

Investigation of Ligand Sphere Perturbations On Mn^{III}-alkylperoxo Complexes

Thursday, 3/14
3:45 pm
RNS 310

Chemistry Seminar

Drawing inspiration from manganese dependent enzymes, a range of synthetic manganese catalysts have been developed to carry out a variety of highly stereoselective oxidation reactions such as olefin epoxidations. In these synthetic catalysts, a key step in the proposed catalytic mechanism invokes the heterolysis of the oxygen-oxygen bond of a Mn^{III}-hydroperoxo intermediate to generate the active oxidant - a manganese(V)-oxo species. However, the geometric and electronic factors controlling this critical O-O activation step remain poorly understood. Work by our group and others has utilized Mn^{III}-alkylperoxo complexes to mimic the key Mn^{III}-hydroperoxo intermediates. From these investigations, there has been evidence that Mn^{III}-alkylperoxo complexes can decay by both O-O homolysis and heterolysis pathways. Presumably, perturbations in the ligand-sphere of these Mn^{III}-alkylperoxo complexes, specifically at positions trans to the O-O bond, could be employed to modulate the decay process. To that end, a new Mn^{III}-alkylperoxo complex has been developed to investigate the effect of trans perturbations on the mechanism of cleavage of the oxygen-oxygen bond. A series of combined computational and kinetic investigations as completed with the goal of probing the effects of such a change to the ligand-sphere on the decay mechanism. These studies have allowed us to gain further understanding of the control of the ligand sphere over the reactivity of Mn^{III}-alkylperoxo adducts.



Sam Brunclik is a 5th-year Ph.D. student at the University of Kansas, working in the group of Professor Timothy Jackson, where he is expected to complete his degree later this year. He received a B.A. in Chemistry from St. Olaf College in 2019 after working in the lab of Professor Elodie Marlier. In 2021, Sam joined the Jackson lab, where his efforts have been focused on the study of manganese complexes using both spectroscopic and computational techniques. Through his work, Sam has utilized techniques such as UV-visible kinetics, low temperature electron paramagnetic resonance spectroscopy, density functional theory (DFT), and has even had the opportunity to travel to the Stanford Synchrotron Radiation Lightsource Laboratory (SSRL) to conduct X-ray absorption spectroscopy. Sam's computational work was recently featured on the front cover of Dalton Transactions in late October.

Sam has also been working to advocate for increased diversity, equity, inclusion, and belonging in chemistry as a member of the LGBTQ+ community. Recently, Sam has served as the student representative on the department committee for diversity, equity, inclusion, and belonging; has planned and hosted a college-wide event celebrating the contributions of LGBTQ+ people in STEM research; and was elected as the future chair of the American Chemical Society's PRIDE subdivision.

Sam Brunclik '19