ELSEVIER

Coordination Chemistry Reviews
159 (1997) 375–383

COORDINATION CHEMISTRY REVIEWS

Inner-sphere reorganization of photo-induced electron transfers on the laser-excitation of ligand-bridged Ru(II)–Rh(III) and Ru(II)–Co(III) compounds

Akio Yoshimura, Koichi Nozaki, Takeshi Ohno *

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Received 22 December 1995

Contents

Abstract 375
1. Introduction 375
2. Formation of excited states, Ru-to-ligand charge transfer and LF ($^3[(d\pi^5)(d\sigma^*)]$) 378
3. Formation of $^2[(d\pi)^6(d\sigma^*)]$ and $^4[(d\pi)^5(d\sigma)^2]$ in the electron transfer 379
4. Deformation of $^4[(d\pi)^5(d\sigma^*)^2]$ (Co(II)) and $^2[(d\pi)^6(d\sigma^*)]$ (Rh(II)) 381
5. Conclusions 382
References 382

Abstract

Intramolecular reorganization for photo-induced electron transfers of Ru(II)-(L)M(III)$^{5+}$ (L = a bridging tetradentate ligand, and M = Co or Rh) and for formation of ligand-field (LF) excited states are investigated. Inner-sphere reorganization energies (λ_{in}) around the metal ions are estimated from the dependence of electron transfer rates on temperature and ΔG°. For back electron transfer processes, the magnitude of λ_{in} around rhodium ion (0.9 eV) is close to that around the cobalt ion. Inner-sphere reorganization after LF emission of rhodium(III) ion is estimated (0.9 eV) from the Stokes shift of the emission. The magnitude of λ_{in} for the electron transfer and the optical transition are interpreted in terms of gain or loss of the dσ^* electron in the metal orbital.. © 1997 Elsevier Science S.A.

Keywords: Photoinduced electron transfer

1. Introduction

Electron transfer reactions in donor–acceptor linked compounds in solution have been extensively studied to clarify the reorganization dynamics of solvent molecules

---

* Corresponding author.

PII S0010-8545(96)01311-2

and atoms of reactants and electronic transition between initial and final states [1–5]. There are two extreme cases of electron transfer controlled by (1) the reorganization dynamics of polar solvent around the charged and/or decharged reactants (solvent relaxation limit) and (2) electron transfer frequency (nonadiabatic limit) [6]. The rate of nonadiabatic electron transfer with weak exergonicity can be written as Eq. (1) shows [7],

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

Each magnitude of reorganization energy (λ) and electronic matrix element (H_{rp}) can be separately determined from the dependence of electron transfer rate on the Gibbs energy change (ΔG°). The maximum rate could be obtained for the reaction with the same magnitude of Gibbs energy change as that of nuclear reorganization. Since the fraction of atoms of reactant molecules and solvent molecules which is displaced to the potential barrier depends on the temperature, each magnitude of λ and H_{rp} could be individually determined based on the temperature dependence of the electron transfer rate [3,9–13], under the condition that the electron transfer frequency is slower than the reorganization rate of the solvent. The activation energy ($E_{\mathrm{a}}=-k_{\mathrm{B}}d(\ln k)/d(1/T)$) and frequency factor ($A=k/\exp(-E_{\mathrm{a}}/k_{\mathrm{B}}T)$) of electron transfer are related to the extent of both the nuclear reorganization energy (λ) and the Gibbs energy change (ΔG°) and the extent of the electronic coupling matrix element, respectively, as shown in Eqs. (2a), (2b) and (2c),

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

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

$$\lambda=\lambda_{\mathrm{out}}+\lambda_{\mathrm{in}} \tag{2c}$$

where λ_{out} and λ_{in} are outer-sphere reorganization energy of low-frequency mode and inner-sphere reorganization energy of high- and medium-frequency mode.

