Proceedings International
Platinum Open Access Journal (ISSN 2668-6384)

Proceedings, Abstract
Volume 3, Issue 2, 2021, 7 - 8
https://doi.org/10.33263/Proceedings32.007008

Activation of Dioxygen: A Unique Copper(II) Complex containing Topoquinone-like Moieties as a Structural and Functional Model for Copper Amine Oxidase †

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† Presented at Virtual International Conference on Physical Sciences (ICPS - 2021)
Received: 1.02.2021; Revised: 3.02.2021; Accepted: 4.02.2021; Published: 5.02.2021

Abstract: Copper amine oxidase (CuAO) is a copper-containing enzyme that catalyzes the oxidation of primary amines to aldehyde. It has inspired the development of several biomimetic homogeneous catalytic systems for amine oxidation. It contains Cu(II) and topoquinone (TPQ) cofactor in the active site. The biogenesis of TPQ in CuAO involves a self-processing mechanism and requires only O2 and Cu(II) in the active site. The latter has been proposed to catalyze the hydroxylation of tyrosine to give TPQ via the generation of dopamine, hydration, and oxidation. The TPQ cofactor and Cu(II) are suggested to aid the oxidative transformation of primary amines to aldehydes in a two-electron process. However, biochemical studies suggest that the Cu(II) active site required for the biosynthesis of the quinone cofactors is not involved in the subsequent amine oxidation. Many metalloenzyme-like catalytic systems, which effect aerobic oxidation under very mild conditions by avoiding the use of copper metal, oxidants, and high temperatures, have been developed in the past.
We have now successfully isolated an unprecedented Cu(II) complex that mimics the active-site structure and the function of CuAO.1 The complex consists of two sterically hindered TPQ-like side-arms that are analogous to the TPQ cofactor of the enzyme. It is obtained by the ambient aerial oxidation of a precursor Cu(II) Schiff base complex. The complex mimics the oxidase activity of CuAO enzyme by converting primary amines to imines in excellent yields at RT using the environmentally benign dioxygen as the oxidant. It is the most efficient and robust homogeneous catalyst for quantitative oxidation of primary benzylic amines to the corresponding secondary imines under ambient conditions within 30 min. The involvement of Cu(II) in the catalysis has been established by using experiments to quench Cu(II) superoxo species and detailed DFT studies. The mechanisms for both the genesis of the TPQ-like moiety from the benzidine moiety and the catalytic oxidation of benzylic amines to imines have been proposed.

Keywords: copper amine oxidase; DFT studies; catalytic reaction.

Funding

This research received no external funding.

Acknowledgments

This research has no acknowledgment.

Conflicts of Interest

The authors declare no conflict of interest.

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