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Comparison between Intra- and Intermolecular Photoinduced Electron Transfer Reactions of Micelle-Solubilized Substances

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The rate constants of intramolecular photoinduced electron-transfer reactions of a linked pyrene–viologen molecule **A** and a linked pyrene–ferrocene molecule **B** solubilized in micellar solutions of a hexadecyltrimethylammonium chloride were determined to be 9×10^8 and 4×10^8 s^{-1} respectively, from the stationary fluorescence intensity. However, the observed fluorescence decay curve of **A** suggests that a large fraction of the molecules have conformations for which the distances between two functional moieties are sufficiently small to permit direct electron transfer. The quasi-first-order rate constants of the intermolecular photoinduced electron-transfer reactions between 1-hexylpyrene (HPy) and dodecylviologen (DDV), and between HPy and butylferrocene (BFc) solubilized in a micellar solution, were also determined to be 9×10^6 and 2×10^7 s^{-1} respectively, from the fluorescence decay curves. It is shown that the rate constants of the intermolecular photoinduced electron-transfer reaction in micelles are determined by the diffusion of the reactants in a micelle. On the other hand, it is suggested that the rate constants of the intramolecular electron-transfer reactions are determined by the molecular conformations of the linked compounds in micelles.

Recently, a number of investigations have been carried out in order to realize such effective artificial solar energy conversion to chemical energy, as in photosynthesis by plants.[1–3] Charge separation in the excited state of a photosensitizer is a very important process for this type photo-energy conversion. In photo-energy conversion using charge separation, it is a very serious problem that back electron transfer occurs and the energy stored by the photoreaction is wasted. The electric field gradient at the surface of a micelle is known to be one of the useful means to prevent this type of back electron transfer. However, other factors may also play important roles in electron-transfer reactions or charge separation in a micelle. It is therefore interesting to study other effects of the micelle solubilization of reactants on the photoinduced electron transfer (PIET) rates between them.

This paper deals with intramolecular PIET reactions of a linked pyrene–viologen molecule and a linked pyrene–ferrocene molecule solubilized in a micelle, as well as with the corresponding intermolecular PIET reactions between the same pairs of donor-acceptor molecules solubilized in micelles. Namely, in the latter case, each solubilizate contains only one of these redox moieties. In these experiments, pyrene, viologen, and ferrocene act as a photosensitizer, an electron acceptor, and an electron donor, respectively.

From a comparison between these intra- and intermolecular PIET reaction rates, the effects of the diffusion processes and the conformations of reactants molecules in a micelle on the rate constants of these PIET reactions are discussed.

Experimental

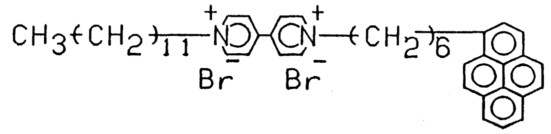
Materials. GR-grade hexadecyltrimethylammonium chloride (CTAC) and butylferrocene (BFc) from Tokyo Kasei Co. were used without further purification.

Dodecylviologen (DDV) was synthesized according to a method from the literature.[4]

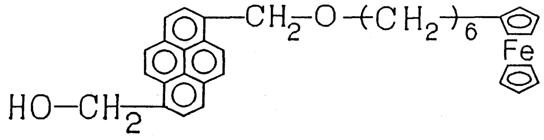
1-Hexylpyrene (HPy) was synthesized by the usual method from pyrene and hexanoyl chloride.

A linked pyrene–viologen compound (**A**) was synthesized from 1-bromo-6-(1-pyrenyl)hexane and 1-dodecyl-4,4′-bipyridinium bromide.[3] 1-Bromo-6-(1-pyrenyl)hexane was prepared from 1-bromo-6-(1-pyrenyl)hexan-6-one by zinc amalgam reduction. 1-Bromo-6-(1-pyrenyl)hexan-6-one was synthesized from 6-bromohexanoyl chloride and pyrene.

