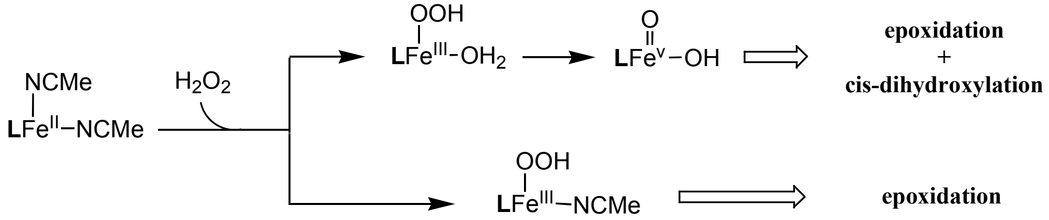
Mechanistic Insights on Bio-inspired Iron Oxidation Catalysts

Yoshimitsu Tachi, Rubén Mas-Ballesté, Lawrence Que, Jr.*

Department of Chemistry & Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant St. S.E. Minneapolis, MN 55455 (e-mail: tachi@chem.umn.edu)

Nonheme iron centers in enzymes can catalyze highly stereo-selective oxidation of C-H and C=C bonds.[1] Inspired by these bioinorganic systems, our group has found that iron(II) complexes of tetradentate N4 ligands like tpa (tris(2-pyridylmethyl)amine) and bpmen (bis(2-pyridylmethyl)ethylenediamine) can use H_2O_2 as oxidant and catalyze not only the high stereo-selective conversion of an olefin to epoxide but also to the corresponding cis-diol.[1] Towards the end of obtaining a better understanding of the mechanisms of these catalytic processes, we have focused on trapping intermediates that may be involved in the catalysis. Herein we present spectroscopic studies of intermediate species trapped in the reaction of [Fe(bpmen)$(OTf)_2$] with H_2O_2 which have been characterized by UV-vis spectroscopy at low temperature. The results obtained show that the nature of the intermediate detected depends on the amount of water present in solution. Correspondingly, catalysis results with this system show that epoxidation is strongly favored in the absence of added water but cis-hydroxylation becomes more significant in its presence. These observations, together with labeled $H_2{}^{18}O_2$ and $H_2{}^{18}O$ experiments, suggest the participation of two pathways in Fe-bpmen catalysis as shown in the scheme, a water-assisted (top) and a non-waster-assisted mechanism (bottom).



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1) M. Costas, M. P. Mehn, M. P. Jensen, and L. Que, Jr. *Chem. Rev.* **2004**,*104*, 939-986