THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 107, NUMBER 9, MARCH 6, 2003

ARTICLES

Laser Photolysis Studies of Rhodium(III) Porphyrins. Photodissociation of Axial Phosphine Ligand in the Temperature Range 300−200 K

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Received: June 28, 2002; In Final Form: December 13, 2002

Photodissociation of the axial ligand from triphenylphosphine complexes of rhodium(III) octaethyl- and tetraphenyporphyrin halides, $(X^-)(PPh_3)Rh^{III}OEP$ and $(X^-)(PPh_3)Rh^{III}TPP$ ($X = Cl$, Br, and I), in toluene solutions are investigated by the 355-nm laser flash photolysis. The photodissociation yield of PPh_3, Φ, from $(X^-)(PPh_3)Rh^{III}OEP$ is markedly dependent on the nature of X: $\Phi = 0.79$ for $X = I$, $\Phi = 0.48$ for $X = Br$, and $\Phi = 0$ for $X = Cl$. Similar trends are observed for $(X^-)(PPh_3)Rh^{III}TPP$: $\Phi = 0.13$ for $X = I$ and $\Phi = 0$ for $X = Br$ and Cl. The excited triplet state is not detected for $(I^-)(PPh_3)Rh^{III}OEP$ and $(Br^-)(PPh_3)Rh^{III}OEP$ but for $(Cl^-)(PPh_3)Rh^{III}OEP$ and $(X^-)(PPh_3)Rh^{III}TPP$. On the basis of the oxygen quenching study and the temperature dependence of the dissociation quantum yields, the excited state of $(I^-)(PPh_3)Rh^{III}OEP$ and $(Br^-)(PPh_3)Rh^{III}OEP$ from which the dissociation occurs is ascribed to the excited singlet state. For $(I^-)(PPh_3)Rh^{III}TPP$, either the excited singlet and triplet state is found to be responsible for the dissociation of the axial PPh_3. From the quantum yield measurements for the photodissociation of the axial PPh_3, Φ, and the triplet formation, Φ_{ST}, in the temperature range 200−300 K, the ligand dissociation and the intersystem crossing processes of $(I^-)(PPh_3)Rh^{III}TPP$ are demonstrated to be competitive at the excited singlet state. The sum of the quantum yields, Φ plus Φ_{ST}, obtained at 300 K is smaller than unity. This result is discussed by assuming that the energy dissipation process at the excited singlet state is due to the formation of the transient species that have insufficiently dissociated bonds between X and Rh and/or PPh_3 and Rh: the species partly return to the parent molecule without dissociation of the axial PPh_3.

Introduction

Rhodium porphyrins have been extensively studied as catalysts for various organic reactions.[1−11] However, photochemical reactions of rhodium porphyrins have received less attention.[12−14] The laser flash photolysis studies of rhodium(III) porphyrins have shown that the T−T absorption spectra are very similar to those of zinc(II) porphyrins, indicating that the lowest excited state is originated from the porphyrin ligand.[15] Thus, the triplet state is considered to be expressed as $^3(\pi,\pi^*)$ in nature.

The photochemical reactions of rhodium(III) porphyrins studied hitherto are photoinduced electron transfer from the $^3(\pi,\pi^*)$ state to methyl viologen[16] and photodissociation of the axial ligands such as CO,[17] alkyl isocyanide,[14] and pyridine.[16]

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10.1021/jp021529g CCC: $25.00

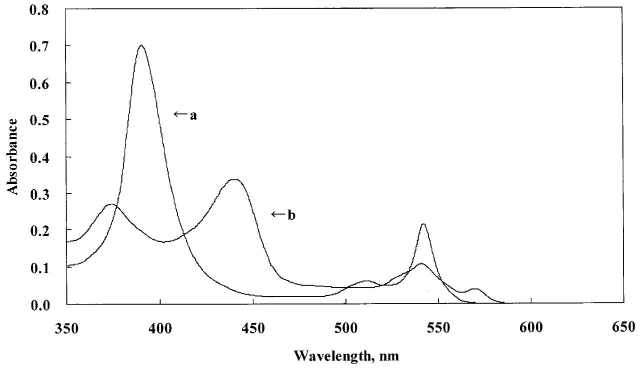


Figure 1. Absorption spectra of 8.5 × 10^{-6} M (a) $(I^-)Rh^{III}OEP$ and (b) $(I^-)(PPh_3)Rh^{III}OEP$ in toluene.

Laser photolysis studies on photoinduced ligand dissociation of rhodium(III) porphyrins have shown that the excited state responsible for the photodissociation of the axial ligands markedly depends on the nature of the ligands: the axial CO molecule is dissociated from the excited singlet state,[14] whereas the axial pyridine is photodissociated via the $^3(\pi,\pi^*)$ state.[16] In the present study, some of (triphenylphosphinato)rhodium(III) octaethyl- and tetraphenylporphyrin halides, $(X^-)(PPh_3)Rh^{III}OEP$ and $(X^-)(PPh_3)Rh^{III}TPP$ (PPh_3 = triphenylphosphine and X = I, Br, and Cl) were found to photodissociate PPh_3. The effects of halide ions on the photodissociation of the axial PPh_3 and the reactive excited state are investigated by the 355-nm laser flash photolysis.

Experimental Section

Rhodium(III) porphyrins were synthesized and purified according to the literature.[18,19] Reagent grade triphenylphosphine supplied from Wako Junnyaku Co. Ltd. was purified by recrystallization from *n*-hexane.

