

Metalloporphyrin Photochemistry

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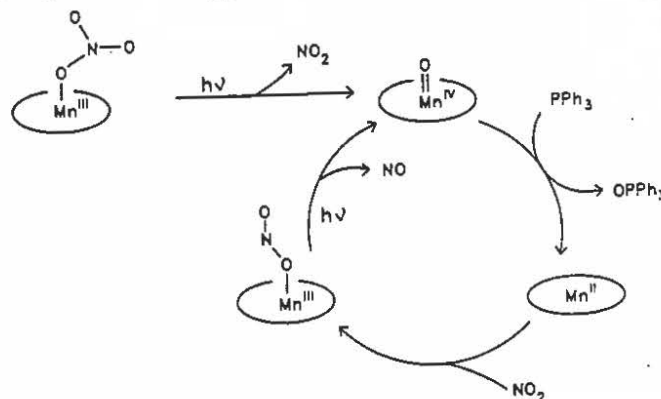
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Metalloporphyrins serve many functions in biological systems. Their important role in the reduction of oxoanions [1] such as nitrite and sulfite in bacteria, and in the oxidation of organic substrates [2] by cytochrome P450 has led us to examine the photochemistry of metalloporphyrin complexes of a number of anions including nitrate and nitrite, sulfate and bisulfate, perchlorate, and chloride. We have also developed the use of matrix isolation photochemistry to examine the mechanism of the photochemistry in metalloporphyrin oxoanion complexes.

The photochemistry of both metal-free porphyrins [3] and metalloporphyrins [4-8] has generated much recent interest. Manganese metalloporphyrins have been especially closely examined, due to the unique mixing of metal e_g orbitals and porphyrin $e_g(\pi^*$ orbitals) [4]. The mixing of these orbitals results in so-called hyper spectra that are characterized by an intense band at low energy (470-480 nm) with additional transitions at higher energy, capable of producing various photochemical reactions. For example, the photoreduction of $\text{Mn}(\text{TPP})(\text{X})$ (where $\text{TPP} = 5,10,15,20$ -tetraphenylporphyrinate(-2)) to $\text{Mn}^{\text{II}}(\text{TPP})$, where $\text{X} = \text{I}, \text{Br}, \text{Cl}, \text{O}_2\text{CCH}_3$, or NCS occurs [6] with quantum yields of approximately 10^{-5} . The photoreduction of water-soluble manganese porphyrins has also been studied extensively [7]. In contrast to these photoreductions, manganese porphyrin perchlorates and periodates undergo photooxidation, possibly via heterolytic β -cleavage, to a putative $\text{O} = \text{Mn}^{\text{IV}}(\text{TPP})^{++}$ species [4a,b]. This metal oxo is a competent oxidant of organic substrates, including alkanes. With both periodate and perchlorate complexes, all four oxygen equivalents are utilized in substrate oxidation. Finally, the formation of a manganese(V) nitrido complex by photooxidation of $\text{Mn}(\text{TPP})(\text{N}_3)$ has also been reported [8].

