Photoinduced Electron Transfer and Back Electron Transfer within Binuclear Complexes of Ru(II) and Co(III)

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Photoinduced electron-transfer (ET) reactions in donor-acceptor bifunctional compounds have been extensively investigated to quantitatively determine the extent of both the electronic coupling between the donor and acceptor and the Franck–Condon factor.[1–6] The extent of electronic coupling and the Franck–Condon factor for ET processes occurring within bifunctional compounds were separately determined by measuring the dependence of ET rates on either energy gap[1–3] or temperature.[4–6] In this communication, it is concluded that (i) the photoinduced ET of Ru(II)–Co(III) binuclear complexes forms ^{2}Ru(III)–^{2}Co(II) with a small innersphere reorganization energy, followed by intersystem crossing, ^{2}Co(II) → ^{4}Co(II), and (ii) the large innersphere reorganization energy (~1.2 eV) and the negative entropy change (–1.3 meV/K) are responsible for the slow back ET, ^{2}Ru(III)–^{4}Co(II) → ^{1}Ru(II)–^{1}Co(III).

According to the classical Marcus theory, the rate parameter is written for a nonadiabatic ET as follows:[7]

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

The preexponential factor (A) and the activation energy (E_a) in $k = A\exp[-E_a/(k_BT)]$ are written as follows for a nonadiabatic ET with no entropy change:

$$A = \frac{2\pi}{\hbar}\frac{{H_{\mathrm{rp}}}^2}{(4\pi k_{\mathrm{B}}T\lambda)^{1/2}} \tag{2a}$$

$$E_{\mathrm{a}} = \frac{(\Delta H^\circ + \lambda)^2}{4\lambda} \tag{2b}$$

The reorganization energy (λ) and matrix element (H_{rp}) can be separately obtained from A and E_a, which are almost independent of temperature.

The determination of λ and H_{rp} is applied to the photoinduced ET and the dark back ET between different metal sites of Ru(II) and Co(III) of binuclear complexes. It is known that the entropy increases to some extent in the thermal processes, Co(III) + e → Co(II), where Co(II) is in the ground state ($^4T_1$). In our cases, the temperature dependence of e[$E^\circ(\mathrm{Ru^{III/II}}) - E^\circ(\mathrm{Co^{III/II}})$] is ascribed to ΔS° of the intramolecular ET, ^{2}Ru(III)–^{4}Co(II) → ^{1}Ru(II)–^{1}Co(III), shown in Table I. λ and H_{rp} are estimated by simulation of temperature-dependent ET rates, where A and E_a are weakly dependent on temperature as eqs 3a and 3b show:[7]

$$A = \frac{2\pi}{\hbar}\frac{{H_{\mathrm{rp}}}^2}{(4\pi k_{\mathrm{B}}T\lambda)^{1/2}}\exp\left[\frac{(\Delta G^\circ + \lambda)\Delta S^\circ}{2\lambda k_{\mathrm{B}}}\right] \tag{3a}$$

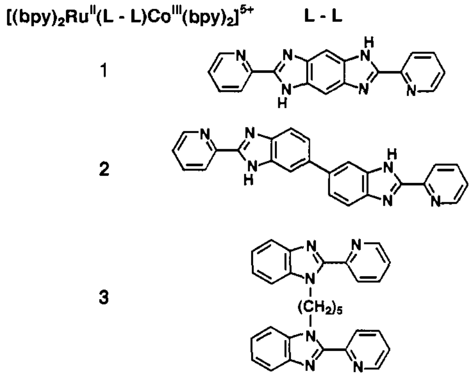
Table I. Physical Parameters for Back ET Following Photoinduced ET within Complexes of Ru(II)–Co(III) in Butyronitrile at 25 °C

complex	ΔG°/ eV	ΔS°/ meV/K	E_a/ meV	λ_{in}/ eV	λ_{out}/ eV	$A/10^7$ s^{-1}	H_{rp}/ meV
1	–0.77	–1.3	77	1.30	0.7	300	5
2	–0.78	–1.3	87	1.15	1.0	50	2
3	–0.79	–1.3	120	1.25	1.1	5	0.8

$$E_{\mathrm{a}} = \frac{(\Delta H^\circ + \lambda)^2 - (T\Delta S^\circ)^2}{4\lambda} \tag{3b}$$

