

In-situ generation of Fe-porphyrin O₂ intermediate for greener oxygenation of small molecules

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Insertion of oxygen or halogen atom onto an organic backbone is crucial to incorporate functional groups. Those oxidation reactions are highly used in industry such as pharmaceutical. However they are often stoichiometric and require harsh conditions. Knowing the economic and environmental situation it is primordial to find greener and economically viable pathway to generate those product and synthetic intermediates.[1] Dioxygen is an abundant and easy accessible oxidant source. However, its triple state makes it unreactive and its activation barrier requires huge energy. Nature is able to easily activate O₂ in mild conditions. Indeed, metalloenzymes such as CytP450 can perform highly efficient and selective oxidation reactions under physiological conditions through the reductive activation of O₂. In this context, we used iron-porphyrin in presence of dioxygen and electrochemistry to generate *in-situ* highly reactive O₂-intermediate and to finally induce oxidation reaction of organic substrates.

In previous work, [2] we have reported thanks to spectroelectrochemistry the O₂ activation mechanism by Fe-Porphyrin complexes revealing that different O₂-intermediate can be generated depending on the value of the applied potential and the reaction medium (presence or absence of proton) (Figure 1).

According to the pertinent potential and reaction conditions applied, the reactivity toward organic substrates can be tuned, promoting -superoxo, or -oxo intermediate.[3] The reactivity will be emphasized on the superoxo intermediate as it is the first one to be reach, thus requiring lower potential to be generated.

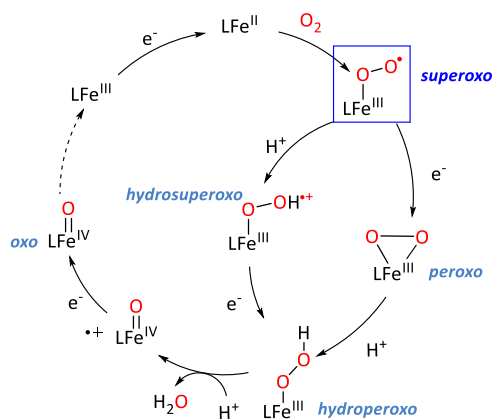


Figure 1: Proposed catalytic cycle of O₂ reductive activation by Fe^{III}-Porphyrin complex.

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