The Excited-state Absorption and Phosphorescence of Rhodium(III) Compounds at Room Temperature

Takeshi OHNO* and Shunji KATO
Chemistry Department, College of General Education, Osaka University, Toyonaka, Osaka 560
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The excited states of rhodium(III) compounds including $[Rh(4,7\text{-diphenyl-}1,10\text{-phenanthroline})_3]^{3+}$ ($[Rh(dp\text{-}phen)_3]^{3+}$), $[Rh(1,10\text{-phenanthroline})_3]^{3+}$ ($[Rh(phen)_3]^{3+}$), $[RhCl_2(dp\text{-}phen)_2]^+$, and $[RhCl_2(phen)_2]^+$, have been investigated by means of emission spectroscopy and laser photolysis spectroscopy. The transient species with the lifetime of 0.055—72 μs are identified as the triplet (π-π^*) excited state of the ligand for $[Rh(dp\text{-}phen)_3]^{3+}$ and $[Rh(phen)_3]^{3+}$ and as the triplet ligand-field excited states for $[RhCl_2(dp\text{-}phen)_2]^+$ and $[RhCl_2(phen)_2]^+$. The molar absorption coefficients of the excited states are 9600 $M^{-1}cm^{-1}$ at 550 nm for $[Rh(dp\text{-}phen)_3]^{3+}$, 2750 $M^{-1}cm^{-1}$ at 560 nm for $[RhCl_2(dp\text{-}phen)_2]^+$, 2300 $M^{-1}cm^{-1}$ at 510 nm for $[Rh(phen)_3]^{3+}$, and 1600 $M^{-1}cm^{-1}$ at 550 nm for $[RhCl_2(phen)_2]^+$. The lifetime of the ligand-field excited state of $[RhCl_2(phen)_2]^+$ (700 ns in acetonitrile) decreases to 55 ns in water.

It has been found that the phosphorescent states of metal complexes containing 2,2′-bipyridine* or 1,10-phenanthroline* as ligands have unusual long lifetimes enabling them to undergo bimolecular electron-transfer reactions. The luminescence or the excited-state absorption (ESA) has been utilized to investigate the photochemical reactions of ruthenium(II),[1] chromium(III),[2,3] and rhodium(III) compounds.[4-6] The lifetime and the quenching reaction of the excited state can be derived from the luminescence measurement. Meanwhile, the formation of the excited state can be determined from the measurement of ESA using the molar-absorption coefficient. Provided that the molar-absorption coefficient of the reaction product is also available, one can estimate the efficiency of the product formation in the quenching of the excited state. However, only a few studies of the elementary reactions of excited-metal complexes have been done, since the molar-absorption coefficients of metal complexes are unknown except for the phosphorescent states of $[Ru(bpy)_3]^{2+}$,[7] $[Cr(bpy)_3]^{3+}$,[3] and $[Cr(4,7\text{-diphenyl-}1,10\text{-phenanthroline}^*)_3]^{3+}$.[3] As for rhodium(III), ESA are known only for $[RhBr_2(bpy)_2]^+$[8] and $[RhCl(NH_3)_5]^{2+}$.[9] We will report here the ESA of four rhodium(III) compounds, ···$[Rh(dp\text{-}phen)_3]^{3+}$, $[RhCl_2(dp\text{-}phen)_2]^+$, $[Rh(phen)_3]^{3+}$, and $[RhCl_2(phen)_2]^+$, which are known to be photoactive.[4,5,10] The molar-absorption coefficients of ESA are also determined for the dp-phen complexes which can be efficiently excited by the second harmonics of a ruby laser (347 nm). The phosphorescences of the rhodium(III) compounds at room temperature are also described for purposes of comparison. The solvent dependence of the lifetimes of the ligand-field excited states at room temperature is discussed in connection with the photo-substitution reaction.

