

# Oxidation of Water to Oxygen with a One-Electron Oxidant Catalyzed by Manganese Porphyrins

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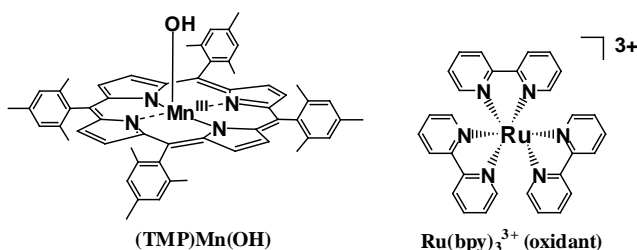
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The oxidation of water to molecular oxygen involves the transfer of four electrons from water to an oxidant, coupled with the release of four protons (eq 1).

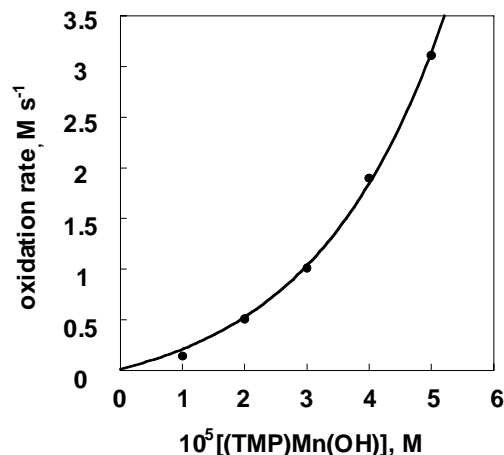


The water oxidation to evolve dioxygen is catalyzed at the oxygen-evolving center (OEC) in photosystem II (PS II) in photosynthesis.<sup>1</sup> Despite recent development on the structural information of OEC,<sup>2</sup> the mechanism of water oxidation at molecular level still remains unresolved mystery.<sup>3-5</sup> Great efforts have been devoted to develop the OEC model complexes which can be applied to artificial photosynthetic systems for the splitting of water that could be utilized in fuel cells. Such systems would solve not only the energy but also environmental problems arising from combustion of fossil fuels. However, the catalytic systems capable of evolving O<sub>2</sub> from water are rare, failing to provide any important mechanistic insight.

We report herein a simple and well-defined catalytic system of the stoichiometric water oxidation to O<sub>2</sub>, in which an outer-sphere one-electron oxidant such as Ru(bpy)<sub>3</sub><sup>3+</sup> (bpy = 2,2'-bipyridine) is employed to oxidize water to O<sub>2</sub>, catalyzed by a manganese porphyrin. The detection of the reactive intermediate in the catalytic oxidation of water and the detailed kinetic analysis provides valuable insight into the catalytic mechanism of water oxidation to O<sub>2</sub>.



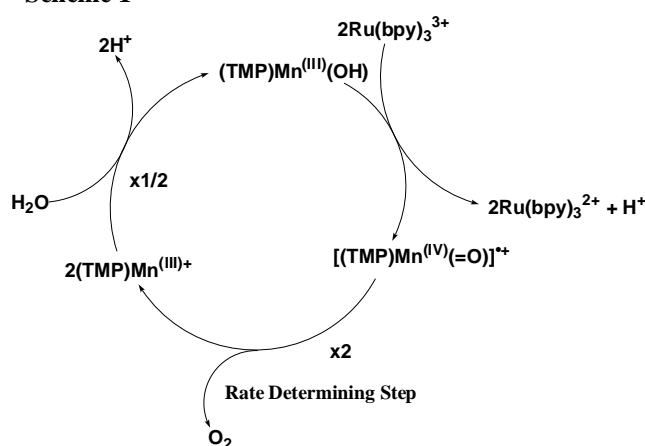
Addition of an outer-sphere one-electron oxidant, Ru(bpy)<sub>3</sub><sup>3+</sup>, to an acetonitrile (MeCN)/H<sub>2</sub>O mixed solution (5 : 1 v/v) containing a catalytic amount of a manganese porphyrin, (TMP)Mn(OH) (TMP<sup>2-</sup> = 5,10,15,20-tetrakis(2,4,6-tri-methylphenyl)porphyrin dianion) results in evolution of stoichiometric amount of O<sub>2</sub> in the four-electron oxidation of water with Ru(bpy)<sub>3</sub><sup>3+</sup>. The two-electron oxidation of (TMP)Mn(OH) by Ru(bpy)<sub>3</sub><sup>3+</sup> to produce (TMP)Mn=O<sup>+</sup> is shown to be essential for the water oxidation to O<sub>2</sub>. The oxidation rate exhibits a second-order dependence with respect to the catalyst concentration (Figure 1). This indicates that the rate-determining step for the catalytic water oxidation to O<sub>2</sub>



**Figure 1.** Plot of  $k_{\text{obs}}$  vs  $[(\text{TMP})\text{Mn}(\text{OH})]$  for the oxidation of water by  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_3$  ( $5.0 \times 10^{-4}$  M) in the presence of  $(\text{TMP})\text{Mn}(\text{OH})$  ( $1.0 - 5.0 \times 10^{-5}$  M) in MeCN/H<sub>2</sub>O (7 : 1 v/v) at 298 K.

with  $\text{Ru}(\text{bpy})_3^{3+}$  is the bimolecular reaction of  $(\text{TMP})\text{Mn}=\text{O}^{+}$  produced by the two-electron oxidation of  $(\text{TMP})\text{Mn}(\text{OH})$  with two equivalents of  $\text{Ru}(\text{bpy})_3^{3+}$  (Scheme 1).

## Scheme 1



The present study is the first demonstration of the stoichiometric evolution of O<sub>2</sub> by the four-electron oxidation of water by four equivalents of one-electron oxidant, Ru(bpy)<sub>3</sub><sup>3+</sup>. The successful detection of the reactive intermediate for the oxidation of water and the second-order kinetic dependence on the catalyst concentration have provided valuable insight into the catalytic mechanism of the O<sub>2</sub> evolution from water.

## References

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