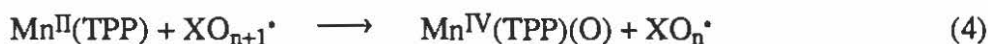
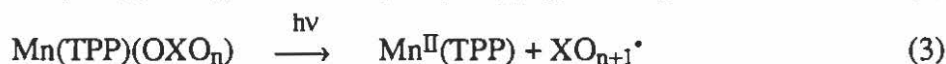
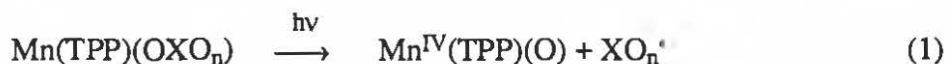
In our work, new nitrate and nitrite complexes of metalloporphyrins have been synthesized and crystallographically characterized, and their photochemistry examined. Irradiation of $\text{Mn}(\text{TPP})(\text{NO}_3)$ and $\text{Mn}(\text{TPP})(\text{NO}_2)$ produces quantitatively the high valent metal-oxo species $\text{O} = \text{Mn}^{\text{IV}}(\text{TPP})$, with quantum yields of 1.6×10^{-4} and 5.3×10^{-4} , respectively. This metal-oxo species is capable of oxidizing substrates as demonstrated in reactions with styrene or triphenylphosphine. In the case of $\text{Mn}(\text{TPP})(\text{NO}_3)$, two oxidizing equivalents are produced, whereas with $\text{Mn}(\text{TPP})(\text{NO}_2)$, only one oxidizing equivalent is available. $\text{Mn}(\text{TPP})(\text{NO}_2)$ is formed as an intermediate in the photolysis of $\text{Mn}(\text{TPP})(\text{NO}_3)$, as shown in Scheme I. Similarly, the photochemistry of $\text{Fe}(\text{TPP})(\text{NO}_3)$ produces substrate oxidation, including C-H hydroxylation, which suggests the photochemical formation of $\text{O} = \text{Fe}^{\text{IV}}(\text{TPP}^{++})$ as the active oxidant. Remarkably, all three oxygen atoms of the initially bound NO_3^- can be used for substrate oxidation. The X-ray crystal structures of $\text{Mn}(\text{TPP})(\text{NO}_3)$ and $\text{Mn}(\text{TPP})(\text{NO}_2)$ have been solved. In the nitrate complex $\text{Mn}(\text{TPP})(\text{NO}_3)$, the nitrate ion is coordinated in an unidentate fashion, with a Mn-O distance of 2.101 Å. $\text{Mn}(\text{TPP})(\text{NO}_2)$ is the first metalloporphyrin complex with oxygen-bound nitrite. The Mn-O distance is 2.059 Å.



Scheme I

New sulfate and hydrogensulfate complexes of metalloporphyrins have also been synthesized and crystallographically characterized, and their photochemistry examined. Irradiation of $[\text{Mn}(\text{TPP})_2(\text{SO}_4)]$ and $\text{Mn}(\text{TPP})(\text{OSO}_3\text{H})$ produces $\text{Mn}^{\text{II}}(\text{TPP})$ quantitatively, with quantum yields of 7.1×10^{-4} and 9.8×10^{-4} , respectively. In contrast to other manganese oxo-anion complexes, metal-oxo species are not formed and oxidation of hydrocarbons does not occur. The X-ray crystal structures of $[\text{Mn}(\text{TPP})_2(\text{SO}_4)]$ and $\text{Mn}(\text{TPP})(\text{OSO}_3\text{H})$ show similar stereochemistry to the analogous iron complexes [9]. In the sulfate complex $[\text{Mn}(\text{TPP})_2(\text{SO}_4)]$, the sulfate ion is coordinated to each metal in an unidentate fashion, with Mn-O distances of 2.109 and 2.008 Å. In $\text{Mn}(\text{TPP})(\text{OSO}_3\text{H})$, the hydrogensulfate ion is coordinated through one of the oxygens, with a Mn-O bond length of 2.078 Å.

In this work with manganese porphyrin oxoanion complexes, two distinct types of reactivity were observed in solution: oxygen atom transfer to the metal and photoreduction of the metal. In the first class, both the nitrate and nitrite complexes underwent β -bond cleavage to form $\text{Mn}^{\text{IV}}(\text{TPP})(\text{O})$ (Equation 1). In the case of perchlorate and periodate [10] complexes, the formation of $[\text{Mn}(\text{TPP})(\text{O})]^+$ (Equation 2) was inferred from the nature of the observed hydrocarbon oxidations. On the other hand, sulfate and bisulfate complexes underwent homolytic α -bond cleavage to form $\text{Mn}^{\text{II}}(\text{TPP})$, as shown in Equation 3. The possibility that all oxoanion complexes may actually undergo initial α -bond cleavage as in Equation 3, followed in some cases by a rapid thermal reaction to form metal-oxo species (Equations 4-5), was also recognized. Solution photochemical studies could not differentiate between these two mechanisms.



