Extremely Slow Long-Range Electron Transfer Reactions Across Zeolite−Solution Interface

Shunichi Fukuzumi,* Yutaka Yoshida, Tsutomu Urano, Tomoyoshi Suenobu, and Hiroshi Imahori

Department of Material and Life Science
Graduate School of Engineering
Osaka University, CREST
Japan Science and Technology Corporation (JST)
2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

Received March 3, 2001

Long-range electron transfer has been studied extensively in both synthetic and biological systems in relation to the central role in photosynthesis and metabolism.[1−8] It is now well-established that the electron transfer rate constant falls off approximately exponentially with increasing the distance between the donor and acceptor molecules, provided that the other parameters such as the driving force and reorganization energy of electron transfer remain the same.[9] Thus, the time scale of electron transfer is expected to increase from femtoseconds to hours and even to days with simply increasing the distance. However, such an extremely slow electron transfer is unprecedented because any other previous study on electron transfer reactions at fixed distances involves the excited state, and the inherent short excited-state lifetime has precluded the study on slow electron transfer processes. Photoexcitation is necessitated to start the electron transfer reactions between the donor and acceptor molecules in the linked systems, since it would be impossible to connect donor and acceptor molecules if the electron transfer occurred thermally. A slow thermal electron transfer would only be achieved if an electron donor or acceptor molecule is encapsulated in a large inert environment which prohibits the close access of the other molecule.

This study reports such a system that utilizes the Y-type zeolite supercage in which an electron acceptor is encapsulated. Encapsulation of chromophore ions in the supercage of zeolite has so far been utilized to retard the back electron transfer across the zeolite−solution interface in photoinduced charge-separation systems.[10−12] However, the electron transfer rates across the zeolite−solution interface have yet to be determined. Addition of an electron donor which cannot penetrate into the zeolite supercage to the acceptor-encapsulated zeolite can start the thermal electron transfer at long distances through the zeolite−solution interface. In the present system, an extremely slow electron transfer such that the completion of electron transfer takes days is observed, in sharp contrast to the corresponding electron transfer reaction in solution which is too fast to be followed even by using a stopped-flow technique. Such extremely slow electron-transfer processes across the zeolite−solution interface between electron donors in solution and electron acceptors inside the zeolite provide valuable insight into thermal electron transfer at long distances.

A metal complex, $\mathrm{Fe(bpy)_3}^{2+}$ (bpy = 2,2′-bipyridine) was loaded into the NaY zeolite by the ship-in-bottle synthesis (see Supporting Information, S1, S2), and the 12 Å dimension of $\mathrm{Fe(bpy)_3}^{2+}$ makes for a secure fit inside the 13 Å supercage. The loaded amount of $\mathrm{Fe(bpy)_3}^{2+}$ was determined from the absorption due to $\mathrm{Fe(bpy)_3}^{2+}$ as 5.4×10^{-5} mol g^{-1}, which corresponds to 1.1 molecules per 10 supercages. Once $\mathrm{Fe(bpy)_3}^{2+}$ is incorporated into the zeolite, no $\mathrm{Fe(bpy)_3}^{2+}$ comes out into solution. Thus, $\mathrm{Fe(bpy)_3}^{2+}$ is not placed on the zeolite surface but inside the supercage. The 12 Å dimension of $\mathrm{Fe(bpy)_3}^{2+}$ is too large to escape from the supercage which has the 7 Å width window. The $\mathrm{Fe(bpy)_3}^{2+}$−zeolite Y was oxidized by exposing the sample under chlorine (1 atm) for 5 min to yield the corresponding $\mathrm{Fe(bpy)_3}^{3+}$−zeolite Y. The completion of the oxidation was confirmed by the disappearance of the absorption at $\lambda_{\max} = 520$ nm due to $\mathrm{Fe(bpy)_3}^{2+}$.

