Copyright Permission

WKU ID #: 800815400

Name: Lee, Ngo Fung

Email (to receive future readership statistics): ngofung.lee785@topper.wku.edu

Type of document: ['Thesis']

Title: PHOTOCHEMICAL GENERATION AND KINETIC STUDIES OF HIGH-VALENT METAL-OXO INTERMEDIATES SUPPORTED BY CORROLE AND Porphyrin LIGANDS

Keywords (3-5 keywords not included in the title that uniquely describe content): Photochemical Generation, Corrole, Porphyrin

Committee Chair: Rui Zhang
Additional Committee Members: Stuart Burris, Kevin Williams

Select 3-5 TopSCHOLAR® disciplines for indexing your research topic in TopSCHOLAR®: In this work, photolysis of highly photo-labile corrole-manganese(IV) bromates or nitrites by visible light was studied in two corrole systems with different electronic environments. The corrole systems under studied include 5,10,15-tris(pentafluorophenyl)corrole (TPFC) and 5,10,15-triphenylcorrole (TPC). As observed in both systems, homolytic cleavage of O-Br or O-N bonds in the ligands resulted in one-electron photo-oxidation to generate corrole-manganese(V)-oxo species, as determined by their distinct UV-vis spectra and kinetic behaviors. The kinetic of oxygen atom transfer (OAT) reactions with various substrates by these photo-generated [MnV(Cor)(O)] were studied in CH3CN and CH2C12 solutions. [MnV(Cor)(O)] exhibits remarkable solvent and ligand effects on its reactivity and spectral behaviors. In the more electron-deficient TPFC system and in the polar solvent CH3CN, MnV-oxo corrole returned MnIII corrole in the end of oxidation reaction. However, in the less polar solvent CH2C12 or in the less electron-deficient TPC systems, MnIV product was formed instead of MnIII. With the same substrates and in the same solvent, the order of reactivity of MnV-oxo corrole was inverted as TPC > TPFC. The spectra and kinetic results are rationalized by a multiple oxidation model, where the electron-demand MnV-oxo species may serve as direct two-electron oxidation for oxygen atom transfer reactions; and less electron-demand systems undergo a disproportionation reaction to form a putative manganese(VI)-oxo corrole as the true oxidant. The choice of pathways is strongly dependent on the nature of the solvent and corrole ligand.

Furthermore, porphyrin-manganese(V)-oxo were produced in organic solvents by visible light irradiation of the corresponding porphyrin-manganese(III) nitrite complexes. The porphyrin systems studied were 5,10,15,20-tetrakis(pentafluoro)phenylporphyrin (TPFPP), 5,10,15,20-tetrakis(2,6-difluorophenyl)porphyrin (TDFPP) and 5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphyrin (TDCPP). Heterolytic cleavage of O-N bond of nitrite ligand results in two-electrons photo-oxidation. Under visible light irradiation, MnV-oxo porphyrins quickly returned to MnIII product. However, in absence of light, MnIV-oxo species were formed, as determined by their distinct UV-vis spectra, which permitted direct kinetic studies. The apparent rate constants for reaction of [MnIV(Por)(O)] species show inverted reactivity order with (TPFPP) < (TDFPP) < (TDCPP) in reactions with ethylbenzene. A model for oxidation under catalytic condition was presented.
Copyright Permission for TopSCHOLAR® (digitalcommons.wku.edu) and ProQuest research repositories:

I hereby warrant that I am the sole copyright owner of the original work. I also represent that I have obtained permission from third party copyright owners of any material incorporated in part or in whole in the above described material, and I have, as such identified and acknowledged such third-part owned materials clearly. I hereby grant Western Kentucky University the permission to copy, display, perform, distribute for preservation or archiving in any form necessary, this work in TopSCHOLAR® and ProQuest digital repository for worldwide unrestricted access in perpetuity. I hereby affirm that this submission is in compliance with Western Kentucky University policies and the U.S. copyright laws and that the material does not contain any libelous matter, nor does it violate third-party privacy. I also understand that the University retains the right to remove or deny the right to deposit materials in TopSCHOLAR® and/or ProQuest digital repository.

[I grant permission to post my document in TopSCHOLAR and ProQuest for unrestricted access.]