A linked pyrene–ferrocene compound (**B**) ($HOCH_2$–Py–$CH_2O(CH_2)_6Fc$) was synthesized from 1-bromo-6-ferrocenylhexane and 1,6-bis(hydroxymethyl)pyrene.[5] 1-Bromo-6-ferrocenylhexane was prepared from 1-bromo-6-ferrocenylhexan-6-one by a zinc amalgam reduction. 1-Bromo-6-ferrocenylhexan-6-one was synthesized from 6-bromohexanoyl



A



B

Fig. 1. Chemical structures of linked compounds **A** and **B**.

chloride and ferrocene.

These compounds were identified by proton magnetic resonance spectroscopy and elemental analysis.

Fluorescence Measurements. 0.1 M (1 M=1 mol dm^{-3}) CTAC solutions were used to solubilize substances for the fluorescence measurements throughout this study. In the measurements of fluorescence intensities of HPy the concentration was kept to be 4 μM; the concentrations of DDV and BFc were varied from 0 to 4 mM.

The fluorescence and absorption spectra were recorded on a Hitachi Model 850 fluorescence spectrophotometer and a Hitachi Model UV 220A spectrophotometer, respectively. The fluorescence decay curves of HPy were recorded with an assembly of instruments, comprising a nitrogen laser, a monochromator, a photomultiplier, and a digital storage oscilloscope.[6] A nitrogen laser oscillator (λ=337.1 nm) made in this laboratory was used with an output power of about 1 mJ per pulse for about a 10-ns duration. Fluorescence emission was monochromatized with a Shimadzu Bausch & Lomb monochromator and detected by a Hamamatsu Photonics Model R 928 photomultiplier. Fluorescence decay curves were monitored on an Iwatsu Model TS-8123 digital storage oscilloscope and transferred to an NEC PC-9801M personal computer system for the storage and analysis of data. The fluorescence decay curves for **A** were recorded by a Horiba NAES-550 Nanosecond Fluorometer equipped with a personal computer system for data analysis.

All stationary and decay fluorescence measurements of the micelle solubilized substances were carried out under a nitrogen atmosphere at room temperature.

Results and Discussion

Intramolecular PIET Reaction Rates of A and B in Micelles. The rate constant, k_q, of the intramolecular PIET reaction of **A** in 0.1 M CTAC solution was determined from the ratio of the respective stationary fluorescence intensities of dilute micellar solutions of **A** and HPy, I/I_0. In this estimation, the value of the intrinsic fluorescence lifetime of the pyrene moiety of **A** was assumed to be equal to that of HPy ($\tau_0=1/k_0$). The rate constant of the intramolecular PIET reaction of **B** was determined similarly. The value of the ratio of the stationary fluorescence intensities (I/I_0), the ratio of the quenching rate constants (k_q/k_0), and the values of k_q are given in Table 1.

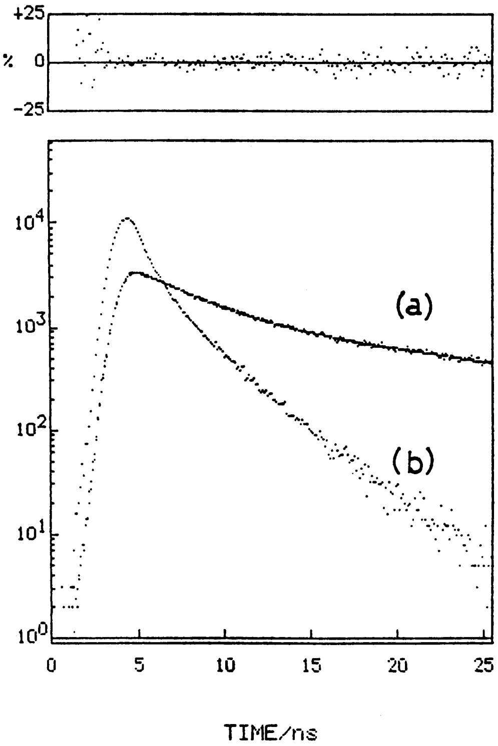


Fig. 2. (a) Fluorescence decay curve for the pyrene-viologen linked compound **A**. (b) Intensity vs. time profile for the light source. The full line shows the curve fitted one by a convoluted three component analysis.

