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Laser flash photolysis production of metal-oxo derivatives and direct kinetic studies of their oxidation reactions

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Abstract

Kinetic studies of oxidation catalysts in real time are necessarily limited by the high reactivity of the active form of the catalysts. One method for direct studies involves photochemical production of the transients in relatively large concentrations using laser flash photolysis methods and kinetic studies under single turnover conditions. Two photochemical entries to high-valent transition metal-oxo derivatives have been developed in our laboratory. In photo-oxidation reactions, irradiation of Compound II and analogues, porphyrin–iron(IV)-oxo species, gave Compound I and analogues, iron(IV)-oxo and porphyrin radical cations. In photo-induced ligand cleavage reactions, metals in n^+ oxidation state with the oxygen-containing ligands perchlorate, chlorate, or nitrate were photolyzed. Homolytic cleavage of the O–X bond in the ligand gives $(n+1)^+$ oxidation state metal-oxo species, and heterolytic cleavage gives $(n+2)^+$ oxidation state metal-oxo species.

Keywords: Photolysis; Porphyrin; Corrole; Metal-oxo; Kinetics

1. Introduction

Transition metal complexes are the central theme for a large number of synthetic homogeneous catalysts. Many of these catalysts are based on a design that mimics the predominant oxidation catalysts in nature, the cytochrome P450 enzymes (P450s). The P450s contain a heme group, iron-protoporphyrin IX, with a thiolate from protein cysteine as the fifth ligand to iron, and hydrogen peroxide or its equivalent provides the oxidizing power for the enzymes [1]. Synthetic homogeneous oxidation catalysts typically contain one of a variety of transition metals, including iron, manganese, chromium, ruthenium, rhodium, osmium in a macrocyclic (porphyrins, corroles) or ‘‘clamp’’-like ligand (salens), and the oxidizing power is provided by sacrificial oxidants such as hydrogen peroxide or peroxy acids [2–4].

In both the synthetic and natural catalysts, high-valent transition metal-oxo species are thought to be the active species [5]. In some cases, metal-oxo species can be observed spectroscopically, but in many cases the putative active metal-oxo species does not accumulate to detectable quantities, and the actual oxidizing species remains speculative. In the P450 enzymes, for example, the putative oxidant is an iron(IV)-oxo porphyrin radical cation that has not been observed under natural enzyme turnover conditions. For homogeneous catalysts, where catalytic species have ready access to one another, high-valent metal-oxo species might be detected, but these species might not be reactive enough to be the true oxidants. Specifically, the observable high-valent metal-oxo species might react by disproportionation to give an intermediate with even a higher metal valence that is the true catalyst but is not produced in detectable amounts [6]. Difficulties in detecting the highly reactive oxidants have resulted in limited physical studies, and measurements of catalytic rate constants are particularly limited. The resulting lack of kinetic and mechanistic information complicates attempts to deduce the identities of the active oxidants. Indeed, most commonly, the nature of the active oxidants in homogeneous oxidation catalysis has been inferred from product studies [5].

Our group initiated a general program for understanding oxidations via high-valent transition metal-oxo species that aims at direct detection of these transients. The model for the

