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Review

O–O bond formation mechanisms during the oxygen evolution reaction over synthetic molecular catalysts

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ARTICLE INFO

Article history:

Received 11 August 2020

Accepted 22 September 2020

Available online 5 April 2021

Keywords:

Oxygen evolution reaction

Water oxidation

O–O bond formation

Transition metal complex

Molecular electrocatalysis

Reaction mechanism

ABSTRACT

Water oxidation is one of the most important reactions in natural and artificial energy conversion schemes. In nature, solar energy is converted to chemical energy via water oxidation at the oxygen-evolving center of photosystem II to generate dioxygen, protons, and electrons. In artificial energy schemes, water oxidation is one of the half reactions of water splitting, which is an appealing strategy for energy conversion via photocatalytic, electrocatalytic, or photoelectrocatalytic processes. Because it is thermodynamically unfavorable and kinetically slow, water oxidation is the bottleneck for achieving large-scale water splitting. Thus, developing highly efficient water oxidation catalysts has attracted the interests of researchers in the past decades. The formation of O–O bonds is typically the rate-determining step of the water oxidation catalytic cycle. Therefore, better understanding this key step is critical for the rational design of more efficient catalysts. This review focuses on elucidating the evolution of metal-oxygen species during transition metal-catalyzed water oxidation, and more importantly, on discussing the feasible O–O bond formation mechanisms during the oxygen evolution reaction over synthetic molecular catalysts.

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1. Introduction

The rapidly increasing energy demands and environmental issues caused by the use of fossil fuels have been compelling scholars to find and use new, renewable, clean, and environmentally benign energy resources. In nature, solar energy is converted to chemical energy via photosynthesis, a reaction that occurs in green plants and other organisms [1]. During photosynthesis, H₂O is first oxidized at the oxygen-evolving center of photosystem II (PSII) to release O₂, which is essential for aerobic life. Moreover, the protons and electrons generated during the process are subsequently used to convert CO₂ to

carbohydrates, which sustain the life circle on Earth. Therefore, the oxygen evolution reaction (OER) is one of the most important reactions of the natural energy conversion cycle. The OER is initiated by the light-induced oxidation of chlorophyll P680, which presents magnesium porphyrin core structure, to form the porphyrin cation radical species P680^{•+}. P680^{•+} is the most oxidizing redox cofactor (redox potential >1.0 V) known in biology and provides the initial oxidizing power for the water oxidation reaction. The subsequent electron transfer from a Mn₄CaO_x cluster of the oxygen-evolving center to P680^{•+} recovers P680 and stores an oxidizing equivalent at the Mn₄CaO_x cluster. After three successive turnovers, four oxidizing equiv-

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This work was supported by the National Natural Science Foundation of China (21101170, 21573139, 21773146), Fok Ying-Tong Education Foundation for Outstanding Young Teachers in University (by the Ministry of Education of China), Fundamental Research Funds for the Central Universities, and the Research Funds of Shaanxi Normal University.

DOI: 10.1016/S1872-2067(20)63681-6 | http://www.sciencedirect.com/journal/chinese-journal-of-catalysis | Chin. J. Catal., Vol. 42, No. 8, August 2021

alents are stored at the Mn_4CaO_x cluster, which triggers the formation of O–O bonds via the coupling of a Mn(IV)-oxyl radical and a di-Mn bridging oxo group [2–7]. Lastly, two H_2O molecules are oxidized to release an O_2 molecule.

As inspired by nature, water splitting is promoted in artificial energy conversion schemes. Owing to its ability to generate O_2 and H_2 via photocatalytic, electrocatalytic, or photoelectrocatalytic processes, water splitting could convert both light and electrical energy to chemical energy. Considering that electrical energy can be generated from renewable but intermittent energy sources, such as solar, wind, and hydropower, the H_2 generated using these processes is, therefore, considered a renewable and clean energy resource. As one of the half reactions of water splitting, water oxidation is a thermodynamically uphill reaction and kinetically sluggish reaction because it requires the combination of the transfer of four electrons, breaking four O–H bonds, and formation of O–O bonds in a concerted manner [8–11]. Therefore, water oxidation is the bottleneck for performing large-scale water splitting. Extensive efforts have been made in the past decades to develop highly efficient water oxidation catalysts (WOCs), and a variety of molecular transition metal complexes have been identified as active WOCs [8,12–20]. However, the water oxidation reaction mechanism, particularly the key O–O bond formation step, has not been fully elucidated. Therefore, it is essential to elucidate the reaction mechanisms and fundamental steps, particularly the O–O bond formation process of the water oxidation reaction, for the rational design of efficient catalysts.

Five main types of O–O bond formation mechanisms have been proposed in the literature (Scheme 1), viz. (1) the water nucleophilic attack (WNA) to a terminal metal oxo/oxyl unit (also known as the acid-base mechanism), (2) coupling between two metal oxo/oxyl units, typically known as the I2M pathway, (3) coupling between two hydroxyl units either on different metal ions (bimolecular hydroxyl coupling; BHC) or the same metal ion (intramolecular hydroxyl coupling IHC), (4)

Scheme 1. Schematic diagrams of proposed O–O bond formation mechanisms: (a) water nucleophilic attack (WNA), (b) coupling between two metal oxo/oxyl units (I2M), (c) bimolecular hydroxyl coupling (BHC), (d) intramolecular hydroxyl coupling (IHC), (e) intramolecular coupling between hydroxyl and bridging oxo (intermolecular oxo/oxyl coupling; IOC), and (f) coupling between two bridging oxo units (redox isomerization; RI).

intramolecular oxo/oxyl coupling (IOC), and (5) redox isomerization (RI). In the following sections, we will discuss the aforementioned mechanisms and summarize the recent experimental and theoretical results that support these mechanisms. This review provides a mechanistic understanding of various metal centers and ligand structures, and sheds light on the rational design of more efficient WOCs.

