Picosecond Photodissociation of Six-Coordinate Iron(II) Porphyrins

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Abstract: Photodissociation of basic axial ligands from ferrous tetraphenylporphyrin (Fe^{II}TPP), ferrous protoporphyrin IX dimethyl ester (Fe^{II}PPDME), and ferrous deuteroporphyrin IX dimethyl ester (Fe^{II}DPDME) has been investigated with picosecond transient absorption spectroscopy. Only one ligand appears to be released upon excitation of the six-coordinate complex. The rate constants for recombination of 10^8–10^9 M^{-1} s^{-1} are in excellent agreement with those reported from slower time-scale measurements. The amplitude of the absorption changes immediately after the 35-ps flash did not depend on ligand concentration between 0.1 and 1.0 M. Analysis of these observations argues against an initial high yield of ligand release followed by rapid geminate recombination. The results suggest that the low photodissociation yields (0.03–0.08) previously reported for similar molecules are largely due to rapid relaxation of the excited six-coordinate complex competing with ligand release. The most likely photodissociative state is a low-lying (d_π, d_{z^2}) ligand-field excited state.

Iron porphyrins are of considerable biological importance, forming the active centers of electron transfer (cytochromes), ligand binding (globin), and catalytic (oxidase, peroxidase, catalase) proteins.[1,2] Most of our understanding of the mechanisms and rates of ligand binding in hemes and heme proteins comes from flash photolysis studies.[3] However, a great deal remains to be learned about the excited-state dynamics of iron porphyrin complexes.

Recently, Lavalette, Momenteau, and Tetreau examined the photodissociation of a variety of basic axial ligands from some simple Fe^{II} porphyrins and Fe^{II} porphyrin chelated compounds in nanosecond flash photolysis experiments.[4] It was found that one ligand was released from the photoexcited six-coordinate complex and that the recombination rates were in the range 10^8–10^9 M^{-1} s^{-1}. The photodissociation yields for ligand release were low (0.03–0.08). The time resolution of these studies did not permit observation of excited states prior to the dissociated one.

In view of the interest in heme photolysis and the reasons for low photodissociation yields in certain protein and metalloporphyrin complexes,[4–6] we have extended the nanosecond work of Lavalette, Momenteau, and Tetreau into the picosecond domain. Here we report the results of picosecond transient absorption and kinetic studies on the photoprocesses of penta- and hexacoordinate

ferrous tetraphenylporphyrin (Fe^{II}TPP), ferrous protoporphyrin IX dimethyl ester (Fe^{II}PPDME), and ferrous deuteroporphyrin IX dimethyl ester (Fe^{II}DPDME). Piperidine and methyl-substituted imidazoles were used as axial ligands. In addition, the ferric porphyrin, Fe^{III}TPP(Cl), was studied as a reference compound, since its picosecond kinetics and those of other nonphotolabile Fe^{III} porphyrins have been reported previously.[7] This work complements picosecond studies of photodissociation in heme proteins[3b,6e,8,9] and in Ni^{II}, Co^{II}, and Co^{III} porphyrins.[10,11]

Experimental Section

The 10-Hz dual-beam picosecond transient absorption spectrometer used for the present studies has been described elsewhere.[10a] For most experiments 35-ps, 300-μJ excitation flashes at 355 nm were employed. For some measurements 532-nm flashes containing 500 μJ were used. The broad-band (450-900 nm) probe flashes, also of ~35-ps duration, were generated from the 1064-nm fundamental in CCl$_4$/CHCl$_3$.

Toluene (OmniSolv MCB) and piperidine (Sigma) were used as received. The purity of the 1-MeIm and 2-MeIm (Aldrich) was checked by NMR. Fe^{III}TPP(Cl) was obtained from Midcentury Chemicals. Fe^{III}PPDME(Cl) and Fe^{III}DPDME(Cl) were prepared by iron insertion[12]

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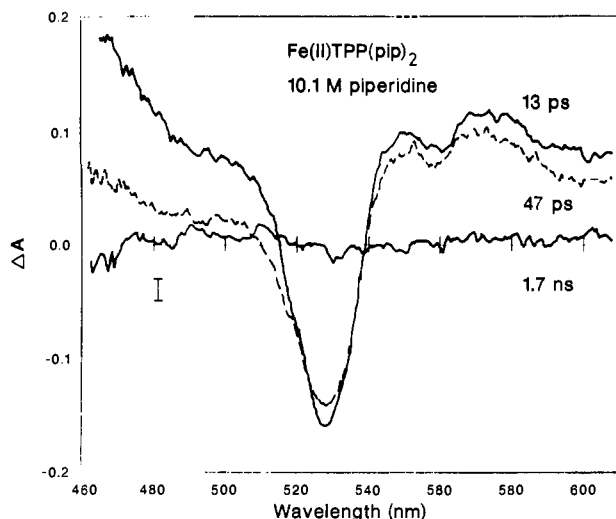
Figure 1. Absorption difference spectra at three time delays with respect to excitation of $Fe^{II}TPP(pip)_2$ in neat (10.1 M) piperidine with 35-ps flashes at 355 nm. Each spectrum here and in Figure 3 represents the average of data employing 500 excitation flashes, with standard deviations in ΔA of ≤ 0.01 over the wavelength region shown, as indicated by the error bars.
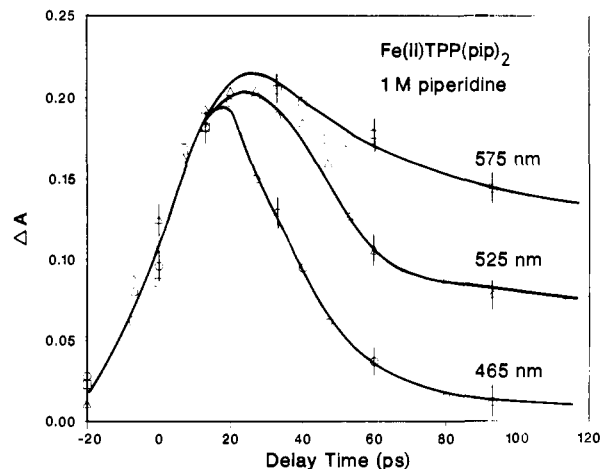
into the free-base compounds (Midcentury). The purity of hemes was checked by TLC, and they were purified by column chromatography where necessary. Glassware was washed with dilute acid to prevent contamination with bases.

