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Temperature-Jump Kinetic Study of a Ferric Porphyrin Monomer-Dimer Equilibrium in Aqueous Solution

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Stability constants have been measured for the monomer-dimer equilibrium of a number of different ferric porphyrins in aqueous solution. The actual species observed and their equilibrium behavior can be described as[2]

$$\mathrm{PFe(H_2O) = PFe(OH)^- + H^+} \tag{1}$$

$$\mathrm{PFe(OH)^- + OH^- = PFe(OH)_2{}^{2-}} \tag{2}$$

$$\mathrm{2PFe(OH)_2{}^{2-} = [(PFe)_2(OH)_2O]^{4-} + H_2O} \tag{3}$$

$$\mathrm{2PFe(OH)^- = [(PFe)_2O]^{2-} + H_2O} \tag{4}$$

$$\mathrm{2FeP(H_2O) = [(PFe)_2O]^{2-} + 2H^+ + H_2O} \tag{5}$$

With an ethylenediamine-substituted protoporphyrin (ENP),[3] reactions 1-3 occur. With a disulfonated deuterohemin (DPS_2),[4] reactions 1 and 4 are found while for the tetrasulfonated tetraphenylporphine ($TPPS_4$),[5] the evidence is only for process 5. The tetra-N-methylated tetrapyridylporphine (TMTPyP)[6] is reported to be similar to ENP, with several unusual features. A stopped-flow study of the kinetics of monomerization of the $FeTPPS_4$ dimer has been done.[5] Previous relaxation studies in this area[3,4,7,8] have involved porphyrins or metalloporphyrin dimers held together by moderate electrostatic polarization forces, in contrast to the oxy bridges found in iron porphyrin dimers. To gain a better understanding of the iron porphyrin monomer-dimer phenomena, we report a temperature-jump kinetic study on reaction 5 with $Fe^{III}TPPS_4$.

Experimental Section

$Fe^{III}TPPS_4$ was made by literature methods.[5] The equilibrium and kinetic studies were run at 20° with 0.05 *M* $NaNO_3$ and 0.02 *M* PIPES buffer. Equilibrium measurements were done with a Beckman Acta III recording spectrophotomer. The equilibrium constant for $FeTPPS_4$ dimerization (reaction 5) was determined in the same manner as described by other workers.[5] Our pK_D of 8.6 ± 0.2 is in good agreement with the value of 8.2 ± 0.3 at $\mu = 0.1$ (20°) reported earlier[5] while kinetic data were collected with a temperature-jump apparatus constructed in this laboratory.[9] The kinetics were followed at wavelengths between 390 and 430 nm, at pH values from 6.09 to 7.50, with total porphyrin concentrations 8.2×10^{-7}–1.7×10^{-5} *M*. The rate constants (±10%) were obtained from transmittance–time data using a nonlinear least-squares program.

Results and Discussion

A spectrophotometric titration of $Fe^{III}TPPS_4$ with base between pH 5 and 8 gave an excellent isosbestic point at 406 nm, and the absorption spectra were unchanged between pH 1 and 5 and from pH 8 to 12. This indicates that only the unhydrolyzed forms of the iron monomer and dimer are in significant concentration. No relaxations were found below pH 5 or above pH 8, where the monomer and dimer forms, respectively, predominate. Between pH 6 and 8 two absorbance changes were observed. The first, with a relaxation time of a few microseconds, was too fast to be resolved. The second, in the 100-msec range, was dependent on pH and total porphyrin concentration.

Assuming a mechanism of the form

$$\mathrm{PFe(H_2O)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{PFe(OH)^- + H^+} \tag{6}$$

$$\mathrm{2PFe(OH)^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{[(PFe)_2O]^{2-} + H_2O} \tag{7}$$

with $PFe(OH)^-$ present as a low concentration intermediate, the reciprocal relaxation time for the slower process, τ^{-1}, is given by the expression

$$\tau^{-1}\left[1 + \frac{4k_1k_2(\mathrm{PFe(H_2O)})}{k_{-1}{}^2(\mathrm{H^+})^2}\right] = \frac{4k_1{}^2k_2}{k_{-1}{}^2}\left[\frac{(\mathrm{PFe(H_2O)})}{(\mathrm{H^+})^2}\right] + k_{-2} \tag{8}$$