2. WNA mechanism

When O–O bonds form via the WNA mechanism, a nucleophilic dissociative H_2O molecule attacks a metal-bound electrophilic oxo group; that leads to the formation of an O–O σ bond, breaking of one of the M–O π bonds, and typical $2e^-$ reduction of the metal center. The metal center should be electrophilic to accept the p electrons from the oxo ligand during the WNA-type O–O bond formation reaction, which indicates that the WNA mechanism would be unfavorable when mediated by later transition metals with numerous d-orbital electrons. The WNA O–O bond formation generates metal-hydroperoxide ($\text{M}-\text{OOH}$) species, which undergo further oxidation to release O_2 . Anions in alkaline solutions, such as the hydroxide, acetate, and nitrate anions, could be potential nucleophiles in this process.

2.1. Traditional WNA mechanism

The WNA mechanism has been extensively studied using Ru-based WOCs. Ru centers are redox-active and the presence of two Ru centers in close proximity was determined to be essential for active WOCs. In their pioneering study, Meyer *et al.* [21] demonstrated the possibility of the multielectron oxidation of H_2O to O_2 , and reported that an oxo-bridged binuclear Ru complex, viz. *cis,cis*- $[(\text{bpy})_2(\text{H}_2\text{O})\text{Ru}(\mu\text{-O})\text{Ru}(\text{H}_2\text{O})(\text{bpy})_2]^{4+}$ (1), where bpy denotes bipyridine, known as the “blue dimer” owing to its characteristic blue color, which contained bipyridyl ligands, could mediate the $4e^-4\text{H}^+$ oxidation of H_2O molecules. It was hypothesized that the $\text{Ru}_2^{\text{III,III}}$ complex was first oxidized to a high-valent $\text{Ru}_2^{\text{V,V}}$ intermediate (two $\text{Ru}^{\text{V}}=\text{O}$ entities) by the added Ce^{IV} oxidants; subsequently, the electron-deficient $\text{Ru}^{\text{V}}=\text{O}$ moiety was nucleophilically attacked by an external H_2O molecule, which resulted in the formation of hydroperoxido species (Scheme 2). The hydroperoxido species would undergo further oxidation to release O_2 . The oxo-bridge was estimated to play a crucial role in electronic delocalization, which would allow a fleet valence equilibrium between the bimetallic centers. This mechanistic scenario was confirmed using isotope-labelling experiments, and ab initio calculations, as reported by Meyer *et al.* [21] and Baik *et al.* [22], respectively. The ab initio calculations revealed that a typical intramolecular ligand-to-metal charge transfer process occurred in the high-valent $\text{Ru}_2^{\text{V,V}}$ intermediate when it reacted with H_2O to generate the $\text{Ru}^{\text{IV}}\text{-O}^\bullet$ radicaloid. The $\text{Ru}^{\text{IV}}\text{-O}^\bullet$ species acted as strong oxidants that attacked H_2O molecules and homolitically cleaved the O–H bonds. However, the calculations performed by Baik *et al.* could not explain the generation of the experimentally observed solvent-derived dioxygen species. Conversely, Hurst *et al.* [23]

Scheme 2. Molecular structure of **1** blue dimer, where bpy denotes bipyridine, and proposed oxo-bridged binuclear Ru complex-mediated water nucleophilic attack O–O bond formation mechanism.

proposed that a H₂O molecule would nucleophilically attack the pyridine ring instead of the Ru^V=O moiety (Scheme 2). Subsequently, the generated Ru₂^{V,IV}-pyridine-OH[•] radicals would be quenched by the attack of a second H₂O molecule, and would further couple to release O₂. The Ru^V=O/Ru^{IV}=OH moieties in the proposed mechanism acted as Lewis bases to facilitate the O–H bonding of the solvent H₂O molecules. Moreover, Mayer *et al.* [24] reported a tripyridyl-containing oxo-bridged binuclear Ru complex, which presented a stable Ru₂^{V,V} intermediate and excellent water oxidation capability.

A variety of mononuclear complexes were reported to mediate the 4e[−] oxidation of H₂O. Thummel *et al.* [25–27] reported a series of mononuclear Ru complexes, which were demonstrated to promote water oxidation. The WNA pathway was proposed as the O–O bond formation mechanisms of the reported mononuclear Ru complexes. Meyer *et al.* [28] performed a detailed mechanistic investigation of the water oxidation promotion using a typical mononuclear Ru aqua complex, viz. [Ru(tpy)(bpm)(OH₂)]²⁺ (**2**), where tpy and bpm denote tripyridine and 2,2′-bipyrimidine, respectively. Two sequential proton-coupled electron transfer (PCET) processes were estimated to occur during the oxidation of Ru^{II}-H₂O to Ru^{IV}=O species. Furthermore, the 1e[−] oxidation of Ru^{IV}=O to Ru^V=O triggered the water oxidation reaction via the WNA mechanism. The formed peroxidic Ru^{III}-OOH complex further underwent 1e[−] oxidation to generate the key intermediate Ru^{IV}-OO. The Ru^{IV}-OO intermediate consisted of a seven-coordinated Ru(IV) center and side-on bidentate peroxide (η²). Calculations indicated that the six-coordinated isomer with a terminal peroxide ligand was less stable. The proposed water oxidation cycle is presented in Scheme 3. The facile coordination of the H₂O molecules at the metal center to a vacant site was important for generating the active catalyst forms of the aqua species. Sakai *et al.* confirmed that the aqua species were the active intermediates and the chloride effect, which facilitated the access to

Scheme 3. Molecular structure of **2** and proposed water oxidation catalytic cycle

vacant coordination sites for H₂O molecules at the metal center, was important [29]. Furthermore, it was demonstrated that the electron-withdrawing groups slowed down the chloride-aqua ligand exchange reaction [29,30]. Berlinguette *et al.* conducted detailed mechanistic studies on [Ru(tpy)(bpy)(OH₂)]²⁺-type complexes and the bpy ligand located *trans* to the Ru-aqua moiety, which affected the catalytic behavior and reaction pathways of mononuclear Ru complexes [30,31]. Meyer *et al.* [32] reported a variety of mononuclear Ru-aqua analogues and proposed that the O–O bond formation mechanism was WNA.

