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Generation of an Isolable, Monomeric Manganese(V)−Oxo Complex from O_2 and Visible Light

Katharine A. Prokop and David P. Goldberg*

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, United States

S *Supporting Information*

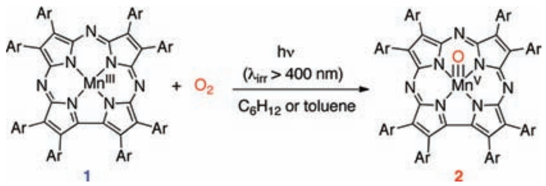
ABSTRACT: The direct conversion of a Mn^{III} complex $[(TBP_8Cz)Mn^{III}$ (**1**)] to a Mn^V−oxo complex $[(TBP_8Cz)Mn^V(O)$ (**2**)] with O_2 and visible light is reported. Complex **1** is also shown to function as an active photocatalyst for the oxidation of PPh_3 to $OPPh_3$. Mechanistic studies indicate that the photogeneration of **2** does not involve singlet oxygen but rather likely occurs via a free-radical mechanism upon photoactivation of **1**.

Heme enzymes such as cytochrome P450 utilize O_2 to generate high-valent metal−oxo species that serve as the active oxidants in a range of selective biochemical oxidations.[1] The development of synthetic metalloporphyrins that can exhibit similar reactivity wherein O_2 is used to generate well-defined, high-valent metal−oxo complexes has been an important yet elusive goal in the modeling of heme enzymes. Although metalloporphyrins have been employed to mimic P450-type activity using sacrificial oxidants such as iodosylbenzene (PhIO) or hydroperoxides in a "shunt" pathway,[2] oxygenation reactions involving O_2 as the oxidant are much less common.[3] A few metalloporphyrin-catalyzed oxidations that utilize O_2 typically require light or heat to cleave open thermally stable μ-oxo porphyrin dimers, which are proposed to generate putative high-valent metal−oxo intermediates.[4] Photo-initiated axial ligand cleavage reactions have been known to generate reduced metalloporphyrins that subsequently react with O_2 to give catalytic oxidations, again possibly through accessing short-lived high-valent metal−oxo intermediates.[5] In contrast, there are very few examples of reactions beginning with metalloporphyrins or other transition-metal complexes that show smooth conversion to well-defined high-valent terminal oxo complexes by treatment with O_2.[6] In addition to mimicking of natural heme systems, there is also compelling motivation to design transition-metal complexes that can use O_2 in catalytic oxidations because of the abundance, low cost, and environmental compatibility of this oxidant.

Herein we describe the reaction of the Mn^{III} complex $(TBP_8Cz)Mn^{III}$ (**1**) [TBP_8Cz = octakis(*p*-*tert*-butylphenyl)-corrolazinato^{3-}] with O_2 and visible light to give the Mn^V−oxo complex $(TBP_8Cz)Mn^V(O)$ (**2**). Either air or pure O_2 gas can be used as the oxidant, which provides the O atom for the terminal oxo ligand. While complexes of reduced +2 metals are well-known to react directly with O_2, there are few examples of +3 first-row transition-metal ions that react with O_2 to give oxygenated metal products. One example is a chromium(III) corrole that reacts directly with O_2 to give a $Cr^V(O)$ complex.[6] A trianionic pincer Cr^{III} complex has also been found to react with O_2 to generate a $Cr^V(O)$ species.[7] Similarly, iron(III) corroles[8] and a tetraamido Fe^{III} complex[4f] have been shown to react with O_2, leading to the formation of stable Fe^{IV}−O−Fe^{IV} dimers. The conversion of **1** to **2** is, to our knowledge, the first example of a clean, direct transformation of a Mn^{III} complex to a $Mn^V(O)$ complex with O_2 as the oxidant.[9] The efficient photocatalytic oxidation of a substrate (PPh_3) under the same conditions (**1** + O_2 + light) is also demonstrated.