Experimental

Apparatus. An NEC SLG-2018 Q-switched ruby laser capable of providing up to 0.17 J per flash at 347 nm was used. The details of the laser apparatus and the monitoring device have been described elsewhere.[3,11] Transient changes in the absorption and decay of luminescence were fed into a Iwatsu 8123 Storagescope, followed by computer analysis using a NEC PC8001 MKII microcomputer. A Hitachi 323 Spectrophotometer and a Hitachi MPF-2A Spectrofluorophotometer were used for the measurements of the absorption and the luminescence spectra, respectively.

Materials. $[Rh(phen)_3]Cl_3\cdot 3H_2O$ was prepared by the method of Harris and McKenzie.[12] $[RhCl_2(phen)_2]Cl\cdot 3H_2O$ was prepared by a catalytic method in the literature,[13] which was applied to the preparation of $[Rh(dp\text{-}phen)_3](ClO_4)_3\cdot 4H_2O$ and $[RhCl_2(dp\text{-}phen)_2]Cl\cdot 3H_2O$. The crude sample were purified by recrystallization; $[Rh(phen)_3]Cl_3\cdot 3H_2O$ and $[RhCl_2(phen)_2]Cl\cdot 3H_2O$ from the aqueous solution, $[Rh(dp\text{-}phen)_3](ClO_4)_3\cdot 4H_2O$ from the ethanol solution (Found; C, 58.79; H, 3.45; N, 5.72. Calcd for $C_{72}H_{56}N_6Cl_3O_{16}Rh$: C, 58.81; H, 3.84; N, 5.72%), and $[RhCl_2(dp\text{-}phen)_2]Cl\cdot 3H_2O$ from the acetonitrile solution (Found: C, 61.40; H, 4.06; N, 5.98. Calcd for $C_{48}H_{38}N_4Cl_3O_3$: C,62.12; H, 4.13; N, 6.04%). Free ligands of dp-phen and phen of analytical grade were used without further purification. Acetonitrile (AN), methanol, and ethanol of G. R. grade were used as supplied by Wako Pure Chemical Co. Water was purified by passing it through a Millipore deionizer and filter. The test solution were deaerated by purging for 15—20 min with nitrogen.

Measurements. All the measurements were done at 13±2°C, unless otherwise noted. The molar absorption coefficients of the excited states were obtained on the assumption that all the molecules in the 10—40 μM (1 M=1 mol dm^{-3}) of $[Rh(dp\text{-}phen)_3]^{3+}$ or $[RhCl_2(dp\text{-}phen)_2]^+$ were excited to the phosphorescent state by one shot of the laser. The complete excitation of the compounds to the phosphorescent state was ascertained by a constant production of the transient absorption, accompanied by an attenuation of the laser intensity.

The decay of ESA was monitored at 500 nm for $[Rh(phen)_3]^{3+}$ and at 560 nm for $[RhCl_2(phen)_2]^+$, $[Rh(dp\text{-}phen)_3]^{3+}$, and $[RhCl_2(dp\text{-}phen)_2]^+$. The decay of the phosphorescence was monitored using an interference filter with the maximum transparency at 510 nm for $[Rh(dp\text{-}phen)_3]^{3+}$, at 597 nm for $[Rh(phen)_3]^{3+}$, or at 669 nm for $[RhCl_2(dp\text{-}phen)_2]^+$ and $[RhCl_2(phen)_2]^+$.

Results

$[Rh(dp\text{-}phen)_3]^{3+}$. The title compound exhibited

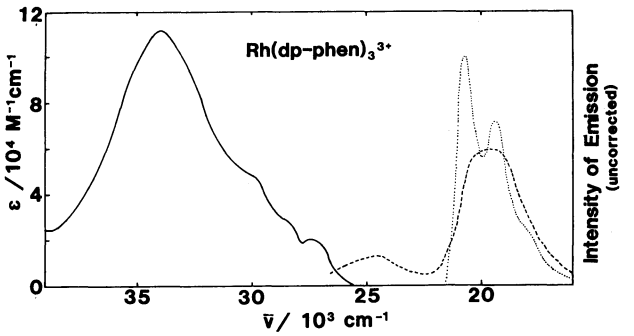

Fig. 1. Absorption and emission spectra of [Rh(dp-phen)$_3$]$^{3+}$.
The full line; the absorption of the 50% AN aqueous solution,the broken line; the emission of the 50% AN aqueous solution (11.4 μM), and the dotted line; the emission of the ethanol-methanol (4:1 by volume) solution (40 μM) at 77 K.

