J. Phys. Chem. A **1999,** *103,* 3672−3677

Laser Photolysis Studies on Photodissociation of Axial Ligands from Isocyanide Complexes of Cobalt(III) and Rhodium(III) Porphyrins in Toluene Solutions. A Comparison with the Photochemistry of Carbonylrhodium(III) Porphyrin

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Received: October 30, 1998; In Final Form: March 9, 1999

Chlorocobalt(III) and iodorhodium(III) tetraphenylporphyrins, (Cl)Co^{III}TPP and (I)Rh^{III}TPP, react with 2,6-dimethylphenyl isocyanide (R−NC) in toluene solutions to give the isocyanide complexes, (Cl)(R−NC)-Co^{III}TPP and (I)(R−NC)Rh^{III}TPP, respectively. The 355-nm laser photolysis studies have shown that these complexes photodissociate the axial ligand, R−NC. The quantum yield, ϕ, for the photodissociation of R−NC from (Cl)(R−NC)Co^{III}TPP is determined as 0.091 in both degassed and oxygen-saturated toluene. On the other hand, (I)(R−NC)Rh^{III}TPP gives $\phi = 0.19$ in degassed toluene and $\phi = 0.07$ in oxygen-saturated toluene. The dissociation of R−NC from (I)(R−NC)Rh^{III}TPP was confirmed to occur from both the excited singlet and triplet states by transient spectroscopic measurements. The small quantum yield obtained with the oxygen-saturated solution is explained by the quenching of the triplet state, $^3(\pi,\pi^*)$ of (I)(R−NC)Rh^{III}TPP. The triplet state decays with a rate constant 9.5×10^4 s^{-1} in degassed toluene and is effectively quenched by oxygen with a bimolecular rate constant 6.7×10^8 M^{-1} s^{-1}. In comparison with (I)(R−NC)Rh^{III}TPP, the lifetime of the $^3(\pi,\pi^*)$ state of (Cl)(R−NC)Co^{III}TPP is too short to be detected by the present laser photolysis system, probably because of the very fast radiationless process, $^3(\pi,\pi^*) \rightarrow {}^3(\pi,d_{z^2}) \rightarrow {}^3(d\pi,d_{z^2})$. The dissociation of R−NC from (Cl)(R−NC)Co^{III}TPP is assumed to occur from the $^3(d\pi,d_{z^2})$ state. The long lifetime of the $^3(\pi,\pi^*)$ state of (I)(R−NC)Rh^{III}TPP is interpreted on the assumption that the $^3(d\pi,d_{z^2})$ is located higher in energy than the $^3(\pi,\pi^*)$ state. The dissociation of R−NC from (I)(R−NC)Rh^{III}TPP at the triplet state is suggested to occur from the thermally populated $^3(d\pi,d_{z^2})$ state. The laser photolysis studies of carbonylrhodium(III) tetraphenylporphyrin are also described to elucidate the ligand dissociation mechanism of rhodium(III) porphyrins.

Introduction

Metalloporphyrins with the central metals, Fe,[1,2] Co,[3,4] Ni,[5,6] Cr,[7,8] Rh,[9,10] and Ru,[11−13] undergo the photoinduced ligand dissociation. The laser photolysis studies of these porphyrins have been extensively carried out to elucidate the nature of the excited-state responsible for the photoinduced ligand dissociation and the mechanisms of the ligand exchange reactions.

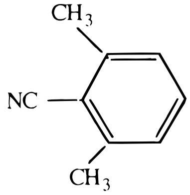
Cobalt(III) tetraphenylporphyrins, (X)(Py)Co^{III}TPP (X = anionic ligands such Cl$^-$, N$_3^-$, and SCN$^-$; Py = pyridine), are known to photodissociate the axial Py.[3] It is assumed that the dissociation of Py occurs from the $^3(d_\pi,d_{z^2})$ state of (X)(Py)-Co^{III}TPP[3] on the basis of the picosecond photolysis study.[14]

The central rhodium(III) atom in rhodium(III)porphyrins has an electronic configuration similar to that of the Co atom in (X)(Py)Co^{III}TPP. In contrast to (X)(Py)Co^{III}TPP, chloro(pyridinato)rhodium(III) tetraphenylporphyrin, (Cl)(Py)Rh^{III}TPP, has been found to photodissociate Py via the triplet state, $^3(\pi,\pi^*)$, of (Cl)(Py)Rh^{III}TPP originating from the porphyrin π system.[10] Therefore, further studies are necessary to elucidate the differences in the photodissociation mechanism of the axial ligands from cobalt(III) and rhodium(III) porphyrins.

The present paper reports the laser photolysis studies of isocyanide complexes of cobalt(III) and rhodium(III) tetraphenylporphyrins in toluene solutions. The photochemistry of carbonylrhodium(III) tetraphenylporphyrins was also investigated to elucidate the effects of the nature of the axial ligand on the photodissociation process of rhodium(III) porphyrins.

