Laser Flash Photolysis Studies of Nitritomanganese(III) Tetraphenylporphyrin. Reactions of O_2, NO, and Pyridine with Manganese(II) Tetraphenylporphyrin

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Laser photolysis of nitritomanganese(III) tetraphenylporphyrin, $Mn^{III}TPP(ONO)$ (**1**), in degassed toluene gives manganese(II) tetraphenylporphyrin, $Mn^{II}TPP$ (**2**), plus NO_2. The quantum yield, Φ, for the formation of Mn^{II}-TPP is dependent on the excitation wavelength: $\Phi = 0.045$ at 355 nm and $\Phi = 0.0064$ at 532 nm. Continuous photolysis studies reveal that the quantum yield for the net photodecomposition of **1** is much smaller (10^{-4}). Thus, $Mn^{II}TPP$ produced by laser photolysis of $Mn^{III}TPP(ONO)$ mostly returns to **1** by recombination with NO_2 according to second-order kinetics with a rate constant 2.2×10^9 M^{-1} s^{-1}. The kinetics for the reactions of $Mn^{II}TPP$ with O_2, NO, and pyridine were investigated in detail. In aerated toluene, $Mn^{II}TPP$ reversibly reacts with oxygen to yield the dioxygen adduct, $MnTPP(O_2)$ (**3**). The rate constants, $k_f(O_2)$ and $k_b(O_2)$, for the formation and dissociation of **3** at 300 K were determined to be 1.93×10^7 M^{-1} s^{-1} and 9.0×10^4 s^{-1}, respectively, and the equilibrium constant, $k_f(O_2)/k_b(O_2)$, is therefore 2.1×10^2 M^{-1}. $Mn^{II}TPP$ reacts with pyridine to give Mn^{II}-TPP(Py) with a rate constant of 9.5×10^8 M^{-1} s^{-1}. $Mn^{II}TPP$ reacts with NO to yield nitrosylmanganese porphyrin, $Mn^{II}TPP(NO)$, with the rate constant 5.3×10^8 M^{-1} s^{-1}. The association reactions of $Mn^{II}TPP$ with NO, pyridine, O_2, and NO_2 are discussed in comparison with those of other metalloporphyrins.

Introduction

Manganese porphyrins have been used as catalysts for oxidation of olefins,[1−10] for oxidative cleavage of DNA,[1,11,12] and for removal of superoxide anion in mammalian cells.[13] It has been suggested that the Mn^{II} (and Mn^{IV}) porphyrins play key roles as intermediates in these catalytic reactions,[1,2] especially in superoxide scavenging.[13,14] Mn^{III} porphyrins have been extensively investigated.[15−17] However, fewer studies have been carried out for Mn^{II} porphyrins, in part because the Mn^{II} porphyrins obtained by chemical reductions of Mn^{III} analogues tend to be unstable in aerobic media. In this context, the flash photolysis technique provides a useful and convenient method for investigating the reactivities of low valent metal porphyrins. Described here are such studies of the reactions of Mn^{II} porphyrins with O_2, NO, and pyridine.

Previous studies have shown that continuous photolysis of various Mn^{III} porphyrins $Mn^{III}Por(X)$ (Por = porphyrin; X = Cl, NO_2, NO_3, Br, I, $OCOCH_3$, or NCS) gives rise to the formation of Mn^{II} porphyrin with low quantum yields ($\leq 10^{-4}$).[18−20] It is noteworthy that continuous photolysis of the nitrito complex $Mn^{III}TPP(ONO)$ (**1**) (TPP = tetraphenylporphyrin) produces $Mn^{IV}TPP(O)$ with a quantum yield of 5×10^{-4}.[19] The present work demonstrates that laser flash photolysis of **1** results in the prompt formation of $Mn^{II}TPP$ (**2**) and NO_2, which recombine to regenerate **1** with quantum yields as high as 0.045 upon irradiation at 355 nm. Thus the flash photolysis technique offers a strategy for studying the reactions of $Mn^{II}TPP$ with O_2, NO, and pyridine (Py) to give the respective adducts, and described here are kinetic studies for the formation of these species at 300 K in toluene solutions.

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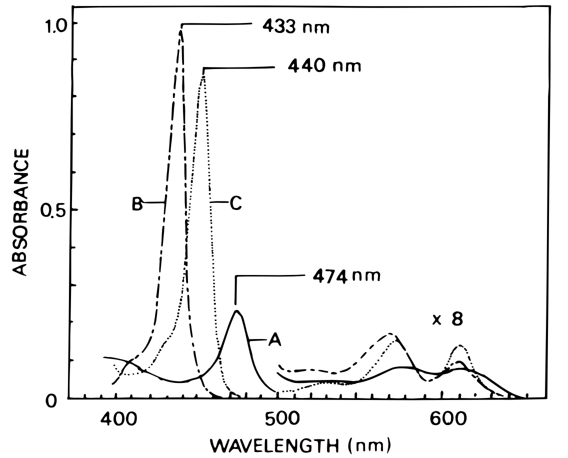

Figure 1. Absorption spectra of 2.8 × 10^{-5} M (A) Mn$^{\rm III}$TPP(ONO), (B) Mn$^{\rm II}$TPP, and (C) Mn$^{\rm II}$TPP(Py) in toluene.