Irradiation of micromolar solutions of **1** in a quartz cuvette at 23 °C with a simple white-light source (a 275 W GE bulb) under an ambient air atmosphere resulted in the rapid conversion of green-brown **1** to the bright-green Mn^V−oxo complex **2** (Scheme 1). Monitoring of this reaction by UV−vis spectroscopy revealed the quantitative conversion of **1** (λ_{max} = 432, 687 nm) to **2** (λ_{max} = 419, 639 nm), with tight isosbestic points being maintained throughout the reaction (Figure 1).

Scheme 1. Production of 2 from 1, O_2, and Visible Light



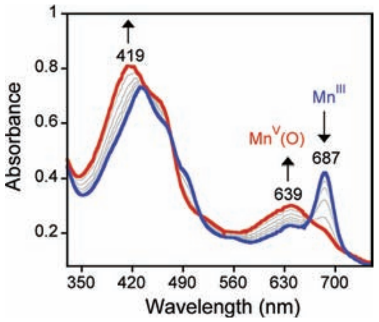


Figure 1. Time-resolved (0−15 min) UV−vis spectral changes observed during the irradiation of an aerobic solution of **1** (12 μM) in cyclohexane (2.5 mL) at 25 °C.

Continued irradiation of the reaction mixture after the appearance of the final spectrum for **2** did not lead to any

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further changes in the UV−vis profile, indicating that **2** is the final product of this reaction.

To determine whether UV light (λ < 400 nm) was necessary for this reaction, a 400 nm long-pass filter was positioned between the light source and the target solution. The filter did not inhibit conversion of **1** to **2**, which continued to proceed smoothly without loss of isosbestic behavior. Since **1** is the only species in solution with an absorption profile above 400 nm, it can be concluded that **1** is the active chromophore that initiates the production of **2** upon irradiation. Control reactions performed in the dark showed that conversion of **1** to **2** does not occur under aerobic conditions in cyclohexane, even after a prolonged period (1 h). Similarly, irradiation of solutions of **1** under a N_2 atmosphere showed no evidence for the production of **2** and no spectral changes that would indicate photoreduction to Mn^{II}, as seen for other photoinitiated metalloporphyrin/O_2 reactions.[5b−d] There was also no observable reaction upon heating (60 °C) of aerobic solutions of **1**. Thus, there is a strict requirement for both light and air as reagents. A similar transformation of **1** to **2** occurred when cyclohexane was replaced with toluene, and tight isosbestic behavior was once again observed (see Figure S1 in the Supporting Information).

Confirmation that **2** was indeed being produced in the photoreaction of **1** + air was obtained by isolation of the green product. The product of the O_2 reaction was purified and isolated via chromatography (silica gel, CH_2Cl_2 eluent), as done previously when **2** was generated from O-atom transfer agents.[10] A major green band was isolated and yielded a green solid, whose ^1H NMR spectrum in CD_2Cl_2 gave rise to peaks exclusively in the diamagnetic region (0−10 ppm). No evidence of broad, paramagnetically shifted peaks associated with the high-spin Mn^{III} starting material were observed. The observed spectrum matches that of the authentic, low-spin (d^2) $Mn^V(O)$ complex **2**,[10a] confirming its production.

To determine whether O_2 was the source of the terminal oxygen atom in **2**, isotope labeling experiments were conducted in combination with analysis by laser desorption ionization mass spectrometry (LDI-MS). When **2** was generated from **1** + light (λ_{irr} > 400 nm) under an ambient air atmosphere, a prominent isotopic cluster centered at *m/z* 1426.8 (Figure 2, top) was observed upon LDI-MS analysis of the reaction mixture. The observed isotope pattern (inset) centered at *m/z* 1426.8 matches that for $(TBP_8Cz)Mn^V(O)$. A less intense cluster centered at *m/z* 1410.8 corresponds to $[(TBP_8Cz)Mn]^+$. In comparison, irradiation of a deaerated solution of **1** in the presence of excess $^{18}O_2$ resulted in a shift of the isotopic cluster consistent with significant ^{18}O enrichment (Figure 2, bottom). To rule out exogenous H_2O as an oxygen source, excess $H_2{}^{18}O$ was added to **1** prior to irradiation under ambient conditions. Immediate analysis of the reaction mixture by LDI-MS after production of **2** showed no evidence of ^{18}O incorporation (Figure S3).[11] These data clearly indicate that O_2 is the source of the terminal oxo ligand in **2**.