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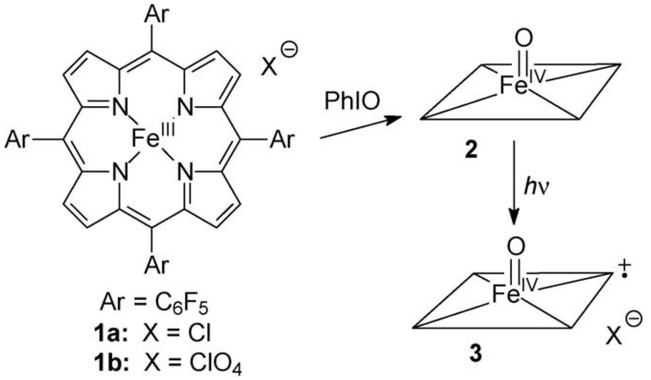
experimental design is that used in direct kinetic and spectroscopic studies of highly reactive organic radicals. Photochemical production of the high-valent metal-oxo species permits formation of these transients in relatively large concentrations, even when they are extremely high in reactivity. By using a laser as the light source, laser flash photolysis (LFP) methods permit very fast kinetic studies, allowing real time studies of species with lifetimes in the nanosecond regime; in comparison, the kinetic limits in even the fastest mixing studies are on the millisecond scale. Finally, one can work with very large concentrations of reductants, such that single turnover reactions with respect to the oxidant and pseudo-first-order kinetic conditions are maintained; this simplifies measurements of second- and higher-order rate constants and mechanistic deductions. Although straightforward in concept, the creation of LFP methods for studies of metal-oxo species requires considerable development of the requisite photochemical methods and especially the photo-labile precursors. This overview describes our progress in the development of two photochemical techniques, photo-oxidation of a metal-oxo species to give a higher valence formal oxidation state of the metal-oxo intermediate and photo-induced ligand cleavage for direct production of high-valent metal-oxo species [6–10].

2. Results and discussion

2.1. Production of Compound I species by photo-oxidation

Peroxidase and catalase enzymes are heme-containing enzymes with iron in the +3 oxidation state in the resting enzymes. Reactions of these enzymes with hydrogen peroxide give observable iron(IV)-oxo porphyrin radical cations that are known as Compound I species from peroxidase chemistry [11]. It is commonly assumed that the active oxidant in the cytochrome P450 enzymes is an iron(IV)-oxo porphyrin radical cation, but this transient is usually called ‘‘iron-oxo’’ in the P450 community. No Compound I derivative of a P450 enzyme has been observed during the natural course of oxidations by these enzymes, nor was a Compound I species observed in low temperature reactions where other iron-oxygen transients were detected [12,13]. Some evidence exists for the production of short-lived Compound I species in reactions of P450 enzymes with sacrificial oxidants [14–16]. In model chemistry, it is possible to produce Compound I derivatives from reactions of some porphyrin iron(III) salts with a sacrificial oxidant such as *m*-chloroperoxybenzoic acid (mcpba) [17].

The photo-oxidation route to Compound I intermediates involves photolysis of a porphyrin–iron(IV)-oxo species with a resulting ejection of an electron into the surrounding medium (Scheme 1). The iron(IV)-oxo derivative, also known as a Compound II species, can be produced from porphyrin–iron(III) salts under some conditions [18]. Experimentally, the photo-oxidation method is complicated by the fact that porphyrin–iron(III) salts are typically photo-reduced to iron(II) species that are strongly absorbing in the UV–vis spectrum. Therefore, the conversion to a porphyrin–iron(IV)-oxo derivative must be highly efficient.



Scheme 1.

We reported the generation of Compound I and its analogues by photo-oxidation of a Compound II analogue in a model system, Compound II of the enzyme horseradish peroxidase, and a Compound II analogue of myoglobin [8]. Scheme 1 shows the reaction sequence in the context of the Compound II derivative prepared by oxidation of the model compound 5,10,15,20-*tetrakis*(pentafluorophenyl)porphyrin–iron(III) chloride (**1a**). Chemical oxidation of iron(III) species **1a** with PhIO gave the known Compound II derivative **2**, and photo-oxidation of species **2** with 355 nm laser light gave the Compound I transient **3**. It is noteworthy that the Compound I derivative formed in the photo-oxidation reaction sequence is not exactly the same as analogous species formed by chemical oxidation. The Compound I analogue has a net +1 charge, requiring a counterion, and the identity of the counterion will affect the properties of the Compound I derivative. For example, oxidation of the porphyrin–iron salt **1b** containing the perchlorate counterion with mcpba produces a Compound I derivative similar to **3**, but with a counterion of either perchlorate or *m*-chlorobenzoate. The photo-oxidation of the neutral poprhyrin–iron(IV)-oxo derivative **2**, however, initially gives a Compound I derivative with no counterion, and complexation of this species with the initial anion present from **1a** would give the Compound I chloride salt.

