Water Oxidation Catalyzed by Dimeric Ru Complexes

Department of Life and Coordination-Complex Molecular Science
Division of Functional Coordination Chemistry

|	
TANAKA, Koji	Professor (–March, 2012)*
OHTSU, Hideki	Assistant Professor*
KOBAYASHI, Katsuaki	IMS Research Assistant Professor*
PADHI, Sumanta Kumar	Post-Doctoral Fellow
NAKANE, Daisuke	Post-Doctoral Fellow
YAMAGUCHI, Yumiko	Secretary
NOGAWA, Kyoko	Secretary

Artificial photosynthesis aimed at carbon dioxide reduction and water splitting has become a top research theme. Two-electron transfer from or to substrates through redox reactions is requisite for stable molecular transformation. Intermolecular electron transfer, however, always generates free radical species, which often causes undesired side reactions. Success of artificial photosynthesis, therefore, depends on the designing of reaction systems that can provide or take out multi-electrons to or from reaction centers.

Irradiation of $[Ru(bpy)_2(pbn)]^{2+}$ (pbn = 2-(2-pyridyl)-benzo[b]-1,5-naphthyridine) with visible light causes proton coupled one-electron reduction, and the subsequent disproportionation affords an NADH model complex, $[Ru(bpy)_2(pbnH_2)]^{2+}$ (pbnH$_2$ = 5,10-dihydro-2-(2-pyridyl)benzo[b]-1,5-naphthyridine) (Scheme 1). Smooth conversion from NAD analog to NADH one under visible light irradiation would lead to a new methodology for utilization of water as the hydrogen source in molecular transformation.
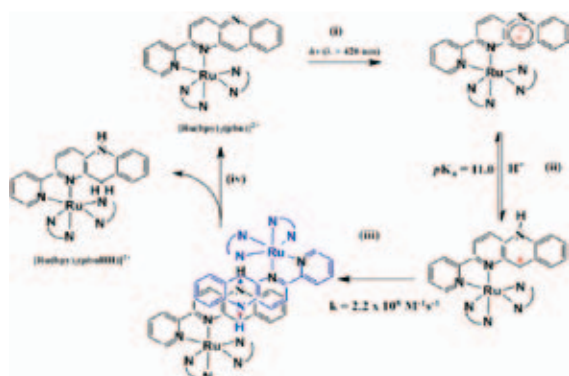
Scheme 1. Photochemical two-electron reduction of $[Ru(bpy)_2(pbn)]^{2+}$.

Three Ru-dioxolene complexes, $[Ru^{II}(Q)(trpy)(OH_2)]^{2+}$, $[Ru^{II}(Q)(trpy)(OH)]^+$, and $[Ru^{II}(Sq)(trpy)(O^{-\bullet})]^0$ (Q = 3,5-dibutylquinone; Sq = 3,5-dibutylsemiquinone) exist as equilibrium mixtures in water with the pK_a values of 5.5 and 10.5, respectively. A novel oxyl radical complex, $[Ru^{II}(Sq)(trpy)$
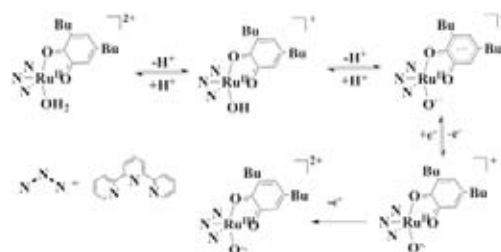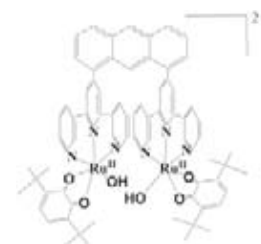

Scheme 2. Two-electron oxidant generation taking advantage of acid-base equilibrium of Ru-aqua(dioxolene) complex.

$(O^{-\bullet})]^0$, undergoes reversible one electron oxidation around 0 V (*vs.* Ag/AgCl), and the subsequent further one electron oxidation creates the unique $Ru^{III}–O^{-\bullet}$ framework in the product (Scheme 2). The oxyl radical and Ru(III) center involved in the product work as simultaneous hydrogen atom and one electron acceptors in two-electron oxidation of alcohols.

