Conclusion

Several factors governing the photoassisted deposition of platinum have been examined. The following points emerge from this study: (i) the deposition occurs from various platinum complexes; (ii) the exhaustion of a solution can reach 1 ppm, and (iii) the deposition is not limited by the saturation of the semiconductor grains by the platinum particles inasmuch as the initially small Pt particles form agglomerates even bigger than the semiconductor grains. On the other hand, the quantum yield could be improved by progresses in the photocatalyst design and/or by addition of hole scavengers.[8,21-23] Such results could lead one to envisage this photodeposition method as a means of noble metal recovery, although, obviously, economical studies would be required to assess

its interest as compared with existing electrochemical and chemical methods.

Registry No. TiO_2, 13463-67-7; H_2PtCl_6, 16941-12-1; Na_2PtCl_6, 16923-58-3; $Pt(NO_2)_2(NH_3)_2$, 14286-02-3; $H_2Pt(OH)_6$, 51850-20-5; Pt, 7440-06-4; O_2, 7782-44-7; Pd, 7440-05-3; Ag, 7440-22-4; Rh, 7440-16-6; Au, 7440-57-5; Ir, 7439-88-5; Cu^{2+}, 15158-11-9; ZnO, 1314-13-2; Nb_2O_5, 1313-96-8; ThO_2, 1314-20-1.

Unexpected Salt Effects on Charge Separation Yields in Phenothiazine Derivatives–Methylviologen Systems

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Neutral salt effects on photoinduced electron-transfer reactions between the singlet excited state of phenothiazine derivatives (PTH) and methylviologen (MV^{2+}) were investigated in homogeneous acetonitrile–water (4/1 v/v) mixture. In the N-methylphenothiazine–MV^{2+} system, the fluorescence quenching reaction was not affected by the addition of neutral salts, whereas the yield of viologen cation radical was greatly improved when some neutral salts having hydrophobic long alkyl chains were added in the solution. The well-known micellar effect was excluded since no preaggregation was found either between salts or between salt and reactant. The increased charge separation yield in the presence of neutral salts was well explained by the suppression of the back-electron-transfer reaction within the geminate ion pair owing to changes in solvation. The effect is discussed with two different and recently developed treatments, (i) solvent friction and (ii) solvation mode.

Introduction

Photoinduced electron-transfer reactions are the basis of photosynthesis, photooxidation, photoconduction, and many other important photochemical processes. The fundamental problem to attain a high chemical yield in photoinduced electron transfer is to achieve efficient charge separation after the primary quenching process. It is known that the forward electron transfer observed as fluorescence quenching proceeds with a diffusion-controlled rate constant if the free energy change (ΔG) of the reaction is more negative than −40 kJ/mol. In such a case, electron-transfer quenching of an excited-state sensitizer (*S) by a quencher (Q) can easily produce a radical ion pair ($S^{\pm}$--$Q^{\mp}$) in polar solvent.[1] However, this does not lead to complete charge separation owing to the back-electron-transfer reaction competing with the dissociation of radical ion pair.

Recently, we reported that the charge separation yield of the photooxidation of leuco dye was improved by the use of ionic sensitizers or by addition of neutral salts such as tetra-n-butylammonium chloride or cetyltrimethylammonium chloride even in a homogeneous solution.[2] It was concluded that a single pair of ions was sufficient to prevent back electron transfer, although molecular aggregates such as micelles or polyelectrolytes were frequently used as the preferable reaction environment to improve charge separation yield.

In this report, we describe salt effects on the photoinduced electron-transfer reaction between the singlet excited state of PTH and MV^{2+} in a homogeneous acetonitrile–water (4/1 v/v) mixture. Suppression of back electron transfer and subsequent improvement of the charge separation yield were demonstrated when certain

salts were added to the solution.

Experimental Section

3-Formyl-10-methylphenothiazine (FMPTH) was synthesized by Buu-Hoï's method.[3] Other PTH derivatives were synthesized by the method described elsewhere.[4] Methylviologen dichloride (Nakarai Chemicals; Guaranteed Reagent grade) was used as supplied. The hydrophobic probes 1-anilinonaphthalene-8-sulfonate (ANS, Tokyo Kasei; Extra Pure grade) and p-dimethylaminobenzonitrile (DMABN, Tokyo Kasei; Extra Pure grade) were used without futher purification.

