

Computational Assessment of Fe(IV)–Oxo–Hydroxo Oxidant Mediated Intramolecular Ligand Hydroxylation and Role of Lewis Acid on O–O Bond Dissociation

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Over the last decades, biomimetic oxidation of alkanes and alkenes by iron complexes in the presence of “ready oxidant” H₂O₂ has been extensively studied. Several iron–oxygen intermediates such as iron(III)–(hydro)peroxo and iron(IV)–oxo species have been generated through reduction of dioxygen by iron(II) complexes. However, the selective oxidation of C–H and C=C bonds by biomimetic complexes using O₂ are rare and remains a major challenge in bioinspired catalysis. In this endeavour, a nucleophilic side-on Fe(II)–hydroperoxo oxidant (I) is proposed to form in the reaction of high-spin iron(II) complex [(TpPh₂)FeII(benzilate)] (1) [TpPh₂=hydrotris(3,5-diphenylpyrazolyl)borate] with dioxygen in benzene at ambient temperature.[1] The concomitant decarboxylation of benzilic acid yields benzophenone. I undergoes O–O bond cleavage to generate an electrophilic Fe(IV)–oxo–hydroxo oxidant (II). The dissociation of O–O bond is facilitated in the presence of a Lewis acid e.g. Sc(OTf)₃. [2] DFT calculations predicted that in the presence of protic acid, the energy barrier for the O–O bond cleavage is lowered.[3] The novel oxidant II exhibits versatile reactivity e.g. cis-dihydroxylation of alkenes, selective oxidization of sulfides to sulfoxides and hydroxylation the strong aliphatic C–H bonds. In the absence of any substrate, the oxidant intramolecularly hydroxylates one of the phenyl rings at ortho position on the facial tridentate TpPh₂ ligand. We have performed DFT calculations to investigate the energetics of the O–O bond cleavage of FeII–hydroperoxo species prior to the generation of II both in the absence and presence of Sc(OTf)₃. Emphasis is also placed on the detailed mechanism of the intramolecular ligand hydroxylation and also the hydroxylation of strong C–H bond of cyclohexane by II.

References:

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