Non-Heme Iron Catalyzed Oxidation of Alkanes to Alcohols via Heterolytic Cleavage of Alkyl Peroxides: Mechanistic and Spectroscopic Insights into Monooxygenase Chemistry

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The ability of the binuclear non-heme ferrous complex $Fe_2^{2+}(H_2Hbamb)_2(N\text{-}MeIm)_2$ (H_2Hbamb: 2,3-bis(2-hydroxybenzamido)2,3-dimethylbutane) to react with oxygen atom donor molecules, peroxides or peracids and catalyze the hydroxylation of alkanes and arenes will be discussed. Mechanistic studies demonstrating the capacity of the ferrous complex to react with either 2-methyl-1-phenylprop-2-yl hydroperoxide (MPPH) or phenylperacetic acid (PPAA) to produce a highly reactive iron-based intermediate exclusively through a pathway characterized by heterolytic O-O bond cleavage will be detailed. Low temperature reactions of the diferrous complex with either oxygen atom donor molecules, MPPH or PPAA cleanly generate a common species ($\square_{max}(\square_M)$ = 295nm (1.3 x 10^4), 430nm (4.8 x 10^3)) that is kinetically competent in its ability to oxidize alkanes to alcohols. Results of temperature-dependent kinetic studies investigating the energetics of reactive intermediate formation and its decay to the μ-oxo diferric dimer will be discussed. The observed reactivity properties, which include the ability to catalyze (50-600 turnovers) the hydroxylation of cyclic alkanes (cyclopentane, cyclohexane, cyclooctane, methyl cyclohexane), straight-chain alkanes (*n*-pentane), branched-alkanes (2,2,3,3-tetramethylbutane), polycyclic alkanes (adamantane, norbornane), and arenes (benzene, toluene) in the presence of MPPH, will be highlighted. In each case, quantification of the MPPH end product showed clean heterolytic O-O bond cleavage with concomitant oxygen atom transfer efficiencies of > 98%. The catalytic oxidation of methane to methanol at ambient temperatures and low pressures will also be discussed. Mechanistic insights obtained from both intermolecular and intramolecular kinetic isotope effect experiments will be presented. In addition, characterization of the intimate mechanism of the oxygen atom transfer step obtained from a series of investigations utilizing radical clock substrates will be presented. Finally, the connections between the observed chemistry and the reaction chemistry catalyzed by both mononuclear and binuclear non-heme iron monooxygenases will be presented.