

Mechanistic Insight into Metal-Catalyzed C-H Oxidation from a DFT Perspective

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Catalytic C-H oxidation is a chemical transformation of high interest. This field is crucial for the development of green and cheap routes for the oxidation of methane to methanol and the selective functionalization of other alkanes. A number of catalytic C-H oxidation systems have been explored computationally. DFT studies on the hydroxylation of toluene by Mn-oxo porphyrins showed that the reaction requires radical character on oxygen, referred to as oxyl, in order to take place.¹ The high spin oxyl states are accessible in energy but they may become unreachable with axial ligands having strong *trans* influence.² The selective oxidation of more complex substrates by means of molecular recognition strategies was also studied, in collaboration with Crabtree. The calculations showed that the success of this approach is based on a flexible double H-bond interaction, combined with the steric protection of the active site (Figure).³ Further studies on the manganese systems showed that they can promote oxidation by both hydroxylation and dehydrogenation. The switch between these two reactions is controlled by the relative orientation of a common radical intermediate.⁴ The iridium-catalyzed stereoretentive hydroxylation of *cis*-decalin was also studied computationally. The $[\pi_{xz}^*(\text{Ir}=\text{O})]^2[\pi_{yz}^*(\text{Ir}=\text{O})]^0$ electronic configuration of this system favors a concerted mechanism without the formation of radicals.⁵ More recently, the copper-catalyzed direct oxidation of benzene to phenol has been studied in collaboration with Pérez.⁶

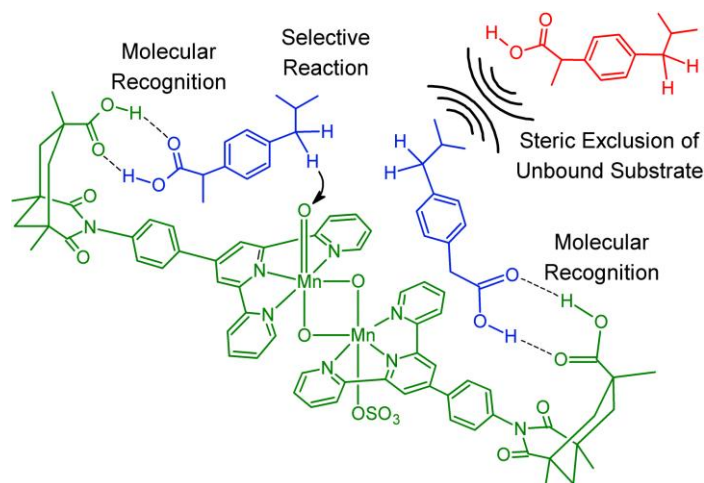


Figure. Manganese-catalyzed selective oxidation of ibuprofen by molecular recognition.