Aspects of the Electron Transfer Reaction Rate for Systems Accompanying a Chemical Equilibrium Change

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In photoinduced electron-transfer systems accompanying chemical equilibrium changes, such as the formation/dissociation of a noncovalent-bonded complex, the calculation method of the charge separation and recombination reaction rates have been derived based on a simple model, in which the formation/dissociation of noncovalent bonding during the electron-transfer reaction is treated as a change of the chemical equilibrium. The effects of the formation/dissociation of noncovalent bonding on the driving forces and the reorganization energies were calculated using the chemical equilibrium constants for the reactant and product states. It has been demonstrated that the formation/dissociation of noncovalent bonding affects the electron-transfer reaction rates not only by stabilizing the charge-separated state, but also by increasing the reorganization energy.

The electron transfer (ET) reaction is one of the most fundamental chemical reactions, and has been extensively studied over the past five decades.[1–15] Particular attention has been focused on biological ET systems, such as photosynthetic reaction centers where efficient energy conversion and transfer are achieved.[15–20] Noncovalent bonding interactions are ubiquitous to biological ET systems, and play an important role to control the ET reaction rates. The non-adiabatic ET reaction rate ($k_{\rm et}$) depends on the electronic coupling matrix element (V), the driving force ($-\Delta G$), and the reorganization energy (λ) as follows:[11–15]

$$k_{\rm et} = \sqrt{\frac{\pi}{\eta^2 \lambda k_{\rm B} T}} V^2 \exp\left\{-\frac{(-\Delta G - \lambda)^2}{4\lambda k_{\rm B} T}\right\}. \tag{1}$$

The effects of noncovalent bonding interactions on the ET parameters of V and $-\Delta G$ have been widely investigated so far.[21–46] For example, optical studies suggested that the V mediated by hydrogen bonding could be larger than that mediated by covalent bonding.[21–26] Electrochemical studies have shown that noncovalent bonding interactions stabilize the charge-separated states, and thus affect the $-\Delta G$ of ET.[39,41] However, it is difficult to estimate the effects of noncovalent bonding on the λ for individual electron donor (D)–acceptor (A) systems, since λ corresponds to the energy for a non-equilibrium state. The Marcus continuum dielectric model has been utilized to evaluate the experimental ET reaction rates.

By using time-resolved electron paramagnetic resonance (TREPR) spectroscopy, we have developed a novel method to determine λ for nanometer-separated radical ion pairs (RIPs) produced by photoinduced intermolecular ET reactions in polar solvents.[47–51] In nonprotic polar solvents, the solvent reorganization energies ($\lambda_{\rm S}$) determined from the TREPR spectroscopy are consistent with the $\lambda_{\rm S}$ values calculated by the continuum dielectric model at the nanometer D–A separation. In the presence of alcohols, on the other hand, the experimental $\lambda_{\rm S}$ values are larger by 0.2 eV than the calculated $\lambda_{\rm S}$ due to the formation of hydrogen-bonded complexes consisting of electron acceptors of quinone and alcohols. Recently, Okamoto et al. also observed large λ values in intramolecular ET reaction systems in which the metal ions strongly bound to the electron acceptor of quinone through noncovalent bonding.[52–54] In previous papers, we proposed that the change in the chemical equilibrium for the noncovalent-bonded complex contributes to the reorganization of ET, and induces a new component of $\lambda_{\rm S}$ in hydrogen-bonding systems.[51,55]

In this work, we calculate the rates of photoinduced ET reactions for systems involving a conformation change, such as the formation/dissociation of noncovalent-bonded complexes. The effects of the formation/dissociation of noncovalent bonding on $-\Delta G$ and λ are taken into account in terms of chemical equilibrium changes during ET reactions. It is revealed that the effects of chemical equilibrium changes induce an increase in λ as well as stabilization of the charge separated state, leading to changes in the ET reaction rates.

Results and Discussion

The photoinduced ET reaction system accompanying chemical equilibrium changes is depicted in Fig. 1. The charge-separation (CS) reaction occurs from a photoexcited state of the reactant. From the product of the charge-separated state, a charge recombination (CR) reaction occurs. Here, the terms of $-\Delta G_{\rm CS}$ and $-\Delta G_{\rm CR}$ indicate the driving forces for the CS and CR processes, respectively. R and P denote the reactant and product, and subscripts of 1 and 2 represent the conformations, respectively. In the reactant state, the compositions of R_1 and R_2 are dependent on the chemical equilibrium constant of $K_{\rm R}$, while those in the product state are dependent on the constant of $K_{\rm P}$:

Published on the web November 11, 2004; DOI 10.1246/bcsj.77.1997

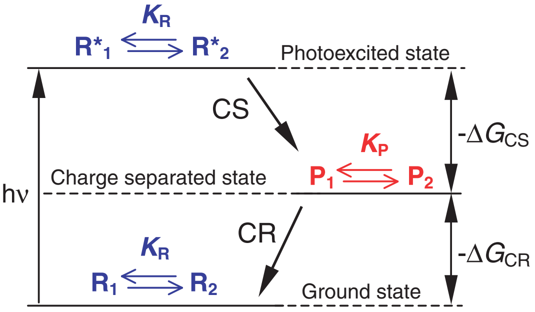

Fig. 1. Reaction scheme for the photoinduced ET reaction accompanying the chemical equilibrium change. R and P denote the reactant and product, respectively and the subscripts of 1 and 2 represent the configurations.

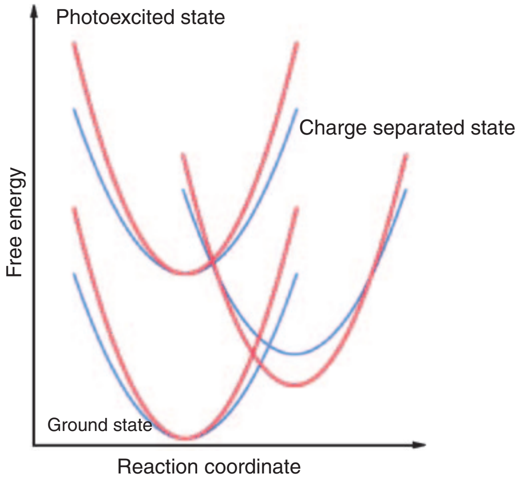

Fig. 2. The free energy surfaces for the ground, photoexcited and charge separated states plotted against the reaction coordinate. The light-blue lines and red lines indicate the energy surfaces in the absence of and presence of the chemical equilibrium changes, respectively.

$$R_1 \overset{K_R}{\rightleftarrows} R_2 \quad K_R = \frac{[R_2]}{[R_1]}, \tag{2}$$

$$P_1 \overset{K_P}{\rightleftarrows} P_2 \quad K_P = \frac{[P_2]}{[P_1]}. \tag{3}$$

Several studies have suggested that the equilibrium constants for the photoexcited states are small, as well as those for the ground state in the liquid phase.[45,54,56] In Fig. 1, for simplicity, the chemical equilibrium for the photoexcited state is assumed to be the same as that for the ground state. When K_R is different from K_P, the chemical equilibrium changes during the CS and CR reactions. It is assumed that the equilibrium states are quickly achieved in the present system.

Figure 2 shows a schematic representation of the energy surfaces for the ground, photoexcited and charge separated states plotted against the reaction coordinate. The red lines denote the energy surfaces in the presence of chemical equilibrium changes, and the light-blue lines indicate the energy surfaces in the absence of chemical equilibrium changes. The charge-separated state is stabilized by the effect of the chemical equilibrium changes, resulting in an increase in $-\Delta G_{CS}$ and a decrease in $-\Delta G_{CR}$. On the other hand, the effects of the chemical equilibrium changes increase λ in both the CS and CR processes.[51,55,56]

The effects of the chemical equilibrium changes on the rates (k_{CS}, k_{CR}) in the CS and CR reactions were calculated using Eq. 1. In the calculations, the following values were used for $-\Delta G^\circ_{CS}$, $-\Delta G^\circ_{CR}$, and the total reorganization energy of λ° in the absence of the effects of the chemical equilibrium changes: $-\Delta G^\circ_{CS} = 1.0$ eV, $-\Delta G^\circ_{CR} = 1.0$ eV, and $\lambda^\circ = 1.5$ eV. These values put the CS and CR processes in the Marcus normal region ($-\Delta G_{CS} < \lambda$, $-\Delta G_{CR} < \lambda$), even when the effects of the chemical equilibrium changes are taken into account. The effects of the chemical equilibrium changes on the driving forces ($-\Delta G^{CEC}_{CS}$, $-\Delta G^{CEC}_{CR}$) in the CS and CR processes are represented by the Nernst equation, respectively:[57]

$$-\Delta G^{CEC}_{CS} = RT \ln\left(\frac{1+K_P}{1+K_R}\right), \tag{4}$$

$$-\Delta G^{CEC}_{CR} = RT \ln\left(\frac{1+K_R}{1+K_P}\right) = -RT \ln\left(\frac{1+K_P}{1+K_R}\right). \tag{5}$$

