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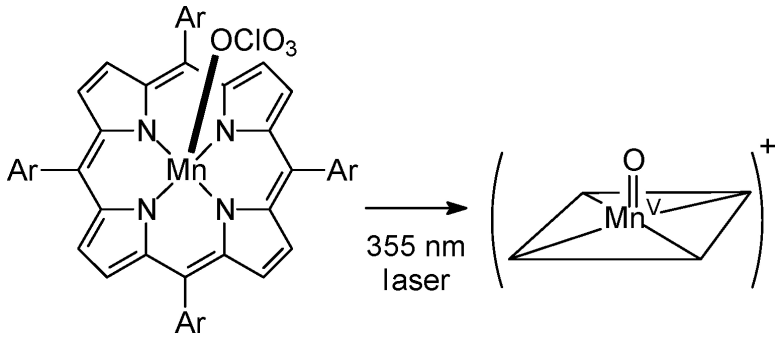

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Laser Flash Photolysis Formation and Direct Kinetic Studies of Manganese(V)-Oxo Porphyrin Intermediates

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High-valent transition metal-oxo intermediates are highly reactive electrophilic oxidants that are produced in the laboratory and in industrial processes from reactions of various metal complexes with sacrificial oxidants.[1] Manganese(V)-oxo species in both porphyrin and Schiff-base complexes are generally accepted to be the key reactive intermediates in useful catalytic oxidations,[1] and high-valent manganese intermediates are produced in photosystem II for oxidation of water to oxygen.[2] Direct spectroscopic observation and isolation of Mn^V-oxo porphyrin intermediates has been a challenging goal due to the high reactivity of these species. A major advance in the chemistry of Mn^V-oxo intermediates was made in 1997 when Groves et al. reported the isolation and characterization of a porphyrin-Mn^V-oxo species,[3] and two other porphyrin-Mn^V-oxo intermediates have since been characterized.[4] These Mn^V-oxo species contained cationic aryl groups on the porphyrin ring and were produced in water, which increases the stability of the intermediates. Non-porphyrin Mn^V-oxo species are known that are stable in comparison to porphyrin species; these include bis-amido-bis-alkoxo, tetraamido, corrole, and corrolazine complexes.[5]

We report here the formation of highly reactive porphyrin-Mn^V-oxo intermediates in acetonitrile via laser flash photolysis (LFP) methods and direct measurements of their rate constants for oxidation reactions. The concept of the studies is based on the general observation of photoactivated oxidations by transition metal complexes in the presence of sacrificial oxidants.[6] More specifically, Suslick et al. reported photocatalytic oxidations by Mn^{III}(TPP)[7] salts in the presence of perchlorate and periodate counterions, and formation of transient Mn^V-oxo species was indicated on the basis of the oxidation products observed.[8]

Treatment of Mn^{III}(TPFPP)(Cl)[7] with $AgClO_4$ in acetonitrile gave a perchlorate complex (**1**), which absorbed in the UV−vis with λ_{max} at ca. 470 nm. Upon addition of substrates such as *cis*-stilbene or diphenylmethane, the absorbance shifted slightly to $\lambda_{max} = 465$ nm. Irradiation with ca. 100 mJ of 355 nm laser light resulted in bleaching of the 465 nm signal and instant formation of a species that absorbed with λ_{max} at 432 nm (Figure 1).[9] We assign the transient produced by LFP as Mn^V-oxo intermediate **2** from heterolytic β-cleavage of an O−Cl bond in the perchlorate precursor on the basis of the reactivity discussed below and the absorbance at 432 nm. Known porphyrin-Mn^V-oxo species in water have λ_{max} in the range 427−443 nm.[3,4] A similar LFP experiment with the nitrate salt of Mn^{III}(TPFPP) gave an Mn^{IV}-oxo intermediate with a weak absorbance at $\lambda_{max} = 425$ nm, from homolytic cleavage of the O−N bond.[10]

