



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: **Mechanistic Insights into the Role of Sulfur Ligation in the Oxidative Reactivity of Non-heme High-valent Iron Complexes**

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SHORT ABSTRACT

This thesis investigates the generation, characterization, and reactivity of various sulfur-ligated high-valent non-heme iron intermediates. Specifically, it focuses on the chemistry of non-heme iron(IV)-oxo, iron(IV)-tosylimido, and iron(III)-alkylperoxo systems. Chapter III demonstrates the significant impact of substituting a sulfur ligand for an N-CH₃ group on the reactivity of the iron(IV)-oxo species. Chapter IV details the creation of a sulfur-ligated iron(IV)-tosylimido complex and compares its properties with those of the iron(IV)-oxo analogue. Chapter V presents the generation of a sulfur-ligated iron(III)-alkylperoxo species and introduces a novel mechanism for its reaction with aldehydes.

This field of bio-inorganic chemistry is both promising and challenging due to its inherent uncertainties. Small modifications can lead to significant changes, complicating predictions. For instance, in Chapter III, replacing the N-CH₃ group with a sulfur ligand alters the reaction mechanism for both sulfoxidation and C-H bond activation. However, in Chapter IV, this substitution does not affect the reaction mechanism. A new direction is explored in aldehyde deformylation reactions, where Chapter V reveals a novel pathway involving the abstraction of an aldehydic-H bond from CCA by a Fe(III)-alkylperoxo species, which then undergoes O-O bond cleavage to produce an iron(IV)-oxo species. Typically, iron(III)-peroxo complexes employ a nucleophilic mechanism for deformylating CCA. Thus, the overall reactivity and mechanisms are influenced by various interacting factors, making it an exciting journey to explore the specific effects that differentiate each species.