Photochemical Reactions of Nitrocobalt(III) Tetraphenylporphyrin and Its Pyridine Complex Studied by Laser Flash Photolysis

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The photochemical reactions of nitrocobalt(III) tetraphenylporphyrin, $(NO_2)Co^{III}TPP$, and its six-coordinated complex with 4-(dimethylamino)pyridine, $(NO_2)Co^{III}TPP(DMAPy)$, in benzene were studied by using a laser flash technique. The structures solved by X-ray analysis show that both compounds are the nitro form (O_2N-Co^{III}) instead of the nitrito form ($ONO-Co^{III}$). The transient absorption spectrum observed 50 ns after laser excitation of $(NO_2)Co^{III}TPP(DMAPy)$ in benzene revealed that the pyridinate complex undergoes photodissociation of the $N-Co^{III}$ bond to yield NO_2 and $Co^{II}TPP(DMAPy)$. These products recombine and regenerate the original complex with a second-order rate constant of 2.5×10^9 dm^3 mol^{-1} s^{-1}. In the case of $(NO_2)Co^{III}TPP$, the transient absorption spectrum detected 50 ns after the laser flash changes to another spectrum which has a longer lifetime and decays according to first-order kinetics with the rate constant of 3.0×10^2 s^{-1}. The former spectrum corresponds to formation of $Co^{II}TPP$ from the photodissociation of the $N-Co^{III}$ bond. The change from the former to latter spectrum is found to follow second-order kinetics with the rate constant of 3.6×10^9 dm^3 mol^{-1} s^{-1}. On the basis of the results obtained, it was concluded that the metastable transient giving the latter spectrum is the nitrito species, $(ONO)Co^{III}TPP$, which undergoes a nitrito → nitro linkage isomerization.

Introduction

The study of the interactions between metalloporphyrins and nitrite ion, as it is the case of the diatomic molecules O_2, CO, and NO,[1] has physiological interest because nitrite-bound metalloporphyrins can be used as models for assimilatory and dissimilatory nitrite reductases. It has been known that the former enzymes contain a heme prosthetic group, siroheme, and catalyze the six-electron reduction of nitrite ion to NH_3.[2] One type of the latter enzymes contains two heme cd_1 units and reduces nitrite ion to NO,[3] a diatomic molecule with important functions in a variety of physiological processes.[4]

Laser flash photolysis has extensively provided useful information regarding the nature of the binding between hemoproteins or synthetic hemes and several diatomic ligands.[5] These studies are based on a reaction where the photodissociation of the iron−ligand bond yields the diatomic ligands and hemes, which later recombine to regenerate the original adducts. Little information is available, however, concerning reactions of the nitrite-bound iron porphyrins, although electrocatalytic reduction of nitrite ion by synthetic iron porphyrins has been studied.[6] The reason seems to be attributable to instability of nitrite-coordinated iron porphyrins with the exception of the picket-fence type porphyrin species.[7,8] Indeed, reaction of nitrite ion with iron porphyrin does not yield the nitrite-coordinated complex but rather produces the nitrosyl complex.[7]

In other related studies, the electrochemical reduction of nitrite-bound polypyridyl complexes of ruthenium and osmium has been proposed as a model reaction for the nitrite reductases.[9] Moreover, it has been reported that photoexcitation of nitritomanganese or nitritochromium porphyrins in solutions undergoes β-bond cleavage to give NO and respective metal-oxo species, O═Mn porphyrin[10] or O═Cr porphyrin.[11] By contrast, photodissociation of NO_2 occurred by α-bond cleavage from nitritomanganese porphyrin in a matrix[12] and oxo(nitrito)molybdenum porphyrin in solution.[13] Studies about the photochemical reaction of nitrite-bound cobalt porphyrin have not been reported previously, although the nitro → nitrito photoisomerization has been observed in several Co(III) complexes: nitropentaamminecobalt(III) ion,[14,15] $[(NH_3)_5Co(NO_2)]^{2+}$, and *trans*-bis(ethylenediamine)(isothiocyanato)nitrocobalt(III) ion,[16] *trans*-$[Co(en)_2(NCS)(NO_2)]^+$.

