Charge Effects in Photoinduced Electron-Transfer Reactions between $[Ru(bpy)_3]^{2+}$ and Viologen Derivatives

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Photoexcited $^*[Ru(bpy)_3]^{2+}$ is oxidatively quenched by methylviologen (MV^{2+}) and 1,1′-bis(2-carboxyethyl)-4,4′-bipyridinium ($BCEBP^{2+}$) with a similar rate constant at pH 2.2; k_q^{obs} = 1.48×10^9 and 1.58×10^9 $mol^{-1}\,dm^3\,s^{-1}$ (30 °C) for MV^{2+} and $BCEBP^{2+}$, respectively. However, $^*[Ru(bpy)_3]^{2+}$ is much more slowly quenched by MV^{2+} than by $BCEBP^0$ at pH 5.0, where the superscript "0" represents that BCEBP is neutral; k_q^{obs} = 1.01×10^9 and 1.74×10^9 $mol^{-1}\,dm^3\,s^{-1}$ for MV^{2+} and $BCEBP^0$, respectively. The reverse electron-transfer reaction between $[Ru(bpy)_3]^{3+}$ and one-electron-reduced $\cdot BCEBP^+$ (k_{rev}^{obs} = 3.33×10^9 $mol^{-1}\,dm^3\,s^{-1}$) proceeds slightly more rapidly than the reaction between $[Ru(bpy)_3]^{3+}$ and $\cdot MV^+$ (k_{rev}^{obs} = 2.80×10^9 $mol^{-1}\,dm^3\,s^{-1}$) at pH 2.2 (30 °C), while the former reaction (k_{rev}^{obs} = 5.85×10^9 $mol^{-1}\,dm^3\,s^{-1}$) proceeds 2-times as rapidly as the latter reaction (k_{rev}^{obs} = 2.74×10^9 $mol^{-1}\,dm^3\,s^{-1}$) at pH 5.0. These differences at pH 5.0 between MV^{2+} and $BCEBP^0$ are interpreted in terms of charge effects on the diffusion and diffusional dissociation of an exciplex and an encounter complex. The electron-transfer reactions in the exciplex and the encounter complex have been analyzed according to Marcus theory. The difference in an electronic coupling matrix element (H_{rp}) between MV^{2+} and $BCEBP^{2+\text{ or }0}$ is discussed in terms of the charge effects and steric effects.

Tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, has been actively investigated so far, because protons in water can be successfully photoreduced to hydrogen gas with this complex, as is well-known.[1—5] This photocatalytic reaction consists of many elementary steps: Namely, the photoexcitation of $[Ru(bpy)_3]^{2+}$ yields the metal-to-ligand charge-transfer triplet excited state (^{3}MLCT) of $[Ru(bpy)_3]^{2+}$ (the ^{3}MLCT excited state of $[Ru(bpy)_3]^{2+}$ is represented with $^*[Ru(bpy)_3]^{2+}$, hereafter), the deactivation of $^*[Ru(bpy)_3]^{2+}$; the formation of an encounter complex, charge separation, and back electron transfer.[1,6] Detailed knowledge of their reaction rates is of crucial importance for a good understanding of the photoinduced electron-transfer reaction of $[Ru(bpy)_3]^{2+}$ and finding an efficient photoenergy conversion system with $[Ru(bpy)_3]^{2+}$.

In order to effectively perform the photoreduction of MV^{2+}, several interesting attempts have been reported.[7—13] In those attempts, polyelectrolytes,[7,8] micelles,[9—11] bilayers,[12] and charged colloids[13] were employed to suppress back electron transfer and/or to accelerate the charge separation by a coulombic repulsion between one electron reduced viologen and the charged aggregate including the ruthenium(III) bipyridine complex. Although such a coulombic repulsion would suppress the oxidative quenching of a photoexcited ruthenium(II) bipyridine complex by viologen, the photoreduction of viologen was certainly accelerated in those attempts. This results suggests that the suppression of back electron transfer and/or the acceleration of charge separation occurs to a greater extent than does the suppression of oxidative quenching. However, the details are still ambiguous. In this regard, it is worth clarifying how elementary steps, such as encounter complex formation, charge separation, and back electron transfer are influenced by the columbic interaction.

Coulombic effects have been investigated in photoinduced electron-transfer reactions between phenotiazines and viologens[14] and between zinc porphyrin and methylviologen.[15] In the above-mentioned elementary processes of the photoinduced electron-transfer reaction between $[Ru(bpy)_3]^{2+}$ and viologens, however, coulombic effects were not investigated in detail, to our knowledge, whereas quenching and reverse electron-transfer reactions between $[Ru(bpy)_3]^{2+}$ and viologen have been investigated in detail in several studies.[16,17]

In the present work, photoinduced electron-transfer reactions of $[Ru(bpy)_3]^{2+}$ with methylviologen (MV^{2+}) and 1,1′-bis(2-carboxyethyl)-4,4′-bipyridinium ($BCEBP^{2+}$) were investigated at pH 2.2[18] and 5.0. Although BCEBP[19] is 2+ positively charged at pH 2.2, it is neutral at pH 5.0, since its pK_a is about 3.7, as described below. On the other hand, MV^{2+} has 2+ charges at both pH regions. We can thus expect to shed clear light on the charge effects by comparing the electron-transfer reactions between MV^{2+} and $BCEBP^{2+}$ at pH 2.2 and 5.0. We mainly performed here: (1) a measurement of the reaction rate constants of the quenching and reverse electron-transfer reactions, (2) estimated the reorganization energy (λ) and the electronic coupling matrix element (H_{rp}) based on Marcus theory,[20,21] and (3) investigated the charge effects in the quenching and reverse electron-transfer reactions and H_{rp}. The main purpose of this work was to clearly elucidate the origin of charge effects in photoinduced electron-transfer reaction between [Ru(bpy)$_3$]$^{2+}$ and viologen derivatives.

Experimental

[Ru(bpy)$_3$]Cl$_2$ was synthesized according to the literature[22] and its purity was ascertained by elemental analysis. Found: C, 49.31; H, 4.46; N, 11.51%. Calcd for $C_{30}H_{24}N_6Cl_2Ru{\cdot}5H_2O$: C, 49.32; H, 4.69; N, 11.50%. Differential thermal analysis clearly indicated that five water molecules were involved in the crystal.

1,1′-bis(2-carboxyethyl)-4,4′-bipyridinium dichloride, [BCEBP]Cl$_2$ was synthesized from 4,4′-bipyridine and acrylic acid in dry chloroform[23] and its purity was ascertained by elemental analysis. Found: C, 50.82; H, 4.94; N, 7.41%. Calcd for $C_{16}H_{18}N_2O_4Cl_2$: C, 51.48; H, 4.86; N, 7.50%. Commercially available methylviologen (Nakalai Tesque Co., Ltd. guaranteed reagent grade) was used without further purification.

The absorption spectra were measured with a spectrophotometer (Hitachi 150-20). The lifetime of *[Ru(bpy)$_3$]$^{2+}$ was measured with a time-resolved fluorometer (Horiba NAES-550) in which the decay of *[Ru(bpy)$_3$]$^{2+}$ was monitored at the emission maximum. The solution employed for the lifetime measurement was prepared by adding [Ru(bpy)$_3$]Cl$_2$ (1.0 or 0.5×10^{-5} mol dm^{-3}) and viologen (0.0—1.5×10^{-3} mol dm^{-3}) to a buffer solution (HCl/KCl for pH 2.2[18] and HOAc/NaOAc for pH 5.0), followed by deaeration through 5 cycles of freeze-pump-thaw, where the ionic strength was adjusted to 0.1 mol dm^{-3} with KCl.

One-electron-reduced viologen was produced when a solution involving [Ru(bpy)$_3$]$^{2+}$ and viologen was irradiated with 355 nm light from a pulsed Nd : YAG laser (Continuum NY-60). The absorption maximum of one-electron-reduced viologen (605 nm for MV^{2+} and 600 nm for BCEBP^{2+}) was monitored with a 150 W Xe-lamp, a monochrometer (JOBIN YVON H-20UV), a photomultiplier (Hamamatsu R955), and a digital oscilloscope (Philips PM3350A). The solution used for this reaction was prepared in the same way as described above, while concentrations of [Ru(bpy)$_3$]Cl$_2$ and viologen were different from the above; [Ru(bpy)$_3$]$^{2+}$ = 1.0—8.0×10^{-4} mol dm^{-3} and [viologen] = 1.0—4.0×10^{-3} mol dm^{-3}. Measurements were repeated 30—100 times for 3 to 5 solutions prepared independently.

The molar extinction coefficient (ε) of one-electron-reduced viologen was measured by monitoring the absorption maxima of viologen and its one-electron-reduced viologen radical, where iron powder was used to produce a one-electron-reduced viologen radical. The solution used for this measurement was deaerated by passing N$_2$ gas for 10 min. The determined ε is 11000 cm^{-1} mol^{-1} dm^3 ($\lambda_{\max}$ = 605 nm) for ·MV$^+$ and 13500 cm^{-1} mol^{-1} dm^3 ($\lambda_{\max}$ = 600 nm) for ·BCEBP$^-$ at pH 5.0.

pK_a of BCEBP^{2+} was spectroscopically determined to be 3.7, where the shift of $\lambda_{\max}$ was plotted against pH. From this result, BCEBP is considered to be neutral at pH 5.0.

Results and Discussion

Quenching of ^{3}MLCT-Excited *[Ru(bpy)$_3$]$^{2+}$. The quenching reaction of *[Ru(bpy)$_3$]$^{2+}$ was carried out at both pH 2.2 and 5.0[18] with MV^{2+} and BCEBP,[19] where the excited-state lifetime (τ) was measured as a function of the concentration of MV^{2+} and BCEBP.[24] As shown in Fig. 1, a plot of τ_0/τ vs. the quencher concentration yields a good linear relation, as expected from the Stern–Volmer relationship, where τ represents the lifetime and subscript "0" represents the absence of a quencher.

