September, 1994] © *1994 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **67**, 2447—2453(1994) 2447

Photoracemization of Ruthenium(II) Complexes with 2,2′-Bipyridine and Di-2-pyridylamine

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(Received March 24, 1994)

The emission lifetime (τ_{obs}) and quantum yield of photoracemization (ϕ_{rac}) for a series of complexes, $[\text{Ru(bpy)}_n\text{(Hdpa)}_{3-n}]^{2+}$ (n=0—3), were studied in aqueous solution at temperatures of between 20 and 60 °C. The values of τ_{obs} of $[\text{Ru(bpy)}_2\text{(Hdpa)}]^{2+}$ were found to vary around 80—200 ns, depending upon temperature, while $[\text{Ru(bpy)(Hdpa)}_2]^{2+}$ and $[\text{Ru(Hdpa)}_3]^{2+}$ did not emit at the temperature studied. The photoracemization reactions of $[\text{Ru(bpy)}_3]^{2+}$, $[\text{Ru(bpy)}_2\text{(Hdpa)}]^{2+}$, $[\text{Ru(bpy)(Hdpa)}_2]^{2+}$, and $[\text{Ru(Hdpa)}_3]^{2+}$ were thermally activated with ϕ_{rac} of $(0.1—1.6)\times10^{-3}$, $(0.5—6)\times10^{-3}$, $(0.04—0.22)\times10^{-3}$, and $(0.1—0.25)\times10^{-3}$, respectively, depending upon the conditions. The photochemical behavior of $[\text{Ru(bpy)}_2\text{(Hdpa)}]^{2+}$ was explained by a set of excited states, which was assumed to include the $^3\text{d}-\pi^*{}_{\text{bpy}}$, $^3\text{d}-\text{d}^*$, and $^3\text{n}-\pi^*{}_{\text{bpy}}$ states. The reactive state, the $^3\text{d}-\text{d}^*$ state, was thermally yielded from the $^3\text{d}-\pi^*{}_{\text{bpy}}$ state. The displacement of a bpy ligand by an Hdpa ligand made the quantum yield of the formation of the $^3\text{d}-\text{d}^*$ state from the $^3\text{d}-\pi^*{}_{\text{bpy}}$ state ($\phi_{\text{d-d}}$) smaller, and the intrinsic quantum yield of photoracemization ($\phi_{\text{rac(d-d)}}$) larger. The fact that ϕ_{rac} for $[\text{Ru(bpy)(Hdpa)}_2]^{2+}$ and $[\text{Ru(Hdpa)}_3]^{2+}$ was smaller than that for $[\text{Ru(bpy)}_3]^{2+}$ and $[\text{Ru(bpy)}_2\text{(Hdpa)}]^{2+}$ could be interpreted by assuming that the displacement of the bpy ligand by the Hdpa ligand diminished the quantum yield of the formation of the $^3\text{d}-\text{d}^*$ state from the $^3\text{d}-\pi^*{}_{\text{bpy}}$ or $^3\text{d}-\pi^*{}_{\text{Hdpa}}$ states considerably, due to the bypath from the $^3\text{d}-\pi^*{}_{\text{bpy}}$ or $^3\text{d}-\pi^*{}_{\text{Hdpa}}$ states through the $^3\text{n}_{\text{Hdpa}}-\pi^*{}_{\text{bpy}}$ or $^3\text{n}_{\text{Hdpa}}-\pi^*{}_{\text{Hdpa}}$ states to the ground state.

During the last two decades, the photochemical and photophysical properties of a number of Ru(II)–polypyridine complexes have been extensively studied.[1,2] A general kinetic model used to explain the observed dynamic behavior of excited states of $[\text{Ru(bpy)}_3]^{2+}$ is as follows.[2—4] Excitation is followed by a rapid intersystem crossing from the initially formed $^1\text{d}-\pi^*{}_{\text{bpy}}$ state to the $^3\text{d}-\pi^*{}_{\text{bpy}}$ state with unit quantum efficiency. The $^3\text{d}-\pi^*{}_{\text{bpy}}$ state decays via radiative (k_{ar}), nonradiative (k_{aq}), and temperature-dependent processes. The thermally activated decay has been ascribed to an internal conversion to a triplet ligand field state, $^3\text{d}-\text{d}^*$, which gives rise to ligand substitution and racemization.

The di-2-pyridylamine (Hdpa) ligand differs from the 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) ligands in that bpy and phen form planar and five-membered chelate rings with metals, whereas Hdpa forms a nonplanar and six-membered chelate ring, furthermore, it has a non-bonding electron pair on the amino nitrogen atom. The absorption and emission spectra of the series of complexes $[\text{Ru(bpy)}_n\text{(Hdpa)}_{3-n}]^{2+}$ (n=0—2) have been reported by Blakley and DeArmond.[5] They suggested that for the excited state of $[\text{Ru(bpy)}_n\text{(Hdpa)}_{3-n}]^{2+}$ (n=0—2) nonbonding orbitals of the bridging amino group of Hdpa were involved in the electronic transition.