In the present work, laser photolysis of nitrocobalt(III) tetraphenylporphyrin, $(NO_2)Co^{III}TPP$, and its six-coordinated complex with 4-(dimethylamino)pyridine, $(NO_2)Co^{III}TPP(DMAPy)$, in benzene solutions has been studied. We have observed that photoexcitation of $(NO_2)Co^{III}TPP$ causes nitro → nitrito linkage isomerization in the recombination process of NO_2 and $Co^{II}TPP$ produced by photodissociation of the $Co-NO_2$ bond, in the case of $(NO_2)Co^{III}TPP(DMAPy)$; however, NO_2 and $Co^{II}TPP$ (DMAPy) produced by the photodissociation simply recombine to yield the original adduct.

Experimental Section

Materials. Reagent-grade benzene, methanol, dichloromethane, and 4-(dimethylamino)pyridine (DMAPy) supplied by Wako Pure Chem. Ind. Ltd. were used without further purification. Cobalt(II) tetraphenylporphyrin, $Co^{II}TPP$, was synthesized and purified according to the literature.[17] Chlorocobalt(III) tetraphenylporphyrin, $ClCo^{III}TPP$, was synthesized from $Co^{II}TPP$ and HCl according to the literature.[18] Nitrocobalt(III) tetraphenylporphyrin, $(NO_2)Co^{III}TPP$, was prepared by replacing Cl anion in $ClCo^{III}TPP$ with NO_2 anion. A methanol solution of $ClCo^{III}TPP$ and $NaNO_2$ was stirred for 3 h at room temperature. The reaction solution was concentrated by evaporation under reduced pressure, and the residual solution was added with a large amount of water to precipitate the crude product. After collection by filtration, the crude product was dissolved in dichloromethane. A single crystal of $(NO_2)Co^{III}TPP$ was obtained by slow evaporation of the solvent. Anal. Calcd

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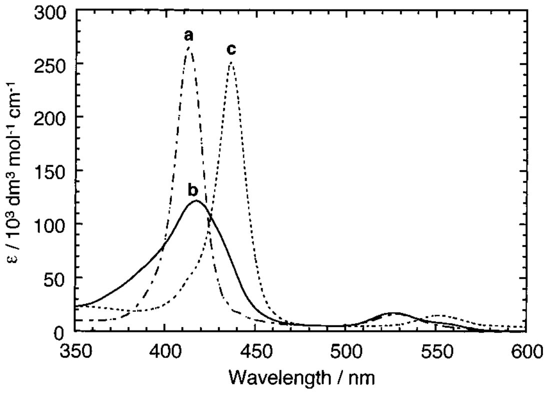

Figure 1. Optical absorption spectra of $Co^{II}TPP$ (dashed line; a), $(NO_2)Co^{III}TPP$ (solid line; b), and $(NO_2)Co^{III}TPPP(DMAPy)$ (dotted line; c) in benzene.

for $(NO_2)Co^{III}TPP(H_2O)(0.7CH_2Cl_2)$: C, 67.77; H, 3.82; N, 8.87; Cl, 6.35. Found: C, 67.52; H, 3.98; N, 8.81; Cl, 6.24.

An axially ligated complex of $(NO_2)Co^{III}TPP$ with 4-(dimethylamino)pyridine, $(NO_2)Co^{III}TPP(DMAPy)$, was synthesized from the solution of $(NO_2)Co^{III}TPP$ and 4-(dimethylamino)-pyridine (DMAPy) dissolved in dichloromethane and was recrystallized also by slow evaporation of the solvent.

Apparatus. Optical absorption spectra were recorded on a Hitachi 330 spectrophotometer. Laser photolysis studies were carried out with the use of the second (532 nm) harmonic of a Nd:YAG from J. K. Laser Ltd: the pulse duration and energy were 20 ns and 100 mJ/pulse, respectively. The detection system of transient spectra has been reported elsewhere.[19] The optical path length of a reaction cell was 10 mm.

