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Catalytic substrate oxidation by transition-metal NHC complexes in water
(水中における遷移金属 NHC 錯体による触媒的基質酸化反応)

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論 文 の 要 旨

The main focus of this doctor thesis is put on formation and characterization of metal-oxyl species, which should have metal-oxygen single bond and are electronically equivalent to the corresponding high-valent metal-oxo species and has never been well investigated yet, and also the reactivity in catalytic oxidation of organic substrates in water. This doctor thesis consists of five chapters as mentioned below.

In chapter 1, general introduction for this research is provided; in particular, the author describes examples of substrate oxidation reactions performed by high-valent metal-oxo species in metalloenzymes and their synthetic model complexes. The author also mentions the theoretical studies on metal-oxyl species, and methodologies of their formation. “Oxo wall” in the periodic table, which is proposed to separate elements forming multiple bonds with oxo ligands or not, is also mentioned from the aspect of formation of metal-oxyl species with elements on the left side of the “oxo wall”. The author also refers the properties of *N*-heterocyclic carbene (NHC) as candidates for a strong σ -donating ligand and reactivity of transition-metal complexes having NHC ligands.

In chapter 2, the author has described the characteristics of two novel ruthenium(II) complexes, having a pincer-type tridentate NHC ligand in a meridional coordination mode. The author also mentions spectroscopic analysis on their $1e^-$ -oxidized species, and performed theoretical studies on their structural optimization, spin-density analysis, and calculations of oscillator strengths. As results, the author has clarified stronger σ -donating ability of the NHC ligand to stabilize the Ru(III) state, compared to the corresponding pyridine ligand or π -conjugated NHC analogs.

In chapter 3, the author describes the catalytic oxidation of organic substrates in water, catalyzed by a novel ruthenium(II)-aqua complex having a tridentate NHC ligand in the facial coordination and

(NH₄)₂[Ce^{IV}(NO₃)₆] under strongly acidic conditions in water at 277 K. In the catalytic substrate oxidation, the reactive species is revealed to be not a normal Ru(IV)-oxo complex, but an unprecedented Ru(III)-oxyl species on the basis of spectroscopic analyses, including resonance Raman spectroscopy, X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and DFT calculations. Furthermore, the author has demonstrated strong radical character of the Ru(III)-oxyl species based on kinetic analysis of catalytic oxidation of benzaldehyde derivatives in water.

In chapter 4, the author describes oxidative cracking of benzene derivatives in acidic water catalyzed by the Ru(III)-oxyl species, referred in chapter 3, to afford formic acid as a hydrogen reservoir at ambient temperature. The author also verifies usability and significance of the benzene cracking by demonstrating conversion of formic acid to dihydrogen with a Rh(III) catalyst reported in literature in the same reaction mixture with simple pH adjustment. In addition, the author has proposed a plausible reaction mechanism for the oxidative benzene cracking, involving electrophilic addition of the Ru(III)-oxyl complex to an aromatic ring on the basis of the kinetic analysis, electronic substituent effects, and product analysis.

In chapter 5, the author describes catalytic oxidative cracking of halogenated benzene derivatives, which the Ru(II)/Ce(IV) system employed in chapter 4 does not show efficient performance, in water with Oxone[®] as an inexpensive sacrificial oxidant and a Pd(II)-NHC catalyst. The author also has proposed a plausible reaction mechanism for oxidative cracking of halogenated benzene derivatives by the Pd catalyst based on the kinetic analysis, substituent effects, and characterization of reactive intermediates obtained from the reaction of the Pd(II) complex with Oxone[®].