A *cis* bipyridyl-based mononuclear Ru photosensitizer complex **3** was analyzed by Llobet *et al.* [33] who determined that the typical photosensitizer **3** was capable of water oxidation (Scheme 4). The Ru^{IV}=O intermediate was estimated to be generated after **3** lost 4e[−] and 4H⁺. The calculated free energy barrier of the WNA-type O–O bond formation step was 24.5 kcal/mol, which was 33.0 kcal/mol lower than the energy barrier of the IOC O–O bond formation reaction. Llobet *et al.* [33] revealed that unpaired spin densities were found on both the Ru and O atoms in the complex formed via the removal of 4e[−] and 4H⁺ from **3**, which indicated that the Ru oxidation state was lower than the typical value of VI and the metal-oxo species presented radicaloid nature. Furthermore, the distinctly high energy barrier of the IOC O–O bond formation pathway confirmed the difficulty of the IOC process at the stable six-coordinated metal center.

A WOC with a strong σ-donating but weak π-accepting ligand would decrease the oxidation potential of the water split-

Scheme 4. Molecular structure of **3**, and water nucleophilic attack (WNA) and intramolecular oxo/oxyl coupling (IOC) O–O bond formation pathways.

ting reaction. Sakai *et al.* [34] reported a mononuclear Ru complex with a σ -donating triazamacrocyclic ligand, which presented lower oxidation potentials for the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ and $\text{Ru}^{\text{IV}}/\text{Ru}^{\text{III}}$ couples than the polypyridyl analogues. Zhao *et al.* [35] reported a series of mononuclear Ru complexes containing tris(2-pyridylmethyl)amine-related ligands, which were demonstrated to be able to mediate the water oxidation reaction via the WNA pathway. Moreover, Llobet *et al.* [36] reported the remarkable water oxidation activity of a series of mononuclear Ru complexes comprising pyridine-functionalized abnormal triazolydene carbene ligands, and their catalytic behavior was ascribed to the strong σ -donating properties of the abnormal carbene ligands.

Kärkäs *et al.* [37] reported that two mononuclear Ru complexes containing benzo[d]imidazole ligands and anionic carboxylate terminal groups, viz. $[(\text{Hhpb})\text{Ru}(\text{pic})_3]^+$ (**4**) and $[(\text{Hhpb})\text{Ru}(\text{pic})_3]^+$ (**5**), where H_3hpb , H_3hpb , and pic denote 2-(2-hydroxyphenyl)-1H-benzo[d]imidazole-7-carboxylic acid, 2-(2-hydroxyphenyl)-1H-benzo[d]imidazol-7-ol, and 4-methylpyridine, respectively, facilitated the WNA-type water oxidation reaction. The excellent catalytic performance of **4** and **5** was attributed to the incorporation of the benzo[d]imidazole moiety in their structures, which enabled the facile protonation or deprotonation and subsequent plausible PCET [38]. Charge accumulation and the formation of damaging high-energy intermediates would be avoided during the PCET processes, which were estimated to facilitate the oxidation of H_2O molecules especially under large overpotentials. Åkermark and Liao [37] proposed that the reaction catalyzed by **4** involved the nucleophilic attack of H_2O on a $\text{Ru}^{\text{VI}}=\text{O}$ species to generate a Ru^{IV} -hydroperoxo intermediate. However, typical $\text{Ru}^{\text{VII}}=\text{O}$ species were formed during the WNA-type O–O bond formation reaction over the phenolate-containing **5**, and **5** would be better described as presenting a Ru^{V} center and 2e $^-$ -oxidized ligand and backbone (Scheme 5). The uncommon formation of such high-valent species was ascribed to the redox-active phenolate terminal groups of the ligand. The combination of benzo[d]imidazole and redox-active ligand contained a high-valent Ru-oxo species, which triggered the subsequent WNA-type O–O bond formation. In addition, Åkermark *et al.* reported a single-site Ru complex, $[\text{Ru}(\text{bpb})(\text{pic})_2]^+$, where H_2bpb denotes *N,N'*-(1,2-phenylene)-bis(2-pyridine-carboxamide), which contained a tetra-coordinated *N*-amidato ligand. The addition of CO to this complex would result in the deactivation of the complex of interest. The *N*-amidato ligand featured strong σ -donating ability, and thus, it could better stabilize the high-valent metal-oxo species. Therefore, a high-valent $\text{Ru}^{\text{VI}}=\text{O}$

Scheme 5. Molecular structures of **4** and **5**, and their respective key intermediates that are nucleophilically attacked by solvent H_2O molecules.

intermediate rather than the typical $\text{Ru}^{\text{V}}=\text{O}$ species was formed, which triggered water oxidation. However, the lack of catalytic properties of the CO-containing complexes for the water oxidation reaction has not been properly elucidated yet [39].

Combined experimental and theoretical investigations were conducted by Llobet *et al.* [40], who reported that the mononuclear Ru complex bearing dangling carboxylate $\text{Ru}(\text{tda})(\text{py})_2$ complex (**6**), where H_2tda and py denote [2,2';6',2'']-terpyridine-6,6''-dicarboxylic acid and pyridine, respectively, could significantly boost water oxidation owing to its ability to decrease the energy barrier of the O–O bond formation reaction. Two sequential PCET processes occurred to generate a seven-coordinated $\text{Ru}^{\text{IV}}=\text{O}$ intermediate. The further oxidation of $\text{Ru}^{\text{IV}}=\text{O}$ to high-valent $\text{Ru}^{\text{V}}=\text{O}$ required the potential of 1.32 V. Then, $\text{Ru}^{\text{V}}=\text{O}$ would be nucleophilically attacked by a H_2O molecule with the activation free-energy barrier of 19.5 kcal/mol. The decrease in the energy barrier of the O–O bond formation reaction was ascribed to the significant intramolecular proton transfer to the dangling carboxylate during the formation of O–O bonds. Tessier *et al.* [41] revisited the role of the seven-coordination during Ru-catalyzed water oxidation reaction. A series of Ru complexes that contained penta-dentate ligands and pyridine were prepared and characterized; moreover the interplay between the six- and seven-coordination at different oxidation states and the important role of the terminal dangling carboxylate located in close proximity to the $\text{Ru}^{\text{V}}=\text{O}$ moiety, which acted both as H-bonding site and internal base to accept proton from the nucleophile H_2O molecule (Scheme 6), was highlighted. The combined experimental data and theoretical results indicated that anionic ligands reduced the redox potential of the $\text{Ru}^{\text{V}}=\text{O}/\text{Ru}^{\text{IV}}-\text{OH}$ couple, and seven-coordination was not necessary particularly for the WNA-type O–O bond formation.