Experimental Section

Reagent grade toluene, benzene, and tetraphenylporphyrin were supplied from Wako Pure Chemical Industries Co. Ltd. 2,6-Dimethylphenyl isocyanide (R−NC) was synthesized and purified according to literature.[15] Chlorocobalt(III) tetraphenylporphyrin, (Cl)Co^{III}TPP, was obtained by air oxidation of cobalt(II) tetraphenylporphyrin in methanol containing 1% HCl.[16] The crude Co^{III}TPP(Cl) was purified by column chromatography on Sephadex LH 20. Rhodium(III) tetraphenylporphyrins, (Y)Rh^{III}TPP (Y = I and Cl), and rhodium(III)



(R-NC)

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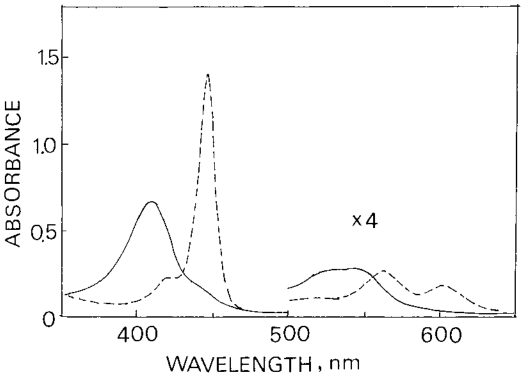

Figure 1. Absorption spectra of 5.9 × 10^{-6} M (Cl)Co^{III}TPP (solid line) in toluene and 5.9 × 10^{-6} M (Cl)(R−NC) Co^{III}TPP (broken line) in toluene containing 1.8 × 10^{-4} M R−NC.

octaethylporphyrins, (Y)Rh^{III}OEP, were synthesized and purified according to the literature.[17,18]

Absorption spectra were recorded on a Hitachi 330 spectrophotometer. Laser photolysis studies were carried out with the use of the Nd:YAG laser (HY 500 from JK Lasers Ltd.) equipped with second, third, and fourth harmonic generators. Samples were irradiated with the third harmonics (355 nm) from the Nd:YAG laser: the duration and the energy of the 355-nm laser pulse are 20 ns and 60 mJ/pulse, respectively. The detection system of the transient spectra was reported previously.[19]

Quartz cells used for the laser photolysis had an optical path length of 1.0 cm. Sample solutions in the quartz cells, if necessary, were degassed on a vacuum line to 10^{-5} Torr. Carbonylrhodium(III) porphyrins were prepared by exposure of CO gas to benzene solutions of (Y)Rh^{III}TPP and (Y)Rh^{III}OEP on the vacuum line. The gas pressures of oxygen and CO were measured by a mercury manometer attached to the vacuum line.

Results

Isocyanide Complex of Cobalt(III) Tetraphenylporphyrin. Figure 1 shows the absorption spectra of (Cl)Co^{III}TPP and the isocyanide complex, (Cl)(R−NC)Co^{III}TPP, in toluene. The spectrum of (Cl)Co^{III}TPP has absorption peaks at 410 and 545 nm. The absorption bands are broad in both the Soret and the Q-band region, showing characteristics of the five-coordinated species, (Cl)Co^{III}TPP.[20]

The addition of R−NC into the toluene solution of (Cl)Co^{III}TPP instantaneously causes the absorption spectral change with isosbestic points at 430 and 555 nm. The reaction is expressed as

$$(\mathrm{Cl})\mathrm{Co^{III}TPP} + \mathrm{R{-}NC} \xrightarrow{k_f(\mathrm{Co})} (\mathrm{Cl})(\mathrm{R{-}NC})\mathrm{Co^{III}TPP} \quad (1)$$

The absorption peaks of (Cl)Co^{III}TPP gradually decrease in intensity with an increase in the concentration of R−NC and new peaks appear at 445, 563, and 602 nm. Both the Soret and Q-bands markedly shift toward the red by forming the six-coordinated (Cl)(R−NC)Co^{III}TPP. The molar absorption coefficient of (Cl)(R−NC)Co^{III}TPP at 445 nm (2.59 × 10^5 M^{-1} cm^{-1}) in the Soret band region is much larger than that of (Cl)Co^{III}TPP at 410 nm (1.11 × 10^5 M^{-1} cm^{-1}). The spectroscopic titration of (Cl)Co^{III}TPP by R−NC in a toluene solution demonstrated the irreversible formation of (Cl)(R−NC)Co^{III}TPP according to eq 1.

Figure 2A shows the transient absorption spectrum observed for an aerated toluene solution of (Cl)(R−NC)Co^{III}TPP containing 1.77 × 10^{-4} M R−NC at 50 ns after the 355-nm laser pulse.

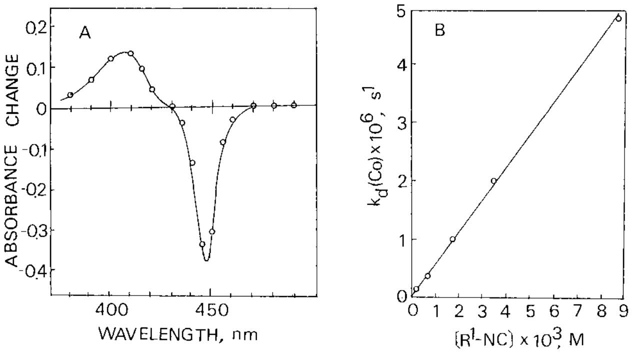

Figure 2. Transient absorption spectrum (A) observed for the toluene solution of (Cl)(R−NC) Co^{III}TPP containing 1.8 × 10^{-4} M R−NC at 50 ns after the 355-nm laser pulse and the plot of k_d(Co) (B) represented as a function of [R−NC].