Results

It has been known that both the nitro form (N-bound) and nitrito form (O-bound) complexes can be prepared for the nitrite-bound pentaammine or bis(ethylenediamine) Co(III) complex, although the latter form is not stable at room temperature.[14−16] Since the structure of nitrite-bound $Co^{III}TPP$(lutidine) is shown to be the nitro complex[20] and nitrite-bound Mn(III)[10] and Cr(III) porphyrin[11] are nitrito complexes, it was necessary to confirm whether the formation of nitro complex alone is a general property for Co(III) porphyrins. The results of a crystallographical analysis for $(NO_2)Co^{III}TPP$ and $(NO_2)Co^{III}TPP$-(DMAPy) have revealed that the nitrite ligand in these compounds binds to the cobalt atom at the N position (nitro form) instead of the O position (nitrito form).[21]

Absorption Spectra of $Co^{II}TPP$, $(NO_2)Co^{III}TPP$, and $(NO_2)Co^{III}TPP$ (DMAPy). Figure 1 shows absorption spectra of $Co^{II}TPP$, $(NO_2)Co^{III}TPP$, and $(NO_2)Co^{III}TPP(DMAPy)$ in benzene solutions. The Soret band in the spectrum of $Co^{II}TPP$ is broadened, and its peak intensity is decreased by formation of the five-coordinated complex, $(NO_2)Co^{III}TPP$. Both Soret and Q-bands in the $(NO_2)Co^{III}TPP$ spectrum are red-shifted by ligation of 4-(dimethylamino)pyridine (DMAPy). The absorption spectrum of $(NO_2)Co^{III}TPP(DMAPy)$ was measured in solutions containing $(NO_2)Co^{III}TPP$ and excess DMAPy. Figure 2A shows the absorption spectral changes in the Q-band region observed for a benzene solution of $(NO_2)Co^{III}TPP$ at various concentrations of DMAPy. The isosbestic point indicates that $(NO_2)Co^{III}TPP$ in solutions containing DMAPy is in equilibrium with $(NO_2)Co^{III}TPP(DMAPy)$, expressed as reaction 1.

$$(NO_2)Co^{III}TPP + DMAPy \rightleftarrows (NO_2)Co^{III}TPP(DMAPy) \quad (1)$$

