

DOCTORAL THESIS

Synthesis and Reactivities of Cobalt(III) Alkylperoxo Complexes Bearing Quaterpyridine Ligand

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Date of Award:
2022

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ABSTRACT

Direct use of dioxygen (O₂) in functionalizing organic molecules is highly desirable. In nature, enzymes perform alkane oxidation efficiently at ambient conditions. The transition metals involved in the active sites of enzymes play vital roles in binding with O₂ and transferring electrons and protons during metabolism. Many metal-oxygen species, such as hydro(alkyl) peroxy complexes, are invoked as reactive intermediates in these biological processes. Given the complexity of enzymes, studying the reactivity of these enzymes with simple synthetic coordination compounds is one of the strategies.

This thesis is mainly concerned with the oxidation of alkanes and alkenes catalyzed by tailor-made cobalt(III) alkylperoxy complexes at ambient conditions. In the first part, we report the design and synthesis of the highly electrophilic cobalt(III) alkylperoxy complex, [Co^{III}(qpy)(OO^tBu)(NCCH₃)]²⁺ (**2**), supported by a planar tetradentate quaterpyridine ligand (qpy = 2,2':6',2'':6'',2''':6''',2''''-quaterpyridine). This complex activates C(sp³)-H bonds of a variety of organic molecules at ambient conditions and yields a series of alkylperoxy complexes with the general formula [Co^{III}(qpy)(OOR)(NCCH₃)]²⁺ [RH = Et₂O (**3**), THF (**4**), ^tBuOMe (**5**), ethylbenzene (**6**), toluene (**7**), cyclopentene (**8**), and 3-hexyne (**9**)], which have been well characterized by various spectroscopic techniques including NMR, ESI-MS, UV-vis, FT-IR, and CHN elemental analysis. The structures of these complexes have also been characterized by X-ray crystallography.

In the second part, the mechanism for the alkane oxidation catalyzed by [Co^{III}(qpy)(OOR)(NCCH₃)]²⁺ was extensively studied at room temperature and one atmospheric pressure. NMR study reveals the reaction stoichiometry. ESI-MS study indicates exogenous O₂ is crucial with the support of ¹⁸O-labeled experiments.

Kinetics study by UV-vis and a significant kinetic isotopic effect resulted for the oxidation of ethylbenzene by **2** suggest a rate-limiting hydrogen-atom abstraction from organic substrates (R'H) by $[\text{Co}^{\text{III}}(\text{qpy})\text{OOR}]^{2+}$ via the proximal oxygen atom of the peroxy group (i.e., $[\text{Co}^{\text{III}}(\text{qpy})\text{OOR}]^{2+} + \text{R}'\text{H} \rightarrow [\text{Co}^{\text{II}}(\text{qpy})]^{2+} + \text{R}' + \text{ROOH}$). The resulting alkyl radical R' bound with O_2 to form alkyl peroxy radical R'OO•, which was rapidly scavenged by the $[\text{Co}^{\text{II}}(\text{qpy})]^{2+}$ to give another alkylperoxy complex $[\text{Co}^{\text{III}}(\text{qpy})\text{OOR}']^{2+}$.

The proposed mechanism in the peroxidation of organic molecules by alkyl(hydro)peroxy complexes is unprecedented. In the third part, we examine the catalytic properties of $[\text{Co}^{\text{III}}(\text{qpy})(\text{OOR})(\text{NCCH}_3)]^{2+}$ in aerobic oxidation of various substrates. Using ethylbenzene, cumene, cyclopentene, and cyclohexene as the substrates, $[\text{Co}^{\text{III}}(\text{qpy})(\text{OOR})(\text{NCCH}_3)]^{2+}$ are found to be active and robust catalysts to produce the corresponding hydroperoxides, alcohols, and ketones catalytically. A turnover of >3000 is achieved in the oxidation of cyclohexene for 7 d.

In the fourth part, the reactivities of $[\text{Co}^{\text{III}}(\text{qpy})\text{OOR}]^{2+}$ with alkenes were explored. Alkenes with weak C–H bonds (e.g., 1,4-cyclohexadiene and cycloalkenes) resulted in C–H functionalization. In case there are no weak C–Hs in the alkenes (e.g., styrene), $[\text{Co}^{\text{III}}(\text{qpy})\text{OOR}]^{2+}$ catalyzes the polymerization of styrenes in O_2 to produce polyalkylperoxy species. The bisalkylperoxy complex, $[\text{Co}^{\text{III}}(\text{qpy})(\text{OOCH}(\text{OO}^t\text{Bu})\text{CH}_2\text{Ph})(\text{NCCH}_3)]^{2+}$ (**11**), has been isolated and characterized by ESI-MS, NMR, and X-ray crystallography.

In summary, this work demonstrates the highly electrophilic character of Co(III) alkylperoxy complexes supported by the qpy ligand. Under ambient conditions, these complexes are suitable catalysts to perform aerobic peroxidation of a variety of alkanes and alkenes.