

as thick as 100 μm , even if the film is deposited on the substrate at 77 K. This molecular orientation can be explained as follows: At a low substrate temperature, the impinging anthracene molecules lose their kinetic energy so rapidly that they are trapped, forming a noncrystalline solid.¹⁹ However, as the film thickness increases the impinging molecules have sufficient surface mobility to form crystallites because the rate of thermal energy dissipation

in the anthracene film is expected to be smaller as the thickness is increased.

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Laser Photolysis Studies of Chlororhodium(III) Tetraphenylporphyrin in Ethanol Solutions. Photoinduced Electron Transfer and Ligand Ejection in the Excited Triplet State

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Chlororhodium(III) tetraphenylporphyrin, ClRh(III)TPP, in ethanol solutions reacts with pyridine, Py, to produce the monopyridine adduct, ClRh(III)TPP(Py), in which Py is located in the axial position. The laser photolysis studies of the adduct revealed that the axial pyridine molecule is dissociated via the porphyrin excited triplet state of ClRh(III)TPP(Py): the quantum yield for the dissociation of pyridine is determined as 0.85 ± 0.05 . The triplet state is found to undergo facile electron transfer to methylviologen, MV²⁺, resulting in the formation of the cation radical, MV^{•+}. The quantum yield for the formation of MV^{•+} was obtained as 0.5 ± 0.1 . This value is much larger than the quantum yield (0.20 ± 0.02) for the formation of MV^{•+} measured for the ethanol solution of ClRh(III)TPP in the presence of MV²⁺. Based on these results, (1) mechanisms for the photoinduced ligand ejection and (2) the effects of the axial pyridine on the electron-transfer reaction are discussed.

Introduction

Physical and chemical properties of synthetic metalloporphyrins have been subjected to numerous studies owing to their importance as model compounds of natural porphyrins that dominate the redox reactions *in vivo*.¹ In photochemistry, studies on photoinduced charge separation of synthetic metalloporphyrins having central metals, Mg and Zn, have been the active area in understanding the role of chlorophylls in photosynthesis.²⁻⁶ In comparison with these porphyrins, metalloporphyrins that have central metals other than Mg and Zn have received less attention.

Recently, we became interested in the role of the central metal and the axial ligands for photoinduced charge separation of metalloporphyrins. The previous studies⁷ have shown that (1) the triplet state of indium(III) tetraphenylporphyrin and methylviologen, MV²⁺, establishes a triplet exciplex which partly undergoes ionic dissociation to yield the methylviologen cation radical, MV^{•+}, and (2) the triplet state of indium(III) tetraphenylporphyrin having two triethanolamine molecules in the axial positions undergoes facile electron transfer toward MV²⁺ without forming the stable triplet exciplex.

The present paper reports the electron-transfer reaction from the excited triplet state of chlororhodium(III) tetraphenylporphyrin, ClRh(III)TPP, to MV²⁺. The effects of the ligand in the electron-transfer reaction were examined with the use of pyridine as an axial ligand. During the course of this study, we found that the axial pyridine in the monopyridine adduct of ClRh(III)TPP, ClRh(III)TPP(Py), was dissociated upon laser excitation. Since photoinduced ligand ejection is one of the current subjects in photochemistry of metalloporphyrins,⁸⁻¹¹ the mechanisms for the ligand ejection were also investigated in detail.

Experimental Section

Chlororhodium(III) tetraphenylporphyrin was synthesized and purified according to the literature.¹² Reagent grade ethanol and pyridine were used as supplied.

Optical absorption spectra were recorded on a Hitachi 330 spectrophotometer. The laser photolysis was carried out by using the second harmonic of a Nd:YAG laser (532 nm) from J. K. Lasers Ltd.: the duration and the energy of a laser pulse were 20 ns and 100 mJ, respectively. The detection system of the transient spectra was described elsewhere.¹³