Fig. 1 shows experimental results for formation of the Compound I transient **3**. The UV–vis spectrum of the Compound II analogue **2** is shown as a dotted line in Fig. 1A; a strong, sharp Soret band absorbance is apparent for the neutral species. This species that will be destroyed in the photochemical oxidation, and one expects a bleaching effect at λ_{max}. Immediately after the photolysis (dashed line in the figure), bleaching is observed at 420 nm, but signal growth also was observed at shorter wavelength, indicating that the Soret band absorbance for the newly formed species is close to that from precursor **2**. The experimental spectrum also shows a bleached signal at $\lambda_{max} = 547$ nm, which is from the Q-band absorbance of species **2**. Using the Q-band bleaching signal as a guide, we scaled the spectrum of precursor **2** and added this scaled spectrum to the observed results from the LFP experiment to obtain the spectrum of the newly formed transient **3** (solid line in Fig. 1A). The Soret band from the newly formed species **3** has a less intense and broader

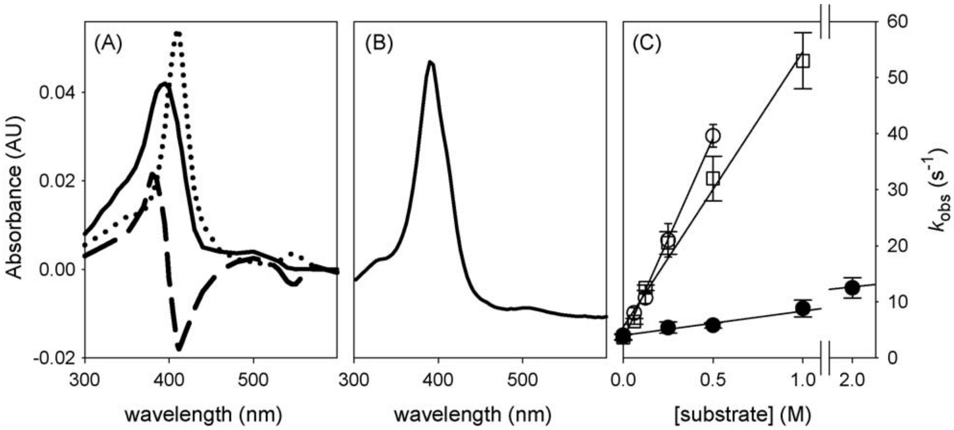


Fig. 1. (A) Results from photo-oxidation experiments from ref. [8]. The spectra are the Compound II analogue **2** (dotted line), observed trace after photolysis (dashed line), and spectrum of Compound I analogue **3a**. (B) Spectrum of Compound I analogue **3b** from mcpba oxidation of **1b**. (C) Kinetic results from reactions of **3a** with cyclohexene (open circles), *cis*-cyclooctene (squares), and ethylbenzene (solid circles).

absorbance than that of species **2**, as expected for a iron(IV)-oxo porphyrin radical cation. As noted above, it is possible to generate a Compound I species by chemical oxidation of perchlorate salt **1b** with mcpba, and Fig. 1B shows the UV–vis spectrum of this species. The difference in the spectra in Fig. 1A and B can be ascribed to the different counterions in the two Compound I analogues.

Fig. 1C illustrates the results of kinetic studies with the Compound I analogue **3**. The transient was produced in CH_3CN solvent and decayed at room temperature with a first-order rate constant of about 3 s^{-1}, possibly from reaction with the solvent. In the presence of an organic reductant in excess, pseudo-first-order conditions were maintained, and the rate constant for decay of transient **3** increased linearly as a function of the concentration of reductant. The kinetic data were analyzed according to Eq. (1) where k_{obs} is the observed rate constant for decay, k_0 the rate constant for decay in the absence of reductant (the background decay reaction), k_{ox} the second-order rate constant for reaction of transient **3** with the reductant, and [Sub] is the concentration of substrate. In the example in Fig. 1C, the observed rate constants for reaction of transient **3** in the presence of substrates are $k_{ox} = 72 \pm 5$, 49 ± 6, and $4.3 \pm 0.5\ M^{-1}\ s^{-1}$ for cyclohexene, *cis*-cyclooctene, and ethylbenzene, respectively.