Meyer *et al.* [42] investigated the electron transfer mediator effects during the water oxidation reaction using $\text{Ru}(\text{bda})(\text{L})_2$ catalysts, where H_2bda and L denote 2,2'-bipyridine-6,6'-dicarboxylic acid and the ligand, respectively, and redox mediators, and revealed the dependence on the redox potential of the mediator. In addition, the experimental results demonstrated the important role of the atom-proton transfer (APT) process and O-atom transfer to the O atom of a H_2O molecule combined with the proton transfer to the added HPO_4^{2-} buffer base during water oxidation over $[\text{Ru}^{\text{V}}(\text{O})]^+$.

The water oxidation mechanism over mononuclear Ru-based catalysts was further investigated by Meyer [28,43–45], Berlinguette [31], Fujita [46], Voorhis [47], Llobet

Scheme 6. Molecular structure of **6** and water nucleophilic attack of the $\text{Ru}^{\text{V}}=\text{O}$ moiety.

[48], Sun [49–52], Sakai [53], Fukuzumi [54], Buda [55], Yang [56], and Chen [57]. The typical water oxidation catalytic cycle mediated by mononuclear Ru complexes, where the O–O bond formation follows the WNA pathway, is summarized in Scheme 7. Two consecutive PCET processes from the Ru-aqua complex, $\text{Ru}^{\text{II}}\text{-OH}_2$, to high-valent $\text{Ru}^{\text{IV}}\text{=O}$ species are followed by the 1e^- -oxidation of $\text{Ru}^{\text{IV}}\text{=O}$ to $\text{Ru}^{\text{V}}\text{=O}$. The $\text{Ru}^{\text{V}}\text{=O}$ species are the key intermediates that are nucleophilically attacked by solvent H_2O molecules to trigger the formation of O–O bonds. The metal-hydroperoxo intermediate, $\text{Ru}^{\text{III}}\text{-OOH}$, is subsequently formed, and further undergoes PCET to be oxidized to the peroxo complex, $\text{Ru}^{\text{IV}}\text{-OO}$. Lastly, O_2 is liberated via substitution with a H_2O molecule, and the $\text{Ru}^{\text{II}}\text{-aqua}$ complex is regenerated. In addition, the $\text{Ru}^{\text{IV}}\text{=O}$ species are responsible for WNA-type O–O bond formation. Alternatively, the peroxo complex, $\text{Ru}^{\text{IV}}\text{-OO}$, is further oxidized to generate the high-valent $\text{Ru}^{\text{V}}\text{-OO}$ intermediate, and the latter complex undergoes rapid O_2 release and deprotonation of the metal-bound H_2O to generate $\text{Ru}^{\text{III}}\text{-OH}$ species.

Similar to Ru centers, Ir centers are redox active and have been widely used as WOCs. Bernhard *et al.* reported a mononuclear cyclometalated Ir complex $[\text{Ir}(\text{ppy})_2(\text{H}_2\text{O})_2]^+$ (**7**), where ppy is cyclometalated phenylpyridine, which presented water oxidation properties in the presence of a Ce^{IV} sacrificial oxidant. It was demonstrated that the preliminary ligand exchange process on the six-coordinated Ir center was necessary for the WNA-type O–O bond formation [58]. The $\text{Ir}^{\text{V}}\text{=O}$ species was hypothesized to be the active catalytic species as $[\text{Ir}(\text{O})(\text{X})(\text{ppy})_2]$, where X could be OH_2 , OH , or O^{2-} depending on the pH. Lledós *et al.* [59] indicated that the X moiety would act as internal base to promote the WNA-type O–O bond formation (Scheme 8), and reported that the $[\text{Ir}(\text{O})_2(\text{ppy})_2]^-$ species with the most basic internal base presented the lowest energy barrier for O–O bond formation.

Author *et al.* [60] reported a mononuclear Ir complex **8** bearing the cyclopentadiene (Cp^*) ligand, which was introduced to increase the electron density and increase the number

Scheme 7. Proposed catalytic cycle of mononuclear Ru-mediated water oxidation; the O–O bond formation mechanism follows the water nucleophilic attack (WNA) pathway.

Scheme 8. Molecular structure of **7** and schematic of base-assisted solvent H_2O nucleophilic attack of the $\text{Ir}^{\text{V}}\text{=O}$ moiety.

of available coordination sites of the Ir center. The water oxidation capability of the Cp^* -containing mononuclear Ir complex was higher than that of the mononuclear Ru counterpart. Subsequently, Author *et al.* substituted the cyclometalated ligand with bipyridine or its analogue to obtain the piano stool-like mononuclear Ir complex **9** [60]. The $\text{Ir}^{\text{V}}\text{=O}$ species was demonstrated to be the key intermediate to trigger the subsequent WNA-type O–O bond formation. Furthermore, it was reported that the nature of the proton acceptor significantly affected the energy barrier of the key O–O bond formation step, and the participation of an outer-sphere H_2O molecule would substantially decrease the energy barrier (Scheme 9). An Ir hydroperoxide species was generated afterward, and that would further undergo oxidation to release O_2 [61]. In addition, Macchioni *et al.* [62] proposed an alternative reaction pathway for the Ir-catalyzed water oxidation reaction, in which the sacrificial oxidant, cerium ammonium nitrate (CAN), presented an important role during the O–O bond formation step (Scheme 9). A significant WNA-type O–O bond formation transition state was identified, in which the $[\text{Ce}^{\text{IV}}(\text{NO}_3)_3(\text{OH})]$ complex directly interacted with the $\text{Ir}^{\text{IV}}\text{-O}^\bullet$ species and a nucleophile H_2O molecule. The energy barrier of the CAN-driven O–O bond formation reaction was calculated to be significantly lower than those of the I2M and conventional WNA pathways.