The fluorescence decay curve of **A** in a 0.1 M CTAC solution is shown in Fig. 2. The observed decay curve was not a single exponential type, and was analyzed as a 3-component exponential curve, $I(t)=\Sigma A_i \exp(-t/\tau_i)$, with good fitness ($\chi^2$=0.988).[7] The result are given in Table 2. They show that the component with the lifetime shorter than 1 ns has a large fraction, i. e. a large A_i value.

If it is assumed that the fluorescence decay curve for the reference compound, HPy, can be represented by $A_0 \exp(-t/\tau_0)$, and the decay curve of the linked compound, **A**, by $\Sigma A_i \exp(-t/\tau_i)$, the stationary fluorescence intensity ratio I/I_0 may be equal to $\Sigma A_i\tau_i/A_0\tau_0$. The value of I/I_0 was calculated to be 0.005 by the above-mentioned relation using the values of A_i and τ_i cited in Table 2 and the values of A_0 (=1) and τ_0 for HPy; it was in good accordance with the experimental

Table 1. Stationary Fluorescence Intensity Ratios, I/I_0, of **A** and **B** to that of HPy in 0.1 M CTAC Solution, the Ratios of the Rate Constants, k_q/k_0, and the Values of k_q for the Intramolecular Photoinduced Electron-Transfer Reactions of **A** and **B** Determined from I/I_0

Compound	A	B
I/I_0	0.0054	0.013
k_q/k_0 [a]	180	80
k_q/s^{-1}	9.0×10^8	4.0×10^8

a) $k_0=5\times10^6$ s^{-1}.

Table 2. Fluorescence Lifetimes, τ_i, for **A** in 0.1 M CTAC Solution Analyzed by the 3-Component Exponential Decay Curves, $\sum A_i \exp(-t/\tau_i)$, and the Corresponding Preexponential Factor, A_i

τ_i/ns	A_i
0.07	0.86
2.34	0.10
18.7	0.04

value for **A** cited in Table 1.

The molecules of the linked compound **A** may have various conformations in micelles. If the distance between the pyrene and the viologen moieties of **A** in some conformation is sufficiently small, a direct electron transfer between the two moieties can occur. The fact that the large fraction of the fluorescence lifetime shown in Table 2 is smaller than 1 ns suggests that a large fraction of **A** molecules have such conformations, for which direct electron transfers are possible.

Accordingly, even though the rate constant of intramolecular PIET reaction estimated by the stationary fluorescence intensity cited in Table 1 is an average value, the rate constants of compound **A** in a large fraction of conformations have values larger than 1×10^9 s^{-1}, nearly equal to 1×10^{10} s^{-1}.

Intermolecular PIET Reaction Rates between HPy and DDV, and between HPy and BFc in Micelles Estimated from the Fluorescence Intensity. Table 3 shows the ratios of the observed stationary fluorescence intensities (I/I_0) of HPy solubilized in CTAC solutions containing various amounts of DDV or BFc, where I_0 is the fluorescence intensity in the absence of quenchers. The variation of I/I_0 shows that HPy fluorescence was strongly quenched as the quencher concentration increased. In these results, the relation between the ratio of the stationary fluorescence intensity and the quencher concentration greatly deviated from the simple Stern-Volmer relation.[8,9] In order to examine the mechanism of the fluorescence quenching process, these experimental results were analyzed according to a method described in the literature[9-14] on the assumption that the distribution of quencher molecules among micelles obeys the Poisson's distribution represented by

$$Pr(x=n)=m^n\exp(-m)/n!. \qquad (1)$$

This equation shows the probability that n quencher molecules are solublized in a micelle when the average quencher number in a micelle is m. In this micellar solution, m is represented by

$$m=[\mathrm{Q}]/[\mathrm{M}], \qquad (2)$$

where [Q] denotes the concentration of the quencher, Q, and [M] the concentration of a CTAC micelle, M.