Absorption spectra were recorded on a Hitachi 330 spectrophotometer. The temperature of sample solutions was controlled with the use of a cryostat (Model DN 1001 from Oxford Instrument).

Laser photolysis was performed with third harmonics (355 nm) from a Nd:YAG laser (Model HY500 from JK Lasers): the duration and energy of a laser pulse are 20 ns and 100 mJ/pulse, respectively. The detection system of the transient spectra has been described elsewhere.[20]

Results

Transient Absorption Spectra. Figure 1 shows the absorption spectra of 8.5 × 10^{-6} M $(I^-)Rh^{III}OEP$ and $(I^-)(PPh_3)Rh^{III}OEP$ in toluene solutions. The absorption peaks of $(I^-)Rh^{III}OEP$ are located at 393 nm ($\epsilon = 8.22 \times 10^4$ M^{-1} cm^{-1}) in the Soret band region and at 543 nm ($\epsilon = 2.47 \times 10^4$ M^{-1} cm^{-1}) in the Q-band region. The absorption spectrum of $(I^-)Rh^{III}OEP$ in the toluene solution gradually changes with the addition of PPh_3 because of the formation of $(I^-)(PPh_3)Rh^{III}OEP$.

$$(I^-)Rh^{III}OEP + PPh_3 \underset{k_b}{\overset{k_f}{\rightleftarrows}} (I^-)(PPh_3)Rh^{III}OEP \tag{1}$$

The spectral change finishes when the equimolar amount of PPh_3 is added into the solution, indicating that the backward rate constant, k_b, is very small, as will be described later.

Figure 2 shows the transient absorption spectra observed for an aerated toluene solution of $(I^-)(PPh_3)Rh^{III}OEP$ containing 1.0 × 10^{-4} M PPh_3 at 30 ns after the 355-nm laser pulse. Because the transient spectrum observed at 30 ns after the pulse is in good accord with the difference spectrum ($(I^-)Rh^{III}OEP$ minus $(I^-)(PPh_3)Rh^{III}OEP$), the axial ligand, PPh_3, is concluded to be photodissociated.

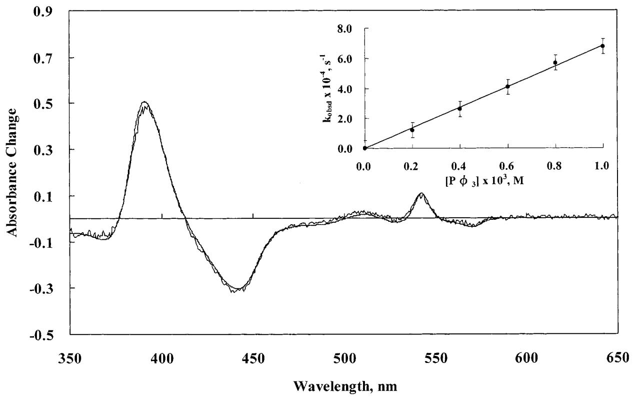


Figure 2. Transient absorption spectrum observed at 30 ns after the 355-nm laser pulse for the degassed toluene solution of $(I^-)(PPh_3)Rh^{III}$ OEP in the presence of 1.0 × 10^{-4} M PPh_3. The solid line is the difference spectrum, $(I^-)Rh^{III}OEP$ minus $(I^-)(PPh_3)Rh^{III}OEP$. The inset is the rate constants, k_{obsd}, represented as a function of PPh_3.

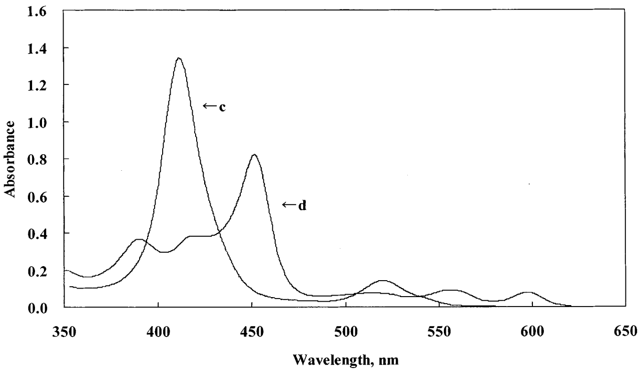


Figure 3. Absorption spectra of 8.8 × 10^{-6} M (c) $(I^-)Rh^{III}TPP$ and (d) $(I^-)(PPh_3)Rh^{III}TPP$ in toluene.

$$(I^-)(PPh_3)Rh^{III}OEP + h\nu \rightarrow (I^-)Rh^{III}OEP + PPh_3 \tag{2}$$

The photochemically produced $(I^-)Rh^{III}OEP$ returns to $(I^-)(PPh_3)Rh^{III}OEP$ by the recombination reaction with PPh_3 (eq 1).

The decay of $(I^-)Rh^{III}OEP$ monitored at 393 nm follows pseudo-first-order kinetics in the PPh_3 concentration range 2.0 × 10^{-4} to 1.0 × 10^{-3} M. According to eq 1, the pseudo-first-order rate constant, k_{obsd}, for the decay of $(I^-)Rh^{III}OEP$ is expressed as

$$k_{obsd} = k_f[PPh_3] + k_b \tag{3}$$

As shown in the inset of Figure 2, the plot of k_{obsd} vs $[PPh_3]$ gives a straight line. From the slope and the intercept of the line, we obtain $k_f = 6.9 \times 10^7$ M^{-1} s^{-1} and $k_b \ll 10^2$ s^{-1}. Other transient species such as the excited triplet state could not be observed for both aerated and degassed toluene solutions of $(I^-)(PPh_3)Rh^{III}OEP$.

