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Low Quantum Yields of Electron-Transfer Reaction of Photoexcited Ru(bpydc)$_3{}^{4-}$with Co(tpy)$_2{}^{3+}$ and Methyl Viologen^{2+} (bpydc:2,2′-Bipyridine-4,4′-dicarboxylate and tpy:2,2′:6′,2”-Terpyridine)

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Quenching reactions of the phosphorescent state of Ru(bpydc)$_3{}^{4-}$ by a cationic ion, Co(bpy)$_3{}^{3+}$, Co(phen)$_3{}^{3+}$, Co(tpy)$_2{}^{3+}$, and methyl viologen (MV^{2+}) to yield ET products were examined for the aqueous solutions by means of transient absorption kinetic spectroscopy and time-correlated single photon counting technique. A molecular complex formed in the ground state, [Ru(bpydc)$_3{}^{4-}$... Co(tpy)$_2{}^{3+}$], produces ET-products in the bulk with a small fraction of 0.3 on the photoexcitation. The fractions of ET product formation in the collisional quenching by Co(tpy)$_2{}^{3+}$ (0.43) is lower than the re-dissociation fraction (0.71) of an encounter complex, Ru(bpydc)$_3{}^{3-}$−Co(tpy)$_2{}^{2+}$, for the reverse ET reaction. A process to reduce the formation of a cage-complex of [Ru(bpydc)$_3{}^{3-}$...Co(tpy)$_2{}^{2+}$], in the collisional quenching is the conversion of unrelaxed cage-complex to the original reactant pair, [Ru(bpydc)$_3{}^{4-}$...Co(tpy)$_2{}^{3+}$] via a potential intersect between the potential energy surfaces (PES) (avoid crossing). Such rapid a deactivation process is suggested by a lower fraction of ET-product formation (0.06) in the bimolecular quenching of ^{3}Ru(bpydc)$_3{}^{4-}$ by MV^{2+} than the re-dissociation fraction (0.18) of the encounter complex for the reverse ET reaction. Both Co(bpy)$_3{}^{3+}$ and Co(phen)$_3{}^{3+}$, which do not form a molecular complex with Ru(bpydc)$_3{}^{4-}$ in the ground state, produce ET-products in the collisional quenching of ^{3}Ru(bpydc)$_3{}^{4-}$ and ^{3}Ru(bpy)$_3{}^{2+}$ with a high fraction (0.93−1.0). The re-dissociation fractions of the encounter complex for the reverse ET reaction are close to unity (0.88−0.99).

Introduction

Yields of photochemical bimolecular redox reactions in solution are not unity always in the presence of an electron donating or accepting molecule.[1−12] Some parts of this inefficiency could originate from fast reverse ET reaction within a cage-complex of the ET-products. Fractions of ET-product formation in the bulk ($F_{\mathrm{ET}}^{\mathrm{obs}}$) are expressed by using the rate-constants of dissociation (k_{dis}) and reverse ET (k_{ret}), $k_{\mathrm{dis}}/(k_{\mathrm{dis}} + k_{\mathrm{ret}})$.[1,2] ET-products form an encounter-complex in the bulk that undergoes reverse ET, yielding the original reactants with a fraction of $F_{\mathrm{RET}}^{\mathrm{obs}} = k_{\mathrm{ret}}/(k_{\mathrm{ret}} + k_{\mathrm{dis}})$ and the rest re-dissociate to the bulk with a fraction of $F'_{\mathrm{ce}} = 1 - F_{\mathrm{RET}}^{\mathrm{obs}}$. As a consequence, the following relation, $F_{\mathrm{ET}}^{\mathrm{obs}} + F_{\mathrm{RET}}^{\mathrm{obs}} = 1$,[1−4] has been found for many redox-quenching reactions of phosphorescent states. However, smaller extents of $F_{\mathrm{ET}}^{\mathrm{obs}}$ than $F'_{\mathrm{ce}} = 1 - F_{\mathrm{ET}}^{\mathrm{obs}}$ have been observed and ascribed to a faster reverse ET within a cage-complex of the ET-products than an encounter complex for the reverse ET.[8] Moreover, an irregular $\Delta G°$-dependence of k_{ret} estimated from $F_{\mathrm{ET}}^{\mathrm{obs}}$ in the quenching of ^{3}Ru(bpy)$_3{}^{2+}$ suggested the participation of nonradiative deactivation of an exciplex formed.[9] Another channel of excitation deactivation was suggested for the collisional quenching of ^{3}Ru(bpy)$_3{}^{2+}$ by MV^{2+} [10] because a regular ΔG°-dependence of reverse ET rates was found for the photoexcitation of a chemically linked donor−acceptor compound, [(bpy)$_2$Ru$^{\mathrm{II}}$(bpy-CH$_2$-CH$_2$-viologen^{2+})]$^{4+}$.[11]

It has been accumulated that a $\Delta G°$-dependence of reverse ET rates within contact ion-pair (CIP) formed in the fluorescence quenching of excited charge-transfer complex is different from that within solvent-separated ion-pair (SSIP) formed in the collisional quenching of fluorescence.[13,14] Yields of ionic-radical formation on the excitation of a charge-transfer (CT) complex between electron-donating and electron-accepting molecules in the ground state are smaller than those in the collisional fluorescence quenching of neutral aromatic molecules. Meanwhile, it has rarely been recognized that the excited triplet state forms a molecular complex in the bi-molecular quenching.[15−17] It is worthwhile to study a photodynamics of a molecular complex formed between an anionic ruthenium(II) compound and a cationic quencher by means of laser kinetic spectroscopy.

Phosphorescence-quenching of an anionic ruthenium(II) compound (Ru(bpydc)$_3{}^{4-}$) by an cationic compound, CoL$_3{}^{3+}$ (L = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), and 2,2′:6′,2′′-terpyridine (tpy)) and methyl viologen (MV^{2+}), were investigated. The extent of $F_{\mathrm{ET}}^{\mathrm{obs}}$ in the quenching were compared with F'_{ce} of the encounter complex, [^{2}Ru(bpydc)$_3{}^{3-}$...^{4}Co(bpy)$_3{}^{2+}$] (^{2}Co(tpy)$_2{}^{2+}$ or ^{2}MV$^+$), formed from the bulk. Ru(bpydc)$_3{}^{4-}$ in the ground state formed a molecular complex with Co(tpy)$_2{}^{3+}$ or methyl viologen for which the quantum yield of ET producuts formation in the bulk on the photoexcitation was investigated. Both the internal conversion of a nonrelaxed cage-complex, [Ru(bpydc)$_3{}^{3-}$...Co(tpy)$_2{}^{2+}$] or [Ru(dcbpy)$^{3-}$...MV$^+$], and the reverse ET reaction within the relaxed cage-complex are proposed to interpret the low yield of ET-product formation in the bimolecular quenching of ^{3}Ru(bpydc)$_3{}^{4-}$.

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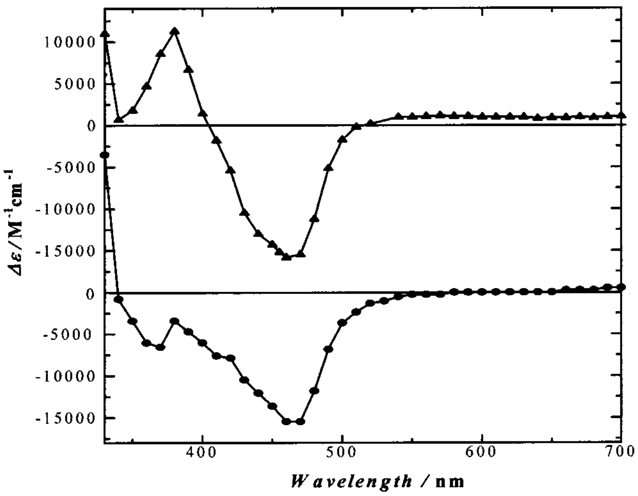

Figure 1. Difference absorption spectra of $^3Ru(bpydc)_3^{4-}$ and $Ru(bpydc)_3^{3-}$. The upper $^3Ru(bpydc)_3^{4-}$ and the bottom: $Ru(bpydc)_3^{3-}$.

