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EFFICIENCIES OF ELECTRON TRANSFER REACTIONS IN THE QUENCHING OF EXCITED RHODIUM COMPOUNDS BY AROMATIC COMPOUNDS

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ABSTRACT

Bimolecular electron transfer reactions of electronically excited rhodium compounds were studied by means of laser photolysis kinetic spectroscopy. Di- and tri-methoxybenzenes and aromatic amines such as diphenylamine, phenylenediamine, and benzidine reduced both π-π* triplet excited state of Rh(4,7-diphenyl-1,10-phenanthroline)$_3^{3+}$ (Rh(dp-phen)$_3^{3+}$), Rh(1,10-phenanthroline)$_3^{3+}$ (Rh(phen)$_3^{3+}$) and ligand field triplet excited states of RhCl$_2$(dp-phen)$_2$ and RhCl$_2$(phen)$_2^+$ with a high efficiency. Back electron transfer, which takes place within a cage complex formed in the primary electron transfer, is retarded by lack of intermolecular electronic exchange interaction and spin-orbit interaction.

INTRODUCTION

Photochemistry of rhodium(III) compounds has drawn attention for one decade. Tervalent rhodium compounds having ammonia or ethylenediamine as ligands are known to emit a broad phosphorescence from the ligand field triplet excited state at liquid nitrogen temperature (refs. 1 and 2) and to be photoactive for ligand substitution at room temperature (refs. 3 and 4). Studies of the phosphorescence, which can provide information about the decay of the excited state, have led to the conclusion that the phosphorescent states of the halogeno-pentammine or dihalogeno bis-ethylenediammine compounds of rhodium(III) ion are responsible for the photo-substitution reaction (refs. 3 and 5). On the other hand, tris(1,10-phenanthroline*)rhodium(III) emits well resolved phosphorescence from the ligand at liquid nitrogen temperature (ref. 2) and undergoes a bimolecular electron transfer reaction at room temperature (ref. 6). Nevertheless, neither the bimolecular quenching rate nor the yield of the primary reaction product in the quenching of Rh(phen)$_3^{3+}$ have been measured, The phosphorescence of rhodium(III) compounds is too weak to be quantitatively studied, and the rhodium(II) compound formed in the quenching is unstable. We utilized excited-state absorptions to clarify the mechanism of photochemical electron transfer reaction, because the formation of the excited state as well as its decay can be quantitatively determined by means of excited-state absorption technique (ref. 7).

Generally speaking, quenching rates of electronically excited states of

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*Following abbreviations will be used, 1,10-phenanthroline:phen, 4,7-diphenyl-1,10-phenanthroline:de-phen, and 2,2'-bipyridine:bpy.

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metal compounds such as Ru(2,2'-bipyridine*)$_3^{2+}$ and Cr(bpy)$_3^{3+}$ have been successfully analyzed in terms of Gibbs' energy change (refs. 8 and 9). Nevertheless, yields of the primary product in the quenching vary with quenchers and are still unpredictable. We ascribed low yields to rapid back electron transfer within a cage complex formed in the quenching (refs. 10-14). When the efficiency of the product formation depends on the cage escape probability of the electron transfer products formed in the quenching, a rate of an effective radius of the back electron transfer process within the cage complex can be estimated from the efficiency of the product formation. Since the rates of the back electron transfer processes within the cage complex are not limited by the diffusion process in the solvent, one can study the substantial dependence of the electron transfer rate on the Gibbs' free energy change in a wide range. It may be possible to discuss unsolved problems of electron transfer processes such as the "inverted region" and nonadiabaticity on the basis of the rate dependence.