The present work describes the photochemistry of $[\text{Ru(bpy)}_n\text{(Hdpa)}_{3-n}]^{2+}$ (n=0—3). The photochemical properties of $[\text{Ru(bpy)}_3]^{2+}$ and $[\text{Ru(bpy)}_2\text{(Hdpa)}]^{2+}$ which emit from the $^3\text{d}-\pi^*{}_{\text{bpy}}$ state, were studied based on the behavior of the emission and photochemical reaction (photoracemization).

Experimental

Materials. $[\text{Ru(bpy)}_3](\text{ClO}_4)_2$[6] and $[\text{Ru(bpy)(Hdpa)}_2](\text{CF}_3\text{SO}_3)_2$[7] complexes were prepared by methods described in the literature; $[\text{Ru(bpy)}_2\text{(Hdpa)}](\text{ClO}_4)_2$ and $[\text{Ru(Hdpa)}_3](\text{CF}_3\text{SO}_3)_2$ complexes were prepared by methods described in a previous paper.[8] The optical resolution of the complexes was carried out using SP-Sephadex cation-exchange column chromatography with sodium chloride used as the eluting agent.[9] The salts of resolved enantiomers were precipitated from the eluent by the addition of NaClO_4 (for n=3, 2) or NaCF_3SO_3 (for n=1, 0). The values of $\Delta\varepsilon$ of the enantiomers agreed well with those of the enantiomers which were resolved by other methods.[7]

Emission Lifetime Measurements. The emission lifetimes were measured with a Hitachi–Horiba (NAES-1100) single-photon counting apparatus. The solutions were deaerated by repeated freeze-pump-thaw cycles. The temperatures of the solutions were controlled to ±0.1°C with a circulating water bath. Excitation was at 460 nm by means of a pulsed hydrogen discharge lamp (10 atm) with 1 ns pulse duration. The emission decay was monitored at the maximum of the emission band by using interference filters.

Quantum Yield of Photoracemization. Irradiation was performed by using a Bausch and Lomb monochrometer along with a 250-W super-pressure mercury lamp and a thermostated cell holder in which a 1-cm square quartz cell was housed. The temperature of the solution was controlled to ±0.1°C. The absorption spectra were measured with a Hitachi (U-3410) spectrophotometer. The CD spectra were measured with a JASCO (J-500) CD spectropolarimeter. Solutions of $(3—5)\times10^{-5}$ mol dm^{-3} complexes in H_2O were used to give an absorbance of about 0.5 for a cell of 1-cm path length at the irradiation wavelengths (436, 365, and 335 nm). The solutions were deoxygenated with a stream of nitrogen gas for 30 min or equilibrated with air prior to irradiation. They were then irradiated for 1—60 min with the desired wavelength while being stirred with a small magnetic bar in order to ensure homogeneity. The intensity of light incident on the solution was determined by using a tris(oxalato)ferrate(III) chemical actinometer for every run.[10)]

Results

Emission Lifetime of $[Ru(bpy)_2(Hdpa)]^{2+}$. The emission decay was found to be strictly single-exponential under all conditions. The temperature dependence of the observed emission life time (τ_{obs}) of $[Ru(bpy)_2(Hdpa)]^{2+}$ in a deoxygenated solution is shown in Fig. 1. The data concerning $[Ru(bpy)_3]^{2+}$ [11)] is also plotted for a comparison. The plots were non-linear, indicating the data did not fit a simple Arrhenius-type equation. Van Houten and Watts[11)] have reported that the temperature dependence of τ_{obs} of $[Ru(bpy)_3]^{2+}$ fitted

$$(\tau_{obs})^{-1} = k_1 + A_2 \exp(-\Delta E_2/RT). \qquad (1)$$

The solid curve in Fig. 1 represents the calculated fit of the data by Eq. 1 with the following parameters: for $[Ru(bpy)_2(Hdpa)]^{2+}$, $k_1=4.54\times10^6$ s^{-1}, $A_2=17.2\times10^{13}$ s^{-1}, and $\Delta E_2=47.8$ kJ mol^{-1}; for $[Ru(bpy)_3]^{2+}$,[11)] $k_1=1.29\times10^6$ s^{-1}, $A_2=1.0\times10^{13}$ s^{-1}, and $\Delta E_2=42.6$ kJ mol^{-1}.

Photoracemization. The $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (n=0—3) complexes were very stable in solution in the dark. No changes in the absorption or CD spectra of the complexes were observed, even after heating at 60 °C for several hours.