The height of the potential barrier for electron transfer is ascribed to reorganization of both the outer-sphere solvent molecules and the inner-sphere atoms of the reactants. The latter, which is the bigger part of total reorganization energy for the slower electron transfer reactions, stems from difference in bond length and vibrational frequency between the reactant and the product [14,15]. The gain of an electron in an antibonding orbital (dσ^*) diminishes the frequency of the Co–N stretching vibration of $\mathrm{Co(NH_3)_6^{2+}}$ and $\mathrm{Co(bpy)_3^{2+}}$ [16], while loss of an electron from an antibonding orbital increases the frequency. Such an elongation of metal–ligand bonds during electron transfer has been expected for rhodium(III)/rhodium(II) chemistry. However, because the chemistry of Rh(II) is very limited due to its high reactivity, structural evidence for the longer bond-length has not been proven. Furthermore, the fast rate of the photo-induced electron transfer reaction [17] suggests a small reorganization energy for the self-exchange electron transfer of $\mathrm{Rh(bpy)_3^{3+/2+}}$ contrary to expectation. Evidence in line with the expectation based on the orbital configuration has been found for the regeneration of Rh(III) in the geminate radical pair formed in the electron transfer quenching of the excited rhodium(III) compound [18]. The regeneration of Rh(III) needed a high reorganization energy (1.7 eV), which consists of outer-sphere reorganization (0.8 eV) and inner-sphere reorganization (0.9 eV).

A vibrational mode with a frequency lower than 300 $\mathrm{cm^{-1}}$ is involved in either the reactant or the product, thus the molecular vibration accessed behaves as an energy acceptor and enhances the effective state density of either a reactant or a product [16,19,20]. When electron transfers involve an entropy change, that change (ΔS°) varies the magnitude of E_a and A as is shown in Eqs. (3a), (3b) and (3c) [21,22]

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

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

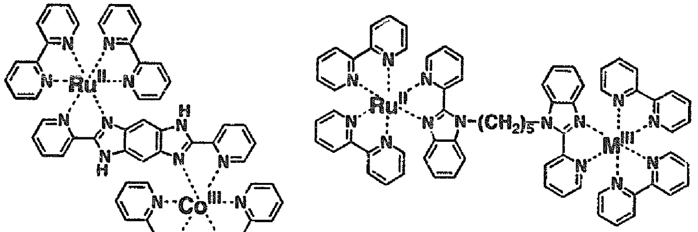
$$E_a=\frac{(\Delta H^\circ+\lambda)^2-(T\Delta S^\circ)^2}{4\lambda} \tag{3c}$$

where ΔH° is the enthalpy change. Recently, large entropy changes due to the change of inner-sphere structure were found for heterogeneous electron transfer reactions of Co(III)/Co(II) [20]. Most of the entropy changes in both homogeneous electron transfer and heterogeneous electron transfer of metal complexes have been ascribed to the temperature-dependent solvation energy of metal complex ions in various solvents [23,24]. As a result of the entropy changes in the electron transfer reactions of Co(III)/Co(II), it is expected that the frequency factor (A) comprises not only the square of electronic coupling matrix element but also the change of state density.

In this article, inner-sphere reorganization energy (λ_{in}) is estimated for the formation of ligand-field excited state [^{3}LF:$(\mathrm{d}\pi)^5(\mathrm{d}\sigma^*)$] [25] and the Ru-to-ligand charge transfer state [26]. The extent of λ_{in} for Co(III) [13,27] and Rh(III) [25] are evaluated from the T- and ΔG°-dependence of the electron transfer rate for M(III) $(\mathrm{d}\pi^6)\rightarrow$M(II) $(\mathrm{d}\pi^6\mathrm{d}\sigma^*$ and/or $\mathrm{d}\pi^5\mathrm{d}\sigma^{*2})$ transfers. In the case of ligand-bridged Ru(II)–Co(III) compounds, the entropy change is taken into account for the temperature-dependence not only of the ^{4}Co(II)-oxidation but also the ^{2}Co(II)-formation and the intersystem crossing (^{2}Co(II)$\rightarrow^4$Co(II)) [27]. Electron transfer processes are examined for the following ligand-bridged Ru(II)–M(III) compounds, $[\mathrm{L'_2Ru(II)(L)M(III)L'_2}]^{5+}$ (L′ = bpy, L = 2,6-bis(2-pyridyl)imidazobenzene(dpimbH$_2$), M = Co:$\underline{\mathbf{a}}$, L′ = bpy, L = 1,5-bis[2-(2-pyridyl)benzimidazoyl]pentane (dpbimPe), M = Co:$\underline{\mathbf{b}}$, and L′ = bpy, L = dpbimPe, M = Rh:$\underline{\mathbf{c}}$).

Molecular structures for $\underline{\mathbf{a}}$, [13,27] for $\underline{\mathbf{b}}$, [13,27] and for $\underline{\mathbf{c}}$ [25] are shown in

Scheme 1. Reaction schemes of photo-induced electron transfers are shown in Scheme 2 for *a* and *b* and Scheme 3 for *c*[1].