Sodium chloride (NaCl, Kanto Chemicals; Extra Pure grade), tetraethylammonium chloride (TEAC, Tokyo Kasei; Extra Pure grade), tetra-n-butylammonium chloride (TBAC, Tokyo Kasei; Extra Pure grade), cetyltrimethylammonium chloride (CTAC, Tokyo Kasei; Extra Pure grade), and sodium dodecyl sulfate (SDS, Tokyo Kasei; Extra Pure grade) were recrystallized repeatedly from deionized water, acetone–methanol, ether–acetone, acetone–ethanol, and ethanol, respectively. Triton X-100 (Kodak, Scintillation grade) was used as supplied.

Solvents were spectro grade (Kanto Chemicals) and used without further purification.

Emission lifetime of PTH was measured by the single photon counting method (Photochemical Research Associates Inc.). Emission quenching experiments were carried out with a Hitachi MPF-4 spectrofluorometer. A 500-W xenon lamp (Ushio Electric) equipped with the combination of glass filters (a Toshiba IR-25S IR cutoff filter, a UV-D33S filter, and a glass plate for UV cutoff) was the light source for the irradiation around 365 nm. Continuous photoreduction of MV^{2+} was monitored spectroscopically at 603

(1) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(2) (a) Tazuke, S.; Kawasaki, Y.; Kitamura, N.; Inoue, T. *Chem. Lett.* **1980**, 251. (b) Kitamura, N. Ph.D Thesis, Tokyo Institute of Technology, 1983.

(3) Buu-Hoï, H. *J. Chem. Soc.* **1951**, 1834.
(4) Kawanishi, Y.; Kitamura, N.; Tazuke, S. *J. Phys. Chem.* **1986**, *90*, 2469.
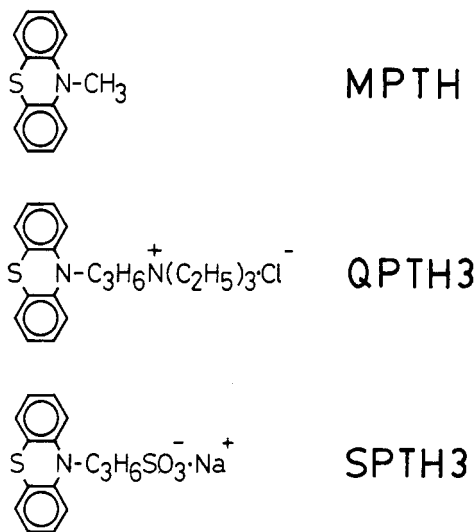
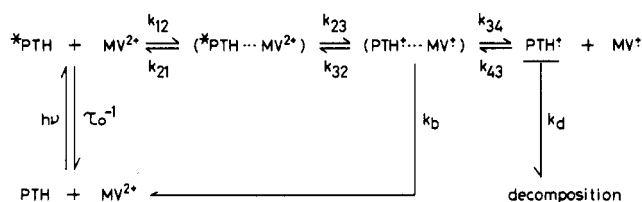Figure 1. Structures and abbreviations of phenothiazine derivatives.

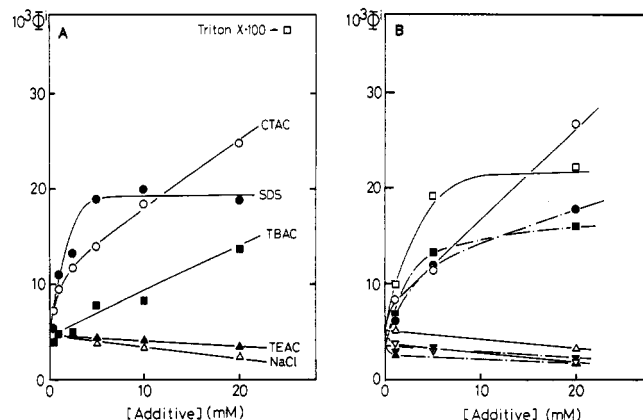Figure 2. Schematic description of the electron-transfer reaction between PTH and MV^{2+}.

