Photodissociation of 1-Methylimidazole Ligand in Ferric Low-Spin Iron Porphyrin

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Photodissociation has been utilized to investigate the association and dissociation rate constants for ligand binding to hemoproteins to provide insight into the relationship between structure and dynamics.[1−4] It has been recently reported that even the water ligand[5] and the proximal histidine ligand[6] are photodissociable in ferrous hemoproteins, much like the other known ligands CO, O_2, and NO. Therefore, it appears that photodissociation will occur with most ligands coordinated to the ferrous low-spin heme iron. For ferric low-spin iron, on the other hand, it is believed that the iron-to-ligand bond is photoinert.[7] There is a difference in d-electron configuration between ferrous low-spin (d_π^4) and ferric low-spin (d_π^3) irons, which may be related to their different properties. We report here the first example of photodissociation in a ferric low-spin complex. In particular, we present preliminary results indicating that nitrogenous ligands photodissociate and rebind to ferric heme iron in a bis(1-methylimidazole) complex of an iron(III) octaethylporphyrinate chloride, $[Fe(OEP)(1\text{-}MeIm)_2]Cl$, in $CHCl_3$ when irradiated by 413.1 nm laser light used for resonance Raman (RR) experiments. The kinetics and dynamics of the photodissociation process will be discussed with the aid of a hypothetical model that accounts for the RR spectral changes as a function of laser power.

The hexacoordinated low-spin complex $[Fe(OEP)(1\text{-}MeIm)_2]Cl$ (P_L) was prepared by adding an appropriate amount of distilled 1-MeIm to [Fe(OEP)Cl] (P_H), purchased from Aldrich, in $CHCl_3$. For RR measurements (Figure 1B), 150-fold excess 1-MeIm was added to 0.36 mM P_H to produce 95% P_L since the binding constant K_b is ca. 7×10^3 M^{-2}.[8] Raman scattering was excited by 413.1 nm Kr ion laser (Spectra Physics model 2580), and the RR light was dispersed with a JEOL 400D Raman spectrometer equipped with a photomultiplier.

Figure 1 (B1−B3) shows three representative RR spectra of the initially prepared 95% P_L in a spinning cell (diameter 7.2 mm, 465 rpm) obtained with a range of incident laser powers. Under spinning conditions, the sample was irradiated by laser light for 1.5 ms per turn (0.13 s). The spectra are substantially in resonance with the porphyrin $\Pi^*-\Pi$ electronic transitions. The two Raman bands near 1500 cm^{-1} are assigned to the ν_3 mode and are well resolved. The intensity of the band at 1495 cm^{-1} increases with increasing laser power while the other at 1507 cm^{-1} decreases. Both ν_2 and ν_{10} are less resolved since the two components of each band have a small frequency separation, and they appear to shift to lower frequency as the laser power increases. Consequently, the RR spectra excited at a higher laser power are similar to the one shown in Figure 1A and the spectra at a lower power are similar to that shown in Figure 1C. On the other hand, the spectral patterns in spectra A and C of Figure 1 are independent of the incident laser power (not shown). Spectra A and C in Figure 1 indicate that the corresponding complexes are in a pentacoordinated ferric high-spin state and hexacoordinated ferric low-spin state, respectively.[9,10] The spectral change illustrated in Figure 1B demonstrates a decrease in the P_L population by photodissociation of 1-MeIm axial ligands, namely the conversion of P_L into P_H. This is the first observation of photodissociation of imidazole ligands bound to ferric iron porphyrins, although photolysis of imidazole ligands was reported for ferrous iron in hemochromes[11] and cytochromes b_5 and c.[6] Moreover, it was proposed that bond cleavage between nitrogenous bases and ferric heme iron is a key step in the photoreduction of pentacoordinated heme complexes irradiated at the charge-transfer bands.[12] However, the photodissociation was directly observed, and it occurs presumably through the porphyrin's $\Pi^*-\Pi$ excitations[13] in the hexacoordinated low-spin complex. Therefore, it is believed that this is the first observation of photodissociation of nitrogenous bases in ferric low-spin hemes.