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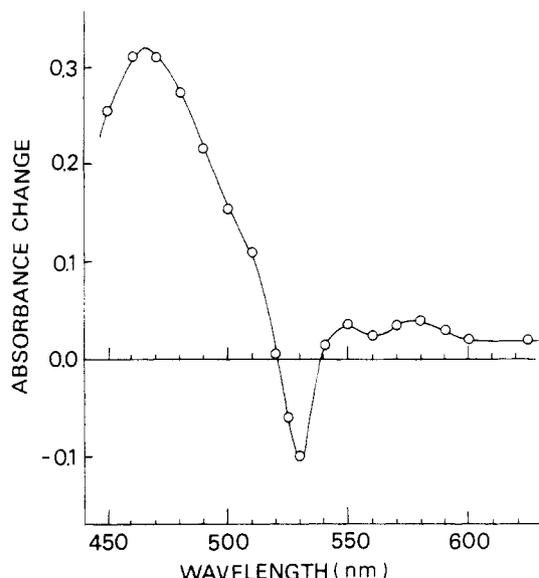


Figure 1. Transient absorption spectrum observed for an ethanol solution of 4×10^{-5} M ClRh(III)TPP at 50 ns after laser pulsing at 532 nm.

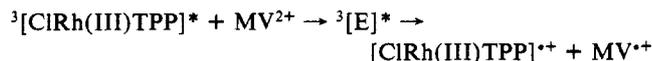
Samples were degassed on a vacuum line by using freeze-pump-thaw cycles.

Results

The optical absorption spectrum of ClRh(III)TPP in ethanol has absorption peaks at 533 and 565 nm in the Q-band region. The molar absorption coefficient at 533 nm was determined as $2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

Figure 1 shows the transient spectrum observed for an ethanol solution of 4×10^{-5} M ClRh(III)TPP at 50 ns after laser pulsing at 532 nm. The positive peak wavelength of the transient spectrum is located around 465 nm. The negative absorbances around 530 nm indicate that ClRh(III)TPP in the ground state is photo-bleached upon laser excitation. Since the transient spectrum is in accord with the absorption spectrum of triplet zinc(II) tetraphenylporphyrin, Zn(II)TPP,¹⁴ the transient species is ascribed to the porphyrin excited triplet state of ClRh(III)TPP. The triplet state decays according to the first-order kinetics with a rate constant of $2.6 \times 10^4 \text{ s}^{-1}$.

The electron-transfer reaction of the triplet ClRh(III)TPP was investigated with the use of MV^{2+} as an electron acceptor. Figure 2 shows the decay rate constants, τ_{obs}^{-1} , of the triplet state represented as a function of MV^{2+} concentration. From the slope of the line, the bimolecular quenching rate constant was obtained as $3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Because of the fact that τ_{obs}^{-1} does not show a leveling off at high concentration of MV^{2+} , we consider that a triplet exciplex between ClRh(III)TPP and MV^{2+} has a very short lifetime. This result differs markedly from the case of chloroindium(III) tetraphenylporphyrin, ClIn(III)TPP, in the excited triplet state: the triplet ClIn(III)TPP in an ethanol solution reacts with MV^{2+} to yield a long-lived triplet exciplex.⁷ In order to confirm whether or not the electron transfer occurs from the triplet ClRh(III)TPP to MV^{2+} , the increase in the absorbance at 610 nm was monitored. The methylviologen cation radical, $\text{MV}^{•+}$, is known to have an absorption band around 610 nm.¹⁵ The rate constant for the formation $\text{MV}^{•+}$ was found to be identical with the decay rate constant of the triplet ClRh(III)TPP. We, therefore, conclude that $\text{MV}^{•+}$ is produced by the electron-transfer reaction from the triplet ClRh(III)TPP to MV^{2+} :



Here, ${}^3[\text{E}]^*$ is assumed to exist as a short-lived exciplex and

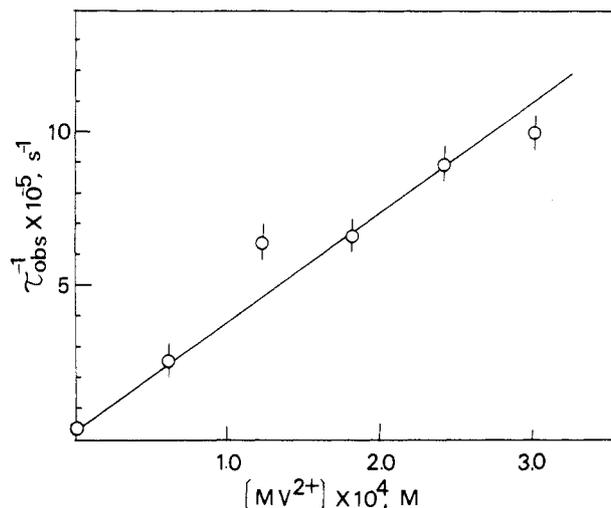


Figure 2. Decay rate constants for the triplet ClRh(III)TPP in ethanol represented as a function of $[\text{MV}^{2+}]$.