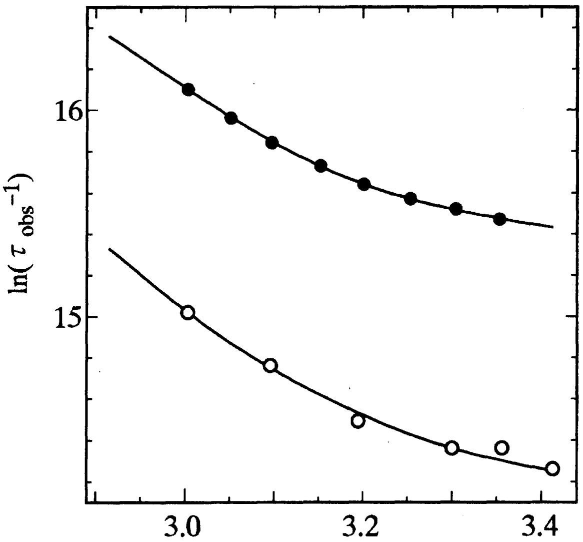


Fig. 1. Plots of $\ln(\tau_{obs}{}^{-1})$ vs. T^{-1} for $[Ru(bpy)_2(Hdpa)]^{2+}$ (●) and $[Ru(bpy)_3]^{2+}$ [11)] (○) in deoxygenated solution. The solid curves were calculated by Eq. 1 with the following parameters: for $[Ru(bpy)_2(Hdpa)]^{2+}$, $k_1=4.54\times10^6$ s^{-1}, $A_2=17.2\times10^{13}$ s^{-1}, and $\Delta E_2=47.8$ kJ mol^{-1}; for $[Ru(bpy)_3]^{2+}$,[11)] $k_1=1.29\times10^6$ s^{-1}, $A_2=1.0\times10^{13}$ s^{-1}, and $\Delta E_2=42.6$ kJ mol^{-1}.

$[Ru(bpy)_2(Hdpa)]^{2+}$: Upon irradiation of both deoxygenated and air-equilibrated solutions, the CD intensity of the solution decreased, although the spectrum pattern did not change. Furthermore, the absorption spectra showed no change in the intensity or spectrum pattern. This indicated that the complex suffered an inversion of the absolute configuration without decomposition upon irradiation under the studied condition. The racemization kinetics followed a linear relationship,

$$\ln((CD)_t/(CD)_0) = -kt, \qquad (2)$$

where $(CD)_0$ and $(CD)_t$ are the CD intensities at $t=0$ and $t=t$, respectively, and k is a rate constant at constant intensity of the exciting light. The rate constant (k) can be related to the quantum yield for photoracemization (ϕ_{rac}).

Table 1 shows ϕ_{rac} between 20 and 60 °C. The values of ϕ_{rac} for an air-equilibrated solution were smaller than those for a deoxygenated solution, when compared at the same temperature. This indicated that the photoracemization was quenched by dioxygen in solution as well as was the emission.

The values of ϕ_{rac} excited at 436 nm were in good agreement with those at 335 nm. The excitations at 436 and 335 nm mainly correspond to the excitations to the d-π^*_{bpy} and d-π^*_{Hdpa} states, respectively. The independence of ϕ_{rac} on the irradiation wavelength suggested that excitations at both MLCT bands gave the same set of the low-lying excited states, and that racemization occurred from them.

Irradiation of the complex in the presence of free ligands (bpy or Hdpa) induced no change in the absorption spectra concerning the intensity or pattern; therefore, the formation of $[Ru(bpy)_3]^{2+}$ or $[Ru(bpy)(Hdpa)_2]^{2+}$ was regarded as being negligible. That is, irradiation of the complex caused only a racemization reaction without an exchange of the ligand. Consequently, it is concluded that photoracemization proceeds via an intramoleculer mechanism under the present conditions.

$[Ru(bpy)_3]^{2+}$: The temperature dependence of ϕ_{rac} of $[Ru(bpy)_3]^{2+}$ was measured for a comparison (Table 1). No decomposition was observed under irradiation, as in the case of $[Ru(bpy)(Hdpa)_2]^{2+}$. Both the photoracemization and the emission were also quenched by dioxygen in solution.

The value of ϕ_{rac} of $[Ru(bpy)_3]^{2+}$ reported by Porter and Sparks was 0.933×10^{-3} at 40 °C,[12)] which was considerably different from the value found in the present work (0.65×10^{-3}). One of reasons for the difference is that the molar absorption coefficient used by them (1.29×10^4) was different from that determined in the present work (1.47×10^4).

The values of ϕ_{rac} excited at 436 nm were larger than those at 335 nm. The excitations at 436 and 335 nm correspond to the excitation to the d-π^*_{bpy} and π-π^*

Table 1. Quantum Yields for Photoracemization of $[\mathrm{Ru(bpy)}_n(\mathrm{Hdpa})_{3-n}]^{2+}$ (n=0—3) (ϕ_{rac}) at Various Temperatures and Various Irradiation Wavelengths

	Temp	$\phi_{\mathrm{rac}}/10^{-3}$			
	°C	Deoxygenated		Air-equilibrated	
$[\mathrm{Ru(bpy)_3}]^{2+}$		436 nm a)	335 nm a)	436 nm a)	335 nm a)
	20	0.16	—	0.12	—
	30	0.34	—	0.22	—
	40	0.65	0.52	0.44	0.34
	50	1.14	0.90	0.76	0.64
	60	1.61	—	1.19	—
$[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$		436 nm a)	335 nm a)	436 nm a)	335 nm a)
	20	0.52	—	0.47	—
	30	1.13	—	0.97	—
	40	2.13	2.04	1.83	1.76
	50	3.61	3.47	3.15	2.96
	60	6.03	—	5.23	—
$[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$		436 nm a)	365 nm a)	436 nm a)	365 nm a)
	20	0.044	0.126	0.044	0.121
	30	0.046	0.110	0.039	0.106
	40	0.056	0.125	0.048	0.104
	50	0.081	0.139	0.073	0.119
	60	0.115	0.216	0.096	0.199
$[\mathrm{Ru(Hdpa)_3}]^{2+}$		436 nm a)	365 nm a)	436 nm a)	365 nm a)
	20	—	0.116	—	0.107
	30	—	0.128	—	0.116
	40	—	0.160	—	0.153
	50	0.132	0.222	0.138	0.207
	60	—	0.249	—	0.243

a) Irradiation wavelength.

states (including the d–d* state slightly), respectively. The dependence of the quantum yield on the irradiation wavelength suggested that the excitations at the ligand-centered transition band (π–π*) yielded the same set of low-lying excited states with different efficiency.