Figure 3. (A) Dependence of the initial quantum yield Φ^i on the concentration of additives in $MPTH-MV^{2+}$ systems. (B) Dependence of the initial quantum yield Φ^i on the concentration of additives in ionic PTH–MV^{2+} systems. $QPTH3-MV^{2+}$: (O) CTAC, (□) SDS, (△) TEAC, (▽) NaCl. $SPTH3-MV^{2+}$: (●) CTAC, (■) SDS, (▲) TEAC, (▼) NaCl.
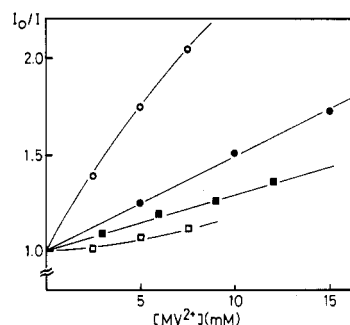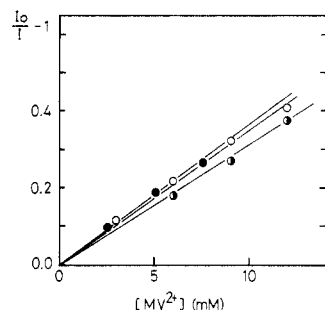

Figure 4. Stern–Volmer plots for the quenching reactions of QPTH3 and SPTH3 by MV^{2+}. $QPTH3-MV^{2+}$: (□) none, (■) 0.1 M TEAC. $SPTH3-MV^{2+}$: (O) none, (●) 0.1 M TEAC.

nm. The quantum yield of the $MPTH-MV^{2+}$ system (4.7×10^{-3})[4] was taken as the standard and that of other combinations was determined by comparison.

The concentrations of PTH and MV^{2+} were kept at 5.0×10^{-4} and 5.0×10^{-3} M, respectively. All sample solutions were deoxygenated by argon gas purging for emission measurements or by several freeze–pump–thaw cycles for the continuous photoirradiation, respectively.

Results and Discussion

General Trends of Salt Effects. Structures and abbreviations for PTH derivatives are shown in Figure 1. Photoinduced electron transfer occurs between the excited singlet state of PTH and MV^{2+} at a diffusion-controlled rate constant because of large and negative ΔG ($\approx$−160 kJ/mol), and the radical ion pair $(PTH^+\cdot -MV^+)$ is produced immediately after encounter[4] (see Figure 2). However, only a small fraction of the radical ion pair dissociates to produce free MV^+, since the fast back electron transfer competes with the dissociation process.

When neutral salts were added to the solution, the quantum yields of MV^+ formation were drastically affected as shown in Figure 3A,B. The initial quantum yields (Φ^i) of $PTH-MV^{2+}$–salt systems are plotted against the concentration of salt where the values of Φ^i were determined from the initial slope of the time–conversion profiles of photoreduction. Regardless of the kind of PTH, Φ^i was increased by the addition of CTAC or SDS, and decreased by the addition of NaCl or TEAC. TBAC and Triton X-100 also catalyzed the reaction of the $MPTH-MV^{2+}$ system.

The quantum yield of photoreduction, Φ, is expressed by eq 1

$$\Phi = E_q F \tag{1}$$

where E_q is the quenching efficiency representing the charge-transfer yield and F is the charge separation efficiency. The rate constants of ionic reactions are strongly affected by the ionic strength (μ) of the reaction medium; this is known as the primary salt effect.[5] Under the condition of high μ, the Coulombic

repulsion and attraction forces between reactants are weakened and therefore, the quenching rate constant will become larger and smaller for the $QPTH3-MV^{2+}$ and $SPTH3-MV^{2+}$ systems, respectively. Stern–Volmer (S–V) plots for the quenching of PTHs by MV^{2+} in the absence and presence of 0.1 M TEAC are shown in Figure 4.[6] The S–V plots for QPTH3 and SPTH3 did not fall on straight lines in the absence of salt, since μ varies with the concentration of MV^{2+} as a quencher. When 0.1 M of TEAC was added to the systems, however, S–V plots gave linear lines and each slope of S–V plots approached to that of the $MPTH-MV^{2+}$ system. Figure 4 indicates that the quenching (the forward electron-transfer process) of *PTH by MV^{2+} is subjected to the primary salt effect. The dissociation rate constant k_{34} will be also affected by μ. If μ becomes higher, the Coulombic repulsion force between the resulting cation radicals ($MPTH^+$ and MV^+) will decrease, and therefore, k_{34} and the charge separation efficiency will be lower. Such primary salt effects on quenching rate constants and on yields of ion radicals have been also observed in tris(2,2′-bipyridine)ruthenium(II)–MV^{2+} systems.[7] The results in Figure 3 indicate that NaCl and TEAC fall in the category of normal salts, although a small difference is seen between the effects of these salts. Apparently, however, CTAC, SDS, TBAC, and Triton X-100 do not behave as normal salts. Specific salt effect should be thus considered. The effect was tested for the fluorescence quenching reaction in the $MPTH-MV^{2+}$ system. The S–V plots for $MPTH-MV^{2+}$, $MPTH-MV^{2+}$–0.1 M TEAC, and $MPTH-MV^{2+}$–0.1 M CTAC systems shown in Figure 5 gave almost identical slopes.[6] The lifetime of the excited singlet MPTH

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(5) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*, 2nd ed.; Wiley: New York, 1961; p 142.