Another special aspect of the back electron transfer is related to an electron spin multiplicity. As long as a phosphorescent state with a triplet spin multiplicity is involved in bimolecular electron transfers, the back electron transfer within a cage complex with a triplet spin multiplicity is prohibited by spin conservation rule from giving the original reactants in the singlet ground state. The following facts clearly indicate that the spin-conservation rule is valid for transition metal compounds. Firstly the spin-forbidden optical transitions of transition metal compounds are much weaker than spin-allowed ones. Secondly when a low spin iron(III) compound with a doublet spin multiplicity is used as an oxidative quencher for the phosphorescent state of phthalocyanine, the spin-allowed back electron transfer from a singlet iron(II) to a doublet phthalocyanine radical is so fast that the cage escape probability of the phthalocyanine radical is close to zero (ref. 14). On the contrary, when a compound of cobalt(III) or benzoquinone with singlet spin multiplicity is used as an oxidative quencher, the spin-forbidden back electron transfer from a doublet cobalt(II) to a doublet phthalocyanine radical is not so fast (ref. 15).

METHODS

Apparatus

An NEC SLG-2018 Q-switched ruby laser capable of providing up to 0.20 J per flash at 347 nm was used. The details of the laser apparatus and the monitoring device have been described elsewhere (ref. 13). Transient changes in absorption and decay of luminescence were fed into a Iwatsu 8123 Storagescope, followed by computer analysis using a NEC PC8001 MKII microcomputer.

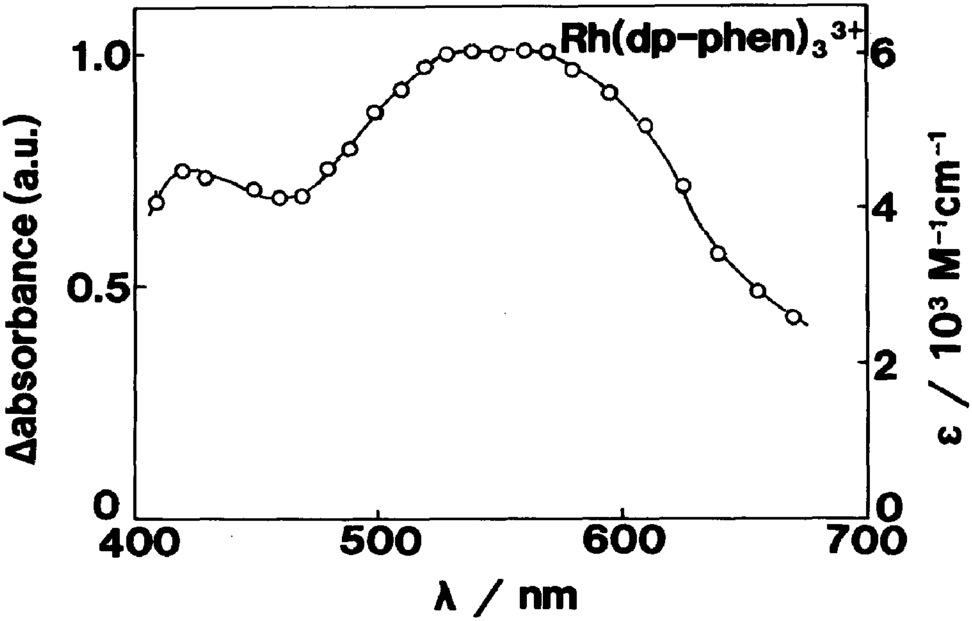

Fig. 1. Excited-state absorption of Rh(dp-phen)$_3^{3+}$ of 11.4 M in AN-water.

Materials

The preparation and purification of $[Rh(phen)_3]Cl_3 \cdot 3H_2O$, $[RhCl_2(phen)_2]Cl \cdot 3H_2O$, $[Rh(4,7\text{-diphenyl-1,10-phenanthroline*})_3]Cl_3 \cdot 4H_2O$ and $[RhCl_2(dp\text{-}phen)_2]Cl \cdot 3H_2O$ were described elsewhere (ref. 7). Acetonitrile (AN) was used as supplied by Wako Pure Chemical Co. Water was purified by passing it through a Millipore deionizer and filter. Following aromatic amines, N,N,N',N'-tetramethyl-1,4-phenylenediamine (TMPD), 1,4-phenylenediamine (1,4-PD), 1,2-phenylenediamine (1,2-PD), N,N,N',N'-tetramethyl-benzidine (TMB), 3,3'-dimethylbenzidine (DMB), diphenylamine (DPA), were purified by sublimation. 1,2,4-Trimethoxybenzene(1,4-DMB) were used without further purification. The test solutions were deaerated by purging for 15-20 minutes with nitrogen.

