Photoinduced ET and back-ET in bimetallated compounds of Ru(II)–Rh(III) and Ru(II)–Co(III)

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Abstract. Intramolecular electron transfer processes in bimetallated donor-acceptor compounds have been investigated by means of laser photolysis kinetic spectroscopy. An excited Ru(II)-moiety of donor-acceptor compounds undergoes intramolecular electron-transfer to either a rhodium(III) ion or a cobalt(III) ion, followed by back-electron transfer, an Arrhenius plot of the electron-transfer-rate gave a straight line of intercept (frequency factor) and slope (activation energy) for the photoinduced electron transfers and the back electron transfers. A common and large frequency factor observed for Ru(II)–Rh(III) compounds is accounted for in terms of solvent-relaxation dynamics. The activation energy observed consists of outersphere rearrangement energy depending on the metal ion-metal ion distance. For the photoinduced electron transfers and subsequent back-electron transfers in the Ru(II)–Co(III) compounds, the electron-transfer-rates are reduced because of weak electronic coupling, large rearrangement energy and negative entropy change.

Keywords. Donor-acceptor linked compound; electron transfer; nuclear tunnelling; temperature-dependence of ET rate; rearrangement energy.

1. Introduction

Electron transfer (ET) is one of the chemical reactions that have been most intensively investigated. The reaction rate of ET is given in (1) below for nonadiabatic ET by assuming no change of force constants between the initial and final states (Kestner *et al* 1974; Ulstrup and Jortner 1975). Equation (1) indicates that the rate depends on many factors, electronic coupling (H_{rp}), energy gap between the reactant and the product (ΔG°), rearrangement energy involved in ET (λ), vibronic coupling strength (S), and angular vibrational frequency of the product (ω).

$$k = \frac{2\pi |H_{rp}|^2}{\hbar(4\pi k_B T \lambda)^{1/2}} \sum_n \frac{(e^{-S} S^n)}{n!} \exp\left(-\frac{(\Delta G + \lambda + n\hbar\omega)^2}{4\lambda k_B T}\right), \quad (1)$$

$$k = \frac{2\pi |H_{rp}|^2}{\hbar(4\pi \lambda k_B T)^{1/2}} \exp\left(-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right), \quad (2)$$

$$\ln kT^{1/2} = \ln A - (E_a/k_B T), \quad (3a)$$

$$A = [2\pi |H_{rp}|^2]/[\hbar(4\pi k_B \lambda)^{1/2}], \quad (3b)$$

$$E_a = (\Delta G^\circ + \lambda)^2/(4\lambda k_B T). \quad (3c)$$

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When the energy gap is much smaller than the rearrangement energy, nuclear tunnelling followed by vibrational excitation of the product can be neglected and the rate formula is close to (2) presented by Marcus earlier (1956, 1965), which is recast to a more simple form (3). A is the frequency factor which depends on nuclear frequency and electronic coupling. E_a is the apparent activation energy depending on energy gap and rearrangement energy. This paper is devoted to the understanding of both A and E_a , which could be obtained from the temperature-dependence of rates of intramolecular ET in donor-acceptor linked compounds.

When the energy gap between initial and final states is so small that no vibrational excitation of the product occurs, decrease in temperature reduces the rate of ET to a large extent. The temperature-dependence of the ET rate allows us to estimate the frequency factor and the activation energy separately.

However, if the force constants of the final state differ from those of the initial state, rearrangement of the inner-coordination shell of the final state gives rise to rearrangement energy and entropy change. The entropy change accompanied by a change of vibrational state density enhances or reduces the frequency factor depending on a positive or negative value of the entropy change, because a term of $\exp[\Delta S^*/k_B]$ appears as a factor in A . It may make the frequency factor hard to interpret without estimation of ΔS^* .

When a high frequency vibrational mode of the product is coupled with ET, the ET rate is weakly dependent on both temperature and energy gap in a high energy-gap region (Liang *et al* 1990; Bixon and Jortner 1991). Only when nuclear tunnelling followed by vibrational excitation in a highly exergonic ET does not occur because of no vibrational overlap between the reactant and the product, the rate of ET might be dependent on temperature.

