

Ethanol Concentration Dependence of Photoinduced Charge Separation Reaction between Zinc Tetraphenylporphyrin and Duroquinone Studied by Laser Flash Photolysis

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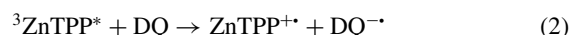
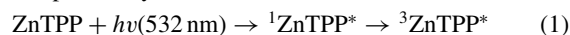
Ethanol concentration dependence of photoinduced charge separation between zinc tetraphenylporphyrin (ZnTPP) and duroquinone (DQ) in benzonitrile was studied by nanosecond laser flash photolysis. Acceleration of the photoinduced charge separation reaction rate by hydrogen bonding between DQ anion radical and ethanol was observed. A simple analysis in the framework of the Marcus theory indicated that the observed electron-transfer reaction rate was affected not only by the decrease of the reaction free energy but also an increase of the reorganization energy in the presence of hydrogen bonding.

Electron transfer (ET) is one of the most fundamental chemical reactions and has been studied extensively over the last six decades. Particular attention has been focused on biological ET systems where the reactions proceed with high efficiency.¹ Hydrogen-bonding interactions are ubiquitous to biological ET systems and have been believed to contribute to efficient ET reactions by stabilizing the charge-separated states. Actually, Fukuzumi et al. have reported the acceleration of charge separation (CS) reactions in the presence of hydrogen-bonding interactions.² According to the Marcus theory, the activation barrier for the ET reactions depends on reaction free energy (ΔG) and reorganization energy (λ).^{3,4} The stabilization of the charge-separated state by hydrogen bonding causes the modulation of the ΔG value for the CS and charge recombination reactions.^{5–11} Recent time-resolved electron paramagnetic resonance (EPR) studies on solvent-separated radical ion pairs generated by photoinduced CS reactions suggest that λ values are also increased by solute–solvent hydrogen-bonding interactions in polar solvents.¹² The results were interpreted with a change of chemical equilibrium for the hydrogen-bonding complex during the ET reactions;¹³ however, the ET reaction rates have not been evaluated directly. It is, therefore, desirable to evaluate ET reaction rates directly in the presence of hydrogen bonding to clarify their role.

In this contribution, we study ethanol concentration dependence of photoinduced CS between zinc tetraphenylporphyrin (ZnTPP) and duroquinone (DQ) in benzonitrile (PhCN) to clarify how the ET reaction rates are affected by the modulation of ΔG and λ in the presence of hydrogen bonding. For this purpose, nanosecond laser flash photolysis experiments were carried out with an apparatus that was essentially the same as an apparatus described elsewhere.¹⁴ The second harmonic (532 nm) of a Nd:YAG laser was used for the selective excitation of ZnTPP (1×10^{-4} M) in the sample solutions. The concentrations of DQ were 0.1–2 mM. To investigate the effect of hydrogen bonding on the CS reaction rates, ethanol (EtOH), which has been known to form hydrogen-bonding complexes with the DQ anion ($\text{DQ}^{\cdot-}$), was added to the sample solution. Since EtOH has a similar viscosity ($\eta = 1.08$ cP)¹⁵ and dielectric constant ($\epsilon =$

24.6)¹⁵ as PhCN ($\eta = 1.24$ cP, $\epsilon = 25.2$),¹⁵ the diffusion coefficients of solutes and macroscopic dielectric properties of solutions were unchanged under the experimental conditions. Therefore, the hydrogen-bonding effects on the CS reactions can be studied with the present photoinduced CS reaction system.

The previous time-resolved EPR study showed that the photoinduced CS reactions proceed between the photoexcited triplet state of ZnTPP and DQ in PhCN.¹⁶ In the PhCN solution, semiquinone radical of DQ is not produced even in the presence of EtOH.^{12b} We can, therefore, describe the photoinduced CS reactions in the present system as follows:



Here, ${}^1\text{ZnTPP}^*$, ${}^3\text{ZnTPP}^*$, and $\text{ZnTPP}^{+\cdot}$ represent the singlet and triplet excited states of ZnTPP, and ZnTPP cation radical, respectively.

Upon irradiation of PhCN solution containing ZnTPP and DQ, a strong T–T absorption band of ${}^3\text{ZnTPP}^*$ was observed around 470 nm.¹⁷ DQ concentration dependence on the time profile of the transient absorption ($A(t)$) was observed at 450 nm.¹⁸ In the presence of DQ, $A(t)$ curves had a fast decay component and an almost constant one. The fast component was assigned to the decay of the T–T absorption of ${}^3\text{ZnTPP}^*$, and the almost constant one can be assigned to the transient absorption of $\text{ZnTPP}^{+\cdot}$ and $\text{DQ}^{\cdot-}$ produced by the photoinduced CS reactions.^{19,20} The DQ concentration dependences of the decay rate constants (k) of ${}^3\text{ZnTPP}^*$ were observed at 450 nm in the presence of the various concentrations of EtOH.¹⁸ In each EtOH concentration, a good linear relationship was observed between k and DQ concentration. From the slopes of these plots, the second-order rate constants (k_q) for the CS reactions of ${}^3\text{ZnTPP}^*$ with DQ were determined. The determined k_q value for each EtOH concentration was smaller than the reaction rate constant for the diffusion-controlled reactions ($5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), indicating that the rate-determining step for CS is the ET and not the encounter process promoted by solute diffusion motions.