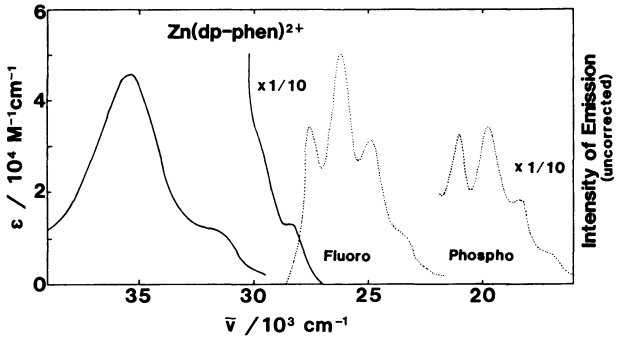

Fig. 2. Absorption and emission spectra of [Zn(dp-phen)]$^{2+}$.
The full line; the absorption of sample containing $Zn(NO_3)_2$ of $(1—5)\times10^{-4}$ M and dp-phen of $(0.2—2)\times10^{-4}$ M in AN-water (1:1) and the dotted line; the emission of the sample containing $Zn(NO_3)_2$ of 2×10^{-4} M and dp-phen of 10^{-4} M in methanol-water (4:1) at 77 K.

almost the same absorption spectrum as the dp-phen coordinated to the zinc(II) ion**, as is shown in Figs. 1 and 2, which is essentially ascribed to the π-π^* transitions of the ligand. The weak band of the free dp-phen at 28800 cm^{-1} (ε=440 M^{-1}cm^{-1}) is strengthened in Zn(dp-phen)$^{2+}$ and [Rh(dp-phen)$_3$]$^{3+}$ by three to thirteen times. As the luminescence spectra in Figs. 1 and 2 show, the coordination of dp-phen to the rhodium(III) ion enormously strengthens the π-π^* phosphorescence, which is shifted to a lower energy with the same fine structure as the phosphorescence of [Zn(dp-phen)]$^{2+}$. While a rise in the temperature weakens the phosphorescence of [Rh(dp-phen)$_3$]$^{3+}$, a phosphorescence with a lifetime of 72 μs and a quantum yield of -10^{-4} is still observed at room temperature. The phosphorescent state of $^3(\pi$-$\pi^*)$ was observed as an absorption by means of laser-photolysis spectroscopy at room temperature. The laser excitation of [Rh(dp-phen)$_3$]$^{3+}$ of 11 μM gives rise to an transient absorption, as is shown in Fig. 3. This transient absorption has the same lifetime (63 μs) as the phosphorescence, so it may be concluded that it is due to the triplet π-π^* state ($^3(\pi$-$\pi^*)$). The molar-absorption coefficient of the $^3(\pi$-$\pi^*)$ is obtained as 9600 M^{-1}cm^{-1} at 550 nm on the condition that the [Rh(dp-phen)$_3$]$^{3+}$ of 11 μM are completely excited to $^3(\pi$-$\pi^*)$ by one shot of the laser, as Fig. 4 shows. The wide ESA of $^3(\pi$-$\pi^*)$ compared to that of the excited free dp-phen indicates the appearance of a new transition. The lifetime of $^3(\pi$-$\pi^*)$ increased by 25% with the increase in the water content in the solvent.

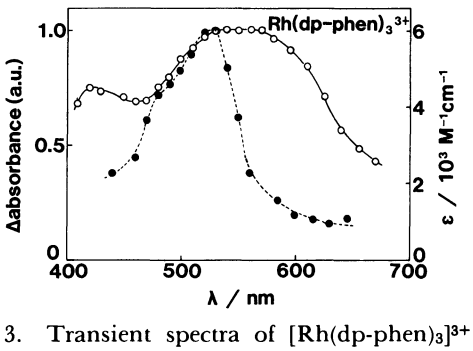

Fig. 3. Transient spectra of [Rh(dp-phen)$_3$]$^{3+}$ and dp-phen.
The full line; [Rh(dp-phen)$_3$]$^{3+}$ of 11.4 μM in AN-water (1:1) and the broken line; dp-phen of 1.21 mM in AN.