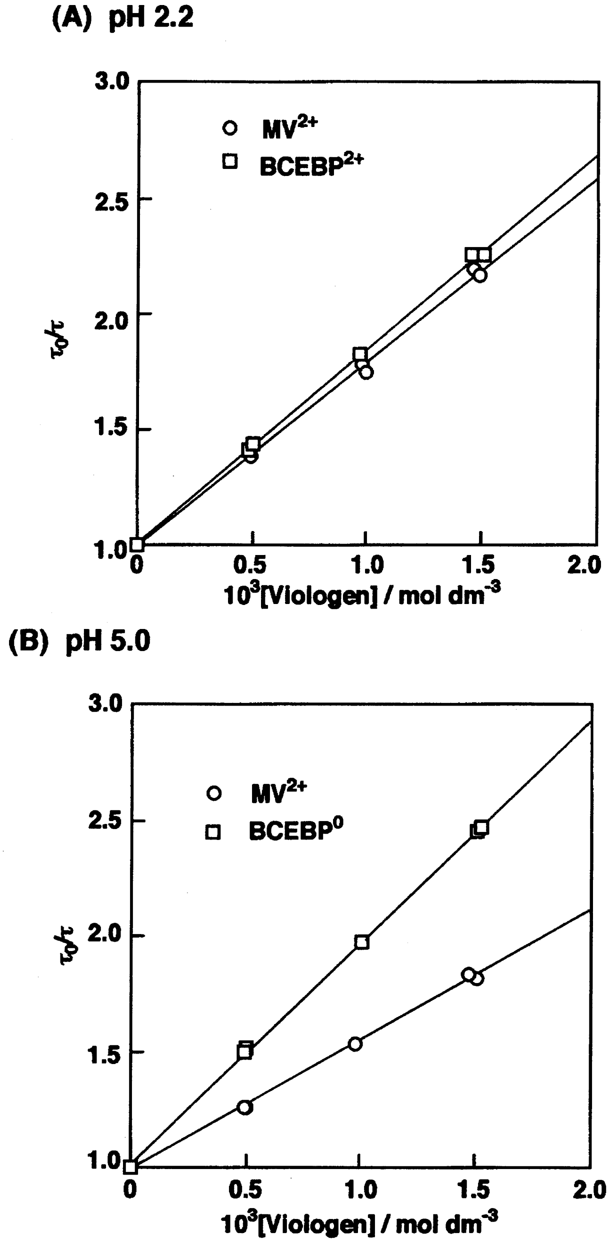


Fig. 1. τ_0/τ of [Ru(bpy)$_3$]$^{2+}$ vs. concentration of methylviologen (MV^{2+}) or 1,1′-bis(2-carboxyethyl)-4,4′-bipyridinium (BCEBP). (A) HCl/KCl buffer at pH 2.2 (μ = 0.1), (B) HOAc/NaOAc buffer at pH 5.0 (μ = 0.1).

At pH 2.2, the Stern–Volmer relation for MV^{2+} coincides well with that for BCEBP^{2+} (Fig. 1A), and the quenching rate constant ($k_q^{\rm obs}$) of MV^{2+} is almost the same as that of BCEBP^{2+} (Table 1). On the other hand, the Stern–Volmer relation is very different between MV^{2+} and BCEBP^0 at pH 5.0 (Fig. 1B), and $k_q^{\rm obs}$ of MV^{2+} is much smaller than that of BCEBP^0.

Although MV^{2+} is positively charged at both pH 2.2 and 5.0, BCEBP^0 is neutral at pH 5.0, since pK_a of BCEBP is 3.7. Thus, the $k_q^{\rm obs}$ difference observed at pH 5.0 between MV^{2+} and BCEBP^0 can be attributed to the charge difference between MV^{2+} and BCEBP^0, as is discussed below in detail.

Table 1. Quenching Reaction Rate Constant k_q^{obs} of Excited State of $[Ru(bpy)_3]^{2+}$ with Methylviologen (MV^{2+}) and 1,1′-Bis(2-carboxyethyl)-4,4′-bipyridinium ($BCEBP^{2+}$) at pH 2.2 and 5.0[a)]

	$10^{-9}\ k_q^{obs}/mol^{-1}\ dm^3\ s^{-1}$	
	pH 2.2	5.0
MV^{2+}	1.48 ± 0.04	1.01 ± 0.02
BCEBP	1.58 ± 0.02	1.75 ± 0.03

a) at 30 °C.

All of the k_q^{obs} values are in the range 1.0—1.8×10^9 $mol\ dm^{-3}\ s^{-1}$. Since these k_q^{obs} values are near to the diffusion rate constant, we must correct k_q^{obs} by taking into consideration the diffusion rate constant. If the overall quenching process is separated into diffusional steps and an electron-transfer step, as shown in Eq. 1, the observed quenching rate constant (k_q^{obs}) is given by Eq. 2 through an approximation

$$^*[Ru(bpy)_3]^{2+} + V_{oxid} \xrightleftharpoons[k^q_{-dif}]{k^q_{dif}} [^*Ru(bpy)_3^{2+} \cdots V_{oxid}] \xrightarrow{k_q^{cor}} [Ru(bpy)_3^{3+} \cdots \bullet V_{red}] \quad (1)$$

of the steady-state concentration of the exciplex $[^*Ru(bpy)_3^{2+} \cdots V_{oxid}]$,[25)] where k^q_{dif} and k^q_{-dif} are the diffusion rate constant for the exciplex formation and the diffusional dissociation rate constant of the exciplex, respectively.

$$k_q^{obs} = \frac{k^q_{dif}\, k_q^{cor}}{k^q_{-dif} + k_q^{cor}}. \quad (2)$$

According to Debye–Smoluchowski, the diffusion rate constant (k_{dif}) of a charged particle was estimated using Eq. 3a.[26)] The diffusional dissociation rate constant (k_{-dif}) was given by Eq. 3b, considering Eigen's treatment of the diffusional dissociation of the encounter complex.[27)] Although several different expressions were reported for $\omega(r,\mu)$,[26,28)] we adopted here Eq. 3c, according to Chiorboli et al.,[26)] since they applied this equation to estimating the diffusion rate constant in the oxidative quenching of $^*[Ru(bpy)_3]^{2+}$ by MV^{2+};

$$k_{dif} = \frac{2k_BTN}{3000\eta}\left(2 + \frac{r_A}{r_B} + \frac{r_B}{r_A}\right)\frac{1}{\alpha \int_\alpha^\infty r^{-2}\exp[\omega(r,\mu)/k_BT]dr}, \quad (3a)$$

$$k_{-dif} = \frac{k_BT}{2\pi\eta}\frac{1}{\alpha^2}\left(\frac{1}{r_B} + \frac{1}{r_A}\right)\frac{\exp[\omega(r,\mu)/k_BT]}{\alpha \int_\alpha^\infty r^{-2}\exp[\omega(r,\mu)/k_BT]dr}, \quad (3b)$$

$$\omega(r,\mu) = \frac{Z_AZ_B}{2Dr}\left(\frac{\exp(\beta\sigma_A\sqrt{\mu})}{1+\beta\sigma_A\sqrt{\mu}} + \frac{\exp(\beta\sigma_B\sqrt{\mu})}{1+\beta\sigma_B\sqrt{\mu}}\right)\exp(-\beta r\sqrt{\mu}), \quad (3c)$$

$$\beta = \{8\pi Ne^2/(1000Dk_BT)\}^{1/2}, \quad (3d)$$

where A and B represent $^*[Ru(bpy)_3]^{2+}$ and viologen, respectively, α is the sum of r_A (diameter of $[Ru(bpy)_3]^{2+}$) and r_B (diameter of quencher), σ_A is the sum of the diameters of $[Ru(bpy)_3]^{2+}$ and a dominant counter ion, and μ is the ionic strength. To estimate k_{dif} and k_{-dif} using Eq. 3, we need values of r_A, r_B, η (biscosity of solvent), and D (dielectric constant of solvent). r_A and r_B were estimated using the following approximation in the usual way;[29)]

$$r = (d_xd_yd_z)^{1/3},$$

where d_x, d_y, and d_z are the diameters of the molecule along the x, y, and z axes, respectively, which were evaluated by the MM2 calculation.[30)] The r_A value was estimated to be 7.1 Å[31)] and the r_B value was 3.6 Å for MV^{2+}, 4.56 Å for $BCEBP^{2+}$ (at pH 2.2), and 4.44 Å for $BCEBP^0$ (at pH 5.0). The molecular size of BCEBP depends on the pH, since BCEBP takes a zwitter ion form at pH 5.0 (vide infra), but a dication form at pH 2.2. The values of η and D were taken from Refs. 29 and 32 (see Ref. 33 for their values).