2. Estimation of rearrangement energy and bridging ligand mediated electronic coupling

(Ohno *et al* 1992) Samples studied in this research on photoinduced ET are donor-acceptor linked compounds. Two kinds of metal ions as donors and acceptors are linked by a bridging ligand containing a biphenyl moiety, benzene moiety, or

Figure 1. Bridging ligands and abbreviations.

methylene chain as a spacer. The general formula of the sample compounds is $[(\text{bpy})_2\text{Ru}(\text{L-spacer-L})\text{M}(\text{bpy})_2]^{5+}$ shown in figure 1, where bpy denotes 2,2'-bipyridine, L denotes a bidentate coordinating group of 2-(2'-pyridyl)imidazole, M denotes ruthenium, rhodium or cobalt. Intramolecular bonds and size of a spacer controls electronic coupling (Larsson 1981, 1984) and rearrangement energy (Brunschwig *et al* 1984; Isied *et al* 1988).

Photoexcitation of a Ru(II)–Rh(III) compound produces either an excited Ru(II) or an excited Rh(III) which undergoes ET to generate a charge-shifted state of Ru(III)–Rh(II) in which a back-ET from Rh(II) to Ru(III) subsequently takes place. It is known that redox processes of both ruthenium and rhodium compounds take place with small changes of the metal–ligand bond and intra-ligand bonds (Creutz *et al* 1982; Sutin and Creutz 1983). In other words, innersphere-rearrangement energy is negligibly small for ET processes of ruthenium and rhodium compounds.

An intramolecular ET within an M(II)–M(III) compound accompanies reorientation of solvent molecules to a charge-shifted state of M(III)–M(II). Charge-transfer photoexcitation of an Ru(II)-moiety causes a small amount of solvent reorientation around the excited Ru(II)–Rh(III) compound. An electron transfer from the Ru(II)-moiety to the Rh(III)-moiety is followed by rearrangement of solvent molecules surrounding the Ru(II)–Rh(III). Otherwise, the electron on the Rh-moiety goes back to the Ru-moiety so that the charge transfer excited state of the Ru-moiety suffers no quenching.

In the optical charge transfer transition of a mixed-valence symmetric Ru(II)–Ru(III) compound, an electron-jump from the left Ru(II) to the right Ru(III) generating a charge-shifted state of Ru(III)–Ru(II) is followed by rearrangement of solvent molecules to generate a newly solvated state of the Ru(III)–Ru(II) compound. Provided that the energy of a charge-shift state (Ru(III)–Ru(II)) is the same as that of original state (Ru(II)–Ru(III)), the transition energy of optical charge transfer is assumed to be the same as the nonvertical rearrangement energy of solvent molecules surrounding a charge-shift state of Ru(III)–Ru(II) (Creutz 1983). The nonvertical rearrangement energy increases with center–center distance between the metal ions because of more solvent molecules reorientating to the Ru(III)–Ru(II) compound.

The extent of bridging ligand-mediated electronic coupling between Ru(II) and Ru(III) can be estimated from an integrated intensity of the optical charge transfer transition (Hush 1967). The electronic coupling strength between the metal ions only depends on the intramolecular bonds and size of a spacer, since coordination bonds

Table 1. Electronic coupling (H_{rp}) and outersphere rearrangement energy (λ) estimated from the intensity and the energy of optical charge transfer transition of $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{L-spacer-L})\text{Ru}^{\text{III}}(\text{bpy})_2]^{5+}$ in acetonitrile at 298 K.

Bridging ligand	Metal–metal distance* (nm)	λ (eV)	H_{rp} (meV)
L_α -benzene- L_α	0.8	0.76	58
L_β -biphenyl- L_β	1.2–1.5	0.91	7.5 ~ 10
L_δ -biphenyl- L_δ	1.3	0.96	22
L_γ -ethane- L_γ	1.1	0.96	8.7

*Estimated by using a molecular model

of 2-(2'-pyridyl)imidazole moieties to metal ions are kept constant among the bridging ligands used here. When the ET process is nonadiabatic, the observed extent of the electronic coupling between metal ions must be reflected on the ET rates.

Broad absorption bands of the Ru(II)-benzene-Ru(III), the Ru(II)-biphenyl-Ru(III), and the Ru(II)-ethane-Ru(III) compounds observed in the near infrared region are assigned to a charge transfer band (Ohno *et al* 1992). Values of rearrangement energy and electronic coupling are estimated from the energy and intensity of the Ru(II)-to-Ru(III) charge-transfer transition (table 1). The extent of electronic coupling between the metal ions decreases with the spacers in the following order, benzene > biphenyl > ethane. The smallest rearrangement energy is obtained for the Ru(II)-benzene-Ru(III) with the shortest metal-metal distance.

