Axial Ligand Studies in Iron Triad Metalloporphyrins

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Knowledge of the chemistry of iron porphyrins is crucial to the understanding of axial ligation in heme proteins. Small molecule binding in these systems is first controlled by the chemistry of the heme unit and then modified by the protein superstructure.[1] Iron porphyrin carbene complexes and carbonyl compounds have been used to further examine the role of porphyrin chemistry in the behavior of heme proteins.[2,3] In particular, energy transfer processes, such as photochemistry or vibrational relaxation, provide insight into small ligand binding and heme protein behavior.[4,5]

Iron porphyrin carbenes and vinylidenes were first synthesized in an attempt to model the reductive deactivation of heme enzymes by halocarbons.[6,7] These complexes are Fe(IV) species with a formal metal-carbon double bond. Upon irradiation of either the Soret or Q band of $Fe(TPP)CX_2$ or $Fe(TPP)(CC(C_6H_4Cl)_2)$ (TPP = 5,10,15,20-tetraphenylporphyrin), the carbene/vinylidene absorbances disappear and the spectrum converts to that of the unligated complex, Fe(TPP) (Figure 1). The formation of this species indicates loss of the axial carbene through a methylene transfer reaction.

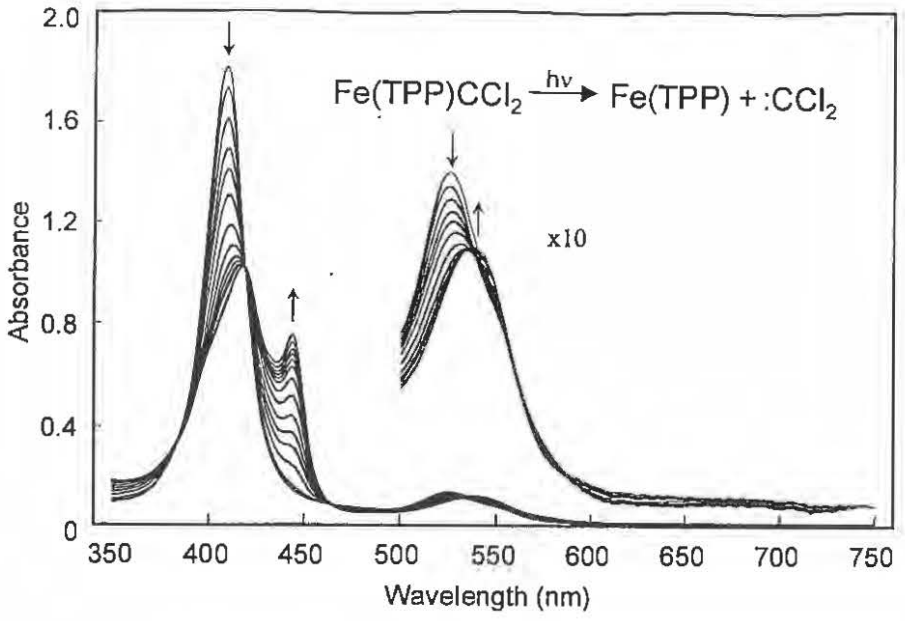


Figure 1. Photolysis of $Fe(TPP)(CCl_2)$ in degassed benzene at 20° C.

Methylene transfer can be confirmed in these photolyses by the formation of cyclopropanes from alkenes.[8] The photolysis of iron porphyrin halocarbenes in the presence of alkene substrates leads to the formation of dihalocyclopropanes in good yield. Methylene transfer can occur through two possible pathways. If the carbene fragment has a stabilized singlet ground state, then a free carbene mechanism can take place. A free carbene is a solvated, transiently stable, singlet diradical that can add to substrates independently of the method of generation. Alternatively, a methylene unit can be transferred through a carbenoid mechanism, where addition to substrates is mediated by a catalyst. This type of reaction is exhibited in

Simmons-Smith cyclopropanations.[9,10] The mechanism of methylene addition in the iron porphyrin carbene photolyses was determined through the use of competitive substrate reactions. The ratio of products in these reactions matched those of a free carbene reaction, haloform generated carbenes, conducted at the same temperature. (Figure 2) This confirms the photoinduced lysis of the metal-carbon double bond and formation of a free carbene in solution. This chemistry has never been observed before in transition metal complexes.[11,12]

