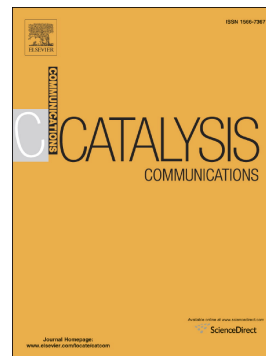


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Direct Reactivity Studies of Non-Heme Iron-Oxo Intermediates toward Alkane Oxidation

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Abstract

Iron complexes $[(S,S)\text{-PDP}^*]\text{Fe}^{\text{III}}(\mu\text{-OH})_2\text{Fe}^{\text{III}}[(S,S)\text{-PDP}^*](\text{OTf})_4$ (**6**), $(S,S)\text{-PDP}^* = N,N'$ -bis(3,5-dimethyl-4-methoxypyridyl-2-methyl)-(S,S)-2,2'-bipyrrolidine, and $[(\text{TPA}^*)\text{Fe}^{\text{III}}(\mu\text{-OH})_2\text{Fe}^{\text{III}}(\text{TPA}^*)](\text{OTf})_4$ (**7**), $\text{TPA}^* =$ tris(3,5-dimethyl-4-methoxypyridyl-2-methyl)amine, catalyze the selective hydroxylation of alkanes with H_2O_2 and peroxycarboxylic acids. Using in situ EPR spectroscopy, direct kinetic data on the reactivity of the iron-oxo intermediates formed in the catalyst systems **6,7**/oxidant/ RCOOH ($\text{RCOOH} =$ acetic acid (AA) or 2-ethylhexanoic acid (EHA)) toward cyclohexane have been obtained for the first time, thus corroborating their key role in the selective C–H oxidation. Intermediates **6a**^{AA}, **6a**^{EHA} and **7a**₂^{EHA} with proposed structures $[(S,S)\text{-PDP}^*]\text{Fe}^{\text{V}}=\text{O}(\text{OC}(\text{O})\text{CH}_3)]^{2+}$, $[(S,S)\text{-PDP}^*]\text{Fe}^{\text{V}}=\text{O}(\text{OC}(\text{O})\text{R}]^{2+}$ and $[(\text{TPA}^*)\text{Fe}^{\text{V}}=\text{O}(\text{OC}(\text{O})\text{R}]^{2+}$ ($\text{RCOOH} =$ EHA) display similar EPR spectra ($g_1 = 2.07$, $g_2 = 2.01$, $g_3 = 1.96$) and have close reactivities toward cyclohexane at $-70\text{ }^\circ\text{C}$ ($k_2 = 2\text{--}3 \times 10^{-3}\text{ M}^{-1}\text{s}^{-1}$).

Keywords

C–H oxidation, enzyme models, EPR spectroscopy, iron, reaction mechanisms

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