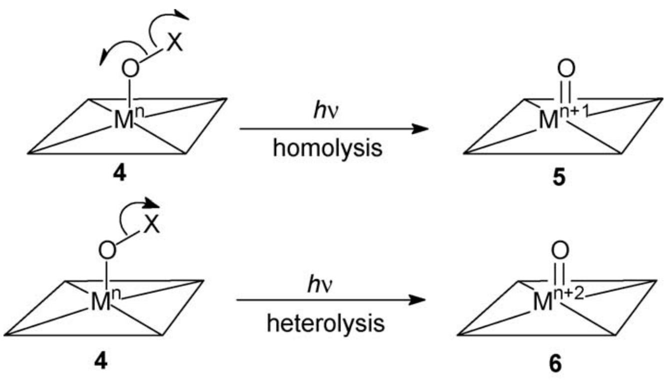
$$k_{obs} = k_0 + k_{ox}\,[\mathrm{Sub}] \qquad (1)$$

2.2. Photo-induced ligand cleavage reactions

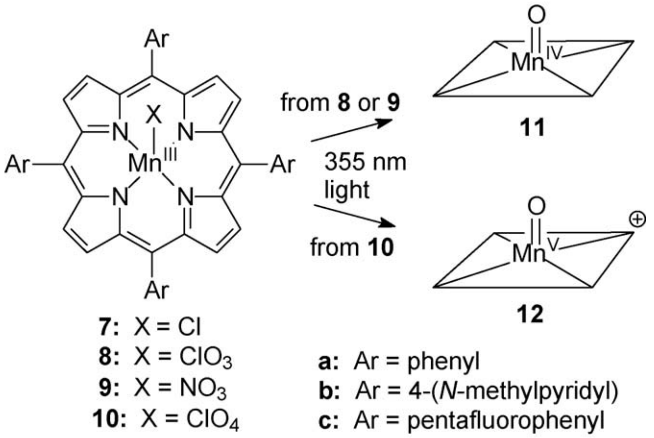
In principle, photo-induced ligand cleavages can generate many types of metal-oxo species. The concept is demonstrated in Scheme 2. Precursor **4** contains a multi-atom ligand with an oxygen atom bound to the transition metal ion in the n^+ oxidation state. Photo-induced homolytic cleavage of the O–X bond of the ligand will give metal-oxo species **5** with the metal ion in the $(n + 1)^+$ oxidation state, and heterolytic cleavage of the O–X bond will give species **6** with the metal ion in the $(n + 2)^+$ oxidation state. Prior to our studies, limited examples of production of metal-oxo species by photo-induced ligand cleavage were known. Porphyrin–manganese(III) nitrates were reported to give porphyrin–manganese(IV)-oxo species with continuous (lamp) irradiation conditions [19]. When porphyrin–manganese(III) chlorides in the presence of silver perchlorate or periodate were irradiated, oxidized substrates were formed, presumably via the intermediacy of porphyrin–manganese(V)-oxo species that were produced by heterolytic cleavage of the periodate and perchlorate complexes [20]. Our initial LFP studies focused on the photochemistry of manganese complexes, in large part due to these reports, and we were able to produce both porphyrin–manganese(V)-oxo species and porphyrin–manganese(IV)-oxo species as a function of the identity of the ligand.

LFP studies of porphyrin–manganese complexes are summarized in Scheme 3. We employed three porphyrin–manganese(III) chlorides as initial reagents (**7**). The different aromatic groups on the porphyrins result in varying electron demand with the phenyl system least electron withdrawing, the 4-(*N*-methylpyridyl) system intermediate, and the pentafluorophenyl system most electron withdrawing. Reactions of chlorides **7** with silver salts exchanged the ligands to give chlorate (**8**), nitrate (**9**), or perchlorate (**10**) complexes.

