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Enhancement of Ligand Binding by Iron(III) Deuteroporphyrin (IX) Dimethyl Ester *via* Interaction with 1,10-Phenanthroline at a Site Remote from the Metal Ion

Sir:

It is well established that porphyrins, metalloporphyrins, and porphyrin-like molecules may form donor-acceptor complexes with either good electron donors or good electron acceptors.[1-11] It has also been observed in heme proteins that aromatic moieties of amino acids like phenylalanine, tyrosine, and histidine are often oriented so as to be parallel to the porphyrin ring and are sufficiently close to it that extensive overlap of their π orbitals with those of the porphyrin must occur.[12-16] As part of an effort to learn how such interactions might modify or "tailor" the reactivity of a metal ion held within the macrocycle, we have been investigating the influence of good aromatic electron donors on the ligand binding of metalloporphyrins. Herein we wish to report thermodynamic evidence indicating that the electron donor 1,10-phenanthroline interacts in a 1:1 stoichiometry with the low-spin complex bis(imidazole)deuteroporphyrin (IX) dimethyl ester iron(III) chlorde at a point remote from the metal ion. This results in stabilization of the low-spin complex and suggests a possible model for cooperative oxygen binding in hemoglobin.

The stepwise addition of imidazole to dichloromethane solutions of the high-spin five-coordinate complex deuteroporphyrin(IX) dimethyl ester iron(III) chloride results in changes of the visible absorption spectrum which show isosbestic points. As with tetraphenylporphine iron(III) chloride,[17] the equilibrium that exists may be satisfactorily accounted for by eq 1[18] in which two imidazole molecules dis-

$$\text{Fe(deut)Cl} + 2\text{Im} \rightleftharpoons \text{Fe(deut)Im}_2{}^+\text{Cl}^- \qquad (1)$$

$$\beta_{12} = \frac{[\text{Fe(deut)Im}_2{}^+\cdot\text{Cl}^-]}{[\text{Fe(deut)Cl}][\text{Im}]^2}$$

place the chloride ion to form the low-spin bisimidazole complex. No detectable concentration of the intermediate monoimidazole complex is observed. With the assumption that the bisimidazole complex is a tightly bound ion pair, β_{12} is found to be $7.75 \times 10^5\ M^{-2}$ at 30°, ΔH is −22 kcal/mol, and ΔS is −46 cal/(mol deg). These values are constant over a hundredfold range of concentrations.

In the presence of 1,10-phenanthroline (phen), variation of imidazole concentration results in spectral changes identical with those in the absence of phen except that in the presence of phen the bisimidazole complex is observed to form at lower concentrations of imidazole. Addition of phen to an equilibrium solution increases the proportion of bisimidazole complex, but no spectral changes are observed when phen is added to solutions of Fe(deut)Cl or of the fully formed $\text{Fe(deut)Im}_2{}^+\text{Cl}^-$. This indicates that phen cannot bind to the metal ion directly under these conditions. Variation of phen concentration at constant total porphyrin and imidazole concentrations gives spectral changes with isosbestic points. These spectral changes are accurately rationalized by addition of eq 2 to eq 1 above. Varing concentration over a hundredfold range, K_m is found to be 2.7×10^2

$$\text{Fe(deut)Im}_2{}^+\text{Cl}^- + \text{phen} \rightleftharpoons \text{Fe(deut)Im}_2{}^+\text{Cl}^-\cdot\text{phen} \qquad (2)$$

$$K_m = \frac{[\text{Fe(deut)Im}_2{}^+\text{Cl}^-\text{phen}]}{[\text{Fe(deut)Im}_2{}^+\text{Cl}^-][\text{phen}]}$$

M^{-1}. For reaction 2 ΔH is −7.7 kcal/mol and ΔS = −15 cal/(mol deg). Since isosbestic points are observed in the presence of phen, $\text{Fe(deut)Im}_2{}^+\text{Cl}^-$ and $\text{Fe(deut)Im}_2{}^+\text{Cl}^-\cdot$ phen are assumed to have identical extinction coefficients.