Siegbahn *et al.* [63] theoretically analyzed the oxidation states of Ir that led to O–O bond formation during the

Scheme 9. Molecular structures of **8** and **9**. Proposed water nucleophilic attack (WNA) pathway of O–O bond formation, which involved the participation of an outer-sphere H_2O molecule or the $[\text{Ce}^{\text{IV}}(\text{NO}_3)_3(\text{OH})]$ complex.

Cp*Ir(bpy)Cl-catalyzed water oxidation reaction. The $[(bpy)Ir(H_2O)_2(CH_3COO)Cl]^+$ species was considered to be the active catalyst at the higher oxidation state. Furthermore, the authors calculated that the O–O bond formation occurred at the high typical oxidation states of Ir^{VI} and Ir^{VII}, rather than Ir^V. A WNA-type O–O bond formation reaction occurred, and was facilitated by the acetate ligand, which acted as internal base during the nucleophilic attack and abstracted a proton.

In addition to the extensive studies on the water oxidation reaction mediated by noble metals, increasing efforts have been made toward the mechanistic elucidation of the O–O bond formation pathways over earth-abundant metal-based WOCs [64–66]. Typically, more experimental details could be found on noble-metal catalyzed reactions than on first-row transition-metal catalyzed reactions owing to the relatively high stability of noble metal-oxygen species. In addition, more mechanistic uncertainties exist for the first-row transition-metal-based reactions owing to the scarce experimental details, complex theoretical approaches, and also the various oxidation states and fluctuating electronic spin populations of these metals. In addition, because first-row transition metal-oxygen species are less stable than their noble metal counterparts, direct coupling of two metal-oxygen radicals to generate O–O bonds scenarios have been rarely reported.

Mn-based WOCs were selected for PSII, and many synthetic Mn-containing complexes were reported as WOCs. In 2007, Sun *et al.* [67] reported the first well-investigated mononuclear site hangman Mn complex **10**. The detailed theoretical analysis of Mn-corrole related complexes revealed that the typical Mn^V=O species were responsible for the formation of the O–O bonds, and the nucleophilic attack of the hydroxide anions on the Mn^V=O species was proposed [68,69]. Borovik *et al.* [70] calculated that the Mn^V=O complex rather than the Mn^{IV}-O• radical was the most oxidized species. In addition, Liao *et al.* [71,72] proposed a PSII-like water oxidation mechanism using a bio-inspired tetranuclear Mn complex, in which the crucial O–O bond formation reaction proceeded via the direct coupling of a Mn^{IV}-oxyl radical and di-Mn bridging oxo group.

Ellis *et al.* [73] reported that the Fe(III)-tetraamido macrocyclic ligand, Fe^{III}-TAML (**11**), catalyst could be an efficient WOC. Fillol *et al.* [74] determined that Fe complexes of tetradentate neutral ligands acted as WOCs at low pH with substantial TON (the representative *cis*-vacant Fe complex **12** is illustrated in Scheme 10). The spectra and kinetic analysis results of these Fe complexes demonstrated that high-valent Fe-oxo species were responsible for the O–O formation reaction. The WNA-type O–O bond formation mechanism was postulated based on the results of the kinetic studies, which indicated that the reaction rate followed first order kinetics in respect to the concentration of the observed Fe^{IV}=O species. $O=Fe^{IV}-(OH)-Ce^{IV}$, which contained a bridging hydroxyl group, was suggested to be the reaction intermediate. The subsequent oxidation of $O=Fe^{IV}-(OH)-Ce^{IV}$ led to the formation of $O=Fe^V-(OH)-Ce^{IV}$, which was nucleophilically attacked by a H₂O molecule, afterward [75]. A series of analogues of **12** with *cis*-vacant coordination sites were also reported [76–79]. Meyer *et al.* [80] proposed the existence of the key Fe^V=O intermediate, which trig-

Scheme 10. Molecular structures of **10**, **11**, **12** and **13**, and proposed **11**-mediated water nucleophilic attack (WNA)-type water oxidation catalytic cycle.

gered the subsequent WNA-type O–O bond formation. In addition, Panda *et al.* [81] confirmed the existence of Fe^V=O species in the reaction mixture. Cramer *et al.* [82] and Liao *et al.* [83] calculated that the oxidation of the initial TAML-Fe^{III}-OH₂ complex led to the formation of TAML•-Fe^V=O species, which subsequently underwent nucleophilic attack by a H₂O molecule, and the TAML of the Fe^V=O species underwent 1e[−] oxidation. The Fe-TAML-catalyzed water oxidation reaction is schematically presented in Scheme 10. The Fe-oxo species responsible for the O–O bond formation process was found to differ with different added sacrificial oxidants. Che *et al.* [84] determined that the key intermediates that triggered the O–O bond formation process were the Fe^{IV}=O or Fe^V=O species when the oxidant reagents were CAN or NaIO₄ (or oxone), respectively.

A WNA-like O–O bond formation mechanism was reported by Liao *et al.* [85]. Water oxidation mediated by a mononuclear Fe complex with a square polypyridine ligand was theoretically investigated, and the typical Fe^V=O intermediate was determined to be directly responsible for O–O bond formation. The energy barrier of the O–O bond formation reaction that occurred via the conventional WNA mechanism using a H₂O nucleophile was calculated to be higher than that of the corresponding reaction in which the nitrate anion was used as the nucleophile.

Nocera *et al.* [86] studied the electrocatalytic water oxidation over Co^{III} hangman corrole complexes **14** bearing β -octafluoro and meso-pentafluorophenyl substituents and reported that the catalytic performance of these complexes was excellent. A Co^{IV}-corrole^{•+} moiety was proposed to be the catalytically active species. Cramer *et al.* [87] and Lai *et al.* [88] further investigated the water oxidation reaction mechanisms. The typical Co^V species (better described as Co^{IV}-corrole^{•+} with cation radical character in the corrole ring) was reconfirmed as the key intermediate to trigger the WNA-type O–O bond formation reaction, rather than Co(IV). In addition, the pendant hangman carboxyl moiety of the complex was determined to act as intramolecular base to facilitate the APT process during the WNA-type O–O bond formation reaction [Scheme 11] [89].