Photolyses of the chlorate complexes **8** with 355 nm laser light gave porphyrin–manganese(IV)-oxo species **11** by



Scheme 2.



Scheme 3.

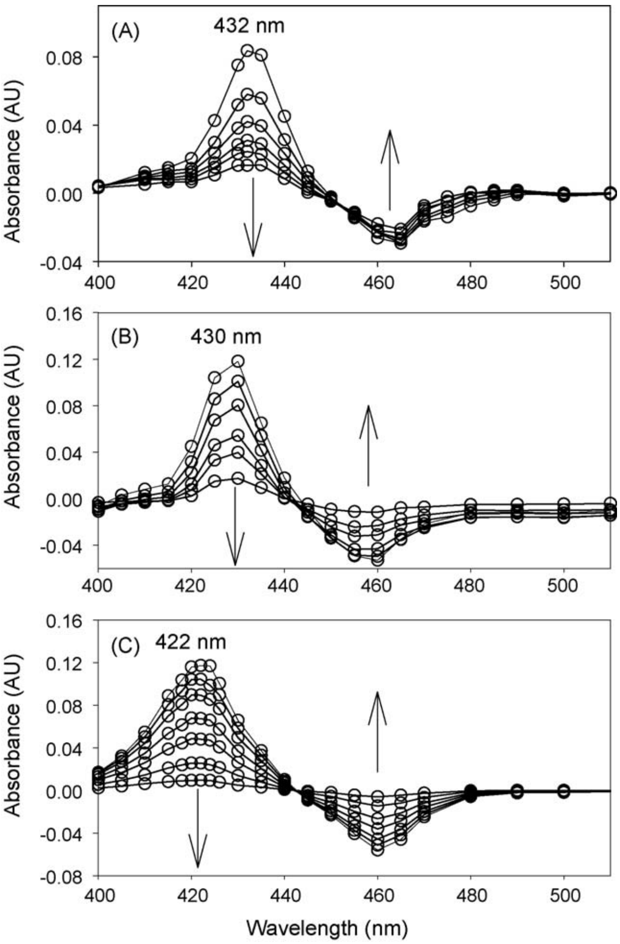


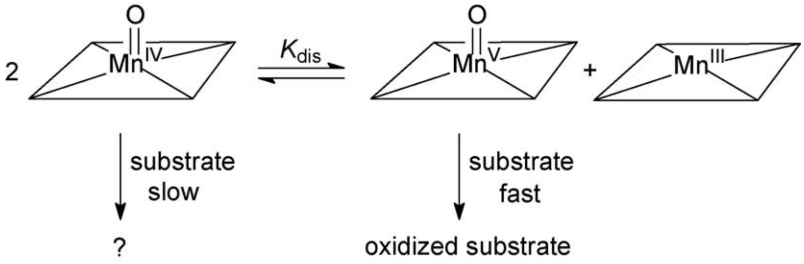
Fig. 2. Examples of formation of porphyrin–manganese-oxo species from [6]. In these time-resolved difference spectra, species with positive absorbance are decaying away with time, and species with negative absorbance are growing in with time. (A) Spectrum in the Soret band region following photolysis of perchlorate salt **10c** in CH_3CN; manganese(V)-oxo species **12c** with λ_{max} at 432 nm was produced in the LFP experiment and is decaying over a total time of 11 ms. (B) Spectrum in the Soret band region from mixing manganese(III) chloride **7c** with *m*-chloroperoxybenzoic acid in CH_3CN/water (3:1, v/v); species **12c** was formed in the oxidation reaction and is decaying over a total time of 0.7 s. (C) Spectrum in the Soret band region following photolysis of chlorate salt **8c** in CH_3CN; manganese(IV)-oxo species **11c** with λ_{max} at 422 nm was produced in the LFP experiment and is decaying over a total time of 5 s.

homolytic cleavage of the O–Cl bond in the ligand. Photolyses of nitrate complexes **9** also gave oxo species **11**, but the efficiencies of the photolysis reactions were substantially reduced [6]. The identities of porphyrin–manganese(IV)-oxo species **11** were confirmed by preparing the same species by chemical oxidation of the chlorides **7** with mcpba in the presence of the one-electron reductant Ph_3N.