Experimental Section

Reagent grade benzene, toluene, and benzophenone were supplied from Wako Pure Chem. Ind. Ltd. Nitric oxide gas (99.99%) was purchased from Takachiho Chem. Co. Ltd. Nitritomanganese(III) tetraphenylporphyrin,[20] Mn$^{\rm III}$TPP(ONO), was synthesized from chloromanganese(III) tetraphenylporphyrin, Mn$^{\rm III}$TPP(Cl), and NaNO$_2$. The crude Mn$^{\rm III}$TPP(ONO) was recrystallized from benzene solutions.

Absorption spectra were recorded on a Hitachi 330 spectrophotometer. Laser photolysis was carried out with the use of third harmonic of a Nd:YAG laser (model HY 500 from JK Lasers Ltd.). Duration and energy of a laser pulse are respectively 20 ns and 100 mJ/pulse. The detection system was previously reported.[21] Continuous photolysis experiments were made with a 250 W high-pressure mercury lamp (Ushio 250 D) with cutoff filters.

Samples were degassed on a vacuum line to 10^{-5} Torr. Nitric oxide and oxygen gases were introduced into sample solutions on the vacuum line: gas pressures were measured by a mercury manometer.

Results

Absorption Spectra of Manganese Tetraphenylporphyrins. Figure 1 shows the absorption spectra of Mn$^{\rm III}$TPP, Mn$^{\rm II}$TPP, and the pyridine complex Mn$^{\rm II}$TPP(Py) in toluene solutions. The molar absorption coefficients of Mn$^{\rm III}$TPP(ONO) in toluene are 8.3 × 10^{3} M^{-1} cm^{-1} at 618 nm and 7.6 × 10^{4} M^{-1} cm^{-1} at 474 nm.

Mn$^{\rm II}$TPP in toluene was produced by photochemical reduction of ClMn$^{\rm III}$TPP in the presence of benzophenone. Benzophenone undergoes photochemical hydrogen abstraction from a toluene molecule to give the ketyl radical,[22] which was found to reduce Mn$^{\rm III}$TPP(Cl), resulting in the formation of Mn$^{\rm II}$TPP, e.g.,

$$(C_6H_5)_2CO + h\nu \rightarrow {}^3(C_6H_5)_2CO^* \quad (1)$$

$${}^3(C_6H_5)_2CO^* + CH_3C_6H_5 \rightarrow (C_6H_5)_2\dot{C}OH + \dot{C}H_2C_6H_5 \quad (2)$$

$$(C_6H_5)_2\dot{C}OH + \mathrm{Mn^{III}TPP(Cl)} \rightarrow (C_6H_5)_2CO + \mathrm{Mn^{II}TPP} + HCl \quad (3)$$

The ESR measurements of the product at 77 K confirmed the formation of Mn$^{\rm II}$TPP.[23] The absorption spectral changes observed for 1.0 × 10^{-5} M Mn$^{\rm III}$TPP(Cl) and 1.0 × 10^{-2} M benzophenone in toluene exhibited isosbestic points upon UV irradiation, indicating that Mn$^{\rm III}$TPP(Cl) was reduced cleanly to give Mn$^{\rm II}$TPP. After the completion of the photoreduction, no further spectral change was observed with UV irradiation. Thus, reduction of Mn$^{\rm II}$TPP by the ketyl radical does not occur. Mn$^{\rm III}$TPP(ONO) is similarly reduced by benzophenone ketyl radical to give **2**. The molar absorption coefficients of Mn$^{\rm II}$-TPP in toluene are 1.24 × 10^{4} M^{-1} cm^{-1} at 563 nm and 3.35 × 10^{5} M^{-1} cm^{-1} at 433 nm.

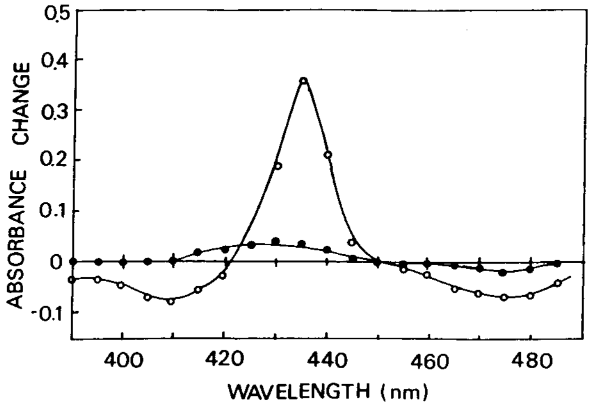

Figure 2. Transient absorption spectra observed for 1.1 × 10^{-5} M Mn$^{\rm III}$TPP(ONO) in degassed toluene at 50 ns (open circles) and 2 ms (closed circles) delay after a 355 nm laser pulse.

