

D052 HIGH-VALENT DINUCLEAR MANGANESE COMPLEXES AS FUNCTIONAL MODELS OF THE CATALASE-LIKE ACTIVITY IN THE OXYGEN EVOLVING COMPLEX

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The oxygen evolving complex (OEC) of Photosystem II is known to catalyze the disproportionation of hydrogen peroxide (Eq. 1) as an alternative substrate under certain conditions.



While this reaction is catalyzed by the Mn catalase enzyme through a low-valent Mn(II,II)/Mn(III,III) cycle, the catalase-like activity of the OEC is believed to proceed through a high-valent Mn(III,III)/Mn(IV,IV) cycle, most likely involving two of the four Mn ions in the site.

This high-valent activity is mimicked by the Mn schiff base complex [Mn^{IV}(SALPN)(O)]₂. [1] The rate of reactivity of this model complex shows striking dependence upon a number of factors, including protonation state, the presence of acid or base sources in solution, electron-donating and withdrawing substituents on the ligand system, and the solvent. The mechanistic details of the catalytic disproportionation of hydrogen peroxide by this complex, as well as its formation by reaction of Mn(III) complexes with hydrogen peroxide, are being studied by comparison of the reaction kinetics under conditions which probe the effects of the perturbations listed above. Addition of a base source is shown to significantly accelerate the catalytic reaction, and numerous solvents have been shown to substantially inhibit this reaction. More subtle perturbations, such as addition of Cl, NO₂, and OCH₃ groups to the phenolate rings of the SALPN ligand, and addition of substoichiometric sources of protons will also be presented. The results of these studies are correlated to the electrochemistry and UV/VIS spectroscopy of these complexes with different electron-withdrawing and -donating groups, different protonation states of the oxo bridges, and different solvents in order to determine the origin of these effects on the reaction kinetics. Additionally, we compare the reactivity of the one-electron reduced Mn(III)Mn(IV) bis oxo-bridged dimer [2] in order to determine its competency as an intermediate in the catalytic disproportionation of hydrogen peroxide.

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