Lei *et al.* [90] systematically investigated the Co-corrole complex-mediated water oxidation reactions. H₂O-Co^{III}-corrole underwent two sequential 1H⁺/1e[−] oxidation steps to form HO•-Co^{III}-corrole^{•+}, which further underwent WNA to generate HOO-Co^{III}-corrole. The calculated energy barrier of the O–O bond formation reaction using an acetate anion as the external

Scheme 11. Molecular structure of **14**, and proposed hangman-assisted water nucleophilic attack (WNA)-type O–O bond formation mechanism.

proton-acceptor base was 11.8 kcal/mol lower than that of the reaction that used a cluster of four H₂O molecules as the proton acceptor (Scheme 12). Furthermore, Cao *et al.* [91] reported the remarkable water oxidation activity of a pyrene-modified Co-corrole complex immobilized on carbon supports, which was attributed to the strong noncovalent π - π interactions between the pyrene moiety and carbon supports. In addition, Cao *et al.* [92–94] reported that the water oxidation catalytic performance of the Co-corrole complexes was increased by connecting them to carbon nanotubes via covalent conjugated links. Furthermore, the effect of the *trans* axial ligand of Co-corroles on the water oxidation activity was investigated [95], and it was determined that the axial ligands on the Co centers presented significant effect on the catalytic OER activity and the Co-corroles with electron-donating *trans* axial ligands were more active. Moreover, Groves *et al.* indicated that the buffer base in the solution played important roles during both the PCET processes and the O–O bond formation step; in addition, more basic buffer base anions led to lower O–O bond formation energy barriers [96].

Cao *et al.* reported a cationic Ni-porphyrin (Ni-Por) complex with meso-tetrakis(*N*-methyl-4-pyridyl) as WOC [97]. The rate-determining O–O bond formation step was proposed to occur between the Por-Ni^{III}-O• radical and a H₂O molecule nucleophile. The energy barrier of the O–O bond formation reaction using acetate anions as proton acceptors was lower than that of a water-cluster induced reaction, and that was similar to the HO•-Co^{III}-corrole+-triggered O–O bond formation process [90]. Sun *et al.* [98] also reported a WNA-type O–O bond formation mechanism, where a Ni^{III} PY5 complex was used to promote water oxidation. Two sequential PCET processes and a subsequent 1e⁻ oxidation reaction formed the key Ni^V=O intermediate species, which was subsequently attacked by a H₂O molecule to form O–O bonds. In addition, it was determined that the added HPO₄²⁻ buffer base acted as the proton acceptor during the proposed APT process of the WNA-type O–O bond

Scheme 12. Molecular structure of **15**, and schematic diagram of two different water nucleophilic attack-type O–O bond formation transition states using a H₂O cluster or an acetate anion as the external bases.

formation.

Meyer *et al.* [99] reported that homogeneous Cu complexes significantly promoted water oxidation, and the simple monomeric [(bpy)Cu(OH₂)₂] complex was proposed as the dominant catalytic species. Subsequently, Lin *et al.* [100] reported that a Cu-bpy related complex with pendant hydroxyl groups could serve as WOC at much lower potentials than those reported by Meyer *et al.* Combined experimental data and theoretical results indicated that the 6,6'-dihydroxy-2,2'-bipyridine ligand was redox non-innocent, which was ascribed to the low redox potentials of the mononuclear Cu complexes. The typical Cu^{IV}-hydroxyl complex (better described as L•-Cu^{III}-OH, where L is the bidentate ligand) was proposed to be the key intermediate to trigger the WNA. The proposed catalytic cycle is presented in Scheme 13. Zhang *et al.* [101] and Pap *et al.* [102] proposed similar WNA-type O–O bond formation pathways. The added buffer base or carbonate anion were determined to act as proton acceptors during the APT process of the WNA-type O–O bond formation process [103,104].

2.2. Single-electron transfer WNA

The concerted typical 2e⁻ reduction of the metal center and O–O bond formation are known to occur during WNA-type reactions. Alternatively, a stepwise single-electron transfer (SET)-WNA mechanism was proposed. Garrido-Barros *et al.* [105] reported a series of mononuclear Cu complexes, **17**, that contained tetraanionic tetradentate amide ligands as WOCs. The low redox potentials of the Cu complex couples were ascribed to the good donating capacity of the anionic ligand and redox non-innocent nature of the ligands. The L•-Cu^{III}-OH complex was treated as the key intermediate to trigger O–O bond formation. Unlike the conventional 2e⁻ WNA-type O–O bond formation, the proposed O–O bond formation was a two-step process: (1) 1e⁻ transfer from the incoming hydroxide anion to the oxidized ligand of L•-Cu^{III}-OH and (2) the reduction of the Cu(III) center during the other 1e⁻ transfer process. Llobet *et al.* [105] labelled this type of O–O bond formation mechanism as SET-WNA. Two consecutive intramolecular SET steps took

Scheme 13. Molecular structure of **16** and proposed water oxidation catalytic cycle.

Scheme 16. Molecular structures of **19** and **20**, and proposed **19**-mediated intramolecular coupling between two metal oxo/oxyl units (I2M)-type O–O bond formation mechanism.

mation process was suggested. These findings were ascribed to the elongated bimetallic distance owing to the orientation introduced by the asymmetric dibenzofuran bridge.

The use of negatively charged ligands decreases the oxidation potentials of WOCs. Sun *et al.* [117] reported a mononuclear Ru complex $[\text{Ru}(\text{bda})(\text{pic})_2]$ (**21**) that contained a tetradentate ligand with anionic carboxylate moieties. An atypical seven-coordinated intermediate Ru(IV) dimeric complex featuring a $[\text{H}_2\text{O}-\text{HO}-\text{H}-\text{OH}-\text{H}_2\text{O}]^-$ (simplified as $[\text{HOHOH}]^-$) bridge was isolated, which indicated that ligand exchange on the octahedral Ru center was not a prerequisite (Scheme 17). The $[\text{HOHOH}]^-$ bridge would act as proton channel for the subsequent water oxidation reaction. The $\text{Ru}^{\text{II}}-\text{OH}_2 \rightarrow \text{Ru}^{\text{III}}-\text{OH}_2 \rightarrow \text{Ru}^{\text{IV}}-\text{OH} \rightarrow \text{Ru}^{\text{V}}=\text{O}$ oxidation process was observed. Water oxidation was suggested to be triggered by the formation of the $\text{Ru}^{\text{V}}=\text{O}$ intermediate, and the O–O bond formation step involved the I2M coupling of two $\text{Ru}^{\text{V}}=\text{O}$ species. The I2M-favored O–O bond formation mechanism was ascribed to the close proximity of the two bimolecular Ru-oxo species owing to the $[\text{HOHOH}]^-$ bridge. In contrast, the mononuclear six-coordinated Ru complex-mediated O–O bond formation generally favors the WNA pathway [118]. Sun *et al.* [119] reported a tridentate dicarboxylate ligand-containing mononuclear Ru complex, $[\text{Ru}(\text{pdc})(\text{pic})_3]$, where H_2pdc and pic denote 2,6-pyridinedicarboxylic acid and picoline, respectively, which facilitated the picoline- H_2O ligand exchange and subsequent WNA-type water oxidation.