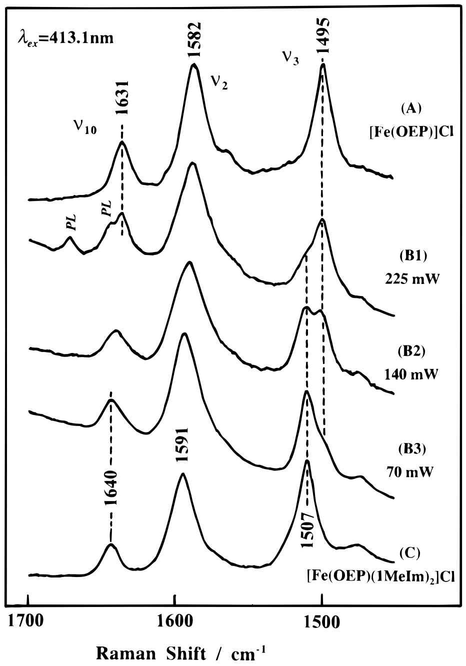

Figure 1. The 413.1 nm excited RR spectra of Fe(OEP) derivatives in $CHCl_3$ at 295 K in the 1450−1700 cm^{-1} region: (A) 0.3 mM [Fe(OEP)Cl]; (B) 0.36 mM [Fe(OEP)Cl] + 150-fold excess 1-MeIm with different laser power; and (C) 0.36 mM [Fe(OEP)Cl] + 20000-fold excess 1-MeIm. Peaks marked PL are due to the laser plasma line.

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(13) Photodissociation was also observed with the excitation at 441.6 and 514.5 nm. Therefore, we suggest that photolysis of 1-MeIm is initiated by $\Pi^*-\Pi$ excitation, not by CT excitation of the porphyrin.

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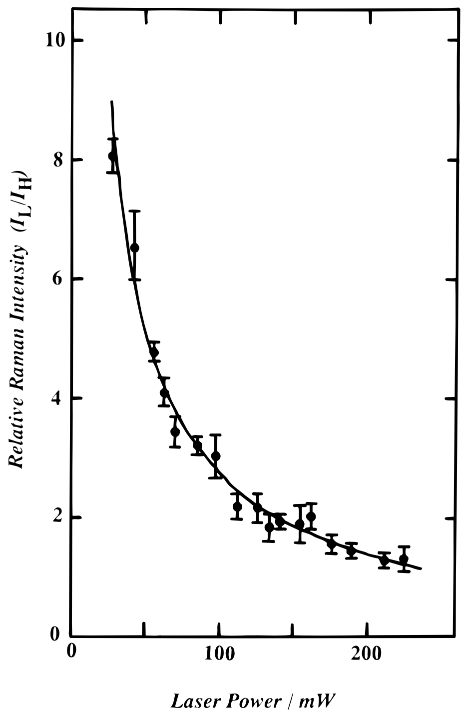

Figure 2. Behavior of the relative intensity ratio of the porphyrin ν_3 1507 cm^{-1} band to the 1495 cm^{-1} band as a function of laser power (mW). The solid curve is discussed in the text.

The solid circles with error bars plotted in Figure 2 represent the laser power dependence of the ratio of the P_L RR band intensity at 1507 cm^{-1} relative to the intensity of the P_H band at 1495 cm^{-1}. The decrease in the ratio reflects the conversion of P_L into P_H through laser excitation. A nearly straight line was obtained when the relative intensity of the ν_3 band to solvent was plotted. Then a simple model for this phenomenon is proposed as the following. P_L excited by the laser relaxes very quickly to P_H so that the total number of molecules of P_0 in the illuminated sample can be given approximately as $[P_0] = [P_L] + [P_H]$ at any time. The rate equation describing the decrease in the ground-state population[14] of P_L entering into the laser focal region ($t_0 =$ 1.5 ms) is as follows:

$$-\mathrm{d}[\mathrm{P_L}]/\mathrm{d}t = \sigma_A I_0[\mathrm{P_L}] + k^-[\mathrm{P_L}] - k^+[\mathrm{L}]^2[\mathrm{P_H}] \qquad (1)$$

where k^- and k^+ represent dissociation and association rate constants, respectively, in the overall reaction for sterically unhindered imidazoles,[15] $P_H + 2L = P_L$. Here, we ignore the pentacoordinated species containing only one 1-MeIm ligand (discussed later). $\sigma_A I_0[P_L]$ is the rate of photodissociation, where σ_A is the absorption cross section of P_L at 413.1 nm and I_0 is the laser power. Since a fresh sample of P_L comes into the laser beam successively, the time evolution of P_L in eq 1, $[P_L](I_0,t)$, is transformed into a spatial distribution $[P_L](I_0,x)$ in the laser beam.[16] The Raman band intensities due to P_L are proportional to the number of molecules, $[P_L](I_0,x)$, obtained from eq 1, and thus, the laser power dependence of the relative Raman intensity of P_L and P_H can be described as follows:

$$I_L/I_H = 0.95\sigma_L\alpha/(\sigma_H((\sigma_A I_0 + a)^2 t_0 - 0.95\alpha)) \qquad (2)$$

where $\alpha = a^2t_0 + \sigma_A I_0[1 + at_0 - \exp\{-(\sigma_A I_0 + a)t_0\}]$ and $a = k^- + k^+[L]^2$. σ_L and σ_H are Raman cross sections of P_L and P_H, respectively. The solid curve in Figure 2 was calculated from eq 2 and has good agreement with the observed data. Using nonlinear least-squares fitting and a relation of $K_b = k^+/k^-$, it is then possible to determine the values of k^+ or k^-. The photon flux is used for data fitting instead of laser power.[17] Both σ_A ($\sigma_A^L = 3.0 \times 10^{-16}$ cm^2, $\sigma_A^H = 1.7 \times 10^{-16}$ cm^2) at 413.1 nm and σ_L/σ_H (=3) for ν_3 RR bands were determined experimentally.

The values of the dissociation rate constant k^- and the association rate constant k^+ obtained in this manner are 5.3 × 10^3 s^{-1} and 3.7 × 10^7 M^{-2} s^{-1}, respectively. The value of k^+ is comparable to that of hemochromes in a chelated porphyrin[11] but is much smaller than those calculated for geminate recombination.[6,18] La Mar et al. monitored the axial ligand exchange rate for [Fe(OEP)(1-MeIm)$_2$]Cl in CDCl$_3$ by ^{1}H NMR line width analysis and found a value of ca. 10^3 s^{-1} at 298 K,[19] which is similar to our k^+ value within experimental error. In this study, the pentacoordinated species with only one 1-MeIm ligand, [Fe(OEP)(1-MeIm)]$^+$, as a photochemical product was ignored because with the RR spectra, it is possible to distiguish two kinds of pentacoordinated species, [Fe(OEP)(1-MeIm)]$^+$ and [Fe(OEP)-Cl].[20] The RR spectrum of the photochemical product is similar to the spectrum of [Fe(OEP)Cl], as shown in Figure 1. By plotting the ratio of the relative intensities of I_L or I_H to solvent band intensity versus the laser power, it was ascertained that the decrease in $[P_L]$ agreed very closely with the increase in $[P_H]$ up to 120 mW. This means that the assumption that $[P_0] = [P_L] + [P_H]$ is a reasonable approximation. It also signifies that [Fe(OEP)-(1-MeIm)]$^+$ is a short-lived species and that both of the two axial ligands eventually photodissociate. The tetracoordinated species, [Fe(OEP)]$^+$, was also ignored as a photochemical product because the associated Cl$^-$ counterion rapidly binds to the transient cationic species. Since the mechanism of photodissociation appears to be complicated, the proposed model may be too simple to evaluate the rate constants quantitatively.

The orientation of the plane of axial ligands perpendicular to the porphyrin plane is related to the distortion of the porphyrin plane and the nature of the chemical bonds between the central metal and the ligands.[21] For instance, it was reported that a weak π interaction between iron (p_π) and imidazole (p_π) in metalloporphyrins is significant in optimizing the orientational preference.[22] Photodissociation might shed light from a completely different point of view on this subject.[23] The fact that photolysis of 1-MeIm is initiated by $\Pi^*-\Pi$ excitation of the porphyrin suggests that there is at least one delocalized molecular orbital in the metal complex which is responsible for the photodissociation. Symmetry considerations require that the MO must consist of porphyrin Π^*, Fe d_π, and 1-MeIm p_π orbitals. Therefore, the data reported in this communication also show the nature of the chemical bond between the ferric iron and an imidazole ligand in porphyrin chemistry. Temperature-dependent experiments are currently being performed to further elucidate the details of the photodissociation process in this ferric low-spin bis-imidazole system.

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[16] Using $P_H + 2L = P_L$, solving rate eq 1 for $[P_L](I_0,t)$, and substituting x/v into t yields $[P_L](I_0,x)$, where x is the distance from the edge of laser beam and v is the speed of the spinning cell. Thus, x_0(the diameter of the laser beam)$/v = t_0$.

[17] An effective photon flux is introduced since the sample is irradiated by laser light for 1.5 ms per turn under spinning conditions. The effective photon flux is almost seven hundred times less than that calculated under static conditions.

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