Unusual Kinetic Stability of a Ground-State Singlet Oxomanganese(V) Porphyrin. Evidence for a Spin State Crossing Effect

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Reactive oxomanganese species are involved in a wide range of biological and catalytic processes involving oxygen activation and transfer.[1−3] Such species are proposed to participate in the oxidation of water to molecular oxygen in photosystem II of green plant photosynthesis[4,5] as well as in certain catalases[6] and peroxidases.[7] Synthetic manganese porphyrins and related Schiff base complexes have also been shown to be versatile catalysts for the oxidation of a wide variety of organic substrates.[8,9] The correlation of electronic structure to the reactivity of such species and a deeper understanding of those reactions has remained an elusive goal. In a recent paper,[10] Collins et al. have shown that the reactivity of an oxoMn(V) tetraamido complex increased upon complexation of metal cations close to an oxoMn(V) center. We show here, by contrast, that moving the site of positive charge toward the oxoMn(V) center in an isomeric set of oxoMn(V) porphyrin complexes[11a] results in an extraordinary kinetic stability as measured by the rates of electron transfer, H atom abstraction, and oxygen transfer reactions. This kinetic stability is shown to be related to the low-spin, d^2 electronic state of the oxidant.

The stoichiometric reaction of Mn(III)TM-2-PyP[11b] with the oxidants HSO_5^- (oxone), *m*-chloroperoxybenzoic acid (*m*-CPBA), and ClO^- at pH 7.4 and 25 °C led immediately to the generation of a new species **1** (Scheme 1) with a strong sharp Soret band at 434 nm (Figure 1).[12] In a few minutes, **1** decayed back to Mn(III)-TM-2-PyP. Treatment of **1** with $NaNO_2$ produced another intermediate, **2**, which had a UV−vis spectrum characteristic of an oxoMn(IV) porphyrin complex.[11a,13] The X-band EPR of **2** at pH 9.0 showed a strong broad resonance at $g_\perp \sim 4.0$ and a weak signal at $g_\parallel \sim 2.0$, similar to those observed for other high-spin, monomeric Mn(IV) species.[14−16] These signals were absent in solutions of **1**.

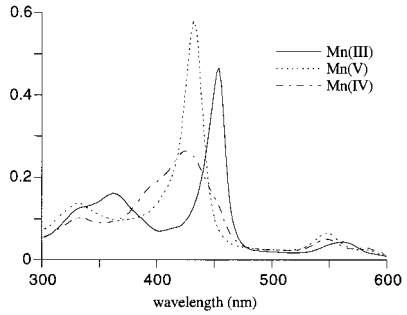
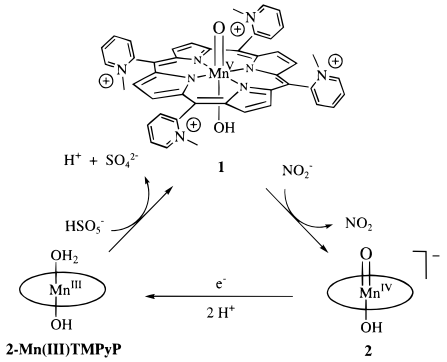


Figure 1. UV−vis spectra MnTM-2-PyP porphyrins. All three are 5 μm in 50 mM pH 7.4 phosphate buffer. OxoMn(V)TM-2-PyP (λ_{max} = 434 nm) was prepared by oxidation of Mn(III)TM-2-PyP (λ_{max} = 454 nm) by 1 equiv of oxone. In situ reduction of Mn(V) by $NaNO_2$ (10 equiv) produced oxoMn(IV)TM-2-PyP (λ_{max} = 426 nm).

Scheme 1



The enhanced stability of **1** at higher pH allowed its characterization by ^{1}H NMR. Figure 2 shows ^{1}H NMR spectra obtained after the reaction of Mn(III)TM-2-PyP with oxone in D_2O at pD 8.7. The starting Mn(III)TM-2-PyP is paramagnetic and displayed characteristically broad signals.[17] Sharp ^{1}H NMR resonances of a clearly diamagnetic compound appeared in the downfield region (δ 8−10) immediately after the addition of oxone. These signals decayed over a few minutes, the same time course for the disappearance of intermediate **1** according to the UV−vis spectra. The very similar ^{1}H NMR spectrum of the transient **1** and those of Zn(II)TM-2-PyP are compared in Figure 2 (trace E). On the basis of these NMR data, we assign to intermediate **1** a low-spin, d^2 oxoMn(V) porphyrin formulation. Possibilities such as an oxoMn(IV) dimer can be ruled out by the facts that the

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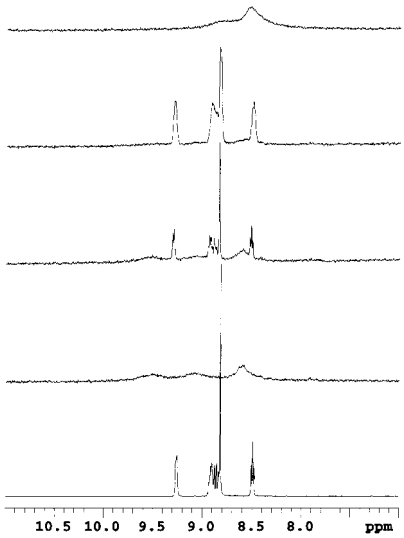

Figure 2. ^{1}H NMR spectra for the oxidation of Mn(III)TM-2-PyP by oxone. All spectra were taken in pD 8.7 phosphate buffered D_2O solution; porphyrin concentrations were all 1 mM: (A) starting Mn(III)TM-2-PyP and (B) 1, (C) 3, and (D) 30 min after mixing with 1.2 equiv of oxone; (E) Zn(II)TM-2-PyP.