3. ET on the excitation of Ru(II)-moiety in Ru(II)-Rh(III) compounds

(Nozaki *et al* 1992) A second harmonic pulse of the nano-second YAG laser excites the Ru-moiety of the Ru(II)-Rh(III) compound into the charge transfer state, which exhibits at a lower temperature a transient absorption spectrum similar to the metal-to-ligand charge transfer excited state of the Ru(II)-Ru(II) compound. The decay of the transient absorption in a mixture of propionitrile and butyronitrile becomes faster as temperature increases.

A nicely linear Arrhenius plot of the decay rate of the excited Ru(II)-moiety was obtained (figure 2). The Ru(II)-benzene-Rh(III) compound displays the fastest decay

Figure 2. Arrhenius plots of photoinduced ET in $[(bpy)_2Ru(L\text{-}spacer\text{-}L)Rh(bpy)_2]^5+$. $\circ$; L_α -benzene- L_α , $\square$; L_β -biphenyl- L_β , $\blacksquare$; L_δ -biphenyl- L_δ , $\triangle$; L_γ -ethane- L_γ .

Table 2. Photoinduced electron transfer of $[(\text{bpy})_2\text{Ru}(\text{L-spacer-L})\text{Rh}(\text{bpy})_2]^{5+}$ in mixed solvent (butyronitrile + propionitrile). Observed and calculated values of energy gap (ΔG°), Arrhenius frequency factor (A), and activation energy (E_a).

Bridging ligand	ΔG° (eV)	A (10^{11} s^{-1})	A^{cal} (10^{11} s^{-1})	E_a (eV)	E_a^{cal} (eV)
L_a -benzene- L_a	-0.02	4.1	5-7	0.166	0.17-0.18
L_β -biphenyl- L_β	-0.13	2.3	4-6	0.200	0.15-0.16
L_δ -biphenyl- L_δ	-0.08	3.2	4-5	0.190	0.185-0.195
L -ethane- L_γ	-0.04	3.2	4-5	0.190	0.205-0.215
L -ethane- L_γ	-0.04	0.6*	1.1-1.6*	0.172*	0.17-0.18*

* In benzonitrile

rate at a given temperature and the smallest slope of the linear plot among the Ru(II)-Rh(III) compounds. Table 2 shows a nearly constant frequency factor (A) of $2 \times 10^{11} \text{ s}^{-1}$ for the Ru(II)-Rh(III) compounds in the mixed solvent, which is in contrast to the variation in the extent of bridging ligand-mediated electronic coupling estimated from the optical charge-transfer transition intensities, and implies that the rate of ET is independent of the spacer.

Replacing the mixed solvent with benzonitrile reduced the frequency factor to 1/5. A slow longitudinal relaxation (5 ps) of benzonitrile compared with butyronitrile (0.5 ps) (Simon 1988) demonstrates that the solvent relaxation dynamics following ET is the rate-determining step. Therefore, the frequency factor is regarded as the nuclear frequency for the adiabatic ET studied.

$$k = \nu^\circ \exp(-E_m/RT) \exp(-\Delta G^*/RT), \quad (4a)$$

$$\Delta G^* = [(\Delta G^\circ + \lambda)^2/4\lambda] - |H_{rp}|. \quad (4b)$$

The nuclear frequency of ET processes can be estimated to be $3.9 \times 10^{11} \text{ s}^{-1}$ in butyronitrile and $0.85 \times 10^{11} \text{ s}^{-1}$ in benzonitrile at 298 K from the rotational and longitudinal relaxation times of the solvent molecules as per Calef and Wolynes (1983). If the temperature-dependence of Debye dielectric relaxation for benzonitrile is similar to that of butyronitrile ($E_m = 45 \text{ meV}$), the nuclear frequency at the infinitely high temperature (ν°) can be calculated as $\sim 5 \times 10^{11} \text{ s}^{-1}$ for benzonitrile and $\sim 23 \times 10^{11} \text{ s}^{-1}$ for butyronitrile.