The spectrum exhibits a positive peak at 410 nm and a negative one at 446 nm. Since the transient spectrum is in good agreement with the difference spectrum ((Cl)Co^{III}TPP minus (Cl)(R−NC)-Co^{III}TPP), the photoreaction is expressed by

$$(\mathrm{Cl})(\mathrm{R{-}NC})\mathrm{Co^{III}TPP} + h\nu \rightarrow (\mathrm{Cl})\mathrm{Co^{III}TPP} + \mathrm{R{-}NC} \quad (2)$$

(Cl)(R−NC)Co^{III}TPP in toluene photodissociates the axial ligand R−NC to give (Cl)Co^{III}TPP. The transient species, (Cl)Co^{III}TPP, decays according to pseudo-first-order kinetics over the whole wavelength region studied. The decay of the transient (Cl)Co^{III}TPP is due to a recombination reaction with R−NC, as shown by eq 1. The first-order decay rate constant, k_d(Co), of the transient spectrum is formulated as

$$k_d(\mathrm{Co}) = k_f(\mathrm{Co})[\mathrm{R{-}NC}] \quad (3)$$

Figure 2B displays the plot of k_d(Co) vs [R−NC], which gives a straight line with an intercept at the origin. From the slope of the line, k_f(Co) is determined as 5.6 × 10^8 M^{-1} s^{-1}.

The quantum yields, Φ_{dis}, for the photodissociation of R−NC from (Cl)(R−NC)Co^{III}TPP in toluene were determined with the use of the laser photolysis technique:[21]

$$\Phi_{dis} I_{abs}/N_A = \Delta D(\lambda)/\Delta\epsilon_{ab}(\lambda) \quad (4)$$

Here I_{abs} is the number of 355-nm photons absorbed by (Cl)(R−NC)Co^{III}TPP in toluene, N_A is Avogadro's number, $\Delta D(\lambda)$ is the initial absorbance change at λ of the sample solution after the 355-nm laser pulse, and $\Delta\epsilon_{ab}(\lambda)$ is the difference in the molar absorption coefficients at the monitoring wavelength λ between (Cl)(R−NC)Co^{III}TPP and (Cl)Co^{III}TPP. A benzene solution of benzophenone was used as a standard for determination of I_{abs}: the absorbance of the solution at 355 nm was adjusted to the same value as that of the sample solution. The 355-nm laser photolysis of benzophenone in benzene gives the triplet benzophenone, which has an absorption peak at 530 nm.[22] Then, the following equation is obtained.

$$\Phi_T I_{abs}/N_A = D(530\ \mathrm{nm})/\epsilon(530\ \mathrm{nm}) \quad (5)$$

where Φ_T is the triplet yield of benzophenone, D(530 nm) is the absorbance at 530 nm observed immediately after the laser pulse, and ϵ(530 nm) is the molar absorption coefficient of the triplet benzophenone at 530 nm. From eqs 4 and 5, we obtain

$$\Phi_{dis} = \Phi_T\{\Delta D(\lambda)/D(530\ \mathrm{nm})\}\{\epsilon(530\ \mathrm{nm})/\Delta\epsilon_{ab}(\lambda)\} \quad (6)$$

With the use of $\Phi_T = 1.0$, $\epsilon(530\ \mathrm{nm}) = 7.8 \times 10^3$ M^{-1} cm^{-1},[22]

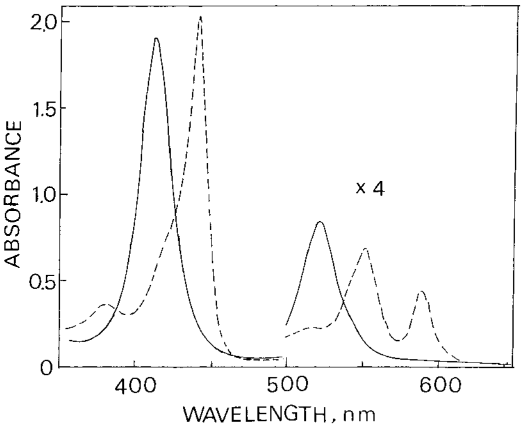

Figure 3. Absorption spectra of 1.4×10^{-5} M (I)Rh$^{\mathrm{III}}$TPP in toluene in the absence (solid line) and in the presence (broken line) of 1.8×10^{-4} M R−NC.

and eq 6, the quantum yield Φ_{dis} for the photodissociation of R−NC from (Cl)(R−NC)Co$^{\mathrm{III}}$TPP is obtained as 0.091 in both degassed and aerated toluene.