Piperidine complexes were prepared by dissolving the hemin in neat piperidine. In neat solution, the hemin autoreduces to the heme rapidly.[13] The piperidine solution was syringed in appropriate amounts into Ar-purged toluene and the resulting solutions flame sealed under vacuum after repetitive freeze–pump–thaw cycles. Imidazole samples do not autoreduce. 1-MeIm complexes were prepared by dissolving the hemin in neat 1-MeIm and reducing the solution with aqueous dithionite ($\simeq 10$ $\mu L/mL$ of solution).[14] 2-MeIm complexes were prepared by purging a saturated ($\simeq 10^{-2}$ M) solution of 2-MeIm and hemin in toluene with argon and reducing the solution with saturated aqueous dithionite ($\simeq 0.5$ mL/mL of toluene). The resulting solutions were transferred by cannula into a cell and sealed under vacuum.

The maximum absorbance of the samples in the 500–600 nm region was 0.4–0.6 in a 2-mm path. Equilibrium constants reported in the literature[15,16] indicate that at the ligand concentrations employed, the ferrous porphyrins were bisligated in the ground state, except in the case of 2-MeIm where only the five-coordinate complex is formed for steric reasons.[17] The ground-state spectra reproduced literature spectra of the known complexes.[15]

Results

$Fe^{II}TPP(pip)_2$. Figure 1 shows representative absorption difference spectra for $Fe^{II}TPP(pip)_2$ in neat (10.1 M) piperidine at three time delays between the peaks of the pump and probe flashes. Transient spectra during the 35-ps, 355-nm excitation flash (13-ps spectrum) exhibit three prominent features: bleaching of the ground state Q(1,0) or β band near 530 nm, broad new absorption to the red of 540 nm (extending to near 700 nm), and a strong absorption increase to the blue of 515 nm increasing in strength to shorter wavelengths. The small dip at 560 nm in the broad absorption increase coincides in wavelength with the weaker Q(0,0) or α peak in the ground-state spectrum and thus probably represents bleaching in this band. The difference spectrum at a 47-ps

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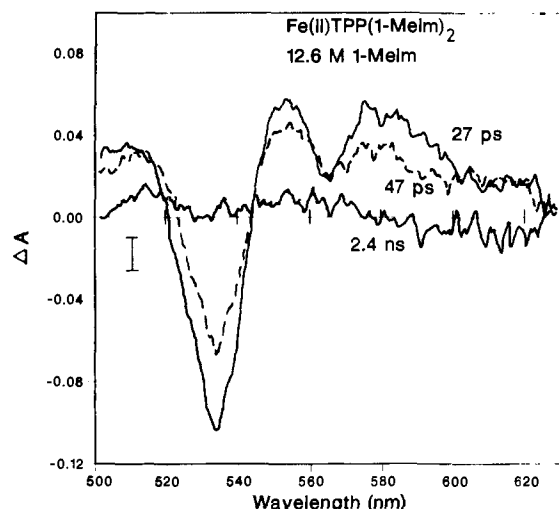(13) DelGaudio, J.; LaMar, G. N. *J. Am. Chem. Soc.* **1978**, *100*, 1112–1119.
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Figure 2. Kinetics of the absorption changes, such as those shown in Figure 1, at three wavelengths produced by excitation of $Fe^{II}TPP(pip)_2$ in 1.0 M piperidine in toluene with 355-nm flashes: 465 (O), 525 (△), and 575 nm (□). The absorption changes were scaled to approximately the same peak value. The absorption difference spectra obtained at this ligand concentration are the same as those shown in Figure 1 for this complex in neat piperidine.