In the following treatment, it is assumed that all of the molecules of HPy, DDV, and BFc are solubilized in micelles, since these molecules have a large hydrophobicity. If the quenching rate constants for HPy in micelles with quencher molecules are very large, only fluorescence from HPy molecules can be detected which are solubilized in micelles without quencher molecules. In this case, I/I_0 is equal to the probability of $n=0$, i. e., $Pr(x=0)$, and is represented by the following equation:[13]

$$I/I_0=\exp(-m)=\exp(-[\mathrm{Q}]/[\mathrm{M}]). \qquad (3)$$

Figure 3 shows plots of ln (I/I_0) vs. [Q] for HPy in CTAC solutions containing DDV or BFc as a quencher, respectively. Both plots deviate from the linear type relation expected from Eq. 3, showing that the quenching rate constants have finite values. In order to estimate these, the following treatment was adopted.

The lifetime, τ_0, of the fluorescence of HPy in a CTAC micellar solution can be written as

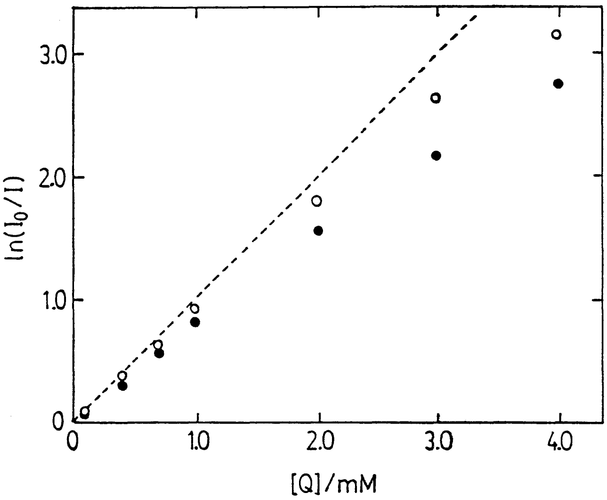


Fig. 3. The plots of ln (I/I_0) vs. [Q] for HPy in 0.1 M CTAC solution containing BFc (○) or DDV (●). Dotted line shows the theoretical one according to Eq. 3, when the aggregation number of the micell is 100.

Table 3. Stationary Fluorescence Intensity Ratios, I/I_0, for HPy Solubilized in 0.1 M CTAC Micellar Solution Containing Varying Amounts of DDV and BFc as Quenchers, and k_q/k_0 Values Estimated from These Data According to Eq. 6 on the Assumption that the Agrregation Number is 100

[Q]/mM	0	0.1	0.4	0.7	1.0	2.0	3.0	4.0
Q=DDV								
I/I_0	1	0.925	0.746	0.574	0.447	0.211	0.115	0.064
k_q/k_0[a]		4	3	4	5	5	5	6
Q=BFc								
I/I_0	1	0.915	0.687	0.534	0.405	0.169	0.073	0.039
k_q/k_0[a]		8	14	10	12	14	17	15

a) $k_0=5\times10^6$ s^{-1}.

$$\tau_0 = 1/(k_e + k_{nr}) = 1/k_0. \tag{4}$$

where k_e and k_{nr} are the luminescence rate constant and the nonradiative inactivation rate constant, respectively; k_0 is their sum. On the other hand, it is assumed that the quenching rate constant is proportional to the number of quencher molecules in a micelle, so that the fluorescence lifetime, τ_n, of an HPy molecule in a micelle containing n quencher molecules can be represented as follows:[9,10,13,14)]

$$\tau_n = 1/(k_0 + nk_q). \tag{5}$$

Where k_q is the quenching rate constant of HPy in a micelle containing only one quencher molecule. Thus, the value of I/I_0 is given by the follwing equation,[9,13)] taking account of the poisson's distribution:

$$I/I_0 = \sum_{n=0}^{\infty} \exp(-m)(m^n/n!)[1/(1 + nk_q/k_0)]. \tag{6}$$

The values of k_q/k_0 estimated by trial and error according to Eq. 6 are listed in Table 3. In this calculation, the aggregation number of a CTAC micelle is assumed to be 100. However, the aggregation numbers reported in the literatures[15-17)] are distributed between 60 and 100. If it is assumed that the aggregation number is 60, no calculation is possible, since the values of k_q/k_0 become negative in certain cases. Therefore, even though the absolute values of k_q/k_0 determined by the stationary fluorescence intensity are not reliable, it is probable that the k_q/k_0 value for HPy and BFc is larger than that for HPy and DDV.

