

Some Very Rapid Reactions of Porphyrins in Aqueous Solution

Robert F. Pasternack,*^{1a} Norman Sutin,*^{1b} and Douglas H. Turner^{1c}

Contribution from the Departments of Chemistry, Ithaca College,

Ithaca, New York 14850, Brookhaven National Laboratory, Upton, New York 11973, and University of Rochester, Rochester, New York 14627. Received August 1, 1975

Abstract: The rate of addition of two water molecules to $\alpha,\beta,\gamma,\delta$ -tetra(4-*N*-methylpyridyl)porphinatonickel(II) to form the six-coordinate diaquo complex has been studied by the laser Raman temperature-jump method. The rate constant for the addition of the first water molecule with the concomitant spin change is $2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C (0.1 M KCl). The laser temperature-jump apparatus has also been used to study the rate of protonation of the metal-free porphyrin. The kinetics are consistent with a mechanism in which the free-base porphyrin exists in solution as a mixture of buckled and planar forms. The relatively low concentration buckled form, with its exposed nitrogen atom, is more susceptible to proton attack. The rate constants for the ring buckling and subsequent proton addition are (25 °C, $\mu = 0.7 \text{ M}$) $\text{PH}_2^{4+} \rightleftharpoons * \text{PH}_2^{4+}$ ($k_1 = 4.6 \times 10^7 \text{ s}^{-1}$, $k_{-1} = 1.2 \times 10^9 \text{ s}^{-1}$), $* \text{PH}_2^{4+} + \text{H}^+ \rightleftharpoons \text{PH}_3^{5+}$ ($k_2 = 5.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{-2} = 8.0 \times 10^6 \text{ s}^{-1}$). The activation energy for the ring buckling is $\sim 2.5 \text{ kcal mol}^{-1}$. The analysis of the amplitudes of the relaxation curves leads to pK values consistent with those obtained from spectrophotometric titrations.

A number of processes have been implicated in porphyrin reactions which have proved too rapid for measurement with conventional temperature-jump techniques. The recent construction of a laser Raman temperature-jump apparatus,^{2,3} having a heating time of 25–30 ns, permits a kinetic investigation of some of these processes. We report on two such reactions here: (1) the protonation of the water-soluble porphyrin $\alpha,\beta,\gamma,\delta$ -tetra(4-*N*-methylpyridyl)porphine $\text{H}_2\text{-(TMpyP)}^{4+}$ and (2) the interconversion of the four-coordinate and six-coordinate forms of the nickel(II) derivative of this porphyrin. Previous work had shown that under the conditions of the present experiments neither the metal-free nor the nickel derivative of TMpyP aggregate in solution.^{4,5} The results of the present study are consistent with the conclusion that the porphyrin species in solution are monomeric. Therefore, although the porphyrin units are not physically isolated from one another as in most metalloporphyrin-protein complexes, they do nevertheless act as independent molecules. The availability of a monomeric porphyrin greatly simplifies the interpretation of kinetic and thermodynamic experimental results.

Experimental Section

The tosylate salt of the porphyrin $\text{H}_2\text{(TMpyP)}^{4+}$ was prepared by literature methods^{4a,6} while the iodide salt was purchased from Strem Chemicals, Inc., Danvers, Mass. Experiments conducted with porphyrin samples from each of the two sources gave identical results. The symbol PH_2^{4+} is used throughout for the free-base form of the porphyrin (Figure 1).

The synthesis and purification of the nickel(II) derivative of TMpyP has been previously described.⁵ It has been shown that this porphyrin may exist in solution as either the four-coordinate species Ni(P)^{4+} or in a six-coordinate form for which, in the case of the diaquo complex, the symbol $\text{Ni(P)(H}_2\text{O)}_2^{4+}$ is used.^{5,7} [The symbol Ni(TMpyP)^{4+} will be used when it is unnecessary to distinguish between Ni(P)^{4+} and $\text{Ni(P)(H}_2\text{O)}_2^{4+}$.] Reagent grade sodium chloride and potassium nitrate were used without further purification. Solutions were freshly prepared (the pH was adjusted by addition of sodium hydroxide and/or hydrochloric acid) and were protected from light until used.

The laser Raman temperature-jump apparatus has been described elsewhere.^{2,3} The xenon probe beam was pulsed to increase the signal-to-noise ratios.^{3b} The filters before the cell were Corning no. 4602 and 5433 and the cell's path length was 0.8 mm. Each of the temperature-jump experiments was conducted at two different wavelengths and a minimum of five relaxation experiments was performed on each solution. The relaxation effects were large and could be measured without appreciable difficulty (Figure 2). The

measured relaxation times for each solution agreed to within $\pm 10\%$. Spectral measurements to be described later were made with a Cary 14 spectrophotometer.

Results and Discussion

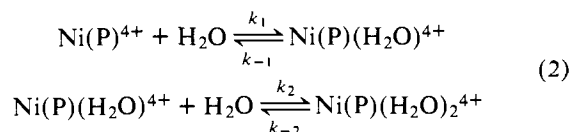
Interconversion of Four- and Six-Coordinate Forms of Ni(TMpyP)^{4+} . A combination of spectral and NMR measurements has been employed to study the properties of Ni(TMpyP)^{4+} in solution.⁵ The conclusion drawn from these studies is that in water Ni(TMpyP)^{4+} exists as a roughly 1:1 mixture of four-coordinate Ni(P)^{4+} and six-coordinate $\text{Ni(P)(H}_2\text{O)}_2^{4+}$. Experimental evidence has also been presented that the addition of acetone or acetonitrile to the aqueous solution displaces the equilibrium to the four-coordinate form while added pyridine or imidazole favors the formation of six-coordinate species.⁵ A recent structural determination⁷ of the perchlorate salt of the nickel porphyrin complex isolated from an imidazole-rich solution demonstrated that the nickel atom was six-coordinate, consistent with the earlier study.

