Proton Coupled Electron Transfers via Phenoxyl Radical Chemistry

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A mechanistic study of the net H-atom transfer (HAT) catalyzed by synthetic mimics of the enzyme galactose oxidase (Gal Ox) will be presented. This work is an effort toward understanding the kinetic barriers in HAT, as these reactions are essential to biomimetic oxidation chemistry. A number of metal phenoxyls have been synthesized, and rate constants for the oxidation of primary alcohols and 9,10-dihydroanthracene to their aldehyde and aromatic product states, respectively, have been measured. In addition to a Marcus-theory analysis of the rate constants, information regarding a five coordinate square pyramidal Zn^{II} species representative of a catalytic intermediate has been gathered via x-ray crystallography and VT-^{1}H NMR. This structure may provide further insight into the mechanistic pathway of oxidation chemistry, and with kinetic information, aid in the development of more efficient metal-phenoxyl catalysts.