In order to avoid any uncertainty regarding these k_q/k_0 values estimated from the stationary fluorescence intensity, the fluorescence decay curves for these systems were also measured.

Intermolecular PIET Rates between HPy and DDV, and, between HPy and BFc in Micelles Estimated from the Fluorescence Decay Curves. The fluorescence decay curve of HPy in the micellar solution without any quencher molecule was recorded at a wavelength of 377 nm. Its logarithmic plot shows that the decay followed a single exponential-type function; the lifetime was determined to be about 200 ns.

In order to determine the rate constants of the electron-transfer reactions between HPy and DDV or between HPy and BFc in micellar solutions, the fluorescence decay curves of HPy solubilized in micellar solutions containing varying amounts of DDV or BFc were recorded. The fluorescence emission of HPy was monitored at a wave length of 377 nm throughout this experiment.

Figures 4 and 5 show the fluorescence decay curves of HPy at varying concentrations of DDV or BFc, respectively. In order to estimate the value of k_q/k_0, semilogarithmic plots of the decay curves were fitted with theoretical curves calculated according to the following equation derived in the literatures,[9,10,13,14)] based on a similar assumption for the derivation of Eq. 6:

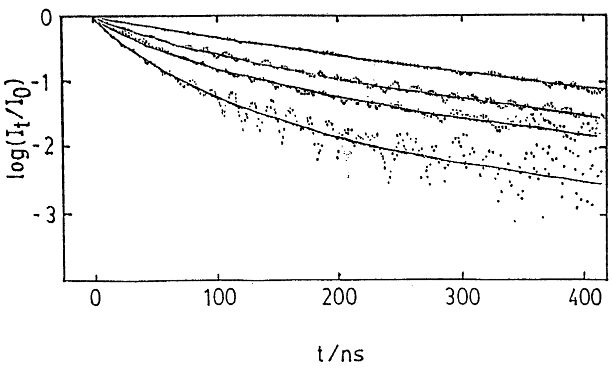


Fig. 4. Fluorescence decay curves of HPy in 0.1 M CTAC solution containing varying amounts of DDV. Upper to lower curves show those for [DDV]=1, 2, 3, 4 mM, respectively.

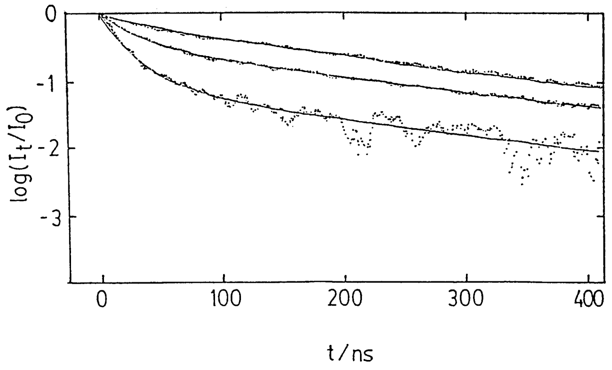


Fig. 5. Fluorescence decay curves of HPy in 0.1 M CTAC solution containing varying amounts of BFc. Upper to lower curves show those for [BFc]=1, 2, 4 mM, respectively.

$$\ln[I(t)/I(0)] = m[\exp(-k_q t) - 1] - k_0 t. \tag{7}$$

The theoretical curves calculated using Eq. 7 with appropriate values of m and k_q/k_0 were fitted with the experimental curves (Figs. 4 and 5). Though the agreement between the experimental and theoretical curves is excellent at a given concentration of the quencher, the parameter k_q/k_0 is not constant and m=[Q]/[M] is not proportional to [Q] for different concentrations of quenchers for their good fitness (as listed in Table 4).