Several approximations for a k_{dif} estimation have been reported. For instance, k_{dif} is approximately represented by considering the Brønsted–Bjerrum ionic strength dependence, as follows:[27)]

$$k_{dif} = k_{dif}(\mu = 0)\exp\left(\frac{\omega(\alpha,0)}{k_BT} + \frac{\beta\alpha\sqrt{\mu}}{1+\beta\alpha\sqrt{\mu}}\right), \quad (4a)$$

$$k_{dif}(\mu = 0) = \frac{2k_BTN}{3000\eta}\left(2 + \frac{r_A}{r_B} + \frac{r_B}{r_A}\right)\frac{\omega(\alpha,0)/k_BT}{\exp[\omega(\alpha,0)/k_BT] - 1}. \quad (4b)$$

In this case, k_{-dif} is given by Eq. 4c through the well-known Fuoss equation (Eq. 4d), which represents the stability of an ion-pair adduct:[34)]

$$k_{-dif} = \frac{k_BT}{2\pi\eta}\frac{1}{\alpha^2}\left(\frac{1}{r_A} + \frac{1}{r_B}\right)\frac{\omega(\alpha,0)/k_BT}{1 - \exp[-\omega(\alpha,0)/k_BT]}, \quad (4c)$$

$$K = \frac{k_{dif}}{k_{-dif}} = \frac{4\pi N\alpha^3}{3000}\exp[-\omega(\alpha,\mu)/k_BT], \quad (4d)$$

$$\omega(\alpha,0) = (Z_AZ_Be^2/D\alpha). \quad (4e)$$

Also, the empirical Eq. 5a was proposed for k_{dif}, where k_{-dif} is given by Eq. 5b through Eq. 4d:

$$k_{dif} = \frac{2k_BTN}{3000\eta}\left(2 + \frac{r_A}{r_B} + \frac{r_B}{r_A}\right)\frac{\omega(\alpha,\mu)/k_BT}{\exp[\omega(\alpha,\mu)/k_BT] - 1}, \quad (5a)$$

$$k_{-dif} = \frac{k_BT}{2\pi\eta}\frac{1}{\alpha^2}\left(\frac{1}{r_A} + \frac{1}{r_B}\right)\frac{\omega(\alpha,\mu)/k_BT}{1 - \exp[-\omega(\alpha,\mu)/k_BT]}. \quad (5b)$$

In our work, we numerically integrated Eq. 3a over the range of $r = (r_A + r_B)$ to 10000 Å, instead of using Eqs. 4 and 5. However, the k_{dif} and k_{-dif} values estimated using Eqs. 4 and 5 are also given in Table 2, to compare Eq. 3 with Eqs. 4 and 5. Although k_q^{cor} of BCEBP is almost the same in all of these equations, k_q^{cor} of MV^{2+} and $BCEBP^{2+}$ increase in the order Eq. 3<Eq. 4<Eq. 5,[35)] as shown in Table 2. Thus, we adopted Eq. 3 here.

Since the diffusion rate constant (6.6—6.7×10^9 $mol^{-1}\ dm^3\ s^{-1}$; see Table 2) is much larger than the deactivation rate constant of $^*[Ru(bpy)_3]^{2+}$ ($k_{deact} = 1.86 \times 10^6\ s^{-1}$ at 30 °C), $^*[Ru(bpy)_3]^{2+}$ can collide and form an adduct with viologen before deactivation. This means that the quenching reaction proceeds through an exciplex formation, as shown in Eq. 1.

Using these k^q_{dif} and k^q_{-dif} values, the rate constant (k_q^{cor}) of electron transfer in the exciplex was estimated according

Table 2. Diffusion Rate Constant (k^{q}_{dif}), Diffusional Dissociation Rate Constant (k^{cor}_{-dif}), and Quenching Rate Constants (k^{cor}_{q}) with the Correction of Diffusion Rate[a)]

	$10^{-9}\ k^{q}_{dif}/mol^{-1}\ dm^{3}\ s^{-1}$		$10^{-9}\ k^{q}_{-dif}/s^{-1}$		$10^{-9}\ k^{cor}_{q}/s^{-1}$	
	pH 2.2	pH 5.0	pH 2.2	pH 5.0	pH 2.2	pH 5.0
Eq. 3						
MV^{2+}	6.59	6.51	6.15	6.26	1.78±0.06	1.15±0.03
BCEBP	6.64	8.91	4.09	2.30	1.28±0.02	0.556±0.011
Eq. 4						
MV^{2+}	5.25	5.16	4.91	4.97	1.92±0.07	1.21±0.03
BCEBP	5.42	8.86	3.34	2.28	1.37±0.03	0.557±0.011
Eq. 5						
MV^{2+}	7.62	7.62	8.68	8.68	2.09±0.07	1.33±0.03
BCEBP	7.81	8.86	5.92	2.28	1.50±0.03	0.557±0.011

a) 30 °C.

to Eq. 2. Interestingly, k^{cor}_{q} of MV^{2+} is larger than that of BCEBP at both pH 2.2 and 5.0, independent of the viologen's charge. Since the redox potential of MV^{2+} is more negative than that of $BCEBP^{2+}$ at both pHs,[36)] the redox potential is not responsible for the larger k^{cor}_{q} of MV^{2+}. Thus, we need to investigate the electron transfer in the exciplex, based on Marcus theory.[20,21)]

Analysis of Electron-Transfer Reaction in the Exciplex by Marcus Theory. According to Marcus theory,[20,21)] the rate constant of the electron-transfer reaction is given by Eq. 6:

$$k = \frac{2\pi}{\hbar}\frac{H_{rp}^{2}}{(4\pi k_{B}T\lambda)^{1/2}}\exp\left[-\frac{(\Delta G^{\circ}+\lambda)^{2}}{4\lambda k_{B}T}\right], \tag{6}$$

where H_{rp} is the electronic coupling matrix element, λ is the reorganization energy, and ΔG° is the Gibbs energy change. From this equation, the following Eq. 7 is easily obtained:

$$\ln(T^{1/2}\ k) = \ln\frac{2\pi}{\hbar}\frac{H_{rp}^{2}}{(4\pi k_{B}\lambda)^{1/2}} - \frac{(\Delta G^{\circ}+\lambda)^{2}}{4\lambda k_{B}T}. \tag{7}$$

This Eq. 7 indicates that a linear relationship must exist between $\ln(T^{1/2}\ k)$ and $1/T$.[37)] Actually, the linear relation is experimentally obtained between $\ln(T^{1/2}\ k^{cor}_{q})$ and $1/T$, as shown in Fig. 2. From its intercept and slope, one can estimate H_{rp} and λ, using the experimentally measured ΔG° value: ΔG° is −0.19 eV at pH 2.2 and −0.18 eV at pH 5.0 when the quencher is MV^{2+}, and −0.28 eV at pH 2.2 and −0.19 eV at pH 5.0 when the quencher is BCEBP, where the redox potential of $^{*}[Ru(bpy)_3]^{2+}$ was taken to be −0.84 eV.[38)] These experimentally estimated λ and H_{rp} are listed in Table 3.

The most important result to be noted is that H_{rp} of BCEBP is similar to that of MV^{2+} at pH 2.2, but much smaller than that of MV^{2+} at pH 5.0. This is a main reason that k^{cor}_{q} of BCEBP is similar to that of MV^{2+} at pH 2.2, but much smaller than that of MV^{2+} at pH 5.0, since the other term, $(1/\lambda)^{1/2}\exp\{-(\Delta G^{\circ}+\lambda)^{2}/(4\lambda k_{B}T)\}$, of $BCEBP^{2+\ or\ 0}$ is similar to that of MV^{2+} at pH 2.2, but much larger than that of MV^{2+} at pH 5.0. The H_{rp} difference at pH 5.0 between MV^{2+} and $BCEBP^{0}$ is easily interpreted in terms of the structure of BCEBP. Since pK_a of BCEBP is 3.7, $BCEBP^{2+}$ has 2+ positive charges at pH 2.2, like MV^{2+}; therefore, the geometry of $BCEBP^{2+}$ is considered to be similar to that of MV^{2+}, except for the $-CH_2CH_2COOH$ groups of $BCEBP^{2+}$, as shown in Fig. 3. Here, we should remember that the 4,4′-bipyridinium moiety must approach the bpy ligand to cause an electron transfer from $^{*}[Ru(bpy)_3]^{2+}$ to viologen. Since the 4,4′-bipyridinium moiety of $BCEBP^{2+}$ is similar to MV^{2+} at pH 2.2, $BCEBP^{2+}$ can approach bpy to a similar extent to MV^{2+}, which leads to a similar H_{rp} value in MV^{2+} and $BCEBP^{2+}$ at this pH.[39)]

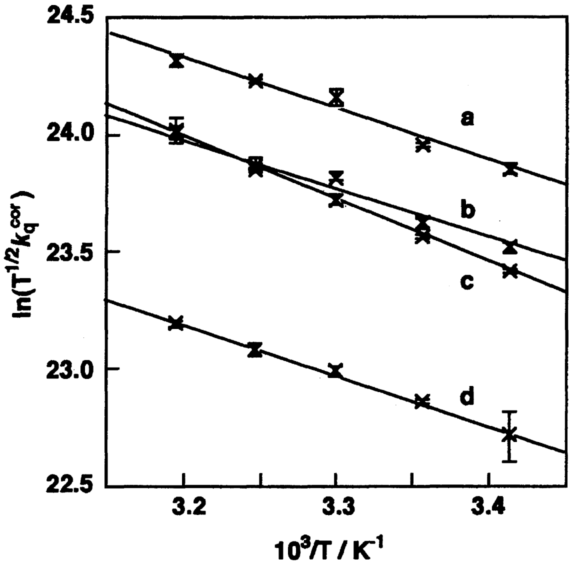
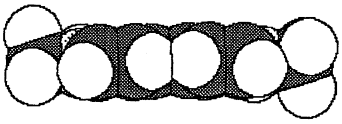


Fig. 2. $\ln(T^{1/2}\ k^{cor}_{q})$ vs. $1/T$, where k^{cor}_{q} is the electron-transfer rate constant in the exciplex after the correction of diffusion rate. (a) MV^{2+} at pH 2.2, (b) $BCEBP^{2+}$ at pH 2.2, (c) MV^{2+} at pH 5.0, (d) $BCEBP^{0}$ at pH 5.0.