Continuous photolysis of a toluene solution of Mn$^{\rm III}$TPP(Cl) and benzophenone in the presence of 1.0 × 10^{-3} M pyridine gives Mn$^{\rm II}$TPP(Py).[24] In the optical absorption spectrum of the latter species, the Soret band was found to be red-shifted by ca. 7 nm from that of Mn$^{\rm II}$TPP. The molar absorption coefficients for Mn$^{\rm II}$TPP(Py) in toluene are 1.19 × 10^{4} M^{-1} cm^{-1} at 572 nm and 2.61 × 10^{5} M^{-1} cm^{-1} at 440 nm.

Continuous Photolysis of Mn$^{\rm III}$TPP(ONO). A degassed toluene solution of Mn$^{\rm III}$TPP(ONO) was irradiated by the mercury lamp with a cutoff filter (λ > 350 nm). The absorption spectral change shows that the peak intensity of **1** located at 474 nm gradually decreased and a new peak appeared at 412 nm during the course of irradiation up to 1.0 h. Judging from the spectral change, the product could be ascribed to oxomanganese(IV) tetraphenylporphyrin, O=Mn$^{\rm IV}$TPP, perhaps formed by an irreversible photodissociation of NO from the coordinated nitrito ligand.[19] The quantum yield for the net photodecomposition of Mn$^{\rm III}$TPP(ONO) was found to be 10^{-4}.

Laser Flash Photolysis. Figure 2 shows the transient absorption spectra observed for a degassed toluene solution of 1.3 × 10^{-5} M of **1** after pulsed laser excitation at 355 nm. The spectrum observed 50 ns after the pulse is the same as the difference spectrum obtained by subtracting the spectrum of Mn$^{\rm III}$TPP(ONO) from that of Mn$^{\rm II}$TPP. Thus the transient is ascribed to formation of **2**.

$$\underset{\mathbf{1}}{\mathrm{Mn^{III}TPP(ONO)}} + h\nu \rightarrow \underset{\mathbf{2}}{\mathrm{Mn^{II}TPP}} + NO_2 \quad (4)$$

The transient Mn$^{\rm II}$TPP decays according to second-order kinetics over the whole wavelength region studied, but the reaction leaves a small residual absorption due to formation of another, long-lived, transient of unknown composition.

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$$\mathrm{Mn^{II}TPP + NO_2 \xrightarrow{k_f(NO_2)} Mn^{III}TPP(ONO)} \tag{5}$$

$$\mathrm{Mn^{II}TPP + NO_2 \rightarrow long\text{-}lived\ species} \tag{6}$$

The rate constant, $k_f(NO_2)$, for the bimolecular reaction between $Mn^{II}TPP$ and NO_2 in toluene is determined as $2.2(\pm0.2) \times 10^9$ M^{-1} s^{-1}. The long-lived transient at 2 ms has a positive peak, at ~430 nm, and a negative one, at ~480 nm, and decays back to the baseline according to first-order kinetics with a rate constant 14 s^{-1}.

Laser flash photolysis of **1** in different media demonstrated that photoinduced dissociation of NO_2 takes place in toluene, diethyl ether, ethyl acetate, or acetonitrile solutions. The reaction between $Mn^{II}TPP$ and NO_2 was modestly solvent sensitive, giving the respective k_b values $3.8(\pm0.4) \times 10^8$, $4.2(\pm0.4) \times 10^8$, and $7.1(\pm0.7) \times 10^8$ M^{-1} s^{-1} in ethyl acetate, diethyl ether, and acetonitrile.

In contrast, photodissociation of NO_2 was not detected in ethanol, a result which was interpreted in terms of **1** in its ground state undergoing ionic dissociation in that solvent:[25]

$$\mathrm{Mn^{III}TPP(ONO) + 2C_2H_5OH \rightarrow Mn^{III}TPP(C_2H_5OH)_2{}^{+} + NO_2{}^{-}} \tag{7}$$

This is further supported by the fact that the absorption spectrum of **1** in alcohols is identical with that of $Mn^{III}TPP(Cl)$ in this same medium. $Mn^{III}TPP(Cl)$ is known to dissociate Cl^- in ethanol.[25]