Figure 3 shows the absorption spectra of 8.8 × 10^{-6} M $(I^-)Rh^{III}TPP$ and $(I^-)(PPh_3)Rh^{III}TPP$ in toluene solutions. The absorption peaks of $(I^-)Rh^{III}TPP$ are located at 413 nm ($\epsilon = 1.52 \times 10^5$ M^{-1} cm^{-1}) and at 523 nm ($\epsilon = 3.07 \times 10^4$ M^{-1} cm^{-1}). As in the case of $(I^-)Rh^{III}OEP$, the spectral changes observed for $(I^-)Rh^{III}TPP$ by addition of PPh_3 end when the equimolar amount of PPh_3 is added into the toluene solution.

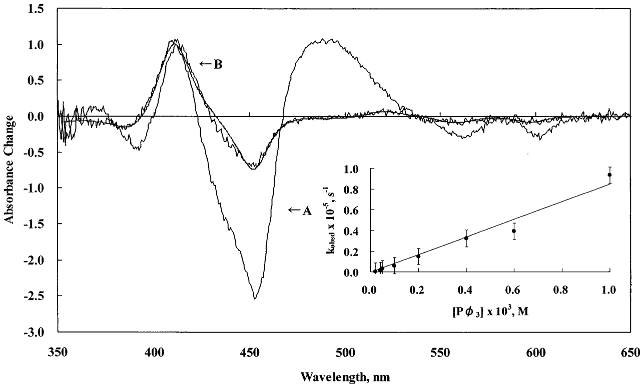


Figure 4. Transient absorption spectra observed at (A) 30 ns and (B) 2 μs after the 355-nm laser pulse for the degassed toluene solution of $(I^-)(PPh_3)Rh^{III}TPP$ in the presence of 1.0×10^{-4} M PPh_3. The solid curve of the spectrum B is the difference spectrum, $(I^-)Rh^{III}TPP$ minus $(I^-)(PPh_3)Rh^{III}TPP$. The inset is the rate constants, k_{obsd}, represented as a function of PPh_3.

Figure 4 shows the transient absorption spectra observed for a degassed toluene solution of $(I^-)(PPh_3)Rh^{III}TPP$ containing 1.0×10^{-4} M PPh_3 at 30 ns and 2 μs after the 355-nm laser pulse. The transient spectrum detected at 30 ns after the pulse has two distinct positive peaks at 413 and 490 nm and a negative peak at 453 nm. The positive absorbance at 490 nm decays according to first-order kinetics with a rate constant 4.37×10^6 s^{-1}, leaving a long-lived transient taken at 2 μs after the pulse. On the basis of the spectral characteristics,[15,16] the transient species with the decay rate constant 4.37×10^6 s^{-1} is ascribed to the excited triplet state of $(I^-)(PPh_3)Rh^{III}TPP$, $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$.

As shown in Figure 4, the transient spectrum observed at 2 μs after the pulse is in good accord with the difference spectrum ($(I^-)Rh^{III}TPP$ minus $(I^-)(PPh_3)Rh^{III}TPP$). Thus, the axial ligand, PPh_3, is concluded to be photodissociated by the 355-nm laser pulse.

$$(I^-)(PPh_3)Rh^{III}TPP + h\nu \rightarrow (I^-)Rh^{III}TPP + PPh_3 \quad (4)$$

The transient $(I^-)Rh^{III}TPP$ reassociates with PPh_3, giving rise to the regeneration of $(I^-)(PPh_3)Rh^{III}TPP$. The decay of $(I^-)Rh^{III}TPP$ monitored at 413 nm follows pseudo-first-order kinetics in the PPh_3 concentration range 2×10^{-5} to 1.0×10^{-3} M. As represented in the inset of Figure 4, the plot of the decay rate constant vs $[(PPh_3)]$ gives a straight line with an intercept at the origin. The slope of the line gives the bimolecular rate constant, 8.4×10^7 M^{-1} s^{-1}, for the reaction between $(I^-)Rh^{III}TPP$ and PPh_3.

It is found by the laser flash photolysis that (1) $(Br^-)(PPh_3)Rh^{III}$ OEP in toluene photodissociates the axial PPh_3 without formation of the triplet state and (2) $(Cl^-)(PPh_3)Rh^{III}OEP$, $(Br^-)(PPh_3)Rh^{III}TPP$, and $(Cl^-)(PPh_3)Rh^{III}TPP$ gave the excited triplet state without photodissociation of the axial PPh_3.

Quantum Yield Measurements by 355-nm Laser Flash Photolysis. When the photochemical reaction is expressed as

$$A + h\nu \rightarrow B \quad (5)$$

the quantum yield for the formation of B is formulated as

$$\phi = \Delta D_a(\lambda)\{\Delta\epsilon_a(\lambda)\}^{-1}(I_{abs})^{-1} \quad (6)$$

where ΔD_a and $\Delta\epsilon_a$ are, respectively, the absorbance change measured at wavelength λ immediately after the pulse and the difference in the molar absorption coefficient between A and B at λ, and I_{abs} stands for the number of photons absorbed.

