Biomimetic Alcohol Oxidations by Iron(III) Porphyrin Complex : Relevance to Cytochrome P-450 Catalytic Oxidation and Involvement of Two-State Radical Rebound Mechanism

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The systematic oxidation reactions of a wide range of alcohols have been carried out by iron porphyrin complex in order to understand their relation to cytochrome P-450 enzymes and to have a practical application to organic synthesis. The iron porphyrin complex catalyzed efficiently alcohol oxidation to the carbonyl compound via high-valent iron-oxo porphyrin intermediate ((Porp)Fe=O$^+$). Several mechanistic studies such as isotope ^{18}O labeling, deuterium isotope effect, linear free energy relationship, and ring-opening of radical clock substrate, have suggested that alcohol is oxidized by the sequence of reactions involving α-hydroxyalkyl radical intermediate and oxygen rebound to form the gem-diol, dehydration of which yields the carbonyl compounds. Moreover, it have been proposed that two-state reactivity mechanism can be also adopted for alcohol oxidation reaction in iron porphyrin model system as shown in P-450 enzymes.