The reorganization energy λ consists of two parts: the reorganization energy of solvent molecules around the binuclear complex, λ_{out}, and the innersphere reorganization energy, λ_{in}. The temperature dependence of λ_{out} (0.3 meV/K for butyronitrile) was also taken into account in the simulation. The λ_{out} in butyronitrile at 25 °C is estimated to be the same as that of binuclear complexes of either Ru(II)–Ru(III)[8] or Ru(II)–Rh(III).[6] Meanwhile, λ_{in} is assumed to be independent of temperature.

We prepared three binuclear complexes of [(bpy)$_2$Ru(L–L)-Co(bpy)$_2$](ClO$_4$)$_5$ (bpy = 2,2′-bipyridine), where L–L are 2,6-bis(2′-pyridyl)benzodiimidazole (dpimbH$_2$),[8a] 2,2′-bis(2″-pyridyl)-bibenzimidazole (bpbimH$_2$),[8b] and 1,5-bis(2′-(2″-pyridyl)-benzimidazoyl)pentane (dpbimPe).[8c] In the binuclear complexes **1**, **2**, and **3**, L–L are dpimbH$_2$, bpbimH$_2$, and dpbimPe, respectively. In the cases of **1** and **2**, 2 mM HClO$_4$ was added to the butyronitrile solutions to avoid the deprotonation of imino groups. The intermetal electronic coupling could be smaller than that between Ru(II) and Ru(III), because a vacant d$_\pi$ orbital is not present in Co(III) but is in Ru(III).



The MLCT excited states of the Ru(II) moiety in Ru(II)–Co(III) complexes in the deaerated butyronitrile were generated by a 532-nm light pulse of a Nd^{2+}:YAG nanosecond[9] and picosecond[10] laser apparatus. Rise and decay of both transient absorption and emission were measured to determine the rate of ET.

The rate of photoinduced ET from the Ru(II) moiety to Co(III) was determined by monitoring the fast rise of the negative transient absorbance at 460 nm. The rate parameters at 25 °C for **1**, **2**, and **3** were >5 × 10^{10} s^{-1}, 6 × 10^9 s^{-1}, and 1 × 10^8 s^{-1}, respectively. The rate parameters for **2** and **3** in ethanol/methanol (1:1 by volume) at 77 K were determined from the decay of emission from the Ru(II) moiety to be 3 × 10^7 s^{-1} and 3 × 10^6 s^{-1}, respectively. The temperature dependence of the rate parameter was measured for **3** as shown in Figure 1A. The activation energy was obtained to be 55 meV. The following two

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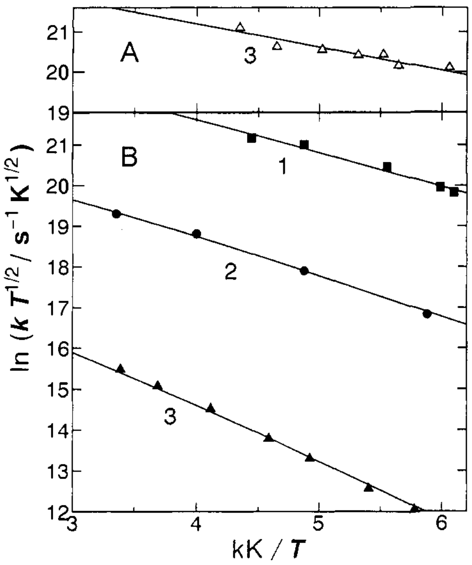

Figure 1. Temperature dependence of the rate parameters of photoinduced ET (A, **3**, △) and back ET (B, **1**, ■; **2**, ●; and **3**, ▲) in butyronitrile. Lines are simulated curves using eq 3 with values in Table I.

schemes for the production of Ru(III)–Co(II) are possible for the photoinduced ET.