For determination of I_{abs}, we use a benzene solution of zinc(II) tetraphenylporphyrin, ZnTPP, which has the absorbance identical with that of the toluene solution of the molecule A at 355 nm. The triplet yield, ϕ_T, of ZnTPP is expressed as

$$\phi_T = \Delta D_T(\epsilon_T)^{-1}(I_{abs})^{-1} \quad (7)$$

where ΔD_T and ϵ_T are the absorbance change at 470 nm immediately after the pulse and the molar absorption coefficient of the triplet ZnTPP at 470 nm, respectively. From eqs 6 and 7, the quantum yield ϕ is formulated as[13,14]

$$\phi = \phi_T(\Delta D_a(\lambda)/\Delta D_T)(\epsilon_T/\Delta\epsilon_a(\lambda)) \quad (8)$$

Because ϕ_T and ϵ_T for the benzene solution of ZnTPP[21] have already been determined as $\phi_T = 0.83$ and $\epsilon_T = 7.3 \times 10^4$ M^{-1} cm^{-1}, the yield ϕ for the formation of B from A can readily be obtained with the use of eq 8.

The laser photolysis of 1.21×10^{-5} M (I^-) $(PPh_3)Rh^{III}TPP$ and 4.0×10^{-4} M PPh_3 in toluene gives two transient species, (I^-) $Rh^{III}TPP$ and the excited triplet state of $(I^-)(PPh_3)$ Rh^{III}-TPP. The triplet state completely disappears within 2 μs after the pulse. However, (I^-) $Rh^{III}TPP$ returns to $(I^-)(PPh_3)$ Rh^{III}-TPP with a half-life of ca. 600 μs. Thus the yield for the formation of $(I^-)Rh^{III}TPP$ was determined by measuring the absorbance change, ΔD(413 nm), at 2 μs after the pulse. The molar absorption coefficients of $(I^-)(PPh_3)Rh^{III}TPP$ and (I^-) $Rh^{III}TPP$ have been determined as 1.52×10^5 and 1.9×10^4 M^{-1} cm^{-1} at 413 nm, respectively. From eq 8, ΔD(413 nm), and the molar absorption coefficients, the quantum yield for the photodissociation of PPh_3 from (I^-) $(PPh_3)Rh^{III}TPP$ in degassed toluene is obtained as 0.17 ± 0.02.

For the measurements of the triplet yield of $(I^-)(PPh_3)Rh^{III}TPP$, the molar absorption coefficient of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ at 490 nm has been determined from the absorption spectrum of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$. The spectrum of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ is obtained as follows. The transients observed for 1.21×10^{-5} M $(I^-)(PPh_3)Rh^{III}TPP$ at 30 ns after the 355 nm laser pulse are composed of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ and $(I^-)Rh^{III}TPP$. The rate for the decay of the triplet state is much faster than that of $(I^-)Rh^{III}TPP$, and thus, the transient spectrum for the triplet state is obtained by subtracting the transient spectrum measured at 2 μs from that at 30 ns. With the use of the absorbances, $D_T(\lambda)$ and $D_0(\lambda)$, of the excited triplet state and the ground state of $(I^-)(PPh_3)Rh^{III}TPP$ at the wavelength λ, the absorbance change, $\Delta D(\lambda)$, of the transient spectrum of the triplet state is expressed as[22,23]

$$\Delta D(\lambda) = k(D_T(\lambda) - D_0(\lambda)) \quad (9)$$

The variable number, k, is the function of the energy of a laser pulse and ranges $0 < k < 1.0$. Equation 9 is transformed to

$$D_T(\lambda) = D_0(\lambda) + \Delta D(\lambda)/k \quad (10)$$

If k is appropriate, the plot of $D_T(\lambda)$ vs λ gives the absorption spectrum of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$. We assume here that the triplet spectrum of $(I^-)(PPh_3)Rh^{III}TPP$ in the Soret band region is not distorted.[22,23] The value $k = 0.6 \pm 0.05$ gives a smooth absorption band centered at 490 nm. Thus, the triplet absorption spectrum is obtained by the plot of $D_T(\lambda)$ vs λ at $k = 0.6 \pm 0.05$. The molar absorption coefficient calculated from the triplet spectrum is obtained as $6.7(\pm 0.06) \times 10^4$ M^{-1} cm^{-1} at 490

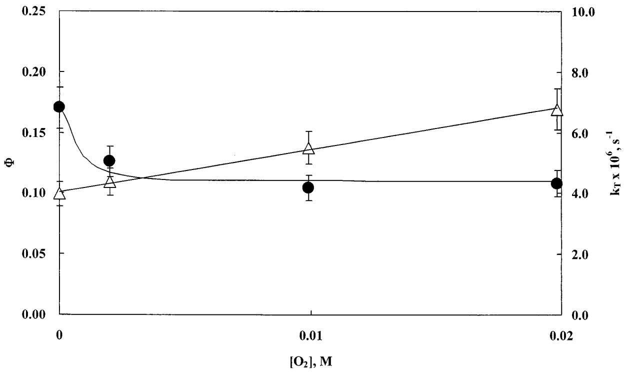


Figure 5. Plots of the dissociation yields, Φ(closed circle), and the triplet decay rate constants, k_T(open triangle), observed for $(I^-)(PPh_3)Rh^{III}$-TPP in toluene, represented as a function of the oxygen concentration.

nm. This value is close to that of the triplet ZnTPP at 470 nm.[21] The quantum yield for the formation of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ is determined as 0.36 ± 0.03.

The quantum yield for photodissociation of the axial PPh_3 from $(I^-)(PPh_3)Rn^{III}OEP$ in both aerated and degassed toluene solutions was obtained as 0.79 by the measurements of the absorbance change at 393 nm at 30 ns after the pulse. Because the excited triplet state could not be detected, the photodissociation of the axial ligand is considered to take place at the excited singlet state, $^1[(I^-)(PPh_3)Rh^{III}OEP]^*$.