Experimental Section

Materials. Methyl viologen ($C_{12}H_{16}N_2Cl_2$) was recrystallized twice from methanol for purification. The other chemicals supplied from Wako Chemicals Co., Sodium borate, NaOH and KCl, were used without further purification.

A ligand of 2,2′-biyridyl-4,4′-dicarboxy acid ($bpydcH_2$) was prepared by permanganate oxidation of 4,4′-dimethyl-2,2′-bipyridine.[18] Anal. $BpydcH_2$ Calcd. For $C_{12}H_8N_2O_4$: C, 59.02; H, 3.30; N, 11.47%. Found: C, 59.02; H, 3.32; N, 11.40%.

$Na_4[Ru(bpydc)_3]$: $BpydcH_2$ (79 mg, 0.3 mmol) and $RuCl_3$-$5H_2O$ (26 mg, 0.1 mmol) in a mixture of ethylene-glycol (10 mL) and HCl acidic water (10 mL) was refluxed for 24 h. On cooling the solution, red precipitates were obtained by the addition of NH_4PF_6. NH_4^+ was exchanged by solving the precipitate into acetone and then by adding concentrated NaOH solution. The compound was purified by using a Sephadex column, LH-20 (30 × 2 cm), and water as an eluent. The yield was about 60%. Anal. $Na_4[Ru(bpydc)_3]8H_2O$ Calcd. For $C_{36}H_{34}N_6Na_4O_{20}Ru$: C, 40.65; H, 3.22; N, 7.90%. Found: C, 40.09; H, 3.36; N, 7.85%.

$[Co(tpy)_2](ClO_4)_33H_2O$, $[Co(tpy)_2]Cl_24H_2O$, $[Co(bpy)_3]Cl_33H_2O$ and $[Co(bpy)_3]Cl_23H_2O$ were prepared by following the literature methods.[19−22] $[Co(phen)_3](ClO_4)_33H_2O$ and $[Co(phen)_3](ClO_4)_2$ were prepared by following the literature methods.[19−23]

Apparatus. Absorption spectra were measured on a Shimadzu spectrophotometer (UV-25000). The emission spectra were measured by using a Hitachi spectro-fluoremeter (MPF-4) or a grating mono-chromator (Jasco CT250) with a silicon diode-array (Hamamatsu S3901−512Q) corrected and a 488 nm line of an Ar laser (Coherent Innova 306) for the excitation of samples. Decay rate of emission was measured by using the second harmonic Nd^{3+}:YAG laser pulse (532 nm) of Continuum Surelite 1−10 or Quantel YG580 as previously described.[24] Shorter lifetimes than 5 ns were measured by means of a time-correlated single photon counting.[25] The excitation laser is the SHG of Ti^{3+}:Sapphire laser excited by using the Ar laser.[25]

Procedure. A transient absorption spectroscopy was carried out to measure the production of $^3CT(Ru)$ and the electron-transfer products, the decay of $^3CT(Ru)$, and the rise-and-decay of the Ru(III) compound. The production of $^3CT(Ru)$ and the oxidized species of $Ru(bpydc)_3^{4-}$ and $Ru(bpy)_3^{2+}$ were determined by using the difference absorption spectra shown in Figure 1. The difference molar absorption coefficient (−15 400 M^{-1} cm^{-1} at 465 nm) for ^3CT of $Ru(bpydc)_3^{4-}$ was determined from the saturated difference absorbance at 465 nm with the laser intensity. The value of $\Delta\epsilon_{465}$ was identical to that determined by utilizing energy-transfer to anthracene (A), $^3CT(Ru) + An \rightarrow Ru(II) + {}^3An$, of which the molar absorption coefficient of triplet excited state is 4.47×10^4 M^{-1} cm^{-1} at 410 nm.[26] The difference molar extinction coefficient for $Ru(bpydc)_3^{3-}$ was determined to be -1.54×10^4 M^{-1} cm^{-1} at 465 nm by assuming the concomitant production of $Ru(bpydc)_3^{3-}$ and MV^+ in the following reaction, $^3Ru(bpydc)_3^{4-} + MV^{2+} \rightarrow Ru(bpydc)_3^{3-} + MV^+$, and referring to the absorption spectrum of MV^+.[27] The difference absorption coefficients for $Ru(bpy)_3^{2+}$ are -9.8×10^3 M^{-1} cm^{-1} at 453 nm for the formation of $^3CT(Ru)$[10] and -14.3×10^3 M^{-1} cm^{-1} at 453 nm for the formation of $Ru(bpy)_3^{3+}$.

Bimolecular rate-constants of reverse ET between photochemical ET products were determined in the following method. Addition of $Co(bpy)_3^{2+}$, $Co(phen)_3^{3+}$, or $Co(tpy)_2^{2+}$ increased the recovery of Ru(II), of which the rates were the first order with respect of the amount of Co(II). The reverse ET rate constants were evaluated from the dependence of the recovery rate on the concentration of Co(II) added.

According to Debye−Smoluchowski,[28,29] the rate-constants of encounter complex formation (k_{ass}) are evaluated by using the following equation

$$k_{\mathrm{ass}} = \frac{2RT}{3\zeta}\left(2 + \frac{r_{\mathrm{a}}}{r_{\mathrm{b}}} + \frac{r_{\mathrm{b}}}{r_{\mathrm{a}}}\right)\frac{1}{a\int_a^\infty r^{-2}\exp\,[w(r,\mu)/k_{\mathrm{B}}T]\mathrm{d}r} \qquad (1)$$

where ζ, a, and $w(r,\mu)$ is the viscosity of solvent (0.89 mPa s), the sum of ion radius of $\mathrm{ion_a}$ and $\mathrm{ion_b}$ (r_{a} and r_{b}) and the work to bring an $\mathrm{ion_a}$ of Z_{a}-charge and an $\mathrm{ion_b}$ of Z_{b}-charge together at the distance of r in an aqueous solution of ionic strength μ, respectively

$$w(r,\mu) = \frac{Z_{\mathrm{a}}Z_{\mathrm{b}}e^2}{8\pi\epsilon_0 Dr}\left(\frac{\exp(\beta\sigma_{\mathrm{a}}\sqrt{\mu})}{1+\beta\sigma_{\mathrm{a}}\sqrt{\mu}} + \frac{\exp(\beta\sigma_{\mathrm{b}}\sqrt{\mu})}{1+\beta\sigma_{\mathrm{b}}\sqrt{\mu}}\right)\exp\,(-\beta r\sqrt{\mu})$$

$$\beta = \sqrt{\frac{2000Ne^2}{\epsilon_0 Dk_{\mathrm{B}}T}}$$

where σ_{a}, σ_{b}, and D are the radius of $\mathrm{ion_a}$-pair, $\mathrm{ion_{b-}}$pair, and the dielectric constant (78) of water, respectively. The rate constant of encounter complex dissociation (k_{dis}) are calculated by using the following equation derived by Eigen[30]

$$k_{\mathrm{dis}} = \frac{k_{\mathrm{B}}T}{2\pi\zeta a^2}\left(\frac{1}{r_{\mathrm{a}}} + \frac{1}{r_{\mathrm{b}}}\right)\frac{\exp[w(a,\mu)/k_{\mathrm{B}}T]}{a\int_a^\infty r^{-2}\exp[w(r,\mu)/k_{\mathrm{B}}T]\mathrm{d}r} \qquad (2)$$

The radius of the complex ions are 0.4 nm for MV^{2+} and MV^+, 0.6 nm for $Ru(bpy)_3^{2+}$, $Ru(bpy)_3^{3+}$, $Co(bpy)_3^{3+}$, $Co(bpy)_3^{2+}$, $Co(phen)_3^{3+}$, and $Co(phen)_3^{2+}$ and 0.8 nm for $Ru(bpydc)_3^{4-}$ and $Ru(bpydc)_3^{3-}$.