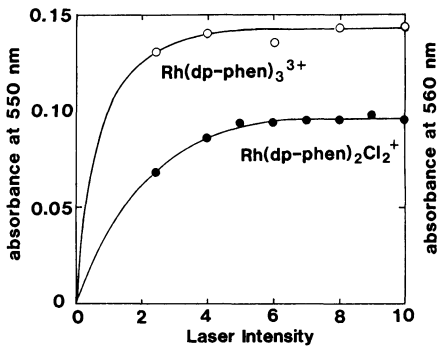

Fig. 4. Dependence of the transient absorbance on the laser intensity.
The open circle; [Rh(dp-phen)$_3$]$^{3+}$ of 11.4 μM in AN-water (1:1) (the left ordinate) and the closed circle; [RhCl$_2$(dp-phen)$_2$]$^+$ of 40 μM in AN (the right ordinate).

[RhCl$_2$(dp-phen)$_2$]$^+$. The pale yellow AN solution of [RhCl$_2$(dp-phen)$_2$]$^+$ emits a weak and broad phosphorescense with a maximum at 690 nm at room temperature (Fig. 5); this can presumably be assigned to the ligand-field phosphorescence ($^3T_1\rightarrow{}^1A_1$)***. It resembles the low-temperature emission of [RhCl$_2$(phen)$_2$]$^+$, with a maximum at 704 nm.[14,15] The lifetime of [RhCl$_2$(dp-phen)$_2$]$^+$ is 1.1 μs at room temperature in AN several hundred times as long as those of [RhX$_2$(NH$_3$)$_4$]$^+$ (X=Cl$^-$ and Br$^-$) in water.[5]

The excited state of $^3T_1$ was also detected by means of laser-photolysis spectroscopy. The transient absorption of the AN solution (Fig. 6) is identified as $^3T_1$ because its lifetime (1.0 μs) is close to that of the phosphorescence. The molar absorption coefficient was obtained as 2750 M^{-1}cm^{-1} at 560 nm from the complete conversion to $^3T_1$, which is ascertained by

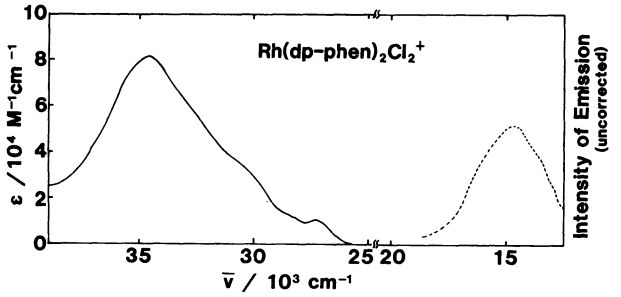

Fig. 5. Absorption spectrum (solid line) and emission spectrum (broken line) of $[RhCl_2(dp\text{-}phen)_2]^+$ in AN.

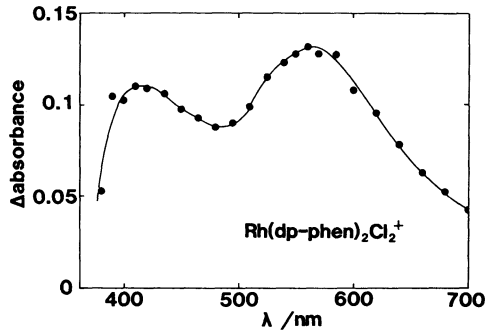

Fig. 6. Transient absorption spectra of $[RhCl_2(dp\text{-}phen)_2]^+$ (50 μM) in AN.

the saturation of the transient absorbance with an attenuation of the laser intensity, as is shown in Fig. 4. The lifetime of $^3T_1$ becomes shorter with the water content in the solvent; the lifetime of 1.02 μs in the AN solution decreases to 340 ns in the 50% AN aqueous solution and to 127 ns in the 20% AN aqueous solution.