Procedure

The production of the excited rhodium(III) compound was determined by using a molar absorption coefficient of the excited-state absorption which is shown in Table 1. The production of one-electron oxidized aromatic compounds was also measured by means of laser-flash spectroscopy. The molar absorption coefficients are shown in Tables 2 and 4.

RESULTS AND DISCUSSION

The excited-state absorption of some rhodium(III) compounds has been already reported by us (ref.7). Laser excitation of Rh(dp-phen)$_3^{3+}$ gave rise to a

TABLE 1

Molar absorption coefficients and lifetimes of excited states.

	$\varepsilon/M^{-1}cm^{-1}$	lifetime/10^{-6}s	(solvent)	lowest excited state
$Rh(dp\text{-}phen)_3^{3+}$	9,800	73	$(AN\text{-}H_2O)$	$^3(\pi\text{-}\pi)$
$RhCl_2(dp\text{-}phen)_2^{+}$	2,750	1.0	(AN)	$^3T_1$
$Rh(phen)_3^{3+}$	2,300	0.41	(H_2O)	$^3(\pi\text{-}\pi)$
$RhCl_2(phen)_2^{+}$	1,600	0.70	(AN)	$^3T_1$

TABLE 2

Quenching rate constants ($k_q/10^9\ M^{-1}s^{-1}$) and efficiencies of product formation in the quenching (F_1).

	$Rh(dp\text{-}phen)_3^{3+}$		$RhCl_2(dp\text{-}phen)_2^{+}$		$Rh(phen)_3^{3+}$		$RhCl_2(phen)_2^{+}$	
	k_q	F_1	k_q	F_1	k_q	F_1	k_q	F_1
1,4-DMB	4.0	0.48	0.44	0.38	4.0	0.34	-	-
1,3,5-TMB	4.0	0.45	<0.1	-	-	-	-	-
1,2,4-TMB	-	-	2.9	0.34	4.0	0.30	0.41	0.065

transient absorption spectrum shown in Figure 1 with the lifetime of 72 μsec in agreement with the lifetime of weak π-π phosphorescence of the ligand. The molar absorption coefficient of the excited-state absorption was obtained as 9,800 M^{-1} cm^{-1} at 550 nm assuming that the complete excitation of $Rh(dp\text{-}phen)_3^{3+}$ to the phosphorescent state was obtained by constant production of the transient absorption, when the laser intensity was attenuated. A transient abosrption of the photo-excited $Rh(phen)_3^{3+}$ at liquid nitrogen temperature can also be identified as the triplet π-π* excited state of coordinating 1,10-phenanthroline by measuring the same lifetime as the π-π* phosphorescence of the ligand at liquid nitrogen temperature. While a rise in temperature replaced the π-π* emission with a broad and red-shifted emission from the ligand-field excited state as Bolletta et al. reported (ref.16), the excited state absorption was not changed so that the broad ligand field emission is ascribed to the thermal activation from the triplet π-π* excited state of 1,10-phenanthroline. The molar absorption coefficient of the excited-state absorption was obtained as 2,300 $M^{-1}cm^{-1}$ at 510 nm by means of complete excitation. Figure 2 shows the constant production of the triplet excited state of $Rh(phen)_3^{3+}$ accompanied by an attenuation of the laser intenisty. The 410 ns lifetime of excited-state absorption at room temperature in water, becomes as short as 50 ns in methanol. On the other hand, the lowest excited state of dichloro-bis-phenanthroline compounds has been assigned to the triplet ligand field excited state (ref.1). Laser excitation