Results

Decay of $^3CT(Ru(II))$ and Formation of ET-Products $Ru(bpydc)_3^{4-}$−$Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$. A buffered (pH = 10.2) aqueous solution of $Ru(bpydc)_3^{4-}$ (40 μM) reveals a difference absorption spectrum on the Nd^{3+}-YAG laser (532 nm) excitation shown in Figure 1. The transient species is identified as $^3CT(Ru)$ because of the same decay rate (k_0 =

1.43×10^6 s^{-1}) as that of phosphorescence at 610 nm. The breaching of a strong absorption-band at 465 nm and formation of a weak absorption-band in the red region is typical of the difference absorption spectrum for ^{3}CT(Ru)-formation. The recovery of the transient bleaching (k_d) occurred in 100 ns on addition of 0.2−10 mM Co(bpy)$_3^{3+}$ or Co(phen)$_3^{3+}$. The bimolecular quenching rate-constant (k_q) are determined 10.7×10^9 M^{-1} s^{-1} from the dependence of the decay rate (k_d) on the Co(III).

After the rapid recovery of the ground-state absorption, more than the half of the bleaching was recovered for a longer time than several miliseconds. The difference absorption spectrum due to the longer lived species after the complete disappearance of ^{3}CT(Ru) is in an agreement with the difference absorption spectrum of photochemically oxidized species (Ru(bpydc)$_3^{3-}$) shown in Figure 1 in the presence of methyl viologen (MV^{2+}). The production of Ru(III) ([Ru(III)]$_0$) in the presence of Co(bpy)$_3^{3+}$ or Co(phen)$_3^{3+}$ was evaluated (>35 μM) from the negative absorbance at 465 nm in the later time region. The amount of Ru(III)-production, [Ru(III)]$_0$, can be written in terms of a fraction of the ET-products formation ($F_{\mathrm{ET}}^{\mathrm{obs}}$) in the bimolecular quenching of ^{3}CT(Ru)

$$[\mathrm{Ru(III)}]_o = F_{\mathrm{ET}}^{\mathrm{obs}}\frac{k_d - k_o}{k_d}[^3\mathrm{CT(Ru)}]_o = F_{\mathrm{ET}}^{\mathrm{obs}} f_q[^3\mathrm{CT(Ru)}]_o \quad (3)$$

where [^{3}CT(Ru)]$_o$ is the initial production of ^{3}CT(Ru), and k_o, k_d, and f_q are the decay rate constants of ^{3}CT(Ru) in the absence and the presence of Co(bpy)$_3^{3+}$ and the fraction of quenching in the decay of ^{3}CT(Ru), respectively

$$^3\mathrm{Ru(II)} \rightarrow {}^1\mathrm{Ru(II)} \qquad k_0$$

$$^3\mathrm{Ru(II)} + {}^1\mathrm{Co(III)} \rightarrow$$
$$^2\mathrm{Ru(III)} + {}^4\mathrm{Co(II)} \text{ or } {}^1\mathrm{Ru(II)} + {}^1\mathrm{Co(III)} \qquad k_q$$

The fraction of Ru(bpydc)$_3^{3-}$ formation in the quenching of ^{3}CT(Ru) by Co(bpy)$_3^{3+}$ or Co(phen)$_3^{3+}$ was so high (0.95−1.0).

Ru(bpydc)$_3^{4-}$−Co(tpy)$_2^{3+}$. In the presence of 10 mM Co(tpy)$_2^{3+}$, the emission of ^{3}Ru(bpydc)$_3^{4-}$ decayed in biexponential mode. The lifetime of fast decay component was determined to be independent of the concentration of Co(tpy)$_2^{3+}$ by means of time-correlated single photon counting as is shown in Figure 2. Though the fast component of the emission decay is not single exponential but multiexponential, the decaying time to the 1/e of the initial emission intensity for the fast decay was 1.1 ns. The fast and the slow decay-components of the excited states are ascribed to the uni-molecular decay of an excited molecular complex, [^{3}Ru(bpydc)$_3^{4-}$...Co(tpy)$_2^{3+}$], and the decay of ^{3}Ru(bpydc)$_3^{4-}$ quenched by Co(tpy)$_2^{3+}$, respectively

$$C(t) = C_f^{\circ}\mathrm{e}^{-k_f t} + C_c^{\circ}\mathrm{e}^{-k_c t} \quad (4)$$

where C_f°, C_c°, and $C(t)$ are the concentration of ^{3}Ru(bpydc)$_3^{4-}$, [^{3}Ru(bpydc)$_3^{4-}$...Co(tpy)$_2^{3+}$] and the sum of both, respectively.

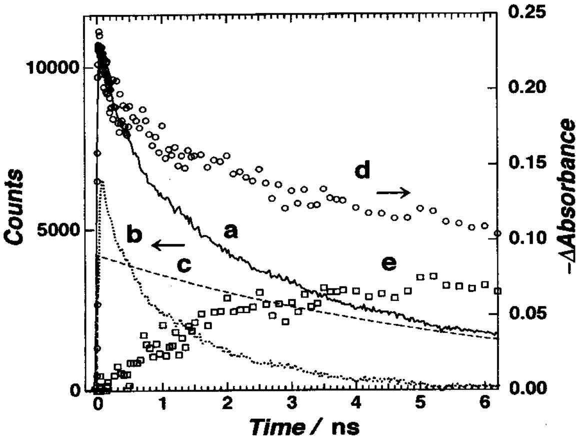

Figure 2. Time-profiles of the emission at 610 nm and the difference absorbance at 465 nm in the presence of 10 mM Co(tpy)$_2^{3+}$. Solid line (a): the emission intensity (I_e), dotted line (b): the short-life component of the emission, broken line (c): the long-life component of the emission, ○(d): the decay of the difference absorbance, □(e): the rise of the difference absorbance due to the formation of Ru(III) compound.

The bleached absorbance at 465 nm was recovered not only during the decay of emission but also after the disappearance of emission. The time-profile of the negative absorbance (ΔA_{455}) during the decay of emission can be decomposed to the decay of ^{3}Ru(bpydc)$_3^{4-}$ ($A_f(t)$), [^{3}Ru(bpydc)$_3^{4-}$...Co(tpy)$_2^{3+}$] ($\Delta A_c(t)$) and the formation of the Ru(III) ($\Delta A_{\mathrm{Ru}^{3+}}(t)$) as shown by eq 5

$$\begin{aligned}\Delta A_{455} &= \Delta A_f(t) + \Delta A_c(t) + \Delta A_{\mathrm{Ru}^{3+}}(t) \\ &= \Delta\epsilon_f C_f^{\circ} e^{-k_f t} + \Delta\epsilon_c C_c^{\circ} e^{-k_c t} + \\ &\quad \Delta\epsilon_{\mathrm{Ru}} F_{\mathrm{ET}}^{\mathrm{obs}} C_f^{\circ}(1 - e^{-k_f t}) + \Delta\epsilon_{\mathrm{Ru}} F_c C_c^{\circ}(1 - e^{-k_c t}) \quad (5)\end{aligned}$$

where $\Delta\epsilon_f$, $\Delta\epsilon_c$, and $\Delta\epsilon_{\mathrm{Ru}}$ are the difference molar absorption coefficients of ^{3}Ru(bpydc)$_3^{4-}$, [^{3}Ru(bpydc)$_3^{4-}$...Co(tpy)$_2^{3+}$], and [Ru(bpydc)$_3$]$^{3-}$, respectively, and F_c is the fraction of ET-product formation in the decay of [^{3}Ru(bpydc)$_3^{4-}$...Co(tpy)$_2^{3+}$]. Because $F_{\mathrm{ET}}^{\mathrm{obs}}$ will be estimated to be 0.43 as described later, the fraction for the excited complex, F_c, is determined 0.3.