Table I. Summary of Kinetic Data for Iron Porphyrins

compound	solvent	[L], M	τ^a	$k \times 10^{-8}$ $M^{-1} s^{-1}$
$Fe^{III}TPP(Cl)$	tol		≤ 35 ps	
$Fe^{II}TPP(pip)_2$	pip	10.1	390 ± 80 ps	2.5 ± 0.5
$Fe^{II}TPP(pip)_2$	tol/pip	1.0	3.6 ± 0.3 ns	2.8 ± 0.3
$Fe^{II}TPP(pip)_2$	tol/pip	0.71	5.5 ± 1 ns	2.6 ± 0.5
$Fe^{II}TPP(pip)_2$	tol/pip	0.1	>10 ns	
$Fe^{II}TPP(1\text{-}MeIm)_2$	1-MeIm	12.6	1.3 ± 0.3 ns	0.6 ± 0.1
$Fe^{II}TPP(2\text{-}MeIm)$	2-MeIm	~ 12	≤ 35 ps	
$Fe^{II}PPDME(pip)_2$	pip	10.1	285 ± 25 ps	3.5 ± 0.3
$Fe^{II}DPDME(pip)_2$	pip	10.1	340 ± 30 ps	2.9 ± 0.4

^{a}All compounds showed a fast component exhibiting a strong absorption increase at $\lambda < 515$ nm having a lifetime of ≤ 35 ps (see text).

delay (dashed spectrum in Figure 1) shows that the shorter wavelength feature has largely decayed, but the broad transient absorption to the red remains at nearly the same amplitude. The shape of the difference spectrum due to this second component remains essentially constant at longer time delays, and by 1.7 ns (Figure 1) transient absorptions have disappeared and the ground-state bleaching has completely recovered. Similar spectral behavior was found for $Fe^{II}TPP(pip)_2$ in lower concentrations of piperidine in toluene (1.0, 0.71, and 0.1 M). Absorption changes similar to those just described for the 570–650 nm region also were observed in neat piperidine following excitation with 532-nm flashes.

The time evolution of the absorption changes at three wavelengths produced by excitation of $Fe^{II}(TPP)(pip)_2$ in 1.0 M piperidine with 355-nm flashes is shown in Figure 2. The time profile for the short-lived component measured at 465 nm (open circles) indicates that the transient decays with a time constant of ≤ 35 ps. However, because of the short lifetime and the possibility for reexcitation of molecules that have returned to the ground state during the excitation flash, the lifetime of the fast component may be much shorter than this value. Decay of the second component measured in the 575-nm absorption increase (squares in Figure 2) follows pseudo-first-order kinetics with a time constant of 390 ± 80 ps (Table I). The time profile for the 525-nm bleaching (triangles) contains contributions from both transients.

At all piperidine concentrations, the absorption increase to the blue of 515 nm decayed almost completely with a time constant ≤ 35 ps, as just discussed for $Fe^{II}TPP(pip)_2$ in 1.0 M piperidine (Figure 2, open circles). After the pump flash, the transient absorption to the red of 540 nm (see dashed spectrum in Figure 1) and a component of the bleaching recovered with pseudo-first-order kinetics; the time constant for the decay depended on

Figure 3. Absorption difference spectra at three time delays with respect to excitation of Fe^{II}TPP(1-MeIm)$_2$ in neat (12.6 M) 1-methylimidazole with 35-ps flashes at 355 nm.

the ligand and its concentration (Table I). There was no evidence for a lag in the growth of the absorption increase between 540 and 615 nm with different concentrations of ligands nor of a significant variation in its initial amplitude as compared to the other spectral features under the various conditions. Thus, the only significant difference observed between the spectral and kinetic behavior with the different ligand concentrations was the time constant for decay of the absorption changes after the excitation flash.

Fe^{II}TPP(1-MeIm)$_2$. Figure 3 shows absorption difference spectra at three time delays for this complex in neat 1-methylimidazole. The broad absorption increases at wavelengths longer than 550 nm and the major component of the ground-state bleaching (dashed spectrum) were found to relax with a time constant of 1.3 ± 0.3 ns, about a factor of 4 slower than that for Fe^{II}TPP in neat piperidine (Table I). Fe^{II}TPP(1-MeIm)$_2$ also showed a ≤35-ps component to the 535-nm bleaching and to the absorption increase to the blue. However, fluorescence from the ligand prevented detailed measurements at wavelengths shorter than 500 nm.

Fe^{II}PPDME(pip)$_2$ and Fe^{II}DPDME(pip)$_2$. We also investigated the bispiperidine complexes of ferrous protoporphyrin and deuteroporphyrin IX dimethyl ester. Absorption difference spectra for these compounds in neat piperidine produced by 355-nm-excitation flashes exhibit the same major features as those discussed above for Fe^{II}TPP(L)$_2$, although differences in detail exist. Spectra during and after the 35-ps excitation flash show bleaching in the Q(0,0) and Q(1,0) (or α and β) bands near 540–560 and 510–530 nm, the former stronger than the latter in these macrocycles as compared to TPP. Transient spectra during the flash have a component to the absorption increase between 450 and 500 nm and the ground-state bleachings that relaxes in ≤35 ps. A broad new absorption extending from 570 nm to the red of 630 nm is present at early times and decays along with the remainder of ground-state bleachings with pseudo-first-order kinetics. The time constant for relaxation of these features in neat piperidine is 285 ± 25 ps for Fe^{II}PPDME and 340 ± 30 ps for Fe^{II}DPDME. A log plot for recovery of bleaching in the 540-nm band of Fe^{II}PPDME is shown in Figure 4, clearly revealing the two components to the decay, as found for the other complexes (Table I).