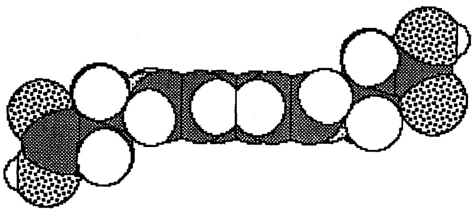
However, a completely different situation appears when the pH changes to pH 5.0 from 2.2. Since deprotonation of carboxylic acid occurs at pH 3.7, BCEBP becomes neutral at pH 5.0. Thus, we might expect that neutral BCEBP more closely approaches $[Ru(bpy)_3]^{2+}$ than does MV^{2+}, because of the absence of a coulombic repulsion. This would lead

Table 3. Electron Coupling Matrix Element (H_{rp}) and Reorganization Energy (λ), ΔG°, and $(1/\lambda)^{1/2}\exp[-(\Delta G^\circ+\lambda)^2/4\lambda k_BT]$[a)]

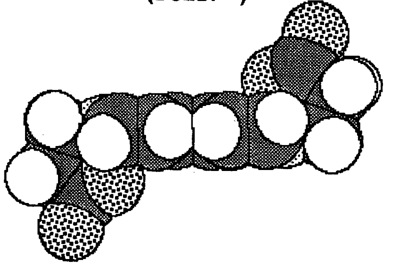
	pH 2.2		pH 5.0	
	MV^{2+}	$BCEBP^{2+}$	MV^{2+}	$BCEBP^0$
(a) Quenching reaction				
H_{rp}/eV	0.012	0.012	0.027	0.0064
λ/eV	1.1	1.3	1.3	1.1
ΔG°/eV	−0.19	−0.28	−0.18	−0.19
$(\Delta G^\circ+\lambda)$/eV	0.91	1.00	1.10	0.91
$(1/\lambda)^{1/2}\exp[-(\Delta G^\circ+\lambda)^2/(4\lambda k_BT)]/eV^{1/2}$	6.3×10^{-4}	3.6×10^{-4}	7.3×10^{-5}	6.3×10^{-4}
(b) Reverse electron-transfer reaction				
H_{rp}/eV	0.023	0.016	0.018	0.0091
λ/eV	0.87	0.84	0.89	0.90
ΔG°/eV	−1.72	−1.64	−1.72	−1.70
$(\Delta G^\circ+\lambda)$/eV	−0.83	−0.76	−0.81	−0.80
$(1/\lambda)^{1/2}\exp[-(\Delta G^\circ+\lambda)^2/(4\lambda k_BT)]/eV^{1/2}$	4.8×10^{-4}	1.4×10^{-3}	8.1×10^{-4}	1.0×10^{-3}



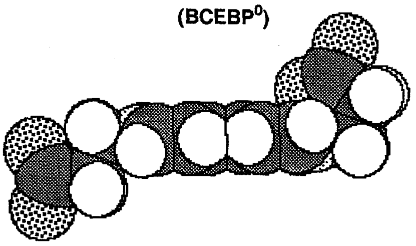
(A) Methylviologen (MV^{2+})



(B) Protonated 1,1′-Bis(2-carboxyethyl)-4,4′-bipyridine ($BCEBP^{2+}$)



(C) Deprotonated 1,1′-Bis(2-carboxyethyl)-4,4′-bipyridine ($BCEBP^0$)



(D) One-electron reduced 1,1′-Bis(2-carboxyethyl)-4,4′-bipyridine (·$BCEBP^-$)

Fig. 3. CPK models of MV^{2+} and $BCEBP^{2+,0,\text{or}\,-}$.

to the larger H_{rp} of $BCEBP^0$ than that of MV^{2+}. However, the H_{rp} value of $BCEBP^0$ is much smaller than that of MV^{2+} (vide supra), against the above expectation. One plausible reason for the small H_{rp} value is a steric repulsion. Since the deprotonated BCEBP involves positively charged quarterly ammonium cation moieties and negatively charged carboxylato groups, BCEBP would take a zwitter ion form, in which the deprotonated carboxylato group takes a position near to the bipyridinium plane due to the coulombic attraction (Fig. 3C). This form would suppress the approach of $BCEBP^0$ to bpy through a steric repulsion by the $-CH_2CH_2COO^-$ moieties. As a result, H_{rp} of $BCEBP^0$ becomes much smaller than that of MV^{2+} at pH 5.0. From the above discussion, it should be concluded here that although the steric effect is a determining factor for H_{rp}, the charge of viologen little influences H_{rp}, against the expectation that neutral $BCEBP^0$ more easily approaches $^*[Ru(bpy)_3]^{2+}$ in the exciplex than does MV^{2+}.

Charge Effects in a Quenching Reaction. We have now completed all preparations for discussing the charge effects in the quenching reaction. At pH 2.2, both MV^{2+} and $BCEBP^{2+}$ have a 2+ charge; therefore, the diffusion rate constant (k^q_{dif}) is similar in MV^{2+} and $BCEBP^{2+}$. The diffusional dissociation rate constant (k^q_{-dif}) of the exciplex of $BCEBP^{2+}$ is slightly smaller than that of MV^{2+}, probably because the molecular size of $BCEBP^{2+}$ is slightly larger than that of MV^{2+}. Though k^{cor}_q of $BCEBP^{2+}$ is slightly smaller than that of MV^{2+}, the smaller k^q_{-dif} of $BCEBP^{2+}$ mostly compensates for the smaller k^{cor}_q. As a result, the quenching reaction occurs with a similar rate constant in these two viologens.

At pH 5.0, $BCEBP^0$ is neutral, unlike MV^{2+}. As a result, the diffusion rate constant (k^q_{dif}) of $BCEBP^0$ is 1.4-times as large as that of MV^{2+}, and the diffusional dissociation rate constant (k^q_{-dif}) of $BCEBP^0$ is about one-third k^q_{-dif} of MV^{2+}. Although k^{cor}_q of $BCEBP^0$ is about one-half k^{cor}_q of MV^{2+}, the larger k^q_{dif} and the smaller k^q_{-dif} of $BCEBP^0$ lead to a larger k^{obs}_q of $BCEBP^0$ than that of MV^{2+}. Thus, although

k_q^{cor} little influences the overall quenching reaction rate, the diffusion and diffusional dissociation are responsible for the more rapid quenching of *[Ru(bpy)$_3$]$^{2+}$ by BCEBP than that by MV^{2+}.

In conclusion, there is no need to consider the charge effects on the electron transfer in the exciplex. This is because H_{rp} depends not on the charge of viologen, but on the steric factor. Thus, the charge effects must be taken into consideration in diffusion and diffusional dissociation; therefore, charge effects on the quenching reaction might be easily predicted by an intuitive consideration of the coulombic interaction on diffusion and diffusional dissociation.

Reverse Electron-Transfer Reaction between [Ru(bpy)$_3$]$^{3+}$ and One-Electron-Reduced Viologen. When a solution of [Ru(bpy)$_3$]$^{2+}$ and viologen is irradiated with pulsed light of 355 nm, a one-electron-reduced viologen radical (•V$_{red}$) is transiently produced. •V$_{red}$ rapidly reacts with one-electron-oxidized [Ru(bpy)$_3$]$^{3+}$ to yield [Ru(bpy)$_3$]$^{2+}$ and viologen, as shown in Fig. 4. This reverse electron-transfer reaction proceeds through an intermediate [Ru(bpy)$_3^{3+}$···•V$_{red}$], as shown in Eq. 8.

$$[\mathrm{Ru(bpy)_3}]^{3+} + \cdot\mathrm{V_{red}} \rightarrow [\mathrm{Ru(bpy)_3^{3+}}\cdots\cdot\mathrm{V_{red}}] \rightarrow [\mathrm{Ru(bpy)_3}]^{2+} + \mathrm{V_{oxid}}. \qquad (8)$$

This intermediate is considered to be the same as the encounter complex formed through a one-electron-transfer in the exciplex [*Ru(bpy)$_3^{2+}$···V$_{oxid}$] (see Eq. 1). Thus, an investigation of the reverse electron-transfer reaction provides knowledge about how the coulombic interaction influences the charge separation.

Since the reverse of the absorbance at λ_{max} of •V$_{red}$ is linearly dependent on the reaction time (Fig. 4), the rate constant (k_{rev}^{obs}) of this reaction is obtained by multiplying the slope by the molecular extinction coefficient of the reduced viologen, where the subscript "rev" represents the reverse electron-transfer reaction. These k_{rev}^{obs} values are given in Table 4. k_{rev}^{obs} of •BCEBP is slightly larger than that of •MV$^+$ at pH 2.2, but much larger than that of •MV$^+$ at pH 5.0, where •BCEBP without a superscript is a general representation for protonated •BCEBP$^+$ (at pH 2.2) and deprotonated •BCEBP$^-$ (at pH 5.5). The large k_{rev}^{obs} of •BCEBP$^-$ at pH 5.0 would be attributed to charge effects, as follows: one-electron-reduced •BCEBP$^-$ is negatively charged at pH 5.0, since the carboxyl group is deprotonated at this pH. On the other hand, one-electron-reduced •MV$^+$ is still positively charged at pH 5.0. Thus, •BCEBP$^-$ more easily approaches [Ru(bpy)$_3$]$^{3+}$ at this pH than does •MV$^+$ due to the coulombic attraction. We examine this difference in more detail below.

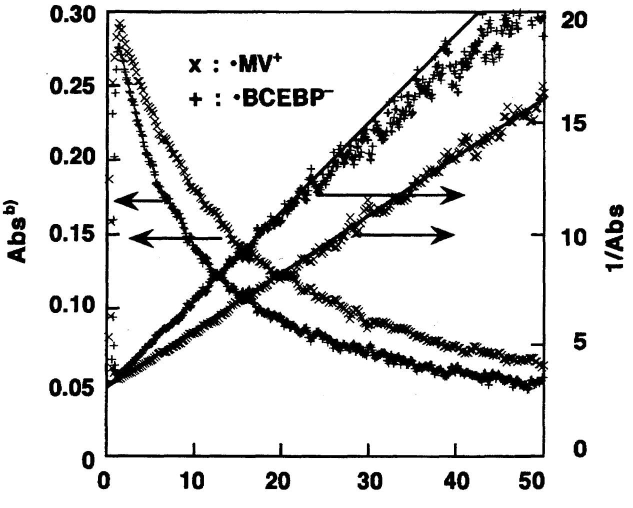


Fig. 4. Decay curves of reduced •MV$^+$ and •BCEBP$^-$ generated by laser flash photolysis of [Ru(bpy)$_3$]$^{2+}$.$^{a)}$
a) HOAc/NaOAc buffer (pH 5.0, $\mu = 0.1$) at 30 °C.
b) Absorbance at 605 nm for •MV$^+$ and 600 nm for •BCEBP$^-$.