The production of C_f° is estimated from the initial amplitude of the second decay component; it was reduced from 40 μM to 35, 34, 16, and 8 μM at 10 ns as the concentration of Co(tpy)$_2^{3+}$ increased from 0 to 0.5, 1, 10, 14.5 mM. The rate of the second decay one was dependent on the quencher concentration. The quenching rate-constant was determined 1.26×10^9 M^{-1} s^{-1} from the dependence.

The formation of [Ru(bpydc)$_3$]$^{3-}$ was obtained from a time profile of the absorbance at 465 nm in a later time region than 300 ns. The fraction of ET product-formation ($F_{\mathrm{ET}}^{\mathrm{obs}}$) in the bimolecular quenching by Co(tpy)$_2^{3+}$ (0.1 mM − 1 mM) were evaluated to be 0.43 from the fraction of quenching, f_q, and the productions of ^{3}Ru(bpydc)$_3^{4-}$ and Ru(bpydc)$_3^{3-}$. The latter, Ru(bpydc)$_3^{3-}$, decayed following the second-order rate-equation to regenerate the original reactant.

Ru(bpydc)$_3^{4-}$—MV^{2+}. Pico-second laser kinetic spectroscopy revealed that ^{3}[Ru(bpydc)$_3$]$^{4-}$ decayed in biexponential mode in the presence of 5 mM MV^{2+}. The formation of ^{3}Ru(bpydc)$_3^{4-}$ just after the laser excitation was constant and the fast decay component exhibited a lifetime of 1 ns independent of the concentration of MV^{2+}. The short-lived species can be an excited molecular complex of [Ru(bpydc)$_3^{4-}$ ... MV^{2+}]. No ET product such as MV$^+$ was observed at all during the fast decay.

The initial amplitude and the lifetime of the slow decay component were smaller as the concentration of MV^{2+} increases. The second decay component of the emission can be assigned to a collisional quenching of ^{3}Ru(bpydc)$_3^{4-}$ by MV^{2+}. The rate constant of collisional quenching is close to the diffusion-controlled one as is shown in Table 2. The production of MV$^+$ was determined from the transient absorbance at 605 nm.[27] The fraction of ET-products formation ion the bulk is small (0.06−0.07) in the quenching of ^{3}Ru(bpydc)$_3^{4-}$.

TABLE 1: Redox Potentials of Ru^{3+}/Ru^{2+}($E°$ ($Ru^{3+/2+}$) and Co^{3+}/Co^{2+} ($E°$ ($Co^{3+/2+}$)) in Acetonitrile, Excitation Energy of the Lowest Excited State of Ru(II) Compound ($E(^3CT(Ru))$) and Co(III) Compound ($E(^3T_{1g})$), and Molar Difference Absorption Coefficients along with the Excitation to $^3CT(Ru)$ ($\Delta\epsilon_{CT}$) and along with the Conversion of Ru(II) → Ru(III) or Co(III) → Co(II)

compound	$E°$ ($Ru^{3+/2+}$) V vs SCE	$E°$ ($Co^{3+/2+}$) V vs SCE	$E°$ ($MV^{2+/+}$) V vs SCE	E ($^3CT(Ru)$)[a] eV	E ($^3T_{1g}$) eV	$\Delta\epsilon_{CT}$ $10^3(M\ cm)^{-1}$	$\Delta\epsilon_{ET}$ $10^3(M\ cm)^{-1}$
$Ru(bpy)_3^{2+}$	1.26[b]			2.17		−9.8[c]	−14.1[d]
$Ru(bpydc)_3^{4-}$	1.54[e]			2.07		−15.4	−15.4
$Co(bpy)_3^{3+}$		0.30[g]			1.74[i]		0
$Co(phen)_3^{3+}$		0.37[g,h]			1.74[j]		
$Co(tpy)_2^{3+}$		0.26[h]			0[k]		−1.3[k]
MV^{2+}			−0.45[l]	−			0

[a] The excitation energy of $^3CT(Ru)$ as the first peak of emission at 77K in the ethanol glass. [b] Steel, P. J.; Lahousse, F.; Lerner, D.; Marzin, C. *Inorg. Chem.* **1983**, *22*, 1488−93. [c] Ohno, T.; Yoshimura, A.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4871−6. [d] Ref 24. [e] $E°$ ($Ru^{3+/2+}$) is assumed to be the same as that of $E°$ ($Ru(L')_3^{3+/2+}$), where L′ is 4,4′-dicarboethoxy-2,2′-bipyridine. [f] Elliott C. M.: Hershenhart, E. T. *J Am. Chem. Soc.* **1982**, *104*, 7519−26. [g] Krishnan, C. V.; Brunshcwig, B. S.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.*, **1985**, *107*, 2005−15. [h] Liu. D. K.; Brunschwig, B. S.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1986**, *108*, 1749−55. [i] Ref 6. [j] $E°$ (Co^{3+}/Co^{2+}) and E ($^3T_{1g}$) are assumed to be the same as those of $Co(bpy)_3^{3+}$. [k] Ref 40. [l] Hünig, S.; Gross, J.; Schenk, W. *Justus. Liebig. Ann. Chem.* **1973**, 324−39.

TABLE 2: Fractions of ET-product Formation in the Quenching (F_{ET}^{obs}), Bimolecular Quenching Rate-Constants (k_q), and Gibbs Energy Change of ET-Quenching (ΔG_{ET}°)

	F_{ET}^{obs}	k_q $10^9(M\ s^{-1})$	$-\Delta G_{ET}^{\circ}$[a] eV
$Ru(bpydc)_3^{4-}-Co(bpy)_3^{3+}$	0.98	10.7	0.63
$Ru(bpydc)_3^{4-}-Co(phen)_3^{3+}$	1.0	10.4	0.70
$Ru(bpydc)_3^{4-}-Co(tpy)_2^{3+}$	0.40	11.5	0.79
$Ru(bpydc)_3^{4-}-MV^{2+}$	0.06	10.1	0.08
$Ru(bpy)_3^{2+}-Co(bpy)_3^{3+}$	0.93	1.2	1.01
$Ru(bpy)_3^{2+}-Co(phen)_3^{3+}$	1.0	1.7	1.08
$Ru(bpy)_3^{2+}-Co(tpy)_2^{3+}$	0.74	1.6	1.17
$Ru(bpy)_3^{2+}-MV^{2+}$	0.19	0.74	0.46

[a] These are derived by putting the redox potentials in to eq 6, which are shown in Table 1.

$Ru(bpy)_3^{2+}$−$Co(bpy)_3^{3+}$, $Co(phen)_3^{3+}$, $Co(tpy)_2^{3+}$, and MV^{2+}. The emission of $Ru(bpy)_3^{2+}$ decayed single-exponentially to produce Ru(III) in the presence of either $Co(bpy)_3^{3+}$, $Co(tpy)_2^{3+}$, or MV^{2+}. The quenching rate-constants of $^3Ru(bpy)_3^{2+}$ are much smaller than those of $^3Ru(bpydc)_3^{4-}$. Although F_{ET}^{obs} are almost unity for $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$, $Co(tpy)_2^{3+}$, and MV^{2+} produced the ET-products less efficiently in the quenching. The fraction of ET-products formation in the bulk are 0.75 and 0.19 in the quenching by $Co(tpy)_2^{3+}$ and MV^{2+}, respectively.