Reaction of $Mn^{II}TPP$ with O_2. When laser flash photolysis studies of $Mn^{III}TPP(ONO)$ were carried out in aerated toluene solutions, the transient spectrum observed 50 ns after the pulse was identical to that seen in degassed toluene. The decay profile, however, proved to be slightly different; a small portion of $Mn^{II}TPP$ initially decays according to first-order kinetics but the second-order decay eventually becomes the major process. The first-order decay component was found to be much more important at higher $[O_2]$. Figure 3 shows the transient absorption spectra measured 20 μs after the laser pulse of toluene solutions of **1** at oxygen pressures over the range 0−2 atm. The spectra exhibit isosbestic points at 420 and 445 nm. Since $Mn^{II}TPP$ produced by photolysis of $Mn^{III}TPP(ONO)$ in degassed toluene decays little within 20 μs after pulsing, the first-order decay component is considered to be associated with the reversible reaction of $Mn^{II}TPP$ and O_2, to give the dioxygen complex, $O_2{\cdots}Mn^{II}TPP$, i.e.,

$$\mathrm{Mn^{II}TPP + O_2 \xrightarrow{k_f(O_2)} \underset{\textbf{3}}{O_2{\cdots}Mn^{II}TPP}} \tag{8}$$

$$\mathrm{O_2{\cdots}MnTPP \xrightarrow{k_b(O_2)} Mn^{II}TPP + O_2} \tag{9}$$

From eqs 8 and 9, the first-order rate constant, $k_{obs}(O_2)$, for the decay of $Mn^{II}TPP$ in oxygenated solutions is expressed as

$$k_{obs}(O_2) = k_f(O_2)[O_2] + k_b(O_2) \tag{10}$$

As displayed in Figure 4, the plot of $k_{obs}(O_2)$ vs dioxygen pressure, P_{O_2}, gives a straight line. From the slope of the line and the Bunsen absorption coefficient of dioxygen (0.222) in toluene at 298 K,[26] $k_f(O_2)$ is obtained as $1.6(\pm0.1) \times 10^7$ M^{-1} s^{-1}. The intercept of the line affords $k_b(O_2) = 0.9\ (\pm0.05) \times 10^5\ s^{-1}$. The equilibrium constant, K, for the formation of the oxygen complex of $Mn^{II}TPP$ is thus calculated as $K = k_f(O_2)/k_b(O_2) = 1.8\ (\pm0.2) \times 10^2\ M^{-1}$.

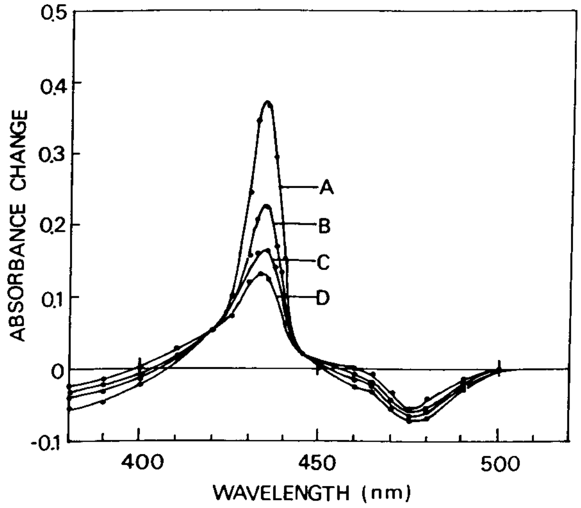

Figure 3. Transient absorption spectra taken at 20 μs after a 355 nm laser pulse, observed for toluene solutions of 1.1×10^{-5} M $Mn^{III}TPP(ONO)$ at various oxygen pressures: A, 0 atm; B, 0.49 atm; C, 1.0 atm; D, 2.0 atm.

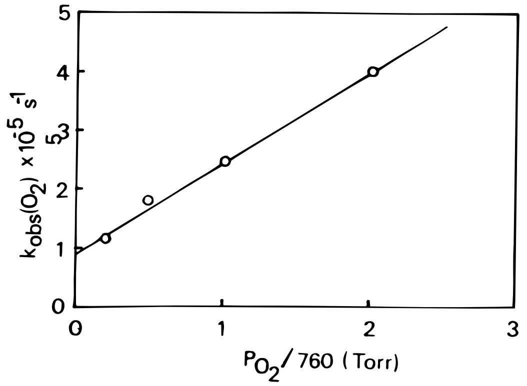

Figure 4. Pseudo-first-order decay rate constants represented as a function of the oxygen pressure.

The equilibrium constant, K, can also be obtained from Figure 3. The absorbance change, ΔD, is formulated as

$$\Delta D - \Delta D_0 = K[O_2](1 + K[O_2])^{-1}(\Delta D_0 - \Delta D_\infty) \tag{11}$$

Here, ΔD_0 and ΔD_∞ are respectively the absorbance change observed at $[O_2] = 0$ and at an “ infinite” concentration of dioxygen. Equation 11 is readily transformed to

$$Y = (\Delta D - \Delta D_0)/(\Delta D_0 - \Delta D_\infty) = K[O_2](1 + K[O_2])^{-1} \tag{12}$$

The plot of Y^{-1} vs $[O_2]^{-1}$ gave a straight line for $\Delta D_\infty = 0.06$. From the slope of the line, K is determined as $K = 1.6(\pm0.2) \times 10^2\ M^{-1}$, in good agreement with the value obtained from the kinetic measurements.