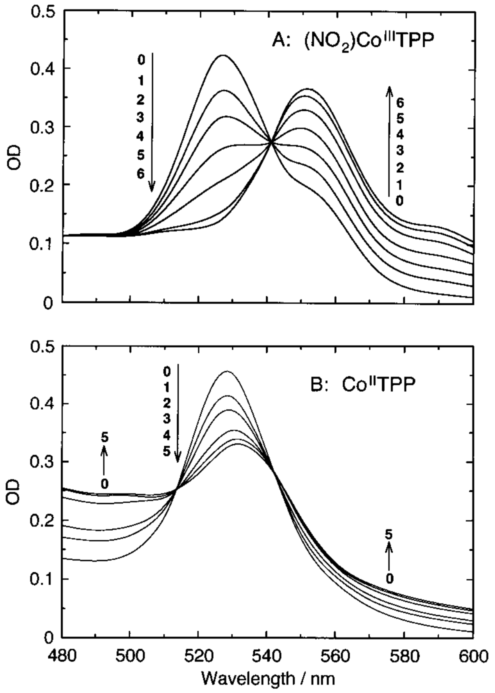

Figure 2. Absorption spectral changes in the Q-band region observed for benzene solutions of $(NO_2)Co^{III}TPP$ and $Co^{II}TPP$ in the presence of DMAPy. (**A**) For a solution containing 2.52×10^{-5} mol dm^{-3} $(NO_2)Co^{III}TPP$ and various concentrations of DMAPy: 0, $[DMAPy]_0$ = 0 mol dm^{-3}; 1, $[DMAPy]_0 = 7.5 \times 10^{-6}$ mol dm^{-3}; 2, $[DMAPy]_0 = 1.04 \times 10^{-5}$mol dm^{-3}; 3, $[DMAPy]_0 = 1.5 \times 10^{-5}$ mol dm^{-3}; 4, $[DMAPy]_0 = 2.0 \times 10^{-5}$ mol dm^{-3}; 5, $[DMAPy]_0 = 2.5 \times 10^{-5}$ mol dm^{-3}; 6, $[DMAPy]_0 = 2.5 \times 10^{-4}$ mol dm^{-3}. (**B**) For a solution containing 3.23×10^{-5} mol dm^{-3} $Co^{II}TPP$ and various concentrations of DMAPy: 0, $[DMAPy]_0 = 0$ mol dm^{-3}; 1, $[DMAPy]_0 = 1.0 \times 10^{-4}$ mol dm^{-3}; 2, $[DMAPy]_0 = 2.0 \times 10^{-4}$ mol dm^{-3}; 3, $[DMAPy]_0 = 1.2 \times 10^{-3}$ mol dm^{-3}; 4, $[DMAPy]_0 = 5.2 \times 10^{-3}$ mol dm^{-3}; 5, $[DMAPy]_0 = 1.0 \times 10^{-2}$ mol dm^{-3}, where $[DMAPy]_0$ refers to the initial concentration of DMAPy.

We followed the method given by Miller and Dorough[22] for the determination of the equilibrium constant (K_1) of reaction 1. The plot of $(D_0 - D)^{-1}$ against $[DMAPy]^{-1}$ gives a straight line, where D_0 and D are the absorbance of $(NO_2)Co^{III}TPP$ at 550 nm in the absence and the presence of various concentrations of DMAPy, respectively. From values of the slope and the intercept of the line, K_1 was determined as 7.1×10^6 dm^3 mol^{-1}.

The absorption spectrum of $Co^{II}TPP$ in benzene changes also with isosbestic points at various concentrations of DMAPy, although the spectral changes in the Soret-band region are very small. The spectral changes in the Q-band region are shown in Figure 2B. We have concluded that $Co^{II}TPP$ in the benzene solution containing DMAPy, is also in equilibrium with Co^{II}=TPP(DMAPy), expressed as

$$Co^{II}TPP + DMAPy \rightleftarrows Co^{II}TPP(DMAPy) \quad (2)$$

The equilibrium constant (K_2) for reaction 2 was determined from the spectral changes by using the same method as in the case of obtaining K_1. The plot of $(D_0 - D)^{-1}$ at 530 against $[DMAPy]^{-1}$ gives a straight line. From the slope and the intercept of the line, K_2 was determined to be 5.6×10^3 dm^3 mol^{-1}. This value of K_2 is more than 10^3 times smaller than that of K_1.

Laser Photolysis of $(NO_2)Co^{III}TPP(DMAPy)$. Figure 3 shows the transient absorption spectrum observed 50 ns after a benzene solution of $(NO_2)Co^{III}TPP(DMAPy)$ was irradiated with laser pulses at 532 nm. The transient spectrum is in good agreement with the difference spectrum obtained by subtracting the spectrum of $(NO_2)Co^{III}TPP(DMAPy)$ from that of $Co^{II}TPP(DMAPy)$. This fact indicates that $(NO_2)Co^{III}TPP(DMAPy)$ photodissociates NO_2 to yield $Co^{II}TPP(DMAPy)$ as a transient photoproduct. The transient spectrum shown in Figure 3 decays uniformly over the whole wavelength range studied without giving any permanent photoproduct. The decay was found to obey second-order kinetics. This indicates that all of the transient photoproduct, $Co^{II}TPP(DMAPy)$, recombines with NO_2 to regenerate $(NO_2)Co^{III}TPP(DMAPy)$. These results obtained by the laser photolysis studies lead to the conclusion that the photochemical reactions of $(NO_2)Co^{III}TPP(DMAPy)$ in benzene are represented as

$$(NO_2)Co^{III}TPP(DMAPy) + h\nu \rightarrow NO_2 + Co^{II}TPP(DMAPy) \quad (3)$$

$$NO_2 + Co^{II}TPP(DMAPy) \rightarrow (NO_2)Co^{III}TPP(DMAPy) \quad (4)$$

From the slope of the straight line given by plotting $[Co^{II}TPP(DMAPy)]^{-1}$ vs time, the second-order rate constant for reaction 4 was determined to be 2.5×10^9 dm^3 mol^{-1} s^{-1}, where $[Co^{II}TPP(DMAPy)]$ is the concentration of $Co^{II}TPP(DMAPy)$ calculated from the absorption change due to reaction 4 and $\Delta\epsilon$, which is obtained by subtracting the molar absorption coefficient of $(NO_2)Co^{III}TPP(DMAPy)$ from that of $Co^{II}TPP(DMAPy)$.