The results were analyzed with the classical Marcus equation combined with the diffusion rate constant (k_{dif}).²¹

$$k_{\text{CS}} = Z \exp \left\{ -\frac{(\Delta G + \lambda)^2}{4\lambda k_{\text{B}} T} \right\} \quad (3)$$

$$\frac{1}{k_q} = \frac{1}{k_{\text{dif}}} + \frac{1}{k_{\text{CS}}} \quad (4)$$

where k_{CS} is CS reaction rate constant, and Z is a pre-exponential factor. Figure 1 shows EtOH concentration dependence of k_{CS} determined for the ZnTPP–DQ system in PhCN with the parameters of $k_{\text{dif}} = 5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.²² The CS reaction was accelerated by the addition of EtOH. Since η for PhCN and EtOH are quite similar, the addition of EtOH to the sample solutions has little

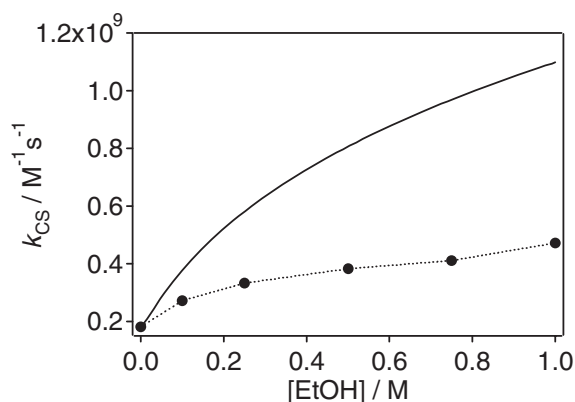


Figure 1. Ethanol concentration ([EtOH]) dependence of charge separation reaction rate constant (k_{CS}) obtained from nanosecond laser flash photolysis (filled circle). Solid line: [EtOH] dependence of k_{CS} calculated by eqs 3–5 with a constant λ value.

effect on the diffusion motion of the solute molecules. The possible parameters affected by the addition of EtOH are ΔG and λ . The formations of hydrogen bonding between quinone anions and protic solvents have been reported from the EPR study,²³ density functional calculation,²⁴ and electrochemical studies.^{5–11} In the presence of the hydrogen-bonding complex, ΔG for the CS reaction can be evaluated with the Nernst equation as follows:²⁵

$$\Delta G = \Delta G_0 - \frac{RT}{F} \ln(1 + K[\text{EtOH}]^n) \quad (5)$$

where ΔG_0 is reaction free energy in the absence of hydrogen bonding, K is the equilibrium constant for the formation of hydrogen-bonding complex consisting of $\text{DQ}^{\cdot-}$ and EtOH, and n is the number of EtOH molecules participating in the one hydrogen-bonding complex. We tried to reproduce the observed EtOH concentration dependence of k_{CS} by using eqs 3–5 with a constant λ value. The hydrogen-bonding effects on ΔG were estimated with the reported equilibrium constant ($K = 83 \text{ M}^{-1.3}$)⁹ for the hydrogen-bonding complex. The other parameters used were $Z = 5.8 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$,^{2a,26} $\lambda = 0.9 \text{ eV}$,²⁷ $\Delta G_0 = -0.04 \text{ eV}$,^{16,28} and $k_{\text{dif}} = 5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.²² The calculated result is indicated by the solid line in Figure 1. The calculation overestimates the effect of hydrogen bonding on k_{CS} . This conclusion is not dependent on the Z and λ values unless λ is smaller than 0.3 eV, which is unlikely for the present ET system.¹⁶ The CS process in the present ET system is in the Marcus normal region ($-\Delta G < \lambda$). The large discrepancy between the calculations and experimental results, therefore, suggests an increase of the λ value by the formation of hydrogen bonding. The increase of the λ value in the presence of 1 M of EtOH was roughly estimated to be 0.1 eV. Fukuzumi et al. reported a similar increase in λ with a decrease in ΔG due to the metal ion–quinone anion complex formation.²⁹ Further quantitative studies to clarify the origin of hydrogen-bonding effects on λ are now in progress.

In conclusion, we have investigated the EtOH concentration dependence of the photoinduced CS reaction between ZnTPP and DQ in PhCN. The CS reactions are accelerated by the effect of hydrogen bonding between $\text{DQ}^{\cdot-}$ and EtOH. The ET reaction modulated by hydrogen bonding induced λ was observed for the first time. The present simple ET system enables us to study the hydrogen-bonding effects on the CS reactions quantitatively.

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