The absorption spectra of the irradiated sample in the presence of free ligands did not change in intensity or spectrum pattern during irradiation. That is, the irradiation of the complex caused only a racemization reaction without an exchange of the ligands. Therefore, as discussed in the case of $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ the photoracemization proceeded via an intramoleculer mechanism. Porter and Sparks have reached the same conclusion based on their measurement of the activation energy of the photoracemization.[12)]

$[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$: For deoxygenated solutions, the CD intensity of the solution decreased, although the spectrum pattern did not change. However, the absorption spectrum showed slight changes in the intensity and spectrum pattern. This indicated that the complexes suffered an inversion of the absolute configuration along with a slight decomposition upon irradiation; the extent of the change was only slightly more appreciable at higher temperature. The amount of the decomposition product was too small to allow us to identify or determine the quantum yield of its formation. Plots of ln (*CD*) vs. time showed a good linear correlation. The racemization kinetics followed Eq. 2. The observed ϕ_{rac}, which actually include both racemization and a very small degree of decomposition, are listed in Table 1.

In air-equilibrated solutions, the complex suffered an inversion of the absolute configuration along with a small extent of decomposition upon irradiation. Plots of ln (*CD*) vs. time were slightly different from those for a deoxygenated solution, in that the plots showed an initial small drop followed by ordinary linearity. Although the reason for this small drop was not clear, ϕ_{rac} at 20—60 °C (Table 1) was calculated based on the part which showed linear plots.

The presence of free ligands (bpy or Hdpa) did not much affect ϕ_{rac}. However, a small increase in the absorbance of a deoxygenated solution at around 460 nm was observed during irradiation in the presence of bpy, indicating that the exchange of an Hdpa of $[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$ by bpy probably took place via some Ru(II) aqua complex. In the presence of Hdpa, such an increase in the absorbance was not observed, which suggested that the coordinating ability of Hdpa was lower than that of bpy. Furthermore, in an air-equilibrated solution the absorbance at around 460 nm did not increase. Probably, the intermediate which formed upon irradiation was readily oxidized to a Ru(III) species, which usually had a pale color.

$[\mathrm{Ru(Hdpa)_3}]^{2+}$: In both deoxygenated and air-equilibrated solutions, the complexes suffered an inversion of the absolute configuration along with a slight decomposition during irradiation. Plots of ln (*CD*) vs. time showed a good linear relationship. The values of ϕ_{rac} obtained at between 20 and 60 °C are given in Table 1.

The presence of free ligands did not greatly affect ϕ_{rac}. Furthermore, no increase in the absorbance spectra of the irradiated solution was observed. This again suggested that the intermediate was very easily oxidized to the Ru(III) species before taking up free ligands to return to the tris complexes.

Discussion

Excited States and the Decay of the Excited States for $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$. Potential energy diagrams of the ground and excited states for $[\mathrm{Ru(bpy)_3}]^{2+}$ and $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ have been proposed on the basis of the absorption and emission studies by Blakley and DeArmond.[5] In their diagrams the lower excited states of $[\mathrm{Ru(bpy)_3}]^{2+}$ included the $^3\mathrm{d}\text{–}\pi^*_{\mathrm{bpy}}$ and $^3\mathrm{d}\text{–}\mathrm{d}^*$ states. On the other hand, the lower excited states of $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ included the $^3\mathrm{d}\text{–}\pi^*_{\mathrm{Hdpa}}$ and $^3\mathrm{n}_{\mathrm{Hdpa}}\text{–}\pi^*_{\mathrm{bpy}}$ states, in addition to the above-mentioned states.

The photochemical behavior of $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ observed in this study can be explained by the mechanisms shown in Scheme 1, which includes the four excited states. The emission lifetime (τ) is expressed as

$$\tau = \{k_{\mathrm{a}} + k_{\mathrm{b}}[k_{\mathrm{d}}/(k_{\mathrm{c}} + k_{\mathrm{d}})] + k_{\mathrm{e}}[k_{\mathrm{g}}/(k_{\mathrm{f}} + k_{\mathrm{g}})]\}^{-1}, \qquad (3)$$

where $k_{\mathrm{a}} = k_{\mathrm{ar}} + k_{\mathrm{aq}}$ and $k_{\mathrm{d}} = k_{\mathrm{dq}} + k_{\mathrm{rac}}$. The observed emission lifetime of $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ fits Eq. 1, which contains only one Arrhenius-type term. Because the term $k_{\mathrm{b}}[k_{\mathrm{d}}/(k_{\mathrm{c}}+k_{\mathrm{d}})]$ is considered to be an Arrhenius-type term, as is shown in the case of $[\mathrm{Ru(bpy)_3}]^{2+}$, the $k_{\mathrm{e}}[k_{\mathrm{g}}/(k_{\mathrm{f}}+k_{\mathrm{g}})]$ term does not depend on the studied temperature. Consequently, it follows that the $^3\mathrm{d}\text{–}\pi^*_{\mathrm{bpy}}$ and $^3\mathrm{n}_{\mathrm{Hdpa}}\text{–}\pi^*_{\mathrm{bpy}}$ states should be almost equal in energy, and that the surface crossing between the states has little activation energy. Equation 3 can be written as