$[\text{ClRh(III)TPP}]^{•+}$ denotes the cation radical of ClRh(III)TPP. Since the $\text{MV}^{•+}$ formation was not observed within the duration of a laser pulse, the excited singlet state of ClRh(III)TPP is hardly concerned with the electron-transfer reaction in the MV^{2+} concentration range studied.

The quantum yield, $\Phi(\text{MV}^{•+})$, for the formation of $\text{MV}^{•+}$ was determined by the laser photolysis technique.¹⁶ The yield is expressed as

$$\Phi(\text{MV}^{•+}) = D(610 \text{ nm}) / I_{\text{abs}} \epsilon(610 \text{ nm}) \quad (1)$$

where $\epsilon(610 \text{ nm})$, I_{abs} , and $D(610 \text{ nm})$ stand for the molar absorption coefficient of $\text{MV}^{•+}$ at 610 nm in an ethanol solution, a laser light intensity absorbed by ClRh(III)TPP, and the absorbance of $\text{MV}^{•+}$ observed at 610 nm after laser pulsing, respectively. For measurement of I_{abs} , the methylcyclohexane solution of Zn(II)TPP having the same absorbance at 532 nm as that for the ethanol solution of ClRh(III)TPP was prepared to monitor the triplet-triplet absorption of Zn(II)TPP at 460 nm after laser pulsing. The value of I_{abs} is represented as

$$I_{\text{abs}} = D(460 \text{ nm}) / \epsilon(460 \text{ nm}) \Phi_{\text{ST}} \quad (2)$$

where Φ_{ST} , $D(460 \text{ nm})$, and $\epsilon(460 \text{ nm})$ are respectively the triplet yield of Zn(II)TPP, the absorbance of the triplet Zn(II)TPP at 460 nm observed immediately after a laser pulse, and the molar absorption coefficient of the triplet Zn(II)TPP at 460 nm. From eq 1 and 2, we obtain

$$\Phi(\text{MV}^{•+}) = \epsilon(460 \text{ nm}) \Phi_{\text{ST}} D(610 \text{ nm}) / \epsilon(610 \text{ nm}) D(460 \text{ nm}) \quad (3)$$

By using the values of $\epsilon(610 \text{ nm}) = (1.38 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$,¹⁵ $\Phi_{\text{ST}} = 0.85$,¹⁷ and $\epsilon(460 \text{ nm}) = 8.98 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$,¹⁷ we determined the quantum yield $\Phi(\text{MV}^{•+})$ at an MV^{2+} concentration of $2.5 \times 10^{-4} \text{ M}$ as 0.19 ± 0.02 . Judging from the decay rate constant of the triplet ClRh(III)TPP at $2.5 \times 10^{-4} \text{ M}$ MV^{2+} , we conclude that 97% of the triplet state is quenched by MV^{2+} . The quantum yield for the $\text{MV}^{•+}$ formation from the triplet ClRh(III)TPP at an infinite concentration of MV^{2+} is evaluated as 0.2 ± 0.02 .

Figure 3 shows the absorption spectra of ClRh(III)TPP in ethanol solutions with and without $2.48 \times 10^{-2} \text{ M}$ pyridine. The absorption peak of ClRh(III)TPP at 532.5 nm ($\epsilon = 2.0 \times 10^4$) is red-shifted by ca. 4.0 nm with the addition of pyridine. Since the spectrum of ClRh(III)TPP in the presence of pyridine is identical with that measured for the ethanol solution after removal

