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Education

Ph. D. (1995): Massachusetts Institute of Technology; B.A. (1989): Williams College

Academic Career

2009: Professor, Department of Chemistry, The Johns Hopkins University

2004: Associate Professor (*tenured*), Department of Chemistry, The Johns Hopkins University

1998: Assistant Professor, Department of Chemistry, The Johns Hopkins University

1995: NIH Postdoctoral fellow, Department of Chemistry, Northwestern University

Awards and Honors

Society of Porphyrins and Phthalocyanines/JPP Young Investigator Award (2006), Japan Society for the Promotion of Science (JSPS) Invitation Fellowship (2004), Alfred P. Sloan Research Fellowship (2002), NSF CAREER Award (2001)

Representative Publications (selected from ~65 peer-reviewed articles)

Prokop, K. A.; Neu, H.; de Visser, S. P.; Goldberg, D. P. "A Manganese(V)-Oxo π -Cation Radical Complex: Influence of One-Electron Oxidation on Oxygen-Atom-Transfer," *J. Am. Chem. Soc.*, **2011**, accepted.

Fukuzumi, S.; Kotani, H.; Prokop, K. A.; Goldberg, D. P. "Electron- and Hydride-Transfer Reactivity of an Isolable Manganese(V)-Oxo Complex," *J. Am. Chem. Soc.*, **2011**, *133*, 1859-1869.

Badiei, Y. M.; Siegler, M. A.; Goldberg, D. P. "O₂ activation by Bis(imino)pyridine Iron(II)-Thiolate Complexes," *J. Am. Chem. Soc.*, **2011**, *133*, 1274-1277.

Prokop, K. A.; de Visser, S. P.; Goldberg, D. P. "Unprecedented Rate Enhancements of Hydrogen-Atom Transfer to a Manganese(V)-Oxo Corrolazine Complex," *Angew. Chem. Int. Ed.*, **2010**, *49*, 5091-5095.

Jiang, Y.; Widger, L. R.; Kasper, G. D.; Siegler, M. A.; Goldberg, D. P. "Iron(II)-Thiolate *S*-Oxygenation by O₂: Synthetic Models of Cysteine Dioxygenase," *J. Am. Chem. Soc.*, **2010**, *132*, 12214-12215.

Namuswe, F.; Hayashi, T.; Jiang, Y.; Kasper, G. D.; Sarjeant, A. A. N.; Moënne-Loccoz, P.; Goldberg, D. P. "Influence of the Nitrogen Donors on Nonheme Iron Models of Superoxide Reductase: High-Spin Fe^{III}-OOR Complexes," *J. Am. Chem. Soc.*, **2010**, *132*, 157-167.

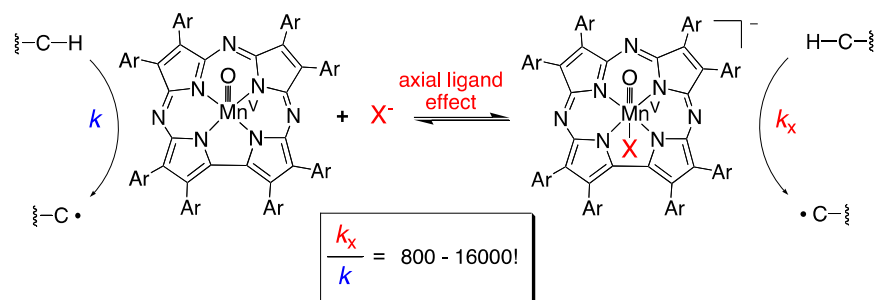
High-Valent Metal-Oxo Corrolazines in Hydrogen-Atom-Transfer and Oxygen-Atom-Transfer

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This presentation will focus on our recent results concerning the stabilization, reactivity, and mechanism of high-valent metal-oxo species.¹ High-valent Mn-oxo and Fe-oxo species play an important role in many biological systems, including a number of heme- and nonheme enzymes. These enzymes catalyze key oxidation reactions in numerous biological pathways, and it is the high-valent metal-oxo species that is believed to function as the critical oxidant. Our lab has constructed the corrolazine platform to stabilize high-valent metal-oxo species, and it is based on the tetrapyrrolic framework common to the heme enzyme cofactor. A key difference is that the corrolazine ligand is ring-contracted, where one of the bridging meso

atoms has been removed and there is a direct pyrrole-pyrrole linkage. In addition, the remaining 3 bridging meso positions are occupied by nitrogen atoms instead of carbon atoms as found in a



regular porphyrin. The Cz ligand platform has allowed us to isolate a rare example of an Mn(V)-oxo complex. The reactivity of this complex as well as a high-valent Fe-oxo complex, will be described. Reactions that are of fundamental importance for both biology (e.g. heme enzymes) and for synthetic catalysts involve oxygen-atom-transfer (OAT) and proton-coupled electron-transfer (PCET). The (Cz)Mn^V-oxo complex exhibits both OAT and PCET reactivity, and mechanistic analyses involving the assessment of products and kinetic parameters for these processes will be presented.² For example, C-H activation mediated by the (Cz)Mn^V(O) complex is shown to proceed through a PCET mechanism, and much of the driving force for this reaction appears to come from the affinity for the proton, or in other words, the basicity of the metal-oxo unit. We have found that dramatic rate enhancements for C-H activation can be induced via axial ligand effects.³ We have also recently prepared the first example of a one-electron-oxidized Mn^V(O)- π -cation-radical complex, and compared its OAT reactivity with the neutral Mn^V(O) complex.⁴ This work has an interesting parallel with the reactivity of Compound-I versus Compound-II in heme enzymes.

References

- (1) McGown, A. J.; Badiei, Y. M.; Leeladee, P.; Prokop, K. A.; DeBeer, S.; Goldberg, D. P. In *Handbook of Porphyrin Science*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; World Scientific Press: Singapore, 2011; Vol. 14, pp 525-599.
- (2) Fukuzumi, S.; Kotani, H.; Prokop, K. A.; Goldberg, D. P. *J. Am. Chem. Soc.*, **2011**, *133*, 1859-1869.
- (3) Prokop, K. A.; de Visser, S. P.; Goldberg, D. P. *Angew. Chem. Int. Ed.*, **2010**, *49*, 5091-5095.
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