Award # DE-SC0004334 FINAL TECHNICAL REPORT
Project title: Membrane-organized Chemical Photoredox Systems
Sponsor: Department of Energy
PI: R. David Britt, University of California Davis, Department of Chemistry

Program Scope:

The key photoredox process in photosynthesis is the accumulation of oxidizing equivalents on a tetranuclear manganese cluster that then liberates electrons and protons from water and forms oxygen gas. Our primary goal in this project is to characterize inorganic systems that can perform this same water-splitting chemistry. One such species is the dinuclear ruthenium complex known as the blue dimer. Starting at the Ru(III,III) oxidation state, the blue dimer is oxidized up to a putative Ru(V,V) level prior to O-O bond formation. We employ electron paramagnetic resonance spectroscopy to characterize each step in this reaction cycle to gain insight into the molecular mechanism of water oxidation.

Publications:

P1: J. A. Stull, R. D. Britt, J. L. McHale, F. J. Knorr, S. V. Lymar, and J. K. Hurst
Anomalous Reactivity of Ceric Nitrate in Ruthenium “Blue Dimer”-Catalyzed Water Oxidation.
J. Am. Chem. Soc., 2012, **134:**19973–19976.
DOI: 10.1021/ja3093532

P2: J. A. Stull, T. A. Stich, J. K. Hurst, and R. D. Britt
Electron Paramagnetic Resonance Analysis of a Transient Species Formed During Water Oxidation Catalyzed by the Complex Ion $[(bpy)_2Ru(OH_2)]_2O^{4+}$.
Inorg. Chem., 2013, **52:**4578–4586.
DOI: 10.1021/ic4001158

Overview:

The ruthenium “blue dimer” is the classic inorganic water oxidation molecular catalyst. For this DOE grant we teamed up with Prof. Jim Hurst, and expert in the chemical characterization of this important molecule, with my lab providing expertise in advanced EPR characterization as honed by years working on the Photosystem II water oxidizing system (nature’s only water splitting catalyst). We published two papers as list above. The results in these papers are described below.

Progress:

P1: J. A. Stull et al. *J. Am. Chem. Soc.,* 2012, **134:**19973–19976.

At high concentrations, nitrate ion alters the dynamics of ruthenium “blue dimer”-catalyzed water oxidation by Ce(IV) such that the oxidation rate is enhanced and a unique reaction intermediate accumulates. This intermediate is characterized by distinct EPR, optical, and resonance Raman (RR) spectra, with the appearance in the latter of a new oxygen isotope-sensitive band. Both Ce(IV) and nitrate are required to generate this intermediate, which suggests ceric-nitrate complexes as the causative agents. Use of ^{18}O-labeled and ^{15}N-labeled materials has established that (1) the new RR band is not an O–O stretching mode (for example, as might be associated with a peroxo species) but involves the O atom coordinated to a Ru center, and (2) the O_2 product does not contain an O atom derived from nitrate, eliminating several plausible pathways involving O-atom transfer to oxidized dimer. Although these results are surprising, similar phenomena have been reported for water oxidation catalyzed by monomeric Ru complexes. The dramatic effects observed for the “blue dimer” make it an ideal candidate for further study.

P2: J. A. Stull et al., *Inorg. Chem.,* 2013, **52:**4578–4586.

The ruthenium “blue dimer” $[(bpy)_2Ru(OH_2)]_2O^{4+}$—the first well-defined molecular complex able to catalyze water oxidation at low overpotentials—has been the subject of numerous experimental and computational studies. However, elements of the reaction mechanism remain controversial. Of particular interest is the nature of the O–O bond-forming step. Herein, we report the first advanced electron paramagnetic resonance (EPR) spectroscopic studies of a high-valent intermediate that appears under conditions in which the catalyst is actively turning over. Results from previous studies have suggested that this intermediate is derived from $[(bpy)_2Ru^V(O)]_2O^{4+}$, denoted **{5,5}**. Under photooxidizing conditions, the corresponding EPR signal disappears at a rate comparable to the turnover rate of the catalyst once the illumination source is removed. In the present work, the electronic and geometric structures of this species were explored using a variety of EPR techniques. Continuous wave (CW) EPR spectroscopy was used to probe the hyperfine coupling of the Ru ions, while corresponding ligand ^{14}N hyperfine couplings were characterized with electron spin echo envelope modulation (ESEEM) and hyperfine sublevel correlation spectroscopy (HYSCORE) methods. Finally, ^{1}H/^{2}H ENDOR was performed to monitor any exchangeable protons. Our studies strongly suggest that the accumulating transient is an $S = 1/2$ species. This spin state formulation of the so-called **{5,5}** species is consistent with only a limited number of electronic structures, each of which is discussed. Notably, the observed large metal hyperfine coupling indicates that the orbital carrying the unpaired spin has significant ruthenyl-oxyl character, contrary to an earlier electronic structure description that had tentatively assigned the signal to formation of a bipyridine ligand radical.

Personnel Development:

The Britt laboratory EPR spectroscopy on this project was primarily carried out by Chemistry Ph.D student Jamie A. Stull, and this work was the core of her Chemistry Ph.D dissertation. Dr. Stull is now a postdoctoral fellow at Los Alamos National Laboratory.