$$\tau = \{k_{\mathrm{a}} + k_{\mathrm{g}}' + k_{\mathrm{b}}[k_{\mathrm{d}}/(k_{\mathrm{c}} + k_{\mathrm{d}})]\}^{-1}, \qquad (4)$$

where $k_{\mathrm{g}}' = k_{\mathrm{e}}[k_{\mathrm{g}}/(k_{\mathrm{f}}+k_{\mathrm{g}})]$ and k_{g}' correspond to a rate constant for the deactivation from the $^3\mathrm{d}\text{–}\pi^*_{\mathrm{bpy}}$ state to the ground state via the $^3\mathrm{n}_{\mathrm{Hdpa}}\text{–}\pi^*_{\mathrm{bpy}}$ state. The following two limiting cases are possible, as was discussed for $[\mathrm{Ru(bpy)_3}]^{2+}$ by several researchers.[2,4] i) When $k_{\mathrm{d}} \gg k_{\mathrm{c}}$, the decay of the $^3\mathrm{d}\text{–}\mathrm{d}^*$ state is much faster than the repopulation of the $^3\mathrm{d}\text{–}\pi^*_{\mathrm{bpy}}$ state. ii) When $k_{\mathrm{c}} \gg k_{\mathrm{d}}$, d–d* state decay is much slower than the repopulation of the $^3\mathrm{d}\text{–}\pi^*_{\mathrm{bpy}}$ state. That is, the two states are in equilibrium. According to the criterion by which Balzani et al. showed that $[\mathrm{Ru(bpy)_3}]^{2+}$ followed the mechanism with case i),[2] $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$, which has 17.2×10^{13} s^{-1} for A_2, can also be concluded to follow Scheme 1 with case i).

Photoracemization Reaction. $[\mathrm{Ru(bpy)_3}]^{2+}$ and $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$: Plots of ln ($\phi_{\mathrm{rac}}$) vs. T^{-1} for $[\mathrm{Ru(bpy)_3}]^{2+}$ and $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ in deoxygenated solution were found to be non-linear (Fig. 2). On the basis of Scheme 1, ϕ_{rac} of $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ can be expressed as

$$\phi_{\mathrm{rac}} = \tau k_{\mathrm{b}} k_{\mathrm{rac}}/(k_{\mathrm{c}} + k_{\mathrm{d}}). \qquad (5)$$

For $[\mathrm{Ru(bpy)_3}]^{2+}$, on the basis of the similar scheme,[13] ϕ_{rac} can also be expressed by Eq. 5. Since the right-hand side of the Eq. 5 contains τ (non-Arrhenius type), ϕ_{rac} is expected not to follow a simple Arrhenius-type equation. This is consistent with the observation. Dividing Eq. 5 by τ, yields

$$\phi_{\mathrm{rac}}/\tau = k_{\mathrm{b}} k_{\mathrm{rac}}/(k_{\mathrm{c}} + k_{\mathrm{d}}). \qquad (6)$$

Two limiting cases are possible for Eq. 6 in the same way as was described for the emission lifetime. In the limiting case i), Eq. 6 is reduced to

$$\phi_{\mathrm{rac}}/\tau = k_{\mathrm{b}} k_{\mathrm{rac}}/k_{\mathrm{d}}. \qquad (7)$$

Since the major contribution to k_{d} is usually regarded as coming from a non-activated process ($k_{\mathrm{d}} \doteqdot k_{\mathrm{dq}}$), Eq. 7 becomes

$$\phi_{\mathrm{rac}}/\tau = A_{\mathrm{b}} A_{\mathrm{rac}}/k_{\mathrm{dq}} \exp[-(\Delta E_{\mathrm{b}} + \Delta E_{\mathrm{rac}})/RT]. \qquad (8)$$