(6) Since no fluorescence spectral shift of PTH was observed in the presence of added salts, we carried out S–V experiments by fluorescence intensity ratio, I_0/I, where I_0 and I are fluorescence intensities in the absence and presence of MV^{2+}, respectively.

(7) (a) Rodgers, M. A. J.; Becker, J. C. *J. Phys. Chem.* **1980**, *84*, 2762. (b) Kalyanasundaram, K.; Neumann-Spallart, M. *Chem. Phys. Lett.* **1982**, *88*, 7.

Figure 5. Stern–Volmer plots for the quenching reactions of MPTH–MV^{2+}–additives systems in CH$_3$CN–H$_2$O (4/1 v/v) mixture: (●) MPTH–MV^{2+}, (○) MPTH–MV^{2+}–0.1 M TEAC, (◑) MPTH–MV^{2+}–0.1 M CTAC.

was also not affected even in the presence of salts. These results indicate the participation of salts after the primary electron-transfer process.

CTAC, SDS, and Triton X-100 are micelle-forming in water above critical micellar concentration. Use of micellar systems has been thought to be a favorable condition for charge separation owing to their high Coulombic potential barrier. Enhanced dissociation and suppressed recombination of ion radicals are expected in ionic micelles.[8] In our systems, the formation of micelles or microaggregates was not at all detected by the fluorescence method with ANS or DMABN as a hydrophobic probe. There is no shift in the spectrum of FMPTH (5 × 10^{-4} M) on addition of enough CTAC (0.1 M) to form micelles.[9] Furthermore, the maximum wavelength and the shape of the MV^{2+} absorption spectra were not affected in the presence of added salts. All the results do not favor aggregation of salts or of reactant with salts and suggest that specific interaction between salts and radical ion pair participates in the charge separation process after the forward electron-transfer reaction. For all PTH–MV^{2+} systems, SDS was the best salt catalyzing MV$^+$ formation as long as μ was low. This is a reasonable observation since negatively charged SDS is more advantageous to interact with positively charged radical ion pair than quaternary ammonium ions.

Kinetic Treatment. According to Figure 2, F is written as[4,10]

$$F = \frac{k_{34}k_d}{k_b k_{43}[\text{MV}^+] + (k_b + k_{34})k_d} \quad (2)$$

where (MV$^+$) is the concentration of viologen radical. The rate of the radical formation, d(MV$^+$)/dt, is given by eq 3 where n

$$d(\text{MV}^+)/dt = nE_qF$$

$$= \frac{nE_q k_{34}k_d}{k_b k_{43}[\text{MV}^+] + (k_b + k_{34})k_d} \quad (3)$$

is the number of absorbed photons per second. From the least-squares fitting of the time profiles of MV$^+$ formation according to (3), we can get the ratios of rate constants (k_{34}/k_b and k_{43}/k_d). The changes in k_{34}/k_b and k_{43}/k_d with the concentration of salt were large and small, respectively. In Table I, the values of k_{34}/k_b in MPTH–MV^{2+} system are listed as a function of the salt concentration. The results indicate that the abnormal increment of Φ in the presence of the salts having long methylene chains such as CTAC, SDS, and Triton X-100 is attributable to the effects on $k_{34}/(k_{34} + k_b)$ representing the initial charge separation yield, [MV$^+$] being zero in eq 2. It must be noted that the obtained parameters are apparent ones since the kinetic scheme (Figure 2) will be no longer usable in the presence of salts. We have attempted to describe the salt effect as a function of [salt] or μ

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(8) Katusin-Razem, B.; Wong, M.; Thomas, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 1679.

(9) FMPTH can be used as a solvent polarity probe since the emission maximum of FMPTH shifts from 500 nm in toluene to 540 nm in acetonitrile.

(10) Kawanishi, Y.; Aoyagi, Y.; Tazuke, S., to be published.