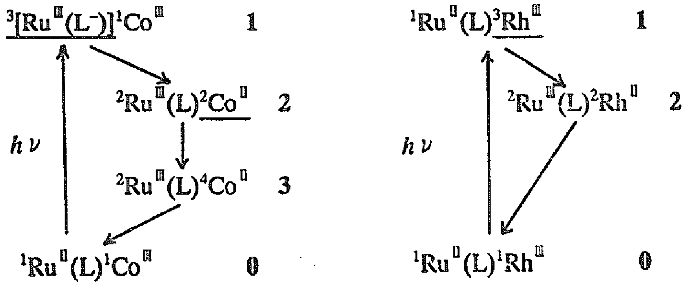


a

b : M = Co

c : M = Rh

Scheme 1.



Schemes 2 and 3.

2. Formation of excited states, Ru-to-ligand charge transfer and LF ($^3[(d\pi^5)(d\sigma^*)]$) [25,27]

Inner-sphere structural change on excitation has been estimated from the spectral profile of absorption and emission. The displacement of atoms in the excited compounds is reflected in the vibrational progressional structure of the electronic transition, where the intensity of the $0-n$ vibronic band (I_n) can be written by using Huang-Rhy factor (S), as follows,

$$I_n = I_0 \frac{S^n e^{-S}}{n!} \tag{4}$$

The magnitude of S is near to n for the strongest vibronic band. The inner-sphere

---

[1] In Schemes 1 and 2, the underline denotes a moiety electronically excited.

reorganization energy (λ_{in}) can be estimated from S as is shown in Eq. (5):

$$\lambda_{\text{in}} = S\hbar\omega' \tag{5}$$

where ω' is angular frequency of vibration. When the vibronic structure of the emission (absorption) is blurred out, the magnitude of inner-sphere reorganization energy has been roughly estimated from Stokes shift.

$Ru(bpy)_2(dpbimPe)^{2+}$ exhibits a structured phosphorescence ($S = 0.9$ and $\Delta\hbar\omega' = 1350$ cm^{-1}) in butyronitrile at 77 K, for which the inner-sphere reorganization is calculated to be 1170 cm^{-1}. The extent of outer-sphere reorganization energy around bpy$^-$ is estimated to be similar from the full width at half-maximum of the 0–0 band by assuming a homogenous broadening. The lowest ^{3}LF excited state of a Rh(III) compound such as $Rh(NH_3)_6^{3+}$ takes an electronic configuration of $(d\pi)^5(d\sigma^*)$, which emits a very broad emission in the red region. $Rh(bpy)_2(mpbim)^{3+}$ (mpbim = *N*-methyl-2-(2-pyridyl)benzimidazole) emits a high-energy structured emission (21 300 cm^{-1}) and a low-energy structureless one (14 300 cm^{-1}) in a higher temperature region than 190 K. The higher energy emission is assigned to $^3(\pi-\pi^*)$ of mpbim, and the lower energy one to ^{3}LF of Rh(III) as for $Rh(1,10\text{-phenanthroline})_2(NH_3)_2^{3+}$ [28]. The reorganization energy of ^{3}LF (emission) is estimated to be 7800 cm^{-1} = 0.97 eV from the differences (800 and 7000 cm^{-1}) in both the state energy and the emission energy between $^3(\pi-\pi^*)$ and ^{3}LF [29,30].