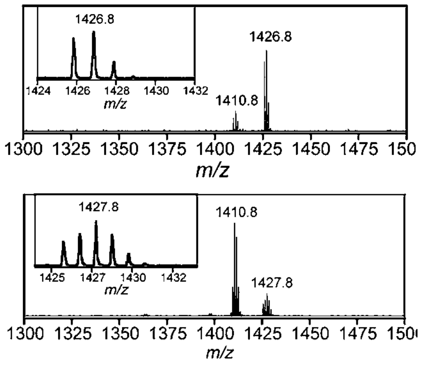
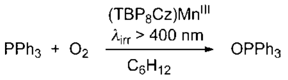


Figure 2. LDI-MS (+ ion mode) of **2** produced from air (top) and $^{18}O_2$ (bottom). The insets show the expanded isotope patterns centered at the molecular ion for **2**. The pattern observed for the bottom inset corresponds to 55% ^{18}O incorporation.[12]

It was shown previously that **2** rapidly reacts with PPh_3 to regenerate **1** and give $OPPh_3$ in good yield.[10a] We thus wanted to determine whether the *catalytic* oxidation of PPh_3 could be performed with O_2 as the oxidant and **1** as the catalyst under photoreaction conditions. Irradiation of a mixture of **1** and excess PPh_3 (1300 equiv) in air-saturated cyclohexane resulted in the rapid production of $OPPh_3$ (Scheme 2). The results of these photocatalytic oxidations are summarized in Table 1. Initial experiments involving air as the oxidant showed that irradiation for 20 min produced $OPPh_3$ with a turnover number (TON) of 80, as observed by ^{31}P NMR spectroscopy. Bubbling of the reaction mixture with a stream of dry O_2 in conjunction with continuous irradiation for 60 min led to a dramatic increase in $OPPh_3$ (TON = 535). Although slow aerobic oxidation of PPh_3 in the absence of a catalyst is known, under our conditions, negligible amounts of $OPPh_3$ were observed in the absence of light or **1** as a catalyst (Table 1, rows 5−7). Similarly, no oxidation products were observed in the presence of the simple Mn coordination complex $Mn(acac)_3$ (Table 1, row 4), indicating that **1** is required for the photocatalytic oxidation of PPh_3 with O_2 as a terminal oxidant.

Scheme 2. Photocatalytic Oxidation of PPh_3



$$PPh_3 + O_2 \xrightarrow[C_6H_{12}]{(TBP_8Cz)Mn^{III},\ \lambda_{irr} > 400\text{ nm}} OPPh_3$$

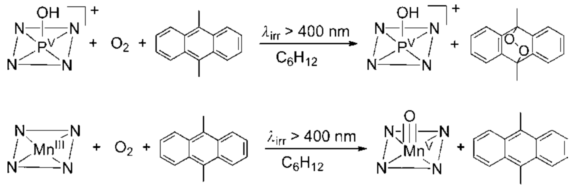
Table 1. Turnover Numbers for Photocatalytic Oxidations[a]

catalyst	t_{irr} (min)[b]	oxidant	TON[c]
1	20	air	80 ± 2
1	30	O_2	252 ± 6
1	60	O_2	535 ± 10
$Mn(acac)_3$	30	O_2	0
none	20	air	0
none	30	O_2	0
none	60	O_2	5 ± 1[d]

[a]Conditions: [catalyst] = 10 or 0 μM and [PPh_3] = 13 mM in cyclohexane at 23 °C. [b]λ_{irr} > 400 nm. [c]TON based on mol $OPPh_3$/mol catalyst as an average of 2 runs. [d]Based on [catalyst] = 10 μM.