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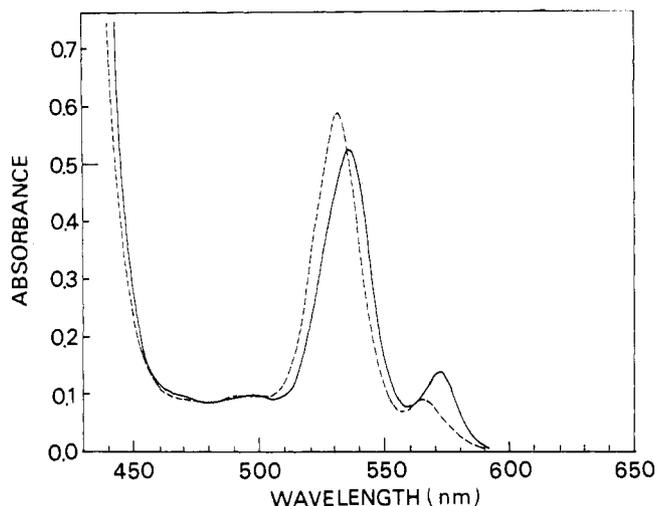


Figure 3. Absorption spectra of ClRh(III)TPP in ethanol with (—) and without (---) 2.48×10^{-2} M pyridine.

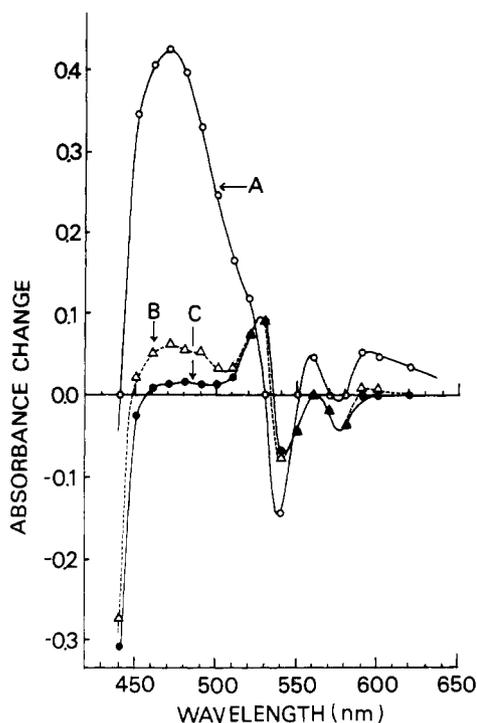
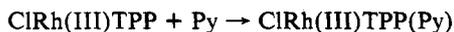


Figure 4. Transient absorption spectra observed at 20 ns (A), 2 μ s (B), and 30 μ s (C) after laser pulsing at 532 nm for an ethanol solution of ClRh(III)TPP(Py) in the presence of 2.48×10^{-2} M pyridine.

of excess pyridine, the following reaction is responsible for the spectral change in absorption:



The 1:1 complex formation between ClRh(III)TPP and pyridine was further confirmed by measurement of the absorption spectral change of ClRh(III)TPP in ethanol by addition of pyridine: (1) the spectral changes of ClRh(III)TPP by addition of pyridine gave isosbestic points, and (2) the spectral changes finished when the concentration of pyridine became the same as that of ClRh(II-I)TPP. Furthermore, the absorption spectrum of ClRh(III)TPP(Py) was identical in the pyridine concentration range 2.48×10^{-4} to 2.48×10^{-2} M. We therefore, consider that the species in the solution is solely ascribed to ClRh(III)TPP(Py) in the pyridine concentration range studied.

Figure 4 shows the transient absorption spectra obtained with laser flash photolysis at 532 nm for the ethanol solution of ClRh(III)TPP(Py) in the presence of 2.48×10^{-2} M pyridine. The transient spectrum observed at 50 ns after pulsing has an absorption peak at 465 nm. Since the spectrum resembles the

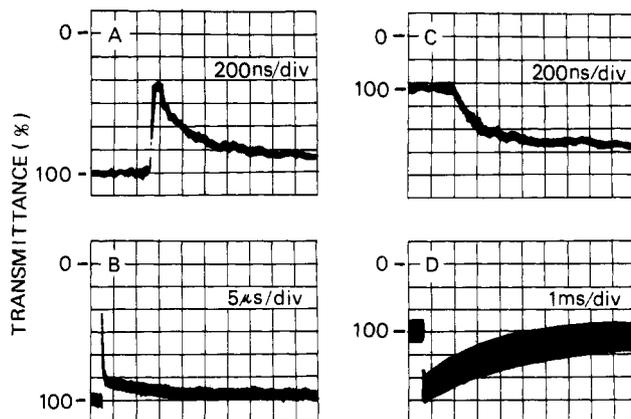
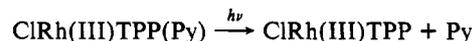


Figure 5. Oscilloscope traces obtained by 532-nm laser photolysis of ClRh(III)TPP(Py) in the ethanol solution containing 2.48×10^{-2} M pyridine: (A) and (B) monitored at 470 nm; (C) and (D) monitored at 440 nm. For details see text.

porphyrin excited triplet-triplet absorption spectrum of ClRh(III)TPP, the transient species is considered to be the porphyrin excited triplet state of ClRh(III)TPP(Py). The decay rate constant of the triplet was determined as $2.7 \times 10^6 \text{ s}^{-1}$. This value is 100 times that of the triplet decay rate of ClRh(III)TPP in ethanol.

