

Abstract

Transition Metal-free Oxygen Activation by Ammonium Based Ionic Liquids for Selective Oxidation Reactions: Experimental and Theoretical Studies

Submitted by-Krishnendu Khamaru

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Developing mild, cost-effective, and selective oxidation methods to convert low-cost and valuable hydrocarbons into useful oxidative compounds is still a major challenge in organic synthesis. In organic chemistry and chemical biology, transition metal catalysts, or metalloenzymes, are typically required for most oxidation reactions. Among various oxidation strategies, the use of dioxygen (O_2) is acknowledged as a highly effective reagent.

The detailed study explores the transition metal-free oxygen (O_2) activation process using ionic liquids for selective oxidation reactions. This thesis shows an efficient, cost-effective, and green protocol to transform hydrocarbons (benzylamine and alcohols) into useful oxidized compounds that are oxygenated (amide) and non-oxygenated (aldehyde, imine, and aromatic heterocycle). These compounds can be used as fine chemicals or as building blocks for chemical synthesis in the lab or in industry. This thesis's research describes first-principles calculations using Density Functional Theory (DFT), revealing that the various reaction coordinates and transition state spin densities demonstrate a unique spin conversion of triplet oxygen to singlet products via a minimum energy crossing point, without the assistance of transition metal ions. It explains about how quaternary alkylammonium-based ionic liquids make the π^* orbital of oxygen more stable, which makes it susceptible for hydrogen atom transfer from desired organic molecule in a mild, metal-free condition. This research elucidates the mechanism of O_2 activation using molecular orbital (MO) theory. The partial density of states (pDOS) calculations suggests a new approach for O_2 activation using quaternary alkylammonium-based ionic liquids instead of metal-based catalysts.

- **Chapter 1** discusses the chemistry of the oxygen molecule and its reactivity in the presence of a transition metal catalyst.
- **Chapter 2** describes the efficient strategy for oxygen activation using quaternary alkylammonium-based ionic liquids, leading to the synthesis of valuable oxidized compounds from benzylamines and alcohols.
- **Chapter 3** presents a detailed mechanistic study of oxygen activation using quaternary alkylammonium-based ionic liquids.

Krishnendu Khamaru
Signature of Candidate

Nakul Chandra Maiti
Signature of Supervisor with Seal

Biswadip Banerji 22/5/24
Signature of Supervisor with Seal

डॉ. नकुल चंद्र माईति / Dr. Nakul C. Maiti
वरिष्ठ प्रधान वैज्ञानिक / Senior Principal Scientist
संरचनात्मक जीवविज्ञान और जैवसूचना प्रभाग
Structural Biology & Bioinformatics Division
सीएसआईआर-भारतीय रासायनिक जीवविज्ञान संस्थान
CSIR-Indian Institute of Chemical Biology
(भारत सरकार / Govt. of India)
कोलकाता - 700 032 / Kolkata - 700 032

डॉ. विश्वदीप बनर्जी / Dr. Biswadip Banerji
PhD (IIT-Kanpur), M. Sc (Cal)
प्रधान वैज्ञानिक / Chief Scientist
आर्गेनिक एवं औषधीय रसायन प्रभाग
Organic & Medicinal Chemistry Division
सीएसआईआर-भारतीय रासायनिक जीवविज्ञान संस्थान
CSIR-Indian Institute of Chemical Biology
(भारत सरकार / Govt. of India)
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