Since k_{rev}^{obs} of 3—6×10^9 mol^{-1} dm^3 s^{-1} is similar to the diffusion rate constant, we need to take into consideration the diffusion rate constant in our discussion. As done for k_q^{obs}, the reverse electron-transfer is separated into diffusional steps and an electron transfer step in the encounter complex (see Eq. 9). The diffusional rate constants, k_{dif}^{rev} and k_{-dif}^{rev}, were evaluated using Eq. 3 for the reaction between [Ru(bpy)$_3$]$^{3+}$ and one-electron-reduced viologen, •MV$^+$ and •BCEBP. Then, the rate constant (k_{rev}^{cor}) for electron transfer

$$[\mathrm{Ru(bpy)_3}]^{3+} + \cdot\mathrm{V_{red}} \underset{k_{-dif}^{rev}}{\overset{k_{dif}^{rev}}{\rightleftharpoons}} [\mathrm{Ru(bpy)_3^{3+}}\cdots\cdot\mathrm{V_{red}}] \xrightarrow{k_{rev}^{cor}} [\mathrm{Ru(bpy)_3^{2+}}\cdots\mathrm{V_{oxid}}] \qquad (9)$$

in the encounter complex was estimated using Eq. 10. These rate constants are summarized in Table 4.

$$k_{rev}^{obs} = \frac{k_{dif}^{rev}\,k_{rev}^{cor}}{k_{-dif}^{rev} + k_{rev}^{cor}}. \qquad (10)$$

At pH 5.0, k_{rev}^{cor} of •BCEBP$^-$ is about one half k_{rev}^{cor} of •MV$^+$. However, the diffusion rate constant (k_{dif}^{rev}) of •BCEBP$^-$ is 1.4-times as large as that of •MV$^+$, and the diffusional dissociation rate constant (k_{-dif}^{rev}) of •MV$^+$ is about 4-times as large as that of •BCEBP$^-$. As a result, k_{rev}^{obs} of •BCEBP$^-$ is larger than that of •MV$^+$ at pH 5.0. The large k_{dif}^{rev} and the small k_{-dif}^{rev} of •BCEBP$^-$ arise from the coulombic attraction between the positively charged [Ru(bpy)$_3$]$^{3+}$ and the negatively charged •BCEBP$^-$.

At pH 2.2, the diffusion rate constant (k_{dif}^{rev}) of •BCEBP$^+$ is similar to that of •MV$^+$. However, the electron-transfer rate constant (k_{rev}^{cor}) in the encounter complex, [Ru(bpy)$_3^{3+}$···•BCEBP$^+$], is slightly smaller than that of [Ru(bpy)$_3^{3+}$···•MV$^+$] and the diffusional dissociation rate constant (k_{-dif}^{rev}) of [Ru(bpy)$_3^{3+}$···•MV$^+$] is slightly larger than that of [Ru(bpy)$_2^{3+}$···•BCEBP$^+$]. Thus, the slightly larger k_{rev}^{obs} of •BCEBP$^+$ at pH 2.2 is attributed to the smaller k_{-dif}^{rev} of •BCEBP$^+$, while it is mostly compensated by the slightly larger k_{rev}^{cor} value. It should be noted that the differences in diffusional rate constants, k_{dif}^{rev} and k_{-dif}^{rev}, between •BCEBP and •MV$^+$ are much smaller at pH 2.2 than those at pH 5.0. This is because both one-electron-reduced •MV$^+$ and •BCEBP$^+$ are positively charged at pH 2.2.

Analysis of Electron-Transfer Reaction in the En-

Table 4. Rate Constant for the Reverse Electron-Transfer Reaction (k^{obs}_{rev}), Diffusion Rate Constant (k^{rev}_{dif}), Dissociation Rate Constant (k^{rev}_{-dif}) of Encounter Complex, and Reverse Electron-Transfer Rate Constant (k^{cor}_{rev}) with the Correction of Diffusion Rate[a)]

	$10^{-9}\ k^{obs}_{rev}$/mol^{-1} dm^3 s^{-1}		$10^{-9}\ k^{rev}_{dif}$/mol^{-1} dm^3 s^{-1}		$10^{-9}\ k^{rev}_{-dif}$/s^{-1}		$10^{-9}\ k^{cor}_{rev}$/s^{-1}	
	2.2	5.0	2.2	5.0	2.2	5.0	2.2	5.0
·MV$^+$	2.80±0.14	2.74±0.05	7.45	7.49	5.34	5.49	3.23±0.24	3.17±0.10
·BCEBP$^{+\ \mathrm{or}\ -}$	3.33±0.22	5.85±0.28	7.39	10.8	3.65	1.38	2.74±0.36	1.64±0.17

a) at 30 °C.

counter Complex by Marcus Theory. We consider here k^{cor}_{rev}, based on Marcus theory, in order to clarify how much the charge of viologen influences k^{cor}_{rev}. A good linear relationship between $\ln(T^{1/2}\ k^{cor}_{rev})$ and $1/T$ was obtained, as shown in Fig. 5. The reorganization energy (λ) and electronic coupling matrix element (H^{rev}_{rp}) were evaluated from the slope and the intercept,[37)] where $\Delta G°$ was estimated with redox potentials of [Ru(bpy)$_3$]$^{2+}$ and viologens (see Table 4 for $\Delta G°$). At pH 5.0, it is noted that k^{cor}_{rev} of ·BCEBP$^-$ is much smaller than that of MV^{2+}. The $(1/\lambda)^{1/2}\exp[-(\Delta G°+\lambda)^2/(4\lambda k_B T)]$ term of ·BCEBP$^-$ is larger than that of ·MV$^+$, but H_{rp} of ·BCEBP$^-$ is about one half H_{rp} of ·MV$^+$ (Table 3). Thus, the smaller H^{rev}_{rp} of ·BCEBP$^-$ is responsible for the smaller k^{cor}_{rev} of ·BCEBP than that of ·MV$^+$. Although ·BCEBP$^-$ is expected to easily approach [Ru(bpy)$_3$]$^{3+}$ because of coulombic attraction, H^{rev}_{rp} of ·BCEBP$^-$ is much smaller than that of ·MV$^+$, unexpectedly. Thus, the reason for the very small H^{rev}_{rp} of ·BCEBP$^-$ is worthy of discussion. Again, it is easily interpreted in terms of the zwitter ion form of ·BCEBP$^-$ at pH 5.0, as follows: Even in the one-electron-reduced ·BCEBP$^-$, one pyridinium moiety is still positively charged, and interacts with the anionic carboxylato group to take a zwitter-ion form (see Fig. 3D). This $-CH_2CH_2COO^-$ moiety suppresses the approach of ·BCEBP$^-$ to the bpy plane of [Ru(bpy)$_3$]$^{3+}$, because of the steric repulsion. On the other hand, ·MV$^+$ can easily approach [Ru(bpy)$_3$]$^{3+}$, because of the lack of the

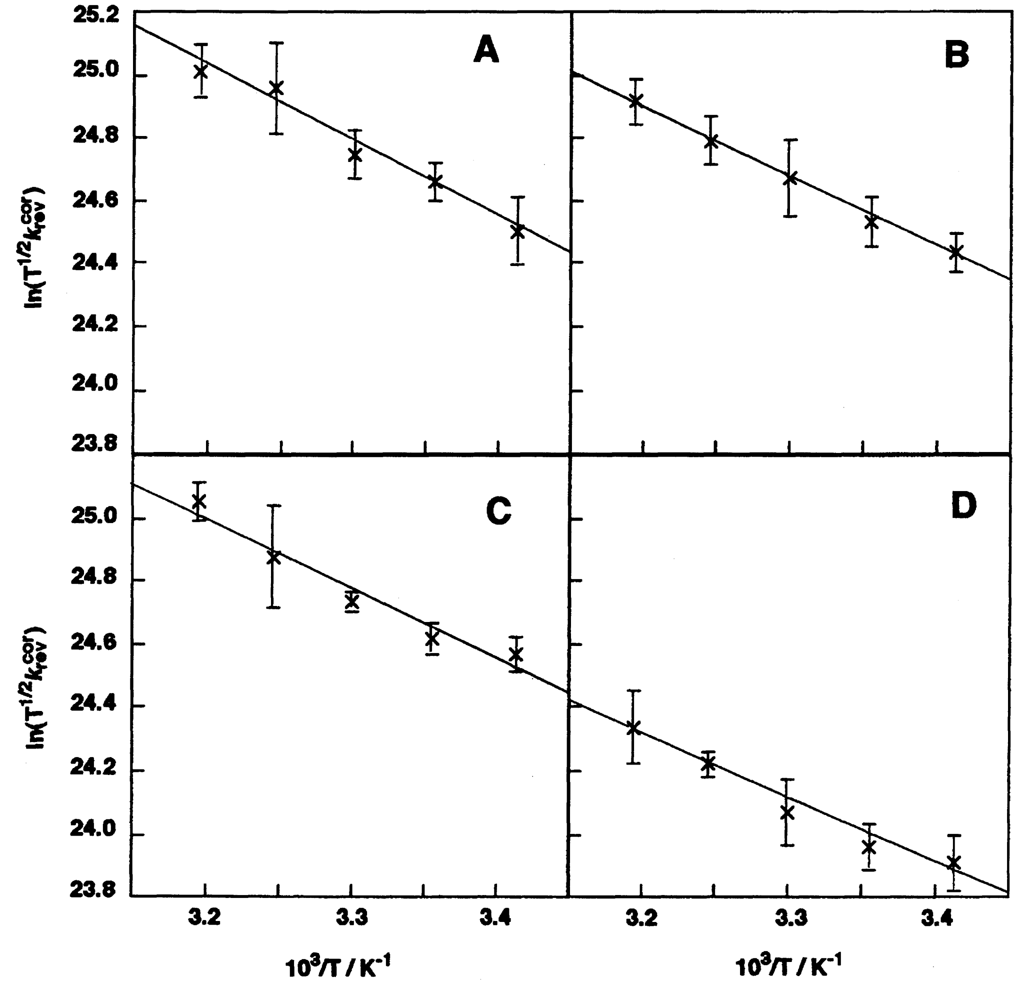


Fig. 5. $\ln(T^{1/2}\ k^{cor}_{rev})$ vs. $1/T$, where k^{cor}_{rev} is the reverse electron-transfer rate constant in the encounter complex after the correction of diffusion rate. a) MV^{2+} at pH 2.2, (b) BCEBP^{2+} at pH 2.2, (c) MV^{2+} at pH 5.0, (d) BCEBP^0 at pH 5.0.