At 2 μ s after pulsing, the absorbance around 470 nm almost disappears, leaving a small amount of the transient absorption. This residual transient absorption has a slow decay rate constant of $3.6 \times 10^4 \text{ s}^{-1}$ and was found to show a marked increase in intensity after the solution was exposed to light. Presumably, a photodecomposition product formed during the sample preparation gives the transient species.

The transient absorption spectrum observed at 30 μ s after pulsing is in good accord with the difference spectrum obtained by subtracting the spectrum of ClRh(III)TPP(Py) from that of ClRh(III)TPP. The decay of the transient follows the first-order kinetics with a rate constant of $3.7 \times 10^2 \text{ s}^{-1}$. These results indicate that the axial pyridine in ClRh(III)TPP(py) is easily photoejected



followed by the recombination reaction between ClRh(III)TPP and Py.

Parts A and B of Figure 5 show the oscilloscope traces monitored at 470 nm after laser pulsing, obtained for the ethanol solution of ClRh(III)TPP(Py) in the presence of 2.48×10^{-2} M pyridine. As mentioned above, two transient species are recognized: (1) the fast-decay component is ascribed to the porphyrin excited triplet state of ClRh(III)TPP(Py), and (2) the slow-decay component is ascribed to the transient species arising from a photoproduct of ClRh(III)TPP(Py). The triplet decay rate was found to be independent of the pyridine concentration. Part C of Figure 5 shows the oscilloscope trace monitored at 440 nm. An increase in the transmittance at 440 nm implies that the photoinduced pyridine ejection occurs after laser excitation. Since the rate constant for the bleaching observed at 440 nm is identical with that for the decay of the fast-decay component measured at 470 nm, the photoinduced ligand ejection is concluded to originate from the porphyrin excited triplet state of ClRh(III)TPP(Py). The quantum yield for the pyridine photodissociation was determined as 0.85 ± 0.05 by the similar method used for measurement of the quantum yield for the formation of MV^{•+} as mentioned previously. The concentration of ClRh(III)TPP produced by a laser flash was determined by monitoring the absorbance change at 530 nm.

Part D of Figure 5 shows the recovery of the transmittance observed at 440 nm after laser pulsing, indicating that the ground-state ClRh(III)TPP produced by photodissociation recombines with a pyridine molecule to regenerate ClRh(III)TPP(Py). The rate for the recombination was found to increase with an increase in the concentration of pyridine. Figure 6 shows the rate constants, k_d , for the recombination between ClRh(II-

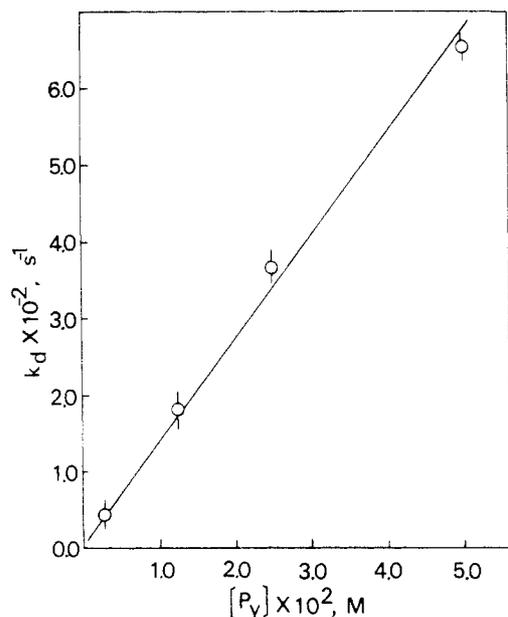


Figure 6. Pseudo-first-order rate constants, k_d , for the recombination reaction between ClRh(III)TPP and pyridine, represented as a function of pyridine concentration, [Py].

