INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

Name of the Student : Sayanta Sekhar Nag

Roll Number : 146122024

Programme of Study : Ph.D.

Thesis Title: Aldehyde deformylation by nonheme metal complexes – a mechanistic study

Name of Thesis Supervisor(s) : Prof. Chivukula V. Sastri

Thesis Submitted to the Department/ Center : Chemistry

Date of completion of Thesis Viva-Voce Exam : 06.07.2021

Key words for description of Thesis Work : Bioinorganic Chemistry, Reaction Mechanism, Deformylation

---

SHORT ABSTRACT

The emission of greenhouse gases and particulate matter has profoundly impacted climate change by unsettling the earth's radiation balance. Fossil fuel burning is the primary reason for increasing the concentration of greenhouse gases and aerosol particles. Many of the so-called first-world countries are reducing their fossil fuel consumption substantially. In economically progressing countries like India, there is a lot of complexity depending on those alternatives. The crude oil refinery industry also produced a wide variety of commodity products for everyday uses. Biomass has particular interest among scientists because it can reduce the dependencies on fossil feedstock by generating both fuels and the necessary chemicals in a net carbon neutral biosynthetic pathway. In a petroleum refinery industry, apart from the extensive use of fuels, hydrocarbons are the primary raw material for producing various commodity products. The prospect of using the biosynthesis of hydrocarbon as an alternative to the crude oil refinery systems accelerated the fascination towards mechanistic enzymology.

Hydrocarbon biosynthesis in nature has evolved several times. There are three types of mechanisms for forming unfunctionalized alkanes utilizing fatty aldehydes as a precursor for three different organisms: plants, insects, and cyanobacteria. The most recently discovered pathway for alkane biosynthesis is the cyanobacterial pathway. Cyanobacterial aldehyde decarbonylase is also known as cyanobacterial aldehyde deformylating oxygenase (cADO). The end product for cADO is entirely different than the other two mechanisms. In this case, the aldehyde carbon transformed into formate instead of any gaseous product, unlike the other two mechanisms. The reactivity of cADO was tested with some model aldehyde substrates having relatively smaller carbon chains than natural fatty aldehydes like nonanal and decanal. In these cases, alcohols and aldehydes with one less carbon atom formed as a product and alkane and formate.

The synthetic model compounds have been used in mimicking different types of biological reactions and study their mechanism. They are relatively easy to synthesize and purify to be used successfully on an industrial scale, provided other parameters are in favor. Though the natural aldehyde decarbonylase enzymes contain mainly Fe at the active site, synthetic models have been generated using different transition metals. A detailed understanding of the

deformylation mechanism by nonheme mononuclear systems would help produce a more efficient catalyst for hydrocarbon biosynthesis.

We have demonstrated the synthesis, characterization, and reactivity of two bispidine Cu(II)-alkylperoxo complexes. In contrast to the earlier report of nucleophilic carbonyl attack by Cu-alkylperoxo species, the species mentioned above exhibit C-H abstraction at the α-position of the aldehyde group. The high KIE value is imperative for rate-determining C-H bond cleavage. It has also been observed that these two complexes show an inverse trend in reactivity for two different types of reactions. The introduction of two benzyl groups instead of methyl groups at the N3 and N7 positions (axial N atoms) of the ligand increases the steric bulk around the metal center, accelerating atom transfer to heteroatoms. Simultaneously, the same phenomenon decreases reaction rates for aldehyde deformylation reactions by reducing the substrate approach feasibility.

Also, we have reported the reactivity of Fe(III)-peroxo complexes in aldehyde deformylation. We have synthesized well-characterized Fe(III)-peroxo intermediates and reinvestigate their mechanism using isotope substitution methods. The result observed suggested that the isotope substitution at the substrate helps in switching the mechanism from electrophilic H-atom abstraction to nucleophilic carbonyl attack.

We have synthesized and characterized a new Mn(III)-peroxo complex and studied its mechanism for deformylation reaction. The result suggested a H-atom abstraction from the aldehyde group for the deformylation of cyclohexanecarbaxaldehyde (CCA). We have also proved that the abstraction of the alpha H atom is not RDS for the deformylation of CCA, as suggested in some earlier reports.

These results enlightened the vision about the aldehyde deformylation by metal(III)-peroxo with a new light. As discussed earlier, aldehyde's transformation to hydrocarbon in a single step by a biochemical process will help reduce greenhouse gases and be an efficient conversion step in synthesizing larger molecules essential for pharmaceutical application. The information obtained from this research will help manipulate the catalyst's efficiency and selectivity of the subject. The successful replacement for fossil fuel might not be possible at the moment on a large scale. Still, those catalysts can replace the use of fossil feedstock to generate other commodity products, and the findings from this research will lead to an essential step towards that direction.