3. Formation of $^2[(d\pi)^6(d\sigma^*)]$ and $^4[(d\pi)^5(d\sigma)^2]$ in the electron transfer [13,25,27]

Photo-induced electron transfers of $[(bpy)_2Ru(L)Co(bpy)_2]^{5+}$ were investigated by means of laser kinetic spectroscopy. Laser excitation of $Ru(L)Co^{5+}$, **a**, with a 532-nm pulse of 20 ps duration generated a transient difference absorption spectrum, which is not assigned to the primary intermediate of $^3[^3Ru(III)(L^-)^1Co(III)]^{5+}$ but the secondary one (see Scheme 2). The secondary intermediate is presumed to be an intramolecular electron-transfer product, $^3[^2Ru(III)(L)^2Co(II)]$ [31], which rapidly decayed to form the third intermediate within 400 ps. The third intermediate exhibits a strong bleaching of Ru-to-dpimbH$_2$ charge transfer absorption around 470 nm, indicating the formation of $^5[^2Ru(III)(L)^4Co(II)]$ in the ground state. Since the secondary intermediate can be most probably identified as a doublet excited state of the Co(II) moiety with a $(d\pi)^6(d\sigma^*)$ configuration, the decay of the secondary intermediate corresponds to the intersystem crossing of $^3[^2Ru(III)(L)^2Co(II)] \rightarrow {}^5[^2Ru(II)(L)^4Co(II)]$. The intersystem crossing of the triplet→quintet (doublet→quartet in the Co(II) moiety), was rapid (2.1×10^{10} s^{-1}) at 180 K. The reorganization energy ($\lambda_{23} = 0.5$ eV) and the electronic coupling matrix element ($H_{23} = 2$ mV) were determined by fitting the *T*-dependent rate to Eq. (3a). The magnitude of reorganization energy is close to the inner-sphere reorganization energy of $^2Co(II) \rightarrow {}^4Co(II)$ estimated from both the optical transition energy ($\hbar\omega = \Delta G_{23}^\circ - \lambda_{23}$) of I$^-$-to-Co(III) charge-transfer of $[Co(bpy)_3]I_3$ [32]. Though the final result is reasonable, there is a question about the validity of Eq. (3a) for the intersystem crossing with a large quantity of $T\Delta S^\circ_{23}$ ($0.6\times T$ meV) compared with ΔH°_{23} (−20 meV), because the Marcus equation (Eqs. (2a), (2b) and (2c)) is not valid for the reactions accompanying a large entropy change see Table 1.

As for ***b***, the decay of a transient absorption due to ^{3}Ru-bpy CT [32] was accompanied by the formation of Ru(III)(L)Co(II) in 1 ns after the ps laser excitation at 298 K. Since the quenching of the MLCT excited state of ***b*** is slower than the intersystem crossing observed for ***b***, the slower quenching of the MLCT excited state is identified as the electron transfer between the Ru(II) and the Co(III) moieties bridged by a dpbimPe. The electron transfer rate of ***b*** was determined to be $1.4\times10^9\ \mathrm{s}^{-1}$ at 298 K. Since the Arrhenius plot of $\ln k_{\mathrm{obs}}T^{1/2}$ against $1/T$ is nonlinear due to the entropy change, the inner-sphere reorganization energy and the matrix element were determined by fitting the observed temperature-dependent rate to Eqs. (3a), (3b) and (3c). The other temperature-dependent quantities, the outer-sphere reorganization energy and the Gibbs energy change, are taken into consideration in the least-square fitting of $\ln k_{12}T^{1/2}$ against $1/T$. The outer-sphere reorganization energy $\lambda_{\mathrm{out},12}(T)$ at a given temperature (Eq. (6))

$$\lambda_{\mathrm{out}}(T)=\frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{2r_1}+\frac{1}{2r_2}+\frac{1}{R}\right)\left(\frac{1}{\epsilon_{\mathrm{op}}(T)}-\frac{1}{\epsilon_{\mathrm{s}}(T)}\right) \tag{6}$$

is estimated from the optical dielectric constant ($\epsilon_{\mathrm{op}}(T)$, square of refractive index) of butyronitrile [33], the static dielectric constant ($\epsilon_{\mathrm{s}}(T)$) [34] and $\lambda_{\mathrm{out},12}$ at 298 K. The magnitude of $\lambda_{\mathrm{out},12}$ at 298 K is estimated to be the same as that of a donor–acceptor compound (Ru(II)(L)Ru(III)) at 298 K [32], for which the radii of Ru(II) and Ru(III) moieties (r_1 and r_2, respectively) and the distance between the metal ions (R) are close to those of Ru(II)(L)M(III), respectively. The extent of $\lambda_{\mathrm{in},12}$ for ***b*** is estimated to be 0.5 eV, which amounts to half of $\lambda_{\mathrm{in},30}$ for the back electron transfer (vide infra).

