Probing the Reactivity of the Photosystem II Manganese Cluster

Thomas Kuntzleman[1,2], Robert M. McCarrick[1], James E. Penner-Hahn[1], and Charles Yocum[1,3]

[1]Department of Chemistry, University of Michigan, Ann Arbor, MI, [2] Department of Chemistry, Spring Arbor University, Spring Arbor MI, [3]Department of Molecular, Cellular, and Developmental Biology, University of Michigan, Ann Arbor, MI

Characterization of reduced derivatives of the photosystem II (PSII) Mn cluster by X-ray absorption spectroscopy revealed a differential reactivity of Mn atoms in the oxygen evolving complex that was dependent on both the reductant (hydroxylamine or hydroquinone) and whether calcium was present during reduction. We have examined this phenomenon further using N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD). XANES spectroscopy shows that reaction of this reductant with PSII Mn is distinct from the reactions catalyzed by either hydroxylamine or hydroquinone; the results indicate that in calcium reconstituted samples, TMPD reduces one Mn^{4+} atom to Mn^{3+}. EXAFS spectroscopy indicates that this reduction produces a minimal perturbation of the metal-metal distances within the Mn cluster. Further characterization by EPR of the reaction between TMPD and the PSII Mn cluster shows that in calcium-reconstituted PSII, TMPD undergoes one-electron oxidation to the stable radical cation $TMPD^{\bullet+}$ ($E_{m,7}$ = +235 mV). In the absence of calcium, however, the reaction of TMPD with PSII exhibits a complex behavior. The cation radical forms rapidly, and then decays. Since the radical is stable in the presence of calcium, the likely cause of its decay in the absence of calcium is a second oxidation reaction catalyzed by the Mn cluster in which the cation radical undergoes a one-electron oxidation to form the quinonediiminium dication ($TMPD^{\bullet+} \rightarrow TMPD^{++}$, $E_{m,7}$ = +850 mV), which has been shown to be unstable. Taken together, we interpret these results to indicate that calcium bound to its site in PSII is topologically positioned so as to block the access of TMPD to one or more Mn atoms whose reduction potentials are higher than those of the Mn atoms that are accessible to, and reduced by, TMPD in the calcium depleted enzyme. This organization of the metals is consistent with models for their participation in catalysis of water oxidization.