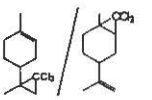
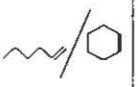
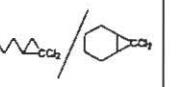
Porphyrin	Substrate	Product	Photolysis Product Ratio	Base Induced Product Ratio
$Fe(TPP)CCl_2$			0.22	0.22
$Fe(TPP)CCl_2$			0.14	0.14
Fe(TPP)CClF		 *syn* F vs. *syn* Cl products	0.55	0.55
Fe(TPP)CClF		 *syn* F vs. *syn* Cl products	0.82	0.82
Fe(TPP)CClF		 *syn* F vs. *syn* Cl products	0.50	0.50

Figure 2. Intramolecular and intermolecular competitive reactivity results for photolyses of $Fe(TPP)CCl_2$ and Fe(TPP)CClF in the presence of alkene substrates.

Like photochemistry, studies in vibrational dynamics can also provide information on heme cofactor/protein relationships. Recent mutant and conformational protein studies found a remarkable correlation between vibrational relaxation and stretching frequencies in bound carbonyls.[13] In order to better understand the factors that lead to this trend, a series of iron triad porphyrin carbonyl complexes, M(porphyrin)(base)(CO), were synthesized. The vibrational frequency of the carbonyl was tuned through varying the metal, axial base, porphyrin structure, and isotopic labeling.

Using the Stanford Free Electron Laser, the first excited vibrational mode of the carbonyl in these complexes was populated with a picosecond pulse and the vibrational relaxation lifetime was then measured.[14] The vibrational relaxation rate increases linearly with decreasing vibrational frequency in both synthetic (5,10,15,20-tetraphenylporphyrin) and natural (protoporphyrin IX dimethyl ester, coproporphyrin IX tetraisopropyl ester) heme models. (Figure 3) This trend demonstrates that vibrational relaxation occurs through anharmonic coupling via π backbonding. This is in contrast with a σ bonding process, which would exhibit increasing vibrational relaxation rates with increasing frequency.[15]

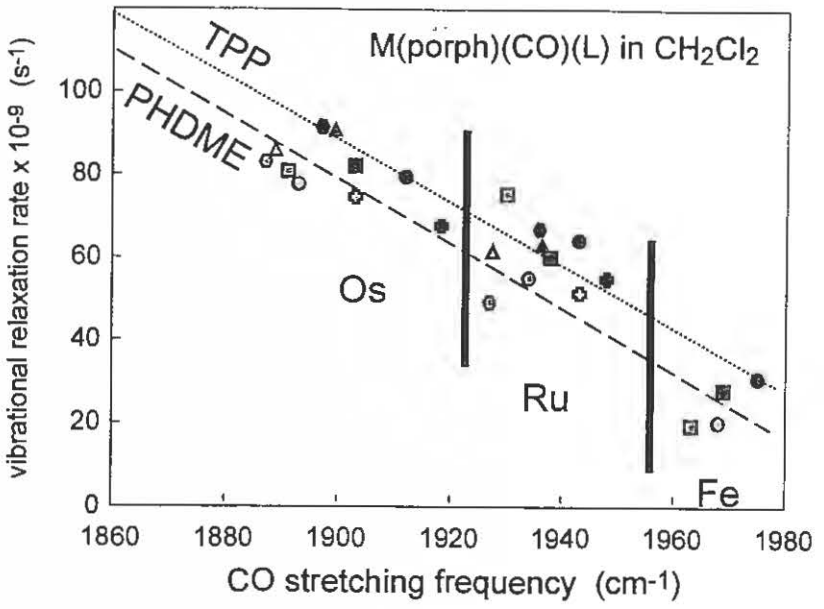


Figure 3. Vibrational relaxation rate versus vibrational frequency in iron, ruthenium, and osmium metalloporphyrin carbonyl complexes.

Further experiments determined the effects of solvent and isotopic labeling. In chlorocarbons, solvent effects did not contribute significantly to vibrational relaxation. These solvents do not have vibrational modes close to that of the excited carbonyl; therefore, intramolecular relaxation processes dominate. Solvents that do have energetically similar vibrational modes, like dibutyl phthalate, did exhibit an increase in vibrational relaxation rate. In addition, isotopic substitution experiments did not alter the relaxation rate in these porphyrin systems. This signifies that vibrational relaxation is dependent on the extent of backbonding with the carbonyl, and not the absolute frequency.

References

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