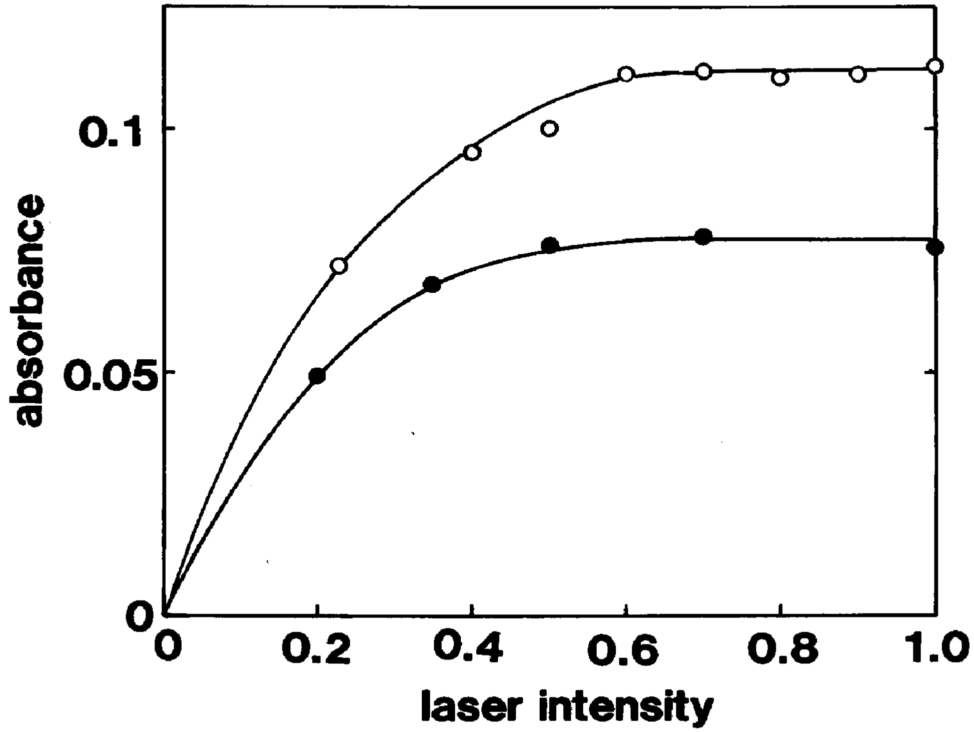

Fig. 2. Dependence of excited-state absorption on the laser intensity attenuated by a filter solutionof chromium alum. The open circles : aqueous solution of $Rh(phen)_3^{3+}$ (98 μM) and the closed circles : an AN solution of $RhCl_2(phen)_2^+$ (100 μM). The cell length is 5 mm.

of the acetonitrile solution produce a transient absorption with a lifetime of 700 ns, which gets as short as 50 ns in pure water. As for $RhCl_2(dp\text{-}phen)_2^+$, a similar excited state absorption with the lifetime of 1 μs in acetonitrile was identified as the ligand field triplet excited state. The shorter lifetime of the ligand field phosphorescence in the aqueous solution indicates that the photo-aquation reaction of the dichloro-bis-phenanthroline compound originates from the low-lying ligand field triplet excited state. Table 1 shows the molar absorption coefficients of excited-state absorptions, which are large enough to determine more than several micro molar concentration of transient species upon laser excitation. Now, we are able to determine the formation of the excited state and quantum yield of electron transfer reactions of the rhodium compounds.

A back electron transfer process within a cage complex is a transient process so that there is no simple relationship between the efficiency of electron-transfer product formation and a rate of back electron transfer process (ref.18). If the rate of back electron transfer within a cage complex can be expressed by using a time-independent rate constant (k_b), the efficiency (F_1) can be written as follows,

$$F_1 = k_{dis}/(k_{dis} + k_b) \tag{1}$$

where k_{dis} is the rate constant of the complex dissociation. Equation 1 is rewritten as,