The faster process has a more complicated concentration dependence and can be written down by standard methods.[10] Rearrangement of eq 8 yields an expression (Table I and Figure 1) whereby a plot of $(R + 1)/\tau^{-1}$ *vs.* R is linear with a slope of $1/k_1$ and an intercept of $1/k_{-2}$. Here, R is $4(\mathrm{PFe(H_2O)})Q/(\mathrm{H^+})^2$ and Q is the equilibrium constant for eq 5; $Q = 2.5 \times 10^{-9}$ $M = k_1{}^2k_2/k_{-1}{}^2k_{-2}$. A least-squares analysis gives $k_1 = 3.37 \pm 0.17$ sec^{-1} and $k_{-2} = 0.90 \pm 0.05$ sec^{-1} at 20°, the "jump" temperature.

The low-concentration approximation on $PFe(OH)^-$ used in the kinetic derivation is in accord with the observed isosbestic point, which indicates a low concentration of $PFe(OH)^-$ with respect to both $PFe(H_2O)$ and the dimer. The assumption, for example, that eq 6 equilibrates rapidly relative to eq 7 is not consistent with the data.

Our results can be compared with those found for the monomerization of the $Fe^{III}TPPS_4$ dimer, measured by stopped-flow techniques.[5] The observed rate law was first order in dimer, with terms dependent ($k_{-3} = 840$ M^{-1} sec^{-1}) and independent ($k_{-2} = 41$ sec^{-1}) of $(\mathrm{H^+})$. While K_D for this porphyrin depends strongly on ionic strength and temperature,[5] our k_{-2} value (0.9 sec^{-1}) is not in agreement with the stopped-flow results. The acid-dependent term k_{-3} is

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(1) (a) Howard University. (b) NIH.

(2) The total charges of the porphyrin species have been omitted for clarity. For example with $FeTPPS_4$, $(PFe)_2O$ has a net molecular formal charge of 8–, with two ionized tetrasulfonated ferric fragments assigned 3– each and the oxygen of the oxy bridge assigned 2–. (P) represents the porphyrin framework.

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Table I. Dependence of Reciprocal Relaxation Times on Concentration and pH[a]

pH	τ^{-1}, sec^{-1}	$4(\mathrm{PFe(H_2O)})Q/(\mathrm{H^+})^2$
6.09	0.76 ± 0.42	0.012
6.09	1.04 ± 0.12	0.082
6.59	1.48 ± 0.28	0.106
6.09	1.00 ± 0.32	0.220
6.42	1.27 ± 0.14	0.499
6.59	1.37 ± 0.07	0.639
7.05	1.37 ± 0.17	0.738
6.59	1.72 ± 0.1	1.408
6.72	1.68 ± 0.1	1.426
7.75	1.63 ± 0.5	1.75
7.36	1.59 ± 0.22	2.10
7.05	1.77 ± 0.13	2.83
7.09	2.22 ± 0.08	4.22
7.10	2.11 ± 0.1	4.72
7.05	2.09 ± 0.13	5.33
7.10	2.68 ± 0.44	7.07
7.10	2.42 ± 0.18	7.72
7.36	2.97 ± 0.21	12.03

[a] $Q = 2.5 \times 10^{-9}\ M$, $T = 20°$, $\mu = 0.1\ M$.

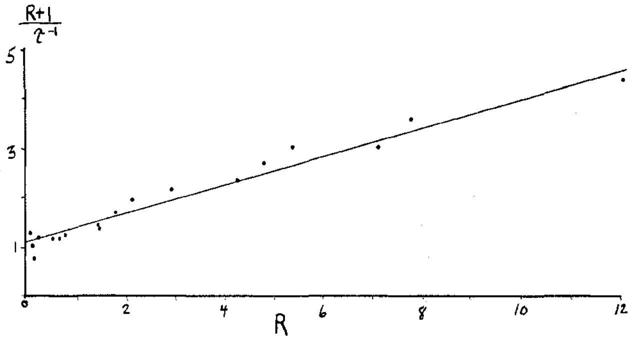

Figure 1. Plot of the kinetic data for the iron porphyrin monomer-dimer reaction at 20°.