The rate of the I2M-type O–O bond formation process was

Scheme 17. (a) Molecular structure of **21**. (b) Isolated seven-coordinated Ru(IV) dimer complex with $[\text{H}_2\text{O}-\text{HO}-\text{H}-\text{OH}-\text{H}_2\text{O}]^-$ bridge. (c) Intramolecular coupling between two metal oxo/oxyl units (I2M) O–O bond formation mechanism between two seven-coordinated $\text{Ru}^{\text{V}}=\text{O}$ (or $\text{Ru}^{\text{IV}}-\text{O}^\bullet$) intermediates.

significantly increased by the introduction of axial isoquinoline (isoq) ligands, as in $[\text{Ru}(\text{bda})(\text{isoq})_2]$ (**22**), which were suggested to facilitate the direct O–O coupling of two typical $\text{Ru}^{\text{V}}=\text{O}$ (or $\text{Ru}^{\text{IV}}-\text{O}^\bullet$) species via the π - π stacking noncovalent interactions between two isoq moieties (Scheme 18) [120]. Conception *et al.* [121] performed detailed mechanistic studies on the I2M origins of $[\text{Ru}(\text{bda})(\text{isoq})_2]$ analogues and revealed that the main contributor to the increase in the reaction rate was entropy, owing to the highly organized transition states. Ahlquist *et al.* [122] investigated the activation energy of the coupling between two $\text{Ru}^{\text{IV}}-\text{O}^\bullet$ radicals. They divided the activation barrier energy into distortion and interaction energy, and their computational analysis results indicated that several aspects, such as solvation, supramolecular properties, and solvent dynamics likely played important roles in the equilibrium between the free typical $\text{Ru}^{\text{V}}=\text{O}$ monomers and $\text{Ru}^{\text{V}}=\text{O} \cdots \text{O}=\text{Ru}^{\text{V}}$ dimer.

Sun *et al.* [123] concluded that the dissociation of axial ligands was the major deactivation cause of the monomeric Ru complexes they analyzed. Furthermore, they investigated the binding affinity of axial ligands and proposed that an axial ligand with high highest occupied molecular orbital energy level could form a highly durable mononuclear Ru complex that would present remarkable catalytic performance. A shorter $\text{Ru}^{\text{V}}=\text{O}$ distance between two facial monomeric complexes would accelerate the I2M-type water oxidation; this inspired the construction of flexibly bridged binuclear Ru complexes, which presented excellent water oxidation performance [124].

Masaoka *et al.* [125] used a pentanuclear Fe complex as WOC. In addition, Liao *et al.* [126] analyzed the metal oxidation states during the O–O bond formation process and determined that the most favorable O–O bond formation mechanism should be the direct I2M coupling of two $\text{Fe}^{\text{IV}}-\text{O}$ radicals.

Nocera *et al.* [115] reported a binuclear Co complex that featured a flexible cavity with two trigonal-bipyramidal scaffolds, which allowed oxo radicals to be brought together and facilitated the I2M-type O–O bond formation.

4. Shifting between WNA and I2M

Llobet *et al.* [127] reported a binuclear Ru complex $[(\text{py}-\text{SO}_3)(\text{OH}_2)\text{Ru}(\mu\text{-Mebbp})\text{Ru}(\text{OH}_2)(\text{py}-\text{SO}_3)]^{3-}$ (**23**) with a planar penta-dentate pyrazole-bridged Mebbp ligand, which separated the bimetallic centers in the equatorial plane. In con-

Scheme 18. Molecular structure of **22**, and π - π stacking noncovalent interaction between two isoquinoline moieties.

trast to the bpp-containing **24**, **23** was found to mediate the O–O bond formation via the WNA mechanism. The Mebbp-ligand in **23** served as bis-meridional scaffold to constrain the bimetallic centers and Mebbp- ligand within the equatorial plane. That generated a very small Ru–N–N–Ru torsion angle (0.4° for the acetate-bridged **23** analogue). Conversely, the Ru–N–N–Ru dihedral angle in bpp-containing **24** was increased to 25.3° . Consequently, the constraints of the bis-meridional scaffold Mebbp- ligand increased the bimetallic distance, and that reduced the through-space interaction of the two Ru–O moieties and shifted the preferred O–O bond formation mechanism to WNA. The different O–O bond formation mechanisms of **23** and **24** demonstrated that the WNA and I2M pathways could be shifted using subtle ligand variations. Thummel *et al.* [128] reported similar water oxidation active binuclear Ru complexes featuring rigid planar bis-tridentate polypyridyl-based ligands. The OER was a first-order reaction in respect to the catalyst concentration, which indicated that the two Ru centers cooperated [25,128]. Less torsion distortions would be expected in the bimetallic centers embedded equational planar, which caused the Ru–Ru distance to increase, and therefore, the O–O bond formation was suggested to follow the WNA mechanism (Scheme 19). More recently, Llobet *et al.* [129] and Meyer *et al.* [130] reported a bbp-based diruthenium water oxidation complex ($[\text{Ru}_2(\text{OH})_2(\text{OAc-bbp})(\text{py})_4]^{2+}$) with a carboxylate anchor at the ligand backbone. It was determined that the effect of the backbone anchor on the electronic properties of the diruthenium centers, and consequently the catalytic water oxidation performance, was insignificant. The $\text{Ru}^{\text{V}}=\text{O}$ was reconfirmed as the key intermediate to trigger the WNA-type O–O bond formation processes.

