**Photosystem II OEC Proposed Mechanism**

The oxidation of water requires the separation of four protons and four electrons from the oxygen atoms of two water molecules.

2 H2O → 4H+ + 4e– + O2

To lower the activation barrier, the protons and electrons can be transferred in a stepwise manner with the assistance of a catalyst. In nature one such catalyst is the oxygen evolving complex of photosystem II. The proposed intermediates in OEC catalytic cycle are named S0 through S4 and are shown in the figure below.

**Instructions**

Add water, photons, protons, and electrons to complete the catalytic cycle. Two water molecules and four photons enter the catalytic cycle. Four protons, four electrons, and oxygen leave. Note that the electrons are removed when the photons are added. (*Science* **2014**, *345*, 804. and *Annu. Rev. Phys. Chem.* **2017**, *68*, 101.) The electrons leaving this cycle are transferred to another catalyst and ultimately to an electron acceptor such as NADP+.



For reference when you are reading, the Mn atoms in the oxygen evolving complex (OEC) are often numbered. The numbers have no meaning other than keeping track of specific atoms.



**Mn dimers as mimics**

Chemists want to mimic the activity of the OEC but these efforts have not yet been entirely successful. In lab you will oxidize water using a synthetic Mn catalyst, but the O2 will be replaced with HSO5–, the active oxidant in Oxone®. Because HSO5– is a two electron oxidant, removing electrons one at a time is not a mechanistic possibility.

Half reactions

Reduction: (HSO5– + H+ + 2e– → SO4 –2 + H2O ) x 2

Oxidation: 2 H2O → 4H+ + 4e– + O2

Overall reaction

2 HSO5– → 2H+ + 2SO4 –2  + O2

**Instructions**

Complete the proposed mechanism below (*J. Chem Ed.* **2005**, *82*, 791) by drawing the species involved in the half reactions entering and leaving the catalytic cycle.

In: 2 H2O and 2 HSO5–

Out: 2H+ + 2SO4 –2  + O2  and 2 H2O

Note that two molecules of water enter the catalytic cycle as reagents for the oxidation half reaction and two molecules of water leave as part of the reduction half reaction. In the balanced equation these cancel however in the catalytic cycle they are not the same water molecules so they should be shown entering and leaving the catalytic cycle.

