

Biomimetic Metal-Oxygen Intermediates in Dioxygen Activation Chemistry

Wonwoo Nam

Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750,
Korea

E-mail: wwnam@ewha.ac.kr

Abstract: Dioxygen is essential in life processes, and enzymes activate dioxygen to carry out a variety of biological reactions. One primary goal in biomimetic research is to elucidate structures of reactive intermediates and mechanistic details of dioxygen activation and oxygenation reactions occurring at the active sites of enzymes, by utilizing synthetic metal-oxygen complexes. A growing class of metal-oxygen complexes, such as metal-superoxo, -peroxo, -hydroperoxo, and -oxo species, have been isolated, characterized spectroscopically, and investigated in various oxygenation reactions. During the past decade, we have been studying the chemical and physical properties of various reactive intermediates in oxygenation reactions, such as high-valent iron(IV)- and manganese(V)-oxo complexes of heme and non-heme ligands in oxo-transfer and C-H activation reactions, non-heme metal-peroxo complexes in nucleophilic reactions, and non-heme metal-superoxo complexes in electrophilic reactions. The effects of supporting and axial ligands on structural and spectroscopic properties and reactivities of metal-oxygen adducts have been extensively investigated as well. In this presentation, I will present our recent results on the synthesis and structural and spectroscopic characterization of mononuclear nonheme metal-dioxygen intermediates as well as their reactivities in electrophilic and nucleophilic oxidation reactions.

General References

1. Wonwoo Nam* "Hydrogen Atom Transfer Reactions by Metal-Oxygen Intermediates" *Acc. Chem. Res.* **2018**, *51*, 2014–2022.
2. Wonwoo Nam* "Synthetic Mononuclear Nonheme Iron-Oxygen Intermediates" *Acc. Chem. Res.* **2015**, *48*, 2415–2423.
3. Wonwoo Nam,* Yong-Min Lee, and Shunichi Fukuzumi* "Tuning Reactivity and Mechanism in Oxidation Reactions by Mononuclear Nonheme Iron(IV)-Oxo Complexes" *Acc. Chem. Res.* **2014**, *47*, 1146–1154.
4. Jaeheung Cho, Ritimukta Sarangi, and Wonwoo Nam* "Mononuclear Metal-O₂ Complexes Bearing Macrocyclic TMC Ligands" *Acc. Chem. Res.* **2012**, *45*, 1321–1330.
5. Wonwoo Nam* "High-Valent Iron(IV)-Oxo Complexes of Heme and Nonheme Ligands in Oxygenation Reactions" *Acc. Chem. Res.* **2007**, *40*, 522–531.
6. Wonwoo Nam* "Guest Editorial: Dioxygen Activation by Metalloenzymes and Models" *Acc. Chem. Res.* **2007**, *40*, 465.