## 1. Direct Evidence for O–O Bond Formation in the Four Electron Water Oxidation

The difficulty of water decomposition results from four-electron oxiation of water rather than that of two-electron reduction. Among various water oxidation catalysts reported so far, much attention has been paid to a dinuclear Ru complex, $[Ru_2(OH)_2(Bu_2q)_2(btpyan)]^{2+}$ (Bu$_2$q = 3,6-di-*tert*-butylquinone, btpyan = 1,8-bis(terpyridyl)-anthracene), known as Tanaka Catalyst because of its high activity toward four-electron oxidation of water. However, any direct evidences for O–O bond formation prior to O$_2$ evolution have not been obtained so far. Four redox centers ($2 \times Ru^{II/III}$ and $2 \times [Q]/[Sq]$) of $[Ru_2(OH)_2$

$(Bu_2q)_2(btpyan)]^{2+}$ is attributable to the high catalytic capacity. So, we tried to detect the O–O bond formation process by decreasing the number of redox centers of an Ru dinuclear complex. Two-electron oxidation of $[Ru^{II}_2(Cl)_2(bpy)_2$ $(btpyan)]^{4+}$ at +1.0 V in a range of pH 2.0 to 3.0 forms $[Ru^{IV}_2(=O)_2(bpy)_2(btpyan)]^{4+}$. The controlled potential electrolysis of $[Ru^{II}_2(\mu\text{-}Cl)(bpy)_2(btpyan)]^{3+}$ at +1.60 V in water at pH 2.6 (H_3PO_4/NaH_2PO_4 buffer) catalytically evolved dioxygen. Addition of a CH_3CN (100 µl) solution of $[Ru^{II}_2(\mu\text{-}Cl)(bpy)_2$ $(btpyan)]^{3+}$ (1.0 µmol) into an aqueous solution (10 ml) of $Ce(NH_4)_2(NO_3)_6$ (2.5 mmol) at pH 1.0 (adjusted with HNO_3) also caused O_2 evolution (414 µmol).

The electronic absorption spectra of the reaction mixture showed a transient band at 688 nm that emerged only in O_2 evolution. The transient complex prepared by the electrolysis of $[Ru^{II}_2(\mu\text{-}Cl)(bpy)_2(btpyan)]^{3+}$ in $H_2{}^{16}O$ and $H_2{}^{18}O$ at +1.40 V displayed two absorption bands at 442 and 824 cm^{-1}, and 426 and 780 cm^{-1}, respectively, in the resonance raman spectra with irradiation at 633 nm. The isotope shifts (Δ 16 and 44 cm^{-1}) between $H_2{}^{16}O$ and $H_2{}^{18}O$ are quite consistent with the calculated values of the ν(Ru–O) and ν(O–O) bands of $[Ru_2$ $(\mu\text{-}O_2)(bpy)_2(btpyan)]^{3+}$. If the $Ru^{IV}=O$ bond of $[Ru^{IV}_2(=O)_2$ $(bpy)_2(btpyan)]^{4+}$ generated by the oxidation of $[Ru^{III}_2(OH)$ $(bpy)_2(btpyan)]^{4+}$ has more or less Ru^{III}–O. oxyl radical character, $[Ru^{III}_2(\mu\text{-}O_2)(bpy)_2(btpyan)]^{4+}$ would be produced by the radical coupling of the two oxo groups of $[Ru^{IV}_2(=O)_2$ $(bpy)_2(btpyan)]^{4+}$. The rate of O_2 evolution by chemical oxidation using Ce(IV) is much faster than that of electrochemical reaction at +1.60 V. Nuclear attack of two water to Ru^{III} of $[Ru^{III}_2(\mu\text{-}O_2)(bpy)_2(btpyan)]^{4+}$ will slowly releases O_2 (Scheme 3). On the other hand, Ce(IV) causes further oxidation of $[Ru^{III}_2(\mu\text{-}O_2)(bpy)_2(btpyan)]^{4+}$ to produce $[Ru^{IV}_2(\mu\text{-}O_2)$ $(bpy)_2(btpyan)]^{6+}$, which smoothly evolves O_2 with regeneration of $[Ru^{III}_2(OH)(bpy)_2(btpyan)]^{4+}$ (Scheme 3). In accordance with this, $[Ru^{III}_2(\mu\text{-}O_2)(bpy)_2(btpyan)]^{4+}$ was detected only after Ce(IV) was consumed in O_2 evolution.
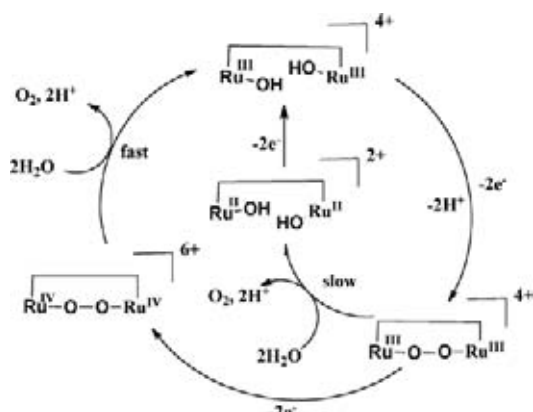
2. Insight for Activity of Tanaka Catalyst toward Water Oxidation

