = \frac{K_P'}{1+K_P'} - \frac{K_R'}{1+K_R'} \tag{6}$$

Similar results are also obtained in the product state.

Results and Discussion

First, we consider the ET system involving 1,4-benzoquinone (BQ) as the electron acceptor and methanol (MeOH) as the hydrogen bonding donor. Uno et al. reported the formation constants for the hydrogen-bonded complexes of BQ with MeOH from cyclic voltammetry and UV absorption measurements in acetonitrile.[12] Figure 3 shows the MeOH concentration dependence of the λ_{CEC} for a one-electron reduction process of BQ calculated from eq 6 with the formation constants of the hydrogen-bonded complexes for the anion and the neutral states of BQ reported at 298 K.[12] The shift ($\Delta E_{1/2}^{red}$) in the reduction potential of BQ due to the formation of the hydrogen-bonded complex is also calculated from the Nernst equation[12-15,28] and depicted in Figure 3 by the dashed line. The $\Delta E_{1/2}^{red}$ monotonically increases with the increasing MeOH concentration. On the other hand, the λ_{CEC} has a maximum value in the presence of 0.48 M MeOH. When the MeOH concentration is higher than 0.48 M, the mol-fraction of the neutral BQ$-$(MeOH)$_2$ complex is increased with the increasing MeOH concentration whereas that of the BQ anion $-$MeOH complex remains constant because almost all of the BQ anions have already formed the hydrogen-bonded complexes in the presence of 0.48 M MeOH. As a result, the change in the chemical equilibrium decreases with the increase in the MeOH concentration under

the condition of [MeOH] > 0.48 M. The MeOH concentration dependence of the λ_{CEC} is different from that of the $\Delta E^{red}_{1/2}$, although both λ_{CEC} and $\Delta E^{red}_{1/2}$ depend on the formation constants of the quinone−alcohol hydrogen bonding complexes.[29]

In the one-electron reduction processes of quinones and flavin, the hydrogen bonding donor concentration dependences of λ_{CEC} are also calculated from eq 6 based on the formation constants of the hydrogen-bonded complexes.[12−14] As listed in Table 1, our model gives 0.06∼0.16 eV for the maximum λ values depending on the formation constants of the hydrogen-bonded complexes in polar solvents. The concentrations of the hydrogen bonding donors that give the maximum λ_{CEC} values also depend on the formation constants of the complexes. The calculated results are in acceptable agreement with the experimental λ values determined in the ET systems involving the duroquinone−alcohols hydrogen-bonded complexes by the TREPR measurements.[21]

The ligand binding, as well as the hydrogen bonding, is ubiquitous to biological ET systems.[1−4] Tezcan et al. investigated the effects of ligation on the one-electron reduction processes of the heme-fragments of cytochrome *c* (cyt *c*) using *N*-acetylmethionine as the ligand in water.[30] Because of the difference in the ligand dissociation constants between the oxidized and reduced forms of the heme-fragments of cyt *c*, the chemical equilibria are expected to change during the ET reactions. The maximum λ_{CEC} values are calculated to be 0.1∼0.4 eV in the one-electron reduction processes of the heme-fragments with the same procedure as was calculated in the hydrogen-bonded systems (Table 1).

In conclusion, the present model successfully gives the explanation for the large λ values observed by the TREPR method in the ET systems involving the hydrogen bonding. Our model offers a new insight into the biological ET mechanism and a clue to design the ET reaction systems such as catalytic ET reaction systems with the noncovalent bonding interaction.

Supporting Information Available: Derivation of eq 7 from eq 6. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Deisenhofer, J., Norris, J. R., Eds.; *The Photosynthetic Reaction Center*; Academic Press: San Diego, CA, 1993; Vols. 1−2.

(2) Hoff, A. J.; Deisenhofer, J. *Phys. Rep.* **1997**, *287*, 1−247.

(3) Möbious, K. *Chem. Soc. Rev.* **2000**, *29*, 129−139.

(4) Gray, H. B.; Winkler, J. R. *Annu. Rev. Biochem.* **1996**, *65*, 537−561.

(5) Levanon, H.; Möbious, K. *Annu. Rev. Biophys. Biomol. Struct.* **1997**, *26*, 495−540.

(6) De Rege, P. J. F.; Williams, S. A.; Therien, M. J. *Science* **1995**, *269*, 1409−1413.

(7) (a) Asano-Someda, M.; Levanon, H.; Sessler, J. L.; Wang, R. *Mol. Phys.* **1998**, *95*, 935−942. (b) Berg, A.; Zohar, S.; Asano-Someda, M.; Levanon, H.; Fuhs, M.; Möbious, K., Wang, R.; Brown, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 7433−7434.

(8) (a) Sessler, J. L.; Brown, C. T.; O'Connor, D.; Springs, S. L.; Wang, R.; Sathiosatham, M.; Hirose, T. *J. Org. Chem.* **1998**, *63*, 7370−7374. (b) Sessler, J. L.; Sathiosatham, M.; Brown, C. T.; Rhodes, T. A.; Wiederrecht, G. *J. Am. Chem. Soc.* **2001**, *123*, 3655−3660.

(9) Williamson, D. A.; Bowler, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 10902−10911.