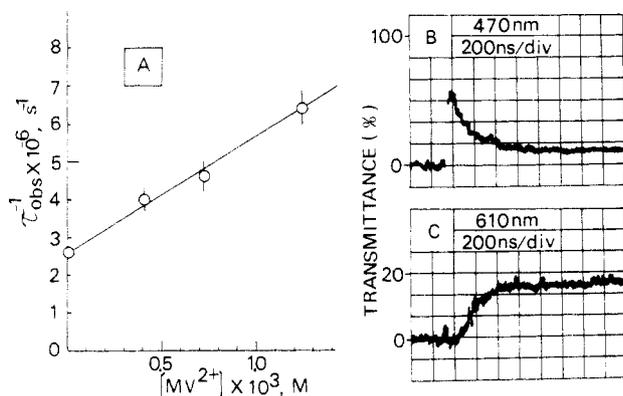


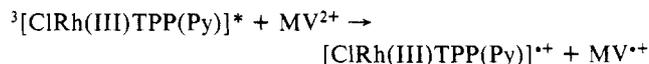
Figure 7. The decay rate constants, τ_{obs}^{-1} , (A) for the triplet ClRh(III)TPP in ethanol solutions containing 2.48×10^{-2} M pyridine, represented as a function of $[\text{MV}^{2+}]$, and oscilloscope traces monitored at 460 (B) and 610 nm (C) after laser pulsing at 532 nm observed for ClRh(III)TPP(Py) in the ethanol solution containing both 2.48×10^{-2} M pyridine and 1.2×10^{-3} M MV^{2+} .

I)TPP and pyridine, represented as a function of pyridine concentration. From the slope of the line, the bimolecular rate constant, k_b , is determined as $1.45 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. It is found that the value of k_b is identical irrespective of the presence or absence of oxygen in ethanol solutions.

The laser photolysis studies of ClRh(III)TPP in ethanol solutions containing 2.48×10^{-2} M pyridine (0 – 1.2) $\times 10^{-3}$ M MV^{2+} were carried out to elucidate the role of axial pyridine in the electron-transfer reaction from the triplet ClRh(III)TPP(Py) to MV^{2+} . Part A of Figure 7 shows the triplet decay rate constant, τ_{obs}^{-1} , represented as a function of MV^{2+} concentration. From the slope of the line, the rate constant for the quenching of the triplet state by MV^{2+} was obtained as $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value is in good agreement with the quenching rate constant of the triplet ClRh(III)TPP by MV^{2+} . Therefore, it is concluded that the quenching rate constant in the triplet state by MV^{2+} is not affected by the axial pyridine.

Parts B and C of Figure 7 show the oscilloscope traces monitored respectively at 460 and 610 nm after laser pulsing, observed for ClRh(III)TPP(py) in the ethanol solution containing 2.48×10^{-2} M pyridine and 1.2×10^{-3} M MV^{2+} . The decay rate of the triplet ClRh(III)TPP(Py) observed at 460 nm is identical with the formation rate of MV^{2+} measured at 610 nm. From these results, the mechanism for the quenching of the triplet ClRh-

(III)TPP(Py) by MV^{2+} is considered to be an electron-transfer reaction:



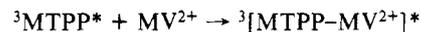
The cation radicals, MV^{*+} and $[\text{ClRh(III)TPP(Py)}]^{*+}$, ultimately disappear according to the recombination reaction to regenerate ClRh(III)TPP(Py) and MV^{2+} . The quantum yield for the formation of MV^{*+} at 1.2×10^{-3} M MV^{2+} was determined as 0.3 ± 0.03 by using the similar method as described for the ClRh(III)TPP and MV^{2+} system. The decay rate constants of ${}^3[\text{ClRh(III)TPP(Py)}]^*$ were obtained as 6.4×10^6 and $2.7 \times 10^6 \text{ s}^{-1}$ with and without 1.2×10^{-3} M MV^{2+} , respectively. From these values, the quantum yield for the formation of MV^{2+} at an infinite concentration of MV^{2+} was estimated as 0.5 ± 0.05 . The fact that the quantum yield (0.5 ± 0.05) for the formation of MV^{*+} from the triplet ClRh(III)TPP(Py) is larger than that (0.2 ± 0.02) from the triplet ClRh(III)TPP implies that the effects of the axial pyridine increase the efficiency of the charge separation in the electron-transfer reaction.