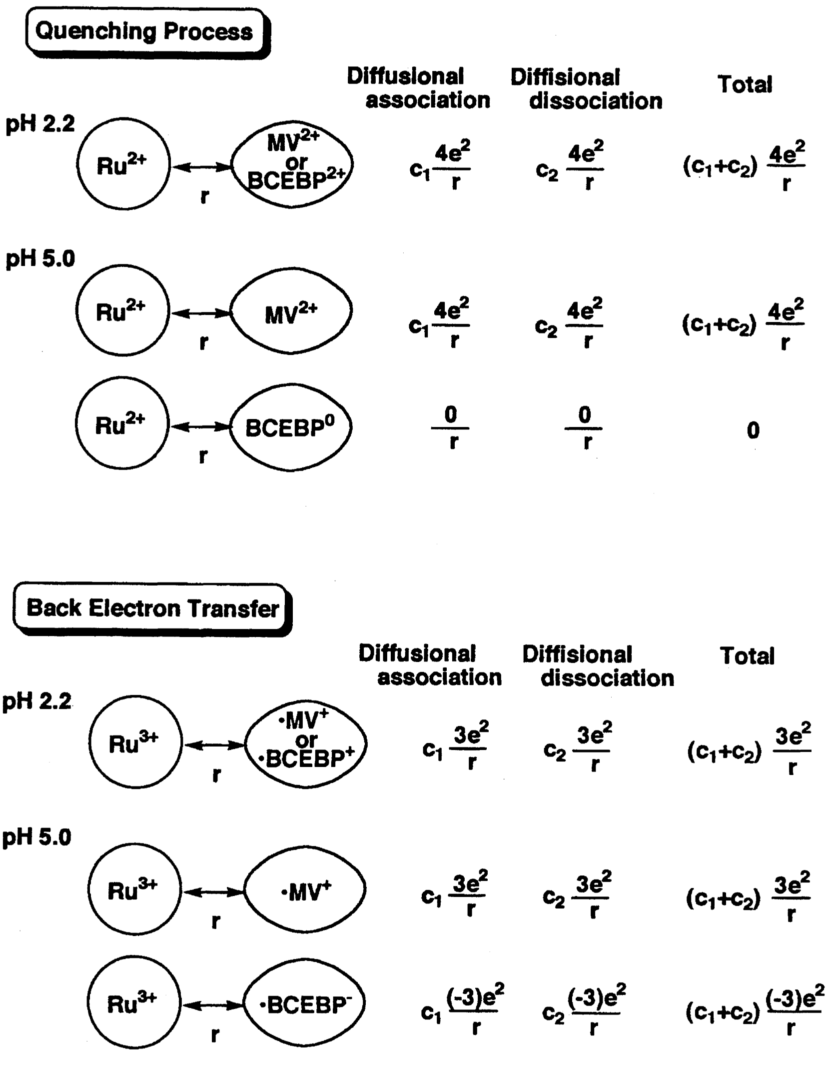
$-CH_2CH_2COO^-$ moieties. Thus, H_{rp}^{rev} of $\cdot BCEBP^-$ is much smaller than that of $\cdot MV^+$.

At pH 2.2, k_{rev}^{cor} of $\cdot BCEBP^+$ is slightly smaller than that of $\cdot MV^+$. Though the $(1/\lambda)^{1/2}\exp[-(\Delta G^\circ+\lambda)^2/(4\lambda k_B T)]$ term of $\cdot BCEBP^+$ is larger than that of $\cdot MV^+$ (Table 3), H_{rp} of $\cdot BCEBP^+$ is about 30% smaller than that of $\cdot MV^+$. Thus, the small H_{rp} is responsible for the small k_{rev}^{cor} of $\cdot BCEBP^+$. However, we must notice that the H_{rp}^{rev} difference between $\cdot BCEBP^+$ and $\cdot MV^+$ is much smaller at pH 2.2 than that at pH 5.0. This is because $\cdot BCEBP^+$ takes a similar geometry to that of $\cdot MV^+$ at pH 2.2 (remember that $\cdot BCEBP^+$ does not take a zwitter ion form at pH 2.2).

From these results, it is reasonably concluded that: (1) the electron-transfer rate constant in encounter complexes, $[Ru(bpy)_3^{3+}\cdots\cdot MV^+]$ and $[Ru(bpy)_3^{3+}\cdots\cdot BCEBP]$, is mainly determined by H_{rp}, and (2) the H_{rp} value depends little on the charge of viologen, but depends much on the steric repulsion.

Understanding the Charge Effects on the Overall Photoreduction of Viologen. Here, we try to clarify the reason why the overall photoreduction of viologen is improved by the acceleration of charge separation and/or the suppression of back electron transfer more than the acceleration of quenching. The charge effects clearly appear at pH 5.0, since BCEBP is neutral but MV^{2+} is positively charged. Therefore, we compare here the quenching and back electron-transfer reactions between MV^{2+} and $BCEBP^0$ at pH 5.0.

Only charge effects on diffusional steps must be examined here, since the electron-transfer reactions in the exciplex and the encounter complex are little influenced by the charge of viologen. In the diffusion step of the quenching reaction, MV^{2+} suffers from a coulombic repulsion with $[Ru(bpy)_3]^{2+}$ and its extent is considered to be proportional to $(2\times2)/r$, as schematically shown in Scheme 1. On the other hand, $BCEBP^0$ does not suffer from a coulombic repulsion. Thus, MV^{2+} is less favorable than $BCEBP^0$, and the difference in charge effects would be approximately represented by $c_1(4/r)$, where c_1 is a proportional coefficient. In the diffusional dissociation step, the difference in the charge effects would be similar to that of the diffusion step, while the proportional coefficient (c_2) would be different from c_1; i.e., $c_2(4/r)$. MV^{2+} is also less favorable than $BCEBP^0$ in this



Scheme 1.

term. Thus, the sum of the charge effects is $(c_1+c_2)\times(4/r)$.

In the diffusion step of the back electron-transfer reaction, the charge effect would be proportional to $c_1(3\times1)/r$ for $\cdot\mathrm{MV}^+$ and $c_1\{3\times(-1)\}/r$ for $\cdot\mathrm{BCEBP}^-$. The diffusional dissociation is also proportional to $c_2(3\times1)/r$ for $\cdot\mathrm{MV}^+$ and $c_2\{3\times(-1)\}/r$ for $\cdot\mathrm{BCEBP}^-$. Thus, the difference in the charge effect between $\cdot\mathrm{MV}^+$ and $\cdot\mathrm{BCEBP}^-$ is $c_1\times(6/r)+c_2\times(6/r)=(c_1+c_2)\times(6/r)$. From the above qualitative consideration, the charge effects are expected to be larger in the charge separation than in the quenching.

We can see that the above expectation agrees well with our experimental results, as follows. In the quenching reaction, the diffusion of BCEBP^0 occurs more rapidly than that of MV^{2+} by ca. 2.4×10^9 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ and the diffusional dissociation of BCEBP^0 takes place less rapidly than that of MV^{2+} by ca. 4×10^9 s^{-1}, as shown in Table 2. Thus, the sum of these charge effects on the quenching is more favorable in BCEBP^0 than in MV^{2+} by ca. 6.4×10^9. In the reverse electron-transfer, the diffusion of $\cdot\mathrm{BCEBP}^-$ for the encounter complex formation occurs more rapidly than does that of $\cdot\mathrm{MV}^+$ by 3.3×10^9 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ and diffusional dissociation of $[\mathrm{Ru(bpy)}_3^{3+}\cdots\cdot\mathrm{BCEBP}^-]$ less rapidly occurs than that of $[\mathrm{Ru(bpy)}_3^{3+}\cdots\cdot\mathrm{MV}^+]$ by 4×10^9 s^{-1}. Thus, $\cdot\mathrm{BCEBP}^-$ is less favorable than $\cdot\mathrm{MV}^+$ in the charge-separation step by 7.3×10^9. This means that the charge-separation step is more sensitive to charge effects than the quenching step, which is consistent with the above-described qualitative discussion. Thus, the suppression of back electron transfer and the acceleration of charge separation are more effective for viologen photoreduction by $[\mathrm{Ru(bpy)_3}]^{2+}$ than the acceleration of oxidative quenching of $^*[\mathrm{Ru(bpy)_3}]^{2+}$ by viologen.