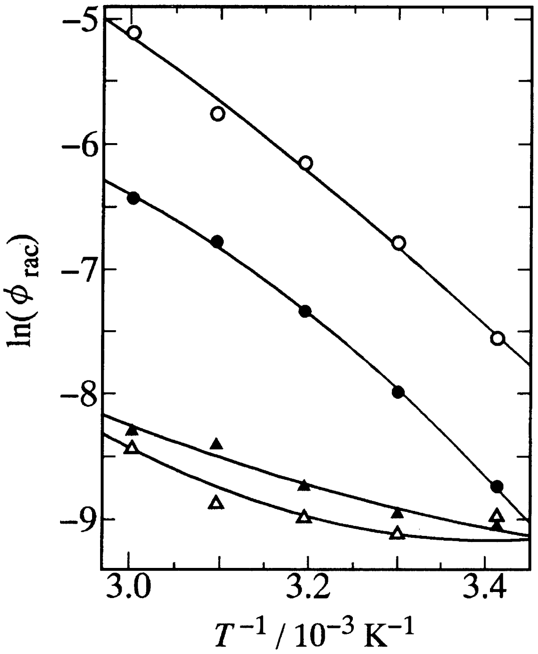
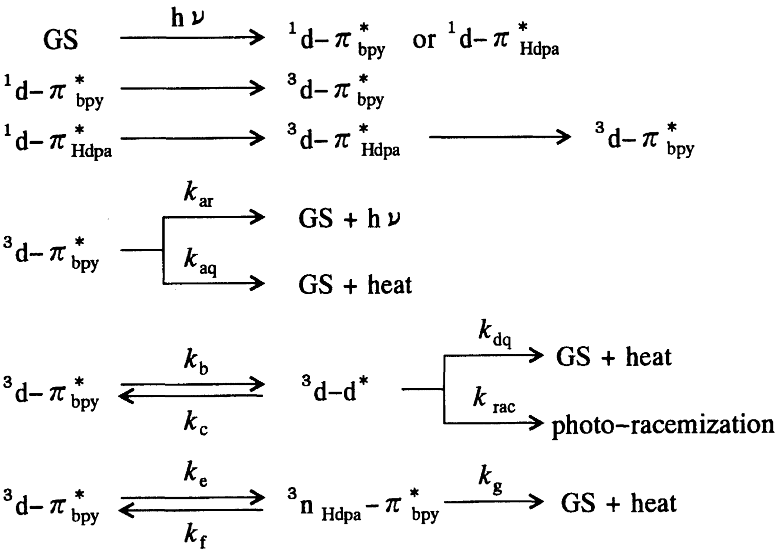


Fig. 2. Plots of ln (ϕ_{rac}) vs. T^{-1} for $[\mathrm{Ru(bpy)}_n\mathrm{(Hdpa)}_{3-n}]^{2+}$ (n = 0—3) in deoxygenated solution. ●: $[\mathrm{Ru(bpy)_3}]^{2+}$ (436 nm), ○: $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ (436 nm), △: $[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$ (365 nm), ▲: $[\mathrm{Ru(Hdpa)_3}]^{2+}$ (365 nm). The values in parentheses are irradiation wavelengths.



Scheme 1. The population and the decay of the excited states for $[\text{Ru(bpy)}_2(\text{Hdpa})]^{2+}$. GS; ground state. $k_{\text{a}}=k_{\text{ar}}+k_{\text{aq}}$. $k_{\text{d}}=k_{\text{dq}}+k_{\text{rac}}$.

Linear plots of $\ln(\phi_{\text{rac}}/\tau)$ vs. T^{-1} indicated that the data fitted an Arrhenius-type equation (Eq. 8). The slope and interception obtained from the plots correspond to $A_{\text{b}}A_{\text{rac}}/k_{\text{dq}}$ and $(\Delta E_{\text{b}}+\Delta E_{\text{rac}})$, respectively. The values are as follows: for $[\text{Ru(bpy)}_2(\text{Hdpa})]^{2+}$, $A_{\text{b}}A_{\text{rac}}/k_{\text{dq}}=40\times10^{13}\ \text{s}^{-1}$, and $(\Delta E_{\text{b}}+\Delta E_{\text{rac}})=62.7$ kJ mol^{-1}; for $[\text{Ru(bpy)}_3]^{2+}$, $A_{\text{b}}A_{\text{rac}}/k_{\text{dq}}=4.3\times10^{13}\ \text{s}^{-1}$, and $(\Delta E_{\text{b}}+\Delta E_{\text{rac}})=62.9$ kJ mol^{-1}.

Table 2 shows the kinetic parameters obtained from the temperature dependences of the emission lifetime and the quantum yields of photoracemization for $[\text{Ru(bpy)}_2(\text{Hdpa})]^{2+}$ and $[\text{Ru(bpy)}_3]^{2+}$ on the basis of the limiting case i). The experimental ϕ_{rac} can be expressed as the product of the quantum yield of the formation of the ^{3}d–d* state from the ^{3}d–π$^*_{\text{bpy}}$ state ($\phi_{\text{d–d}}$) and the intrinsic quantum yield of racemization from the ^{3}d–d* state ($\phi_{\text{rac(d–d)}}$):

$$\phi_{\text{rac}} = \phi_{\text{d–d}}\phi_{\text{rac(d–d)}}. \tag{9}$$

The quantum yield, $\phi_{\text{d–d}}$, is expressed in terms of the constants (since $k_{\text{d}}\gg k_{\text{c}}$) in Scheme 1 as

$$\phi_{\text{d–d}} = k_{\text{b}}/\{k_{\text{a}}+k_{\text{g}}'+k_{\text{b}}\}. \tag{10}$$

Therefore,

$$\phi_{\text{d–d}} = A_{\text{b}}\exp(-\Delta E_{\text{b}}/RT)/\{k_{\text{a}}+k_{\text{g}}'+A_{\text{b}}\exp(-\Delta E_{\text{b}}/RT)\}. \tag{11}$$

Equation 11 allows us to calculate $\phi_{\text{d–d}}$ by using the values in Table 2; the temperature dependence of $\phi_{\text{d–d}}$ is plotted in Fig. 3A. The $\phi_{\text{d–d}}$ for $[\text{Ru(bpy)}_2(\text{Hdpa})]^{2+}$ was smaller than that for $[\text{Ru(bpy)}_3]^{2+}$ within the temperature range studied, due to the presence of decay through the ^{3}n$_{\text{Hdpa}}$–π$^*_{\text{bpy}}$ state (k_{g}') in the former.