The reason for these variations of k_q/k_0 with the concentration of quenchers may be due to a limitation of the model based on the poisson's distribution, especially concerning the assumption represented by Eq. 5. On the other hand, the fact that the value of m is not proportional to [Q] shows that the aggregation number, N_{agg}, of CTAC micelles varied with the concentration of the quenchers,[18,19)] since this fact indicates that the value of [M]=[CTAC]/N_{agg} varied with the concentration of the quencher, in spite of the constant value of [CTAC]. It is worthwhile noting

Table 4. The Ratio of the Rate Constants k_q/k_0 of the Intermolecular Photochemical Electron-Transfer Reactions between HPy and DDV, and between HPy and BFc in 0.1 M CTAC Solution, Determined by Curve Fitting as Shown in Figs. 4 and 5

[Q]/mM	HPy-DDV			HPy-BFc		
	k_q/k_0 a)	m b)	N_{agg} c)	k_q/k_0 a)	m b)	N_{agg} c)
1.0	1.4	0.6	60	2.5	0.6	60
2.0	1.6	1.6	80	4.0	1.3	65
3.0	1.8	2.4	80	4.2	2.2	73
4.0	1.8	4.0	100	4.5	2.8	70
Mean value	1.7			3.8		
k_q (mean)/s^{-1}	8.5×10^6			1.9×10^7		

a) $k_0=5\times10^6$ s^{-1}. b) $m=[Q]/[M]$. c) N_{agg}: The aggregation number of the CTAC micelle.

that the values of m or N_{agg} of the micelle can be determined independently by such curve fitting, since Eq. 7 approaches $\ln[I(t)/I(0)]=-m-k_0t$ for long time; the intercept obtained by extrapolating the line to $t=0$ is equal to $-m$. It is interesting that the values of aggregation numbers determined by curve fitting are also distributed between 60 and 100, as are values found in the literature.[15–17]

Though the reason for the differenece between the values of the rate constants for intermolecular PIET reactions determined by a stationary method and those determined by fluorescence decay curves is not clear, the latter values are likely to be more reliable than the former, as described above.

Comparison of the Rate Constants for Intramolecular PIET Reactions of A and B, with Those of the Corresponding Intermolecular PIET Reactions in Micellar Solutions. The rate constants of the PIET reactions of **A** and **B** in CTAC micellar solutions are larger than those of the corresponding intermolecular PIET reactions by a factor of 10 to 100. These large difference between the rate constants of intra- and intermolecular PIET reactions is mainly attributable to the difference in the size of the effective space for these PIET reactions, as shown below. The rate constants for the intermolecular PIET reactions between HPy and DDV or HPy and BFc in micellar solutions are defined to be those in micelles containing a pair of HPy and DDV or HPy and BFc. In such situations, the local concentrations of the reactants in a micelle is determined by the volume of the micelle. If the shape of the micelle is assumed to be spherical, the concentration of the reactants is easily calculated from the value of the micellar radius. From the results cited in Table 4, the aggregation number of the CTAC micelle takes on values between 60 to 100. If we assume that the density of the micelle is about 1 g cm^{-3}, the volume and the radius of the micelle can be calculated from the aggregation number and the molecular weight of CTAC. The radius of the micelle, thus calculated, has takes values between 18 and 22 Å.

Table 5. Second Order and Quasi-First-Order Rate Constants for Diffusion-Controlled Reaction in CTAC Micelle

D a)/cm^2 s^{-1}	k_d b)/M^{-1} s^{-1}	$k_1=k_dC$ c)/s^{-1}	
		r=18 Å	r=22 Å
3×10^{-7}	3.6×10^8	2.5×10^7	1.4×10^7

a) Calculated by Eq. 9. b) Calculated by Eq. 8. c) C: The concentration of reactants in the micelle which contains only a pair of reactants.

In intermolecular PIET reactions between HPy and DDV or BFc, the free-energy change of these reactions are smaller than -1 eV/molecule. Such highly exothermic electron transfer reactions are usually diffusion-controlled reactions. If the diffusion coefficients of the reactants in the micelle is known, the second-order rate constant of a diffusion-controlled reaction, k_d, can be estimated by the Smoluchowski equation,[20]

$$k_d=4\pi(D_A+D_B)(r_A+r_B), \tag{8}$$

where D_A, D_B, r_A, and r_B are the diffusion coefficients and the molecular radii of the reactants A and B, respectively. The diffusion coefficient, D, can generally be represented by the Stokes-Einstein equation,[20]