Isocyanide Complex of Rhodium Porphyrins. Figure 3 shows the absorption spectra of (I)Rh$^{\mathrm{III}}$TPP and (I)(R−NC)-Rh$^{\mathrm{III}}$TPP in toluene solutions. (I)Rh$^{\mathrm{III}}$TPP has absorption peaks at 412 nm ($\epsilon = 1.3 \times 10^5$ M^{-1} cm^{-1}) in the Soret band region and at 522 nm in the Q-band region. With an increase in the concentration of R−NC, the absorption peaks of (I)Rh$^{\mathrm{III}}$TPP gradually decrease in intensity and new peaks appear at 441, 552, and 588 nm owing to the formation of (I)(R−NC)Rh$^{\mathrm{III}}$-TPP.

$$(\mathrm{I})\mathrm{Rh^{III}TPP} + \mathrm{R{-}NC} \xrightarrow{k_f(\mathrm{Rh})} (\mathrm{I})(\mathrm{R{-}NC})\mathrm{Rh^{III}TPP} \tag{7}$$

From the spectroscopic titration of (I)Rh$^{\mathrm{III}}$TPP by R−NC in toluene, eq 7 is found to be an irreversible reaction. Both the Soret and Q-bands of (I)Rh$^{\mathrm{III}}$TPP markedly shift toward the red and the Q-band is split into two bands by forming the isocyanide complex. The molar absorption coefficient of (I)(R−NC)Rh$^{\mathrm{III}}$-TPP in toluene is obtained as 1.4×10^5 M^{-1} cm^{-1} at 441 nm.

Similarly, (Cl)Rh$^{\mathrm{III}}$TPP in toluene was found to react with R−NC. The absorption peak of (Cl)Rh$^{\mathrm{III}}$TPP located at 420 nm in the Soret band region shifts to the red by 10 nm due to the formation of (Cl)(R−NC)Rh$^{\mathrm{III}}$TPP.

The laser photolysis studies were carried out for the oxygen-saturated toluene solution of (I)(R−NC)Rh$^{\mathrm{III}}$TPP in the presence of 4.58×10^{-5} M R−NC. Two transients were observed: one disappeared within 0.5 μs after the pulse, and the other had a lifetime of ca. 20 μs. As will be shown later, the short-lived species is the triplet state, $^3(\pi,\pi^*)$ of (I)(R−NC)Rh$^{\mathrm{III}}$TPP. Here, we initially describe the kinetics of the long-lived species. As shown in Figure 4A, the transient absorption spectrum observed at 1.0 μs after a 355-nm laser pulse is in good accord with the difference spectrum ((I)Rh$^{\mathrm{III}}$TPP minus (I)(R−NC)Rh$^{\mathrm{III}}$TPP). Thus, the photoreaction of (I)(R−NC)Rh$^{\mathrm{III}}$TPP is shown by

$$(\mathrm{I})(\mathrm{R{-}NC})\mathrm{Rh^{III}TPP} + h\nu \rightarrow (\mathrm{I})\mathrm{Rh^{III}TPP} + \mathrm{R{-}NC} \tag{8}$$

The transient spectrum decays according to pseudo-first-order kinetics with a rate constant of 5.5×10^3 s^{-1}. Since no photoproducts were detected after the photolysis of (I)(R−NC)-Rh$^{\mathrm{III}}$TPP, the transient (I)Rh$^{\mathrm{III}}$TPP is considered to disappear by the recombination reaction with R−NC (eq 7). The decay rate constant, k_d(Rh), was measured as a function of [R−NC]. Figure 4B shows the plot of k_d(Rh) vs [R−NC]. The plot gives a straight line with an intercept at the origin.

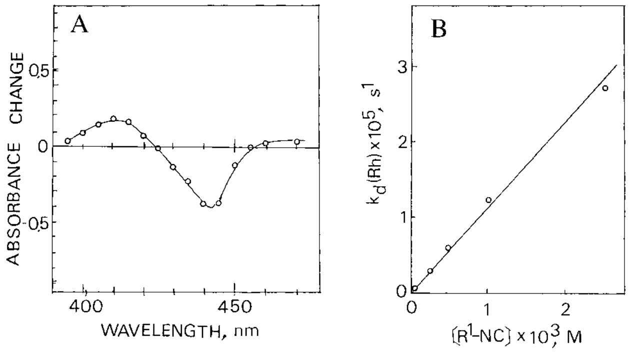

Figure 4. Transient absorption spectrum (A) observed for the oxygen-saturated toluene solution of (I)(R−NC)Rh$^{\mathrm{III}}$TPP in the presence of 4.58×10^{-5} M R−NC at 1 μs after the 355-nm laser pulse and the plot of k_d(Rh) (B) represented as a function of [R−NC].