Photolyses of perchlorate complexes **10** with 355 nm light gave distinctly different species than those produced by photolyses of complexes **8** and **9**, and we characterized the new transients as porphyrin–manganese(V)-oxo derivatives **12**. Fig. 2A shows a representative example for manganese(V)-oxo species **12c** from photolysis of perchlorate complex **10c**, which is decaying rapidly in CH_3CN solvent. For each system studied, the Soret band absorbances of **12** were red-shifted by ca. 10 nm from those of complexes **11**, as one can see by comparing the spectrum of **12c** with that for complex **11c** produced by photolysis of the chlorate **8c** (Fig. 2C). Transients **12** were much more reactive that species **11** in self-decay reactions and reactions with reductants, as discussed below. An important point for the identification of the porphyrin–manganese(V)-oxo intermediates **12** was that it was possible to produce these species by chemical oxidations of precursors **7** albeit as short-lived species and/or as mixtures with the manganese(IV)-oxo species[21]. The formation of species **12c** by chemical oxidation is especially noteworthy because the transient is so highly reactive when prepared in CH_3CN solution that it cannot be detected in fast mixing experiments; this transient decays with a 0.7 ms lifetime in CH_3CN at room temperature (Fig. 2A). Surprisingly, we found that species **12c** was nearly three orders of magnitude less reactive in a mixture of water—acetonitrile (Fig. 2B), and the UV–vis spectrum was quite similar to that formed in CH_3CN in the LFP experiments [6]. The origin of the considerable stabilizing effect of water on the porphyrin–manganese(V)-oxo species is not apparent, and this subject deserves further study.

The ability to measure kinetics readily is a significant advantage for formation of the high-valent metal-oxo species by LFP methods instead of mixing methods, and we were able to measure rate constants for reactions of porphyrin–manganese(V)-oxo species **12** with variety of substrates [6]. The reactivities in the series of transients **12** are consistent with expectations. For any substrate, the reactivity order was **12c** > **12b** > **12a**; that is, the transient with the most electron demand by the porphyrin macrocycle (**12c**) was most reactive, and the transient with the least electron demand (**12a**) was least reactive. Representative rate constants for the reaction of oxo species **12c** at ambient temperature in CH_3CN solvent are $k_{ox} = 6 \times 10^5\ M^{-1}\ s^{-1}$ for *cis*-stilbene and $k_{ox} = 1.3 \times 10^5\ M^{-1}\ s^{-1}$ for ethylbenzene.

Rate constants for reactions of the porphyrin–manganese(IV)-oxo species **11** also could be measured, but the mechanisms of these reactions were complex [6]. For example, the velocities of the reactions were effectively second-order in transient **11**, suggesting the possibility that **11** reacted in disproportionation reactions to give **12** and a porphyrin–manganese(III) species and that transient **12** was the actual

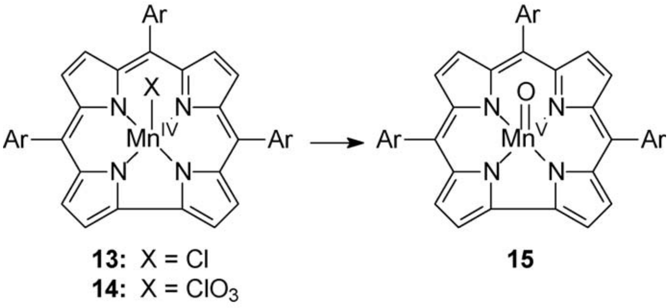


Scheme 4.

oxidant in the reactions (Scheme 4). This conclusion was supported by the observation that the reactivity pattern for species **11** with any organic reductant evaluated was inverted from expectations based on electron demand from the macrocycle, with **11a** appearing to be most reactive and **11c** appearing to be least reactive. If Scheme 4 is a correct description of the mechanisms of oxidation with manganese(IV)-oxo species **11**, then the equilibrium constant for formation of **12c** from **11c** should be the least favorable, resulting in a small concentration of **9c** and a slow overall reaction [6].