$$1/F_1 - 1 = k_b/k_{dis} \tag{2}$$

If the rate constant, k_b, is expressed in Eq. 3 according to Marcus (ref.17),

$$k_b = \nu\kappa\ \exp(-\Delta G_b/RT) \tag{3}$$

$$\Delta G_b = \lambda/4(1 + \Delta G_b^o/\lambda)^2 \tag{4}$$

$$\lambda = 1/2(\lambda_1 + \lambda_2) \tag{5}$$

where ν, κ, ΔG^o and λ are the frequency along the reaction coordinate, the transmission coefficient, the Gibbs' free energy change and the intrinsic barrier in the back electron transfer process, λ_1 the intrinsic barrier in the self-exchange process of Rh(III)/Rh(II) couple, λ_2 that of D/D$^+$ couple. Since λ_1 and λ_2 are estimated to be 0.8 eV, one can obtain values of k_b depending on ΔG^o on assuming κ=unity. The calculated k_b has a parabolic form against ΔG^o (as is shown in Fig. 3) and a maximum value ($6.2\text{x}10^{12}\ s^{-1}$) at $\Delta G^o = -\lambda$. When a diffusional process is required from the bulk for the electron transfer, the maximum of k_b is restricted by the diffusion controlled value of $8.5\text{x}10^9 M^{-1}s^{-1}$ in water-AN as is shown by a dotted line in Fig. 3. Since the back electron transfer within a cage complex needs no diffusional process, one can find a real dependency of electron transfer rate on ΔG^o in a wider range.

We define the efficiency of the electron transfer product formation in the quenching of the excited triplet rhodium(III) compound in terms of measurable rate constants,

$$F_1 = k_{et}/(k_{et} + k_d) \tag{6}$$

where k_{et} and k_d are the bimolecular rate constants of electron transfer product formation and deactivation, respectively.

$$^3\text{Rh(III)} + \text{D} \rightarrow {}^2\text{Rh(II)} + {}^2\text{D}^{\dot{+}} \qquad k_{et} \tag{7}$$

$$^3\text{Rh(III)} + \text{D} \rightarrow \text{Rh(III)} + \text{D} \qquad k_d \tag{8}$$

A sum of k_{et} and k_d, which is the quenching rate constant (k_q), were obtained by plotting the decay rate constants of ^{3}Rh(III) against the concentration of a donor molecule (D). The k_{et} were also obtained by plotting a ratio of the production of D$^{\dot{+}}$ to that of ^{3}Rh(III) against $[D]\times\tau$, where τ is the lifetime of ^{3}Rh(III) in the presence of donor molecule.

$$\frac{[\text{D}^{\dot{+}}]_0}{[^3\text{Rh(III)}]_0} = k_{et}[\text{D}]\tau \tag{9}$$

Productions of ^{3}Rh(III) and D$^{\dot{+}}$ can be obtained by using the molar absorption coefficients mentioned above. Methoxybenzenes having a high redox potential (1.1-1.5 V) reduce the ^{3}Rh(III) compounds with F_1 of 0.06-0.48, as Table 2 shows. The donor radical and the Rh(II) compound escaped from the cage complex in the quenching of the triplet states of RhCl$_2$(dp-phen)$_2^+$ and RhCl$_2$(phen)$_2^+$ whose lowest excited states have ligand field excited state ($^3T_1$) character. The larger efficiency observed for the former compound than that for the latter is caused by the slower back electron transfer between Rh(II) and $D^{\cdot+}$. Within the cage complex consisting of $RhCl_2(dp\text{-}phen)_2$ and $D^{\cdot+}$, an electron in the d_σ* orbital of rhodium(II) ion may be prohibited from transferring to the π-orbital of 1,2,4-trimethoxybenzene by the bulky ligand of dp-phen. A similar prohibition of electron transfer has been observed in the back electron transfer within the cage complex of $Cr(dp\text{-}phen)_3^{3+}$-aromatic amine radical (ref.13). The large efficiencies were also observed in the quenching of $Rh(dp\text{-}phen)_3^{3+}$ and $Rh(phen)_3^{3+}$, of which the lowest excited states is the triplet π-π* state localized in the ligand. Therefore it is probable that the rhodium(III) ion in the tris-chelate compounds is reduced by the methoxybenzenes in the triplet π-π* state of the ligand and the d_σ* electron of the rhodium(II) ion is protected by the bulky ligands against the back transfer.

