



Physical Chemistry Student Seminar Series

Water-Nucleophilic Attack Mechanism for the $\text{Cu}^{\text{II}}(\text{pyalk})_2$ Water-Oxidation Catalyst

Who? Dr. Benjamin Rudshiteyn, Friesner group

When? Wednesday, September 26th, 2018 at 5:30 pm

Where? 711 Havemeyer

Abstract

I will discuss one of my PhD projects (Yale University, Batista Group) involving the investigation of the mechanism of water oxidation catalyzed by the $\text{Cu}^{\text{II}}(\text{pyalk})_2$ complex.¹ My role involved using density functional theory and comparing to experimental measurements (Brudvig and Crabtree groups) of turnover frequencies, UV-visible spectra, H/D kinetic isotope effects (KIEs), electrochemical analysis, and synthesis of a derivative complex. We found that only in the *cis* form does $\text{Cu}^{\text{II}}(\text{pyalk})_2$ convert water to dioxygen. In a series of alternating chemical and electrochemical steps, the catalyst is activated to form a metal oxyl radical species that undergoes a water-nucleophilic attack defining the rate-limiting step of the reaction. The experimental H/D KIE (3.4) is in agreement with the calculated value (3.7), shown to be determined by deprotonation of the substrate nucleophile upon O–O bond formation. The reported mechanistic findings are particularly valuable for rational design of complexes inspired by $\text{Cu}^{\text{II}}(\text{pyalk})_2$. I will cover the problem of water oxidation, the calculation of KIEs, the accounting for concentration effects, and computational electrochemistry as pedagogical concepts.