The reversible binding of O_2 to $Mn^{II}TPP$ is also observed for cyclohexane solutions. The forward and backward rate constants for the formation of $O_2{\cdots}MnTPP$ were respectively $2.5(\pm0.2) \times 10^8$ M^{-1} s^{-1} and $1.5(\pm0.1) \times 10^5$ s^{-1}, giving a K value of $1.7(\pm0.2) \times 10^3$ M^{-1} in this solvent.

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(26) *IUPAC Solubility Data Series*; Battino, R., Ed.; Pergamon Press: New York, 1985; Vol. 7.

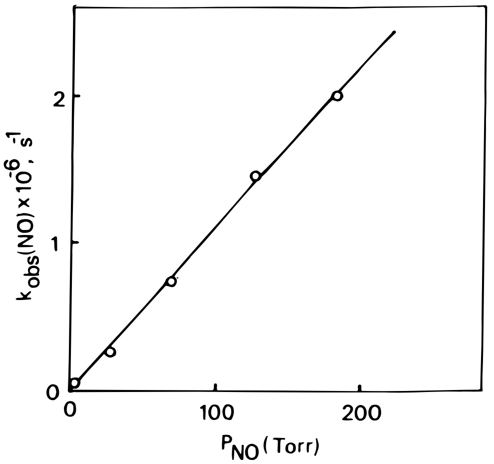

Figure 5. Pseudo-first-order decay rate constants represented as a function of the NO pressure, P_{NO}.

The formation of the dioxygen adduct of $Mn^{II}TPP$ could not be measured in acetonitrile, ethyl acetate, and diethyl ether solutions.

Reaction of $Mn^{II}TPP$ with NO. Laser photolysis studies were carried for a toluene solution of **1** at a NO pressure $P_{NO} = 185$ Torr. The photochemical formation of $Mn^{II}TPP$ affords the transient spectrum observed at 50 ns after the laser pulse. The spectrum gradually changes over a few microseconds to give a transient spectrum (after 3.5 μs) with a positive peak at 412 nm and a negative one at 450 nm (Figure S1 of the Supporting Information). This can be compared to the absorption spectrum of $Mn^{II}TPP(NO)$ (the inset of Figure S1 of the Supporting Information) which was obtained by exposure to a toluene solution of **2**, produced by photochemical reduction of $ClMn^{III}TPP$ in the presence of benzophenone, to NO. The difference spectrum ($Mn^{II}TPP$ minus $Mn^{II}TPP(NO)$) is the same as that of the 3.5 μs transient spectrum. Thus, the change in the transient spectrum (Figure S1 of the Supporting Information) is interpreted in terms of the formation of $Mn^{II}TPP(NO)$:

$$\mathrm{Mn^{II}TPP + NO \xrightarrow{k_f(NO)} Mn^{II}TPP(NO)} \qquad (13)$$

The formation of $Mn^{II}TPP(NO)$ follows pseudo-first-order kinetics. Figure 5 displays the pseudo-first-order rate constant, $k_{obs}(NO)$, as a function of P_{NO}. The plot gives a straight line with an intercept at the origin. From the slope of the line and the Bunsen absorption coefficient of NO in toluene (0.275),[27] $k_f(NO)$ was determined to be $5.3(\pm 0.5) \times 10^8$ M^{-1} s^{-1}. The $k_b(NO)$ term for the dissociation of NO from $Mn^{II}TPP(NO)$ could not be measured, but the negligible value of the intercept gives the upper limit to $k_b(NO)$ of 10^4 s^{-1}; thus, a lower limit for the equilibrium constant is $K = k_f(NO)/k_b(NO) > 5 \times 10^4$ M^{-1}.

The transient absorption spectrum of $Mn^{II}TPP(NO)$ gradually decays over a few milliseconds to regenerate $Mn^{III}TPP(ONO)$. This result suggests that $Mn^{II}TPP(NO)$ eventually reacts with the equivalents of NO_2, leading to the formation of **1** either by direct replacement of axial NO with NO_2 or more likely by oxidation of coordinated NO by N_2O_3, which would have been formed by the nearly diffusion-limited reaction of NO_2 with excess NO.[28]

$$\mathrm{Mn^{II}TPP(NO) + N_2O_3 \rightarrow Mn^{III}TPP(ONO) + 2NO} \qquad (14)$$

Laser photolysis studies of MnTPP(NO) in ethanol were carried out in order to examine the effects of solvent on the rate constant for the reaction between **2** and NO. $Mn^{II}TPP$ was readily formed upon mercury lamp irradiation of $Mn^{III}TPP(Cl)$ in degassed ethanol containing 10^{-2} M acetone. Exposure of this solution to NO results in the formation of $Mn^{II}TPP(NO)$. Laser flash photolysis of $Mn^{II}TPP(NO)$ leads to NO photodissociation to $Mn^{II}TPP$ which returns to $Mn^{II}TPP(NO)$ by the recombination reaction.[29] In the presence of excess NO, k_{obs} for this reaction increases with increasing P_{NO}. A plot of k_{obs} vs P_{NO} gives a straight line with an intercept at the origin. From the slope of this line and the solubility of NO,[28] the bimolecular rate constant for the reaction between $Mn^{II}TPP$ and NO in ethanol was calculated to be $4.9(\pm 0.2) \times 10^5$ M^{-1} s^{-1}, 3 orders of magnitude slower than in toluene.

