Auxiliary Proton-Influenced Metal-Mediated Reactions

Christopher S. Letko Final Seminar October 6, 2011

The oxygen reduction reaction (ORR) is vital to aerobic organisms, powering the proton gradient used to drive phosphorylation of adenosine diphosphate. Although Nature has evolved elaborate methods to effect the $4e^-$ reduction of O_2, the development of hydrogen fuel cells has been stalled by slow advancements in the design of efficient cathodic catalysts. Platinum metal, the current industrial standard, exhibits ORR overpotentials on the order of hundreds of millivolts along with slow reaction kinetics.[1] Enzymatic systems operate at lower overpotentials than Pt, with some evolving methods for activating O_2 assisted by pendant proton donors. In example, laccases, enzymes that reduce O_2 at a tricopper active site, have been proposed to effect O–O bond cleavage with the assistance of a proton transferred from a coordinated aquo ligand (Figure 1).[2]

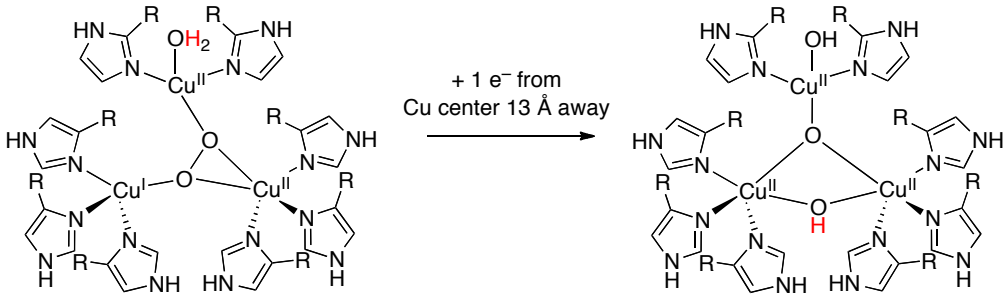

Figure 1. Proposed proton transfer event to assist O_2-cleavage in the active site of laccase.

Although laccases demonstrate properties of finely tuned cathodic catalysts, the large size of each enzyme offers low current densities when adsorbed onto an electrode's surface.[3] An opportunity to circumvent the excess mass of an enzyme's structure resides in designing small biomimetic models that replicate the function of an active site.[4] Tricopper complexes are known to form stable μ-oxo or hydroxo species.[5] Dicopper sites, such as the one found in hemocyanin, are also capable of activating O_2, and such fragments serve as blueprints for the design of ORR catalysts. Although removing a Cu center does not assist the $4e^-$ equivalents needed for the reduction of O_2 to H_2O, it remains to be known whether the addition of ancillary proton donors to hemocyanin models can imbue such small molecules the O_2 reduction properties of laccase.

The incorporation of hydrogen-bonding groups into the second coordination sphere of Cu complexes was demonstrated to enhance their reactivity with O_2. Cu(I) salts of hydroxyl-functionalized tripodal ligands were found to oxidize in the presence of O_2 to form mixed valence Cu dimers. Similar reactivity is not observed for the methoxylated derivative or the structurally analogous Cu(I)[tris(2-picolinyl)methane]$^+$ complex reported by Kodera and coworkers.[6] Formation of the mixed valence dimers is proposed to proceed through initial deprotonation of the hydroxy group to form a diCu(I) complex, which can be independtly synthesized. Heterogeneous electrocatalysis studies comparing the monocopper(I) salts of the

hydroxy, methoxy, and methyl functionalized tripods show the Cu complex of the hydroxylated tripod to have the lowest ORR overpotential by at least 100 mV.

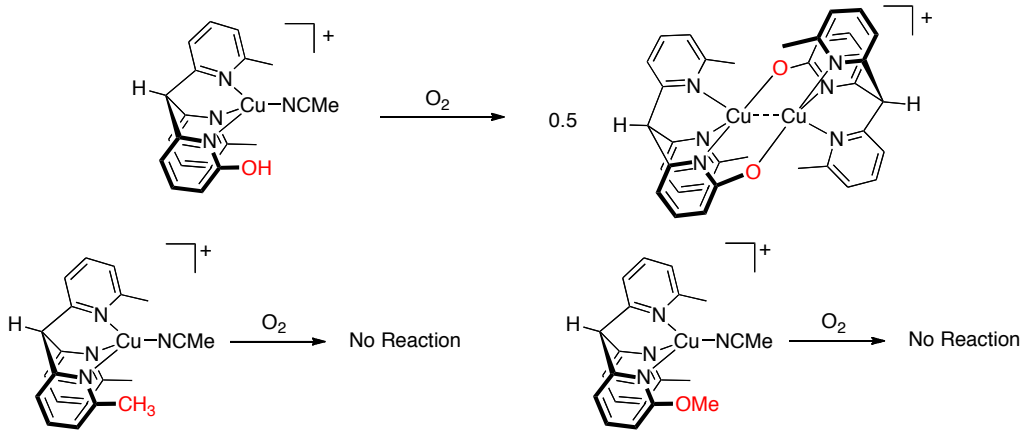

Figure 2. O_2 reactivity of a Cu(I) complex having a hydroxylated tripodal ligand.