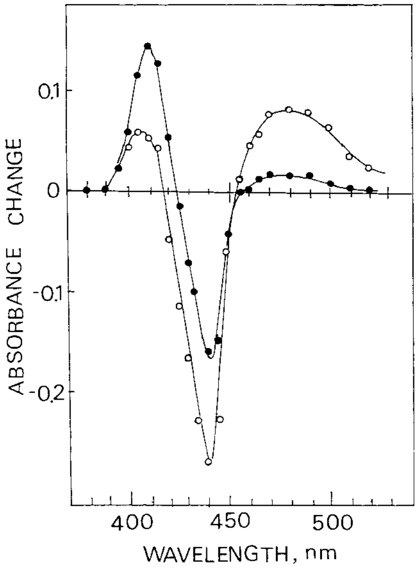

Figure 5. Transient absorption spectra observed at 50 ns (open circle) and at 40 μs (closed circle) after the 355-nm laser pulse for the degassed toluene solution of (I)(R−NC)Rh$^{\mathrm{III}}$TPP in the presence of 4.58×10^{-5} M R−NC.

$$k_d(\mathrm{Rh}) = k_f(\mathrm{Rh})[\mathrm{R{-}NC}] \tag{9}$$

From the slope of the line, the bimolecular rate constant k_f(Rh) is obtained as 1.1×10^8 M^{-1} s^{-1}.

As mentioned above, the laser photolysis of an oxygen-saturated toluene solution of (I)(R−NC)Rh$^{\mathrm{III}}$TPP gives rise to the formation of (I)Rh$^{\mathrm{III}}$TPP and another transient with a lifetime shorter than 0.5 μs. To investigate the short-lived transient, laser flash photolysis studies of (I)(R−NC)Rh$^{\mathrm{III}}$TPP in degassed toluene were carried out.

Figure 5 shows the transient absorption spectra observed for the degassed toluene solution of (I)(R−NC)Rh$^{\mathrm{III}}$TPP in the presence of 4.58×10^{-5} M R−NC. The transient spectrum detected at 50 ns after the laser pulse has positive peaks at 410 and 480 nm and a negative one at 440 nm. The positive peak intensity at 480 nm gradually decreases according to first-order kinetics with a rate constant $(9.5 \pm 0.5) \times 10^4$ s^{-1}. The increase in the peak intensity at 410 nm follows first-order kinetics and the rate constant is the same as that of the decay measured at 480 nm.

The transient spectrum measured at 40 μs is identical with that observed for the oxygen-saturated toluene solution at 1.0

μs after the pulse. Further, the decay rate constant of the 40-μs transient spectrum is the same as that measured in the oxygen-saturated solution, indicating that the photodissociation of R−NC from (I)(R−NC)Rh^{III}TPP occurs in the degassed solution.

The first-order decay component in the transient spectrum observed 50 ns after the laser pulse has a strong absorption around 480 nm. The 480-nm transient is ascribed to the excited triplet state of (I)(R−NC)Rh^{III}TPP originating from the porphyrin π system. It has been reported that the excited triplet states of metallotetraphenylporphyrin originating from the porphyrin π-system have a strong absorption band around 470−480 nm.[9] The rate constant, k_T, for the decay of the triplet (I)(R−NC)Rh^{III}TPP is obtained as $(9.5 \pm 0.5) \times 10^4$ s^{-1} from the first-order plot of the transient absorbance at 480 nm. (I)Rh^{III}-TPP and the triplet state produced by laser photolysis of (I)(R−NC)Rh^{III}TPP are, respectively, detected by monitoring the absorbances at 410 and 480 nm in the transient spectrum. Since the rise of the absorbance at 410 nm has a rate constant identical with the decay of the absorbance at 480 nm, we conclude that the excited triplet state of (I)(R−NC)Rh^{III}TPP photodissociates the axial R−NC in degassed toluene.

The porphyrin triplet state is readily quenched by oxygen. The decay rate constant, k_T, of the triplet (I)(R−NC)Rh^{III}TPP in toluene was measured as a function of the oxygen pressure in the range 0−395 Torr. The O_2 concentration in toluene was obtained from the partial pressure of oxygen and the Bunsen coefficient of O_2.[23] The plot of $k_T(O_2)$ vs the oxygen concentration gives a straight line, i.e.,

$$k_T(O_2) = (6.7 \pm 0.5) \times 10^8[O_2] + (9.5 \pm 0.5) \times 10^4 \ (s^{-1}) \qquad (10)$$

The triplet quenching by oxygen would be due to the energy transfer mechanism.[24]

The quantum yields, ϕ, for the photodissociation of R−NC from (I)(R−NC)Rh^{III}TPP were determined according to the method described above. The yield obtained is 0.19 ± 0.02 in degassed toluene and 0.07 ± 0.01 in O_2-saturated toluene at 1 atm. Clearly, the quenching of the triplet state by oxygen leads to a small quantum yield in O_2-saturated toluene.

The laser photolysis study of (Cl)(R−NC)Rh^{III}TPP in toluene was carried out for comparison with that of (I)(R−NC)Rh^{III}-TPP. The transient observed in the degassed toluene is solely the triplet state, $^3(\pi,\pi^*)$ of (Cl)(R−NC)Rh^{III}TPP. The triplet state with an absorption peak at 470 nm decays according to first-order kinetics with a rate constant 2.0×10^4 s^{-1}. Photodissociation of the axial R−NC from (Cl)(R−NC)Rh^{III}TPP could not be detected in both aerated and degassed toluene.