Photo-induced ligand cleavage reactions producing corrole–manganese(V)-oxo species also were possible (Scheme 5) [9]. We studied three corrole systems with different aromatic groups on the macrocycle. Corrole ligands are tri-anions, as opposed to the porphyrin ligand di-anions, and corrole–manganese(IV) salts should be considered the analogues of porphyrin–manganese(III) salts. We produced the corrole–manganese(IV) chlorates **14** from the chlorides **13** by ligand exchange with $AgClO_3$. Laser photolysis of species **14** with 355 nm light resulted in homolytic cleavage of the O–Cl bond in the ligand to give corrole–manganese(V)-oxo species **15**. The photochemical reaction is directly analogous to the reactions of the porphyrin–manganese(III) chlorates **8**, which gave species **11**. As with the porphyrin–manganese-oxo intermediates, we identified transients **15** by preparation via oxidation of the neutral manganese(III) species with chemical oxidants to give the same intermediates [22].

Kinetic studies of photo-generated corrole–manganese(V)-oxo species were not straightforward. The neutral transients **15** were quite stable, resulting in some operational difficulties in the studies. More importantly, the rate constants for oxidations by species **15** were inversely dependent on the concentration of the oxo species. That is, the rate constants for the oxidation reactions were only partial order in oxo species **15**, with the effect that the oxidation reactions were very slow when the concentration of **15** was high. Moreover, addition of a variety of manganese species resulted in reduced rate constants for oxidations by **15**. Our working hypothesis is that oxo species **15** can complex with another molecule of **15** or with other manganese species to produce a non-reactive, sequestered form of the oxidant (Scheme 6). Equilibrium dissociation of the sequestered complexes to give low concentrations of active oxidant would result in partial kinetic order, as observed experimentally.



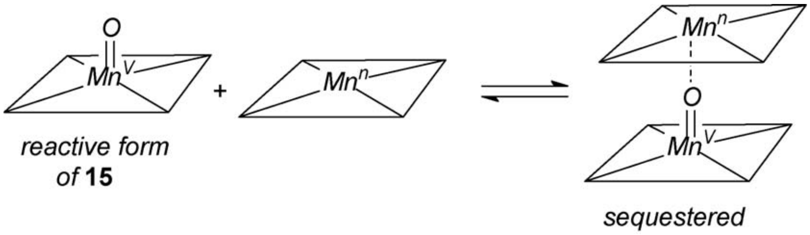
Scheme 5.

In what we believe to be a very important advance, we recently have extended the photo-induced ligand cleavage reactions to an iron macrocycle system [10]. Photolyses of porphyrin–iron(III) salts are known to give iron(II) species by photo-reduction [23]. The photochemistry of iron(IV) complexes, however, appears to present a reaction manifold similar to that of the manganese(IV) systems.

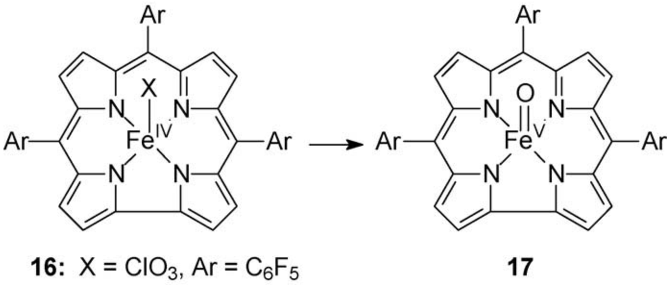
The corrole–iron(IV) chlorate **16** was prepared by ligand exchange from the corresponding chloride. Photolysis of **16** gave a new transient that we tentatively identified as the corrole–iron(V)-oxo species **17** on the basis of its extremely high reactivity and by analogy to the reactions of the corresponding corrole–manganese species. The iron(V)-oxo isomer **17** is not expected to be the low energy isomer of this system; by analogy to porphyrin–iron species, an iron(IV)-oxo corrole radical cation should be more stable than **17** [24]. Nonetheless, it appears that isomerization of **17** to a more stable isomer has a significant energy barrier, such that the iron(V)-oxo species reacts with organic reductants faster than it isomerizes. For example, oxo species **17** reacts with ethylbenzene with a rate constant of 570 $M^{-1} s^{-1}$, which is six to seven orders of magnitude faster than expected for reaction of an isomeric iron(IV)-oxo corrole radical cation [10]. Further studies in this area undoubtedly will give interesting results (Scheme 7).