An equilibrium constant $K_{12} = [\text{Ni(P)(H}_2\text{O)}_2^{4+}] / [\text{Ni(P)}^{4+}] = 1.23$ at 25 °C has been previously determined for reaction 1.⁵



Temperature-jump experiments over a fourfold range of concentration of the nickel porphyrin resulted in a single relaxation effect, independent of metalloporphyrin concentration, with $\tau = 40 \text{ ns}$ (0.10 M KCl). The relaxation process was studied at 420 nm which is near the Soret maximum for Ni(P)^{4+} and at 440 nm which is near the Soret maximum for $\text{Ni(P)(H}_2\text{O)}_2^{4+}$. The observed absorbance changes were in opposite directions with the 420-nm peak increasing and the 440-nm peak decreasing with temperature. These results are consistent with the model and with the finding that $\Delta H^\circ = -9.4 \text{ kcal mol}^{-1}$ for equilibrium 1.⁵ Addition of 15% acetone to the nickel porphyrin solution led to the total disappearance of the relaxation effect at both wavelengths.

It is likely that the addition of water to Ni(P) proceeds in two stages.^{8,9}



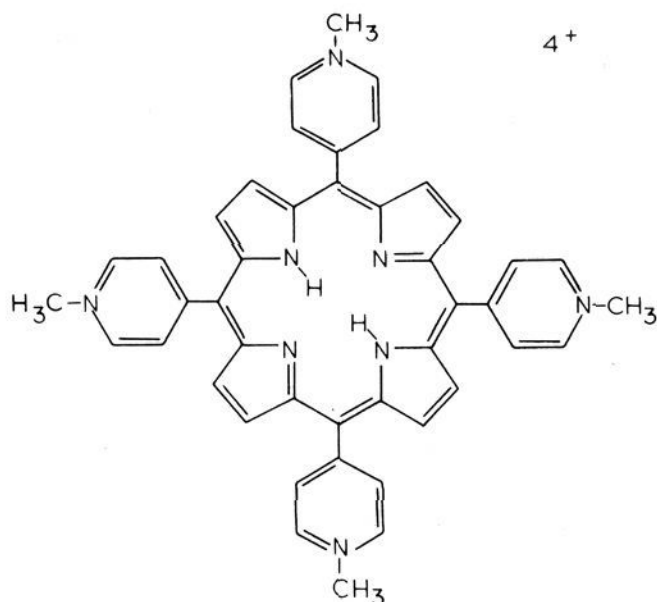


Figure 1. Structure of $\alpha,\beta,\gamma,\delta$ -tetra(4-*N*-methylpyridyl)porphine, $\text{H}_2(\text{TMpyP})^{4+}$. This form of the porphyrin in which two of the pyrrole nitrogens are protonated is referred to as the neutral porphyrin or free base form, PH_2^{4+} .

Since the change of nickel coordination number from four to five involves a change in spin state, the first step in the above mechanism is likely to be rate determining. Applying the steady-state approximation to $\text{Ni}(\text{P})(\text{H}_2\text{O})^{4+}$, we obtain

$$\frac{1}{\tau} = k_1[\text{H}_2\text{O}] \left(1 + \frac{1}{K_{12}} \right) \quad (3)$$

which leads to $k_1 = 2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. It has been previously shown that $k_1 = 6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the planar to octahedral conversion of $\text{Ni}(2,3,2\text{-tet})^{2+}$ through the addition of water molecules.⁸⁻¹⁰ The porphyrin environment evidently accelerates the uptake of water molecules and the concomitant spin-state change as compared to (2,3,2-tet), but the effect is not a pronounced one.

From the values of k_1 and K_{12} we can calculate the reverse rate constants ($k_r = k_{-1}k_{-2}/k_2[\text{H}_2\text{O}] = k_{-1}/K_2$) for the two systems where $K_2 = [\text{Ni}(\text{P})(\text{H}_2\text{O})_2^{4+}]/[\text{Ni}(\text{P})(\text{H}_2\text{O})^{4+}][\text{H}_2\text{O}]$. For the $\text{Ni}(2,3,2\text{-tet})^{2+}$ system $k_r = 1 \times 10^4 \text{ s}^{-1}$ while $k_r = 2 \times 10^5 \text{ s}^{-1}$ for $\text{Ni}(\text{TMpyP})^{4+}$. The rate enhancement by the porphyrin ligand may reflect both a smaller value of K_2 and a larger value of k_{-1} . It is known that the porphyrin environment stabilizes a coordination number of five for certain metal ions such as zinc(II) and high-spin iron(II) and iron(III) presumably because steric restrictions force the metal out of the porphyrin plane.¹¹ The ionic radius of nickel(II) is such as to allow it to remain in plane. Therefore, while it is possible that $\text{Ni}(\text{P})(\text{H}_2\text{O})^{4+}$ is more stable relative to $\text{Ni}(\text{P})(\text{H}_2\text{O})_2^{4+}$ than is $\text{Ni}(2,3,2\text{-tet})(\text{H}_2\text{O})^{2+}$ to $\text{Ni}(2,3,2\text{-tet})(\text{H}_2\text{O})_2^{2+}$, there is no direct evidence for this effect. It is known, however, that porphyrins exert a marked labilizing influence¹²⁻¹⁶ on the bond between a metal and its axial ligands and we might therefore anticipate that k_{-1} would be larger for $\text{Ni}(\text{P})(\text{H}_2\text{O})^{4+}$ than for $\text{Ni}(2,3,2\text{-tet})(\text{H}_2\text{O})^{2+}$.