The rate constant (k_b) of the back electron transfer is estimated to be 1.5×10^{10} s^{-1} from the F_1 value assuming the rate constant of cage-complex dissociation to be 1.4×10^{10} s^{-1}, using the Eigen equation (18) for an ion pair dissociation process. According to the Marcus equation of electron transfer, k_b is calculated to be less than 10^7 s^{-1}, assuming the intrinsic barrier of the $Rh(phen)_3^{3+}/Rh(phen)_3^{2+}$ couple to be the same as that for $Rh(bpy)_3^{3+}$ (ref.19) so that the discrepancy in the value between the k_b observed and calculated indicates an absence of "inverted region" in the back electron transfer process.

In order to clarify whether "inverted region" is absent or not, the efficiencies of Rh(II) production were examined by using some aromatic amines having a

TABLE 3

Redox potentials of amines (E^o), quenching rate constants ($k_q/10^9M^{-1}s^{-1}$), and efficiencies of product formation (F_1).

	E^o vs SCE	$\varepsilon/M^{-1}cm^{-1}$ (λ_{max})	k_q	F_1
DPA	1.07[a]	b	9.7	0.38
3,3'-DMB	0.89[a]	32,000 (460nm)	8.4	0.55
1,2-PD	(0.79)[c]	d	8.1	0.64
TMB	0.67[a]	41,000 (474nm)[e]	-	0.58
1,4-PD	0.42[a]	7,000 (460nm)[f]	6.3	0.78
TMPD	0.25[a]	12,000 (610nm)[f]	-	0.88

[a] C.K.Mann and K.K.Barnus, "Electrochemical Reactions In Nonaqueous Systems", Marcel Dekker, N.Y.(1970).

[b] Production of DPA radical was obtained after its conversion to 3,3'-DMB radical.

[c] ref. 14.

[d] Production of 1,2-PD radical was obtained after its conversion to 1,4-PD radical.

[e] S.A.Akaitis and M.Gratzel, J.Am.Chem.Soc.,98(1976)3549-3554.

[f] P.S.Rao and E.Hayon, J.Phys.Chem.,79(1975)1063-1066.

