MECHANISTIC STUDY OF C-H HYDROXYLATION REACTIONS BY Fe(^{X}PyTACN) CATALYST. REBOUND MECHANISM vs. ASYNCHRONOUS CONCERTED PROCESS

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The selective oxidation of inactivated hydrocarbons, in general, and alkanes in particular, remains a challenge in synthetic chemistry. All the same, these reactions are very common in many biological processes and often they are catalyzed by enzymes containing a high-valent iron-oxo group as active center [1,2]. Biomimetic catalysts Fe[^{X}PyTACN], developed in the experimental QBIS laboratories, act as very efficient catalysts in several oxidative transformations including alkane hydroxylation [3], olefin cis-hydroxylation [4,5] or water oxidation [6].

A proposed mechanism for the alkane hydroxylation using Fe[^{X}PyTACN] as catalysts and H_2O_2 as the oxidant is analyzed in detail by means of DFT calculations. The evidences given by the DFT calculations allow the rationalization of unexpected experimental labeling results, which indicate that the level of oxygen coming from the water incorporated into the hydroxylated products is highly dependent on the specific substitution in the pyridine ring of the ^{X}PyTACN ligand backbone [7]. Further studies for the alkane hydroxylation mechanism for different substrates (methane, primary-carbon alkane, secondary-carbon alkane and tertiary-carbon alkane) have been done in order to compare their reactivity and mechanism details. Three different models have been used to study the alkane hydroxylation mechanism: i) Gas-phase geometry optimization including the effect of the dispersion (Grimme D3) through single points calculations; ii) Gas-phase geometry optimizations including the effect of the dispersion (Grimme D3) and solvent (PCM-SMD) corrections through single point calculations; iii) Geometry optimization taking into account the dispersion forces and the solvent. Different mechanism have been obtained depending on the theoretical model used. Depending on the substrate, the consideration of the solvent during the optimization process not only changes the reaction free energies and barriers but also the alkane hydroxylation mechanism. These insights will be very useful for further studies in alkane hydroxylation processes.

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