The quantum yields for the photodissociation of the axial PPh_3 from $(I^-)(PPh_3)Rh^{III}TPP$ in degassed and aerated toluene are obtained as 0.13 ± 0.01 and 0.17 ± 0.02, respectively. As mentioned above, photolysis of $(I^-)(PPh_3)Rh^{III}TPP$ yields the excited triplet state. To examine the contribution of the triplet state to the photoreaction, the quantum yields, Φ, for the photodissociation of PPh_3 and the rate constant, k_T, of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ monitored at 490 nm were measured at various concentrations of oxygen.

Figure 5 shows the plots of k_T and Φ vs $[O_2]$. The rate constants, k_T, for the decay of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ depend on the oxygen concentration, $[O_2]$. When the triplet state is quenched by oxygen, the rate constant, k_T, is expressed as

$$k_T = k_T^{\ 0} + k_q[O_2] \tag{11}$$

Here $k_T^{\ 0}$ and k_q are the rate constant of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ in degassed toluene and the quenching rate constant of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ by oxygen, respectively. The plot of k_T vs $[O_2]$ gives a straight line. The slope of the line gives $k_q = 1.4 \times 10^8\ M^{-1}\ s^{-1}$. The decay rate constant of $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ in degassed toluene is found to be $k_T^{\ 0} = 3.8 \times 10^6\ s^{-1}$, irrespective of the absence or presence of PPh_3.

The quantum yield, Φ, initially decreases with an increase in $[O_2]$ and approaches to a limiting value at higher concentrations of oxygen. The assumption that the photodissociation of the axial ligand occurs via both the excited singlet and the triplet state leads to the following equation.

$$\Phi = \Phi_S + \Phi_T \frac{k_T^{\ 0}}{k_T^{\ 0} + k_q[O_2]} \tag{12}$$

where Φ_S and Φ_T are the quantum yields for the photodissociation of the axial ligand at the excited singlet state and at the excited triplet state of $(I^-)(PPh_3)Rh^{III}TPP$, respectively. The solid curve in Figure 5 is the calculated quantum yield Φ with the use of eq 12, $\Phi_S = 0.11 \pm 0.01$, $\Phi_T = 0.06 \pm 0.005$, $k_T^{\ 0} = 3.8 \times 10^6\ s^{-1}$, and $k_q = 4.4 \times 10^8\ s^{-1}$. Because the calculated curve reproduces well the quantum yields obtained, it is concluded that the axial PPh_3 is photodissociated from both the excited singlet and the triplet state of $(I^-)(PPh_3)Rh^{III}TPP$.

The laser photolysis of $(Br^-)(PPh_3)Rh^{III}OEP$ gives a transient spectrum identical with the difference spectrum ($(Br^-)Rh^{III}OEP$ minus $(Br^-)(PPh_3)Rh^{III}OEP$). The excited triplet state could not be detected. Thus, $(Br^-)(PPh_3)Rh^{III}OEP$ is concluded to photodissociate the axial PPh_3 at the excited singlet state. The quantum yield for the photodissociation is determined as 0.5 ± 0.05. In Table 1 are listed the quantum yields for photodissociation of the axial PPh_3, the triplet yield, and the rate constants for the recombination between rhodium(III) porphyrins and PPh_3.

TABLE 1: Quantum Yield, Φ, for Photodissociation of the Axial PPh_3 from Triphenylphosphine Adducts of Rhodium(III) Porphyrins, the Triplet Yield, Φ_{ST}, and the Bimolecular Rate Constant, k_f, for the Reaction between Rhodium(III) Porphyrin and PPh_3 at 300 K

	Φ	Φ_{ST}	k_f, $M^{-1}\ s^{-1}$
$(Cl^-)(PPh_3)Rh^{III}TPP$	ND[a]	0.69	
$(Br^-)(PPh_3)Rh^{III}TPP$	ND	0.72	
$(I^-)(PPh_3)Rh^{III}TPP$	0.18[b]	0.36	8.4×10^7
$(Cl^-)(PPh_3)Rh^{III}OEP$	ND	0.35	
$(Br^-)(PPh_3)Rh^{III}OEP$	0.48[c]	N.D	1.3×10^6
$(I^-)(PPh_3)Rh^{III}OEP$	0.79[c]	N.D	4.6×10^7

[a] Not detected. [b] The sum of the quantum yields for the photodissociation of PPh_3 at both the excited singlet (0.12) and the triplet state (0.06). [c] The quantum yields for the photodissociation of PPh_3 at the excited singlet state.

Temperature Dependence of the Quantum Yields for the Photodissociation of PPh_3. The quantum yields for the photodissociation of the axial PPh_3 from $(I^-)(PPh_3)Rh^{III}OEP$ were measured in the temperature range 170−300 K. The transient species observed after the laser pulse is solely $(I^-)Rh^{III}OEP$. As will be mentined later, it is found that (1) the quantum yield for the photodissociation of PPh_3 from $(I^-)(PPh_3)Rh^{III}OEP$ diminishes at low temperatues and (2) the excited triplet state of $(I^-)(PPh_3)Rh^{III}OEP$ could not be detected in the temperature range studied. This finding indicates that the suppression of the ligand dissociation does not result in the formation of the excited triplet state of $(I^-)(PPh_3)Rh^{III}OEP$. Thus, we concluded that the excited triplet state of $(I^-)(PPh_3)Rh^{III}OEP$ is not responsible for the photodissociation of the axial PPh_3.