Reaction of $Mn^{II}TPP$ with Pyridine. The ligation of pyridine to $Mn^{II}TPP$ was studied by laser photolysis of **1** in toluene solutions containing pyridine. The absorption spectrum of **1** is not changed by the addition of $0-10^{-1}$ M pyridine. The transient absorption spectra were measured by the flash photolysis of a toluene solution of **1** and 6.2×10^{-4} M pyridine (Figure S2 of the Supporting Information). The spectrum detected at 50 ns after pulsing is the same as that observed for toluene solution of $Mn^{III}TPP(ONO)$ in the absence of pyridine. Over several microseconds, the positive peak intensity of the transient at 435 nm decreased and a new peak appeared at 440 nm. The spectrum observed at 3.5 μs is identical with the difference spectrum calculated for formation of $Mn^{II}TPP(Py)$ ($Mn^{II}TPP(Py)$ minus **1**):

$$\mathrm{Mn^{II}TPP + Py \xrightarrow{k_f(Py)} Mn^{II}TPP\ (Py)} \qquad (15)$$

The rate for the formation of $Mn^{II}TPP(Py)$ follows pseudo-first-order kinetics. The pseudo-first-order rate constants, $k_{obs}(Py)$, were measured as a function of the pyridine concentration, [Py]. The plot of $k_{obs}(Py)$ vs [Py] gives a straight line with the intercept at the origin. The slope affords the bimolecular rate constant, $k_f(Py) = 1.1(\pm 0.1) \times 10^9$ M^{-1} s^{-1}. The rate constant for the dissociation of pyridine from $Mn^{II}TPP(Py)$ is negligibly small ($\ll 10^5$ s^{-1}).

Continuous photolysis of **1** in a toluene solution containing 10^{-3} M pyridine gave $Mn^{II}TPP(Py)$ as a product which returned to **1** within a few tens of minutes. It is suggested that NO_2 photodissociated is trapped by pyridine to form the charge-transfer complex, $NO_2^{\delta-} \cdots Py^{\delta+\bullet}$, and therefore, the rate for the recovery of **1** becomes very slow.

As described above, $Mn^{II}TPP(Py)$ is readily prepared by continuous photolysis of a toluene solution of $Mn^{III}TPP(Cl)$ in the presence of benzophenone and pyridine. The 355-nm laser flash photolysis of $Mn^{II}TPP(Py)$ in the toluene solution gives no transient, indicating that photodissociation of pyridine does not occur from $Mn^{II}TPP(Py)$.

Quantum Yield Measurements. The quantum yield for the photochemical formation of $Mn^{II}TPP$ from $Mn^{III}TPP(ONO)$ was determined by a published method.[30] The absorbance change, ΔD, observed for a toluene solution of **1** immediately after flash photolysis is shown by

$$\Delta D = (\Delta\epsilon)\Phi[I_{abs}(\lambda)]/N_A \qquad (16)$$

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(27) *IUPAC Solubility Data Series*; Young, C. L., Ed.; Pergamon Press: New York, 1985; Vol. 8.

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where $\Delta\epsilon$ and Φ are respectively the difference in the molar absorption coefficient between **2** and **1** and the quantum yield for the formation of **2**, $I_{abs}(\lambda)$ is the number of photons absorbed by the toluene solution, and N_A is Avogadro's number. $I_{abs}(\lambda)$ is a function of the solution absorbance at the laser excitation wavelength, λ.

For determination of $I_{abs}(\lambda)$ upon excitation at 355 and 532 nm, benzene solutions of benzophenone and zinc(II) tetraphenylporphyrin, ZnTPP, were used as standard solutions: the triplet yield, Φ_T, and the difference in the molar absorption coefficient of the triplet state, $\Delta\epsilon_T$, have already been reported as $\Phi_T = 1.0$ and $\Delta\epsilon_T = 7.6 \times 10^3$ M^{-1} cm^{-1} at 530 nm for triplet benzophenone[31] and $\Phi_T = 0.83$ and $\Delta\epsilon_T = 7.3 \times 10^4$ M^{-1} cm^{-1} at 470 nm for triplet ZnTPP.[32] When the absorbance of the standard solution at the laser excitation wavelength is the same as that of the toluene solution of **1**, the absorbance change, ΔD_T, due to the triplet formation by laser photolysis is given by