These equilibria data indicate that phen interacts with $\text{Fe(deut)Im}_2{}^+\text{Cl}^-$ to form a 1:1 complex. The lack of change in spectrum for the complex formed indicates that the point(s) of attachment are far removed from the metal ion. $\text{Fe(deut)Im}_2{}^+\text{Cl}^-$ is an ion pair and is probably more polar than Fe(deut)Cl. Since phen is highly polar, one might attribute enhanced formation of $\text{Fe(deut)Im}_2{}^+\text{Cl}^-$ to a general increase in solvent polarity. A number of arguments may be raised against this. First K_m is functionally a good 1:1 constant over a wide range of conditions. Second, we have studied other highly polar species which are not donors such as nitrobenzene and have found that they have virtually no effect over the same concentration range. Third, other less polar aromatic donors including phenanthrene and imidazole itself are currently being studied and are found to behave similarly to phen. It should also be pointed out that we observe similar effects in other solvents and with other porphines such as tetraphenylporphine.

Although these thermodynamic data reveal neither the structure of the interacting species nor the nature of the interactions, it is apparent that the donor molecule phen interacts with the low-spin bisimidazole complex much more strongly than with the high-spin Fe(deut)Cl. Evidently, the site of interaction is far removed from the metal ion, a point made all the more striking by the fact that the bisimidazole complex is stabilized over the reactant despite the greater steric requirement of the bisimidazole complex. Whatever the detailed interpretation of this interaction, it is important to consider the possible biological implications of the ability of such a donor molecule to stabilize the low-spin iron(III) state by interaction remote from the metal ion site. It is well known that the heme sites of hemoglobin bind oxygen cooperatively. This means that when each heme of a hemoglobin molecule binds an oxygen molecule the equilibrium constant for binding subsequent oxygen molecules increases for the other sites. One view of cooperativity is that the binding of oxygen at one site causes a structural change in the protein which enhances the equilibrium constant for binding of oxygen at another site.[19-21] If one considers the state of the iron when oxygen is bound to be low-spin iron(III), it may

be suggested that the binding of oxygen at one site of hemoglobin causes a structural change which juxtaposes aromatic amino acid donor moieties with a heme at another site. Stabilization of the low-spin state may occur at this second site by means analogous to those responsible for the effects of phen reported above. The consequence is that oxygen will be bound more strongly and K_2 will be greater than K_1.

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Photoreduction by Hydrazinium Ions, Quenching by Hydrazines

Sir:

We wish to report that hydrazines, which are reducing agents in thermal processes, quench photoexcited ketones in water efficiently, with little photoreduction; however, certain monoprotonated hydrazinium ions, normally less effective thermal reducing agents, are good photoreducing agents.

Photoreduction of aromatic ketones by amines proceeds *via* rapid initial formation of a charge transfer complex, CTC, characterized by rate constant k_{ir}, followed either by regeneration of the ground state reactants, k_e, or by H transfer and formation of radicals, k_h, eq 1.[1] Formation of

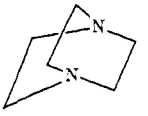
$$\begin{array}{l} \mathrm{Ar,Ar'C{=}O^*(T_1) + R'CH_2NR_2 \longrightarrow [Ar,Ar'\dot{C}{-}\bar{O}\ R'\overset{+\cdot}{C}H_2NR_2]} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \swarrow^{k_e} \quad \downarrow^{k_h} \\ \mathrm{Ar,Ar'C{=}O(S_0) + R'CH_2NR_2 \qquad Ar,Ar'COH + RCHNR_2} \end{array} \qquad (1)$$

the CTC facilitates the subsequent hydrogen transfer, so that ketones which are not photoreduced by alcohols are photoreduced by amines, particularly tertiary amines.[1b,2] Values of k_{ir} increase regularly with increasing electron availability in the amine.[3,4] With very favorable ionization potentials or negative values of σ^+, values of k_{ir} approach diffusion control,[4,5] but the quantum yields for photoreduction may become very small.[4] In such cases the charge transfer complexes are relatively stable and lead to quenching, as the hydrogen transfer requires excessive activation energy. Low electron availability, caused by electron withdrawing substituents, decreases k_{ir}, and may also decrease quantum yield,[4] as insufficient development of positive charge in the CTC fails to facilitate adequately transfer of a proton from α-C.