Fe^{II}TPP(2-MeIm). In neat 2-methylimidazole, only one ligand is bound to make a five-coordinate Fe^{II} complex in the ground state.[15,17] Excitation of this compound with 355-nm flashes gave a broad, very weak transient absorption over the 460–630 nm region, broken by ground-state bleachings centered at 535, 570, and 610 nm. The absorption changes were present only during the excitation flash, giving a time constant of ≤35 ps for decay of the transient. Unlike the six-coordinate complexes discussed

above, there was no evidence for formation of a longer-lived component (Table I).

Fe^{III}TPP(Cl). The difference spectrum obtained upon excitation of this complex in toluene with 355-nm flashes (not shown) exhibits strong absorption near 460 nm decreasing in amplitude to longer wavelengths, tailing past 600 nm. There is a trough at 505 nm due to bleaching in the ground-state absorption band. The spectral features appear to decay with a time constant of 15–30 ps. However, because of possible recycling during the 35-ps excitation flash we report an upper limit of ≤35 ps for the relaxation. The time profile for the absorption changes is similar to that observed at 465 nm for Fe^{II}TPP(L)$_2$ in Figure 2 (open circles).

Our spectral and kinetic observations on Fe^{III}TPP(Cl) are consistent with previous picosecond work on this complex.[7b,c] A strong transient absorption peak near 450 nm was assigned to the lowest porphyrin triplet excited state, $^3T(\pi,\pi^*)$, formed in low quantum yield from the short-lived $^1Q(\pi,\pi^*)$. Its observation was attributed to multiple recycling through the short-lived states during the 7-ps excitation flash. Our transient difference spectrum (not shown) is consistent with that reported by Cornelius et al.,[7b] although we could not monitor at short enough wavelengths to resolve the peak of the absorption in the blue.

Discussion

Photodissociation of the Six-Coordinate Complex. A priori, photolysis might result in the loss of either one or two axial ligands from the initially excited six-coordinate complex to give the five-coordinate or four-coordinate hemes, respectively. For most nitrogenous bases, ground-state spectra of the five-coordinate species are not known. Titration experiments have shown that binding of the second ligand is substantially greater than that of the first,[15,16] and no five-coordinate heme is observed. Hindered bases, such as 2-methylimidazole, do form five-coordinate species, however.[17] Figure 5 shows difference spectra calculated for loss of one imidazole [Fe^{II}TPP(2-MeIm) minus Fe^{II}TPP(1-MeIm)$_2$] (solid) and loss of two imidazoles [Fe^{II}TPP minus Fe^{II}TPP(1-MeIm)$_2$] (dashed) taken from the work of Brault and Rougee.[15]

In their nanosecond experiments, Momenteau and Lavalette[4a] assigned the difference spectrum observed upon photolysis of Fe^{II}TPP(1-MeIm)$_2$ to the formation of the five-coordinate complex by comparing the transient difference spectrum with a calculated static difference spectrum. The transient difference spectra observed in our picosecond study for Fe^{II}(TPP)(1-MeIm)$_2$ are shown in Figure 3. These spectra do not agree in amplitude feature for feature with either calculated difference spectrum in Figure 5 but resemble that expected for the five-coordinate complex to a much greater extent than that expected for the four-coordinate complex. The transient spectra show a broad absorption to the red of the ground-state bleachings and absorption increases of similar magnitude near 550 and 580 nm. These features are expected for the five-coordinate complex. However, after normalization of the spectra at 500 or 580 nm, the amplitude of the bleaching at 535 nm in the transient spectra is about 20% smaller than that in the calculated spectrum. The transient spectra observed by Momenteau and Lavalette also showed a smaller extent of bleaching in the 535-nm ground-state band than in the calculated spectrum, although the two spectra matched very well in the 550–600 nm and Soret band regions. The discrepancy in the amplitude of the 535-nm bleaching seen in both studies may arise from spectral differences between the five-coordinate 2-methylimidazole complex and the five-coordinate transient in which 1-methylimidazole (or piperidine discussed below) is the axial ligand. It is possible that the position of the metal with respect to the heme plane is not the same in these pentacoordinate species.[18]

Additional spectral support for the rapid formation of a five-coordinate transient is observed upon comparison of the static difference spectra with the picosecond spectra for Fe^{II}TPP(pip)$_2$ shown in Figure 1. (The ground-state spectra in the visible region for the six-coordinate 1-methylimidazole and piperidine complexes

(18) Scheidt, W. R.; Gouterman, M. In ref 1, Part I, Chapter 2.

of Fe^{II}TPP are very similar, except for a 5-nm wavelength shift.) The features in the broad absorption increase between 540 and 630 nm at the 47-ps delay (dashed spectrum in Figure 1) are in very good agreement with those in the calculated five-coordinate spectrum (solid curve in Figure 5). The absorption changes in this region during the excitation flash (13-ps spectrum) are the same shape within experimental error as those at longer delays, indicating that the five-coordinate complex is formed in ≤35 ps.