Rates of electron transfer from various electron donors in solution to $\mathrm{Fe(bpy)_3}^{3+}$ inside the zeolite across the zeolite−solution interface were followed by monitoring an increase in absorbance at 520 nm due to $\mathrm{Fe(bpy)_3}^{2+}$. Addition of ferrocene to $\mathrm{Fe(bpy)_3}^{3+}$−zeolite Y suspended in MeCN results in a gradual increase in the absorption at 520 nm due to $\mathrm{Fe(bpy)_3}^{2+}$ (see Supporting Information, S3). The free energy change of electron transfer in MeCN is exergonic ($\Delta G^0{}_{\mathrm{ET}} = -0.69$ eV) judging from the higher one-electron reduction potential of $\mathrm{Fe(bpy)_3}^{3+}$ (1.06 V vs SCE)[13,14] than the one-electron oxidation potential of ferrocene (0.37 V vs SCE).[15] In such a case, the electron transfer occurs rapidly, and the rate of electron transfer from ferrocene to $\mathrm{Fe(bpy)_3}^{3+}$ in solution was in fact too fast to be followed even with use of a stopped-flow technique. In contrast, the observed electron transfer from ferrocene to $\mathrm{Fe(bpy)_3}^{3+}$−zeolite Y is extremely slow such that the completion of the electron transfer takes days. From the absorbance in a prolonged reaction time (24 h), the amount of $\mathrm{Fe(bpy)_3}^{3+}$ reduced was determined as 4.6×10^{-5} mol g^{-1} which corresponds to 85% yield based on $\mathrm{Fe(bpy)_3}^{2+}$ loaded in the zeolite.

Such an extremely slow electron transfer from ferrocene in solution to $\mathrm{Fe(bpy)_3}^{3+}$ inside the zeolite suggests the occurrence of a long-range electron transfer. The first-order plot of $\ln([\mathrm{Fe}^{2+}]_\infty - [\mathrm{Fe}^{2+}])/[\mathrm{Fe}^{3+}]_0$ versus time is not linear. It is common practice to fit such kinetic curves to a multiexponential expression. However, it seems impractical to consider too many multiexpo-

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10.1021/ja015751v CCC: $20.00

nential expressions. Albery et al.[16] has presented an alternative model, in which there is a Gaussian distribution of the activation free energy about some mean and which introduces only one additional parameter, that is, the width of the distribution (γ). The rate of electron transfer from an electron donor to $Fe(bpy)_3^{3+}$ inside zeolite should vary depending on the distance r between the electron donor adsorbed on the zeolite surface and $Fe(bpy)_3^{3+}$ placed in various places inside the zeolite. In such a case there should be a dispersion of r according to a normal Gaussian distribution, $\exp(-x^2)$, about some mean value (r_{av}): $r = r_{av} - \gamma x$. On the other hand, the rate constant k_{ET} of electron transfer may be given as a function of the distance r between an electron donor and an acceptor, $k_{ET} = C_0 \exp[-\beta(r - r_0)]$, where r_0 is the distance of the close contact separation between the electron donor and acceptor, C_0 is the rate constant at $r = r_0$, and β is a constant which is related to the magnitude of interaction between an electron donor and an acceptor. Integrating across the normal distribution, $\exp(-x^2)$, the time dependence of the term $([Fe^{2+}]_\infty - [Fe^{2+}])/[Fe^{3+}]_0$ is given by eq 1, which is essentially the same as that Albery et al. derived with dispersion of the activation free energy of reactions.[16] When $\gamma = 0$, there is no dispersion, and the system will behave in a classical homogeneous fashion. The experimental data can be well fitted to eq 1 by adjusting only two parameters, k_{ETav} which is the rate constant at $r = r_{av}$ and $\beta\gamma$ as shown by the solid line calculated based on eq 1 (see S4).

$$\frac{[Fe^{2+}]_\infty - [Fe^{2+}]}{[Fe^{3+}]_0} = \frac{\int_{-\infty}^{+\infty} \exp(-x^2) \exp[-k_{ETav} t \exp(\beta\gamma x)]\,dx}{\int_{-\infty}^{+\infty} \exp(-x^2)\,dx} \quad (1)$$

The dependence of k_{ETav} on the concentration of ferrocene was examined, and the k_{ETav} was constant even at very low concentrations of ferrocene. Such a constant dependence of k_{ETav} on the ferrocene concentration indicates that the actual concentration of ferrocene adsorbed on the zeolite surface is constant since the small concentration of ferrocene such as 2.0×10^{-4} M may be enough to cover the zeolite surface.[17]

The temperature dependence of k_{ETav} is also examined, and there was no activation energy observed for the electron transfer despite the extremely slow rates. The absence of activation energy is understandable, judging from the highly exothermic nature of the electron transfer (vide infra).