Reverse ET to $Ru(bpydc)_3^{3-}$ and $Ru(bpy)_3^{3+}$ from the Co(II) Complex or Methyl Viologen$^+$. After the complete decay of $^3CT(Ru)$ in the presence of Co(III) compound, the negative absorbance due to the bleaching of $Ru(bpydc)_3^{4-}$ or $Ru(bpy)_3^{2+}$ were recovered in several miliseconds. The recovery of the Ru(II) occurred almost in a bimolecular reaction between ET-products, the Ru(III) and the Co(II) compounds. The recovery-rates of Ru(II) are dependent on the concentration of $Co(bpy)_3^{2+}$, $Co(phen)_3^{2+}$ or $Co(tpy)_2^{2+}$ added. The bimolecular rate-constants of reverse ET (k_{RET}^{obs}) were obtained from the concentration dependence of the recovery rate as are shown in Table 2. The reverse ET of $Ru(bpy)_3^{3+}$ are much slower than that of $Ru(bpydc)_3^{3-}$ because the electrostatic repulsion between the cations reduces the rate-constant, as was seen in the case of quenching reaction. The small rate-constant of reverse ET from $Co(phen)_3^{2+}$, which is 1/5 of that observed in 1 M ionic strength solution,[5] is consistent with the high value of F_{ET}^{obs}.

In the case of the reverse ET between $Ru(bpydc)_3^{3-}$ and MV^+, the rate-constant of reverse ET process (k_2) was obtained as a second-order one with respect to either [$Ru(bpydc)_3^{3-}$] or [MV^+]. The second-order disappearing rate-constant of MV^+ observed at 610 nm was in agreement with that of $Ru(bpydc)_3^{3-}$ at 465 nm, 7.3 × $M^{-1}\ s^{-1}$. The reverse ET processes between $Ru(bpy)_3^{3+}$ and MV^+ were determined by using a Guggenheim method because both $Ru(bpy)_3^{3+}$ and MV^+ decay following to a mixed equation of the first- and second-order rates. The second-order rate-constant of reverse ET monitored at 465 nm and at 610 nm was $5.5 \times 10^9\ M^{-1}\ s^{-1}$ and $8.5 \times 10^9\ M^{-1}\ s^{-1}$, respectively.

Discussion

Decay of Excited Molecular Complexes, [$Ru(bpydc)_3^{4-}$...$Co(tpy)_2^{3+}$] and [$Ru(bpydc)_3^{4-}$...MV^{2+}]. The phosphorescence decay of $Ru(bpydc)_3^{4-}$ was bi-phasic in the presence of the $Co(tpy)_2^{3+}$ or MV^{2+}. Because the lifetime of the fast decay component was independent of the quencher concentration, 1 ns for MV^{2+} and 1.1 ns for $Co(tpy)_2^{3+}$, the fast decay component is identified to that of the excited molecular complex. The formation constant of molecular complex in the ground state, [$Ru(bpydc)_3^{4-}$...$Co(tpy)_2^{3+}$] and [$Ru(bpydc)_3^{4-}$...MV^{2+}], was determined $1.8 \times 10^2\ M^{-1}$ and $<1 \times 10^2\ M^{-1}$ from the ratio of the intensity of the fast decay component to that of the slow one. The molecular complexes are prepared by not only electrostatic force but also intermolecular one,[31] because the trivalent cations of $Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$ do not form a molecular complex. The picosecond laser-flash photolysis revealed that a part of the excited molecular complex, [$^3Ru(bpydc)_3^{4-}$...$Co(tpy)_2^{3+}$], was converted to the ET-products with a fraction of 0.3 for $Co(tpy)_2^{3+}$. No MV^+ was produced on the excitation of the molecular complex, [$Ru(bpydc)_3^{4-}$...MV^{2+}]. The smaller yield of $Ru(bpydc)_3^{3-}$ on the excitation of molecular complex indicates that the excited triplet state of [$Ru(bpydc)_3^{4-}$...$Co(tpy)_2^{3+}$] generates a cage-complex, [$Ru(bpydc)_3^{3-}$...$Co(tpy)_2^{2+}$], which experiences faster reverse ET than a cage-complex formed in the collisional quenching (vide infra).

Fractions of ET Quenching in the Quenching and Mechanism of Quenching. Some of Co(III) complexes have been considered to be oxidants for long-lived excited states of Ru(II) [5,6,24,32−37] and Cr(III) compounds.[38] Both the formation yields of ET-reaction products and the dependence of quenching rate-constant on $\Delta G°$ for ET reaction have been pursued to present evidence of ET[5,6,24,32−37] because it has been difficult to deny other processes, e.g., energy transfer, involved in the quenching of excited state. To ascertain the ET-quenching of $^3CT(Ru)$, the magnitude of the standard Gibbs energy-change

TABLE 3: Fractions of ET Product Formation in the Quenching (F_{ET}^{obs}), Bimolecular Reverse Electron Transfer from the Bulk (k_{ret}^{obs}), Rate Constants of Association (k'_{ass}), and Dissociation (k'_{dis}) of an Encounter Complex Formed between the ET Products, Dissociation Fraction of the Encounter Complex (F'_{ce}), Uni-molecular Rate Constants of Reverse ET (k_{ret} and k'_{ret}, Respectively) within a Cage-complex and an Encounter Complex, a Fraction of ET Quenching (F_{ET}), and Standard Gibbs Energy Change Involved in the Reverse ET (ΔG°_{ret})[a]

	F_{ET}^{obs}	k_{ret}^{*1} / 10^9 s^{-1}	k_{ret}^{obs} / 10^9 (M s)$^{-1}$	k'_{ass} / 10^9 (M s)$^{-1}$	k'_{dis} / 10^9 s^{-1}	F'_{ce}	F_{ET}	k'_{ret} / 10^9 s^{-1}	$-\Delta G^{\circ}_{ret}$ / eV
$Ru(bpydc)_3^{3-}-Co(bpy)_3^{2+}$	0.98	0.009	1.1	9.8	0.44	0.89	1.1	0.056	1.24
$Ru(bpydc)_3^{3-}-Co(phen)_3^{2+}$	1.0	−	1.2	9.8	0.44	0.88	1.0	0.061	1.17
$Ru(bpydc)_3^{3-}-Co(tpy)_3^{2+}$	0.43*2	0.66	2.8	9.8	0.44	0.71	0.60	0.176	1.28
$Ru(bpydc)_3^{3-}-MV^{+}$	0.06*2	12.8	7.3	8.9	0.82	0.18	0.30	3.8	1.99
$Ru(bpy)_3^{3+}-Co(bpy)_3^{2+}$	0.93	0.34	0.056	4.8	4.5	0.99	0.94	0.045	0.96
$Ru(bpy)_3^{3+}-Co(phen)_3^{2+}$	0.93	0.34	0.028	4.8	4.5	0.99	1.0	0.026	0.89
$Ru(bpy)_3^{3+}-Co(tpy)_2^{2+}$	0.75	1.6	0.35	4.8	4.5	0.93	0.80	0.36	1.00
$Ru(bpy)_3^{3+}-MV^{+}$	0.19	24.7	3.2	5.0	5.8	0.36	0.53	10.3	1.71

[a] The ionic strength of the sample solution is 0.06 M. *1 Calculated on the assumption that the reverse ET within the cage-complex is responsible for the F_{ET}^{obs} smaller than unity, *2 Formation of a molecular complex in the ground state.

for ET quenching of ^{3}CT(Ru) is evaluated by using the following equation

$$\Delta G^{\circ}_{ET} = -E^{\circ}(Co^{3+}/Co^{2+}) + E^{\circ}(Ru^{3+}/Ru^{2+}) - E(^3CT) + \Delta G^{\circ}_{4-2} \quad (6)$$

where E° is the redox potential vs SCE in CH_3CN solution, and ΔG°_{4-2} is standard Gibbs energy-change involved in a transition from the ground state of Co(II) compound to the doublet state, which is assumed to be 0.2 eV for $Co(bpy)_3^{2+}$ [39] and $Co(phen)_3^{2+}$, and 0 eV for $Co(tpy)_2^{2+}$. [40] Quantities of the redox potentials, E°, and the excitation energy of ^{3}CT(Ru), $E(^3CT)$, are shown in Table 1. Because the ΔG°_{ET} are in a range of −0.70 eV ∼ −1.22 eV except for MV^{2+}, the most probable quenching mechanism are electron-transfer even if the water solvent would make a small change of the redox potential. In the case of MV^{2+}, there is no other mechanism of quenching than electron-transfer.