Protonation of $\text{H}_2(\text{TMpyP})^{4+}$. In contrast to the diacid form of most porphyrins, which is violet, the diacid form of the meso-substituted porphyrins such as TMpyP is green in solution.¹⁷ Evidence has also been presented that the monoacid form of the meso-substituted porphyrins is never present in significant concentrations relative to the free base or diacid forms.¹⁸ More recent experiments have failed to confirm this conclusion for water-soluble porphyrins; these studies show instead that the monoacid form of the meso-substituted porphyrins is in fact present in aqueous solution although only over a very limited pH range.^{4,19} That isosbestic points are obtained during the spectrophotometric ti-

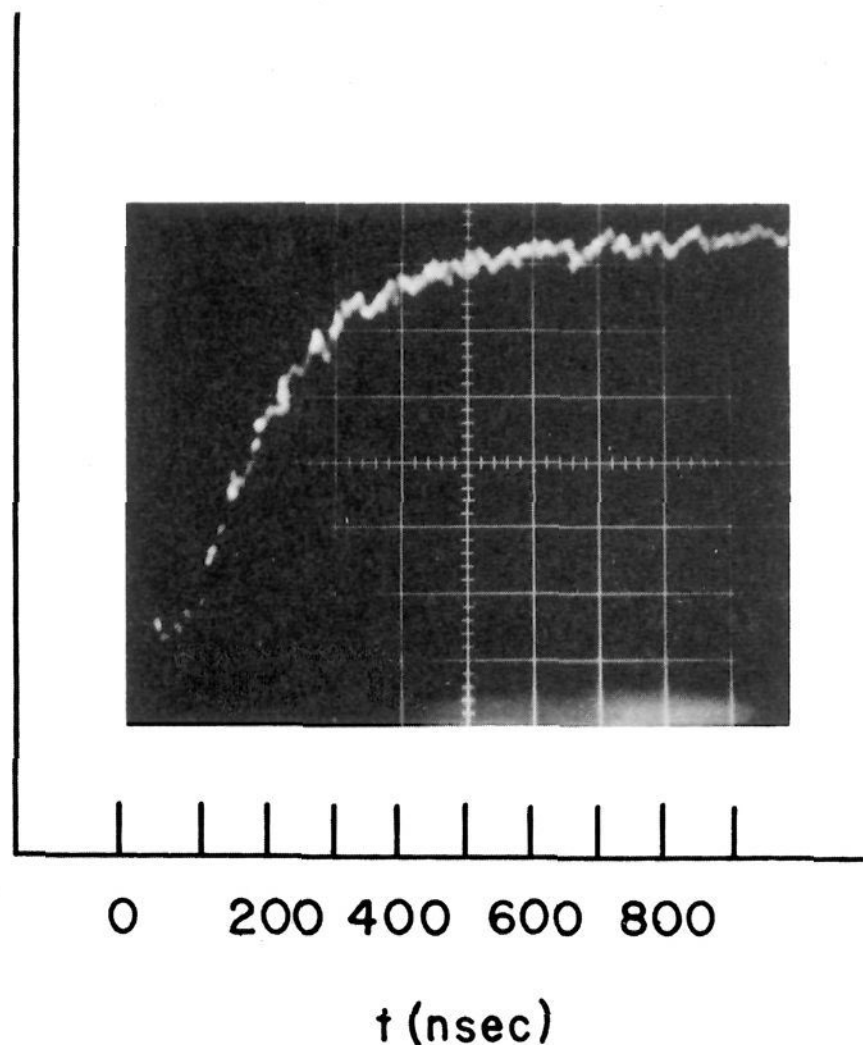
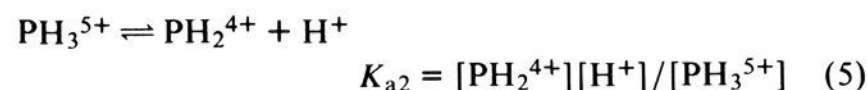
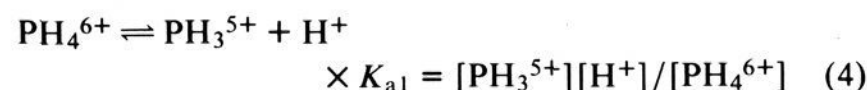


Figure 2. An oscillograph of a relaxation experiment as obtained by the laser Raman temperature-jump technique for the equilibration of the various acid forms of TMpyP. The conditions are: $[\text{TMpyP}]_{\text{total}} = 1.2 \times 10^{-4} \text{ M}$, $[\text{H}^+] = 1.94 \times 10^{-3} \text{ M}$, $\mu = 0.7 \text{ M}$, and $T = 5 \text{ }^\circ\text{C}$. This effect was obtained at 446 nm and the observed relaxation time for this solution is 140 ns.

tration of TMpyP in the Soret region^{6,19} implies that although three porphyrin forms PH_2^{4+} , PH_3^{5+} , and PH_4^{6+} are present under the conditions used, two of these forms (probably the latter two) have very similar spectra in the Soret region. Baker et al. have shown that pH-invariant isosbestic points are not obtained in the visible region.¹⁹

We have conducted a titration experiment at 5 °C and $\mu = 0.7 \text{ M}$ in NaCl and have obtained results qualitatively similar to those obtained by Baker et al. at a higher temperature.¹⁹ The relevant equilibria are shown in eq 4 and 5.



Consistent with the above equilibria, spectrophotometric titration in the visible region did not lead to a set of pH-invariant isosbestic points (Figure 3). Equation 6

$$\frac{1}{(A_b - A)} = \frac{K_{a2}}{(A_b - A_m)[\text{H}^+]} + \frac{1}{(A_b - A_m)} \quad (6)$$

where A_b and A_m are the absorbances of the free base and monoacid forms at a given total concentration of the porphyrin and A is the measured absorbance, was used to analyze the high-pH data at 519 nm. A plot of $1/(A_b - A)$ vs. $1/[\text{H}^+]$ is shown in Figure 4 and leads to a value of $\text{p}K_{a2} = 2.3$ at 5 °C and $\mu = 0.7 \text{ M}$. A value of $\text{p}K_{a1} = 1.2$ was estimated from the remaining data. We repeated the titration experiments at 25 °C and $\mu = 0.7 \text{ M}$ and obtained $\text{p}K_{a1} = 0.7$ and $\text{p}K_{a2} = 1.8$ in good agreement with the values of 0.7 and 2.0 obtained by Baker et al. at 26 °C.¹⁹

A model suggested by Fleischer accounts for the unusual color change when free base meso-substituted porphyrins