Through the researches described in this thesis, the author successfully constructed a unique and useful catalytic system for substrate oxidation. Moreover, the author has provided a break-through in metal-oxo chemistry using strongly σ -donating NHC ligands, as represented by a rule-breaking Ru^{III}-oxyl complex, which shows unique catalytic oxidations in water in sharp contrast to those performed by conventional Ru^{IV}=O complexes. In addition, using the metal-oxyl complexes as reactive intermediates, this work also has provided an efficient methodology for conversion of benzene derivatives as harmful and robust pollutants to useful materials such as formic acid as a hydrogen reservoir. Therefore, the Ru^{III}-O• complex, described in this thesis, should be recognized as important species in oxidation chemistry from the viewpoints of worldwide efforts to solve energy and environmental problems. This research will pave a reliable way to the establishment of a sustainable society and improvement of our lives through the selective and oxidative conversion of persistent pollutants in environments into useful energy sources under mild conditions.

審 査 の 要 旨

[批評]

The contents of the doctor thesis are excellent and the parts of the thesis have been already published in high-impact academic journals including *Angew. Chem. Int. Ed.* and *ACS Catalysis*. In this thesis, the author has described preparation, characterization, and reactivity of novel metal-oxyl complexes formed in water. As presented in chapter 3, the author succeeded in the formation and characterization of an unprecedented Ru(III)-oxyl complex, which is electronically equivalent to the corresponding Ru(IV)-oxo complex bearing strong radical character. The author has clarified the oxidation state of the Ru center using XANES analysis and the single bond character of the Ru-O bond using resonance Raman spectroscopy. DFT

calculations also support the electronic structure of the Ru(III)-oxyl species. The reactivity of the Ru(III)-oxyl species has been demonstrated using benzaldehyde derivatives in acidic water; the rates of oxidation reactions are analyzed in the light of the Hammett equation to visualize an almost no substituent effects on the reactions. This result clearly supports strong radical character of the species. The finding of the Ru(III)-oxyl complex, without doubt, has provided a break-through in the metal-oxo chemistry.

In chapter 4, the author has described very unique oxidative cracking of aromatic rings to afford formic acid, from which H₂ gas can be obtained using a known Rh(III) catalyst with simple pH adjustment. This reaction is of great significance in terms of the fact that harmful pollutants dispersing in water can be detoxified and converted to an energy source. In this reaction, the author has clarified the electrophilic character of the Ru(III)-oxyl complex in the light of substituent effects of benzene derivatives. Another feature of this reaction is that benzene derivatives having aliphatic substituents can be oxidized to afford carboxylic acids with the substituents; this is due to the strong electrophilic character of the species. The author also gained mechanistic insights into the oxidative benzene cracking to demonstrate that muconic acid can be formed as an intermediate, which is proposed to generate via electrophilic addition of the Ru(III)-oxyl complex to the benzene ring to form a benzene oxide-oxepin mixture.

In chapter 5, the author describes oxidative perhalogenated benzene derivatives, which cannot be efficiently degraded by the Ru(III)-oxyl complex, with use of a novel Pd(II) complex with a NHC-containing tridentate ligand and a cheaper oxidant of Oxone[®] in water. The catalytic system has been demonstrated to oxidatively crack halogenated benzene derivatives, especially chlorinated benzenes. Scrutiny has been also given to observe reactive intermediates in the reaction using spectroscopic and ESI-TOF-MS measurements. Although the responsible species has yet to be identified, the author has detected a relatively stable intermediate, a Pd(II)-OOS(O)OH complex, which is proposed to react further with the oxidant to afford a oxidatively responsible species. The findings described in this chapter are also very important from a viewpoint of development of a strategy to establish clean water environments.

All reviewers of this thesis have recognized the quality and excellence of the achievements described in this thesis.

In summary, in the light of the quality and significance of the contents, this doctor thesis provided by the author should be acceptable.

[最終試験結果]

The final examination committee conducted the fi defense seminar on February 13, 2019. The applicant provided an overview of dissertation, addressed questions and comments raised during Q&A session. All of the committee members reached a final decision that the applicant has passed the final examination.

[結論]

Based on the results of the above-mentioned dissertation defense and final examination, the final

examination committee approved that the applicant is qualified to be awarded Doctor of Philosophy in Science.