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Catalytic Oxidation of Water and Organic Substrates by Iron, Nickel, Manganese and Ruthenium Complexes
鐵、鎳、錳以及釕化合物用於水和有機物的氧化

Submitted to
Department of Biology and Chemistry
生物與化學系
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
哲學博士學位

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September, 2012
二零一二年九月

Abstract

The thesis is made of four parts. The first part describes chemical and visible light-driven water oxidation using simple iron salts as precatalysts. The second part discloses chemical-driven water oxidation using simple nickel salts as precatalysts. The third part is about the oxygenation of organic substrates driven by visible-light using a manganese nitrido complex as catalyst. The fourth part concerns the activation of ruthenium-oxo complexes by Lewis acids towards alkane oxidation.

In part one, simple iron salts are used as precatalysts for water oxidation. Both chemical and visible light-driven water oxidation are highly efficient in borate buffer at pH 7.5 – 8.5. For chemical water oxidation using $Ru(bpy)_3(ClO_4)_3$ as oxidant, turnover number of up to 394 was obtained. Under visible light irradiation in the presence of $Ru(bpy)_3Cl_2$ as photosensitizer and $Na_2S_2O_8$ as sacrificial oxidant, oxygen evolved at turnover number up to 1115. Fe_2O_3 nanoparticles are found to be formed during water oxidation, which are the actual catalyst.

In part two, simple nickel salts are used as precatalysts for water oxidation. Using $Ru(bpy)_3(ClO_4)_3$ as oxidant, oxygen evolution catalysed by nickel processed smoothly in borate buffer at pH 7.5 – 8.5 with a maximum turnover number of 170.

Large particles (0.3 mm to 2 mm) were observed during chemical-driven water oxidation through dynamic light scattering (DLS) measurement.

In part three, the manganese(V) nitrido complex, $(PPh_4)_2[Mn(N)(CN)_4]$ is found to be an efficient catalyst for the visible-light driven oxygenation of organic substrates in water using $[Ru^{II}(bpy)_3]^{2+}$ as a photosensitizer and $[Co^{III}(NH_3)_5Cl]^{2+}$ as the sacrificial oxidant. Alkenes are oxidized to epoxides and alcohols are oxidized to carbonyl compounds with turnover numbers high up to 117 and 137, respectively. ^{18}O-isotopic labeling study for epoxidation of styrene confirmed that the oxygen atoms incorporated into styrene came from water.

In part four, the high-valent ruthenium-oxo complexes, $[Ru^{VII}O_4]^-$ and $[Ru^{VI}O_2Cl_3]^-$ were activated by Lewis acids, such as $FeCl_3$, BF_3, or $Sc(OTf)_3$, to oxidize alkanes to the corresponding alcohols and ketones. Oxidation occurs rapidly under argon atmosphere, and excellent yields up to 46% were achieved in the oxidation of cyclohexane to cyclohexanone with $[Ru^{VI}O_2Cl_3]^-/BF_3$ in acetonitrile at 296 K. The accelerating effect of BF_3 on the oxidation of methane by $[Ru^{VII}O_4]^-$ and $[Ru^{VI}O_2Cl_3]^-$ have also been studied computationally by the Density Functional Theory (DFT) method. A significant decrease in the reaction barrier resulting from BF_3 coordination to ruthenium-oxo complexes was observed.

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List of abbreviations

WOC = water oxidation catalyst

PS II = Photosystem II

TON = turnover numbers

TOF = turnover frequency

py = pyridine

Cp* = 1,2,3,4,5-pentamethylcyclopentadiene

^{t}*Bu* = tertiary butyl

TBHP = tert-butyl hydroperoxide

bpy = 2,2’-bipyridine

qpy = 2,2’:6’,2”:6”,2”’-quaterpyridine

NMO = *N*-methylmorpholine-*N*-oxide

AcOOH = acetic peroxide

AcOH = acetic acid

TBP = tributyl phosphate

c-CyO = cyclohexanone

c-CyOH = cyclohexanol

c-CyCl = cyclohexyl chloride