Carbonylrhodium(III) Porphyrins. Isonitrile and CO are the ligands with similar chemical property.[25] The difference between them would be that isonitrile is a better σ-donor and a poorer π acceptor than CO. We have studied the photochemistry of the carbonyl rhodium(III) porphyrin for comparison with that of the isocyanide complexes. (Y)Rh^{III}TPP (Y = I and Cl) reacts with CO to give the adduct (Y)(CO)Rh^{III}TPP. Our previous study has shown that (Cl)(CO)Rh^{III}TPP in benzene undergoes photodissociation of CO to give (Cl)Rh^{III}TPP.[9] In the present study, the laser photolyses of both (Y)Rh^{III}TPP and (Y)Rh^{III}-OEP in benzene were carried out.

Figure 6A shows the absorption spectra of (I)Rh^{III}OEP in benzene and (I)(CO)Rh^{III}OEP in CO saturated benzene at 1 atm. The absorption peak of (I)Rh^{III}OEP located at 393 nm ($\epsilon = 3.9 \times 10^4$ M^{-1} cm^{-1}) shifts to 425 nm owing to the formation of (I)(CO)Rh^{III}OEP. Figure 6B shows the transient absorption spectrum of (I)(CO)Rh^{III}OEP in benzene saturated with CO gas at 1.0 atm, observed 20 ns after laser pulsing. The transient spectrum is in good agreement with the difference spectrum ((I)Rh^{III}OEP minus (I)(CO)Rh^{III}OEP), indicating that CO is photodissociated.

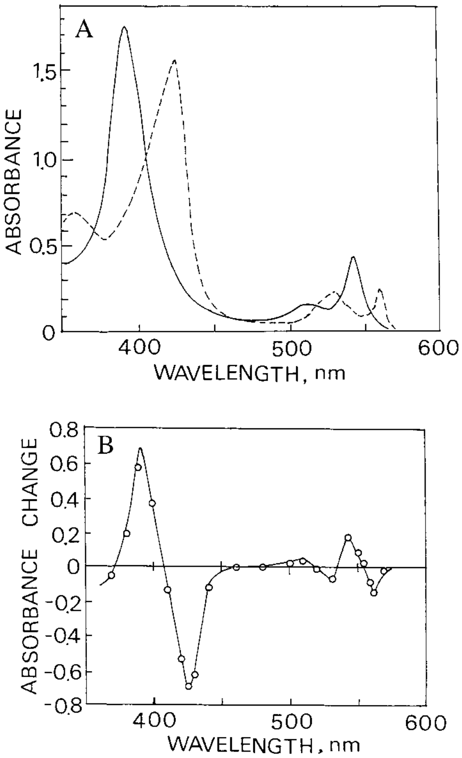

Figure 6. Absorption spectra (A) of (I)Rh^{III}OEP (solid line) and (I)(CO)Rh^{III}OEP (broken line) in toluene and transient absorption spectrum (B) observed at 50 ns after the 355-nm pulse for the benzene solution of (I)(CO)Rh^{III}OEP saturated with CO gas at 1 atm.

$$(I)(CO)Rh^{III}OEP + h\nu \rightarrow (I)Rh^{III}OEP + CO \qquad (11)$$

The quantum yields for the photodissociation of CO from (X)(CO)Rh^{III}TPP are determined as 0.93 ± 0.05 for X = I and 0.68 for X = Cl.

The excited triplet state of (X)(CO)Rh^{III}TPP is detected in the case of X = Cl: the lifetime of the triplet state is determined as 2.4×10^6 s^{-1}. It is found that the triplet state formation and the photodissociation of CO take place within 20 ns after the laser pulse. Since the decay of the triplet (Cl)(CO)Rh^{III}TPP does not accompany the formation of (Cl)Rh^{III}TPP, it is concluded that the CO dissociation does not occur from the excited triplet state. This conclusion is further supported by the fact that the triplet state of (Cl)(CO)Rh^{III}TPP is efficiently quenched by oxygen, but the yield of the CO dissociation is irrerspective of the presence or absence of oxygen. The photodissociation of CO from (X)(CO)Rh^{III}TPP is suggested to occur most probably from the excited singlet state, $^1S^*$.

The excited triplet states of (I)(CO)Rh^{III}TPP and (I)(CO)-Rh^{III}OEP were not detected because of a high quantum yield (ca. 1.0) for photodissociation of CO. In Table 1 are listed the quantum yield, $\phi_{(CO)}$, for the photodissociation of CO and the triplet yields, $\phi_{(T)}$, obtained for (X)(CO)Rh^{III}TPP and (X)(CO)-Rh^{III}OEP. These results mentioned above lead to the conclusions that (1) photodissociation of CO occurs from the excited singlet state, $^1S^*$, and (2) the excited triplet state is not responsible for the photodissociation of CO.