The quantum yield, $\Phi_{react.3}$, for the photodissociation of NO_2 from $(NO_2)Co^{III}TPP(DMAPy)$ was measured by using a laser photolysis technique. The quantum yield is expressed as

$$\Phi_{react.3} = \Delta D_\lambda^{50ns}/(\epsilon_\lambda P - \epsilon_\lambda R)I_{abs} \quad (5)$$

where ΔD_λ^{50ns} is the absorbance change at a wavelength λ observed 50 ns after a laser pulsing (λ was fixed here mainly at 412.5 nm, where the absorption peak of $Co^{II}TPP(DMAPy)$ exists); ϵ_λ^P and ϵ_λ^R are the molar absorption coefficients at the wavelength λ of $Co^{II}TPP(DMAPy)$ and $(NO_2)Co^{III}TPP(DMAPy)$ in benzene, respectively; I_{abs} is the excitation light (532 nm) intensity absorbed by $(NO_2)Co^{III}TPP(DMAPy)$ in the solution. For measurement of I_{abs} a benzene solution of ZnTPP having the same absorbance at 532 nm as that for the solution under study (0.2) was prepared as a standard solution to monitor the triplet−triplet absorption of ZnTPP at 470 nm after laser pulsing. I_{abs} is represented as

$$I_{abs} = \Delta D_{470}{}^T/\epsilon_{470}{}^T\Phi_T \quad (6)$$

where $\Delta D_{470}{}^T$, $\epsilon_{470}{}^T$, and Φ_T are the absorbance of the triplet ZnTPP at 470 nm observed for the standard solution immediately after laser pulsing, the molar absorption coefficient of the triplet at 470 nm in benzene, and the quantum yield of the triplet for the standard solution. By using the reported values of $\epsilon_{470}{}^T = 7.3 \times 10^4$ dm^3 mol^{-1} cm^{-1},[23] $\Phi_T = 0.83$,[23] and $(\epsilon_{412.5}{}^P - \epsilon_{412.5}{}^R) = 1.99 \times 10^5$ dm^3 mol^{-1} cm^{-1}, the value of $\Phi_{react.3}$ was determined to be 0.071.

Laser Photolysis of $(NO_2)Co^{III}$ TPP. Figure 4 shows the transient absorption spectra observed for a benzene solution of $(NO_2)Co^{III}TPP$ in the absence of DMAPy at 50 ns and 800 μs after 532-nm laser pulsing. There are apparent differences in the wavelengths giving zero absorbance and peaks between those two transient spectra; that is, spectrum A (observed at 50 ns) exhibits zero absorbance at 398 and 423 nm and a peak at 412.5 nm, while spectrum B (observed at 800 μs) subsequently appears with zero absorbance at 380 and 417 nm and a peak at 406 nm.

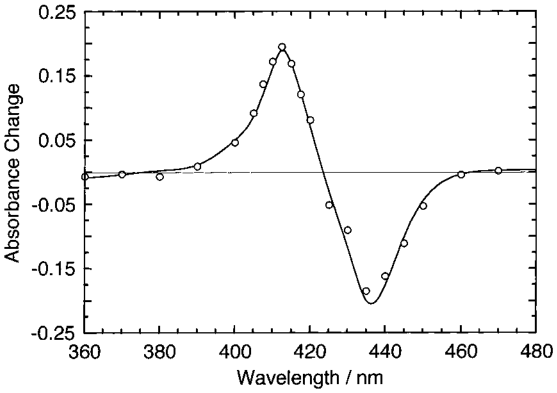

Figure 3. Transient absorption spectrum observed for a benzene solution of $(NO_2)Co^{III}TPP$ (7.84×10^{-6} mol dm^{-3}) in the presence of DMAPy (2×10^{-3} mol dm^{-3}) at 50 ns after 532-nm laser pulsing. It was confirmed in advance by measuring the absorption spectrum for the above solution that all the $(NO_2)Co^{III}TPP$ (>99%) was converted to $(NO_2)Co^{III}TPP(DMAPy)$ in the solution.

