Oxoiron(IV) Porphyrin Cation Radical Complexes with a Chameleon Behavior in Cytochrome P450 Model Reactions

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There has been an intriguing, current controversy on the involvement of multiple oxidizing species in oxygen transfer reactions by cytochromes P450 and iron porphyrin complexes. The primary evidence for the "multiple oxidants" theory was that products and/or product distributions obtained in the catalytic oxygenations were different depending on reaction conditions. In the present work, we carried out detailed mechanistic studies on competitive olefin epoxidation, alkane hydroxylation, and C=C epoxidation versus allylic C-H hydroxylation in olefin oxygenation with in situ-generated oxoiron(IV) porphyrin π-cation radicals (**1**) under various reaction conditions. We found in the studies that the products and product distributions were markedly different depending on reaction conditions. These results demonstrate that **1** can exhibit diverse reactivity patterns under different reaction conditions, leading us to propose that the different products and/or product distributions observed in the catalytic oxygenation reactions by iron porphyrin models might not arise from the involvement of multiple oxidizing species but from **1** under different circumstances. This study provides strong evidence that **1** can behave like a "chameleon oxidant" that changes its reactivity and selectivity under the influence of environmental changes.