TABLE 1: Quantum Yields for Photodissociation of Axial Ligands, the Rate Constants for Ligand Association, and the Decay Rate Constants of the ($\pi\pi$*) Triplet States (Experimental Errors within ±10%

	Φ_{dis}[a]	$\Phi_{dis(T)}$[b]	k_f,[c] M^{-1} s^{-1}	$k_T(\pi\pi^*)$,[d] s^{-1}
(Cl)(R−NC)Co^{III}TPP	0.091	0.0	5.6×10^8	n.m.
(I)(R−NC)Rh^{III}TPP	0.19	0.12	1.1×10^8	9.5×10^4
(Cl)(R−NC)Rh^{III}TPP	0.0	0.0	n.m.	2.0×10^4
(I)(CO)Rh^{III}TPP[e]	0.93	0.0	1.33×10^8	n.m.
(Cl)(CO)Rh^{III}TPP[e]	0.68	0.0	3.6×10^5	2.4×10^6
(I)(CO)Rh^{III}OEP[e]	0.90	0.0	6.6×10^8	n.m.
(Cl)(CO)Rh^{III}OEP[e]	0.52	0.0	2.5×10^5	2.4×10^6
(Cl)(Py)Rh^{III}TPP[f]	0.85	0.85	1.4×10^4	2.7×10^6

[a] The quantum yields for the photodissociation of axial ligands, R−NC, CO, and Py. [b] The quantum yields for the photodissociation of the axial ligands from the triplet (π,π*) states. [c] The rate constants for the association of the axial ligands. [d] The rate constant for the decay of the triplet state. [e] Benzene is used as a solvent. [f] Ethanol is used as a solvent.[10] n.m. = not measured.

Discussion

Recently, we found that chloroaquachromium(III) tetraphenylporphyrin, (Cl)(H_2O)Cr^{III}TPP, reversibly reacts with R−NC to yield the adducts (Cl)(R−NC)Cr^{III}TPP.[25] The laser flash photolysis studies revealed that (Cl)(R−NC)Cr^{III}TPP in toluene photodissociates the axial R−NC. The rate constant for the reaction between the five-coordinate (Cl)Cr^{III}TPP and R−NC is determined as 4.4×10^8 M^{-1} s^{-1}.[26]

An earlier laser photolysis study of the bis(isocyanide) complex of protoheme dimethyl ester in toluene have shown that the axial isonitrile is photodissociated to give the five-coordinate isocyanide complex, which returns to the bis(isocyanide) complex by recombination with the isonitrile. The bimolecular rate constant for the recombination reaction is 2.5×10^8 M^{-1} s^{-1}.[27,28] The present work has shown that the rate constants for association of R−NC toward (Cl)Co^{III}TPP and (I)Rh^{III}TPP are respectively 5.6×10^8 and 1.1×10^8 M^{-1} s^{-1}. Thus, the rate constants for the reaction between isonitrile and metalloporphyrins are on the order of 10^8 M^{-1} s^{-1}, irrespective of the nature of the central metal studied.

Photodissociation of R−NC is confirmed to occur from both the $^1S^*$ and $^3T^*$ states of (I)(R−NC)Rh^{III}TPP. The photochemical reactions of (I)(R−NC)Rh^{III}TPP are represented by

$$\text{(I)(R-NC)Rh}^{III}\text{TPP} + h\nu \rightarrow {}^1S^* \tag{12}$$

$$^1S^* \rightarrow {}^3T^* \tag{13}$$

$$^1S^* \rightarrow \text{(I)(R-NC)Rh}^{III}\text{TPP} \tag{14}$$

$$^1S^* \rightarrow \text{(I)Rh}^{III}\text{TPP} + \text{R-NC} \tag{15}$$

$$^3T^* \rightarrow \text{(I)(R-NC)Rh}^{III}\text{TPP} \tag{16}$$

$$^3T^* \rightarrow \text{(I)Rh}^{III}\text{TPP} + \text{R-NC} \tag{17}$$

The quantum yield measured in the degassed solution is 0.19. Thus we obtain

$$\phi_d(^1S^*) + \phi_d(^3T^*) = 0.19 \tag{18}$$

where $\phi_d(^1S^*)$ and $\phi_d(^3T^*)$ are the quantum yields for the photodissociation of R−NC at the excited singlet and the triplet state, respectively.

In oxygen-saturated toluene at 1 atm, the quantum yield was determined to be 0.07. On the assumption that only the triplet state is quenched by oxygen, the following equation is obtained

$$\phi_d(^1S^*) + \phi_d(^3T^*)k_T/k_T(O_2, 1\text{ atm}) = 0.07 \tag{19}$$

where k_T and $k_T(O_2$, 1 atm) are respectively the decay rate constants of $^3T^*$ measured in the absence of oxygen and in the oxygen-saturated system at 1 atm. From eq 11, we obtain $k_T = 9.5 \times 10^4$ s^{-1} and $k_T(O_2, 1\text{ atm}) = 5.7 \times 10^6$ s^{-1}. With the use of k_T, $k_T(O_2$, 1 atm), and eqs 18 and 19, the quantum yields are determined as $\phi_d(^1S^*) = 0.06_8$ and $\phi_d(^3T^*) = 0.12_2$, respectively. Thus the photodissociation yield of R−N=C from the excited triplet state of (I)(R−NC)Rh^{III}TPP is ca. 2 times larger than that from the excited singlet state.

