

COMMUNICATION

Theoretical Study on Sulfoxidation Reactivity by a Nickel Acylperoxo Complex

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Abstract: The mechanism of the biomimetic nonheme complexes has been experimentally and theoretically studied in recent years, owing to their capability to activate various substrates. According to the previous studies, the mechanisms were different in the presence/absence of acid. In this paper, we used density functional theoretical (DFT) methods to study the mechanism of the sulfoxidation of sulfide by a nickel acylperoxo complex [Ni-(Tp^{CF₃Me})(κ²-mCPBA)] in the presence of the *m*-chloroperbenzoic acid(mCPBA). Both the concerted and the stepwise radical mechanisms were proposed and it was demonstrated that the former is preferred.

AMS subject classifications: 65D18, 74M40, 78M50

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Introduction

In the past few years, a large number of biomimetic nonheme complexes have been designed and developed to catalyze the hydroxylation, epoxidation, or cis-dihydroxylation

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of hydrocarbon substrates with high stereoselectivity [1-3]. Despite intensive research efforts, the catalysis mechanism was still a formidable challenge to chemists, especially for the genuine oxidant and intermediate involved. Thus, experimental and theoretical studies have been performed to investigate the mechanism, which may lead to new insight in biocatalysis as well as enlighten new approaches for industrial catalysis.

According to the previous studies, it was found that the mechanisms were different with and without acid. In 2001, Que et al. proposed a general mechanism for alkane oxidation by $\text{Fe}^{\text{II}}(\text{TPA})$ (TPA=tris(3,5-dimethyl-4-methoxypyridyl-2-methyl)amine) family of catalysis in combination with H_2O_2 , in which both $\text{Fe}^{\text{III}}\text{-OOH}$ and $\text{Fe}^{\text{V}}(\text{O})\text{OH}$ oxidants could play a vital role in alkane hydroxylation [4]. In 2006, Que et al. characterized a family of nonheme iron catalysts and performed olefin epoxidation, cis-dihydroxylation using H_2O_2 as the oxidant. The resultant intermediate was observed as the ferric hydroperoxo complex $\text{Fe}^{\text{III}}\text{-OOH}$, whose spin state was modulated by the electronic and steric properties of the ligand environment. In $\text{Fe}^{\text{II}}(\text{TPA})/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ system, the intermediate is $\text{Fe}^{\text{III}}\text{-OOH}$, which decays via water-assisted heterolytic O-O bond cleavage to form a real oxidant $\text{Fe}^{\text{V}}(\text{O})\text{OH}$ [5, 6]. The kinetic evidence for such pathway and the mass spectral evidence of the oxidant has been reported [7,8]. Overall, the available data reveal a surprising complex reaction landscape that the transformation is carried out by the common $\text{Fe}^{\text{V}}(\text{O})\text{OH}$ oxidant.

The addition of acetic acid could alter the mechanism and improve both catalytic activity and selectivity [6, 9-11]. In the $\text{Fe}^{\text{II}}(\text{TPA})/\text{H}_2\text{O}_2/\text{AcOH}$ system, Que et al. [12] have observed the intermediate and it was proposed that the oxidant was the $[(\text{TPA})\text{Fe}^{\text{V}}(\text{O})(\text{OC}(\text{O})\text{CH}_3)]$, Talsi et al. performed EPR spin trapping and found that $g=2.7$ [13]. The further support has also been built on the basis of DFT calculations. Gopalan et al. explored two possible high-valent species generated from the cleavage of O-O bond of $\text{Fe}^{\text{III}}\text{-OOH}$ species, which revealed that the species underwent heterolytic cleavage to form a transient $\text{Fe}^{\text{V}}=\text{O}$ oxidant, then it underwent an electrophilic attack and eventually led to the ortho-hydroxylated product [14]. Wang et al. also performed the calculations, and the results showed that the oxidant was an oxoiron (V) species $[(\text{TPA})\text{Fe}^{\text{V}}(\text{O})(\text{OC}(\text{O})\text{CH}_3)]$ which was isomerized by $[(\text{TPA})\text{Fe}^{\text{IV}}(\text{O})(\text{OC}(\text{O})\text{CH}_3)$ radical] [15]. Que et al. observed the change in olefin oxidation products when the acetic acid replaced the water and they proposed the modification of the water-assisted mechanism to a carboxylic-acid-assisted version [16]. In the $\text{Fe}^{\text{II}}(\text{S,S})\text{-PDP}/\text{H}_2\text{O}_2/\text{AcOH}$ system [17], the catalyst was the cyclic ferric peracetate complex and it could convert to a transient oxoiron (IV)-ACO species that performed alkane hydroxylation. Elena and co-workers observed the unusual $g=2.7$ EPR signal in the presence of carboxylic acid and postulated that this chromophore was an acylperoxoiron(III) intermediate and the oxidant might be unobserved higher-valent oxidant [18].