$$\Delta D_T = (\Delta\epsilon_T)\Phi_T[I_{abs}(\lambda)]/N_A \tag{17}$$

Equations 16 and 17 lead to

$$\Phi = \Phi_T(\Delta\epsilon_T/\Delta\epsilon)(\Delta D/\Delta D_T) \tag{18}$$

With the use of $\Delta\epsilon = 4.4 \times 10^5$ M^{-1} cm^{-1} and eq 18, the quantum yields for the formation of $Mn^{II}TPP$ from $Mn^{III}TPP(ONO)$ were determined as 0.045 and 0.0064 upon excitation at 355 and 532 nm, respectively.

Discussion

$Mn^{II}TPP$ and NO_2 are produced by laser photolysis of $Mn^{III}TPP(ONO)$ in toluene solutions with wavelength-dependent quantum yields. According to the absorption spectra of manganese(III) porphyrins, 355 and 532 nm laser pulses are respectively absorbed by the B- and Q-bands both of which have porphyrin to Mn charge-transfer character.[17] The charge-transfer character of the excitation band is probably essential for **1** to dissociate NO_2. It is postulated that the excitation of a higher energy band brings forth a large excess energy for dissociation of the O−Mn bond in $Mn^{III}TPP(ONO)$, leading to the larger quantum yield.

The very low yield photodecomposition of **1** seen under continuous photolysis may be the result of a minor secondary thermal reaction of $Mn^{II}TPP$. However, an alternative, for which there is precedent in the photochemistry of the chromium(III) analogue, $Cr^{III}TPP(ONO)$, would be a competing low quantum yield photodissociation of NO from the coordinated nitro ligand **1** to give $O{=}Mn^{IV}TPP$.[33]

The second-order rate constants for the recombination between $Mn^{II}TPP$ and NO_2 are quite large in each of the solvents investigated ($3.8 \times 10^8 - 2.1 \times 10^9$ M^{-1} s^{-1}) although they do fall in the order toluene > acetonitrile > diethyl ether ∼ ethyl acetate. Since this order does not correlate with differences in solvent viscosity, a logical explanation would be that these rate differences reflect the weak coordination of the various solvents in the axial position(s) of $Mn^{II}TPP$.

Scheme 1

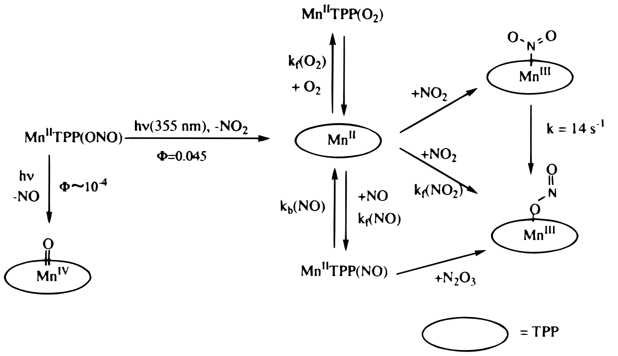

Table 1. Rate and Equilibrium Constants for the Reaction of $Mn^{II}TPP$ with NO, O_2, NO_2, and Pyridine

	solvent	k_f (M^{-1} s^{-1})[a]	k_b (s^{-1})[b]	K (M^{-1})
$Mn^{II}TPP + NO$	toluene	5.3×10^8		
	ethanol	4.9×10^5		
$Mn^{II}TPP + O_2$	toluene	1.9×10^7	9.0×10^4	2.1×10^2
	cyclohexane	2.5×10^8	1.5×10^5	1.7×10^3
$Mn^{II}TPP + NO_2$	toluene	2.2×10^9		
	ethyl acetate	3.8×10^8		
	diethyl ether	4.2×108		
	acetonitrile	7.1×10^8		
$Mn^{II}TPP + NO$	toluene	1.1×10^9		

The flash photolysis of $Mn^{III}TPP(ONO)$ in toluene reveals that a residual transient spectrum is observed after the decay of $Mn^{II}TPP$. Since the transient spectrum detected at 50 ns after the pulse is strictly in accord with the difference spectrum ($Mn^{II}TPP$ minus $Mn^{III}TPP(ONO)$), the residual transient is likely to be a recombination product between $Mn^{II}TPP$ and NO_2, i.e., the linkage isomer of **1**, nitromanganese(III) tetraphenylporphyrin, $Mn^{III}TPP(NO_2)$. The decay of this to **1** would be a first-order linkage isomerization analogous to that seen in the photochemical reaction of nitrocobalt(III) tetraphenylporphyrin.[34]

The second-order nature of the back-reaction of **2** with NO_2 to give **1** allows one to probe the kinetics of the reactions of $Mn^{II}TPP$ with other reagents, such O_2, NO, and Py, which have been added in large excess (Scheme 1). The rate constants measured are summarized in Table 1.