Photodissociation of the axial pyridine from chloro(pyridinato)rhodium(III) tetraphenylporphyrin, (Cl)(Py)Rh^{III}TPP, in ethanol has been reported: (Cl)(Py)Rh^{III}TPP dissociates the axial pyridine in the excited triplet state with the quantum yield 0.85.[10] In contrast to the case of (I)(R−NC)Rh^{III}TPP, the photodissociation of Py from the excited singlet state could not be detected.

A number of studies on the photodissociation of the axial ligands from various metalloporphyrins have been carried out.[1−13] Picosecond photolysis studies of Co^{III} porphyrins suggest that the lifetime of the $^3(d\pi,d_{z^2})^*$ states is very short (ca. 20−40 ps).[14] The ligand ejection is considered to occur at the $^3(d\pi,d_{z^2})^*$ state within the lifetime. The present study shows that (Cl)(R−NC)Co^{III}TPP in toluene photodissociates R−NC within the duration of a laser pulse (20 ns). Presumably, the dissociation of R−NC takes place at the $^3(d\pi,d_{z^2})$ state of (Cl)(R−NC)Co^{III}TPP, as in the case of the pyridine dissociation from (X)(Py)Co^{III}TPP.[10]

A marked difference in the photophysical properties between Co^{III}TPP and Rh^{III}TPP is the lifetime of the triplet state originating from the porphyrin π ligand. The very short lifetime of the (π,π*) triplet of Co^{III}TPP is interpreted in terms of the fast excitation energy dissipation sequence, $^3(\pi,\pi^*) \rightarrow {}^3(\pi,d_{z^2}) \rightarrow {}^3(d\pi,d_{z^2})$.[14]

The $^3(d\pi,d_{z^2})$ efficiently undergoes radiationless transition to the ground state of Co^{III}TPP. The triplet lifetime of Rh^{III}TPP, however, is a few tens of microseconds. This indicates that the $^3(\pi,\pi^*)$ of Rh^{III}TPP is the lowest excited state; i.e., the $^3(\pi,d_{z^2})$ and $^3(d\pi,d_{z^2})$ states of Rh^{III}TPP are higher in energy than the $^3(\pi,\pi^*)$ state. On the assumption that the $^3(d\pi,d_{z^2})$ state is a thermally accessible triplet state lying higher in energy than the $^3(\pi,\pi^*)$ state, we consider that the ligand dissociation from the excited triplet states of either (Cl)(Py)Rh^{III}TPP and (I)(R−NC)Rh^{III}TPP occurs via the thermally populated $^3(d\pi,d_{z^2})$ state.

The lifetime of the $^3(\pi,\pi^*)$ state Rh^{III}TPP is expected to depend on the energy difference, ΔE, between the $^3(d\pi,d_{z^2})$ and the $^3(\pi,\pi^*)$ state. When ΔE is small, the $^3(\pi,\pi^*)$ state has a decay channel to the ground state via the thermally populated $^3(d\pi,d_{z^2})$ state. As shown in Table 1, the triplet lifetime of (Cl)(R−NC)Rh^{III}TPP is ca. 5 times longer than that of (I)(R−NC)Rh^{III}TPP. This is explained by assuming that ΔE of (Cl)(R−NC)Rh^{III}TPP is larger than that of (I)(R−NC)Rh^{III}TPP. In fact, photodissociation of the axial R−NC is not observed for (Cl)(R−NC)Rh^{III}TPP at the excited triplet state. This result supports the view that the $^3(d\pi,d_{z^2})$ state of (Cl)(R−NC)Rh^{III}TPP is unlikely to be thermally accessible owing to the larger ΔE of (Cl)(R−NC)Rh^{III}TPP than that of (I)(R−NC)Rh^{III}TPP.

As mentioned above, photodissociation of CO from (X)(CO)Rh^{III}TPP occurs solely at the $^1S^*$ state. Since the ligand CO is a π acceptor toward the central metal of porphyrins, it is postulated that $^1S^*$ concerns with the photodissociation of the acceptor type ligands. In contrast, photodissociation of pyridine occurs only from the $^3(d\pi,d_{z^2})$ state via the $^3(\pi,\pi^*)$ state of (Cl)(Py)Rh^{III}TPP. Taking into account the fact that pyridine is a σ donor ligand, we consider that the $^3(d\pi,d_{z^2})$ state is responsible for dissociation of the σ donor type ligand at the axial position of rhodium porphyrins. Isonitriles are the ligands having both characters, σ donor and π acceptor, and thus, the dissociation of R−NC would occur at the two states, the $^1S^*$ and $^3(d\pi,d_{z^2})$ states of (I)(R−NC)Rh^{III}TPP.

We could not detect the photodissociation of R−NC even from the excited singlet state of (Cl)(R−NC)Rh^{III}TPP. It, therefore, is necessary to study the pico- or femtosecond photolysis of rhodium porphyrins for full elucidation of the nature of their higher excited states.

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