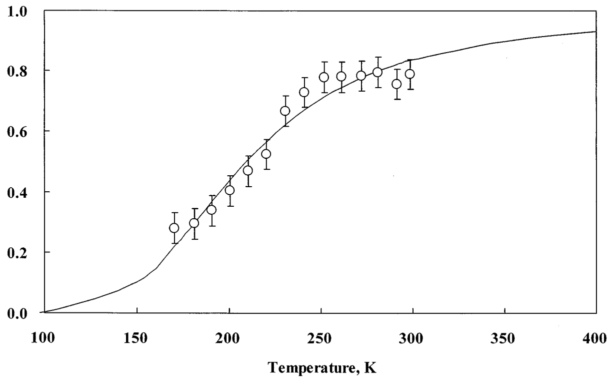


Figure 6. Plot of the dissociation yield, Φ, of $(I^-)(PPh_3)Rh^{III}OEP$ in toluene, represented as a function of temperature. The solid line is the calculated one (see text).

Figure 6 shows the quantum yields for the photodissociation of the axial PPh_3 from $(I^-)(PPh_3)Rh^{III}OEP$, represented as a function of the temperature. The yield is 0.8 ± 0.08 at 300 K.

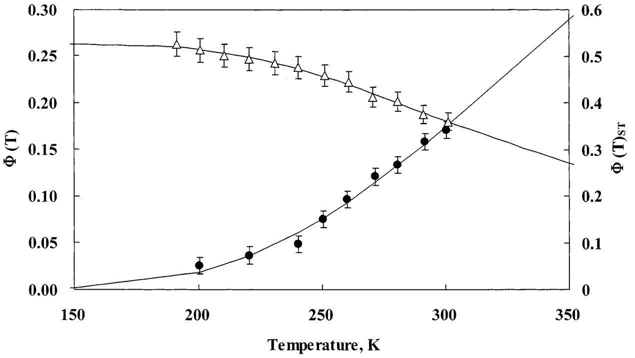
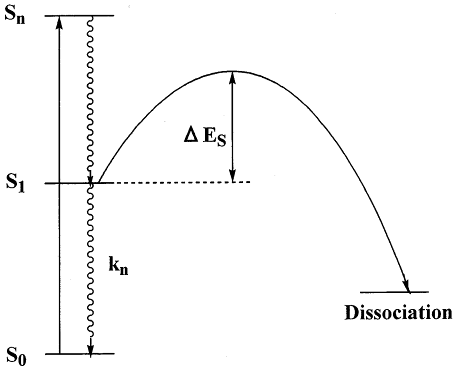


Figure 7. Plots of the dissociation yields, Φ(T) (closed circle), and the triplet yields, $\Phi(T)_{ST}$(open triangle) observed for $(I^-)(PPh_3)Rh^{III}TPP$ in toluene, represented as a function of temperature. The solid lines are the calculated ones (see text).

SCHEME 1



With a decrease in the temperature, the yield gradually decreases. The photodissociation diagram of PPh_3 is shown in Scheme 1. By assuming the activation energy, ΔE, for the photodissociation of the axial PPh_3, the quantum yield Φ is represented as

$$\Phi = \frac{k_{S0}\exp(-\Delta E/RT)}{k_n + k_{S0}\exp(-\Delta E/RT)} \tag{13}$$

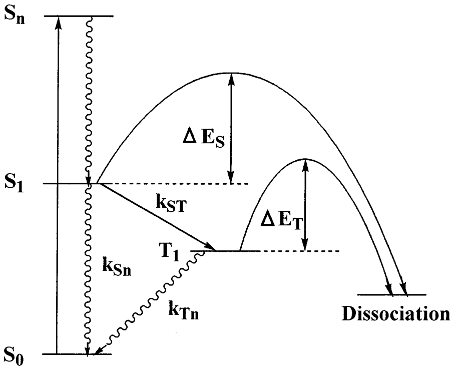
Here k_{S0} is the preexponential factor of the Arrhenius expression for the rate constant of the PPh_3 dissociation, and k_n is the rate constant for the internal conversion process of the excited singlet state. With the use of eq 13 and the least-squares fitting program, we obtained the parameters, $\Delta E = 2.3$ kcal/mol, and $k_n/k_{S0} = 4.3 \times 10^{-3}$. The solid line in Figure 6 is the quantum yields calculated according to eq 13 with the use of these parameters mentioned above.

The photodissociation of the axial PPh_3 from $(I^-)(PPh_3)Rh^{III}TPP$ takes place from both the excited singlet and triplet state. Figure 7 shows the quantum yields for the photodissociation of the axial ligand, PPh_3, represented as a function of the temperature. The quantum yield for the photodissociation of the axial ligand,Φ(T), is represented as a sum of the yields, $\Phi(T)_S$ and $\Phi(T)_T$, at both the singlet and triplet excited states.

$$\Phi(T) = \Phi(T)_S + \Phi(T)_T \tag{14}$$

Scheme 2 shows the diagram of the photodissociation of PPh_3 from $(I^-)(PPh_3)$ $Rh^{III}TPP$ in toluene. It is assumed that, as in the case of $(I^-)(PPh_3)Rh^{III}OEP$, (1) the dissociation of PPh_3 requires the activation energy and (2) the internal conversion rate constant, k_n, and the intersystem crossing rate constants, k_{ST} and k_{Tn}, are the activationless processes.