TABLE I: Salt Effects on the Ratio (k_{34}/k_b) in MPTH–MV^{2+}–Salt Systems

additives	concn, mM	k_{34}/k_b
none		0.035
CTAC	0.5	0.046
	1.0	0.065
	2.5	0.076
	5.0	0.097
	10.0	0.17
	20.0	0.23
SDS	0.5	0.051
	1.0	0.071
	2.5	0.084
	5.0	0.13
	10.0	0.14
	20.0	0.15
TBAC	0.5	0.027
	1.0	0.031
	5.0	0.058
	10.0	0.067
	20.0	0.12
Triton X-100^a	25.0	0.34
TEAC	5.0	0.036
	10.0	0.032
	20.0	0.027
NaCl	5.0	0.023
	10.0	0.021
	20.0	0.017

^{a} Nonionic surfactant.

under assumption of some additional kinetic schemes. However, no meaningful relationship has been obtained. Kinetic analysis of the overall reaction is difficult in the presence of salt since salt will affect some elementary processes simultaneously. Therefore, our discussion in following sections is limited to the salt effect as increment of the apparent rate parameter k_{34}/k_b.

The Origin of Salt Effects. Similar salt effects observed in benzophenone (BP)–leuco dye (LC) systems[2] are explained by the ion-pair exchange mechanism.[11] In the BP–LC system, the geminate ion radical pair (BP$^-$–LC$^+$) and the added quaternary ammonium halide exchange counterions with each other. Once such counterion exchange occurs, the Coulombic attraction force between BP$^-$ and LC$^+$ reduces and the dissociation process becomes more likely. In the MPTH–MV^{2+} system, however, the resulting ion radicals have the same positive sign and repel each other. Thus, ion-pair exchange cannot contribute to the increment of F and Φ in the sense of Coulombic interaction.

Some quaternary ammonium salts are known as structure-forming ions which promote iceberg structure of water around their hydrophobic alkyl chains. The structure-forming effect was confirmed even in nonaqueous medium such as methanol or acetonitrile.[12] When hydrophobic chains approach the radical ion pair, polar solvent molecules will be excluded from the solvation shell by lyophobic interaction.[13] As a consequence, the effective microscopic dielectric constant around the radical ion pair will decrease and the Coulombic repulsion will increase to promote ionic dissociation. However, the improvement in Φ occurs even in the SPTH3–MV^{2+} system where any repulsion force within ion radical pair is not expected, since oxidized SPTH3 has no net electric charge. Therefore, we conclude that the changes in the solvation affect not only the Coulombic interaction but also more intrinsically the back-electron-transfer reaction itself. Actually, we have observed that the rate of back electron transfer between PTHs and viologens depends strongly upon the solvent.[4] Thus, we must consider the salt effect in a way relevant to the solvent effect.

The rate constant of electron-transfer reaction (k) is expressed as[14]

$$k = A \exp(-\Delta G^{\ddagger}/RT) \quad (4)$$

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(11) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6142.

(12) Criss, C. M.; Mastroianni, M. J. *J. Phys. Chem.* **1971**, *75*, 2532.

(13) Siegel, B.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 6869.

where A is the collision frequency factor and $\Delta G^{\ast}$ is the intrinsic activation barrier. $\Delta G^{\ast}$ is related to outer- and inner-shell reorganization terms (λ_{os} and λ_{is}, respectively), and the standard free energy change (ΔG°).

$$\Delta G^{\ast} = \lambda (1 + \Delta G^{\circ}/\lambda)^2/4$$

$$\lambda = \lambda_{is} + \lambda_{os} \qquad (5)$$

λ_{is} is a solvent-independent term associated with bond distortion of reactants, whereas λ_{os} is a solvent-dependent term given by eq 6 where e is the electronic charge, a_1 and a_2 are the radii of the

$$\lambda_{os} = e^2 \, (\tfrac{1}{2}a_1 + \tfrac{1}{2}a_2 - 1/r)(1/n^2 - 1/D_s) \qquad (6)$$

reactants (1 and 2), respectively, r is the distance between reactants, and n^2 and D_s are optical and static dielectric constants, respectively. On the other hand, we have concluded that the back-electron-transfer reaction in the PTH–MV^{2+} system occurs from the ion radical state to the vibronically excited state with a small and positive free energy change and (5) is simplified to $\Delta G^{\ast} \approx (^1/_4)\lambda$, and $\Delta G^{\ast}$ has been calculated to be about 2.2 kcal/mol with the estimated k_b value.[4] If ca. 10-fold increment of k_{34}/k_b in the presence of salts is ascribed to the reduction of k_b, the activation barrier must increase by 1.4 kcal/mol to 3.6 kcal/mol. Since λ_{is} is not affected by the surrounding medium and λ_{os} takes a rather small value under the low effective dielectric constant, any increment in $\Delta G^{\ast}$ will not be anticipated. The above consideration indicates the changes in the preexponential term A. A is written as $A = K\kappa_{el}\nu_n$ where K is the formation constant of the precursor complex (being unity for the back-electron-transfer reaction within the ion radical pair), κ_{el} is the electronic transmission coefficient (being unity for an adiabatic electron-transfer reaction), and ν_n is the nuclear frequency factor. The nuclear frequency is described as (eq 7) containing bond vibrations