It is well established that the driving-force dependence on the ET rate constants (k_{ET}) is given by eq 2,

$$k_{ET} = [4\pi^3/(h^2\lambda k_B T)]^{1/2}\,|V|^2 \exp[-(\Delta G^0{}_{ET} + \lambda)^2/(4\lambda k_B T)] \quad (2)$$

where V is the electronic coupling matrix element and T is the absolute temperature.[9] When the reorganization energy $\lambda = -\Delta G^0{}_{ET}$, the activation enthalpy ($\Delta H^\ddagger$) becomes zero. Thus, the k_{ETav} value of $Fe(C_5H_5)_2$ may correspond to the maximum value in the driving-force dependence of the rate constant of electron transfer in eq 2.[18]

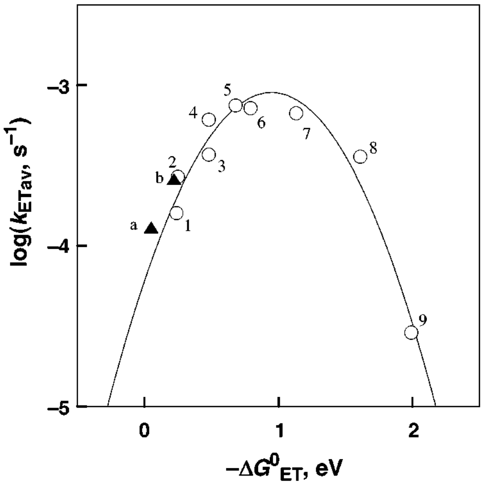

Figure 1. Dependence of averaged electron-transfer rate constants (k_{ETav}) on driving force ($-\Delta G^0{}_{ET}$) of electron transfer in deaerated acetonitrile at 298 K. (○) Electron transfer from electron donors to $Fe(bpy)_3^{3+}$−zeolite Y (1: $Fe(C_5H_4COCH_3)_2$, 2: 10-methyl-9,10-dihydroacridine, 3: $Fe(C_5H_5)(C_5H_4COCH_3)$, 4: 1-benzyl-1,4-dihydronicotinamide, 5: $Fe(C_5H_5)_2$, 6: $Fe(C_5H_4Me)_2$, 7: $Fe(C_5Me_5)_2$, 8: $Mn(C_5Me_5)_2$, 9: $Co(C_5H_5)_2$). (▲) Electron transfer from $Fe(bpy)_3^{2+}$−zeolite Y to electron acceptors (a: $Ru(Me_2bpy)_3^{3+}$, b: $Ru(bpy)_3^{3+}$).

To confirm the driving-force dependence of the electron-transfer rate constant (eq 2), the k_{ETav} values of a variety of electron donors are determined together with the one-electron oxidation potentials ($E^0{}_{ox}$)[15,19−22] of the electron donors and the free energy change of electron transfer ($\Delta G^0{}_{ET}$) (see S5). Electron donors are chosen such that the reorganization energies of electron transfer are similar to the value of $Fe(C_5H_5)_2^+/Fe(C_5H_5)_2$ (1.01 eV).[23] The unknown $E^0{}_{ox}$ values of electron donors were determined by using the cyclic voltammetry and the second harmonic ac voltammetry methods (see S2). A plot of log k_{ETav} versus $-\Delta G^0{}_{ET}$ in Figure 1 exhibits a parabolic dependence of k_{ETav} on $-\Delta G^0{}_{ET}$ as expected from eq 2. The k_{ETav} value decreases in order $Fe(C_5H_5)_2 > Fe(C_5Me_5)_2 > Mn(C_5Me_5)_2 > Co(C_5H_5)_2$ as the driving force, which is in the Marcus inverted region (Figure 1), increases.

Electron-transfer reactions of the reversed direction are also examined by using $Fe(bpy)_3^{2+}$−zeolite Y as an electron donor instead of $Fe(bpy)_3^{3+}$−zeolite Y. Electron transfer from $Fe(bpy)_3^{2+}$−zeolite Y to $Ru(bpy)_3^{3+}$ and $Ru(Me_2bpy)_3^{3+}$ was also examined, and these data (see S6) also fit the Marcus parabolic relation as shown in Figure 1.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research Priority Area (No. 11228205) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Experimental procedures (S1, S2), observed spectral change of the electron transfer (S3), first-order plot of the electron transfer and the fit by eq 1 (S4), tables of the kinetic data (S5, S6) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA015751V

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[17] Since a typical particle size of zeolite Y is a dimension of 5000 Å diameter, the surface area is estimated as 6.8×10^{20} Å^2 g^{-1}. Then, the surface area of 6 mg of the zeolite used for the measurement would be 4.1×10^{18} Å^2. The 2.0×10^{-4} M ferrocene in 3 cm^3 MeCN includes 3.7×10^{17} ferrocene molecules. The surface area per one ferrocene molecule is thereby estimated as 11 Å^2 which is smaller than that required for the coverage of one ferrocene molecule.

[18] By using the β value of 1.1 Å^{-1},[1] the average distance for electron transfer from $Fe(C_5H_5)_2$ to $Fe(bpy)_3^{3+}$−zeolite Y is evaluated as 33 Å.

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