Proton-influenced reactivity was additionally discovered to expand the scope of transfer hydrogenation catalysis with the previous finding that a Lewis acidic metal center capable of activating H_2 can be accessed via protonation of 16e$^-$ Ir(III)– or Ru(II)–bisamido complexes of type, (arene)M(TsDPEN–H) (TsDPEN–H = HNCH(Ph)CH(Ph)NTs).[7] Coordination of anions to [Cp*Ir(TsDPEN)]$^+$ was found to generate a pair of diastereomers (α and β) which exhibit first order kinetics in the isomerization to the thermodynamically favored α-isomer (Figure 3).[8] The mechanism of diastereomerization is proposed to depend on the donation strength of the anion, where weakly coordinating anions (Cl^-, $H_3CC(O)NH^-$, NO_2^-) quickly dissociate and coordinate to form a single observed diastereomer and strong donors (H^-, CN^-, $H_3CC(NH)S^-$) slowly isomerize via an intermediate in which the M(TsDPEN) chelate ring is open.

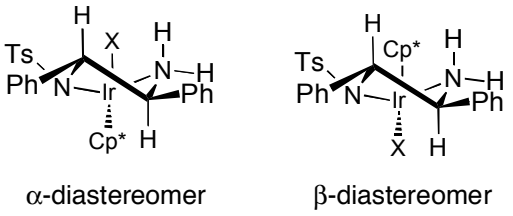

Figure 3. Diastereomers formed upon coordinating anions (X) to [Cp*Ir(TsDPEN)]$^+$.

Protonation of Cp*Ir(TsDPEN–H) with H_3PO_4 was found to generate a H_2O-soluble salt capable of reducing the ketone 2-hydroxyacetophenone to 1-phenyl-1,2-ethanediol in aqueous solution.[9] The catalyst was observed to gradually degrade to [Cp*$_2$Ir$_2$(μ-H)$_3$]$^+$ over long reaction

periods. Deactivation of the catalyst is proposed to proceed through protonation of the NTs amido group, followed by hydrogenolysis of the TsDPEN ligand.

References

1. Alonso-Vante, N. Platinum and Non-Platinum Nanomaterials for the Molecular Oxygen Reduction Reaction. *ChemPhysChem* **2010**, *11*, 2732-2744.

2. Augustine, A. J.; Quintanar, L.; Stoj, C. S.; Kosman, D. J.; Solomon, E. I. Spectroscopic and Kinetic Studies of Perturbed Trinuclear Copper Clusters: The Role of Protons in Reductive Cleavage of the O–O Bond in the Multicopper Oxidase Fet3p. *J. Am. Chem. Soc.* **2007**, *129*, 13118-13126.

3. Blanford, C. F.; Heath, R. S.; Armstrong, F. A. A Stable Electrode for High-Potential, Electrocatalytic O2 Reduction Based on Rational Attachment of a Blue Copper Oxidase to a Graphite Surface. *Chem. Commun.* **2007**, 1710-1712.

4. Armstrong, F. A.; Hirst, J. Reversibility and Efficiency in Electrocatalytic Energy Conversion and Lessons from Enzymes. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 14049-14054. Collman, J. P.; Boulatov, R.; Sunderland, C. J.; Fu, L. Functional Analogues of Cytochrome c Oxidase, Myoglobin, and Hemoglobin. *Chem. Rev.* **2003**, *104*, 561-588.

5. Tsui, E. Y.; Day, M. W.; Agapie, T. Trinucleating Copper: Synthesis and Magnetostructural Characterization of Complexes Supported by a Hexapyridyl 1,3,5-Triarylbenzene Ligand. *Angew. Chem., Int. Ed.* **2011**, *50*, 1668-1672. Mirica, L. M.; Stack, T. D. P. A Tris(μ-hydroxy)tricopper(II) Complex as a Model of the Native Intermediate in Laccase and Its Relationship to a Binuclear Analogue. *Inorg. Chem.* **2005**, *44*, 2131-2133.

6. Kodera, M.; Kajita, Y.; Tachi, Y.; Kano, K. Structural Modulation of Cu(I) and Cu(II) Complexes of Sterically Hindered Tripyridine Ligands by the Bridgehead Alkyl Groups. *Inorg. Chem.* **2003**, *42*, 1193-1203.

7. Heiden, Z. M.; Rauchfuss, T. B. Proton-Induced Lewis Acidity of Unsaturated Iridium Amides. *J. Am. Chem. Soc.* **2006**, *128*, 13048-13049. Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. The Hydrogenation/Transfer Hydrogenation Network: Asymmetric Hydrogenation of Ketones with Chiral η^6-Arene/N-Tosylethylenediamine-Ruthenium(II) Catalysts. *J. Am. Chem. Soc.* **2006**, *128*, 8724-8725.

8. Letko, C. S.; Heiden, Z. M.; Rauchfuss, T. B.; Wilson, S. R. Coordination Chemistry of the Soft Chiral Lewis Acid [Cp*Ir(TsDPEN)]+. *Inorg. Chem.* **2011**, *50*, 5558-5566.

9. Letko, C. S.; Heiden, Z. M.; Rauchfuss, T. B. Activation and Deactivation of Cp*Ir(TsDPEN) Hydrogenation Catalysts in Water. *Eur. J. Inorg. Chem.* **2009**, 4927-4930.