The fraction of ET-product formation in the quenching can be written as a product of fractions of cage-complex formation of ET-products in the quenching (F_{ET}) and F_{ce}, the latter of which is written as a ratio of the dissociating rate (k_{dis}) to the decay rate ($k_{dis} + k_{ret}$) of the cage complex formed in the ET quenching and is occasionally called "cage-escape-probability"

$$F_{ET}^{obs} = F_{ET}F_{ce} = F_{ET}\frac{k_{dis}}{k_{dis} + k_{ret}} \quad (7)$$

The low value of F_{ET}^{obs} are ascribed to either a slow dissociation rate of the cage-complex to the bulk (k_{dis}), a fast reverse ET (k_{ret}) or participation of other quenching of ^{3}CT(Ru) from electron transfer. Provided that F_{ET} is unity as were seen in the quenching of excited methyleneblue with iron(III) compounds[2] and aromatic amines,[3,4] the magnitude of k_{ret} can be estimated from those of F_{ET}^{obs} and k_{dis}.

Even if most of the cage-complex dissociates into the bulk, the ET products encounter to undergo the reverse ET reproducing the original reactants in a competition with re-dissociation of the encounter complex. The bimolecular rate-constant of the reverse ET (k_{ret}^{obs}) can be related to a re-dissociation fraction of an encounter complex, F'_{ce}, which is written in terms of k'_{ret} and k'_{dis}

$$k_{ret}^{obs} = k'_{ass}(1 - F'_{ce}) = k'_{ass}\frac{k'_{ret}}{k'_{dis} + k'_{ret}} \quad (8)$$

$$1 - F'_{ce} = k_{ret}^{ob}/k'_{ass} = \frac{k'_{ret}}{k'_{dis} + k'_{ret}} \quad (8')$$

where k'_{ass} is the association rate constant of ET-products. Consequently, the fraction of ET reaction in the quenching, F_{ET}, can be evaluated from the quantities of F_{ET}^{obs} and F'_{ce} under the assumption that F'_{ce} is equal to F_{ce}. The rate-constant of association (k'_{ass}) of $Ru(bpydc)_3^{3-}$ with $Co(bpy)_3^{2+}$ can be theoretically estimated to be 9.8×10^9 M^{-1} s^{-1} by putting the following parameters, $r_a = 0.8$ nm, $r_b = 0.6$ nm, $\sigma_a = 1.1$ nm and $\sigma_b = 0.9$ nm, into Debye−Smoluchowski equation. The magnitude of k'_{ass} is close to the largest rate of quenching of $^3RuL_3^{2+}$ (L = bpy, phen and 4,4′-dimethyl-bpy) by $Co(bpydc)_3^{3-}$ in an aqueous solution of the same ionic strength (9.5×10^9 M^{-1} s^{-1}).[24] The fraction of the cage-complex formation in the quenching (F_{ET}) can be determined from the measurable quantity, F_{ET}^{obs}, and the calculated quantity, F'_{ce}. Rates of reverse ET within the cage-complexes have been estimated under a further assumption of $F_{ET} = 1$.

$Ru(bpydc)_3^{4-}-Co(bpy)_3^{3+}$ and $Co(phen)_3^{3+}$. The high fraction of ET products-formation in the quenching of $^3[Ru(bpydc)_3]^{4-}$ by $Co(bpy)_3^{3+}$ ($F_{ET}^{obs} = 0.93$) definitely indicates the ET is the major in the quenching. Since the re-dissociation fraction of an encounter complex formed between $^2Ru(bpydc)_3^{3-}$ and $^4Co(bpy)_3^{2+}$ (F'_{ce}) is estimated (0.90) from the small rate-constant of bimolecular reverse ET (1.1×10^9 M^{-1} s^{-1}), and the formation rate of the encounter complex. The quenching of $^3Ru(bpydc)_3^{4-}$ by $Co(phen)_3^{3+}$ gave a high fraction of $Ru(bpydc)_3^{3-}$ formation ($F_{ET}^{obs} = 1$) (See Table 3). The extent of F'_{ce} for the re-dissociation of the encounter complex is estimated to be close to one. So, the fraction of ET reaction giving the ET-products in the bulk is estimated unity for both the cases. The exclusive ET reaction of $^3Ru(bpy)_3^{2+}$ has been found in the quenching by $Co(bpy)_3^{3+}$ and $Co(bpydc)_3^{3-}$.[24]

$Ru(bpydc)_3^{4-}-Co(tpy)_2^{3+}$. The observed yield of ET products in the bulk, F_{ET}^{obs}, were not high and weakly dependent on the temperature (0.30 at 283 K, 0.43 at 298 K, and 0.43 at 317 K) for the collisional quenching. The smaller magnitude of F_{ET}^{obs} for the excitation of the molecular complex (0.30 at 298 K) is in agreement with a general trend that F_{ET}^{obs} on the excitation of molecular complex is smaller than F_{ET}^{obs} in the collisional quenching of fluorescence.[12,13] Meanwhile, the bimolecular rate constant of reverse ET from the bulk (2.8×10^9 M^{-1} s^{-1}) was not large compared with the encounter-

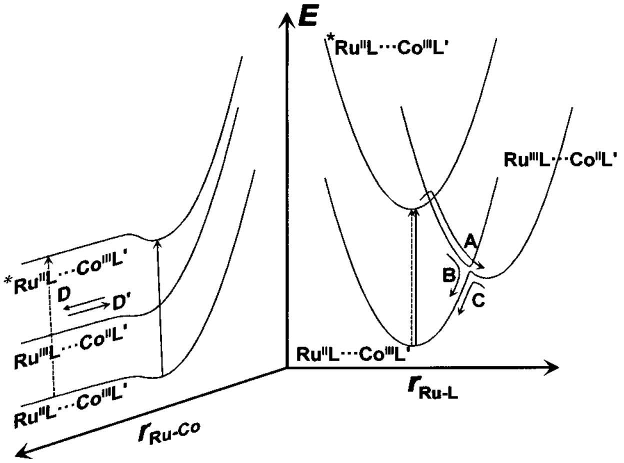

Figure 3. Reaction schemes of bimolecular quenching (A, B) and reverse ET (C and D, D′, and C) along potential energy surfaces (PESs) of the ground state, the excited state, the ET-products state of [Ru(bpydc)$_3{}^{4-/3-}$...Co(tpy)$_2{}^{3+/2+}$]. a: a deep well of PES displayed along the distance of Ru−N where the distance of Ru−Co is constant, b: a shallow well of PES displayed along the distance of Ru−Co where the distance of Ru−N is constant. The solid arrow and the brocken one represent the photoexcitation of a free Ru(II) compound and a complex of a Ru(II) compound and Co(tpy)$_2{}^{3+}$, respectively.

complex formation from the bulk, which is estimated to be 9.8 × 10^9 M^{-1} s^{-1} by using Debye−Smoluchowski equation and ionic radii of 0.6 nm for Co(tpy)$_2{}^{2+}$ and of 0.8 nm for Ru(bpydc)$_3{}^{3-}$. The smaller fraction of cage escape ($F_{\mathrm{ET}}^{\mathrm{obs}}$ = 0.43) than that of re-dissociation (F'_{ce} = 0.71) implies that only 60% of emission quenching produces a cage-complex of [Ru(dcbpy)$_3{}^{3-}$...Co(tpy)$_2{}^{2+}$] based on eq 7.