Conclusions

A detailed investigation was carried out on the quenching reaction of $^*[\mathrm{Ru(bpy)_3}]^{2+}$ with MV^{2+} and BCEBP and the reverse electron-transfer reaction of $[\mathrm{Ru(bpy)_3}]^{3+}$ with one-electron-reduced viologen radical. In this work, we focused on the charge effects in these electron-transfer reactions. It is our intention here to first present a detailed discussion on the origin of the charge effects of photoinduced electron-transfer reaction of $[\mathrm{Ru(bpy)_3}]^{2+}$.

The quenching reaction rate constant ($k_\mathrm{q}^\mathrm{obs}$) is similar in MV^{2+} and BCEBP^{2+} at pH 2.2, while the quenching by MV^{2+} proceeds much more slowly than that by BCEBP^0 at pH 5.0. At pH 2.2, the electron-transfer rate constant ($k_\mathrm{q}^\mathrm{cor}$) in the exciplex $[^*\mathrm{Ru(bpy)}_3^{2+}\cdots\mathrm{MV}^{2+}]$ is slightly larger than that of $[^*\mathrm{Ru(bpy)}_3^{2+}\cdots\mathrm{BCEBP}^{2+}]$. The diffusion rate constant for exciplex formation is similar in MV^{2+} and BCEBP^{2+}, while the diffusional dissociation of the exciplex $[^*\mathrm{Ru(bpy)}_3^{2+}\cdots\mathrm{MV}^{2+}]$ occurs slightly more rapidly than that of $[^*\mathrm{Ru(bpy)}_3^{2+}\cdots\mathrm{BCEBP}^{2+}]$. This slightly faster dissociation of $[^*\mathrm{Ru(bpy)}_3^{2+}\cdots\mathrm{BCEBP}^{2+}]$ mostly compensates for the slightly faster $k_\mathrm{q}^\mathrm{cor}$ of MV^{2+}. As a result, the quenching reaction by MV^{2+} occurs with a similar rate constant to the quenching by BCEBP^{2+} at pH 2.2.

At pH 5.0, the diffusion of BCEBP^0 for exciplex formation occurs much more rapidly than that of MV^{2+}, and the diffusional dissociation of $[^*\mathrm{Ru(bpy)}_3^{2+}\cdots\mathrm{BCEBP}^0]$ takes place more slowly than that of $[^*\mathrm{Ru(bpy)}_3^{2+}\cdots\mathrm{MV}^{2+}]$. Although the electron transfer in the exciplex $[^*\mathrm{Ru(bpy)}_3^{2+}\cdots\mathrm{MV}^{2+}]$ occurs more rapidly than in $[^*\mathrm{Ru(bpy)}_3^{2+}\cdots\mathrm{BCEBP}^0]$ (see $k_\mathrm{q}^\mathrm{cor}$ in Table 3), the more rapid diffusion of BCEBP for the exciplex formation and the slower diffusional dissociation of the exciplex lead to the more rapid quenching by BCEBP^0 than that by MV^{2+}. This means that the diffusion and diffusional dissociation are the determining factors for the quenching reaction at pH 5.0.

Why is the diffusion rate similar in MV^{2+} and BCEBP^0 at pH 2.2, but much different between them at pH 5.0? An important difference is the charge of viologen; BCEBP^0 is a neutral zwitter ion at pH 5.0, while it has 2+ charges at pH 2.2, like MV^{2+}. Since both MV^{2+} and BCEBP^{2+} take 2+ charges at pH 2.2, the diffusion rate constant is similar in MV^{2+} and BCEBP^{2+} at this pH. At pH 5.0, on the other hand, the diffusion of BCEBP^0 for exciplex formation occurs more rapidly and the diffusional dissociation of $[^*\mathrm{Ru(bpy)}_3^{2+}\cdots\mathrm{BCEBP}^0]$ occurs much more slowly than those of MV^{2+}, due to the neutral charge of BCEBP.

In conclusion, not the electron transfer in the exciplex, but the diffusion and diffusional dissociation, are determining factors for the quenching of $^*[\mathrm{Ru(bpy)_3}]^{2+}$, and significantly depend on the charge of viologen.

In the reverse electron-transfer reaction between $[\mathrm{Ru(bpy)_3}]^{3+}$ and one-electron-reduced viologen, $\cdot\mathrm{BCEBP}^+$ reacts with $[\mathrm{Ru(bpy)_3}]^{3+}$ slightly more rapidly than does $\cdot\mathrm{MV}^+$ at pH 2.2, but much more rapidly than does $\cdot\mathrm{MV}^+$ at pH 5.0. At pH 2.2, the diffusion ($k_\mathrm{dif}^\mathrm{rev}$) for the encounter complex formation similarly proceeds in $\cdot\mathrm{MV}^+$ and $\cdot\mathrm{BCEBP}^+$. Though the electron transfer takes place in the encounter complex $[\mathrm{Ru(bpy)}_3^{3+}\cdots\cdot\mathrm{MV}^+]$ slightly more rapidly than in $[\mathrm{Ru(bpy)}_3^{3+}\cdots\cdot\mathrm{BCEBP}^+]$, $[\mathrm{Ru(bpy)}_3^{3+}\cdots\cdot\mathrm{MV}^+]$ dissociates slightly more easily than does $[\mathrm{Ru(bpy)}_3^{3+}\cdots\cdot\mathrm{BCEBP}^+]$, which results in the slightly smaller $k_\mathrm{rev}^\mathrm{obs}$ of $\cdot\mathrm{MV}^+$ than that of $\cdot\mathrm{BCEBP}^+$. At pH 5.0, the electron transfer occurs much more rapidly in the encounter complex $[\mathrm{Ru(bpy)}_3^{3+}\cdots\cdot\mathrm{MV}^+]$ than in $[\mathrm{Ru(bpy)}_3^{3+}\cdots\cdot\mathrm{BCEBP}^-]$. However, $k_\mathrm{dif}^\mathrm{rev}$ of $\cdot\mathrm{BCEBP}^-$ is much larger than that of $\cdot\mathrm{MV}^{2+}$, and $k_{-\mathrm{dif}}^\mathrm{rev}$ of $\cdot\mathrm{BCEBP}^-$ is much smaller than that of $\cdot\mathrm{MV}^+$, due to the negative charge of $\cdot\mathrm{BCEBP}^-$. As a result, $k_\mathrm{rev}^\mathrm{obs}$ of BCEBP is larger than that of $\cdot\mathrm{MV}^+$.

From the above findings, reasonable conclusions emerge, as follows. Although the electron-transfer rate constant in the exciplex and the encounter complex are different between MV^{2+} and BCEBP, they are not a determining factor for both quenching and reverse electron-transfer reactions. The overall rate constants of the quenching and reverse electron-transfer reactions are mainly determined by the diffusion and diffusional dissociation rate constants, which are very much influenced by the charge effects of viologen. Thus, the charge effects should be taken into consideration only concerning the diffusion and diffusional dissociation rate constants when attempting to construct an efficient photoreaction system. Actually, various efficient photoreaction systems were successfully constructed by simple and intuitive consideration of the charge effects.[7—13]

The electron-transfer rate constants in the exciplex and the encounter complex were successfully analyzed with Marcus theory. We found that H_{rp} of MV^{2+} is similar to that of $BCEBP^{2+}$ at pH 2.2. This is probably because the 4,4′-bipyridinium moiety of $BCEBP^{2+}$ is similar to MV^{2+}. However, H_{rp} of $BCEBP^0$ is much smaller than that of MV^{2+} at pH 5.0 in both quenching and reverse electron-transfer reactions, against our expectation that $BCEBP^0$ and $\cdot BCEBP^-$ can more closely approach $[Ru(bpy)_3]^{2+}$ than MV^{2+} and $\cdot MV^+$ because of either the absence of a columbic repulsion or the presence of a coulombic attraction. This result is clearly interpreted in terms of the steric repulsion caused by the zwitter-ion forms of $BCEBP^0$ and $BCEBP^-$ at pH 5.0. Thus, it should be concluded that not the charge, but the steric effect, of viologen is a determining factor for H_{rp}. This is the reason that we take into consideration the charge effects only in diffusional steps.

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References

1) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, and A. V. Zelewsky, *Coord. Chem. Rev.*, **84**, 85 (1988).

2) a) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2858 (1975); b) N. Sutin and C. Creutz, *Pure Appl. Chem.*, **52**, 2717 (1980); c) G. M. Brown, B. S. Brunschwig, C. Creutz, J. F. Endicott, and N. Sutin, *J. Am. Chem. Soc.*, **101**, 1298 (1979); d) C. V. Krishnan, B. S. Brunschwig, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **107**, 2005 (1985).

3) K. Kalyanasundaram, J. Kiwi, and M. Gräzel, *Helv. Chim. Acta*, **61**, 2720 (1978).

4) M. Kirch, J.-M. Lehn, and J.-P. Sauvage, *Helv. Chim. Acta*, **62**, 1345 (1979).

5) a) P. J. DeLaive, B. P. Sullivan, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **101**, 4007 (1979); b) W. J. Dressick, T. S. Meyer, B. Durham, and D. P. Rillena, *Inorg. Chem.*, **21**, 3451 (1982).

6) For instance: a) K. Mandal and M. Z. Hoffman, *J. Phys. Chem.*, **88**, 185 (1984); b) K. Mandal and M. Z. Hoffman, *J. Phys. Chem.*, **88**, 5632 (1984); c) M. Z. Hoffman, *Inorg. Chem.*, **28**, 978 (1989); d) N. Sabbatini, S. Dellonte, A. Bonazzi, M. Ciano, and V. Balzani, *Inorg. Chem.*, **25**, 1738 (1986); e) D. K. Liu, B. S. Brunschwig, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **108**, 1749 (1986); f) N. Kitamura, H. B. Kim, S. Okano, and S. Tazuke, *J. Phys. Chem.*, **93**, 5750 (1989).