Photolysis of the bispiperidine complexes of Fe^{II}PPDME and Fe^{II}DPDME gives an overall picture similar to that discussed above for Fe^{II}TPP. The transient difference spectra do not allow distinction between a four- and a five-coordinate intermediate because the ground-state difference spectra for these two species are so similar.[15] However, the kinetic results (Figure 4 and Table I) are again consistent with the bimolecular recombination (at times longer than 50 ps) of one ligand with a five-coordinate transient state that appears to be formed early in the excitation flash.

Ligand Rebinding. The rate constants for ligand recombination found in this study are very similar to those found previously by Lavalette et al.[4b] using nanosecond flash photolysis techniques, even though the ligand concentration varies a total of 10^5-fold between the two studies. Ligand rebinding for Fe^{II}TPP(pip)$_2$ occurs with a rate constant of 2.5–2.8×10^8 M^{-1} s^{-1} in the picosecond study and 3.4×10^8 M^{-1} s^{-1} in the nanosecond study. Similarly, the rate constants for Fe^{II}TPP(1-MeIm)$_2$ are 6.5×10^7 and 1.6×10^8 M^{-1} s^{-1}, respectively. The small differences between the two studies are probably due to changes in solvation of the complex and in the viscosity of the medium. In both studies rebinding of piperidine is approximately four times faster than that of 1-methylimidazole. This has been ascribed by Lavalette et al.[4b] to the larger dipole moment of the imidazole, resulting in an increased electrostatic repulsion and hence a slower rebinding.

Lavalette, Momenteau, and Tetreau found in nanosecond experiments that the overall yields of photodissociation were low, <10%.[4] We have probed the reason for this by investigating the kinetics of Fe^{II}TPP(pip)$_2$ at four ligand concentrations: neat (10.1 M) and 1.0, 0.7, and 0.1 M in toluene. In all four sets of experiments only two decays were seen, a fast decay ($\tau \leq 35$ ps) and a slow decay whose lifetime was inversely related to the concentration of piperidine. (In 0.1 M piperidine a lower limit on the lifetime of >10 ns was found, consistent with the value of 36 ns expected from the results with the other piperidine concentrations (Table I).) The amplitude of the absorption changes immediately after the flash did not depend on the ligand concentration between 0.1 and 10.1 M.

These observations are consistent with a rebinding scheme that explains the low quantum yield as due to fast relaxation of the excited six-coordinate complex rather than rapid geminate recombination. For rebinding to occur mainly in a primary cage (that formed upon photodissociation), the bimolecular rate would have to be that of diffusion control. This is not the case, as seen in the table. The bimolecular rates measured are approximately an order of magnitude slower than the calculated diffusion-controlled value of $\sim 5 \times 10^9$ M^{-1} s^{-1} in these solvents.

Rebinding from a secondary cage is often important in radical reactions.[19] In the present experiment the analogous process would involve rebinding of initial FeL, L pairs which have separated by one or more solvent molecules but returned to rebind. In neat solution, however, where the solvent is the ligand, any solvent molecule can bind to the heme. This would imply that the amount of five-coordinate compound observed shortly after the flash should be smaller in neat ligand than in dilute solution (assuming that the initial five-coordinate transient has a spectrum different from the six-coordinate ground state). As described above, this was not the case. These arguments do not exclude

any geminate recombination, but they indicate that the major reason for the low quantum yield is not geminate recombination.

Excited-State Deactivation. We now discuss the photophysics of Fe^{III}TPP(Cl) and address three important points regarding the photophysical and photochemical behavior of the hexacoordinate ferrous porphyrins: (A) the nature of the photodissociative state responsible for the ligand release that is observed, (B) the reason for the low photodissociation yields, and (C) assignment of the transient responsible for the initial absorption changes that decay in ≤35 ps.

Iron porphyrins are radiationless, exhibiting fluorescence quantum yields <10^{-6}, implying $^1Q(\pi,\pi^*)$ lifetimes of <1 ps.[20,21] In these and other nonluminescent porphyrins, it is thought that the normally emissive (π,π^*) excited states deactivate rapidly via lower energy ring $\leftrightarrow$ metal (π,d) or (d,π^*) charge transfer (CT) excited states or ligand field (d,d) excited states.[20]

Rapid excited-state decays have been reported previously from picosecond transient absorption studies on iron porphyrins: <2 ps for ferrous and ferric cytochrome c,[7a] ≤13 ps for Fe^{III}OEP(Cl) in toluene or pyridine,[7d] and 25–50 ps for Fe^{III}TPP(Cl) in benzene.[7b,c] In the present study we have examined the transient behavior of Fe^{III}TPP(Cl) in toluene and have placed an instrument-limited time constant of ≤35 ps on the relaxation of the absorption changes between 460 and 630 nm. On the basis of the earlier work, it is reasonable to assign the transient observed here as the $^3T(\pi,\pi^*)$,[7b] which can build up by recycling of shorter lived states during the 35-ps, 355-nm excitation flash. It is important to note that this assignment is consistent with the (π,π^*) excited-state difference spectra reported for other metallo-TPP complexes, which exhibit a strong new absorption peak between 420 and 500 nm, broad weak absorption in the visible, and one or two weaker absorption peaks in the near infrared.[10,11,22] We attribute the short lifetime to rapid deactivation of the (π,π^*) states via even shorter lived CT or (d,d) excited states. The $S = {}^5/_2$ electronic configuration and presence of the half-filled d$_\pi$ and d$_{z^2}$ orbitals between the porphyrin filled-π and empty-π^* orbitals makes a number of low-energy states possible in this complex.[20] Quenching states such as the $(a_{2u}(\pi),d_\pi)$ CT are placed below the $^1Q(\pi,\pi^*)$ by calculations and assignments of the ground-state absorption spectrum.[20,23]

