

Correlation between the Reactivity and Selectivity of Low-Spin and High-Spin Oxo-Iron(V) Complexes in the Oxidation of (+)-Sclareolide

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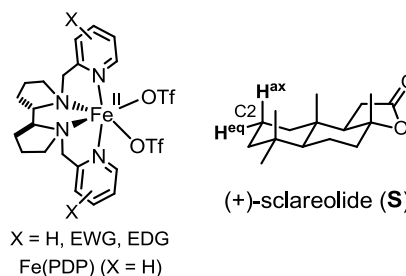
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The milestone discovery of Fe(PDP)-type catalyst system [1] has been inspiration for subsequent progress of bioinspired catalyst systems for C=C and C–H oxidation of complex organic molecules [2]. In recent years, the main mechanistic peculiarities of catalyst systems based on non-heme Fe complexes with aminopyridine ligands, including the key role of perferryl intermediates, have been reliably established. However, disclosing correlations between the electronic structure (and spin state) of the key perferryl intermediates and their selectivity profile remains the subject of experimental and theoretical studies.

Notably, while perferryl intermediates in Fe(PDP)-based catalyst systems exhibit clear “reactivity-selectivity” relationship in the enantioselective epoxidation of olefins [3], such correlations in C–H oxidation reactions have been elusive until recently. Herewith, we report the first example of “reactivity-selectivity” correlation in Fe(PDP) catalyzed C–H oxidation of (+)-sclareolide (S).

The catalyst systems exhibiting the most reactive oxoiron(V) intermediates in the series, have been found to display the lowest (51-55%) C2 oxidation regioselectivity (to yield alcohol and ketone, $S^{2(\text{eq})-\text{OH}}$ and $S^{2=\text{O}}$). Contrastingly, the systems featuring the least reactive intermediates, exhibit the highest C2 oxidation regioselectivity



(64-65%). The chemoselectivity of C2 oxidation, assessed by the $S^{2(\text{eq})-\text{OH}}/S^{2=\text{O}}$ ratio, also increases with decreasing reactivity of the oxoiron(V) intermediates (from 1.6 for up to 5.0). These results demonstrate that besides steric effects, electronic effects may play important role in directing the C–H oxidation chemo- and regioselectivity, which should be taken into account when designing biomimetic catalyst systems for late-stage oxidation of complex substrates of natural origin.

Acknowledgement. The authors thank the Russian Science Foundation (grant 22-13-00225) for financial support.

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