In the case of Ru(II)(L)Rh(III) (***c***), two kinds of excited states underwent electron transfer from the Ru(II) moiety to the Rh(III) moiety. The 355-nm light excitation of Ru(II)(L)Rh(III) generates the ^{3}LF of Rh(III) ($\hbar\omega=2.7$ eV) and $^3(\pi^*-\pi)$ of dpbimPe ($\hbar\omega=2.6$ eV). The ^{3}LF state of Rh(III), which exhibits a

Table 1
Gibbs energy change (ΔG°), entropy change (ΔS°), rate constant (k), activation energy (E_{a}), and frequency factor (A) of the electron transfer of photoexcited Ru(II)(L)M(III) (M=Co or Rh) or the intersystem crossing of Co(II) in butyronitrile at 298 K [25,27]

Compound	ΔG° (eV)	ΔS° (meV K^{-1})	k ($10^8\ \mathrm{s}^{-1}$)	E_{a} (meV)	λ_{in} (eV)	λ_{out} (eV)	A_{ij} (s^{-1})	H_{ij} (meV)	Process
a	−0.2	0.6	620[a]	53	0.3	0	2×10^{11}	1.4	2→3
b	−1.14	0.6	14	54	0.5	1.1	2×10^{10}	0.7	1→2
c	−0.8	–	80	~0	0	0.8	–	–	1→2

[a] Estimated by extrapolation of the Arrhenius plot in the range of 173–230 K.

transient weak band in a visible region, underwent electron transfer from the Ru(II) moiety to the Rh(III) moiety as is shown in Scheme 3. The rate of Ru(III) formation ($8 \times 10^9\ s^{-1}$) was greater by two orders of magnitude than that of the excitation to Ru-ligand CT. The electron transfer rate was independent of temperature so that the reorganization energy is estimated to be as high as $|-\Delta G_{12}^{\circ}|$ (0.8 eV). The major part of the inner-sphere reorganization energy is attributable to the outer-sphere one. Actually, the electronic configuration, $^2[(d)^6(d\sigma^*)]$ of the product, Rh(II), is not so different from that of $^3[(d\pi)^5(d\sigma^*)]$ of the precursor, ^3LF. It is expected that the back electron transfer from $d\sigma^*(Rh)$ to $d\pi(Ru)$ reorganizes the inner-sphere structure of the rhodium ion (vide infra). It was observed by means of ns laser kinetic spectroscopy that the excited state of Ru(II)-bpy CT ($h\omega = 2.0$ eV) performed electron trasnfer with a rate $k_{et} = 9 \times 10^7\ s^{-1}$ at 298 K. Since the electron transfer rate was dependent on the temperature, the magnitude of the reorganization energy (0.9 eV) and the electronic matrix element (2 meV) were estimated from the slope and the intercept of a plot, $\ln k_{et} \sim 1/T$. Since the reorganization energy is ascribed to the outer-sphere reorganization, the electron transfer is suggested not to be to the $d\sigma^*$ orbital but to the π^* orbital of pyridyl-benzimidazole. If this is so, Scheme 3 cannot be applied to the quenching of the Ru-ligand CT state.

4. Deformation of $^4[(d\pi)^5(d\sigma^*)^2]$ (Co(II)) and $^2[(d\pi)^6(d\sigma^*)]$ (Rh(II)) [25,27]

The starting species of Ru(II)(L)Co(III), **a** and **b**, were slowly recovered in the last stage of the photo-induced electron transfer reaction. The rates of back electron transfer were determined from the recovery of the MLCT absorption at 460 nm. The rates of back electron transfer $(0.3–2.1) \times 10^8\ s^{-1}$ and $(0.13–1.6) \times 10^6\ s^{-1}$ for **a** and **b**, respectively, are more dependent on temperature than are the preceding processes. The magnitude of H_{30} and $\lambda_{in,30}$ are determined as shown in Table 2 from the temperature dependence of the back electron transfer rate. The temperature dependencies of ΔG_{30}° and $\lambda_{out,30}$ are taken into consideration during the analyses. Since the reoxidation rate of the Co(II) moiety is slow compared with the initial electron transfer, the substantial inner-sphere reorganization energy of the Co(III)/Co(II) moiety is thought to be involved in the back electron transfer. Large

Table 2
Gibbs energy change (ΔG°), entropy change (ΔS°), rate constant (k), activation energy (E_a), and frequency factor (A) of the back electron transfer of $^{4,2}M(II)$-to-$^2Ru(III)$ in butyronitrile at 298 K [25,27]