$[Rh(phen)_3]^{3+}$. The coordination of phen to the rhodium(III) ion strengthens the lowest transition of free phen by thirteen times, which is symmetry forbidden.[16] On excitation with the second harmonics of the ruby laser, a transient species with an absorption maximum at 510 nm was observed in an alcoholic solvent at room temperature, as well as they at 77 K, as is shown in Fig. 7. Since the transient absorption has as long a lifetime as the phosphorescence (48 ms) from $^3(\pi\text{-}\pi^*)$ at 480 nm,[15] the transient absorption is ascribed to $^3(\pi\text{-}\pi^*)$. The molar-absorption coefficient of the ESA in water was obtained as 2300 $M^{-1}cm^{-1}$ from the complete conversion to the excited state. The lifetime of the $^3(\pi\text{-}\pi^*)$, as monitored by the ESA, decreased at room temperature to 60 ns in methanol, 85 ns in AN–water (4:1), and 440 ns in water. Correspondingly, the $\pi\text{-}\pi^*$ phosphorescence was replaced by a broad emission with the maximum at 580 nm, which has been assigned by Bolleta[17] to the phosphorescence from $^3T_1$. The same lifetime of the phosphorescence from $^3T_1$ as the ESA of $^3(\pi\text{-}\pi^*)$ supports the idea that the thermal activation from $^3(\pi\text{-}\pi^*)$ to $^3T_1$ is responsible for the broad phosphorescence at room temperature.[17] The $^3(\pi\text{-}\pi^*)$ in water has the longest lifetime, in contrast to the triplet ligand-field excited states of $[RhCl_2(dp\text{-}phen)_2]^+$ and $[RhCl_2(phen)_2]^+$, which have the shortest

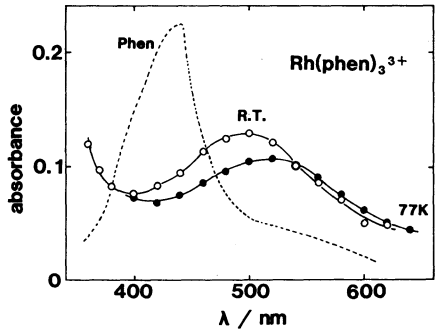

Fig. 7. Transient absorption spectra of $[Rh(dp\text{-}phen)_3]^{3+}$ and free phen.
The open circle; $[Rh(dp\text{-}phen)_3]^{3+}$ of 100 μM in water, the closed circle; $[Rh(dp\text{-}phen)_3]^{3+}$ of 100 μM in ethanol-methanol (4:1) at 77 K, the solid line; phen of 0.04 M in AN.

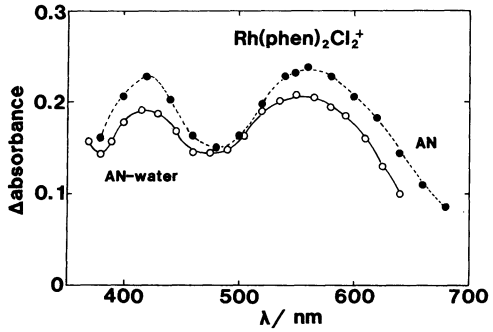

Fig. 8. Transient absorption spectra of $[RhCl_2(phen)_2]^+$ (200 μM) in AN–water (1:1) (open circle) and AN (closed circle).

lifetime in water (*vide infra*). It should be noted that the ESA of $[Rh(phen)_3]^{3+}$ disagrees with that of free phen, with the maximum at 440 nm.

$[RhCl_2(phen)_2]^+$. The lowest excited state of $[RhCl_2(phen)_2]^+$ is $^3T_1$ of the ligand-field excitation, which emits a broad phosphorescence at 77 K.[14,15] The weak phosphorescnce with the lifetime of 680 ns in the AN solution was observed at room temperature, too. The ESA of $^3T_1$ with the molar absorption coefficient of 1600 $M^{-1}cm^{-1}$ at 550 nm is also observed by means of laser photolysis spectroscopy as Fig. 8 shows; it is independent of the solvent. The lifetime of the ESA in the AN solution (700 ns) agrees with that of the ligand field phosphorescence and becomes as short as to 200 ns in the 50% AN aqueous solution and 55 ns in the aqueous solution.