Porphyrins are well-known photosensitizers that can produce singlet oxygen ($^1O_2$),[13] and it was important to determine whether $^1O_2$ played a role in the observed **1**/O_2 photooxidation chemistry. The $^1O_2$ trap 9,10-dimethylanthracene (DMA) was employed to test the ability of **1** to generate $^1O_2$ upon exposure to light.[14] DMA reacts with $^1O_2$ to give an endoperoxide product with a rate constant of $k \approx 10^5$−10^6 M^{-1} s^{-1}.[14] In a test reaction, the closed-shell phosphorus(V) corrolazine $[(TBP_8Cz)P^V(OH)](OH)$[15] was irradiated under the same conditions as **1** in air in the presence of excess DMA (Scheme 3). The UV−vis spectrum of this reaction prior to irradiation

Scheme 3. Detection of $^1O_2$ with DMA



was consistent with the combination of phosphorus−Cz and DMA, in which multiple, sharp bands between 300 and 400 nm arise from the DMA component (Figure S2). After 10 min of irradiation, the spectrum showed the loss of all peaks associated with DMA, consistent with the formation and trapping of $^1O_2$. It can be concluded that the closed-shell $(TBP_8Cz)P^V$ complex is an effective photosensitizer for the production of $^1O_2$, with DMA functioning as an efficient $^1O_2$ trap in the presence of the corrolazine. An aerobic solution of **1** (18 μM) was next charged with excess DMA (0.24 mM) and then irradiated (λ_{irr} > 400 nm) for 20 min at 23 °C. No decrease in the absorption bands for DMA at 300−400 nm was observed, and complete formation of **2** proceeded smoothly without any significant inhibition from the presence of the $^1O_2$ trap (Figure 3). These results rule out a significant role for $^1O_2$ as the oxidant in the photoreaction involving **1**. The absence of $^1O_2$ is not surprising in this case because the Mn^{III} complex **1** contains an open-shell d^4 metal ion, in contrast to the closed-shell P^V complex used for the $^1O_2$ test reaction.

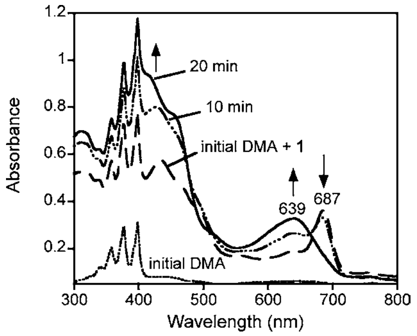


Figure 3. UV−vis spectra of an aerobic solution of **1** (18 μM) and DMA (0.24 mM) following irradiation (λ_{irr} > 400 nm) over 20 min in cyclohexane (3 mL).

The kinetics of the formation of **2** from **1** + O_2 + light was monitored to gain information regarding the mechanism of this reaction. The absorbance-versus-time profiles for the decay of **1** and production of **2** in cyclohexane (Figure 4) were obtained by following the change in their respective Q bands. The time profiles clearly exhibit a sigmoidal shape, and these distinct and reproducible curves are characteristic of a radical chain mechanism, where an induction period is required.[16,17] Similar profiles were observed when the solvent was changed to toluene (Figure S1). Interestingly, the reaction rate was highly dependent upon continuous irradiation. As shown in Figure 4, a dramatic decrease in rate was seen when the lamp was turned off, and this could then be reversed upon continued irradiation following another short induction period. These results suggest that radical chain termination events may be rapid and that constant irradiation is needed to maintain the initiation and propagation of the potential radical chain pathway.

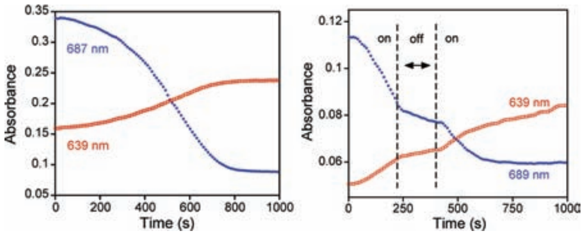
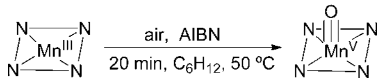


Figure 4. (left) UV−vis time profiles for the irradiation of **1** (12 μM) in cyclohexane (2.5 mL) at 25 °C showing the loss of **1** (687 nm) and the formation of **2** (639 nm). (right) Dependence of the reaction profile on the light source (lamp on/off denoted by the vertical lines).