Preliminary studies of photoreduction in water of 4-benzoylbenzoate anion by some hydrazines, amines, and their protonated forms are summarized in Table I.

Hydrazine is an efficient quencher at pH 12, $k_{ir} = 5.3 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, but it is not a good photoreducing agent, $\varphi \sim 0.01$. At pH 7, where it is 91% monoprotonated, reducing efficiency is increased manyfold, $\varphi = 0.29$. From 0.005 to 0.10 M hydrazine at pH 7, φ rises from 0.14 to 0.31, and a linear plot of $1/\varphi$ *vs.* $1/c$ may be constructed, slope = 0.022 M, intercept = 3.1, limiting quantum yield 0.32, and $k_d/k_{ir} = 0.007\ M$. Methylhydrazine shows, on protonation, a similar increase in quantum yield for photoreduction of the carbonyl compound. However, tetramethylhydrazine shows little more increase in quantum yield than would result from the change in reduction product, from hydrol at pH 12 to pinacol at pH 7.[5] The quantum yield at pH 7 remains low, ~0.026, despite the presence of ample α-CH which normally leads to photoreduction by amines. Tetramethylhydrazine is only 17% protonated at pH 7, and the unprotonated base may be quenching most of the excited ketone. Yet hydrazine and methylhydrazine appeared to show efficient photoreduction when only partly monoprotonated at pH 9. The monoprotonated forms of the polyalk-

Table I. Photoreduction of 0.003 M 4-Benzoylbenzoate by 0.04 M Amine Compound in Water. Effect of pH on Quantum Yield

Compound	pK_a	pH	>NH^{+d} (%)	φ^e	$10^{-8}k_{ir}$,^{f} M^{-1} sec^{-1}
H_2NNH_2	8.07[a]	12	0	0.011	0.53
H_2NNH_2		9	9	0.16	
H_2NNH_2		7	91	0.29	
CH_3NHNH_2	7.87[a]	12	0	0.011	
CH_3NHNH_2		9	7	0.12	
CH_3NHNH_2		7	88	0.21	
$(CH_3)_2NN(CH_3)_2$	6.3[b]	12	0	0.011	
$(CH_3)_2NN(CH_3)_2$		7	17	0.026	
$(CH_3)_2NCH_2CH_2N(CH_3)_2$	9.1[b,c]	12	1	0.73	2.04
$(CH_3)_2NCH_2CH_2N(CH_3)_2$		7	99	1.30	
$(CH_3CH_2)_3N$	10.75[c]	12	5	0.70	2.09
$(CH_3CH_2)_3N$		7	100	0.35	
	8.8[b,c]	12	0	0	1.69
		7	98	~0.003	

[a] Reference 6. [b] Determined by titration. [c] Reference 7. [d] Per cent of monoprotonated form at the indicated pH, calculated from pK_a. [e] The quantum yield for photoreduction by triethylamine at pH 12 was determined by ferrioxalate actinometry at 334 nm, ref 5. This solution was used as a secondary actinometer, irradiated simultaneously with the other solutions on a rotating wheel. Solutions were degassed by the freeze–thaw method and irradiated under argon. [f] Determined by quenching of phosphorescence of 0.008 M ketone by 0.0002 M amino compound in water pH 12, excitation at 350 nm, emission at 450 nm, $\tau_0 = 4.34 \times 10^{-5}$ sec.