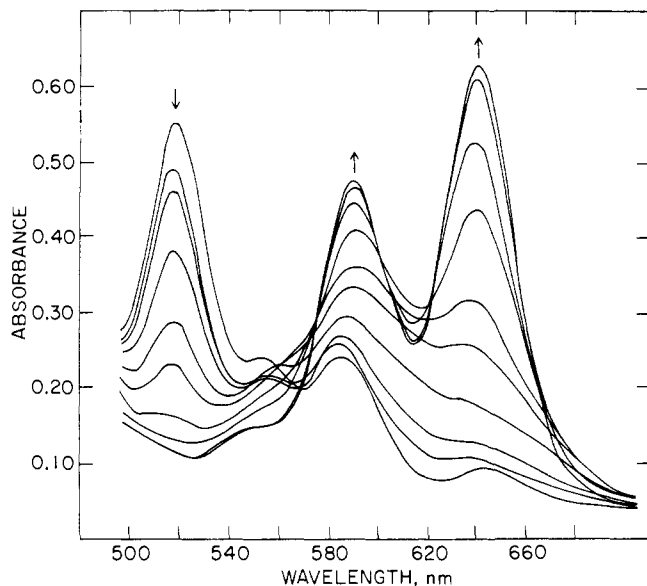


Figure 3. Absorption spectra of TMpyP in the visible region when titrated with HCl at $\mu = 0.7$ M, 5 °C. The spectra cover the pH range of 0.3–7.0. The arrows in the figure show the influence of decreasing pH on the various absorption bands. The porphyrin concentration in this study was 3.57×10^{-5} M.

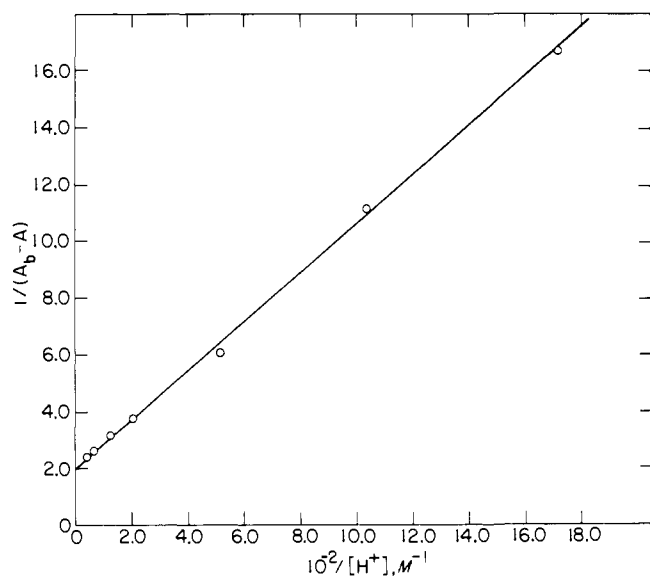


Figure 4. Plot of $1/(A_b - A)$ vs. $1/[H^+]$ to determine K_{a2} at 5 °C.

are converted to acid forms, for the spectral similarity of PH_3^{5+} and PH_4^{6+} , and for the relative instability of the monoacid form in solution.¹⁷ The protonation of a pyrrole nitrogen to form the PH_3^{5+} species involves a large change in the porphyrin structure. The van der Waals and coulombic repulsions among the three porphyrin-core hydrogens lead to a loss of planarity of the ring system. The porphyrin skeleton is thus partially buckled allowing for interactions between the pyridyl (or phenyl) substituents at the meso positions and the porphyrin π system. This interaction is believed to be the source of the green color.¹⁷ Furthermore, the loss of planarity of the porphyrin skeleton exposes the heretofore unprotonated nitrogen thereby diminishing the repulsive forces which arise upon further protonation.

We have conducted relaxation experiments for TMpyP at 5 and 25 °C and $\mu = 0.7$ M using the laser Raman temperature-jump technique. Plots of τ^{-1} vs. $[H^+]$ are shown in Figure 5. Outside the hydrogen ion concentration range

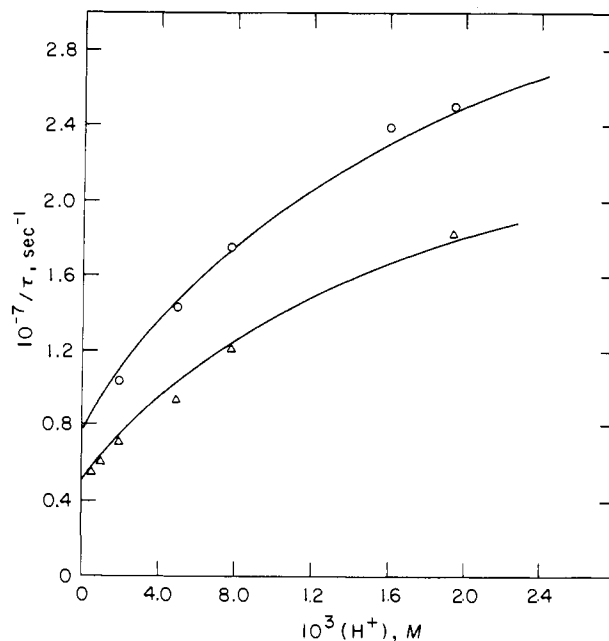


Figure 5. Plot of τ^{-1} vs. $[H^+]$ from temperature-jump data at $\mu = 0.7$ M. The circles represent studies at 25 °C and the triangles at 5 °C.