Matrix isolation techniques can prevent, in principle, the thermal reactions shown in Equations 4 and 5, and thus distinguish between initial α - and β -bond cleavage as the primary photoreaction. In polymer films and solvent glasses at 10K, both $\text{Mn}(\text{TPP})(\text{NO}_3)$ and $\text{Mn}(\text{TPP})(\text{NO}_2)$ produce $\text{Mn}^{\text{II}}(\text{TPP})$ upon irradiation. In contrast to the solution photochemistry, no formation of $\text{Mn}^{\text{IV}}(\text{TPP})(\text{O})$ was detected. The quantum yields (ϕ) for $\text{Mn}^{\text{II}}(\text{TPP})$ formation in the matrix is only slightly larger than those measured for $\text{Mn}^{\text{IV}}(\text{TPP})(\text{O})$ formation in solution, and the ratio of $\phi(\text{Mn}(\text{TPP})(\text{NO}_3))/\phi(\text{Mn}(\text{TPP})(\text{NO}_2))$ is the same both in solution and in matrix. Taken together, these data demonstrate that the initial photoreaction is reduction of the metal, followed by rapid thermal reactions in solution give $\text{Mn}^{\text{IV}}(\text{TPP})(\text{O})$. The photoreduction of the metal center is consistent with other known porphyrin photochemistry and appears to be a general mechanism. The subsequent thermal chemistry is probably determined by several factors, including the relative stabilities of the leaving groups and the remnant porphyrin species, as well as relative solvation energies of products.

References

1. Cole, J. A.; Ferguson, S. J., eds. *The Nitrogen and Sulphur Cycles*, Cambridge University Press, Cambridge, 1988.
2. Ortiz de Montellano, P. R., ed. *Cytochrome P450*, Plenum, New York, 1985.
3. (a) Blauer, G.; Sund, H., eds. *Optical Properties of Tetrapyrroles*, W. DeGruyter, Berlin, 1985.
(b) Gouterman, M.; Rentzepis, P. M.; Straub, K. D., eds. *Porphyrins: Excited States and Dynamics*, ACS Symp. Series #321, Washington, D. C., 1986.
(c) Andreoni, A.; Cubeddu, R., ed. *Porphyrins in Tumor Phototherapy*, Plenum Press, New York, 1984.
(d) Gomer, C. J. *Seminars in Hematology* 1986, 26, 27.
(e) van der Bergh, H. *Chim. Brit.* 1986, 22, 430.
4. (a) Suslick, K. S.; Acholla, F. V.; Cook, B. R. *J. Am. Chem. Soc.* 1987, 109, 2812.
(b) Suslick, K. S.; Acholla, F. V.; Cook, B. R. Kinnaird, M. G. *Rec. Trav. Chim.* 1987, 106, 329.
(c) Hendrickson, D. N.; Kinnaird, M. G.; Suslick, K. S. *J. Am. Chem. Soc.* 1987, 109, 1243.
5. (a) Zerner, M.; Gouterman, M. *Inorg. Chem.* 1966, 5, 1699.
(b) Zerner, M.; Gouterman, M. *Theor. Chim. Acta.* 1966, 4, 44.
(c) Gouterman, M. *Porphyrins*, Dolphin, D., ed., Academic Press, New York, 1978, vol. 3, pp. 1-166.
6. Imamura, T.; Jin, T.; Suzuki, T.; Fujimoto, M. *Chem. Lett.* 1985, 847.
7. (a) Carnier, N.; Harriman, A. *J. Photochem.* 1981, 15, 341.
(b) Harriman, A.; Porter, G. *J. Chem. Soc., Faraday II* 1980, 76, 1429.
(c) Harriman, A.; Porter, G. *J. Chem. Soc., Faraday II* 1979, 75, 1543.
8. Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* 1983, 105, 2073.
9. (a) Scheidt, W. R.; Lee, Y. J.; Bartzcak, T.; Hatano, K. *Inorg. Chem.* 1984, 23, 2552.
(b) Scheidt, W. R.; Lee, Y. J.; Finnegan, M. G. *Inorg. Chem.* 1988, 27, 4725.
10. Suslick, K. S.; Acholla, F. V.; Cook, B. R. *J. Am. Chem. Soc.* 1987, 109, 2818.