

Title	Generation of Metal(V)-Oxo Complexes by Dioxygen Activation and the Catalytic Oxidation Reactivity
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Osaka University

Abstract of Thesis

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Title

Generation of Metal(V)-Oxo Complexes by Dioxygen Activation and the Catalytic Oxidation Reactivity
(分子状酸素による金属(V)オキソ錯体の生成とその反応性)

Abstract of Thesis

Dioxygen activation catalyzed by metal complexes to form high-valent metal-oxo complexes has been in the focus of attention because extensive efforts have been devoted to (1) modeling of biological oxidations, (2) design and utilization of new catalysts for oxidative transformations of organic substrates, and (3) use of O₂ as a cheap oxidant in the manufacture of fine and bulk chemicals. However, the mechanistic insight of O₂ activation has yet to be well understood and oxygenation reactions with high-valent metal-oxo complexes using O₂ as an oxidant are much less common. In this thesis, I focus on the investigation of the mechanistic insight of generation of high-valent metal-oxo complexes by dioxygen activation and the catalytic oxidation reactivity.

In chapter 1, formation of a manganese(V)-oxo complex [Mn^V(O)] from the manganese(III) in the presence of O₂ as the clean oxidant and toluene derivatives under visible light irradiation has been examined to reveal a new method for the selective oxidation of benzylic C–H bonds. And, based on the photodynamics, together with the effect of added substrate and the large kinetic isotope effects (KIEs), the mechanism of photochemical oxidation reaction is proposed.

In chapter 2, the photocatalytic oxygenation of 10-methyl-9,10-dihydroacridine by O₂ with manganese complexes has been examined. The mechanistic findings in chapter 1 suggest that when an appropriate substrate is oxidized by Mn^V(O) to regenerate Mn^{III}, photocatalytic oxidation of the substrate by O₂ can be achieved by using Mn complexes. In chapter 2, photocatalytic oxygenation of a substrate which has a weaker C-H bond was achieved and the reactivities of manganese complexes ligated porphyrin as well as corrolazine are compared.

In chapter 3, an effect of an acid on the photocatalytic reactivity of manganese corrolazine complex for oxygenation of toluene derivatives with O₂ has been examined by using an acid, [H(OEt₂)₂]⁺[B(C₆F₅)₄]⁻ or triflic acid. Protonation of a manganese corrolazine complex was observed by spectral titration and the protonated site of mono- and diprotonated manganese(III) complex was identified by the X-ray crystal structural analysis of the protonated manganese species. In the presence of hexamethylbenzene as a substrate, photocatalytic oxygenation of hexamethylbenzene by O₂ with mono-protonated manganese(III) complex has been confirmed, yielding the corresponding alcohol and the protonated high-valent manganese complex. Mechanism of photocatalytic oxygenation is clarified based on the kinetic study and the detection of the intermediates.

Chapter 4 describes mechanism of catalytic two-electron reduction of O₂ with a high-valent manganese-imido complex, which acts as a catalyst precursor for the catalytic two-electron reduction of O₂ by octamethylferrocene (Mes₈Fc) to produce H₂O₂ in the presence of trifluoroacetic acid in acetonitrile. The rate of the catalytic reduction of O₂ obeyed zeroth-order kinetics with respect to concentrations of Mes₈Fc and an acid, whereas the rate increased linearly with increasing concentrations of the manganese-imido complex and O₂, indicating the rate-determining step is electron transfer from the manganese(III) complex to O₂.

In chapter 5, the rate constants of electron self-exchange of high-valent oxo and imido complexes of chromium(V/IV) corrole have been determined in acetonitrile and toluene at various temperatures by EPR linewidth broadening. The observed activationless electron self-exchange transfer resulted in extremely fast electron-transfer reactions of chromium(V)-oxo and –imido corrole in sharp contrast with slow electron-transfer reactions of other high-valent metal-oxo and –imido complexes.

Chapter 6 describes the photocatalytic water oxidation with a cobalt complex at low pH in the presence of a Ru(II) complex as a photocatalyst, which is oxidized to the Ru(III) complex by oxidative quenching of the photoexcited state with O₂ in the presence of H₂SO₄ to produce H₂O₂. The quantum yield was determined to be 37% with 0.25% of conversion efficiency from solar energy to chemical energy.

論文審査の結果の要旨及び担当者

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	論文審査の結果の要旨	
<p>In this thesis, generation of metal(V)-oxo complexes by dioxygen activation and the catalytic oxidation reactivity has been described, focusing on mechanisms of formation of high-valent metal-oxo complexes via reductive activation of oxygen molecule and oxidative activation of water.</p> <p>In chapter 1, the mechanism for the selective oxidation of benzylic C–H bonds involving only O₂, light, and a manganese(III) corrolazine complex, [(TBP₈Cz)Mn^{III}], to give the high-valent manganese(V)-oxo complex has been clarified. Femtosecond laser flash photolysis measurements have led to the first direct spectroscopic observation of a novel photoexcited state ([[(TBP₈Cz)Mn^{III}][*] (⁷T₁)), which was found to be responsible for the initial reaction with O₂. (TBP₈Cz)Mn^{III} has been shown to act as a photocatalyst in the oxygenation of 10-methyl-9,10-dihydracridine (AcrH₂) by O₂. In chapter 2, the reactivity of manganese porphyrins in photocatalytic oxidation of AcrH₂ by O₂ has been compared with that with a manganese corrolazine complex. Based on the results in chapters 1 and 2, the author has developed photocatalytic oxidation of substrates by O₂ using manganese complexes. In chapter 3, photocatalytic oxygenation of hexamethylbenzene by O₂ with a manganese corrolazine has been described in the presence of an acid. The author revealed that photocatalytic oxygenation ability of manganese corrolazine was much enhanced by the addition of an acid. It should be noted that this is the first example of photocatalytic oxygenation of toluene derivatives using metal complexes in the presence of an acid. In chapter 4, the author found the first example of the homogeneous catalytic two-electron reduction of O₂ to produce H₂O₂ using a high-valent manganese-oxo complex. This study paves a new way to develop Mn-based catalysts for the selective two-electron reduction of O₂ by modifying the ligands to control the redox potential of the Mn^{III}/Mn^{IV} couple. In chapter 5, unique electron-transfer properties of high-valent chromium complex, (tpfc)Cr^V(O) and (tpfc)Cr^V(NTs), with much smaller reorganization energies as compared with other high-valent metal-oxo complexes have been scrutinized. This is a new way to utilize them as efficient electron-transfer catalysts, which are now under investigation. In chapter 6, efficient photocatalytic production of H₂O₂ from H₂O and O₂ in water containing H₂SO₄ or Sc(NO₃)₃ has been achieved using a photocatalyst and a WOC. The photocatalytic production of H₂O₂ using solar energy provides the most convenient and sustainable solar fuel that can be converted to electricity using an H₂O₂ fuel cell.</p> <p>This thesis provides valuable insights both into mechanism of formation of high-valent metal-oxo complexes via reductive activation of dioxygen and into oxidative activation of water to realize artificial photosynthesis, paving a new way to develop efficient catalytic systems using O₂ as an environmentally benign oxidants. I, therefore, believe that the present study will merit considerable interest as a doctoral thesis.</p>		