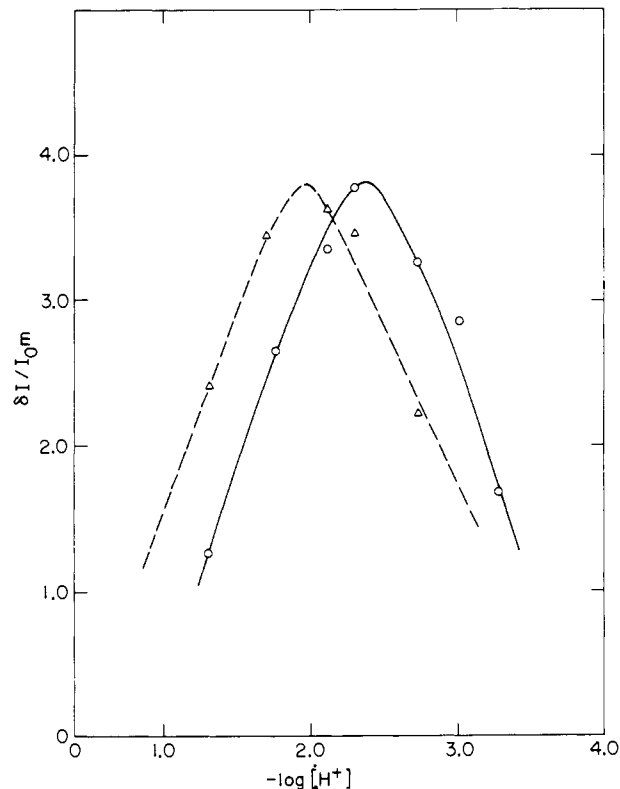


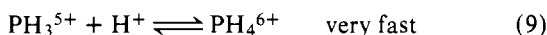
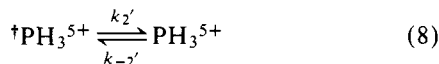
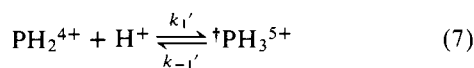
Figure 6. A plot of the normalized amplitudes of relaxation effects as a function of $[H^+]$. The broken curve is the 25 °C data and the unbroken curve is for data obtained at 5 °C.

shown in this figure, the amplitude of the relaxation effect decreases rapidly to very small levels. The dependence of the amplitude on hydrogen ion concentration is shown in Figure 6. The amplitude maxima occur at $-\log [H^+] = 2.0$ at 25 °C and 2.4 at 5 °C. All other conditions remaining constant, the sudden temperature rise produced in a temperature-jump experiment leads to the largest change in concentration of the porphyrin species (i.e., the largest relaxation amplitude) when the concentrations of PH_2^{4+} and PH_3^{5+} are about equal.²⁰ Thus, the amplitude profile pro-

vides a set of titration data and the pK_{a2} estimates obtained from the amplitudes are in good agreement with the pK_{a2} values determined spectrophotometrically.

The above model for porphyrin protonation leads to three reaction mechanisms. The first mechanism involves proton attack on the planar (or near planar) porphyrin molecular ion to form the unstable planar species $\dagger\text{PH}_3^{5+}$. This form then undergoes the buckling process described above to form PH_3^{5+} which adds a proton in a very rapid step to form PH_4^{6+} .

Mechanism I:

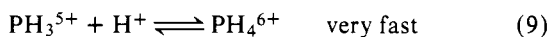
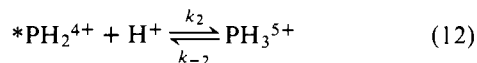
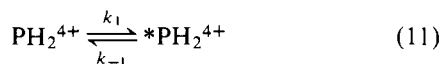


By using standard techniques²⁰ the following expression is obtained for the reciprocal relaxation time for the above mechanism.

$$\tau^{-1} = \frac{k_{1'}k_{2'}[\text{H}^+]}{k_{-1'} + k_{2'}} + \frac{k_{-1'}k_{-2'}}{(1 + [\text{H}^+]/K_{a1})(k_{-1'} + k_{2'})} \quad (10)$$

A second mechanism involves the free base porphyrin existing in two forms, a planar form (PH_2^{4+}) and a buckled form ($*\text{PH}_2^{4+}$). The proton preferentially attacks the buckled form because the nitrogen atom is partially exposed to form PH_3^{5+} . The monoacid form then adds a proton in a rapid step.

Mechanism II:

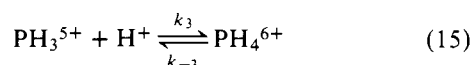
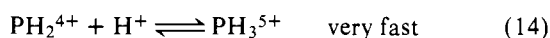


The reciprocal relaxation for this mechanism is given by eq 13.

$$\tau^{-1} = \frac{k_1k_2[\text{H}^+]}{k_{-1} + k_2[\text{H}^+]} + \frac{k_{-1}k_{-2}}{(1 + [\text{H}^+]/K_{a1})(k_{-1} + k_2[\text{H}^+])} \quad (13)$$

The above two mechanisms assume that reaction 5 is rate determining. A third mechanism that needs to be considered is one in which reaction 4 is rate determining (but with the change in porphyrin structure still occurring in reaction 5).

Mechanism III:



Under the conditions used in our experiments the reciprocal relaxation time for this mechanism is given by eq 16.

$$\tau^{-1} = \frac{k_3[\text{H}^+]^2}{K_{a2} + [\text{H}^+]} + k_{-3} \quad (16)$$

All the above expressions for the relaxation time assume that $[\text{H}^+]$ is much larger than the total porphyrin concentration. Mechanism I (eq 10) predicts that the reciprocal relaxation time increases with increasing $[\text{H}^+]$, mechanism II (eq 13) predicts an approach to rate saturation with in-

Table I. Rate Constants for the Protonation of TMpyP

	5 °C	25 °C
k_1, s^{-1}	3.4×10^7	4.6×10^7
k_{-1}, s^{-1}	1.0×10^9	1.2×10^9
$k_2, \text{M}^{-1} \text{s}^{-1}$	4.5×10^{10}	5.0×10^{10}
k_{-2}, s^{-1}	5.0×10^6	8.0×10^6

creasing $[\text{H}^+]$, while mechanism III (eq 16) predicts a second-order dependence on $[\text{H}^+]$ when $K_{a2} \gg [\text{H}^+]$ and a linear dependence on $[\text{H}^+]$ when $[\text{H}^+] \gg K_{a2}$. Evidently the kinetic data (Figure 5) are consistent with mechanism II but not with mechanism I or III (the expression for the reciprocal relaxation time for mechanism II is derived in the Appendix). The curves drawn through the experimental points in Figure 5 were calculated from eq 13 using the rate constants listed in Table I and the values of K_{a1} obtained from the titration data. The agreement between the experimental data and the calculated curve is satisfactory.

