

O₂ Evolution and Permanganate Formation from High-Valent Manganese Complexes

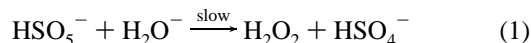
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The O₂-evolving complex (OEC) in photosystem II (PSII) contains a μ -oxo-bridged manganese tetramer that oxidizes water by four electrons, producing O₂.^{1–4} The exact structure of the tetramer has remained elusive, as has the mechanism of water oxidation. Whereas there are many high-valent multinuclear manganese oxo complexes,^{5,6} the first characterized one being the Mn(III,IV)–bpy di- μ -oxo dimer (bpy = 2,2'-bipyridine),⁷ there is only one reported manganese-based homogeneous water oxidation catalyst,⁸ a dimanganese–porphyrin complex. Meyer⁹ has characterized a dimeric Ru system that oxidizes water through a Ru^V=O species and, more recently, Halfen et al.¹⁰ reported a Cu dimer that can reversibly cleave an O–O bond. One current idea is that the OEC contains a terminal Mn^V=O species in the S₄ state that goes on to form O₂.¹¹ There are no characterized clusters containing Mn^V=O moieties, but monomeric complexes have been isolated.^{12,13} With this in mind, we have been studying the reactivity of manganese complexes, in particular [Mn(dpa)₂][–] (dpa = dipicolinate),¹⁴ with oxone, a highly oxidizing oxygen atom transfer reagent.

Potassium peroxydisulfate (oxone) has an estimated *E*⁰ of 1.82 V vs NHE,¹⁵ making it one of the most powerful commercially available oxidants. Oxone can epoxidize water-soluble olefins and is used in the preparation of pyridine *N*-oxides, quinones, and sulfones. In conjunction with metal catalysts, oxone can oxidize olefins and hydrocarbons, presumably via M=O species, and in particular has been used with Mn(III)–tetraphenylporphyrin,¹⁵ and [Mn₃O₄(bpy)₄(H₂O)₂](ClO₄)₃.¹⁶ Oxone is kinetically stable in acidic solution over the pH range 1–7, showing only a very slow hydrolysis to hydrogen peroxide:



In basic solution the decomposition product is O₂:

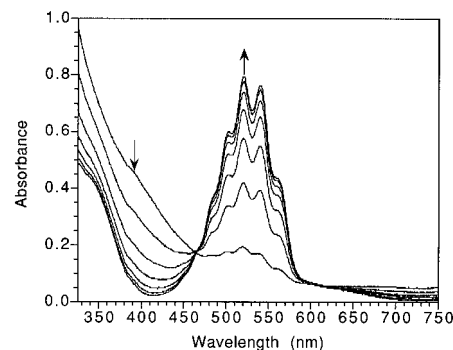
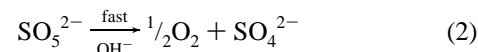


Figure 1. Visible absorption spectra showing the reaction between the green Mn-dpa intermediate ($\lambda_{\text{max}} = 400$ nm) and oxone to form MnO₄[–] ($\lambda_{\text{max}} = 520$ nm). The data were taken over a period of 12 min with a scan every 2 min. Reactions were done in 4 mL of 0.1 M acetate–H₂SO₄ buffer, pH 4.3, with [Mn(II)] = 0.25 mM.



Here we report a reaction between oxone and [Mn(dpa)₂][–] to form a Mn(III/IV) dimer that can then react further to evolve O₂ along with a novel alternate pathway that leads to the stoichiometric formation of MnO₄[–]. We believe that this MnO₄[–] forming reaction is unique to this system. All reported reactions were carried out in buffered aqueous solution over the pH range 3–6 using 0.023 M oxone, as the oxone salt is stable to decomposition in this range.

When [Mn(dpa)₂][–] was added to a solution of oxone, a green complex formed and O₂ was evolved in a reaction that was catalytic below pH 3.5 (Figures 1 and 2).^{17,18} Control experiments with Lewis acids, Ni(SO₄)₂, Zn(SO₄)₂, or AlCl₃, and bpy (M:bpy = 2:1) gave no O₂, suggesting that the reaction is not simple hydrolysis of oxone to form hydrogen peroxide (eq 1) followed by disproportionation to O₂. Permanganate was added to the Lewis acid/oxone solutions in these control experiments, as it is known to react rapidly with hydrogen peroxide to form O₂, and in no case was O₂ detected. This implies that redox activity is required for O₂ evolution. The green intermediate was characterized by both UV/vis ($\lambda_{\text{max}} = 400$ nm)¹⁹ and EPR spectroscopy, which showed a 16-line spectrum diagnostic of an antiferromagnetically exchange-coupled Mn(III/IV) dimer^{6,20} and no other signals.