The most possible mechanism of the other quenching than the formation of a cage- complex is the following. ^{3}Ru(bpydc)$_3{}^{4-}$ forms an encounter complex with Co(tpy)$_2{}^{3+}$, which is converted to a cage-complex of [Ru(bpydc)$_3{}^{3-}$...Co(tpy)$_2{}^{2+}$] within 2 ns on the photoexcitation. As Figure 3 shows, most of the unrelaxed cage-complexes are relaxed to a loose complex in cage (path A), which dissociates to the bulk along the distance of Ru−Co (path D) in competition with the reverse ET (path C). The rest of the un-relaxed cage-complexes are converted to the molecular complex of [Ru(bpydc)$_3{}^{4-}$...Co(tpy)$_2{}^{3+}$] in the ground state via an intersect of PESs between the molecular complex and the loose cage-complex, [Ru(bpydc)$_3{}^{3-}$...Co(tpy)$_2{}^{2+}$], (path B). A considerable extent of Ru−Co interaction is necessary for the conversion of [^{2}Ru(bpydc)$_3{}^{3-}$...^{2}Co(tpy)$_2{}^{2+}$]→ [^{1}Ru(bpydc)$_3{}^{4-}$...^{1}Co(tpy)$_2{}^{3+}$] (avoid crossing) to occur. The involvement of metal−metal interaction is rationalized by both the formation of the molecular complex of [Ru(bpydc)$_3{}^{4-}$...Co(tpy)$_2{}^{3+}$] and the efficient reverse ET within the re-encounter complex of [Ru(bpydc)$_3{}^{3-}$...Co(tpy)$_2{}^{2+}$] via a potential intersect (path D′ and C).

A picosecond laser kinetic spectroscopy revealed that the yield of the ET-product was close to 50% in the case of [(tpy)Ru^{II}(tpy-C$_6$H$_4$-tpy)Co^{III}(tpy)]$^{5+}$, where the accepting moiety is (tpy)Co(tpy)$^{3+}$. The low-yield formation of ET-product ([(tpy)Ru^{III}(tpy-C$_6$H$_4$-tpy)Co^{II}(tpy)]$^{5+}$) in 10 ps was distinguished from the following reverse-ET generating the original compound in several hundreds ps Such a low yield of the ET product was not met if the accepting moiety was -(L−L)Co(bpy)$_2{}^{3+}$ (L−L: 2,6-(2-pyridyl)benzodiimidazole,[36,37] 2,2′-bis(2-pyridyl)bibenzimidazole,[36,37] and tetrapyrido-phenazine).

The second candidate explainable for the low faction of ET quenching is an excitation energy-transfer of ^{3}CT to Co(tpy)$_2{}^{3+}$, of which ^{3}T$_{1g}$ is inferred to lie at 1.7 eV as high as ^{3}T$_{1g}$ of Co(bpy)$_3{}^{3+}$.[6] There is no reason Co(tpy)$_2{}^{3+}$ is the better energy acceptor than Co(bpy)$_3{}^{3+}$ and Co(phen)$_3{}^{3+}$.

On the assumption that the quenching produces ET-products in cage (F_{ET} = 1), a rate of uni-molecular reverse ET (k_{ret}) within the cage-complex is estimated to be 0.66 × 10^9 s^{-1} from $F_{\mathrm{ET}}^{\mathrm{obs}}$ (0.43) and the calculated rate of cage-escape (0.44 × 10^9 s^{-1}). The uni-molecular rate of the reverse ET within [Ru(bpydc)$_3{}^{3-}$...Co(tpy)$_2{}^{2+}$] formed from the bulk (k'_{ret}) is also estimated to be only 0.18 × 10^9 s^{-1} from the observed rate of $k_{\mathrm{ret}}^{\mathrm{obs}}$ (2.8 × 10^9 M^{-1} s^{-1}) and the calculated rates of k'_{dis} and k'_{ass}. The higher rate of the former reverse ET (k_{ret}) than the latter (k'_{ret}) could be explained in terms of spin-dependent inner-sphere rearrangement energy of the reverse ET. Provided that (i) the intersystem crossing of ^{2}Co(II) → ^{4}Co(II) is slow compared with the dissociation-rate of the cage-complex and (ii) the extent of k'_{ret} is exactly estimated, the nascent Co(tpy)$_2{}^{2+}$ with doublet spin-multiplicity undergoes a faster reverse ET than Co(tpy)$_2{}^{2+}$ with spin-multiplicity of doublet or quartet in a thermal equilibrium in the bulk.[40] Because the fraction of ^{2}Co(tpy)$_2{}^{2+}$ in the bulk can be estimated to be 0.6 at 283 K, 0.5 at 298 K and 0.4 at 317 K from Δ$G°$ and Δ$H°$ for the spin-equilibrium, the rate of the reverse ET from the bulk, k'_{ret}, should be a half of k_{ret} within the cage-complex at 298 K. This might be the case. However, the slow rate of intersystem crossing (<10^8 s^{-1}) has been never met for both Co(tpy)$_2{}^{2+}$ [41] and [(bpy)$_2$Ru(L−L)$^{4/2}$Co(bpy)$_2$]$^{5+}$ (L−L:2,6-(2-pyridyl)benzodiimidazole,[36,37] 2,2′-bis(2-pyridyl)bibenzimidazole,[36,37] and tetrapyrido-phenazine).

Ru(bpydc)$_3{}^{4-}$−MV^{2+}. The re-dissociation fraction of the encounter pair for the reverse ET, F'_{ce}, is estimated to be 0.18 from the rates of reverse ET ($k_{\mathrm{ret}}^{\mathrm{obs}}$) and encounter-complex formation (k'_{ass}). The smaller extent of $F_{\mathrm{ET}}^{\mathrm{obs}}$ than F'_{ce} implies a participation of another deactivation process of the excited-state competing with the formation of ET-products in cage.