The results of a recent study²¹ of the protonation reactions of $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine, $\text{H}_2(\text{TPP})$, in 90% (v/v) DMSO- H_2O have been interpreted in terms of a model in which the monoacid form is never present in significant amounts. Relaxation times measured for the protonation reactions of $\text{H}_2(\text{TPP})$ in this mixed solvent system were of the order of 100 μs compared to the 100-ns relaxation times observed in the present study. The kinetic data for $\text{H}_2(\text{TPP})$ were interpreted in terms of a relatively rapid proton addition to the free base followed by the slower addition of a proton to the monoacid form. The data are not necessarily inconsistent with the results presented here considering the difference in the media used and the fact that the rate of porphyrin buckling measured by us for TMpyP is more rapid than the rate-determining process in the Hibbert and Hunte study.

Returning to mechanism II, reaction 12 involves protonation of a basic site which is poised to accept the proton. We might anticipate that this process would be at or near the diffusion-controlled limit. Diffusion-controlled ion combination in solution in the absence of external fields has been considered by Debye.²² The theory encompasses the effect of a finite radius for the reacting species and a spherical electrostatic potential of interaction. The expression for the rate constant for a diffusion encounter is (in units of $\text{M}^{-1} \text{s}^{-1}$)

$$k_{\text{diff}} = \frac{4\pi N_0}{1000} a_{ij}(D_i + D_j)\Phi_{ij}$$

where N_0 is Avogadro's number, a_{ij} is the distance of closest approach of the reacting species (which are assumed to be spherical), D_i and D_j are the diffusion coefficients of the reacting species, and Φ_{ij} is a function which depends upon the interaction potential. The function Φ_{ij} has been calculated for a simple electrostatic model in water ($\epsilon = 79$, $T = 298 \text{ K}$), and plots have been constructed of $k/(D_i + D_j)$ as a function of a_{ij} for ions of different charge type.²³ Although this model is a rather rough approximation to our system, it will provide some insight into whether the value of k_2 derived from the kinetic data is reasonable.

The formal charge type of the porphyrin species PH_2 is +4. However, the charges are localized at four positions on the periphery of the molecule and it would be valuable to have an estimate of the effective charge of this type of porphyrin. The dimerization of porphyrins and metalloporphyrins having formal charges of -4 have been studied,^{4,24} and the aggregation has been considered as a function of ionic strength.²⁵ Application of the Debye-Hückel limiting law showed that the porphyrins behaved as ions of charge less

than two. The relative rates of substitution reactions of $\text{Co}^{\text{III}}(\text{TMpyP})$ lead to the conclusion that this ion, having a formal charge of +5, has an effective charge type of between +1 and +2.¹² Therefore, it is probably an overestimate to consider PH_2 as a +2 ion in determining k_{diff} . Nevertheless, using this value and taking a_{ij} as 4 Å and $D_{\text{H}^+} + D_{\text{PH}_2} \approx D_{\text{H}^+} = 9.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, we obtain $k_{\text{diff}} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. For comparison, the measured rate constant for the protonation of $\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ at 10 °C and $\mu = 0.1 \text{ M}$ is $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.²⁶ Since our study involves an ion of smaller effective charge and was conducted at an ionic strength of 0.7 M, our derived value of k_2 , although large, is not unreasonable.

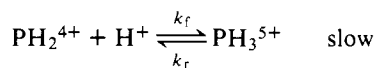
The ratio $k_{-1}/k_1 = 30$ at 5 °C and 26 at 25 °C. Therefore, our results suggest that less than 5% of the free base porphyrin exists in the nonplanar form at any pH significantly above $\text{p}K_{\text{a}2}$. For any mechanism to be acceptable it must predict a large ratio of k_{-1}/k_1 or else we would expect to observe the nonplanar form spectrophotometrically throughout the pH range. The ratio $k_{-1}k_{-2}/k_1k_2$ provides a kinetic estimate of $K_{\text{a}2}$ and although the value of $\text{p}K_{\text{a}2}$ (kinetic) = 2.4 at 25 °C is only in fair agreement with the value obtained from the spectrophotometric and amplitude titrations, the value of $\text{p}K_{\text{a}2}$ (kinetic) = 2.5 at 5 °C is in excellent agreement with the result obtained by other techniques.

We conclude that mechanism II is consistent with the known acid-base properties of TMpyP. In this work we have determined the rate constant for the buckling of the porphyrin ring system to be $4.6 \times 10^7 \text{ s}^{-1}$ at 25 °C and $2.4 \times 10^7 \text{ s}^{-1}$ at 5 °C leading to $E_a \sim 2.5 \text{ kcal mol}^{-1}$. Although this estimate of the activation energy should be regarded as tentative at this time, its magnitude does suggest that the barrier to porphyrin ring ruffling is not large. In this connection it is tempting to propose that the reaction of the free base form of the porphyrin with metal ions also involves buckling of the porphyrin ring system. The observed kinetics, however, do not indicate a rate-determining ring buckling in the complex formation reactions that have been studied.

Acknowledgment. This research was performed in part at Brookhaven National Laboratory and was supported by the Energy Research and Development Administration, the National Institutes of Health (Research Grant GM-17574), the Research Corporation through a Cottrell College Science Grant, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Appendix

Derivation of the Relaxation Expression for Mechanism II. For the two-step process



the rate law is

$$\frac{-d[\text{PH}_2^{4+}]}{dt} = k_f[\text{PH}_2^{4+}][\text{H}^+] - k_r[\text{PH}_3^{5+}]$$

Neglecting the charges on the porphyrin species and defining

$$[\text{PH}_2] = [\text{PH}_2] + \delta[\text{PH}_2]$$

$$[\text{PH}_3] = [\text{PH}_3] + \delta[\text{PH}_3]$$

$$[\text{PH}_4] = [\text{PH}_4] + \delta[\text{PH}_4]$$

$$[\text{H}^+] = [\bar{\text{H}}^+] + \delta[\text{H}^+]$$

where [] refers to equilibrium concentrations we obtain

$$-\frac{d\delta[\text{PH}_2]}{dt} = k_f\{\text{PH}_2\}\delta[\text{H}^+] + [\bar{\text{H}}^+]\delta[\text{PH}_2] - k_r\delta[\text{PH}_3]$$