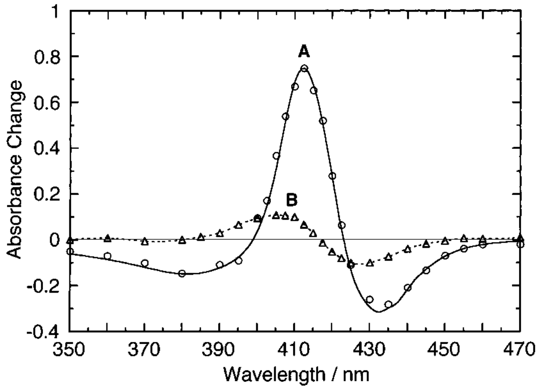

Figure 4. Transient absorption spectrum observed for a benzene solution of $(NO_2)Co^{III}TPP$ (5.09×10^{-6} mol dm^{-3}): spectrum A at 50 ns (○) after 532-nm laser pulsing and spectrum B (△) at 800 μs after 532-nm laser pulsing.

The transient spectrum A is in good agreement with the difference spectrum obtained by subtracting the spectrum of $(NO_2)Co^{III}TPP$ from that of $Co^{II}TPP$. This fact indicates that $(NO_2)Co^{III}TPP$ photodissociates NO_2 to yield $Co^{II}TPP$ as a transient photoproduct. It was confirmed that spectrum A has changed completely to the long-lived spectrum B at 800 μs after laser pulsing, while spectrum B scarcely starts to decay at that time. The changing of spectrum A to B was found to occur according to second-order kinetics. Spectrum B decays to give the original spectrum of $(NO_2)Co^{III}TPP$; that is, no permanent products were detected spectrophotometrically. The decay of spectrum B was found to obey first-order kinetics with a rate constant of 3.0×10^2 s^{-1}. On the basis of these results, photochemical reactions of $(NO_2)Co^{III}TPP$ in benzene is expressed as

$$(NO_2)Co^{III}TPP + h\nu \rightarrow NO_2 + Co^{II}TPP \quad (7)$$

$$NO_2 + Co^{II}TPP \rightarrow \text{long-lived transient} \quad (8)$$

$$\text{long-lived transient} \rightarrow (NO_2)Co^{III}TPP \quad (9)$$

where the long-lived transient term expressed in reactions 8 and 9 means the transient species giving spectrum B. The second-order kinetics for the decay of $Co^{II}TPP$ was carried out by means

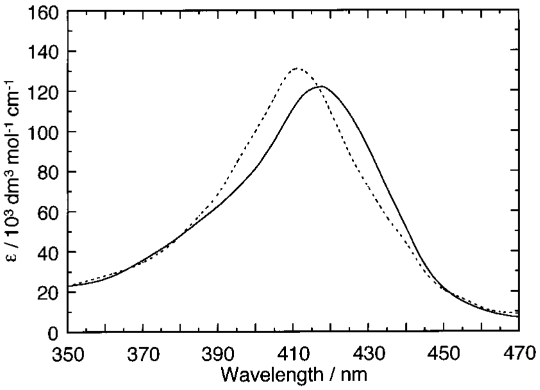

Figure 5. Absorption spectrum for the long-lived transient (dotted line), which was assigned to $ONO-Co^{III}TPP$. The spectrum was estimated from the use of eq 10. The spectrum of $(NO_2)Co^{III}TPP$ (solid line) is also shown for comparison.

of time-resolved absorbance changes at several different wavelengths in the Soret-band region, but mainly at 380 and 417 nm, where the transient spectrum B shows no absorbance. The second-order rate constant for the decay of $Co^{II}TPP$ was determined to be 3.6×10^9 dm^3 mol^{-1} s^{-1} with the use of the value of $\Delta\epsilon$ obtained by subtracting the molar absorption coefficients of $(NO_2)Co^{III}TPP$ from that of $Co^{II}TPP$ at 380 or 417 nm ($\Delta\epsilon_{380} = -2.93 \times 10^4$, $\Delta\epsilon_{417} = 1.06 \times 10^5$ dm^3 mol^{-1} cm^{-1}).