Lever and his co-workers¹⁸ have measured the quantum yield for the photoreduction of MV^{2+} by acetato(tetraphenylporphyrinato)rhodium(III) in the presence of triethanolamine. The yield (0.5) is identical with that for the photoreduction of MV^{2+} by ClRh(III)TPP(Py), obtained in the present study.

Discussion

Triplet Exciplex and Charge Separation. There is clear evidence that the formation of the triplet exciplex between the triplet metalloporphyrins and electron donor or acceptor molecules takes place.^{19–22} It is also recognized that the triplet metalloporphyrins undergo efficient electron transfer to the electron acceptor molecules. In an earlier paper,⁷ we reported the laser photolysis studies of ClIn(III)TPP in methanol solutions containing MV^{2+} as electron acceptors. The triplet ClIn(III)TPP was found to react with MV^{2+} to yield the triplet exciplex, which partly dissociates to form MV^{*+} and the cation radical of ClIn(III)TPP, $[\text{ClIn(III)TPP}]^{*+}$. The present study revealed that the triplet ClRh(III)TPP in ethanol solutions undergoes efficient electron transfer toward MV^{2+} . However, no triplet exciplex formation was detected. This result is interpreted by assuming that the triplet exciplex between the triplet ClRh(III)TPP and MV^{2+} has a short lifetime owing to the facile ionic dissociation in the exciplex state.

The assumption that the electron transfer occurs via the triplet exciplex leads to



Here, MTPP represents metallotetraphenylporphyrin. Therefore, the yields for the ionic dissociation are suggested to be closely related to the nature of the triplet exciplex, ${}^3[\text{MTPP-MV}^{2+}]^*$. We consider that the yield increases with an increase in the charge-transfer character in ${}^3[\text{MTPP-MV}^{2+}]^*$. It is expected that MV^{2+} interacts with the porphyrin ligand in analogy with the ground-state complex between metalloporphyrin and electron acceptors. Accordingly, the central metal, M, results in the changes of the ionization potential of the porphyrin ligand, leading to the variation of the charge-transfer character in the triplet exciplex, and hence, the yield of charge separation is presumed to be dependent on the nature of the central metal.

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The Role of Axial Ligand in Electron-Transfer Reaction. The triplet Zn(II)TPP and 1,4-benzoquinone have been known to form the triplet exciplex in nonpolar solvents, while they undergo ionic dissociation in polar solvents.²³ Harriman and his co-workers³ have investigated the relationship between the yields for ionic dissociation and the dielectric constants of the solvents. They have found that an increase in the dielectric constants of solvents results in an increase in the yields for ionic dissociation. These facts imply that stability of the triplet exciplex is dependent on the solvent polarity: the exciplex tends to undergo ionic dissociation in highly polar solvents. The solvent effects on the lifetime and the ionic dissociation of the triplet exciplex of porphyrins have been also studied by Roy and Whitten.²⁴

In comparison with the solvent effects, the role of axial ligands in the electron-transfer reaction has received less attention. Since the nature of the axial ligand affects the electronic structure of the central metal, and therefore leads to a change in the ionization potential of the porphyrin ligand, it is expected that the axial ligand plays an important role in the electron-transfer reaction from the triplet porphyrin to MV^{2+} . Previously, we have studied the effects of axial triethanolamine (TEA) in electron-transfer reaction from the triplet $[In(III)TPP]^{+*}$, $[In(III)TPP(TEA)]^{+*}$, and $[In(III)TPP(TEA)_2]^{+*}$ to MV^{2+} .⁷ It was concluded that (1) the triplet states of $[In(III)TPP]^{+*}$ and $[In(III)TPP(TEA)]^{+*}$ react with MV^{2+} to form triplet exciplexes and (2) the triplet $[In(III)TPP(TEA)_2]^{+*}$ undergoes facile electron transfer toward MV^{2+} . The results suggest that the triplet exciplex between $[In(III)TPP(TEA)_2]^{+*}$ and MV^{2+} has a very short lifetime owing to the ionic dissociation to produce separated ions, MV^{+} and the porphyrin cation radical. Evidently, two axial TEA molecules accelerate the charge separation of the triplet exciplex.

