by comparison with the analogous H_2-$I_2^*(B^3\Pi_0, v' = 15)$ system.[10] Here, V-T events occur with a cross section of ~1/6 gas kinetic. This is expected to be an upper limit to the V-T rate in ICl*-H_2, since the energy level spacing in ICl* is greater than that in I_2^*. The result is that ~75% of the ICl* which reacts does so from within three vibrational levels of the originally excited level. Figure 2 shows the quantum yield (proportional to k_1) as a function of the excitation energy. About 600 cm^{-1} (3 kT) of vibrational energy increases the rate constant by a factor of e.[11]

Halogen atoms, formed from sufficiently energetic collisions of ICl*, could conceivably be contributing to the measured quantum yields. The dissociation probability, however, should decrease by ~$1/e$ for each 200 cm^{-1} (kT) of vibrational energy,[12] dashed line in Figure 2. (Experiments[13,14] on $I_2(B^3\Pi_0)$ which seem to show higher dissociation quantum yields have not allowed for hot band absorption.) I atoms formed simply recombine, and Cl atoms are mostly scavenged by the fast reaction $Cl + ICl \rightarrow Cl_2 + I$;[15] when ICl is excited 1400 cm^{-1} above dissociation there is a low quantum yield of HCl (Figure 2), implying that, for excitation well below dissociation, radical reactions are not important. Finally, a quenching gas may be added to the system. Experiments with added argon at λ 616.8 nm ($v' = 15$) give quantum yields in very good agreement with those predicted from the measured quenching rate constant for ICl* by Ar $(4.9 \pm 0.5) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (dashed line in Figure 1). These results prove conclusively that radicals are not important, since Ar should not inhibit their reactions, and that $ICl^*(A^3\Pi_1)$ is the reactive species.

The reactivity of ICl* may be related to the fact that the dipole moment changes sign upon excitation[16] to I^-Cl^+. The positive Cl atom, with its partially filled valence shell, might be expected to be very reactive.

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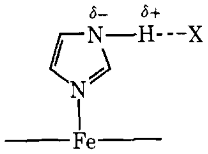
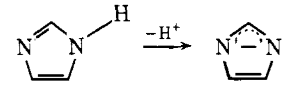
Imidazolate Complexes of Ferric Porphyrins

Sir:

The importance of imidazole as an axial ligand in hemoproteins is evident from the fact that histidine residues provide one or both axial ligands to iron in the majority of those proteins for which pertinent information is available.[1] Model studies of iron porphyrins have often been carried out using *N*-alkylimidazoles rather than imidazole itself, however, for a variety of reasons such as stability[2] or crystallizability[3] of the desired products. Recent studies of the binding of imidazole and *N*-alkylimidazoles to ferric porphyrins have established that their binding constants can differ by as much as 10^3.[4] These studies have also implicated hydrogen bonding of bound imidazole as a factor stabilizing ferric porphyrin-imidazole complexes.[4,5] Examination of published x-ray crystal structures of several heme proteins such as myoglobin,[6] cytochrome *c*,[7] and cytochrome b_5[8] reveals that histidylimidazoles bound to heme iron are hydrogen bonded to other residues on the polypeptide chain. Hydrogen bonding or actual deprotonation of imidazole ligands provides a means whereby the tertiary structure of the protein could moderate the reactivity or redox potential of the iron center.[9] For this reason, we have undertaken an investigation of imidazolate (Im^-) complexes of ferric porphyrins, since deprotonation is the limiting case of strong hydrogen bonding of imidazole (ImH).





ImH Im⁻

The bisimidazole complex $[Fe(TPP)(ImH)_2]^+$ (TPP, tetraphenylporphine) (**1**) is prepared by reaction of Fe(TPP)Cl with a large excess of ImH in several different solvents.[4] Titration of solutions of **1** in benzene, toluene, dichloromethane, and dimethyl sulfoxide with several different bases[10] (hydroxide, *tert*-butoxide, and imidazolate) results in virtually identical visible spectral changes. A titration with OH^- in CH_2Cl_2 is shown in Figure 1. Stepwise addition of 1 equiv of OH^- occurs with an isosbestic point at 585 nm. Further addition of hydroxide produces yet another species. The same spectral shifts and isosbestic point are observed for all three bases in CH_2Cl_2. We believe that we are observing the stepwise deprotonation of **1** as indicated in reaction 1.

$$\mathbf{1} \xrightarrow{-H^+} \underset{\mathbf{2}}{Fe(TPP)(ImH)(Im)} \xrightarrow{-H^+} \underset{\mathbf{3}}{[Fe(TPP)(Im)_2]^-} \quad (1)$$

The bisimidazolate complex **3** can also be prepared by direct reaction of Fe(TPP)Cl with excess Im^- in CH_2Cl_2 (eq 2).

$$Fe(TPP)Cl \xrightarrow{Im^-} \mathbf{4} \xrightarrow{Im^-} \underset{\mathbf{3}}{[Fe(TPP)(Im)_2]^-} \quad (2)$$

An intermediate **4** is observed in this reaction at low levels of Im^-. The blue shift of the Soret band of **4** relative to that of Fe(TPP)Cl, **1**, **2**, and **3** and the positions of the α,β bands imply that **4** is a high spin complex (see Table I). When reaction 2 is followed by EPR at 77 K, the typical high spin spectrum of Fe(TPP)Cl (g = ~6, ~2) disappears and no signal is observed for **4**.[11] Subsequent additions of Im^- produce the low spin EPR spectrum of **3** (g = 2.73, 2.28, 1.76). We believe that **4** may be a high spin imidazolate bridged dimer such as $[(TPP)Fe$-Im-$Fe(TPP)]^+$.