Concurrent with catalytic O₂ evolution is a reaction that converts the green intermediate into MnO₄[–] with isosbestic points at 465 and 607 nm (Figure 1). The effect of pH on the rates of both O₂ evolution and MnO₄[–] formation from

(17) Chandra et al.¹⁴ isolated and solved the crystal structure of a red manganese–dpa complex that was formulated as [(Mn(dpa)₂)[–](Mn(dpaH₂)(dpa))[–]·5H₂O]. However, we found that their synthesis initially produced a violet powder that had different spectroscopic characteristics when compared to the red Na[Mn(dpa)₂]·2H₂O complex which we have structurally characterized (see Supporting Information). In the present study, the Mn(III)–dpa complex was added to an aqueous oxone solution as a violet solution in methanol, which on addition to water immediately converted to a red solution of the structurally characterized [Mn(dpa)₂][–].

(18) O₂ was detected with a YSI Standard Oxygen Probe at 25 °C. In a typical experiment, an aliquot (10–50 μ L) of 0.015 M aqueous Mn(II) or [Mn(dpa)₂][–] in methanol was added to 4 mL of 0.023 M oxone in 0.1 M acetate–H₂SO₄ buffer. When Mn(III) was used, the initial rates of O₂ evolution were measured 20 s after mixing, as the initial 20 s included a mixing artifact from methanol. A control experiment was done without the acetate (pH 4.3) and the reaction still occurred at the same rate.

(19) UV/vis spectra were recorded on a Perkin-Elmer Lambda 2B spectrophotometer. The rate of formation of MnO₄[–] was determined from the absorbance change at 550 nm. In each run, 50 μ L of 6.8 mM [Mn(dpa)₂][–] in methanol was added to 4 mL of 0.023 M oxone in 0.1 M acetate–H₂SO₄ buffer in a cuvette which was then shaken and placed in the spectrophotometer.

(20) Spectra of frozen aqueous samples were recorded on a Varian E-9 X-band EPR spectrometer at 10 K.

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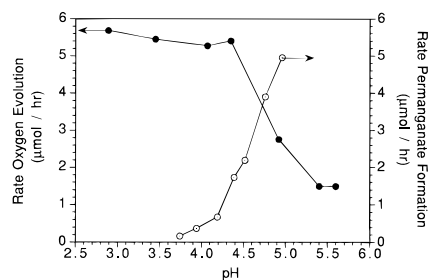


Figure 2. Plot showing the effect of pH on the initial rates of O₂ evolution (filled circles) and MnO₄⁻ formation (open circles). Reactions were done in 4 mL of 0.1 M acetate-H₂SO₄ buffer with [Mn(dpa)₂]⁻ = 0.09 mM.



Figure 3. Proposed structure of the green complex formed by the reaction between oxone and [Mn(dpa)₂]⁻.

Table 1. Initial Rates of O₂ Evolution from Mn(II)-Ligand Complexes^a

ligand	rate of O ₂ evolution (μmol/h)	turnovers before deactivation (mol of O ₂ /mol of Mn)
dipicolinate (dpa)	3.7	0.6 (pH 4.3) 2.0 (pH 2.5)
2,2'-bipyridine (bpy)	0	0
1,10-phenanthroline (phen)	5.7	0.25
picolinate (pic)	0.4	0.1
2,2':6',2''-terpyridine (terpy)	61	>50 ^b

^a Reactions were done in 4 mL of 0.1 M acetate-H₂SO₄ buffer, pH 4.3, with [Mn] = 125 μM. ^b No deactivation after 1 h.

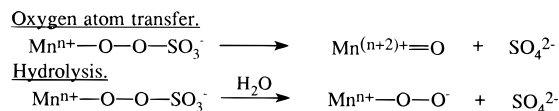
[Mn(dpa)₂]⁻ is shown in Figure 2. Clearly, MnO₄⁻ formation is favored by higher pH and lowering the pH allows multiple turnovers of the O₂-evolving reaction.