2.3. The reactive oxidants in homogeneous oxidation catalysis

One of the objectives of our studies is to identify the true oxidants formed during turnover conditions when sacrificial (or terminal) oxidants are employed with transition metal catalysts. Attempts to control catalytic oxidation reactions, especially in terms of selectivities, require an understanding of the identity of



Scheme 6.



Scheme 7.

the oxidant. In a typical catalytic reaction, however, the concentrations of active oxidants will not build up to concentrations that permit detection. Moreover, as our work with porphyrin–manganese(IV)-oxo species **11** indicates, a high-valent metal-oxo species detected in a reaction might not be the true oxidant but a precursor to the true oxidant that is formed in small, undetectable amounts [6,9].

One method to test the identity of the oxidants under turnover conditions is to determine the selectivity found in competitive oxidation reactions where one oxidant is presented with two reductants. In the simple case, the ratio of products from competitive oxidations of two substrates will be equal to the ratio of rate constants for the two oxidation reactions. If the ratio of rate constants found in the competitive oxidation reaction is the same as that obtained from the absolute rate constants for reaction of a particular metal-oxo species with the two substrates, then one can infer that the oxo species under catalytic and single turnover conditions are the same. For example, the ratio of rate constants for reaction of porphyrin–manganese(V)-oxo species **12c** and **12b** with organic substrates is similar to the ratio of products found in competitive catalytic oxidations (Table 1) [6]. Differences in inherent reactivities of the reductants obviously influence the ratio of products, but the close match between the ratios of absolute rate constants and the ratios of products from the competition experiment strongly suggests that species **12c** and **12b** were the active oxidants in the catalytic oxidation reactions, even though they could not be detected during the reactions.

Table 1
Relative rate constants for porphyrin–manganese-oxo reactions

Oxo species	Substrates[a]	Oxidant	k_{rel}
12c	Stilbene/Ph_2CH_2	LFP results	4.7
		PhIO	4.6
		mcpba	6.5
12c	Ph_2CH_2/PhEt	LFP results	1.1
		PhIO	1.0
		mcpba	1.2
12c	PhEt/PhEt-d_{10}	LFP results	2.3
		PhIO	2.1
		mcpba	2.6
12b	Stilbene/Ph_2CH_2	LFP results	7.5
		mcpba	8.8

Relative rate constants from LFP results with (porph)Mn(V)(O) and for competitive oxidations with catalytic (porph)Mn(III)Cl at ambient temperature in CH_3CN solvent from ref. [6].

[a] The more rapidly reacting substrate is listed first.

3. Conclusion

Photochemical production of high-valent transition metal-oxo derivatives appears to have general utility. Highly reactive transients can be produced within a few nanoseconds, and the kinetics of their reactions can be studied with sub-microsecond temporal resolution. Photo-oxidation methods have been shown to be generally useful for oxidation of Compound II and its analogues to Compound I species, and it is possible that the method can be extended to production of Compound I species in cytochrome P450 enzymes. Previously unknown high-valent iron-oxo species, possibly iron(V)-oxo derivatives, apparently already have been produced by the photo-induced ligand cleavage reactions. These new methods should be expected to provide mechanistic insight concerning the identities of the active oxidants and oxidation reaction pathways of commercially important catalysts as well as the catalytic oxidizing enzymes in nature.

Note added in proof

Production of Compound I in a cytochrome P450 enzyme by photo-oxidation of the Compound II derivative was reported [25].

Acknowledgement

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