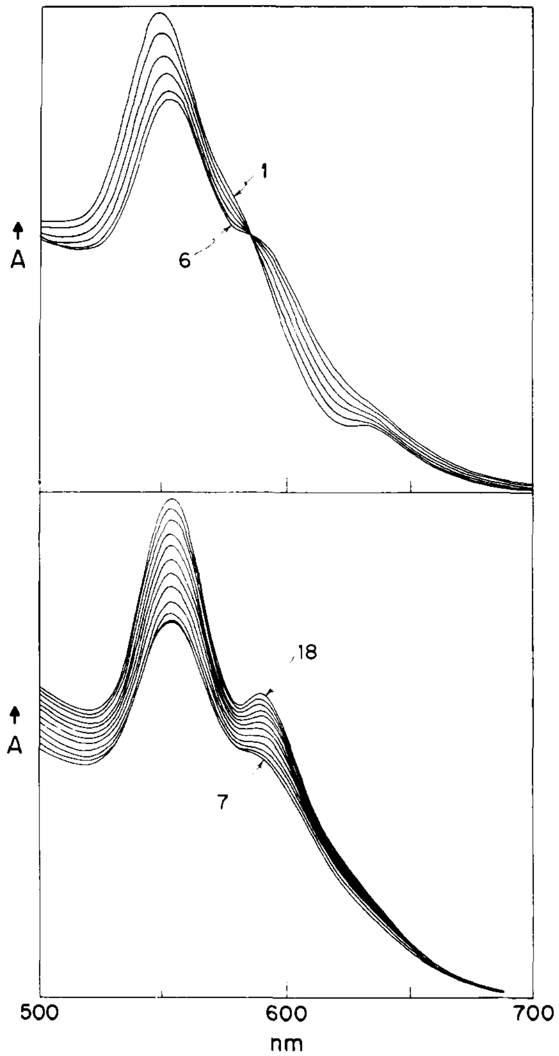


Figure 1. Titration of 3 mL of 10^{-4} M $FeTPP(ImH)_2^+$ in CH_2Cl_2 with 0.1 M Bu_4NOH in methanol/benzene by successive 0.5-μL additions. Six additions correspond to 1 equiv.

Table I

Compd	Visible absorption band positions, nm[a]		
$[Fe(TPP)(ImH)_2]^+$ (**1**)	416 (S)[b]	548	580 (sh)[c]
Fe(TPP)(ImH)(Im) (**2**)	418 (S), 444 (sh)	552	585 (sh)
$[Fe(TPP)(Im)_2]^-$ (**3**)	425 (S), 444 (sh)	556	595
4	403 (S)	561	595 (sh)
$[Fe(TPP)]_2O$	406 (S)	569	612

[a] In CH_2Cl_2. [b] S, Soret band. [c] sh, shoulder.

Addition of acid to solutions of the deprotonated species **3** or **2** results in reversion of the visible spectra to that of the bisimidazole complex **1**. Addition of imidazole to solutions of the bisimidazolate complex **3** results in a shift of the spectrum to that of the monodeprotonated species **2**.

Attempts to isolate **2**, **3**, and **4** have been unsuccessful owing to precipitation of the insoluble polymer $[Fe(TPP)(Im)]_n$.[12] Solution susceptibility measurements have not been possible because of precipitation of the polymer at concentrations appropriate for NMR.

Addition of fluoride ion[13] to **1** results in spectral changes very similar to those observed upon addition of the three bases described above. These spectral changes have previously been attributed to hydrogen bonding of F^- to bound imidazole,[14] but our results and the high basicity of F^- in the gas phase[15] and in aprotic solvents[16] lead us to conclude that fluoride is essentially deprotonating bound imidazole.

Results similar to those described above are obtained upon titration of $Fe(PPIXDME)(ImH)_2^+$ with OH^- in CH_2Cl_2.[17] Singly and doubly deprotonated species are observed analogous to **2** and **3**. The monodeprotonated species has a visible spectrum very similar to that observed for the high pH form of the methemoglobin-imidazole complex.[18] The pK_a of imidazole bound to iron(III) in methemoglobin is known to have dropped from 14 to ~10 upon coordination.[18] This does not exclude the possibility, however, that strong hydrogen bonding or actual deprotonation of histidylimidazole ligands in ferric hemoproteins may occur at physiological pH in the nonaqueous hydrophobic cavity near the iron atom.

Further characterization of these imidazolate complexes and related species is continuing.

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Gas Phase Reactions of Anions with Nitrous Oxide and Carbon Dioxide

Sir:

Nitrous oxide and carbon dioxide are linear, isoelectronic molecules whose gas phase negative ion chemistry remains intriguing and important.[1] We wish to report that both species react readily with a variety of organic anions under the conditions of a flowing afterglow system. For N_2O the reaction process may be characterized as addition, followed by loss of H_2O, N_2, or CH_2O depending upon the nature of the anion;