SCHEME 2



The quantum yields, $\Phi(T)_S$ and $\Phi(T)_T$, are formulated as

$$\Phi(T)_S = \frac{k_{S0}\exp(-\Delta E_s/RT)}{k_{Sn} + k_{ST} + k_{S0}\exp(-\Delta E_s/RT)} \tag{15}$$

and

$$\Phi(T)_T = \Phi(T)_{ST}\frac{k_{T0}\exp(-\Delta E/RT)}{k_{Tn} + k_{T0}\exp(-\Delta E_T/RT)} \tag{16}$$

Here k_{S0} and ΔE_S are the preexponential factor and the activation energy for the dissociation of PPh_3 at the excited singlet state, and k_{T0} and ΔE_T are those at the excited triplet state, respectively. The triplet yield, $\Phi(T)_{ST}$, in eq 16 is represented as

$$\Phi(T)_{ST} = \frac{k_{ST}}{k_{Sn} + k_{ST} + k_{S0}\exp(-E_S/RT)} \tag{17}$$

Figure 7 shows the temperature dependence of the triplet yield, $\Phi(T)_{ST}$, and the dissociation yield, Φ(T), observed for the toluene solution of $(I^-)(PPh_3)Rh^{III}TPP$ by the 355-nm laser photolysis. The triplet yield, $\Phi(T)_{ST}$, is found to increase with a decrease in the temperature. With the use of the triplet yield (0.36) at 300 K, eq 17, the curve fitting, and a least-squares method, k_{Sn}/k_{ST}, k_{S0}/k_{ST}, and ΔE_S are obtained as 0.88, 1.81×10^2, and 3.2 kcal/mol, respectively. Thus, eq 17 is rewritten as

$$\Phi(T)_{ST} = \frac{1}{1.88 + 1.81 \times 10^2 \exp(-3.2 \times 10^3/RT)} \tag{18}$$

As represented by eq 15, the quantum yield, $\Phi(T)_S$, for the photodissociation of PPh_3 at the excited singlet state is governed by the factors ΔE_S and $(k_{Sn} + k_{ST})/k_{S0}$. From $\Phi(T)_S = 0.11$ at 300 K, $\Delta E_S = 3.2$ kcal/mol, and eq 15, $(k_{Sn} + k_{ST})/k_{S0}$ is obtained as 0.04. Then eq 15 is rewritten as

$$\Phi(T)_S = \frac{\exp(-3.2 \times 10^3/RT)}{0.04 + \exp(-3.2 \times 10^3/RT)} \tag{19}$$

As mentioned above, the total dissociation yield of PPh_3, Φ(T), is expressed as a sum of the yields, $\Phi(T)_S$ and $\Phi(T)_T$. With the use of eqs 16, 18, and 19, Φ(T) in eq 14 can be formulated as a function of T. The parameters, k_{Tn}/k_{T0} and ΔE_T, in eq 16 were determined by a curve fitting of Φ(T) and a least-squares

TABLE 2: Activation Energies for the Dissociation of the Axial PPh_3 at the Excited States

	ΔE_S, kcal/mol[a]	ΔE_T, kcal/mol[b]
$(I^-)(PPh_3)Rh^{III}TPP$	3.2	2.9
$(Br^-)(PPh_3)Rh^{III}OEP$	NM[c]	
$(I^-)(PPh_3)Rh^{III}OEP$	2.3	

[a] Activation energy for the dissociation of the axial PPh_3 at the excited singlet state. [b] Activation energy for the dissociation of the axial PPh_3 at the excited triplet state. [c] Not measured.

method: $k_{Tn}/k_{T0} = 0.036$ and $\Delta E_T = 2.9$ kcal/mol. Equation 16, therefore, is rewritten as

$$\Phi(T)_T = \Phi(T)_{ST}\frac{\exp(-2.9 \times 10^3/RT)}{0.036 + \exp(-2.9 \times 10^3/RT)} \quad (20)$$

Here $\Phi(T)_{ST}$ has already been formulated by eq 18. Equations 14, 19, and 20 predict that the dissociation occurs solely at $^1[(I^-)(PPh_3)Rh^{III}TPP]^*$ at an "infinite" temperature with the yield of 0.97. In Table 2 are listed the activation energies for the PPh_3 dissociation at the reactive excited states.

Discussion

Photodissociation of axial ligands from various metalloporphyrins has been extensively studied with an aim to elucidate the reaction mechanisms for association and dissociation of the axial ligands. For instance, alkylaluminum(III)-[24] and alkylindium(III) porphyrins,[25] $R-Al^{III}P$ and $R-In^{III}P$ (P = porphyrin), undergo the homolytic cleavage of the carbon-metal bond to give $Al^{II}P$ and $In^{II}P$. Zinc(II) tetraphenylporphyrin reversibly binds or releases a pyridine molecule at the axial position in the excited singlet state.[26] The pyridine complex of chlorochromium(III) porphyrins, $(Cl^-)(Py)Cr^{III}P$ (Py = pyridine as the axial ligand) photochemically dissociate Py.[27] Similarly, $(Py)_2Fe^{II}P$,[28] $(Cl^-)(Py)Co^{III}P$,[29] $(Cl^-)(Py)Rh^{III}P$,[16] and $(Py)_2Ni^{II}P$[30,31] readily release Py upon laser excitation.