In the absence of reactive substrates, **2** decayed over ca. 30 ms in a biexponential process. In the presence of reactive substrates, the fast decay component accelerated as a function of substrate concentration, and the slow decay component was unaltered. Second-order rate constants for the reactions were determined by eq 1, where k_{obs} is the pseudo-first-order rate constant for the fast decay process, k_0 is the background decay rate constant, k_{ox} is the rate constant for oxidation of substrate, and [sub] is the concentration of substrate. Results for two substrates are shown in Figure 2, and second-order rate constants are listed in Table 1. Epoxidation of *cis*-stilbene was faster than oxidation of diphenylmethane and ethylbenzene, and the kinetic isotope effect for the reaction of **2** with PhEt is 2.3.[11]

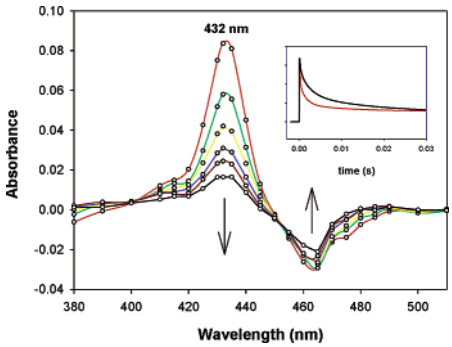

Figure 1. Time-resolved spectrum following LFP of complex **1** in acetonitrile. The bleached signals from **1** are negative absorbances, and the signals from **2** are positive absorbances. Time slices are at 0.13, 0.5, 1.2, 2.4, 4.4, and 11.2 ms. The inset shows decay traces at 432 nm from reactions in the absence of substrate (black) and in the presence of 1×10^{-3} M *cis*-stilbene (red), where the signal intensities of the traces have been scaled such that the initial absorbances are equal.

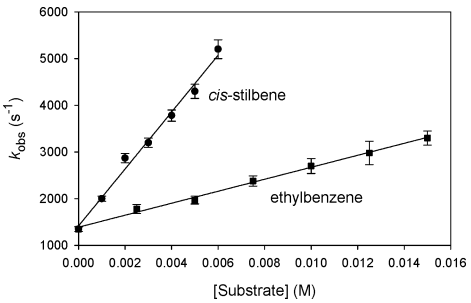

Figure 2. Observed fast decay rate constants for reactions of **2** in the presence of *cis*-stilbene and ethylbenzene in acetonitrile solutions.

$$k_{obs} = k_0 + k_{ox}[\text{sub}] \quad (1)$$

The kinetic results with **2** were confirmed by conducting competition oxidations under catalytic turnover conditions. Thus, oxidations of mixtures of substrates were conducted with 0.1 mol % of the porphyrin-Mn^{III}(Cl) salt and *m*-CPBA[7] or PhIO as the sacrificial oxidants. The results of the competition reactions between *cis*-stilbene and diphenylmethane and between PhEt-d_0 and PhEt-d_{10} listed in the Supporting Information are in good agreement with the ratios of the absolute rate constants for the respective reactions, although the relative rate constants were sensitive to the identity of the sacrificial oxidant and solvent.[12] Consistent with the established oxygen insertion pathway for reaction of **2**, we observed

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Table 1. Rate Constants for Reactions of Mn^V-Oxo Intermediates[a]

Mn^V-oxo	substrate	k_{ox} (M^{-1} s^{-1})
2	*cis*-stilbene	$(6.1 \pm 0.3) \times 10^5$
	diphenylmethane	$(1.3 \pm 0.3) \times 10^5$
	ethylbenzene	$(1.28 \pm 0.03) \times 10^5$
	ethylbenzene-d_{10}	$(5.5 \pm 0.5) \times 10^4$
4	*cis*-stilbene	$(1.1 \pm 0.1) \times 10^4$
	diphenylmethane[b]	$<2 \times 10^3$
6	*cis*-stilbene	$(4.3 \pm 0.3) \times 10^4$
	diphenylmethane	$(5.8 \pm 0.1) \times 10^3$

[a] In acetonitrile at (22 ± 2) °C. The results for **2** are from 2 to 4 determinations, and those for **4** and **6** are from 1 to 2 determinations. [b] The reaction was too slow to determine a rate constant accurately; the value is the lower limit of the method.

