Carboxylic Acid-Directed C—H Oxidations and Desaturations using a Non-heme Iron Catalyst and H_2O_2

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Non-heme iron enzymes are a class of oxygen-activating metalloenzymes that catalyze a variety of remarkable C—H oxidations, including hydroxylation, desaturation, and halogenation. The non-heme iron model complex Fe(PDP) **1** has been reported to catalyze predictably site-selective C—H oxidations of 2° and 3° C—H bonds when using H_2O_2 as terminal oxidant. Interestingly, oxidation of carboxylic acid-containing substrates leads to the unexpected observation of 'double oxidation' products featuring two adjacent sites of formal C—H oxidation. Mechanistic analysis suggests that these products arise from oxidation of *in situ* generated olefins, and that these olefins, in turn, arise from a short-lived carbon-centered radical. Based on our analysis, non-heme iron complexes are demonstrated for the first time to exhibit mixed oxygenase/desaturase activity on unactivated, aliphatic C—H bonds.

Catalytic DNA with Phosphatase Activity

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Catalytic DNA sequences (deoxyribozymes) have been identified by in vitro selection to perform Zn^{2+}-dependent phosphomonoester hydrolysis of tyrosine and serine side chains, i.e., exhibit phosphatase activity. The rate enhancement of the best new deoxyribozyme is at least 4×10^{14}, decreasing the uncatalyzed half-life for phosphoserine from $>10^{10}$ years to <1 h. The phosphatase activity also occurs with non-peptidic substrates but with reduced efficiency, indicating that this new deoxyribozyme prefers phosphopeptides. The newly identified deoxyribozyme can function with multiple turnover using free peptide substrates and has activity in the presence of human cell lysate or bovine serum albumin, suggesting broader application of DNA catalysts as artificial phosphatases.