Compound	ΔG° (eV)	ΔS° (meV K^{-1})	k ($10^8\ s^{-1}$)	E_a (meV)	λ_{in} (eV)	λ_{out} (eV)	A_{ij} (s^{-1})	H_{ij} (meV)	Process
a	−0.77	−1.3	2100	60	1.3	0.7	300×10^7	5	3→0
b	−0.79	−1.3	16	78	1.1	1.1	8×10^7	0.9	3→0
c	−1.95	–	(260)[a]	–	0.9	1.0	–	–	2→0

[a] Estimated by extrapolation of the Arrhenius plot in the range of 173–230 K.

values of $\lambda_{\mathrm{in},30}$ (1.1 and 1.3 eV) are determined for **a** and **b**, respectively. These large $\lambda_{\mathrm{in},30}$ values are consistent with large differences (~0.20 Å) in the bond-length between the ^{4}Co(II)–nitrogen and ^{1}Co(III)–nitrogen of analogous Co(III)/Co(II) redox couples [8,35].

The frequency factors of the back electron transfer are much smaller than the electron transfer of the excited state. The extent of A_{30} is reduced by $\exp[(\Delta G_{30}{}^{\circ}+\lambda_{30})\Delta S_{30}{}^{\circ}/2\lambda_{30}k_{\mathrm{B}}]=1\times10^{-2}$ and 8×10^{-3} for **a** and **b**, respectively. A frequency factor corrected by the negative entropy term gives rise to the large extent of matrix element for **a** and **b**, as shown in Table 2. Since a part of the entropy change can be attributable to the difference in the vibrational frequency between the ^{4}Co(II)–nitrogen and the ^{1}Co(III)–nitrogen, the inner-sphere reorganization during the back electron transfer is responsible for both the small frequency factor and the high activation energy.

In the case of Ru(II)(L)Rh(III), **c**, the Ru(III) formed in the electron transfer quenching of the excited LF state of the Rh(III) moiety was detected by means of ps laser kinetic spectroscopy. The rate of Ru(III) disappearance (2.6×10^9 s^{-1}) was determined for $\Delta G^{\circ}=-1.95$ eV. The magnitude of reorganization energy of the back electron transfer was estimated to be 1.9 eV from the ΔG°_{20} dependence of the rate for the analogous compounds, L$'_2$Ru(III)(L)Rh(II)L$''_2$ (L = 1,4-bis[2-(2-pyridyl)benzimidazoyl]buthane, L′ = 4,4′-di-ethoxycarbonyl-bpy, bpy, or 4,4′-dimethyl-bpy, L″ = bpy). The extent of the inner-sphere reorganization energy for loss of a dσ^* electron is calculated to be as large as 0.9 eV.

The extent of $\lambda_{\mathrm{in},20}$ is in agreement with those observed for both the formation of the ^{3}LF (Rh(III) moiety) with a electronic configuration of dπ^5dσ^* and the regeneration of Rh(III) from the geminate radical pair between a Rh(II) and a cation radical of aromatic donor [18]. A dσ^* electron of Rh(II) gives rise to as a large displacement of Rh(II)–N bonds as two dσ^* electrons of cobalt(II).

5. Conclusions

Photoexcitation of ligand-bridged Ru(II)(L)M(III) compounds (M = Co and Rh) leads to electron transfer of Ru(II)→M(III), followed by back electron transfer of M(II)→Ru(III). Dependence of electron transfer rates on temperature and Gibbs energy change demonstrates both the inner-sphere and the outer-sphere reorganization are involved in the processes. Reorganization of Co–N bonds occurs during electron transfers of Ru-to-Co and Co-to-Ru and intersystem crossing ^{2}Co(II)→^{4}Co(II). A similar displacement of Rh–N bonds in a Ru(II)(L)Rh(III) compound occurs during the photoexcitation to ^{3}LF of the rhodium(III) moiety and Rh-to-Ru electron transfer.

References

[1] G.C. Walker, P.F. Barbara, S.K. Doorn, Y. Dong and J.T. Hupp, J. Phys. Chem., 96 (1991) 5712.
[2] D.A.V. Kliner, K. Tominaga, C. Walker and P.F. Barbara, J. Am. Chem. Soc., 114 (1992) 8323.