$$D=kT/6\pi\eta r, \tag{9}$$

where η is the viscosity of the media in which the spherical particles of radius r is diffusing. The microviscosity of the interior of a CTAC micelle was estimated to be about 20 cP (1 cP=10^{-3} Pa s) by using a fluorescent perylene probe.[21] The radius of the reactants could not be strictly defined in the present case, because they were not spherical. However, we assumed that the reactants are spherical particles with a mean radius of r, determined by their molecular volume. The mean molecular radius of pyrene was estimated to be about 4 Å.[22] The molecular radii of ferrocene and methylviologen were also estimated to be about 4 Å by considering their molecular weights. The diffusion coefficient calculated by Eq. 9 and the second-order rate constant for a diffusion-controlled reaction in the CTAC micelle calculated by Eq. 8 using these estimated values are listed in Table 5. The quasi-first-order rate constants for diffusion-controlled reactions in a micelle, calculated by considering the local concentration of the reactants in the micelle, are also listed in Table 5, for two extreme values of the radii of micelles.

The quasi-first-order rate constants listed in Table 5 agreed fairly well with the experimental rate constants found for the intermolecular PIET reactions (Table 4). This result shows that the intermolecular PIET reactions between HPy and DDV or BFc in the CTAC micelles are diffusion-controlled. The difference between the rate constants for the two intermolecular PIET reactions may be attributable to the difference of the location of the reactants for each reaction, as will be described in the conclusion.

The intramolecular PIET reactions of **A** and **B** can be treated similarly, if we assume that these intramolecular PIET reactions of the linked compounds (**A** and **B**) in the CTAC micelle are equivalent to the intermolecular PIET reactions between the two functional moieties (pyrene, ferrocene, and viologen) of the linked compounds in a small sphere with a diameter equal to the length between the functional moieties when the molecule have a completely extended structure. Such a length of compounds **A** and **B** were estimated to be 16 Å for **A** and 18 Å for **B**, considering the bond length of these compounds. If the functional moieties of these compounds are randomly distributed in such a sphere, and react with each other in a diffusion-controlled manner, the rate constants of the intramolecular PIET reaction of **A** and **B** in a CTAC micelle are considered to be the rate constants of a quasi-first-order diffusion-controlled reaction in the small type sphere mentioned above. The rate constants calculated in this way are listed in Table 6 for several values of radius r. A radius of 8 Å corresponds to compound **A** and 9 Å corresponds to compound **B**. These quasi-first-order rate constants are larger than those cited in Table 4 by the factor of 10 or more, but agreed fairly well with the rate constants estimated by the stationary fluorescence intensity for the intramolecular PIET reaction (Table 1) and are smaller than the value estimated by the fluorescence decay curve of **A**.

As shown in the above discussions, the rate constants of the intermolecular PIET reactions are primarily determined by the diffusion of the reactants in a micelle. However, the rate constant of the intramolecular electron-transfer reaction may be determined by the molecular conformation of the linked compound.

Though diffusion-controlled reactions in a micelle have been studied by several authors,[23-26] the models treated in their papers are not necessarily appropriate to our experiment. In their papers, the following three cases were treated: (a) one reactant resides at the center of a spherical micelle and the other reactant moves freely in the micelle; (b) both reactants move freely on the surface of a micelle; and (c) one reactant moves freely in the micelle and reacts with other reactants which reside over the entire surface of the micelle. Though it is the most probable case that both reactants move freely in the micelle, an analytical solution for this case has not yet been obtained.

Table 6. Quasi-First-Order Rate Constant for Diffusion-Controlled Reaction in a Sphere of Radius r which Have Microviscosity Equal to That of CTAC Micelle

$k_1=k_dC^{a)}/\mathrm{s}^{-1}$			
r=6 Å	r=7 Å	r=8 Å	r=9 Å
6.6×10^8	4.2×10^8	2.8×10^8	2.0×10^8

a) C: The concentration of reactants in the micelle which contains only one molecule for each reactants.

The treatment mentioned above is not exact, but it is important that this model can be used to interpret the main features of the intermolecular PIET reactions in a micelle.

The difference between the rate constants for the intermolecular PIET reactions may be attributable to a difference in the location of the reactants for each reaction.

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