The quantum yield for the photodissociation of NO_2 from $(NO_2)Co^{III}TPP$, $\Phi_{react.7}$, was measured by the same method used for determination of $\Phi_{react.3}$; however, $\epsilon_\lambda{}^{P}$ and $\epsilon_\lambda{}^{R}$ used in the eq 5 were replaced by $\epsilon_\lambda{}^{P\prime}$ and $\epsilon_\lambda{}^{R\prime}$, which stand for the molar absorption coefficients of $Co^{II}TPP$ and $(NO_2)Co^{III}TPP$ at the wavelength λ, respectively. The value of $\Phi_{react.7} = 0.077$ was calculated with $\epsilon_\lambda{}^{P\prime} - \epsilon_\lambda{}^{R\prime} = 1.49 \times 10^5$ and -6.24×10^4 dm^3 mol^{-1} cm^{-1} at the respective wavelengths of 412.5 and 430 nm. This value of $\Phi_{react.7}$ is very close to the value of $\Phi_{react.3} = 0.071$ for the NO_2 dissociation from $(NO_2)Co^{III}TPP(DMAPy)$.

Discussion

The following equation,

$$\epsilon_\lambda{}^{L} - \epsilon_\lambda{}^{R\prime} = \Delta D_\lambda{}^{800\mu s}/[Co^{II}TPP]^{50ns} \qquad (10)$$

can be applied to the spectral changes when all of $Co^{II}TPP$ produced by reaction 7 converts to the long-lived transient through reaction 8. In eq 10, $\epsilon_\lambda{}^{L}$ and $\epsilon_\lambda{}^{R\prime}$ are the molar absorption coefficients of the long-lived transient and $(NO_2)Co^{III}TPP$ at a wavelength λ, $\Delta D_\lambda{}^{800\mu s}$ is the absorbance change at the wavelength λ observed 800 μs after laser pulsing for the solution of $(NO_2)Co^{III}TPP$, and $[Co^{II}TPP]^{50ns}$ is the concentration of $Co^{II}TPP$ at 50 ns after laser pulsing. The value of $[Co^{II}TPP]^{50ns}$ was determined by using the absorbance change observed at 50 ns and $\epsilon_\lambda{}^{P\prime} - \epsilon_\lambda{}^{R\prime} = 1.49 \times 10^5$ dm^3 mol^{-1} cm^{-1} at 412.5 nm. Since the value of $\epsilon_\lambda{}^{R\prime}$ has been obtained already, as shown in Figure 1, the value of $\epsilon_\lambda{}^{L}$ can be calculated from eq 10. The calculated values of $\epsilon_\lambda{}^{L}$ were plotted against the corresponding λ in the Soret-band region. The resultant spectrum is shown in Figure 5 as the spectrum for the long-lived transient. The shape and molar absorbance of the resultant spectrum are very close to those of $(NO_2)Co^{III}TPP$ also shown in Figure 5, although the peak wavelength of the resultant spectrum (410 nm) is shifted from that of $(NO_2)Co^{III}TPP$ (418 nm). This fact suggests that the structure of the long-lived transient is analogous to that of $(NO_2)Co^{III}TPP$. Furthermore, by considering that the decay process of the transient to $(NO_2)Co^{III}TPP$ follows first-order kinetics, we concluded that the long-lived transient has the structure of the nitrito form, $ONO-Co^{III}TPP$, an isomer of $(NO_2)Co^{III}TPP$. The decay of the transient can be assigned, therefore, to a nitrito → nitro linkage isomerization. We also calculated the value of $\epsilon_\lambda{}^{L}$ for case where a part of $Co^{II}TPP$ produced through reaction 7 recombines with NO_2 to give the nitro complex without passing through the nitrito form. For the calculation of $\epsilon_\lambda{}^{L}$ in such a case, eq 10 was used with $[Co^{II}TPP]^{50ns}$ multiplied by a variable factor r ($0 < r < 1$). The spectrum for the nitrito form calculated by using the corrected $\epsilon_\lambda{}^{L}$ was distorted, especially when $r < 0.7$. This observation indicates that most of the $Co^{II}TPP$ produced by photodissociaton of $(NO_2)Co^{II}TPP$ recombines with NO_2 to yield the nitrito form, followed by isomerization to the nitro form.