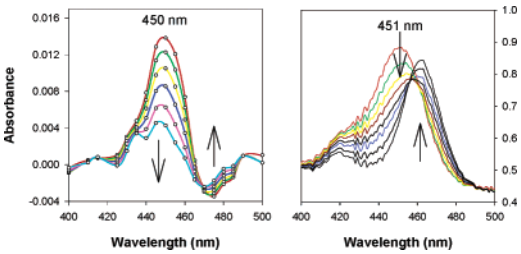

Figure 3. Left: Time-resolved spectrum of **6**, produced by LFP of complex **5** in acetonitrile, reacting with diphenylmethane over 11 ms. Right: Time-resolved spectrum from reaction of Mn^{III}(TMPyP)(Cl) with *m*-CPBA in acetonitrile over 40 s. The growing absorbances are from Mn^{III} species. Note that the formation of **6** in acetonitrile was "instant" in the stopped-flow unit under our reaction conditions.[3]

highly stereoselective formation of *cis*-stilbene oxide (>95:5, cis:trans) from oxidations of *cis*-stilbene by catalytic Mn^{III}(TPFPP)(Cl) with *m*-CPBA and by photoactivated (300−400 nm irradiation) $Mn^{III}(TPFPP)(ClO_4)$ in CH_3CN and in $PhCF_3$ solutions.

Manganese(V)-oxo species also were generated by LFP of $Mn^{III}(TPP)(ClO_4)$[7] (**3**), giving oxo species **4**, and of $Mn^{III}(TMPyP)(ClO_4)$[7] (**5**), giving oxo species **6**. Groves et al. produced the Mn^V-oxo species **6** via stopped-flow methods in water, where λ_{max} was at 443 nm,[3] but **6** has λ_{max} at 451 nm in acetonitrile.[13] Figure 3 shows time-resolved UV−vis spectra of **6** produced by photolysis of the perchlorate salt **5** and from the reaction of Mn^{III}(TMPyP)(Cl) with *m*-CPBA. In the absence of substrates, decay of **6** was faster than formation of Mn^{III} species.[8] In the reaction with *m*-CPBA, we used 3 equiv of oxidant to drive the reaction to formation of the Mn^V-oxo species **6**, and the rate of decay of **6** is a measure of the rate of consumption of *m*-CPBA. We note that Mn^V-oxo species **2** was not detected from reaction of Mn(TPFPP)(Cl) with *m*-CPBA.

Second-order rate constants for reaction of **4** with *cis*-stilbene and for reaction of **6** with *cis*-stilbene and diphenylmethane are listed in Table 1. The reactivities of the Mn^V-oxo intermediates with *cis*-stilbene and with diphenylmethane are in the order **2** > **6** > **4**, which is in agreement with the general observation that more highly electrophilic metal-oxo complexes, by virtue of the electron-withdrawing aryl groups, are more reactive oxidants.[14]

LFP formation of Mn^V-oxo species demonstrates that highly reactive transition metal-oxo intermediates can be produced photochemically and studied directly. The method permits measurements of absolute rate constants for oxidations of substrates rather than relative rate constants that are obtained under catalytic turnover conditions, and comparisons of the reactivity of various metal-oxo species with one substrate are possible. Given that Mn^V-oxo intermediates are more reactive than analogous iron-oxo species, the potential is good for extending the methods for studies of iron-oxo species and possibly for generation of iron-oxo intermediates in enzymes.[15]

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Supporting Information Available: Experimental details, results of LFP experiments, and results of competition experiments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Abbreviations: TPP = tetraphenylporphyrinato, TPFPP = tetrakis-(pentafluorophenyl)porphyrinato; TMPyP = tetra(4-(*N*-methylpyridiniumyl))porphyinato; *m*-CPBA = *m*-chloroperoxybenzoic acid.
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