The laser photolysis studies of ClRh(III)TPP in ethanol solutions containing MV^{2+} have confirmed that the quantum yield for the formation of MV^{+} is 0.20 ± 0.05 at an infinite concentration of MV^{2+} . When ClRh(III)TPP(Py) is used instead of ClRh(III)TPP, the yield for the formation of MV^{+} is evaluated as 0.5 ± 0.05 . These results indicate that the effects of axial pyridine increase the yield of the charge separation from the triplet exciplex. Presumably, the electron-donating nitrogen atom of the axial pyridine molecule causes a decrease in the electronegativity of the central rhodium atom, resulting in a decrease in the ionization potential of the porphyrin ligand. Therefore, it is expected that (1) the charge-transfer character in the triplet exciplex increases owing to the effect of axial pyridine and (2) the yield of the ionic dissociation from the triplet exciplex becomes larger.

Photoinduced Ligand Ejection. Photoinduced ligand ejection of metalloporphyrins is an area of current interest.⁸⁻¹¹ In particular, photodissociation of O_2 , CO, and NO from their adducts of natural and synthetic metalloporphyrins has been extensively studied.^{11,25-29}

As to the metalloporphyrins having nitrogenous bases in the axial position, Ni, Co, and Fe porphyrins were found to release the axial ligands upon laser excitation.⁸⁻¹¹ These porphyrins have the d orbitals between the highest occupied and lowest vacant π orbitals of the porphyrin ligand. The lifetimes of the excited state responsible for the ligand ejection are found to be extremely short. Picosecond photolysis, therefore, is necessary to investigate the nature of the excited states.

In the present study, the triplet ClRh(III)TPP(Py) is found to have a long lifetime compared with the duration of the laser flash. Accordingly, we can observe directly the photoinduced ligand ejection from ClRh(III)TPP(Py) by using a conventional laser photolysis. Since the triplet ClRh(III)TPP(Py) transfers an electron to MV^{2+} , the nature of the triplet state is considered to be the porphyrin-originating $\pi-\pi^*$ triplet. The fact that the triplet spectrum resembles that of the ligand porphyrin in the triplet state also supports the consideration mentioned above.

The kinetics of the transient spectra observed for the ethanol solution of ClRh(III)TPP(Py) confirmed that the axial pyridine molecule is released via the $\pi-\pi^*$ triplet state. However, direct dissociation of the axial pyridine from the $\pi-\pi^*$ triplet state is unlikely because of the fact that the axial pyridine interacts with the central rhodium atom but it does not with the porphyrin ligand.

Recently, Tait and his co-workers carried out the picosecond photolysis of cobalt(III) porphyrins.¹⁰ The dissipation processes of the excitation energy is expressed as a chain of the excited states: $(\pi-\pi^*) \rightarrow (\pi-d_{z^2}) \rightarrow (d_x-d_{y^2})$. The ejection of the axial ligand from the cobalt(III) porphyrins is postulated to occur from the $^3(d_x-d_{y^2})$ state. Since the rhodium(III) atom has an electronic configuration similar to the cobalt(III) atom, it is likely that the ejection of the axial pyridine takes place from the $^3(d_x-d_{y^2})$ state of the central rhodium in ClRh(III)TPP(Py).

The decay rate of the triplet ClRh(III)TPP(Py) is markedly greater than that of the triplet ClRh(III)TPP. On the assumption that, in analogy with the case of cobalt(III) porphyrins, the excitation energy dissipates as a chain of the excited states, $^3(\pi-\pi^*) \rightarrow ^3(\pi-d_{z^2}) \rightarrow ^3(d_x-d_{y^2})$, the axial pyridine increases the nonradiative decay rate from $^3(\pi-\pi^*)$ to $^3(d_x-d_{y^2})$. An increase in the nonradiative decay rate by an axial ligand is also observed for the triplet state of chloro(tetraphenylporphyrinato)carbonylrhodium(III), ClRh(III)TPP(CO), in benzene solutions.³⁰

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Registry No. ClRh(III)TPP, 77944-60-6; MV^{2+} , 4685-14-7; Py, 110-86-1; ClRh(III)TPP(py), 103933-55-7; MV^{+} , 25239-55-8; $[ClIn(III)TPP]^{+*}$, 97644-35-4.

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