[3] K. Nozaki, T. Ohno and M. Haga, J. Phys. Chem., 96 (1992) 10880.
[4] G.L. Closs, L.T. Calcaterra, N.J. Green, K.W. Penfield and J.R. Miller, J. Phys. Chem., 90 (1986) 3673.
[5] M.D. Newton, Chem. Rev., 91 (1991) 767.
[6] I. Rips and J. Jortner, J. Chem. Phys., 87 (1987) 2090.
[7] R.A. Marcus, J. Chem. Phys., 24 (1956) 966.
[8] B.S. Brunshwig, C. Creutz, D. Macartney, T.-K. Sham and N. Sutin, Faraday Discuss. Chem. Soc., 74 (1982) 113.
[9] (a) S.S. Isied, C. Kuehn, G. Worosila, J. Am. Chem. Soc., 106 (1984) 1722; (b) S.S. Isied, A. Vassilian, J.F. Wishart, C. Creutz, H.A. Schwartz, N. Sutin, J. Am. Chem. Soc., 110 (1988) 635.
[10] H. Heitele, P. Finckh, S. Weeren, F. Pollinger and M.E. Michel-Beyerle, J. Phys. Chem., 83 (1989) 5173.
[11] M. Liang, J.R. Miller and G.L. Closs, J. Am. Chem. Soc., 112 (1990) 5353.
[12] J. Liu and J. Bolton, J. Phys. Chem., 96 (1992) 1718.
[13] A. Yoshimura, K. Nozaki, N. Ikeda and T. Ohno, J. Am. Chem. Soc., 115 (1993) 7521.
[14] N. Sutin, Progr. Inorg. Chem., 30 (1984) 441.
[15] J.F. Endicott, G.R. Brubaker, T. Ramsami, K. Kumar, K. Dwarakanath, J. Cassel and D. Johnson, Inorg. Chem., 22 (1983) 3754.
[16] D. Richardson and P. Sharpe, Inorg. Chem., 30 (1991) 1412.
[17] C. Creutz, A.D. Keller, H.A. Chwartz, N. Sutin and A.P. Zipp, ACS Symp. Ser., 198 (1982) 385.
[18] T. Ohno, T.A. Yoshimura and N. Mataga, J. Phys. Chem., 84 (1990) 4871.
[19] J.T. Hupp, G.A. Neyhart, T.J. Meyer and E.M. Kober, J. Phys. Chem., 96 (1992) 10820.
[20] P.W. Crawford and F.A. Schultz, Inorg. Chem., 33 (1994) 4344.
[21] R.A. Marcus and N. Sutin, Biochim. Biophys. Acta, 811 (1985) 265.
[22] R.A. Marcus and N. Sutin, Comments Inorg. Chem., 5 (1986) 119.
[23] J.T. Hupp and M.J. Weaver, Inorg. Chem., 23 (1984) 256, 3639.
[24] J.T. Hupp and M.J. Weaver, J. Phys. Chem., 89 (1985) 2795.
[25] K. Nozaki and T. Ohno, 11th International Symposium on Photophysics and Photochemistry of Coordination Compounds, Abstract Book, 1995, p. 127.
[26] A. Yoshimura, K. Nozaki, N. Ikeda and T. Ohno, Bull. Chem. Soc. Jpn., 69 (1996) 2791.
[27] A. Yoshimura, K. Nozaki, N. Ikeda and T. Ohno, J. Phys. Chem., 100 (1996) 1630.
[28] M.T. Indelli and F. Scandola, Inorg. Chem., 29 (1990) 3056.
[29] A large reorganization energy of ^{3}LF (8800 cm^{-1}) is estimated for *trans*-dicyano(1.4.8.11-teraazacyclotetra-decane)rhodium(III) ion from the Stokes shift. L.J. McClure and P.C. Ford, J. Chem. Phys., 96 (1992) 6460.
[30] X. Song, Y. Lei, S.V. Wallendal, M.W. Perkovic, J.F. Endicott and D.P. Rillema, J. Phys. Chem., 97 (1993) 3225.
[31] R. Billing, R. Benedix, G. Stich and H. Hennig, Z. Anorg. Allg. Chem., 583 (1990) 157.
[32] T. Ohno, K. Nozaki and M. Haga, Inorg. Chem., 31 (1992) 4256.
[33] J.A. Riddick, W.B. Bunger and T.K. Sakano (eds.), Organic Solvents, 4th Edn., John Wiley and Sons, New York, 1986.
[34] $\epsilon_s(T)$ of butylonitrile is estimated on the assumption that the temperature dependence of $\epsilon_s(T)$ is the same as that (see Ref. [32]) of acetonitrile.
[35] J.F. Endicott, B. Durham and K. Kumar, Inorg. Chem., 21 (1982) 2437.