The axial coordination of dioxygen to metalloporphyrins has long been of major interest in porphyrin chemistry.[1−14] For manganese porphyrins, absorption spectroscopy and ESR studies at low temperatures suggest the structure of the dioxygen adduct to be $Mn^{IV}(O_2^{2-})TPP$.[25] However, kinetic studies for the formation of such dioxygen adducts have not been previously reported. The present data for the formation of $Mn^{II}TPP(O_2)$ in oxygenated toluene and cyclohexane solutions demonstrates that the rate and equilibrium constant for the formation of the dioxygen adduct are each about 1 order of magnitude higher in cyclohexane than in toluene under analogous conditions (300 K). This again can be interpreted as indicating modest differences in solvation of **2**; i.e., $Mn^{II}TPP$ is better solvated by toluene than by cyclohexane.

Reversible dioxygen binding has been investigated for the iron(II) porphyrins in solutions containing nitrogenous bases at temperatures below −40 °C.[35−39] The kinetic studies for the

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formation of the dioxygen adducts have been made with the use of "pocket" and "picket-fence" iron(II) porphyrins.[40−43] The magnitudes of the rate constants, k_f, for the formation of the dioxygen adducts range from 10^6 to 10^8 M^{-1} s^{-1}, and those of the back-reaction, k_b, from 10^2 to 10^4 s^{-1}.[40] The equilibrium constant is ca. 10^3 M^{-1} for many of the "pocket" and "picket-fence" porphyrins. The present study revealed that, despite the difference in the nature of the central metal, Fe(II) and Mn(II) porphyrins give similar values for the forward and back rate constants and the equilibrium constant for the formation of the dioxygen adducts.

As in the cases of Fe^{II}TPP and Mn^{II}TPP, the Co^{II} porphyrin, Co^{II}TPP, yields the dioxygen adduct at low temperatures.[44,45] However, formation of $Co^{II}TPP(O_2)$ is hardly detected at room temperature, so the equilibrium constant for the reversible binding of O_2 must be small. Thus, O_2 binding follows the order $Fe^{II}TPP \approx Mn^{II}TPP > Co^{II}TPP$.

Laser photolysis studies of Mn^{III}TPP(ONO) in toluene in the presence of excess NO demonstrate that Mn^{II}TPP reacts with NO with a rate constant (5.3×10^8 M^{-1} s^{-1}) somewhat slower than the values found for Fe^{II}TPP (5.2×10^9 M^{-1} s^{-1})[29] and Co^{II}TPP (2.5×10^9 M^{-1} s^{-1})[29] in 300 K toluene. In ethanol, the analogous rate constant measured by flash photolysis of Mn^{II}TPP(NO) was 3 orders of magnitude smaller. Again, this difference can be rationalized in terms of solvent coordination at axial sites of Mn^{II}TPP by the stronger donor ligand ethanol which blocks the axial position of Mn^{II}TPP. In this context, it is notable that recent studies of the hydrostatic pressure and temperature effects on the rates of nitrosylation of the water-soluble iron(III) complexes $Fe^{III}TPPS(H_2O)_2$ (TPPS is sulfonated TPP) clearly point to a mechanism requiring dissociation of an axial ligand before the reaction with NO.[46]

Kinetic studies on the coordination of nitrogenous bases have been extensively studied by using the laser photolysis method.[47−52] For example, the rates of pyridine reactions with Co^{III} or Fe^{II} porphyrins have been determined by flash photolysis of the pyridine adducts in benzene and toluene, respectively. In contrast, no photodissociation of pyridine was detected upon photoexcitation of Mn^{II}TPP(Py) in toluene. The present work has shown that the laser photolysis of **1** is a convenient method to produce Mn^{II}TPP which, in the presence of pyridine, reacts to give the five-coordinate species, Mn^{II}TPP(Py). The rate constant, 1.1×10^9 M^{-1} s^{-1}, for the formation of Mn^{II}TPP(Py) is almost identical with those for the formation of Fe^{II}TPP(Py) and Co^{III}TPP(Cl)(Py): 1.1×10^9 and 9.8×10^8 M^{-1} s^{-1}, respectively. The spin states are $S = {}^5/_2$ for both Mn^{II}TPP and Mn^{II}TPP(Py), $S = 2$ for both Fe^{II}TPP and Fe^{II}TPP(Py), and $S = 0$ for both Co^{III}TPP(Cl) and Co^{III}TPP(Cl)(Py). The fact that no reorganization of d-electrons is necessary for these metalloporphyrin to form their pyridine adducts may be one rationalization for the identical rate constants of pyridine association.[29]

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Supporting Information Available: Figures S1 and S2, showing the transient absorption spectra observed for toluene solutions of Mn^{III}TPP(ONO) in the presence of NO and pyridine (2 pages). Ordering information is given on any current masthead page.

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