$$\nu_n = [(\nu_{os}^2 \Delta G^{\ast}_{os} + \nu_{is}^2 \Delta G^{\ast}_{is})/(\Delta G^{\ast}_{os} + \Delta G^{\ast}_{is})]^{1/2} \qquad (7)$$

(ν_{is}), solvent reorganization frequencies (ν_{os}), and outer- and inner-shell reorganization energies ($\Delta G^{\ast}_{os}$ and $\Delta G^{\ast}_{is}$, respectively).[14] In most cases, $\nu_{is}^2 \Delta G^{\ast}_{is}$ is calculated to be a sufficiently large value that could decide the nuclear frequency. Recently, however, it has been reported that the theoretically predicted ν_n cannot explain solvent effects on the rate of electrochemical electron-transfer reactions and that the solvent friction associated with the longitudinal solvent dielectric relaxation time (τ_L) is very important and ν_n takes a small value for high friction solvents.[15] Furthermore, the rate of intramolecular electron transfer is also related to τ_L which indicates motion of the solvent clusters around the

excited state.[16] Our present results are well explainable with this solvent friction model: When the hydrophobic long alkyl chains of the salts associate with the ion radical pair, they will promote structure formation of the neighboring polar solvent molecules. Under such conditions, outer-sphere reorganization of the back-electron-transfer reaction is difficult owing to the low mobility (high friction) of the quasi-frozen solvent molecules and to that of the ions having long alkyl chains; namely, ν_n becomes small and thus, the back electron transfer would be highly restricted.

Another possible explanation is based on a new theory of photoinduced electron-transfer reaction proposed by Kakitani and Mataga, which provides a unified interpretation on the rate of electron transfer over a large variation of ΔG.[17] According to their calculation, the rate of electron transfer shows strong dependence not only on the energy gap between the states before and after electron transfer, but also on the shape of energy surfaces in terms of solvent coordinate around reactants. They introduced a parameter β: $\beta = k_i/(k_f - k_i)$ where k_i and k_f are phonon force constants of the solvent surrounding the reactants in their initial and final states, namely, before and after electron transfer, respectively. Since solute–solvent interaction strongly depends on the charge of solute in a polar solvent, the shape and the force constants of these two energy surfaces are quite different from each other, and β takes a finite value (see Figure 1 in ref 17a). If the long alkyl chains of salts associate with the radical ion pair, the solute–solvent interaction becomes so small that the shape of energy surfaces before and after the back electron transfer will be almost identical ($k_i = k_f$), and β approximates to an infinite value. The rate of the back electron transfer (k_b) is extremely susceptible to the change in parameter β. As mentioned above, ΔG of the back reaction takes a small and positive value in the MPTH–MV^{2+} system. In such a ΔG region, k_b decreases drastically with increasing β (see Figure 3 in ref 17a).

Although the real description of salt effects is not yet obtained, it must be emphasized that the rate decrease of only back electron transfer can occur in the presence of appropriate salts. Molecular assembly effects have been studied relevant to the photoinduced electron-transfer reactions: micelles, polyelectrolytes, membranes, and so forth. However, it has never been reported that the microscopic changes of solvation improve the charge separation efficiency by the addition of the salts having hydrophobic alkyl chains. This effect should be taken into consideration in order to accomplish highly efficient electron transport systems.

(14) Sutin, N. *Progr. Inorg. Chem.* **1983**, *30*, 441.
(15) (a) Weaver, M. J.; Gennett, T. *Chem. Phys. Lett.* **1985**, *113*, 213. (b) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787. (c) Opa-Ho, M.; Kapturkiewicz, A. *Electrochim. Acta* **1985**, *30*, 1301.

(16) Kosower, E. M.; Huppert, D. *Chem. Phys. Lett.* **1983**, *96*, 433.
(17) (a) Kakitani, T.; Mataga, N. *J. Phys. Chem.* **1985**, *89*, 8. (b) Kakitani, T.; Mataga, N. *Chem. Phys.* **1985**, *93*, 382.