High catalytic ability of $[Ru_2(btpyan)(3,6\text{-}di\text{-}Bu_2Q)_2$ $(OH_2)]^{2+}$ (Tanaka catalyst) toward water oxidation produces disputes about the electronic structures in the catalytic cycle. DFT computational works reported so far are not consistent with each other in the viewpoints of the relative stability between the closed-shell (Ru^{II}-Q) and open-shell (Ru^{III}-SQ) electronic structures, and the pathway to the O–O bond formation. On the other hand, broken-symmetry hybrid density functional computations have provided a rational reaction mechanism for water oxidation (Scheme 4). Deprotonation of waters in ^{1}**1** affords the key tetraradical intermediate ^{1}**3** via one-electron transfer (OET) in ^{1}**2**. The oxygen-radical pair in ^{1}**3** is local triplet diradical (LTD), suppressing facile O–O bond formation by the radical coupling (RC) mechanism. The two-electron removal from ^{1}**3** provides the hexaradical species ^{3}**4**. The oxygen radical pair (^{3}A) is still LTD-type, indicating the necessity of spin inversion (SI) for generation of local singlet diradical (LSD) pair in ^{1}**5**. The RC mechanism in ^{1}**5** is facile, giving the peroxide species ^{1}**6**. The next step for generation of oxygen dianion may become the rate-determining step as shown in ^{1}**7**. The β-spin at the terminal oxygen anion in ^{1}**7** is moved to the Ru_2(III) site with the α-spin to form the singlet pair as shown in ^{1}**8**. The spin exchange (SE) between ↓•Ru_1(III) and SQ_1•↑ to generate ↑•Ru_1(III) and SQ_1•↓ is necessary for one more OET from superoxide anion to ↑•Ru_1(III) to afford triplet molecular oxygen in ^{1}**9**. The SE process is easy because the exchange coupling for the •O–O–Ru(III)• is weak. Thus the SQ_1• radical plays an important role for spin catalysis. The two-electron removal from ^{1}**9** is necessary for reproduction of ^{1}**1**. Thus the BS computational results provide the orbital and spin correlation diagram for water splitting reaction.

Scheme 3. Four-electron oxidation of water catalyzed by $[Ru^{III}_2(OH)_2(bpy)_2(btpyan)]^{4+}$.
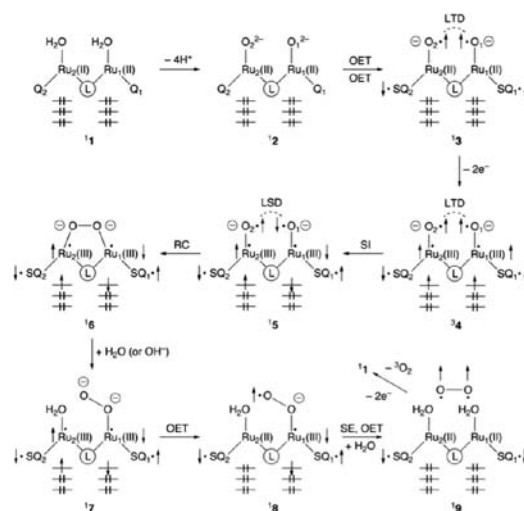
Scheme 4. Proposed mechanism for water oxidation catalyzed by Tanaka catalyst.