Discussion

The $^3(\pi\text{-}\pi^*)$ of $[Rh(dp\text{-}phen)_3]^{3+}$ and $[Rh(phen)_3]^{3+}$ have some different characters from those of the ligand-field excited states of $[RhCl_2(dp\text{-}phen)_2]^+$ and $[RhCl_2(phen)_2]^+$. The $^3(\pi\text{-}\pi^*)$ of $[Rh(dp\text{-}phen)_3]^{3+}$ has a longer lifetime and a larger molar absorption than the $^3T_1$ of the $[RhCl_2(dp\text{-}phen)_2]^+$. The longest phosphorescent lifetime of $[Rh(dp\text{-}phen)_3]^{3+}$ can be explained as follows. The $^3(\pi\text{-}\pi^*)$ of $[Rh(dp\text{-}phen)_3]^{3+}$

is localized in the large ligand of dp-phen so that the spin-orbit interaction due to the rhodium(III) ion is not effective on the internal conversion ($^3(\pi\text{-}\pi^*)\rightarrow{}^1A_1$). The much shorter lifetimes of the ligand-field triplet-excited states in the aqueous solution may be closely related to the aquation reaction of $[RhCl_2(phen)_2]^+$.[5,18] It can be explained in terms of a competition between the phosphorescence and the aquation that $[RhCl_2(phen)_2]^+$, with less photoactivity (ϕ=0.01),[10] has a longer lifetime (55 ns) than that (1 ns)[5] of *cis*-$[RhBr_2(NH_3)_4]^+$ in the aqueous solution, which undergoes a photoaquation reaction with the quantum yield of 0.3.

The $^3T_1$ of $[RhCl_2(dp\text{-}phen)_2]^+$ and $[RhCl_2(phen)_2]^+$ have large molar-absorption coefficients (2750 $M^{-1}cm^{-1}$ and 1600 $M^{-1}cm^{-1}$, respectively), which can be explained not by the parity-forbidden ligand-field transition, but by a charge-transfer transition ($\pi\rightarrow d_\pi$). As for $[Rh(dp\text{-}phen)_3]^{3+}$, the wide absorption of $^3(\pi\text{-}\pi^*)$ with the absorption coefficient of 9600 $M^{-1}cm^{-1}$ indicates the appearance of a charge-transfer transition ($d_\pi\rightarrow\pi^*$) in addition to the ($\pi\text{-}\pi^*$) transition of the excited free ligand. Such an appearance of the charge-transfer transition ($\pi\rightarrow d_\pi$) in the ESA also has been proposed in the cases of excited doublet states of chromium(III) compounds.[3] By using these large molar-absorption coefficients, one can estimate the formation of the excited state on photoexcitation. The formation of the excited state is indispensable to an estimation of the efficiency of product formation in the quenching process of the excited rhodium(III) compound, which has been qualitatively studied by several workers.[4,19] Both $^3(\pi\text{-}\pi^*)$ and $^3T_1$ of the rhodium(III) compounds studied are subjected to electron-transfer quenching by some aromatic amines. The efficiencies of product formation in the quenching are calculated to be more than 0.1 by using these absorption coefficients. The details of the electron transfer quenching will be reported elsewhere.

References

* The following abbreviations will be used; 2,2′-bipyridine: bpy; 1,10-phenanthroline: phen; and 4,7-diphenyl-1,10-phenanthroline: dp-phen.

** The enhancement of the lowest band of dp-phen on its coodination confirmed the formation of $Zn(dp\text{-}phen)^{2+}$ in dilute solutions of $Zn(NO_3)_3$ and free dp-phen.

*** The rhodium(III) compounds studied do not belong to the Oh group, but the electronic states are denoted by the irreducible representations of the Oh group for the sake of convenience.

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