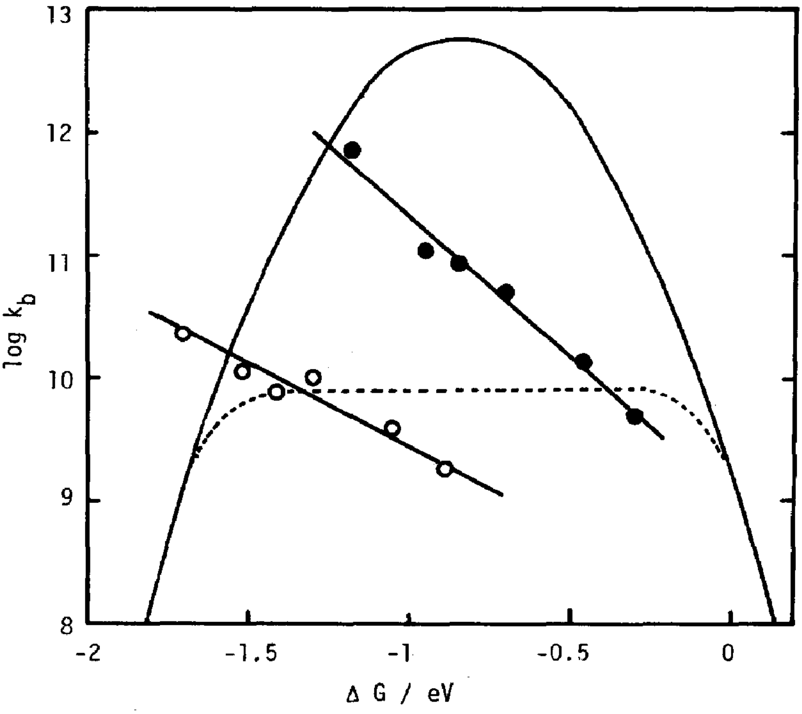

Fig. 3. ΔG^o-dependence of k_b calculated on Eqs. 3-5 (λ=0.84 eV and ν=6.2x10^{12} s^{-1}) and k_b obtianed from F_1. The solid curved line:monomolecular process within a cage complex the dotted curved line:bimolecular process from the bulk (k_{diff}=8.5x$10^9M^{-1}s^{-1}$), the open circles: ^{2}Rh(dp-phen)$_3^{2+}$ + ^{2}Amine$^+$ and the closed circles: ^{3}Cr(dp-phen)$_3^{2+}$ + ^{2}Amine$^+$.

redox-potential in a range of 0.25-1.1 V (Table 4). The efficiencies of amine radical formation in the quenching of Rh(dp-phen)$_3^{3+}$ were obtained by using the molar absorption coefficient of the amine radical (see Table 3). They are high and not dependent on ΔG^o (-1.7 - -0.9 eV). The values of k_b obtained by using k_{dis} = 1.4x10^{10} s^{-1} span a range of 1.3x10^9 - 3x10^{10} s^{-1}. The dependence of log k_b on ΔG^o is weak, different from the parabolic form predicted from Eqs. 3-5. The less steep slope (σlog $k_b/\sigma\Delta G^o$ = -1.2 V^{-1}) suggests a larger intrinsic barrier in the self exchange electron transfer process of Rh(dp-phen)$_3^{3+}$/Rh(dp-phen)$_3^{2+}$. However, it is improbable that the Rh(dp-phen)$_3^{3+}$ has a large intrinsic barrier compared to the small one of 0.8 eV for Rh(bpy)$_3^{3+}$/Rh(bpy)$_3^{2+}$ couple (ref.20). We have obtained weak dependences of k_b on ΔG^o for five kinds of reaction systems (see Table 4). A nearly normal dependence (-2.4 V^{-1}) was observed for spin-inverted electron transfer between dπ orbital of Cr(II) (ref. 13) or Fe(III) and π-orbital of aromatic compounds (ref.12), in which electronic exchange interaction is estimated to be stronger than that between the dσ* electron on rhodium ion and the nonbonding electron on the amine radical. Spin-inverted electron transfers between organic radicals containing no heavy atom

TABLE 4

Dependences of k_b on ΔG^o.

Reactions	$(\partial \log k_b/\partial \Delta G^o)/V^{-1}$	Reference
$Fe(C_5H_5)^+{}_2$ $(^3(d\pi)^5)$ + $amine^{\cdot +}$	-2.4	12
$Cr(dp\text{-}phen)_3{}^{2+}$ $(^3(d\pi)^4)$ + $amine^{\cdot +}$	-2.4	13
$Rh(dp\text{-}phen)_3{}^{2+}$ $(^2(d\sigma^*)$ + $amine^{\cdot +}$	-1.2	this work
Al(phthalocyanine)• + $amine^{\cdot +}$	-1.0	14
methylene blue• + $amine^{\cdot +}$	-1.0	12

have the most strange dependence of ΔG^o ($-1.0\ V^{-1}$) (refs.12 and 14), though electron exchange interaction may not be small. Therefore, these spin-inverted back electron transfers are substantially nonadiabatic processes in which both intermolecular exchange interaction and the spin-orbit interaction control the rate. Another explanation for the weak dependency of k_b on ΔG^o is as follows. When a part of the back electron transfer process within a cage complex can be regarded as an intramolecular radiationless process as Mataga et al. pointed out (ref.21), the rate of back electron transfer does not decrease with the decrease of ΔG^o, because the rate of radiationless transition follows the "energy gap law."

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