Table 2. Kinetic Parameters for $[\text{Ru(bpy)}_3]^{2+}$ and $[\text{Ru(bpy)}_2(\text{Hdpa})]^{2+}$ on the Basis of the Limiting Case i)

	$[\text{Ru(bpy)}_3]^{2+}$	$[\text{Ru(bpy)}_2(\text{Hdpa})]^{2+}$
$(k_{\text{a}}+k_{\text{g}}')/10^6\ \text{s}^{-1}$ [a)]	1.29[b)]	4.54
$A_{\text{b}}/10^{13}\ \text{s}^{-1}$	1.0[b)]	17.2
ΔE_{b}/kJ mol^{-1}	42.6[b)]	47.8
$A_{\text{rac}}/k_{\text{dq}}$	4.3	2.3
ΔE_{rac}/kJ mol^{-1}	20.3	14.9

a) For $[\text{Ru(bpy)}_3]^{2+}$, since the transitions which involved the n$_{\text{Hdpa}}$–π$^*_{\text{bpy}}$ state do not exist, the value of k_{a} was presented.[13)] b) Ref. 11.

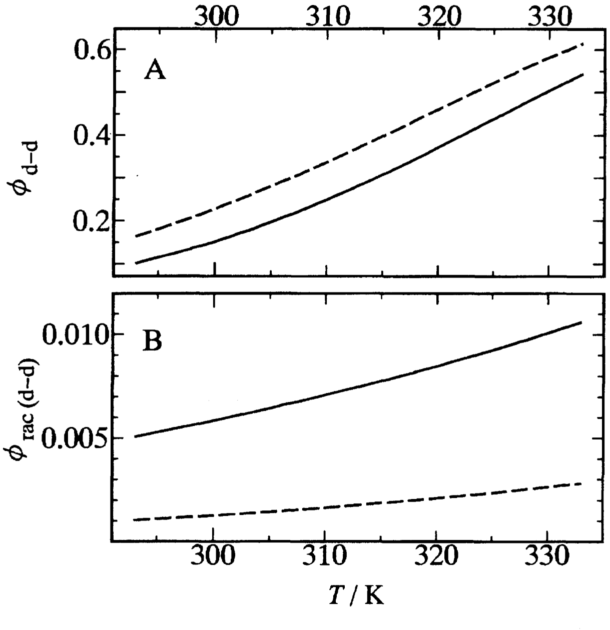


Fig. 3. The calculated temperature dependence of $\phi_{\text{d–d}}$ (A) and ϕ_{rac} (d–d) (B). ——; $[\text{Ru(bpy)}_2(\text{Hdpa})]^{2+}$, - - -; $[\text{Ru(bpy)}_3]^{2+}$.

That is, the replacement of a bpy ligand by an Hdpa ligand appeared to make the complex photo-inert.

In terms of the constants in Scheme 1 (since $k_{\mathrm{rac}} \ll k_{\mathrm{dq}}$), $\phi_{\mathrm{rac(d-d)}}$ is given by

$$\phi_{\mathrm{rac(d-d)}} = k_{\mathrm{rac}}/k_{\mathrm{dq}}, \tag{12}$$

$$\phi_{\mathrm{rac(d-d)}} = A_{\mathrm{rac}}/k_{\mathrm{dq}} \exp\left[-(\Delta E_{\mathrm{rac}})/RT\right]. \tag{13}$$

The calculated temperature dependence of $\phi_{\mathrm{rac(d-d)}}$ by using the values in Table 2 is shown in Fig. 3B. The $\phi_{\mathrm{rac(d-d)}}$ for $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ is larger than that for $[\mathrm{Ru(bpy)_3}]^{2+}$ within the temperature range, indicating that the ^{3}d–d* state of $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ has a higher reactivity than does that of the latter. The photo-reactivity of the complexes is dependent on two factors, $\phi_{\mathrm{d-d}}$ and $\phi_{\mathrm{rac(d-d)}}$, which have opposite effects on ϕ_{rac}. Since the effect of the latter was bigger, the overall quantum yield ϕ_{rac} was bigger for $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$.