The conservation equations are

$$0 = \delta[\text{PH}_2] + \delta[\text{PH}_3] + \delta[\text{PH}_4]$$

$$0 = \delta[\text{H}^+] + \delta[\text{PH}_3] + 2\delta[\text{PH}_4]$$

Moreover since $[\text{PH}_3][\text{H}^+] = K_{\text{a}1}[\text{PH}_4]$ it follows that

$$[\text{PH}_3]\delta[\text{H}^+] + [\bar{\text{H}}^+]\delta[\text{PH}_3] = K_{\text{a}1}\delta[\text{PH}_4]$$

These equations together with the relaxation expression for systems returning to equilibrium after a small perturbation (Langevin equation)

$$\frac{d\delta c}{dt} = \frac{-\delta c}{\tau}$$

give

$$\tau^{-1} = k_f[\text{H}^+] + \frac{k_r}{(1 + [\text{H}^+]/K_{\text{a}1})}$$

provided $[\text{H}^+]$ is much larger than the total porphyrin concentration.

The rate constants k_f and k_r are composites of the rate constants shown in mechanism II. Applying the steady-state approximation to $[\text{*PH}_2]$, we obtain

$$[\text{*PH}_2] = \frac{k_1[\text{PH}_2] + k_{-2}[\text{PH}_3]}{k_{-1} + k_2[\text{H}^+]}$$

This leads directly to

$$\tau^{-1} = \frac{k_1k_2[\text{H}^+]}{k_{-1} + k_2[\text{H}^+]} + \frac{k_{-1}k_{-2}}{(1 + [\text{H}^+]/K_{\text{a}1})(k_{-1} + k_2[\text{H}^+]})$$

References and Notes

- (1) (a) Ithaca College. Research Collaborator, Brookhaven National Laboratory. (b) Brookhaven National Laboratory. (c) University of Rochester. Research Collaborator, Brookhaven National Laboratory.
- (2) J. V. Beitz, G. W. Flynn, D. H. Turner, and N. Sutin, *J. Am. Chem. Soc.*, **92**, 4130 (1970).
- (3) (a) D. H. Turner, G. W. Flynn, N. Sutin, and J. V. Beitz, *J. Am. Chem. Soc.*, **94**, 1554 (1972); (b) D. H. Turner, R. Yuan, G. W. Flynn, and N. Sutin, *Biophys. Chem.*, **2**, 385 (1974).
- (4) (a) R. F. Pasternack, P. R. Huber, P. Boyd, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G. C. Ventura, and L. deC. Hinds, *J. Am. Chem. Soc.*, **94**, 4511 (1972); (b) R. F. Pasternack, *Ann. N.Y. Acad. Sci.*, **206**, 614 (1973).
- (5) R. F. Pasternack, E. G. Spiro, and M. Teach, *J. Inorg. Nucl. Chem.*, **36**, 599 (1974).
- (6) P. Hambright and E. B. Fleischer, *Inorg. Chem.*, **9**, 1757 (1970).
- (7) J. F. Kirner, J. Garofalo, Jr., and W. R. Scheidt, *Inorg. Nucl. Chem. Lett.*, **11**, 107 (1975).
- (8) K. J. Ivin, R. Jamison, and J. J. McGarvey, *J. Am. Chem. Soc.*, **94**, 1763 (1972).
- (9) C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **95**, 7177 (1973).
- (10) G. W. Hoffman, *Rev. Sci. Instrum.*, **42**, 1643 (1971).
- (11) J. L. Hoard, *Science*, **174**, 1295 (1971).
- (12) R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, **14**, 866 (1975).
- (13) (a) R. F. Pasternack and M. A. Cobb, *J. Inorg. Nucl. Chem.*, **35**, 4327 (1973); (b) R. F. Pasternack and M. A. Cobb, *Biochem. Biophys. Res. Commun.*, **51**, 507 (1973).
- (14) E. B. Fleischer, S. Jacobs, and L. Mestichelli, *J. Am. Chem. Soc.*, **90**, 2527 (1968).
- (15) (a) E. B. Fleischer and M. Krishnamurthy, *J. Coord. Chem.*, **2**, 89 (1972); (b) *J. Am. Chem. Soc.*, **93**, 3784 (1971).
- (16) G. B. Kolski and R. A. Plane, *J. Am. Chem. Soc.*, **94**, 3740 (1972).
- (17) E. B. Fleischer, *Acc. Chem. Res.*, **3**, 105 (1970), and references cited therein.
- (18) E. Fleischer and L. Webb, *J. Phys. Chem.*, **67**, 1131 (1963).
- (19) H. Baker, P. Hambright, and L. Wagner, *J. Am. Chem. Soc.*, **95**, 5942 (1973).
- (20) M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry", Vol. VIII, Part II, 2d ed, A. Weissberger, Ed., Interscience Publishers, New York, N.Y., 1963.
- (21) F. Hibbert and K. P. P. Hunte, *J. Chem. Soc., Chem. Commun.*, 728

- (1975).
 (22) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).
 (23) M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Prog. React. Kinet.*, **2**, 286 (1964).

- (24) R. F. Pasternack, L. Francesconi, D. Raff, and E. Spiro, *Inorg. Chem.*, **12**, 2606 (1973).
 (25) R. F. Pasternack, G. Engasser, and D. Raff, unpublished results.
 (26) G. Ertl and H. Gerischer, *Z. Elektrochem.*, **66**, 560 (1962).