If any quenching process except for the formation of ET-products in cage were not involved in the quenching (F_{ET} = 1), the uni-molecular rate constant of reverse ET within the cage complex, [Ru(bpydc)$_3{}^{3-}$...MV$^+$], could be estimated 12.8 × 10^9 s^{-1} from $F_{\mathrm{ET}}^{\mathrm{obs}}$ and k_{dis}. It is 4 time as large as that (3.8 × 10^9 s^{-1}) for the reverse ET within an encounter complex [Ru(bpydc)$_3{}^{3-}$...MV$^+$] formed from the bulk, as is seen for the reverse ET between ^{2}Ru(III) and ^{2}Co(tpy)$_2{}^{2+}$. A similar estimate of the uni-molecular rate for the reverse ET k_{ret} within the cage-complex, [Ru^{III}L$_3{}^{3+}$...MV$^+$], lead an unexplainable ΔG°_{ret}-dependence of reverse ET rates.[10] A direct rate-determination of the reverse ET within donor−acceptor compounds, [(bpy)$_2$Ru^{III}(bpy-CH$_2$−CH$_2$-viologen$^+$)]$^{4+}$, by means of ps-laser kinetic spectroscopy lead a regular bell-shaped ΔG°_{ret}-dependence of ET-rate.[11] Inhibition of exciplex formation by the methylene chain may be responsible for the normal ΔG°_{ret}-dependence of ET-rates. Consequently, it can be derived that the formation of a charge-transfer complex in the collisional quenching by MV^{2+} is responsible for the lower fraction of $F_{\mathrm{ET}}^{\mathrm{obs}}$ than F'_{ce}. In a course of energy relaxation of charge-transfer complex, [Ru(bpydc)$_3{}^{3-}$...MV$^+$], a transition to [Ru(bpydc)$_3{}^{4-}$...MV^{2+}] may occur via a potential intersect between [Ru(bpydc)$_3{}^{4-}$...MV^{2+}] and [Ru(bpydc)$_3{}^{3-}$...MV$^+$]. A similar deactivation process might occur more on the photoexcitation of the 1:1 molecular complex, [Ru(bpydc)$_3{}^{4-}$...MV^{2+}]. Kikuchi et al., recently demonstrated that the formation of exciplex in the collisional quenching of fluorescent state reduced the yield of ET-products in the bulk, for which ΔG°_{ET} was weakly negative.[8]

$Ru(bpy)_3{}^{2+}$−$Co(bpy)_3{}^{3+}$, $Co(phen)_3{}^{3+}$, $Co(tpy)_2{}^{3+}$, and MV^{2+}. ^{3}CT(Ru) of $Ru(bpy)_3{}^{2+}$ was quenched by $Co(bpy)_3{}^{3+}$, $Co(phen)_3{}^{3+}$, $Co(tpy)_2{}^{3+}$, or MV^{2+} to produce the ET-products with a similar rate constant of quenching shown in Table 2. F_{ET}^{obs} for the quenching by $Co(bpy)_3{}^{3+}$ and $Co(phen)_3{}^{3+}$ are close to unity, whereas F_{ET}^{obs} for the quenching by $Co(phen)_3{}^{3+}$ was one-half in a reference.[5] The extent of F_{ET}^{obs} for the quenching of $^3Ru(bpy)_3{}^{2+}$ was substantially larger for $Co(tpy)_2{}^{3+}$ and MV^{2+} than in the quenching of $^3Ru(bpydc)_3{}^{4-}$ because of the smaller chance of the reverse ET in the shorter lives of cage-complexes. The increasing order of F_{ET}^{obs}, $Co(bpy)_3{}^{3+} > Co(tpy)_2{}^{3+} > MV^{2+}$, is the same as the increasing order of the re-dissociation fraction (F'_{ce}) of encounter-complex formed from the bulk. However, the extent of F_{ET}^{obs} is smaller than F'_{ce} except for $Co(bpy)_3{}^{3+}$ and $Co(phen)_3{}^{3+}$. The fraction of ET-products formation in cage, F_{ET}, is estimated to be 0.80 for $Co(tpy)_2{}^{3+}$ and 0.53 for MV^{2+} by using eq 7, suggesting the formation of a CT-complex, followed by the avoid-crossing to generate $[Ru(bpydc)_3{}^{4-}...Co(tpy)_2{}^{3+}]$ during the energy relaxation of CT-complex.

Rates of the Reverse ET within Re-encounter Pairs Formed from the Bulk. Bimolecular rate constants of the reverse ET from the bulk k_{ret}^{obs} were determined from either the pseudo first-order rate of $[Ru(bpydc)_3]^{3-}$ disappearing in the presence of $CoL_n{}^{2+}$ ($n = 2$ or 3) or the second-order rate of MV^+ disappearing. By using the rate-constants of pair-formation and pair-dissociation evaluated, uni-molecular rate of the reverse ET k'_{ret} are calculated; 0.056×10^9 s^{-1}, 0.175×10^9 s^{-1}, and 3.8×10^9 s^{-1} for $^4Co(bpy)_3{}^{2+}$, $^2Co(tpy)_2{}^{2+}$ and $^2MV^+$, respectively. The increasing order of the rate may be related to the decreasing order of the inner-sphere reorganization energy of the electron-donor, $^4Co(bpy)_3{}^{2+} > {}^2Co(tpy)_2{}^{2+} > {}^2MV^+$. The uni-molecular rate-constants k'_{ret} of reverse ET, $^2Ru(bpy)_3{}^{3+} + {}^2Co(tpy)_2{}^{2+}$ (or MV^+) $\rightarrow Ru(bpy)_3{}^{2+} + Co(tpy)_2{}^{3+}$ (or MV^{2+}), are twice or three times as large as those of $[Ru(bpydc)_3]^{3-}$. Carboxylate groups of $[Ru(bpydc)_3]^{3-}$ might inhibits dπ-electrons of the Ru(III) from electronically interacting with the reduced quencher in the encounter complex. Otherwise, formation of an ion-pair, $[Ru(bpy)_3]^{3+}...BO_3{}^-$, might enhance the reverse ET rate compared with the reduction of $[Ru(bpydc)_3]^{3-}$ by MV^+, as was seen for an ion-pair between $[Ru(bpy)_3]^{3+}$ and $ClO_4{}^-$.[42]

Conclusion

Bimolecular quenching reactions of $^3Ru(bpydc)_3{}^{4-}$ in aqueous solution were studied by using $Co(bpy)_3{}^{3+}$, $Co(phen)_3{}^{3+}$, $Co(tpy)_2{}^{3+}$, and methyl viologen (MV^{2+}) as a quencher. $Co(tpy)_2{}^{3+}$ form a molecular complex with $Ru(bpydc)_3{}^{4-}$ in the ground state, which produces the ET-products in 2 ns with a small fraction (0.3) on the photoexcitation. The fraction of ET-products formation, F_{ET}^{obs}, in the collisonal quenching of $^3Ru(bpydc)_3{}^{4-}$ are not unity but 0.43 for $Co(tpy)_2{}^{3+}$ and 0.06 for MV^{2+}. Meanwhile, the fraction of ET products re-dissociating to the bulk again (F'_{ce}) are estimated to be much larger (0.71 and 0.18) for $Co(tpy)_2{}^{2+}$ and for MV^+, respectively, from the rates of the reverse ET rate and the encounter-complex formation from the bulk. The lower extent of F_{ET}^{obs} for the quenching of $^3Ru(bpydc)_3{}^{4-}$ by $Co(tpy)_2{}^{3+}$ or MV^{2+} than F'_{ce} indicates the fast conversion of the un-relaxed CT complex, $[Ru(bpydc)_3{}^{3-}...Co(tpy)_3{}^{2+}]$, to $[Ru(bpydc)_3{}^{4-}...Co(tpy)_2{}^{3+}]$ via a potential intersect of PESs during the energy relaxation of the former.

The others cationic quenchers, $Co(bpy)_3{}^{3+}$ and $Co(phen)_3{}^{3+}$, underwent ET reaction with $^3Ru(bpydc)_3{}^{4-}$ - and produced the ET-products very efficiently ($F_{ET}^{obs} = 0.98 - 1$). The reverse ET from the bulk to regenrate $Ru(bpydc)_3{}^{4-}$ was slow compared with the diffusion-controlled rate. The quenching mechanism is assigned as ET reaction.

The quenching of $^3Ru(bpy)_3{}^{2+}$ by a cationic electron accepting molecule was also studied. The smaller fractions of ET-products formation in the bulk (F_{ET}^{obs}) than the re-dissociation fraction of the ET-products into the bulk were found for the collisional quenching by $Co(tpy)_2{}^{3+}$ and MV^{2+} . It is proposed that the quenching of $^3Ru(bpy)_3{}^{2+}$ produces a molecular complex with MV^{2+} which is partly converted to the original reactants not to produce the ET-products.

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