Complete inhibition of the photogeneration of **2** was observed in the presence of the known radical inhibitors 2,4-di-*tert*-butylphenol (DTBP) and diphenylamine (DPA).[17] While these findings suggest that the reaction of **1** with light is a free-radical process, a direct reaction occurs between **2** and both DTBP and DPA to generate complex **1**. These findings led us to find an alternative test for a free-radical mechanism. The thermally activated radical initiator azobis(isobutyronitrile) (AIBN) was added in place of light to promote the O_2-mediated oxidation of **1** to **2**. Excess AIBN (12 mM) was added to an aerobic solution of **1** (8 μM) in cyclohexane (2.5 mL), and the reaction mixture was heated to 50 °C in the dark (Scheme 4). Complete conversion of **1** to **2** was observed by UV−vis spectroscopy (Figure S4).

Scheme 4. Use of AIBN as a Radical Initiator for the Generation of 2 from 1 and O_2



Taken together, our results provide strong support for the conclusion that the photogeneration of **2** occurs via a free-radical mechanism. Scheme 5 outlines a basic free-radical mechanism that follows the major steps for autoxidation involving hydrocarbon substrates and O_2[18] and is instructive in discussing the reaction of **1** + O_2 + light. In fact, autoxidation reactions are well-known to be catalyzed by transition-metal complexes, although the direct generation and identification of oxygenated metal complexes in these reactions is quite rare.[16] Initiation presumably involves light-induced excitation of **1** followed by reaction with O_2, which may produce Mn^{IV}−superoxide ($Mn^{IV}OO\cdot$). This species could then abstract a hydrogen atom from the solvent (RH) to give Mn^{IV}−OOH (Scheme 5), which in turn could cleave to give $(Cz)Mn^V(O)$ + $OH\cdot$. The solvent-derived alkyl radicals ($R\cdot$) would then function in the usual chain propagation steps to produce

Scheme 5. Free-Radical Chain Mechanism

Initiation

$Mn^{III} + h\nu \longrightarrow Mn^{III*}$

$Mn^{III*} + O_2 \longrightarrow Mn^{IV}OO\bullet$

$Mn^{IV}OO\bullet + RH \longrightarrow Mn^{IV}OOH + R\bullet$

$Mn^{IV}OOH \longrightarrow Mn^{V}O + OH\bullet$

Propagation

$R\bullet + O_2 \longrightarrow ROO\bullet$

$RH + ROO\bullet \longrightarrow ROOH + R\bullet$

Termination

$2\ ROO\bullet \longrightarrow ROH + R{=}O + O_2$

alkylperoxy/alkylhydroperoxide species, which can also serve as oxidants to convert **1** to **2**. We have shown that *t*-BuOOH can cleanly convert **1** to **2** in an independent reaction (Figure S5).

The conversion of a discrete Mn^{III} complex (**1**) into an isolable $Mn^{V}(O)$ complex (**2**) via reaction with O_2 has been demonstrated. To our knowledge, this transformation is unprecedented for Mn^{III}. Photoactivation of **1** by visible light is needed to produce **2**, but photosensitization of $^1O_2$ by **1** has been ruled out. The proposal of a detailed mechanism is not yet possible, but the combined mechanistic evidence indicates that the photogeneration of **2** occurs through a free-radical chain process. In addition, **1** has been shown to function as an active and robust photocatalyst for the conversion of PPh_3 to $OPPh_3$ with O_2 as the oxidant. A limiting factor in constructing transition-metal catalysts that use O_2 is a lack of understanding of the fundamental rules that govern transition metal + O_2 chemistry. The reactivity of a Mn^{III} complex with O_2 presented here should provide a new entry into this arena for further study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

dpg@jhu.edu

Notes

The authors declare no competing financial interest.

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(12) The cause of the incomplete ^{18}O incorporation has not yet been determined.

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