One reaction scheme consists of an ET process in which the triplet MLCT state of the Ru(II) moiety produces a ^{2}Ru(III) and a ^{4}Co(II) ($^4T_1$) in the ground state. The $\Delta G°$ of the photoinduced ET at 25 °C is estimated to be −1.25 eV from both the energy level of the MLCT triplet state of the Ru(II) moiety (2.04 eV) and $\Delta G°$ for the back ET (−0.79 eV). The entropy increases by 1.3 meV/K. The extent of λ_{in} is estimated to be 0.4 eV from the activation energy, which is much smaller than the value obtained for the following back ET (1.25 eV). If the λ_{in} were as big as 1.25 eV, the activation energy might be much bigger (200 meV) than that observed (55 meV). Therefore, this scheme should not be dominant.

In an alternative scheme, an ET process producing ^{2}Ru(III) and ^{2}Co(II) (^{2}E) is followed by $^2E \rightarrow {}^4T_1$ intersystem crossing of Co(II). $\Delta G°$ for ^{2}E production (−0.85 eV) is less negative than that for $^4T_1$ production by the energy difference between ^{2}E and $^4T_1$ (0.4 eV), which is assumed to be the same as the spectroscopic data of Co(bpy)$_3^{2+}$.[11] The entropy change for ^{2}E-(Co^{2+}) production is assumed to be 0. The simulated curve is shown in Figure 1A, and the obtained λ_{in} and A values are 0.3 eV and 2 × 10^9 s^{-1}, respectively. This small value of λ_{in} is not strange, because the bond length of Co(II)–ligands might not be much lengthened during ^{2}E formation. The small λ in photoinduced ET is in accord with the work by Guardado and van Eldik,[12] where the activation volume of the photoinduced reaction, Fe(II)–Co(III) → Fe(III)–Co(II), is much smaller (~0) than that of the thermal ET (+30 mL/mol). The intersystem crossing, $^2E \rightarrow {}^4T_1$, of the Co(II) moiety occurs after the ET. The sequential scheme is more reasonable than the direct formation of high-spin Co(II) described above. Very recently, an intramolecular rapid ET (8 × 10^9 s^{-1}) from an excited Ru(II) moiety to a Co(III) was not accounted for by $^4T_1$ formation but by ^{2}E formation.[13]

The rates of back ET were determined from the recovery of ground-state absorption at 460 nm. The back ET for **1**, **2**, and **3** are more dependent on temperature than the photoinduced ET, as shown in Figure 1B. The solid lines in the figure show simulated curves using the λ_{in} and A as parameters, and the fitted parameters are shown in Table I. The large values of λ_{in} are consistent with longer bond lengths of Co(II)–ligands in the $^4T_1$ state than those of Co(III)–ligands, which are seen for many cobalt compounds.[14] The preexponential factor is expressed by eq 3a, because the oxidation of Co(II) in the $^4T_1$ is accompanied by entropy change of −1.3 meV/K. The negative entropy changes reduce the preexponential factors in the normal region, where $\exp[(\Delta G° + \lambda)\Delta S°/(2\lambda k_B)]$ in eq 3a are 0.01 (**1**) and 0.007 (**2** and **3**). The H_{rp} estimated from A and the entropy-dependent term changes with the bridging ligands. The H_{rp} decreasing in the order of **1**, **2**, **3** indicates a weak nonadiabticity, since the similar trend has been observed spectroscopically for H_{rp} between a Ru(II) and a Ru(III) linked by these bridging ligands.[6]

It has been also reported that the oxidation of Co(II) by Ru(III) is much slower than the photoinduced reduction of Co(III) by Ru(II).[13,15–18] The slower oxidation process has been ascribed to less exergonicity[18] and less electronic coupling.[13,15–16] However, the rates of Co(II) oxidation may be reduced by a negative entropy change[19] and a large innersphere reorganization of the Co(II) moiety.

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