usually attributed[11] to the reaction

$$\mathrm{L\text{-}Fe(OH)^- + L\text{-}Fe(H_2O) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [(L\text{-}Fe)_2O]^{2-} + H^+ + H_2O} \qquad (9)$$

where the L represents various ligands coordinated to the ferric ion. We find no evidence of eq 9 making any contribution to the $\mathrm{FeTPPS_4}$ kinetics in the pH range 5-7. The monomerization study was run below pH 3, where such a process could occur.

Our k_{-2} term for $\mathrm{Fe^{III}TPPS_4}$ (0.9 sec^{-1} at 20°) is similar to those found for other iron complexes at 25°, for example,[11] EDTA (1.2 sec^{-1}), HEDTA (4.0), CyDTA (9.0), and $\mathrm{H_2O}$ (0.35). It has been suggested that the attacking nucleophile on such oxy-bridged dimers is a water molecule, which forms an unstable dihydroxy intermediate. Since it has been demonstrated that the Fe-$\mathrm{TPPS_4}$ system, which shows no equilibrium evidence for $\mathrm{[PFe(OH)]^-}$, goes through this species to form the dimer, systems in which there is definite evidence for $\mathrm{[PFe(OH)]^-}$ (ENP, $\mathrm{DPS_2}$, and TMTPyP) might behave in a similar fashion. Studies are underway to prove this point. Preliminary results indicate that five- or six-coordinated $\mathrm{TPPS_4}$-metal complexes do not aggregate in aqueous solution, as found here with the pure monomer and dimer forms of $\mathrm{FeTPPS_4}$. Many four-coordinate $\mathrm{TPPS_4}$ metalloporphyrins dimerize.

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Palladium(II), Platinum(II), and Rhodium(III) Complexes of a Chelating Di(tertiary stibine), 1,3-Bis(diphenylstibino)propane. The Spectrochemical Position of a Distibine Ligand

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Very few coordination complexes of di(tertiary stibine) ligands have been reported[1] in contrast to the extensive studies of the phosphorus and arsenic analogs.[2,3] Bis(diphenylstibino)methane, $\mathrm{Ph_2SbCH_2SbPh_2}$, behaves as a monodentate or bridging bidentate ligand[4] toward class B metals. Replacement of the methylene backbone by dimethylene or trimethylene should increase the tendency of the ligand to function as a chelating diantimony donor, and since all reported attempts to prepare 1,2-bis(diphenylstibino)ethane have failed,[5-7] we have investigated the palladium(II), platinum(II), and rhodium(III) complexes of 1,3-bis(diphenylstibino)propane. This forms part of a general investigation we are making of the donor properties of stibine ligands.[4,8]

Experimental Section

1,3-Bis(diphenylstibino)propane (dsbp) was prepared in ~50% yield by the reaction of sodium diphenylstibine and 1,3-dibromopropane in liquid ammonia.[9] *Anal.* Calcd for $\mathrm{C_{27}H_{26}Sb_2}$: C, 54.5; H, 4.4. Found C, 54.2; H, 4.3; mp 54° (lit. value 52-53°[4]).

$\mathrm{Pd(dsbp)Cl_2}$. Potassium tetrachloropalladate(II) (0.327 g, 1.0 mmol) and dsbp (0.594 g, 1.0 mmol) were stirred together under reflux in a 1:1 mixture of ethanol-dichloromethane for 1 hr, and the yellow product was filtered off, recrystallized from dichloromethane, and dried *in vacuo*. Yield ~75%.

$\mathrm{Pd(dsbp)X_2}$ (X = Br, I, SCN) were obtained similarly in the presence of an excess of NaX. Yields 50-70%.

$\mathrm{Pt(dsbp)X_2}$ (X = Cl, Br, I, SCN) were obtained from sodium tetrachloroplatinate(II), NaX, and dsbp in a water-ethanol-dichloromethane mixture under reflux for 2 hr. Recrystallization from dichloromethane yielded crystalline complexes in 50-70% yield.

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