Dpa, being a planar tridentate ligand, is expected to form a dimer with open sites for solvent coordination. A possible structure for the green intermediate is shown in Figure 3. To test the hypothesis that complexes with open coordination sites are more reactive, we studied the oxone-manganese reaction using a series of other ligands (Table 1). In all cases, a Mn(III/IV) dimer was observed as an intermediate, as determined by observation of a 16-line EPR signal and no other EPR signals.²⁰ In the cases of bpy, phen, and pic, di-μ-oxo Mn(III/IV) dimers have been previously characterized.^{7,21,22} However, this is the first observation of a Mn(III/IV) dimer with terpy or dpa. These results suggest that oxone may be generally useful as an oxidant to make high-valent Mn complexes.

With pic, the O₂-evolving reaction occurred at a rate 10 times slower than with dpa. With phen, the initial reaction rate was about the same as with dpa, but the activity was entirely lost after just 1/4 of a turnover. No O₂ evolution was observed with bpy. In a key finding, when terpy, being a planar tridentate ligand like dpa, was used, rapid catalytic O₂ evolution was observed. Moreover, catalysis of O₂ evolution by the terpy complex was far more robust with a turnover number of 49 h⁻¹ at pH 4.35 and no deactivation even after 1 h. This arises because there is no buildup of MnO₄⁻, in contrast to the dpa system where catalysis of O₂ evolution was lost as MnO₄⁻ built up. We conclude that tridentate ligands capable of meridional coordination are optimal for O₂ evolution.

Bpy, phen and pic form di-μ-oxo Mn(III/IV) dimers that are coordinatively saturated and, hence, unreactive toward catalysis.

Scheme 1



As these dimers build up in solution any O₂ evolving reactivity is lost as species with exchangeable solvent coordination sites are consumed. However, we did observe some MnO₄⁻ formation with bpy and pic (no isosbestic points were seen in the corresponding UV/vis spectra and the reaction was much slower than with dpa), but none with phen. All the ligands must dissociate to allow MnO₄⁻ to form, so it would be expected that the more tightly bound the ligand the harder it would be to form MnO₄⁻, as was observed. This result is consistent with the work of Manchanda et al.,²³ who found that the rate of acid-induced ligand dissociation from the di-μ-oxo Mn(III,IV)-bpy dimer was up to 10 times faster (pH 3.0) than ligand dissociation from the phen dimer. The difference in dissociation rates was attributed to free rotation about the single bond connecting the aromatic rings in the case of bpy. By the same criterion, bpy, pic, and dpa can dissociate with much greater facility than terpy or phen. This may explain why the terpy complex cannot go on to form MnO₄⁻ at a significant rate. Finally, the observation that the dpa complex forms MnO₄⁻ faster than either the bpy or pic complexes is best explained by the presence of exchangeable solvent coordination sites on the dpa-manganese dimer.

The possible mechanisms of O₂ evolution fall into two categories: those involving oxygen-atom transfer from oxone and those involving hydrolysis of a manganese-bound oxone. These are summarized in Scheme 1. Oxygen-atom transfer leads to the formation of a Mn^V=O species as an intermediate. Such a complex could then form an O-O bond via a bimolecular reaction with either another Mn^V=O or a second oxone molecule in an overall four-electron process. Alternatively, hydrolysis of a bound oxone would produce a Mn-O-O⁻ complex (Mn = III or IV) and O₂ formation would then be a simple two-electron reductive decomplexation. Preliminary results have shown that Mn(II) and terpy react with dimethyldioxirane to produce O₂, supporting the idea of a Mn=O intermediate since this reagent is only an O atom, and not an O₂²⁻ or O₂ donor. The mechanism of O₂ evolution must be considered together with the mechanism of MnO₄⁻ formation. EPR and UV/vis spectroscopic studies show that a Mn(III/IV) dimer is the only complex present in significant concentrations in the reaction mixture. For MnO₄⁻ to form from a Mn(III/IV) dimer, an oxidation step is needed, presumably involving oxygen-atom transfer. This would involve the formation of a Mn^V=O species which could be a common intermediate in both the MnO₄⁻ and O₂ forming reactions. On the other hand, it is conceivable that oxone bound to Mn can undergo either oxygen-atom transfer or hydrolysis, with the former leading to MnO₄⁻ and the latter leading to O₂. Here, the fate of the bound oxone would be dependent on pH with protonation of the oxone-manganese intermediate favoring hydrolysis. We are currently undertaking experiments with H₂¹⁸O to look for label incorporation into the O₂, sulfate, and MnO₄⁻ that form in order to answer these questions.

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Supporting Information Available: Synthesis and X-ray characterization of Na[Mn(dpa)₂]-2H₂O (17 pages). See any current masthead page for ordering and Internet access instructions.

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