Similar considerations are important for understanding the transient behavior of the hexacoordinate ferrous porphyrins. These complexes have a d^6 electronic configuration and $S = 0$. They also are nonfluorescent, implying that one or more states lie in energy below the normally emissive $^1Q(\pi,\pi^*)$.[20] There are three states that one might consider to lie below the $^1Q(\pi,\pi^*)$. These are the ring $\rightarrow$ metal (d$_\pi$,e$_g(\pi^*)$) CT, the metal $\rightarrow$ ring (a$_{2u}$-(π),d$_{z^2}$) CT, and the ligand field (d$_\pi$,d$_{z^2}$) states. For brevity, these are referred to as (d,π^*), (π,d), and (d,d) states in the subsequent discussion. Two of these states, the (d,d) and the (π,d), are expected to be dissociative with respect to the axial ligands employed here, because electron density is transferred to the d$_{z^2}$ orbital. This orbital is antibonding toward σ-bonded ligands. The nitrogenous bases used in the present study as axial ligands are mainly σ-bonded, with π-back-bonding not being substantial. The (π,π^*) and (d,π^*) are not expected to be dissociative toward such ligands.

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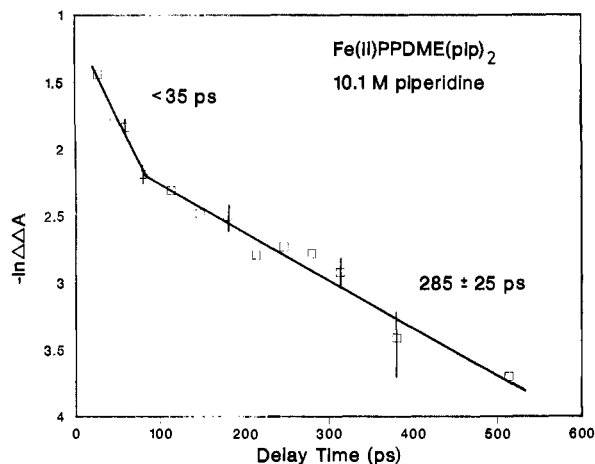
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Figure 4. log plot showing the biphasic decay kinetics observed upon excitation of Fe[II]PPDME(pip)$_2$ in neat piperidine with 355-nm flashes. The quantity $\Delta\Delta A$ in the ordinate is the difference in ΔA between the broad absorption increase at 610 nm and the ground-state bleaching at 525 nm. Kinetic data for this and other complexes are summarized in Table I.
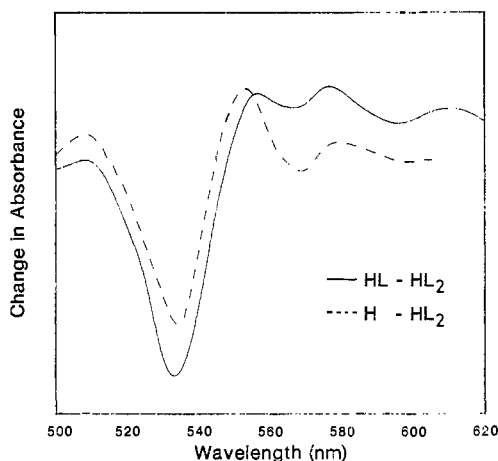
Figure 5. Difference spectra calculated from the spectra of ref 15 for Fe[II]TPP complexes with methyl-substituted imidazoles. The solid curve (—) is the spectrum for Fe[II]TPP(2-MeIm) minus that for Fe[II]TPP(1-MeIm)$_2$; it represents the difference spectrum for the loss of one ligand from the six-coordinate complex. The dashed curve (- - -) is the spectrum for Fe[II]TPP minus that for Fe[II](TPP)(1-MeIm)$_2$; it represents the difference spectrum for the loss of two ligands from the six-coordinate complex.

It must first be noted that there is at least one photodissociative state beneath the visible $^1Q(\pi,\pi^*)$ state in energy. This follows from the observations that the absorption changes seen after excitation of the hexacoordinate ferrous porphyrins with 355-nm flashes (this work) were very similar to those observed with 532-nm flashes (this work and ref 4). The reasoning does not mean that a second photoactive state does not lie in energy between the ring visible $^1Q(\pi,\pi^*)$ and near-UV Soret $^1B(\pi,\pi^*)$ states but that there must be at least one photodissociative state lower than the ^1Q-(π,π^*).