Therefore, the driving forces including the effects of the chemical equilibrium changes are obtained by the following equations:

$$-\Delta G_{CS} = -\Delta G^\circ_{CS} - \Delta G^{CEC}_{CS}, \tag{6}$$

$$-\Delta G_{CR} = -\Delta G^\circ_{CR} - \Delta G^{CEC}_{CR}. \tag{7}$$

The effect of the chemical equilibrium changes on λ (λ^{CEC}) is expressed with the equilibrium constants, K_R and K_P, in the CS and CR processes:[55]

$$\lambda^{CEC} = \left\{RT \ln\left(\frac{K_P}{K_R}\right)\right\} \mathrm{d}n, \tag{8a}$$

$$\mathrm{d}n = \frac{K_P}{1+K_P} - \frac{K_R}{1+K_R}. \tag{8b}$$

The derivation of Eq. 8 is described in Appendix. The λ value is thus represented as

$$\lambda = \lambda^\circ + \lambda^{CEC}. \tag{9}$$

Figure 3 displays the K_P/K_R value dependences of $-\Delta G_{CS}$, $-\Delta G_{CR}$, and λ, calculated by Eqs. 4–9 with the parameters of $K_R = 0.1$, 1, and 10, respectively. The λ value is increased with increasing K_P/K_R, as shown in Fig. 3b. The $-\Delta G_{CS}$ values are also increased with increasing the K_P/K_P, while $-\Delta G_{CR}$ is decreased with increasing K_P/K_R due to stabilization of charge-separated state.

Figure 4 shows the K_P/K_R dependences of k_{CS} and k_{CR}, calculated by Eq. 1, with the parameters of $K_R = 0.1$, 1, and 10, respectively. For calculating ET reaction rates, the parameters of V and T in Eq. 1 were set at 1 cm^{-1} and 298 K, respectively, throughout in this study, assuming non-adiabatic long-range ET reactions. In the absence of chemical equilibrium changes, k_{CS} and k_{CR} were calculated to be 4.2×10^7 sec^{-1}. In the CS process, the increase in $-\Delta G_{CS}$ due to chemical equilibrium changes accelerates the CS reaction, whereas an increase in λ reduces the CS reactions in the normal region. In the case of $K_R = 0.1$ (red line in Fig. 4a), the magnitude of λ^{CEC} calculated from Eq. 8 is larger than that of $-\Delta G^{CEC}_{CS}$ obtained

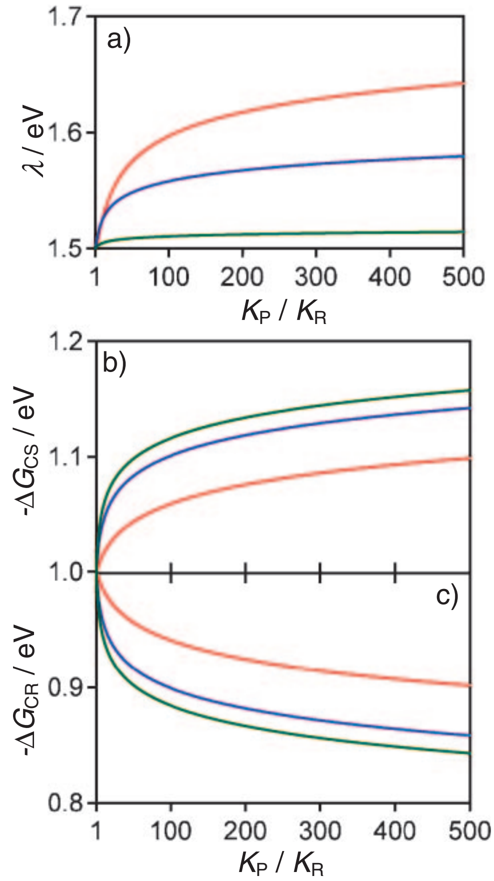

Fig. 3. K_P/K_R dependences of (a) reorganization energy (λ), (b) driving forces ($-\Delta G_{CS}$) for the charge separation, and (c) driving forces ($-\Delta G_{CR}$) for the charge recombination calculated by Eqs. 4–9 with the parameters of $K_R = 0.1$ (red), $K_R = 1.0$ (blue), and $K_R = 10$ (green), respectively.

by Eq. 4, leading to the reduction of k_{CS} with increasing K_P/K_R. On the contrary, when the parameter of $K_R = 1$ or $K_R = 10$ is used, k_{CS} is increased by the effect of the chemical equilibrium changes, since the magnitudes of λ^{CEC} are smaller than those of $-\Delta G_{CS}^{CEC}$.