It has been reported that the photoreaction of solid $[Co(NH_3)_5(NO_2)]^{2+}$ or *trans*-$[Co(en)_2(NCS)(NO_2)]^+$ produces the corresponding isomeric nitrito complex.[14–16] The nitrito complex isomerizes back to the corresponding nitro complex, which is known to have a larger thermodynamic stability than the corresponding nitrito complex.[14–16] The results from the present study show that the photochemical and thermodynamical behavior in the solution of $(NO_2)Co^{III}TPP$ is similar to $[Co(NH_3)_5(NO_2)]^{2+}$ or *trans*-$[Co(en)_2(NCS)(NO_2)]^+$ in the solid, although the lifetime of the nitrito form of the porphyrin is much shorter (2.3 ms at room temperature) than that of the solid pentaammine or ethylenediamine complexes (more than several days at 283 *K*[15,16]).

The thermal nitrito → nitro isomerization of the pentaammine or ethylenediamine complexes has been shown to occur not only in the solid state but even in the solution via an intramolecular process involving a seven-coordinated transition state, where the cobalt atom is bonded to both the N and one of the O atoms of the nitrite ligand.[15,16,24] On the basis of the changes in powder diffraction patterns, a similar intramolecular mechanism was suggested for the photochemical nitro → nitrito isomerization of the ethylenediamine complex in solid.[16] Further, Balzani et al. concluded that, even in solution, the nitro → nitrito photoisomerization of the pentaammine complex occurs through an intramolecular process, since they found that complete separation of two fragments produced by the $Co-NO_2$ homolytic bond scission causes decomposition of the complex in solution.[14]

The present results clearly show that photoexcitation of $(NO_2)Co^{III}TPP$ in solution brings about complete separation of the two fragments, NO_2 and $Co^{II}TPP$, produced by cleavage of the O_2N-Co bond (reaction 7) and the nitrito form is produced in the recombination process of the two fragments (reaction 8). Consequently, the photochemical nitro → nitrito isomerization of $(NO_2)Co^{III}TPP$ cannot proceed through an intramolecular process, although the thermal nitrito → nitro isomerization (reaction 9) is an intramolecular process, as is the case for the pentaammine complex in aqueous solution.[24] This is supported by the results from kinetic analysis for both processes described above; that is, the former process follows second-order kinetics, and the latter process follows first-order kinetics. Photoexcitation of $(NO_2)Co^{III}TPP(DMAPy)$ in solution also causes complete separation of the two fragments, NO_2 and $Co^{II}TPP(DMAPy)$, produced by cleavage of the O_2N-Co bond (reaction 3). However, formation of the nitrito form was not observed in the recombination process of the two fragments (reaction 4), in contrast to the photoreaction of $(NO_2)Co^{III}TPP$. This difference in the recombinations of NO_2 with $Co^{II}TPP$ and $Co^{II}TPP(DMAPy)$ may be attributable to the following reason. That is, at the first step in the recombination process of NO_2 and $Co^{II}TPP$, the positively charged cobalt atom of $Co^{II}TPP$ must prefer access of the O atom to the N atom of the NO_2, because the electron density on the N−O bond is shifted onto the O atom from the N atom. The recombination of NO_2 and Co^{II}-TPP, thus, results in formation of the nitrito form as a metastable compound, which causes then intramolecular rearrangement to yield the thermodynamically more stable nitro form, whereas the positive charge on the cobalt atom of $Co^{II}TPP(DMAPy)$ should be neutralized more or less by ligation of DMAPy. Consequently, the O atom cannot easily access the cobalt atom or even if it could access it, the resulting nitrito form is not stable enough to be detectable.

References and Notes

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