For an adiabatic ET controlled by solvent relaxation dynamics, the ET rate can be expressed as in (4), where ΔG^* is given by energy gap (ΔG°), rearrangement energy (λ), and electronic coupling (H_{rp}). Let us assume that ΔG° is similar to ΔH° in magnitude and λ is close to the outersphere rearrangement energy.

$$\ln A = \ln \nu^\circ + \frac{\alpha}{2k_B n^3} \frac{dn}{dT}, \quad (5a)$$

$$E_a = \frac{\Delta H^\circ}{2} + \frac{\alpha}{4n^2} \left(1 + \frac{2T}{n} \frac{dn}{dT} \right) - |H_{rp}| + E_m. \quad (5b)$$

The value of outersphere rearrangement energy is estimated from the optical charge transfer transition energy mentioned above. Finally, we obtained (5) for frequency

factor and activation energy for weakly exergonic ET, where α is structural constant depending on sizes of metal ions and metal-metal distance. The second terms of (5) come from the temperature dependence of refractive index ' n ', which the outersphere-rearrangement energy is a function of. The values of A and E_a are calculated to be in the order of $2 \times 10^{11} \text{ s}^{-1}$ and $\sim 0.2 \text{ eV}$, respectively, by using (5a) and (5b), which are in agreement with the observed ones except for the Ru-biphenyl-Rh(III) compound, as table 2 shows.

4. ET and back ET on the excitation of Rh-moiety in Ru(II)-Rh(III) compounds

(Nozaki *et al* 1993) When the Rh-moiety of a Ru(II)-spacer-Rh(III) compound is excited by 317 nm picosecond pulse, ET from Ru to Rh is expected to occur rapidly because the energy gap of 0.6 eV is much larger than the energy gap of ET ($< 0.1 \text{ eV}$) on the excitation of Ru-moiety. The subsequent back-ET could be distinguished from the rapid ET.

Time evolution of transient absorption showed the fast decay of excited rhodium-moiety with a rate constant of $\sim 10^{10} \text{ s}^{-1}$ and the subsequent recovery of the Ru(II)-moiety with a rate constant of $1.2 \times 10^9 \text{ s}^{-1}$ for the Ru(II)-pentane-Rh(III) compound. The Ru(II)-propane-Rh(III) exhibited only a faster recovery of the Ru(II)-moiety with a rate constant of $4.7 \times 10^9 \text{ s}^{-1}$. The decay of the excited Rh-moiety of Ru(II)-propane-Rh(III) was hardly observed because of such a fast process. The back-ET of the Ru(II)-biphenyl-Rh(III) compound is a little faster (of the order of 10^{10} s^{-1}) at ambient temperature. Meanwhile, the ET rate estimated by putting the energy gap and the rearrangement energy into the classical Marcus equation of (3) is smaller than 10^8 s^{-1} because the energy gap is much larger ($\sim 2 \text{ eV}$) than the rearrangement energy. Nuclear tunnelling followed by the vibrational excitation is

Figure 3. Arrhenius plots of photoinduced ET and subsequent back-ET in $[(bpy)_2Ru(L_7-pentane-L_7)Co(bpy)_2]^{5+}$; Δ ; photoinduced ET, $\blacktriangle$; back-ET.

the only explanation for the much faster back-ET compared to the rate estimated by using the classical Marcus equation (3). The decreasing order of the rates in the Ru(II)-spacer-Rh(III) compounds (benzene > biphenyl > ethane > propane > pentane) is suggestive of non-adiabaticity of the back-ET processes in the spacer compounds.

5. ET and back ET on the excitation of the Ru(II)-moiety in Ru(II)-Co(III) compounds

(Yoshimura *et al* 1993) The second samples of donor-acceptor linked compounds studied consist of a ruthenium (II) ion and a cobalt (III) ion. The energy gap of the back-ET, which follows ET from an excited Ru(II)-moiety to a cobalt(III)-moiety, is changed from 880 meV at 200 K to 750 meV at 300 K. The standard entropy change (ΔS°) of -1.3 meV/K is responsible for the energy-gap change with temperature. An activation entropy (ΔS^*) is suspected to be involved in the activation process, because the transition state may have an intermediate amount of entropy between the entropy values of the reactant and the product (Hupp and Weaver 1984; Marcus and Sutin 1986). Provided that the activation entropy due to the rearrangement of the inner-coordination shell around a cobalt ion is as negligibly small as that around a ruthenium ion, (3) can be recast by using a temperature-dependent ΔG° into (6). The entropy change (ΔS°) even in this case reduces apparent values of A and E_a , from which the frequency factor and the activation energy are obtained as shown in (6).

$$k = \frac{2\pi}{\hbar} \frac{|H_{rp}|^2}{(4\pi k_B T \lambda)^{1/2}} \exp\left(\frac{(\Delta G^\circ + \lambda)\Delta S^\circ}{2\lambda k_B}\right) \exp\left(-\frac{(\Delta H^\circ + \lambda)^2 - (T\Delta S^\circ)^2}{4\lambda k_B T}\right). \quad (6)$$

