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論　文　内　容　の　要　旨

氏　名　（朴　志齋　）	
論文題名	Reactivity Enhancement of a Nonheme Iron(IV)-Oxo Complex by Lewis Acids for Oxidation of Substrates (非ヘム鉄(IV)オキソ錯体の酸化反応性のルイス酸による活性化)

論文内容の要旨

In this thesis, remarkable acceleration effects of Lewis acids, such as a $Sc(OTf)_3$ (OTf = $CF_3SO_3^-$), perchloric acid ($HClO_4$) and triflic acid (HOTf), on the reactivity of a nonheme iron(IV)-oxo complex, $[(N4Py)Fe^{IV}(O)]^{2+}$ toward various organic substrates such as thioanisole derivatives and toluene derivatives have been systematically investigated in relation with the MCET and PCET reactions of $[(N4Py)Fe^{IV}(O)]^{2+}$.

Chapter 1 describes the switch of a reaction mechanism from direct oxygen atom transfer to MCET by the addition of a metal ion (Sc^{3+} ion) to the reaction system of sulfoxidation of thioanisole derivatives by a $[(N4Py)Fe^{IV}(O)]^{2+}$. In Chapter 2, the mechanism of oxidative dimerization and *N*-demethylation of *N,N*-dimethylaniline, which was enhanced in the presence of Sc^{3+} ions, has been clarified. Chapter 3 describes a PCET pathway for sulfoxidation of thioanisole derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$. In Chapter 4, remarkable acceleration effects of $HClO_4$ on the reactivity of $[(N4Py)Fe^{IV}(O)]^{2+}$ in the C–H bond cleavage of toluene derivatives are shown to result from PCET from toluene derivatives to protonated $Fe^{IV}(O)$ species with no deuterium kinetic isotope effect. The reactivity of $[(N4Py)Fe^{IV}(O)]^{2+}$ in the oxidation of toluene and thioanisole derivatives in the presence of HOTf and $Sc(OTf)_3$ has been well analyzed as unified PCET and MCET driving force dependence of the rate constants of PCET and MCET pathways in light of the Marcus theory of electron transfer (Chapter 5). Such a unified PCET driving force dependence of the rate constant is also applied for oxidation of styrene derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$ (Chapter 6).

The unified view of enhancement of oxidative C–H bond cleavage of toluene derivatives, sulfoxidation of thioanisole derivatives and epoxidation of styrene derivatives by a nonheme iron(IV)-oxo complex via PCET and MCET demonstrated in this study provides generalized understanding of a variety of PCET and MCET pathways for oxidation of substrates by metal-oxygen species.

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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

In this thesis, remarkable acceleration effects of Lewis acids, such as a $Sc(OTf)_3$ (OTf = $CF_3SO_3^-$), perchloric acid ($HClO_4$) and triflic acid (HOTf), on the reactivity of a nonheme iron(IV)-oxo complex, $[(N4Py)Fe^{IV}(O)]^{2+}$ (N4Py: *N,N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methyl amine), toward various organic substrates such as thioanisole derivatives and toluene derivatives have been systematically investigated in relation with the metal-coupled electron-transfer (MCET) and proton-coupled electron transfer (PCET) reactions of $[(N4Py)Fe^{IV}(O)]^{2+}$.

Chapter 1 describes the switch of a reaction mechanism from direct oxygen atom transfer to MCET by the addition of a metal ion (Sc^{3+} ion) to the reaction system of sulfoxidation of thioanisole derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$. In Chapter 2, the mechanism of oxidative dimerization and *N*-demethylation of *N,N*-dimethylaniline, which was enhanced in the presence of Sc^{3+} ions, has been clarified. Chapter 3 describes a PCET pathway for sulfoxidation of thioanisole derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$. In Chapter 4, remarkable acceleration effects of $HClO_4$ on the reactivity of $[(N4Py)Fe^{IV}(O)]^{2+}$ in the C–H bond cleavage of toluene derivatives are shown to result from PCET from toluene derivatives to protonated $Fe^{IV}(O)$ species with no deuterium kinetic isotope effect. The reactivity of $[(N4Py)Fe^{IV}(O)]^{2+}$ in the oxidation of toluene and thioanisole derivatives in the presence of HOTf and $Sc(OTf)_3$ has been well analyzed as unified PCET and MCET driving force dependence of the rate constants of PCET and MCET pathways in light of the Marcus theory of electron transfer (Chapter 5). Such a unified PCET driving force dependence of the rate constant is also applied for epoxidation of styrene derivatives by $[(N4Py)Fe^{IV}(O)]^{2+}$ (Chapter 6).

The unified view of enhancement of oxidative C–H bond cleavage of toluene derivatives, sulfoxidation of thioanisole derivatives and epoxidation of styrene derivatives by a nonheme iron(IV)-oxo complex via PCET and MCET demonstrated in this study provides generalized understanding of a variety of PCET and MCET pathways for oxidation of substrates by metal-oxygen species.