The lowest energy CT excited state for Fe[II]P(L)$_2$ should be the (d,π^*). Although it is unclear from the Hückel calculations whether this state is below the (π,π^*),[20,21a,b,23a] recent ab initio calculations indicate that this may be so.[23c] If it is lower in energy than the (π,π^*) state, it could serve as a quencher. However, it is not expected to be photodissociative toward the σ-bonded ligands studied here, as mentioned above.

Recent theoretical work suggests that the (π,d) state lies above the $^1Q(\pi,\pi^*)$.[21a,23c] Raman studies on the bisimidazole complex of Fe[II] protoporphyrin place the (π,d) CT in the Soret region.[24]

This state could be dissociative when 355-nm flashes are used. However, as pointed out above, no significant differences in transient spectra and kinetics were observed between experiments employing 355- and 532-nm excitation flashes. Therefore, the (π,d) CT is not expected to be a major contributor to the quenching or dissociation that is observed.

On the basis of previous theoretical and experimental work, it appears that the most likely candidate for the photodissociative state is the (d,d).[20,21a,23a,25] Iterative extended Hückel calculations place the filled metal orbitals d_{xy} and d_π slightly above the highest filled ring $a_{1u}(\pi)$ and $a_{2u}(\pi)$ orbitals and the empty metal d_{z^2} and $d_{x^2-y^2}$ above the ring lowest empty $e_g(\pi^*)$.[20,21a,b,23a] There appears to be a consensus from these calculations that the (d,d) is lower in energy than the lowest (π,π^*). In addition, it has been suggested that the $^1(d_\pi,d_{z^2})$ may be responsible for the weak ground-state absorption band observed near 800 nm in these complexes.[20,21a,25] The (d,d) state should be dissociative with respect to σ-bonded axial ligands such as the nitrogenous bases investigated here, as has been discussed above and previously for similar ligand-field (d,d) excited states in Co[III] and Ni[II] porphyrins[10,11] and carbonylhemoglobin.[8a,f,25a,26]

Dissociation of the base occurs with a low quantum yield. As discussed above, this is not due to an initial high yield of photodissociation followed by fast cage recombination. Therefore, rapid deactivation of the six-coordinate complex must compete with ligand release to account for the low quantum yields. Two relaxation schemes are possible. First, the (π,π^*) state could decay to the (d,d) state followed by rapid deactivation competing with dissociation. The nondissociative (d,π^*) CT could be an intermediate state either between the (π,π^*) and (d,d) or (d,d) and ground state. Second, the (π,π^*) decay pathway could branch, occurring predominantly to the ground state via a short-lived (d,π^*) with a minor decay route through the dissociative (d,d) state. Although we cannot distinguish these two possibilities on the basis of our results, the first scheme seems more likely because relaxation in either the singlet or triplet channel probably proceeds through all the low-lying states of a given multiplicity.

Assignment of the (d_π,d_{z^2}) as the state responsible for dissociation does not necessarily mean that it is responsible for the ≤ 35-ps transient absorption observed for all the hexacoordinate Fe[II] complexes. In fact, the absorption changes observed during the excitation flash *are not* consistent with those expected for a metalloporphyrin (d,d) excited state. Recent picosecond studies on Ni[II] and Co[III] porphyrins indicate that such states exhibit absorption bands similar to, but red shifted from, those found in the ground state,[10,11] as predicted by theory.[27] It is possible that the short-lived transient is the (d,π^*) CT excited state, which is expected to have an absorption difference spectrum similar to that resulting from the production of the metalloporphyrin π-anion radical. However, this state may decay too quickly. A more likely candidate for the ≤ 35-ps transient is that it is the $^3T(\pi,\pi^*)$ excited state of the ring. The strong absorption to the blue of the Q-band bleachings is consistent with the state so assigned for Fe[III]TP-P(Cl)[7b] and (π,π^*) states of other metallo-TPP complexes,[10,11,22] as discussed above. Whether this transient feeds the dissociative state and whether it is observed because of recycling during the excitation flash is unclear from the present measurements.

Finally, we have found that excitation of the five-coordinate Fe[II]TPP(2-MeIm) does not yield a long-lived dissociative state but simply results in deactivation in ≤ 35 ps. This confirms the earlier report[4a] from nanosecond measurements that this complex is not photolabile. This complex has $S = 2$, the metal displaced from the heme plane, and half-filled d_π and d_{z^2} orbitals between the ring filled-π and empty-π^* orbitals. Therefore relaxation may occur very rapidly via a manifold of low-lying nondissociative CT

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states, as discussed above for Fe^{III}TPP(Cl) and analogous pentacoordinate complexes.