Table 1. Comparative Second Order Rate Constants for MnTM-2-PyP and MnTM-4-PyP[a]

Reaction	MnTM-2-PyP[d]	MnTM-4-PyP[e]
Mn(V) $\xrightarrow{NaNO_2}$ Mn(IV)	2.0×10^4	1.5×10^7
Mn(V) $\xrightarrow{CBZ^b}$ Mn(III)	~10^2	6.5×10^5
Mn(V) $\xrightarrow{HPA^c}$ Mn(III)	8.8×10^3	3.4×10^6
Mn(IV) $\xrightarrow{NaNO_2}$ Mn(III)	7.6×10^1	1.4×10^2
Mn(IV) $\xrightarrow{HPA}$ Mn(III)	1.4×10^4	9.1×10^4

[a] Reaction kinetic profiles were collected in the photomultiplier mode on the HI-TECH SF-61 DX2 stopped-flow spectrophotometer with single or double-mixing modes. oxoMn(V) (**1**), oxoMn(IV) (**2**), and Mn(III)TM-2-PyP were monitored at 434, 426, and 454 nm, respectively. All reactions were pseudo first order in reductant concentrations. [b] Carbamazepine, (5*H*-dibenzo[*b*,*f*]azepine-5-carboxamide). [c] 4-Hydroxyphenylacetic acid. [d] This work. [e] Rate constants reported in ref 11a.

chemical shifts of the pyrrole protons are nearly identical with those reported for other monomeric diamagnetic metalloporphyrins[18a] and distinctly different from known Mn(IV)-μ-oxo dimers.[18b]

Oxomanganese(V) complexes are rare. Two characterized species[10,19,20] involve the use of tetraanionic ligands to stabilize the high-valent manganese center. Both compounds are diamagnetic, as are the isoelectronic nitridomanganese(V)[21] and oxochromium(IV)[22] porphyrin complexes.

The reactivity of **1** was elucidated by analysis of its reactions with reducing substrates. Table 1 shows comparative rate constants for MnTM-2-PyP and its isomer MnTM-4-PyP. The reactions were carried out at pH 7.4 in 50 mM phosphate buffer to allow direct comparison with our earlier data.[11a] Under these reaction conditions, oxoMn(V)TM-2-PyP, **1**, had a half-life of 95 s, which is about 200 times greater than that of its 4-pyridyl isomer, oxoMn(V)TM-4-PyP. OxoMn(V)TM-2-PyP was found to be significantly less reactive than oxoMn(V)TM-4-PyP toward a range of oxidizable species. For the selected reductants, nitrite (electron transfer), a carbamazipine (olefin epoxidation), and 4-hydroxyphenylacetic acid (hydrogen abstraction), the reduction rates for oxoMn(V)TM-2-PyP are all about *3 orders of magnitude slower* than those of the isomeric oxoMn(V)TM-4-PyP. Significantly, the two isomeric oxoMn(IV)TMPyP species show similar reactivity toward nitrite and phenols,[23] suggesting a kinetic stabilization that is unique to the Mn(V) oxidation state (**1**).

To which effects can we attribute the dramatic differences in the reactivity of these regioisomers? Steric effects and general field effects are unlikely since these should show similar trends in the Mn(IV)/Mn(III) reaction rates as well. Indeed, electron-withdrawing groups close to an electrophilic oxidant would be expected to increase its reactivity, as has been generally observed.[9,10] Further, the redox potential for the Mn(III)/Mn(II) couple for MnTM-2-PyP is 0.22 V vs NHE while that of MnTM-4-PyP is 0.06 V,[11b,24] also as expected.

We suggest that the differences in reactivity observed for the three reaction types studied reflect electronic factors and involve kinetic barriers due to *spin state crossing effects* as recently suggested by Shaik and Schwarz.[24] Reduction of the *low-spin*, d^2 oxoMn(V) species will lead to *high-spin* Mn(IV) and Mn(III) states which requires the promotion of a d_{xy} electron to $d_{(xz,yz)}$. This effect could also be described as a vibronic effect due to the elongation of the very short Mn−oxo bond upon reduction. Significantly, this promotion is not required for the reductions of Mn(IV) to Mn(III) or Mn(III) to Mn(II), which would explain the more typical behavior of those couples. The ortho isomer free base, H_2TM-2-PyP, is unusual in that it resists protonation even at pH 0 ($pK_a = -0.9$ and 2.4 for H_2TM-2-PyP and H_2TM-4-PyP, respectively[25]). This low pK_a is a measure of the charge distribution of the porphyrin pyrrole ring and can account for the dramatic differences in their kinetic reactivity. The reduced σ-electron donor properties of the 2-methylpyridyl porphyrin ligand would be expected to lower the energy of the *nonbonding* electron pair in d_{xy} and thus increase the $d_{xy} - (d_{xz}, d_{yz})$ energy gap.[26] Thus, in a two-state reaction profile,[24] the singlet manifold of the starting materials would have to cross to a high-spin manifold at some point, thus allowing the promotion energy to be expressed in the transition state. The case of a low-spin d^2 oxoMn(V) complex described here could suggest other cases in which kinetic effects of this type might be found.[27] Such studies are under continued investigation.

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Supporting Information Available: Figure 3, X-band EPR spectrum of **2**, and Figures 4 and 5, kinetic data for the reaction of **1** with nitrite and phenols (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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