A nicely linear plot between the natural logarithms of rate constant and the reciprocal of temperature gives values of an intercept and a slope (figure 3), from which the frequency factor and activation energy are obtained after the correction of entropy term as are shown in table 3. The extent of electronic coupling decreases from the Ru(II)-benzene-Co(III) to the Ru(II)-pentane-Co(III) compound. Since a similar trend in the extent of electronic coupling between an Ru(II) and an Ru(III) of the Ru(II)-Ru(III) compound, was obtained as mentioned above, the back-ET from Co(II) to Ru(III) can be regarded as a nonadiabatic process.

The rearrangement energy of ~ 2 eV observed can be decomposed to an innersphere-rearrangement energy of 1 eV and an outersphere-rearrangement energy of ~ 1 eV. The large innersphere rearrangement energy is consistent with the longer bond-

Table 3. Back electron transfer in $[(\text{bpy})_2\text{Ru}(\text{L-spacer-L})\text{Co}(\text{bpy})_2]^{5+}$ in butyronitrile: Energy gap (ΔG°), entropy change (ΔS°), Arrhenius frequency factor (A), activation energy (E_a), rearrangement energy (λ) and electronic coupling (H_{rp}).

Bridging ligand	ΔG° (eV)	ΔS° (meVK ⁻¹)	A (10 ⁹ s ⁻¹)	E_a (meV)	λ (eV)	H_{rp} (meV)
L _a -benzene-L _a	-0.65	-1.3	300	77	1.8	5
L _β -biphenyl-L _β	-0.75	-1.3	40	87	2.05	2
L _γ -pentane-L _γ	-0.70	-1.3	1.5	120	2.2	0.4

distances of the Co(II)-ligand bonds than with those of the Co(III)-ligand bonds, which are seen for many cobalt compounds (Buhks *et al* 1979; Endicott *et al* 1981; Newton 1991). This may call into question the application of (6) to the Co(II)-to-Ru(III) electron-transfer. While the estimation of rearrangement energy might yield more error, the estimated values of ~ 1 eV are not so strange.

Photoinduced ET of Ru(II)-moiety-to-Co(III) was also observed for Ru(II)-biphenyl-Co(III) and Ru(II)-pentane-Co(III) compounds. The rate of the forward-ET with the exergonicity of 0.6 eV is the following $\sim 1 \times 10^8 \text{ s}^{-1}$ for the Ru(II)-pentane-Co(III) compound, $6 \times 10^9 \text{ s}^{-1}$ for the Ru(II)-biphenyl-Co(III) compound and $> 5 \times 10^{10} \text{ s}^{-1}$ for the Ru(II)-benzene-Co(III) compound at ambient temperature. This trend suggests the nonadiabaticity of the forward-ET, though the frequency factors are not determined by extrapolating an Arrhenius plot of the ET rate constants. A very small activation energy of 0.045 eV for Ru(II)-pentane-Co(III) implies the formation of the doublet excited state of the Co(II)-moiety without change in entropy, which is followed by a rapid relaxation to the quartet ground state of the Co(II)-moiety.

6. Conclusions

Both rearrangement energy and extent of ligand-mediated electronic coupling between metal ions, which are estimated from transition energy and intensity of intramolecular CT transition band of Ru(II)-Ru(III) bimetalated compound, are dependent on the intramolecular bonds and the size of the spacer.

Meanwhile, the extent of electronic coupling and rearrangement energy involved in ET processes with a small exergonicity are evaluated from the temperature-dependence of ET rate.

Frequency factors for ET from an excited ruthenium-moiety to a rhodium-moiety with a small exergonicity is determined by solvent relaxation dynamics. Outersphere rearrangement energy estimated from the activation energy are dependent on the size of spacers of bridging ligands. Back-ET occurring via nuclear tunnelling from Rh(II) to Ru(III) with a high exergonicity is nonadiabatic.

ET from an excited ruthenium(II)-moiety to a cobalt-moiety with an intermediate exergonicity is nonadiabatic. Frequency factors for back-ET from a cobalt(II)-moiety to a ruthenium(II)-moiety is reduced by weak electronic coupling between the metal ions, and reduction in entropy. Activation energy for the back-ET of the Ru(III)-spacer-Co(II) compounds are also reduced by a negative entropy change and by an innersphere rearrangement energy in addition to the outersphere one.

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