Determination of the reactive excited states of metalloporphyrins responsible for the dissociation of the axial ligands has also been one of the principal subjects of the metalloporphyrin photochemistry. Femtosecond laser photolysis of $[Fe^{III}P]^+$,[32] $[Co^{III}P]^+$,[33] and $Ni^{II}P$[34] suggests that the dissociation of axial ligands occurs from the d−d*, MLCT, or LMCT excited states. Nanosecond photolysis of $(Cl^-)(L)Cr^{III}P$ (L = axial ligand) revealed that the axial ligand L is dissociated from both the $^4S_1$ and the $^6T_1$ (and/or $^4T_1$) state.[23] Alkylindium(III) porphyrins have been confirmed to dissociate the alkyl group via the excited triplet state originating from the porphyrin ligand.[35]

The reactive excited states for the photodissociation of the axial ligands of rhodium(III) porphyrins have been found to depend on the nature of the axial ligands. For alkylrhodium(III) porphyrins, the excited singlet state, $^1(\pi,\pi^*)$, has been demonstrated to play the key role in the cleavage of the carbon−Rh bond.[13] The laser photolysis studies of $(Cl^-)(Py)Rh^{III}TPP$ suggest that the reactive excited state responsible for the dissociation of the axial pyridine molecule is the thermally accessible $^3(d\pi,d^*)$ state produced via the $^3(\pi,\pi^*)$ state.[14,16] In the case of $(I^-)(CO)Rh^{III}TPP$, the photodissociation of CO takes place at the $^1(\pi,\pi^*)$ state. Furthermore, $(I^-)(R-NC)Rh^{III}TPP$ has been found to dissociate the axial R−NC at both the $^1(\pi,\pi^*)$ state[14] and the thermally accessible $^3(d\pi,d^*)$ state.[14]

The quantum yield for the photodissociation of PPh_3 from $(X^-)(PPh_3)Rh^{III}OEP$ at the excited singlet state was found to depend on the nature of the axial halide ion, X^-: the yield increases in the order Cl^-, Br^-, and I^-. On the basis of the electron affinity of halide atoms, it is suggested that an important factor, which dominates the yield for the dissociation of the axial PPh_3, is the charge-transfer interaction between the halide ions and the central rhodium(III) atom at the excited singlet state. Presumably, the charge transfer from X^- to the Rh(III) atom labilizes the bond of the $Rh-PPh_3$ at the trans position. The similar trend was observed for $(X^-)(PPh_3)Rh^{III}TPP$. The photodissociation of the axial PPh_3 is detected solely for X = I.

Because the excited triplet state could not be detected, the reactive excited state responsible for the dissociation of the axial PPh_3 from $(I^-)(PPh_3)Rh^{III}OEP$ and $(Br^-)(PPh_3)Rh^{III}OEP$ is assumed to be the $^1(\pi,\pi^*)$ state. The laser photolysis of $(Cl^-)(PPh_3)Rh^{III}OEP$ has shown that the excited triplet state is formed without the dissociation of the axial PPh_3. This fact indicates that the axial Cl^- suppresses the dissociation of the axial PPh_3 at the excited singlet state, and thus, the triplet state is readily produced by intersystem crossing.

$(I^-)(PPh_3)Rh^{III}TPP$ undergoes photodissociation of the axial PPh_3 at both the excited singlet and the triplet state. The quantum yield measurements in the temperature range 300−200 K indicate that the triplet formation and the dissociation of the axial PPh_3 are the competitive processes at the excited singlet state. At an "infinite" temperature, the dissociation yields estimated by eqs 19 and 20 are $\Phi(\infty)_S = 0.96$ and $\Phi(\infty)_T = 5 \times 10^{-3}$, respectively. Thus, the major processes at elevated temperatures are supposed to be the dissociation of the axial PPh_3 at $^1[(I^-)(PPh_3)Rh^{III}TPP]^*$.

Rhodium(III) porphyrins studied here hardly exhibit fluorescence. The sum of the quantum yields of the triplet formation, Φ_{ST}, and the dissociation of the axial PPh_3, Φ, is smaller than unity at 300 K, suggesting that the electronic energy of the excited singlet state is partly dissipated into the thermal energy. A previous study has shown that the triplet yields of Zn, Mg, Al, and Ga porphyrins are larger than 0.75 and the sum of the yields, the triplet formation plus fluorescence, are close to unity.[36] These results lead to the assumption that, in general, the rate constant, k_{nr}, for internal conversion of metalloporphyrins is principally smaller than that, k_{ST}, for the intersystem crossing process. In the case of rhodium porphyrins, the rate constant, k_{ST}, is expected to become large owing to the heavy atom effects and thus, $k_{ST} \gg k_{nr}$. From these considerations, the electronic energy dissipation process of $^1[(X^-)(PPh_3)Rh^{III}OEP]^*$ and $^1[(X^-)(PPh_3)Rh^{III}TPP]^*$ is not solely ascribed to the internal conversion process. The possible energy dissipation process is suggested to be, at least in part, due to the formation of the short-lived species having insufficiently dissociated bonds between PPh_3 and the Rh(III) atom and/or X and the Rh(III) atom at the excited singlet state. It is likely that the full dissociation of the axial PPh_3 takes place from the short-lived species, which has the weakened bond between PPh_3 and the Rh(III) atom.

The rhodium porphyrins, $(I^-)(PPh_3)Rh^{III}TPP$, undergo the photodissociation of the axial PPh_3 at both $^1[(I^-)(PPh_3)Rh^{III}TPP]^*$ and $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ similarly to the case of the isonitrile complexes, $(I^-)(R-NC)Rh^{III}TPP$. Thus, the dissociation of the axial PPh_3 at $^3[(I^-)(PPh_3)Rh^{III}TPP]^*$ is suggested to occur via the thermally accessible $^3(d\pi,d^*)$ state.

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