In the CR process, the effect of the chemical equilibrium changes restrains the CR reaction by decreasing $-\Delta G_{CR}$ and increasing λ in the Marcus normal region, as depicted in Fig. 4b. Thus, it is expected that the lifetime of the charge-separated state becomes longer in the presence of the effects of the chemical equilibrium changes. The long-lived charge-separated states with the formation of noncovalent-bonded complexes, obtained by Okamoto et al., are consistent with the present result.[53,54]

In conclusion, based on the chemical equilibrium change model, we calculated the reaction rates for photoinduced ET systems accompanying a conformation change, which is induced by a specific interaction of the noncovalent bonding. It has been revealed that the chemical equilibrium changes modulate λ as well as the driving forces, leading to a change in the ET reaction rate. The results offer a key to understand the ET mechanisms in biological systems where noncovalent bonding interactions play important roles.

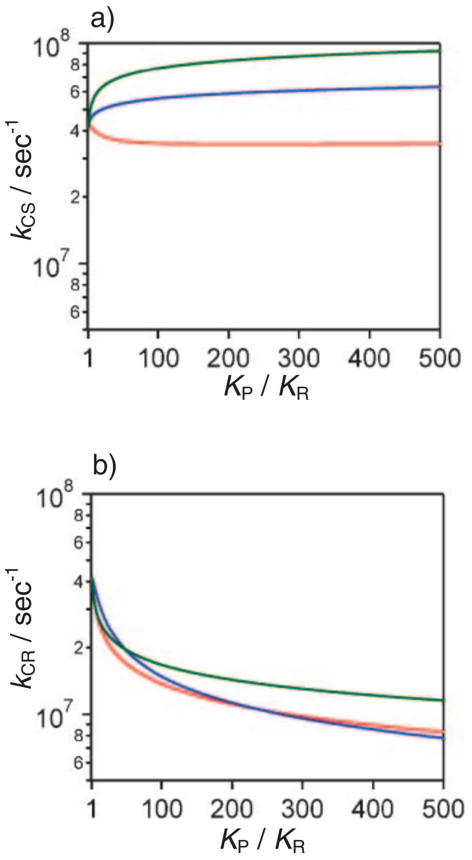

Fig. 4. K_P/K_R dependences of (a) charge separation reaction rate (k_{CS}) and (b) charge recombination reaction rate (k_{CR}) calculated by Eq. 1 with the parameters of $K_R = 0.1$ (red), $K_R = 1.0$ (blue), and $K_R = 10$ (green), respectively. $V = 1\ \mathrm{cm}^{-1}$, $T = 298$ K.

This research has been partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

Appendix

In order to obtain the λ^{CEC} values from the K_R and K_P values, the change in the Gibbs energy (dG) is considered in the reactant state along the reaction coordinate of the chemical equilibrium change. At the equilibrium reaction coordinate of the product sate, the reactant state is in the non-equilibrium state because of the difference in the chemical equilibria among the reactant and the product states. The energy for this non-equilibrium state corresponds to the reorganization energy of λ^{CEC}.[55,56] In the non-equilibrium state, where dn of R_1 turns into R_2 from the equilibrium state, dG at constant pressure and temperature is given by[58]

$$dG = \lambda^{CEC} = -\mu_1 dn + \mu_2 dn. \tag{A1}$$

Here μ_1 and μ_2 are the chemical potentials for P_1 and P_2, respectively, and are represented by

$$\mu_1 = \mu_1^\circ + RT \ln\left(\frac{[R_1]}{[R_1]+[R_2]}\right), \tag{A2}$$

$$\mu_2 = \mu_2^\circ + RT \ln\left(\frac{[R_2]}{[R_1]+[R_2]}\right), \tag{A3}$$

where μ_1° and μ_2° are the chemical potentials for the standard states of P_1 and P_2, respectively. The substitution of Eqs. A2 and A3 to Eq. A1 results in

$$\lambda^{\rm CEC} = \left\{\mu_2^\circ - \mu_1^\circ + RT\ln\left(\frac{[R_2]}{[R_1]}\right)\right\}{\rm d}n. \qquad ({\rm A4})$$

The term of $\mu_2^\circ - \mu_1^\circ$ can be obtained with K_R as

$$\mu_2^\circ - \mu_1^\circ = \Delta G^\circ = -RT\ln K_R, \qquad ({\rm A5})$$

where ΔG° is the change in the Gibbs energy when 1 mol of P_1 turns into P_2. In Eq. 8, the term $[R_1]/[R_2]$ in Eq. A4 is replaced by K_P.

Similar results were also obtained for the product state.

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