(10) (a) Klenifeld, D.; Okamura, M. Y.; Feher, G. *Biochim. Biophys. Acta* **1984**, *766*, 126−140. (b) Labahn, A.; Paddock, M. L.; McPherson, P. H.; Okamura, M. Y.; Feher, G. *J. Phys. Chem.* **1994**, *98*, 3417−3423. (c) Labahn, A.; Bruce, J. M.; Okamura, M. Y.; Feher, G. *Chem. Phys.* **1995**, *197*, 355−366. (d) Paddock, M. L.; Feher, G.; Okamura, M. Y. *Biochemistry* **1997**, *36*, 14328−14249.

(11) (a) Haller, B. A.; Holten, D.; Kirmaier, C. *Science* **1995**, *269*, 940−945. (b) Kirmaier, K.; Weems, D.; Holten, D. *Biochemistry* **1999**, *38*, 11516−11530. (c) Kirmaier, K.; He, C.; Holten, D. *Biochemistry* **2001**, *40*, 12132−12139. (d) Kirmaier, K.; Cua, A.; He, C.; Holten, D.; Bocian, D. F. *J. Phys. Chem. B* **2002**, *106*, 495−503.

(12) Uno, B.; Okumura, N.; Goto, M.; Kano, K., *J. Org. Chem.* **2000**, *65*, 1448−1455.

(13) (a) Ge, Y.; Lilienthal, R. R.; Smith, D. K. *J. Am. Chem. Soc.* **1996**, *118*, 3976−3977. (b) Ge, Y.; Miller, L.; Ouimet, T.; Smith, D. K. *J. Org. Chem.* **2000**, *65*, 8831−8838.

(14) (a) Breinlinger, E.; Niemz, A.; Rotello, V. M. *J. Am. Chem. Soc.* **1995**, *117*, 5379−5380. (b) Niemz, A.; Rotello, V. M. *Acc. Chem. Res.* **1999**, *32*, 44−52.

(15) Gupta, N.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 6384−6391.

(16) (a) Kawai, K.; Wata, Y.; Ichinose, N.; Majima, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 4327−4329. (b) Kawai. K.; Majima, T. *J. Photochem. Photobiol. C: Photochem. Rev.* **2002**, *3*, 53−66. (c) Kawai, K.; Wata, Y.; Hara, M.; Tojo, S.; Majima, T. *J. Am. Chem. Soc.* **2002**, *124*, 3586−3590.

(17) (a) Fukuzumi, S.; Yoshida, Y.; Okamoto, K.; Imahori, H.; Araki, Y.; Ito, O. *J. Am. Chem. Soc.* **2002**, *124*, 6794−6795. (b) Fukuzumi, S.; Okamoto, K.; Yoshida, Y.; Imahori, H.; Araki, Y.; Ito, O. *J. Am. Chem. Soc.* **2003**, *125*, 1007−1013.

(18) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966−978. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265−322.

(19) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401−449.

(20) (a) Kjaer, A. M.; Ulstrup, J. *J. Am. Chem. Soc.*, **1987**, *109*, 1934−1942. (b) Kjaer, A. M.; Ulstrup, J. *J. Am. Chem. Soc.*, **1988**, *110*, 3874−3879.

(21) Yago, T.; Kobori, Y.; Akiyama, K.; Tero-Kubota, S. *Chem. Phys. Lett.* **2003**, *369*, 49−54.

(22) Okamoto, K.; Imahori, H.; Fukuzumi, S. *J. Am. Chem. Soc.* **2003**, *125*, 7014−7021.

(23) (a) Kobori, Y.; Akiyama, K.; Tero-Kubota, S. *J. Chem. Phys.* **2000**, *113*, 465−468. (b) Kobori, Y.; Yago, T.; Tero-Kubota, S. *Appl. Magn. Reson.* **2003**, *23*, 269−287.

(24) (a) Kobori, Y.; Yago, T.; Akiyama, K.; Tero-Kubota, S. *J. Am. Chem. Soc.* **2001**, *123*, 9722−9723. (b) Yago, T.; Kobori, Y.; Akiyama, K.; Tero-Kubota, S. *J. Phys. Chem. B* **2002**, *106*, 10074−10081.

(25) Muss, L. T., Atkins, P. W., McLauchlan, K. A., Pederson, J. B., Eds.; *Chemically induced magnetic polarization*; Reidel: Dordrecht, The Netherlands, 1977.

(26) This assumption is appropriate when the concentrations of X are high. When the concentrations of X are low, the diffusion motion dominates the formation rates of the noncovalent-bonded complexes. The formation of the noncovalent-bonded complexes after the ET event may not contribute to the reorganization of ET.

(27) Atkins, P. W. *Physical Chemistry*, 3rd ed.; Oxford University Press: Oxford, 1986; Chapter 8, pp 160−191.

(28) Meites, L. *Polarographic Techniques*, 2nd ed.; John Wiley & Sons: New York, 1965; Chapter 5, pp 267−301.

(29) The decreases in the λ with the addition of X were recently observed in the intramolecular ET systems in which X of the metal ions strongly bound to the electron acceptor of naphthoquinone, see ref 22.

(30) Tezcan, F. A.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1998**, *120*, 13383−13388.

(31) Kuehen, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689−702