The photoracemization of $[\mathrm{Ru(bpy)_3}]^{2+}$ occurs by a rearrangement through a trigonal-bipyramidal intermediate which contains a one-ended bpy ligand; the activation energy, ΔE_{rac}, corresponds to the energy for the formation of a five-coordinated intermediate.[4,12] Because the photoracemization of $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ proceeds via an intramoleculer mechanism, like that of $[\mathrm{Ru(bpy)_3}]^{2+}$, it is considered that the type of intermediate is also similar for both cases. The difference of ΔE_{rac} between the two complexes indicates that the five-coordinated intermediate from the ^{3}d–d* state for $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$ forms more easily than does that for $[\mathrm{Ru(bpy)_3}]^{2+}$. This is explained by considering the weaker coordination ability and higher degree of flexibility of the Hdpa ligand than the bpy ligand.[14]

$[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$ and $[\mathrm{Ru(Hdpa)_3}]^{2+}$: The lower excited states of $[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$ include five states: ^{3}d–π^*_{bpy}, ^{3}d–π^*_{Hdpa}, $^3\mathrm{n_{Hdpa}}$–π^*_{bpy}, $^3\mathrm{n_{Hdpa}}$–π^*_{Hdpa}, and ^{3}d–d*. The kinds of lower excited states of $[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$ are similar to those of $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$, except for the presence of the $^3\mathrm{n_{Hdpa}}$–π^*_{Hdpa} state. It was found that ϕ_{rac} depended on the irradiation wavelength, and that activation to the upper levels gave a larger quantum yield. This is explained as follows. Excitation to the ^{1}d–π^*_{bpy} and ^{1}d–π^*_{Hdpa} states is followed by an intersystem crossing to the ^{3}d–π^*_{bpy} and ^{3}d–π^*_{Hdpa} states, respectively. Although in the case of $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$, the ^{3}d–$\pi^*_{\mathrm{Hdpa}}$ state converts to the ^{3}d–π^*_{bpy} state, which passes to the ^{3}d–d* state, for $[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$, the ^{3}d–$\pi^*_{\mathrm{Hdpa}}$ state converts to both the ^{3}d–π^*_{bpy} and ^{3}d–d* states competitively. That is, excitation to the ^{1}d–π^*_{Hdpa} state deactivates through two paths to the ^{3}d–d* state, as indicated by Nakamaru[15] and Wacholtz et al.[16] Consequently, activation by shorter wavelength light gives a larger ϕ_{rac}.

The lower excited states of $[\mathrm{Ru(Hdpa)_3}]^{2+}$ include three states: ^{3}d–π^*_{Hdpa}, $^3\mathrm{n_{Hdpa}}$–π^*_{Hdpa}, and ^{3}d–d*. Although Blakley and DeArmond stated that the lowest excited state of $[\mathrm{Ru(Hdpa)_3}]^{2+}$ was the ^{3}d–d* state,[5] the wavelength dependece of ϕ_{rac} indicated that the ^{3}d–π^*_{Hdpa}, $^3\mathrm{n_{Hdpa}}$–π^*_{Hdpa} states, besides the ^{3}d–d* state, played important roles in photochemical reactions. The irradiation with the light of lower energy (436 nm), which was not sufficient to excite to the ^{1}d–π^*_{Hdpa} state, and involved excitation to the $^1\mathrm{n_{Hdpa}}$–π^*_{Hdpa} state, gave a lower quantum yield. This indicated that the $^{1,3}\mathrm{n_{Hdpa}}$–π^*_{Hdpa} state can not pass to the ^{3}d–d* state, and, accordingly, the ϕ_{rac} value became lower. The process may not be probable, since it involves a two-electron transition via the ^{3}d–π^*_{Hdpa} state, which has a higher energy than does the $^3\mathrm{n_{Hdpa}}$–π^*_{Hdpa} state.

The similarity in the photochemical behavior between $[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$ and $[\mathrm{Ru(Hdpa)_3}]^{2+}$, in that they both showed weak or no emission at room temperature, and the values of ϕ_{rac} were on the order of 10^{-4} (Fig. 2), revealed features of the excited states of the two complexes. The fact that the decomposition was recognized upon irradiation could be explained by the higher reactivity of the ^{3}d–d* state for the complexes. If for $[\mathrm{Ru(Hdpa)_3}]^{2+}$ only the lowest excited state, ^{3}d–d*, played an important role in the photochemical reaction, $\phi_{\mathrm{d-d}}$ in Eq. 9 would be nearly equal to unity, hence, ϕ_{rac} might be larger than those of $[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$, which was not the case. Consequently, for $[\mathrm{Ru(Hdpa)_3}]^{2+}$, the ^{3}d–$\pi^*_{\mathrm{Hdpa}}$ and $^3\mathrm{n_{Hdpa}}$–π^*_{Hdpa} states, besides the ^{3}d–d* state, contributed to the photochemical reactions. In conclusion, the deactivation of the ^{3}d–π^*_{bpy} or ^{3}d–π^*_{Hdpa} states through the paths to the $^3\mathrm{n_{Hdpa}}$–π^*_{bpy} or $^3\mathrm{n_{Hdpa}}$–π^*_{Hdpa} states, respectively, reduce $\phi_{\mathrm{d-d}}$ for $[\mathrm{Ru(bpy)(Hdpa)_2}]^{2+}$ and $[\mathrm{Ru(Hdpa)_3}]^{2+}$; therefore, their ϕ_{rac} will be smaller than those of $[\mathrm{Ru(bpy)_3}]^{2+}$ and $[\mathrm{Ru(bpy)_2(Hdpa)}]^{2+}$.

The authers wish to thank Dr. Mikio Hoshino of The Institute of Physical and Chemical Research (RIKEN) for measuring of the emission lifetime. We would also like to thank Mrs. Hiroko Hirota née Miki and Mr. Tomonori Hirose for their technical assistance. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 61470048 from the Ministry of Education, Science and Culture.

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