Nitrosylmetalloporphyrins. III. Synthesis and Molecular Stereochemistry of Nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(1-methylimidazole)iron(II)^{1,2}

W. Robert Scheidt* and Paul L. Piciulo

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. Received June 2, 1975

Abstract: The preparation and molecular structure of nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(1-methylimidazole)iron(II) are described. The title compound crystallizes, as the chloroform solvate, in the orthorhombic space group $P2_12_12_1$ with $a = 17.733$ (13), $b = 25.339$ (22), and $c = 9.752$ (10) Å. Calculated and experimental densities are 1.35 and 1.36 g/cm³, respectively, at 20 °C. Measurement of diffracted intensities employed ω scanning with Mo $K\alpha$ radiation on a four-circle diffractometer; the 4148 reflections retained as observed were used for the determination and refinement of structure. Final discrepancy indices are $R_1 = 0.052$ and $R_2 = 0.074$. Equatorial bond distances in the FeN₆ coordination group average to 2.008 Å; Fe-N_{NO} is 1.743 (4) Å. The Fe-N-O bond angle is $\sim 140^\circ$. The Fe-N_{Im} bond trans to the nitric oxide is quite long at 2.180 (4) Å. The importance of these results in understanding some properties of nitrosylhemoglobin is discussed.

Complexes of metalloporphyrins with diatomic molecules have been intensively investigated, primarily as model heme protein systems.³⁻⁶ We have been investigating the reactions and stereochemistry of nitrosylmetalloporphyrins and report herein the preparation and molecular stereochemistry of nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinato(1-methylimidazole)iron(II), to be written as Fe(TPP)(NO)(1-MeIm). With nitric oxide and 1-methylimidazole as the axial ligands, Fe(TPP)(NO)(1-MeIm) is a particularly cogent model system for the coordination group geometry of nitrosyl heme protein derivatives. We compare the stereochemistry and spectral properties of Fe(TPP)(NO)(1-MeIm) with the closely related five-coordinate derivative nitrosyl- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatoiron(II).¹ The results are discussed in terms of some observations recently made on nitrosylhemoglobin.

Experimental Section

Preparation and Characterization of ON(1-MeIm)FeTPP. All reactions were carried out under argon using Schlenk glassware. ClFeTPP was prepared as previously described.⁷ A solution of 0.20 g of ClFeTPP in 50 ml of dry chloroform and 8 ml of 1-methylimidazole was carefully degassed. Nitric oxide, purified by passing through a KOH column, was bubbled into the solution for 15–20 min. Excess NO was then removed by bubbling argon through the solution and dry methanol slowly added until crystals of Fe(TPP)(NO)(1-MeIm) appeared. Filtration, under argon, yielded the crystalline complex. These bulk preparations were frequently contaminated with varying amounts of the five-coordinate complex ONFeTPP, as judged from ir spectra. Pure six-coordinate complexes could always be prepared by very slow crystallizations as described below.

The infrared spectrum of Fe(TPP)(NO)(1-MeIm) was recorded on a Perkin-Elmer 457 spectrometer using a KBr pellet; the strong absorption at 1625 cm⁻¹ was assigned as the NO stretching frequency. The absorption spectrum of Fe(TPP)(NO)(1-MeIm) shows peaks at 4150, 4600, 5450, 5800 (shoulder), and 6425 Å with extinction coefficients of 181×10^3 , 18.1×10^3 , 9.72×10^3 , 6.0×10^3 , and 1.12×10^3 M⁻¹ cm⁻¹, respectively. The magnetic susceptibility is 2.2–2.3 μ_B . Anal. (FeC₄₈H₃₄N₇O·CHCl₃) calcd, C, 65.38; H, 3.92; N, 10.89; Fe, 6.2. (FeC₄₈H₃₄N₇O·½CHCl₃)

calcd, C, 69.31; H, 4.14; N, 11.67; Fe, 6.6; found, C, 67.04; H, 3.95; N, 11.53; Fe, 5.9.

Crystallographic and X-Ray Data. Crystals of Fe(TPP)(NO)(1-MeIm) suitable for x-ray study were grown by vapor diffusion of anhydrous methanol into a chloroform solution of the complex, prepared in situ, under an argon-nitric oxide atmosphere. Lattice constants, $a = 17.733$ (13) Å, $b = 25.339$ (22) Å, and $c = 9.752$ (10) Å (λ 0.71069) came from a least-squares refinement that utilized the setting angles of 30 reflections, each collected at $\pm 2\theta$, at $20 \pm 1^\circ$. The calculated density for a cell content of 4[FeON₇C₄₈H₃₄·CHCl₃] is 1.35 g/cm³; the experimental density is 1.36 g/cm³.

X-ray intensity data were collected using graphite-monochromated Mo $K\alpha$ radiation on a Syntex P1 diffractometer. A freshly prepared crystal with approximate dimensions of $0.8 \times 0.5 \times 0.3$ mm was mounted in a thin-walled glass capillary filled with argon. All independent reflections in the range $3 < 2\theta < 55^\circ$ ($\sin \theta/\lambda < 0.65$ Å⁻¹) were measured by the ω -scan technique.⁸ The ω scan was performed in 0.027° increments of ω and extended $\pm 0.15^\circ$ from the calculated peak position. When the observed peak position did not coincide with the calculated peak position, one or two additional steps were taken to assure centering of the scan. Background counts were taken at $\pm 0.5^\circ$ ω displacement from the peak center for a duration of one-half the time required for the scan. Four standard reflections that were well distributed in reciprocal space were used for periodic checking (every 50 reflections) on the alignment and possible deterioration of the crystal; only random variations in intensity were noted during the course of measurements. With a linear absorption coefficient of 0.56 mm⁻¹ for Mo $K\alpha$ radiation, the maximum error in any structure amplitude resulting from the neglect of absorption corrections was seen to be <3.5%. Consequently, intensity data were reduced and standard deviations calculated as described previously.⁹ Data was retained as objectively observed if $F_o > 3\sigma(F_o)$; 4148 data were retained, some 81% of the total number possible in the range of 2θ examined.

The structure was solved by the usual heavy-atom method.¹⁰ During the latter stages of structure development, it became apparent that the chloroform molecule of crystallization was disordered. The disorder appeared to be rotational disorder, and was approximated by assigning four positions for the three chlorine atoms. Subsequent unconstrained refinement of the occupancy factors for these atoms gave 2.82 for the sum, to be compared to the theoretical value of 3.00.