Copper Carbonyls, Cu(CO) and Cu(CO)₃: Matrix Isolation ESR Study

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Abstract: ESR spectra of copper carbonyls, Cu(CO) and Cu(CO)₃, generated in argon matrices were observed and analyzed. The g tensors and the hyperfine coupling tensors of the Cu and ^{13}C nuclei in each complex were determined. The Cu(CO)₃ spectra were complicated by forbidden transitions induced by severe anisotropy of the hyperfine coupling tensor and the nuclear quadrupole interaction of the Cu nucleus; the effect was demonstrated and the quadrupole interaction tensor was determined. Both carbonyls are formed by a σ-type dative interaction between the lone-pair electrons of CO and vacant hybrid sp orbital(s) of Cu and π-type back-donation from the Cu atom to the vacant π* orbitals of the CO moiety. In Cu(CO) the back-donation is from the filled d$_\pi$ orbitals, and the semifilled orbital is an sp$_\sigma$ orbital of Cu pointing away from the ligand. Cu(CO)₃ is trigonal planar, and the back-donation results from interaction of the semifilled p$_\pi$ orbital of Cu with the vacant π* orbitals of CO molecules.

Introduction

The stability of mononuclear transition metal carbonyls such as Cr(CO)$_6$ or Ni(CO)$_4$ is well known. The bonding scheme of these complexes invokes a σ-type dative interaction of the lone-pair electrons of CO with the vacant valence orbitals of the metal atom, and π-type back-donation from the filled d$_\pi$ orbitals of the metal atom to the vacant π* orbitals of CO molecules.[1] Thermally stable carbonyls of the group 1B metal atoms (Cu, Ag, and Au), however, are not known. It is ascribed to the extra stability of the completed nd^{10} configuration of these atoms.

Ogden,[2] earlier, and Ozin and his co-workers,[3] later, showed that mononuclear carbonyls of group 1B metal atoms were formed when the metal atoms and CO molecules were cocondensed in rare gas matrices at cryogenic temperature (~4-20 K). A thorough analysis of vibrational spectra of the Cu/CO/Ar system by Ozin et al.[3] revealed the formation of Cu(CO), Cu(CO)$_2$, and Cu(CO)$_3$. It also showed that Cu(CO)$_2$ was linear, while Cu(CO)$_3$ was trigonal planar. In a separate paper Ozin reported on ESR (electron spin resonance) spectra of Cu(CO)$_3$ with a preliminary analysis, and a brief reference to an ESR spectrum of Cu(CO).[4] Cu(CO)$_2$ of a linear structure would have a $^2\Pi$ ground state, and its ESR spectrum would not be observed.

Accurate descriptions of the semifilled orbitals of these complexes, if obtained, should be extremely elucidative of the structures and bonding schemes involved. We report here ESR spectra of copper carbonyls observed from the Cu/CO/Ar system, and their detailed analyses. The g tensors and the hfc (hyperfine coupling) tensors with the Cu and ^{13}C nuclei of Cu(CO) and Cu(CO)$_3$ were determined. As expected no ESR signal attributable to Cu(CO)$_2$ was observed. It is shown that the semifilled orbital of Cu(CO) is a hybrid sp$_\sigma$ orbital of Cu pointing away from the ligand, while the semifilled orbital of Cu(CO)$_3$ represents the back-donation from the Cu 4p$_\pi$ orbital into the π* orbitals of CO molecules.

Experimental Section

A liquid helium cryostat that would enable trapping of vaporized metal atoms in an inert gas matrix and examination of the resulting matrix by ESR has been described earlier.[5] In the present series of experiments, copper atoms were generated from a resistively heated (~1400 °C) tantalum cell and were trapped in argon matrices containing a controlled amount of carbon monoxide (~1-4%).

The ESR spectrometer used was an IBM Model ER200D system, and a low-frequency (375 Hz) field modulation was used for the signal detection. All the spectra reported here were obtained while the matrix was maintained at ~4 K. The spectrometer frequency locked to the sample cavity was 9.4250 GHz, and a typical microwave power level was ~5 μW.

Research grade argon and CP grade carbon monoxide were obtained from Matheson, and ^{13}C-enriched (enrichment >90%) carbon monoxide was obtained from MSD Isotopes.

Results

The ESR spectrum of Cu atoms (3d^{10}4s^1) isolated in rare gas matrices has already been analyzed.[6] There are two naturally abundant Cu isotopes, ^{63}Cu (natural abundance = 69%, $I = 3/2$, $\mu = 2.2206\beta_n$) and ^{65}Cu (natural abundance = 31%, $I = 3/2$, $\mu = 2.3790\beta_n$). Owing to the large hfc interaction with those nuclei, the ESR spectrum of Cu atoms observed with an X-band spectrometer shows only two resonance transitions; one corresponds to the "NMR" transition ($M_S = 1/2$, $M_I = -1/2 \leftrightarrow -3/2$) and occurs at 1.5 and 2.0 kG for ^{63}Cu and ^{65}Cu, respectively, and the other corresponds to the ESR transition ($M_S = -1/2 \leftrightarrow +1/2$, $M_I = -3/2$), and occurs at 5.8 and 6.0 kG.

Figure 1 shows the ESR spectrum observed from the Cu/CO-(2%)/Ar system. Three types of signals A, B, and C are indicated. The signals A are those of isolated Cu atoms described above. The signals B and C were observed only when Cu and CO were cocondensed. When the CO concentration was low (~1%), the A and B signals dominated the spectrum, and, when the CO concentration was high (~4%), the C signals were the most dominant. The color of the argon matrix changed from pale blue to purple with increasing CO concentration. Thus, based on these observations and in cognizance of conclusions reached in the IR

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