7) a) D. Meisel and M. S. Matheson, *J. Am. Chem. Soc.*, **99**, 6577 (1977); b) D. Meisel, D. Meyerstein, and M. S. Matheson, *J. Phys. Chem.*, **82**, 985 (1978); c) D. Meyerstein, J. Rabani, M. S. Matheson, and D. Meisel, *J. Phys. Chem.*, **82**, 1879 (1978); d) C. D. Jonah, M. S. Matheson, and D. Meisel, *J. Phys. Chem.*, **83**, 257 (1979).

8) R. E. Sasson and J. Rabani, *J. Phys. Chem.*, **84**, 1319 (1980); b) S. Kelder and J. Rabani, *J. Phys. Chem.*, **85**, 1637 (1981); c) R. E. Sasson, Z. Aizenshtat, and J. Rabani, *J. Phys. Chem.*, **89**, 1182 (1985).

9) a) T. Nagamura, K. Takura, Y. Tsutsui, and T. Matsuo, *Chem. Lett.*, **1980**, 503; b) T. Nagamura, T. Kurihara, T. Matsuo, M. Sumitani, and K. Yashihara, *J. Phys. Chem.*, **86**, 4368 (1982); c) T. Osako, T. Sakamoto, and T. Matsuo, *J. Phys. Chem.*, **89**, 222 (1985).

10) Y. Kaizu, H. Ohta, K. Kobayashi, and H. Kobayashi, *J. Photochem.*, **30**, 93 (1985).

11) T. Miyashita, T. Murakata, Y. Yamaguchi, and M. Matsuda, *J. Phys. Chem.*, **89**, 497 (1985).

12) T. Nagamura, N. Takeyama, K. Tanaka, and T. Matsuo, *J. Phys. Chem.*, **90**, 2247 (1986).

13) A. J. Frank, I. Willner, Z. Goren, and Y. Degani, *J. Am. Chem. Soc.*, **109**, 3568 (1987), references are therein.

14) Y. Kawanishi, N. Kitamura, and S. Tazuke, *J. Phys. Chem.*, **90**, 2469 (1986).

15) M. C. Richoux and A. Harriman, *J. Chem. Soc., Faraday Trans. 1*, **78**, 1873 (1982).

16) a) S. L. Larson, C. M. Elliott, and D. F. Kelly, *J. Phys. Chem.*, **99**, 6530 (1995); b) L. A. Kelly and M. A. J. Rodgers, *J. Phys. Chem.*, **99**, 13132 (1995).

17) C. D. Clark and M. Z. Hoffman, *J. Phys. Chem.*, **100**, 7526 (1996).

18) pH 2.2 was rather arbitrarily taken here, since a solution whose pH is lower than 2 cannot be easily prepared. Almost all portion of BCEBP is, however, protonated at pH 2.2 and deprotonated at pH 5.0; (only 3% of BCEBP remains as a deprotonated species at pH 2.2 and as a protonated species at pH 5.0). Thus, we can expect to investigate charge effects of viologen at pH 2.2 and 5.0.

19) The positively charged BCEBP at pH 2.2 and the neutral BCEBP at pH 5.0 are represented here with $BCEBP^{2+}$ and $BCEBP^0$, respectively, and BCEBP without a superscript is used as a general name for $BCEBP^{2+}$ (at pH 2.2) and $BCEBP^0$ (at pH 5.0).

20) a) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); b) R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 21 (1960); c) R. A. Marcus, *J. Chem. Phys.*, **43**, 679 (1965); d) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964); e) R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, **811**, 265 (1985); f) R. A. Marcus and N. Sutin, *Comments Inorg. Chem.*, **6**, 209 (1987), references are therein.

21) M. D. Newton and N. Sutin, *Ann. Rev. Phys. Chem.*, **35**, 437 (1984).

22) I. Fujita and H. Kobayashi, *Ber Bunsenges. Phys. Chem.*, **76**, 115 (1972); R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966).

23) I. Willner, N. Lapidot, A. Riklin, R. Kasher, E. Zahavy, and E. Katz, *J. Am. Chem. Soc.*, **116**, 1428 (1994).

24) The measurement was in general carried out two times on the two samples which were independently prepared. The difference between two measurements was less than 1.5%. The τ values at 30 °C are given here as an example; $\tau/\mathrm{ns} = 539\pm8$, 388 ± 9, 306 ± 8, and 247 ± 5 at pH 2.2 and 552 ± 1, 440 ± 1, 361, and 303 ± 1 at pH 5.0 for $[MV^{2+}]/\mathrm{mol\,dm^{-3}} = 0.0$, 0.5×10^{-3}, 1.0×10^{-3}, and 1.5×10^{-3}, respectively, and $\tau/\mathrm{ns} = 539\pm8$, 379 ± 2, 291, and 239 ± 4 at pH 2.2 and 554 ± 1, 374 ± 5, 281, and 225 ± 1 at pH 5.0 for $[BCEBP]/\mathrm{mol\,dm^{-3}} = 0.0$, 0.5×10^{-3}, 1.0×10^{-3}, and 1.5×10^{-3}, respectively.

25) M. Eigen, W. Kruse, G. Maass, and L. De Maeyer, *Prog. React. Kinet.*, **2**, 287 (1964).

26) C. Chiorboli, M. T. Indelli, M. R. A. Scandola, and F.

Scandola, *J. Phys. Chem.*, **92**, 156 (1988), references are therein.

27) M. Eigen, *Z. Phys. Chem. (Munich)*, **1**, 176 (1954).

28) J. Keizer, *Chem. Rev.*, **87**, 167 (1987).

29) B. S. Brunschwig, S. Ehrenson, and N. Sutin, *J. Phys. Chem.*, **90**, 3657 (1986).

30) a) Chem 3D was used for MM calculations with standard parameters. Chem 3D version 3.0 for Apple Macintosh, Cambridge Scientific Computing, Inc., Massachusetts; b) In the MM calculations, the Ru–N distance was taken to be the same as the experimental bond distance (2.056 Å). See: D. P. Rillema and D. S. Jones, *J. Chem. Soc., Chem. Commun.*, **1979**, 849.

31) This value is similar to the previous one estimated from CPK model; 7.1 Å (C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan, and J. K. Nagle, *J. Am. Chem. Soc.*, **101**, 4815 (1979)), 7.0 Å (C. D. Clark and M. Z. Hoffman, *J. Phys. Chem.*, **100**, 7526 (1996); and C. D. Clark and M. Z. Hoffman, *J. Phys. Chem.*, **100**, 14688 (1996)), and 6.8 Å (E. H. Yonemoto, G. B. Saupe, R. H. Schmehl, S. M. Hubig, R. L. Riley, B. L. Iverson, and T. E. Malloul, *J. Am. Chem. Soc.*, **116**, 4786 (1994)).

32) "Lange's Handbook of Chemistry," 11th ed, ed by J. A. Dean, McGraw-Hill, New York (1973), pp. 10-288, 10-148.

33) $\eta/\mathrm{mPa\,s} = 1.005$, 0.8937, 0.8007, 0.7225, and 0.6560, and $D = 80.36$, 78.54, 76.76, 75.03, and 73.35, for 20, 25, 30, 35, and 40 °C, respectively. D for 25 °C is referred from Ref. 29, and the others are from Ref. 32.

34) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

35) The error of $k_\mathrm{q}^\mathrm{cor}$ comes from the error of $k_\mathrm{q}^\mathrm{obs}$ (see Eq. 2).

36) The redox potential of BCEBP is −0.50 V at pH 2.2 and −0.54 V at pH 5.0, and that of MV^{2+} is −0.59 V at pH 2.2 and −0.58 V at pH 5.0 (vs. Ag/AgCl), where a HCl/KCl buffer and a HOAc/NaOAc buffer were used for CV measurements at pH 2.2 and pH 5.0 respectively.

37) If ΔG° depends on the temperature, this plot is meaningless. However, the redox potentials of MV^{2+}, BCEBP, and $[\mathrm{Ru(bpy)_3}]^{2+}$ little depend on the temperature, as follows, where the redox potentials at 10 and 40 °C are given for brevity; $\mathrm{E}^{2+/+}$ (V vs. Ag/AgCl) of MV^{2+} is −0.58 and −0.59 at pH 5.0 on 10 and 40 °C, respectively, and −0.59 at pH 2.2 on both 10 and 40 °C. $E^{0/-\text{ or }2+/+}$ (V vs. Ag/AgCl) of BCEBP is −0.55 and −0.54 at pH 5.0, −0.51 and −0.50 at pH 2.2 on 10 and 40 °C, respectively. $E^{3+/2+}$ (V vs. Ag/AgCl) of $[\mathrm{Ru(bpy)_3}]^{2+}$ is 1.15 and 1.14 at pH 5.0 on 10 and 40 °C, respectively, and 1.14 at pH 2.2 on both 10 and 40 °C. $E^{3+/2+*}$ (V vs. Ag/AgCl) of ${}^*[\mathrm{Ru(bpy)_3}]^{2+}$ is −0.75 at pH 5.0 and −0.77 at pH 2.2 on both 10 and 40 °C.

38) C. Creutz and N. Sutin, *Inorg. Chem.*, **15**, 496 (1976).

39) According to this discussion, H_rp of MV^{2+} must be similar in both pH 2.2 and 5.0. However, H_rp of MV^{2+} is larger in pH 2.2 than in pH 5.0. Although we cannot find a concrete reason of this result, at the present stage, one of the plausible reason is anion effects: At pH 2.2, only the chloride anion exist but the acetate anion also exists in the reaction solution. Hoffman reported that the anion would influence the quenching reaction.[17] Since the most popular buffer at pH 5.0 involves the acetate anion and any buffer solution at pH 2.2 does not involve the acetate anion, we cannot compare H_rp between pH 2.2 and 5.0, in the presence of the same anion. We wish here to focus on the difference in H_rp between MV^{2+} and BCEBP at pH 2.2 and 5.0.