Sun *et al.* [50] reported a similar mononuclear Ru complex $[\text{Ru}(\text{bda})(\text{DMSO})(\text{L})]$ (**25**), where DMSO denotes dimethyl sulfoxide, with axially coordinated DMSO and imidazole. The WOC simulation demonstrated that the Ce^{IV} -driven water oxidation was better than the **25**-mediated one and the O–O bond formation occurred via an I2M mechanism. A similar seven-coordinated intermediate $\text{Ru}^{\text{IV}}\text{-OH}$ with axial $\text{Ru}^{\text{IV}}\text{-O}(\text{DMSO})$ bond was analyzed. Sun *et al.* suggested that the smaller collisions between the axial and equatorial ligands favored the I2M-type O–O bond formation (Scheme 20). In contrast, the WNA O–O bond formation pathway was proven to be more favorable when mediated by the monomeric Ru complex $[\text{Ru}(\text{pda})(\text{pic})_2]$ (**26**), where H_2pda denotes 1,10-phenanthroline-2,9-dicarboxylic acid, which contained a rigid phenanthroline dicarboxylate ligand. The increased collisions of the axial picoline moieties introduced by the confinement of the rigid ligand prevented the two typical $\text{Ru}^{\text{V}}=\text{O}$ species from approaching each other, which significantly increased

Scheme 19. Schematic diagram of origins of different O–O bond formation mechanism mediated by **23** and **24**.

Scheme 20. Schematic diagram of origins of different O–O bond formation mechanism mediated by **25** and **26**.

the energy barrier of the direct I2M-type O–O coupling [49].

The changes in substituents in Co-porphyrin complexes can alter the O–O bond formation mechanism. Sakai *et al.* [131] proposed that the rate determining step of the water oxidation reaction should proceed via the radical coupling of two CO-oxyl radicals when the substituents of Co-porphyrin complex **27** were less bulky (Scheme 21). However, the WNA-type O–O bond formation was suggested for bulky Co-porphyrin complex **28** [132]. In addition, it was suggested that the WNA pathway was preferred for O–O bond formation when mononuclear Co complexes with non corrole or porphyrin-related ligands were used as WOCs [133–136].

5. Other O–O bond formation mechanisms

In addition to the aforementioned WNA and I2M mechanisms of O–O bond formation, three more O–O bond formation mechanisms are reviewed in the following sections.

5.1. IHC and BHC mechanisms

O–O bond would be directly formed via couplings between two metal-bound hydroxyl groups. For the IHC mechanism, unimolecular dihydroxo coupling is suggested to occur, which leads to the generation of metal-hydroperoxides and their subsequent oxidations would release O_2 .

Milstein *et al.* [137] reported a non-aromatic mononuclear Ru pincer complex **29**, which was determined to consecutively promote the generation of H_2 and O_2 from H_2O . The pincer complex rapidly reacted with H_2O and led to ligand aromatization and the formation of a *trans* hydrido-hydroxo complex. The formed hydrido-hydroxo complex further reacted with H_2O to generate a *cis*-dihydroxo complex. H_2^{17}O and H_2^{18}O isotopic labelling experiments indicated unequivocally that H_2O_2 was released from the dihydroxo intermediate and O–O bond for-

Scheme 21. Molecular structures of **27** and **28**, and proposed water nucleophilic attack (WNA) or coupling between two metal oxo/oxyl units (I2M) O–O bond formation mechanisms.

mation occurred via the IHC mechanism (Scheme 22). The alternative BHC mechanism for O–O bond formation was ruled out using isotopic labelling experiments. Hall *et al.* [138] used time-dependent density functional theory (TD-DFT) calculations to predict that the breaking of the two strong Ru–O bonds and formation of the O–O bond during this photolytic reaction involved low-energy triplet states and singlet-triplet crossings. In addition, Fang *et al.* [139] proposed an alternative reaction pathway, in which H₂O₂ was not suggested to be an important intermediate for O₂ formation. Instead, the formation of triplet O₂ molecules consisted of two steps: concerted hydrogen transfer and dehydration. The light-induced OER was determined to be a nonadiabatic process, and the O–O bonds was formed via unimolecular metal-oxo coupling.

Crabtree *et al.* [140] developed a single-site Ir complex **30** with a C,C-chelating *N*-heterocyclic carbene (NHC) ligand (Scheme 23). The singlet NHC was proven to possess good σ -donating ability to stabilize high-valent metal centers, which would subsequently result in low oxidation potentials and the high stability of the Ir^{IV}-intermediate. A series of sequential 1e-oxidations were observed during water oxidation, and a BHC-type O–O bond formation mechanism was estimated because the kinetic survey established that the order of the water oxidation reaction was close to 2. In contrast, Hetterscheid *et al.* [141] reported a Me₂-NHC based mononuclear Ir complex **31** for the water oxidation reaction. An incubation process was observed when the complex generated the active Ir-aqua catalyst. The excellent water oxidation rate of **31** was ascribed to the electron-donating normal carbene and open coordination sites of the aqua species. A mononuclear IHC-type O–O bond formation pathway was proposed for the water oxidation reaction [141,142].

Lu *et al.* [141] reported a robust macrocyclic mononuclear Ni complex **32** as WOC [143]. Significant isomerization was suggested to occur between the *trans*-bis(aqua) Ni^{III} complex and *cis*-bis(aqua) Ni^{III} species; in addition, the *cis* isomer was proposed to be the active catalyst form. The formed *cis*-Ni^{IV}-bis(hydroxyl) could trigger HO–OH coupling on the Ni center. Theoretical studies revealed that the energy barrier of the IHC-type O–O bond formation was significantly lower than

Scheme 23. Molecular structures of **30** and **31** and their respective key intermediates for hydroxyl coupling O–O bond formation.

that of the WNA-type O–O bond formation. The proposed catalytic cycle is illustrated in Scheme 24. Similar IHC-type O–O bond formation mechanisms were reported in other papers [144,145].

Recently, Cao *et al.* [146] reported low overpotential water oxidation at neutral pH catalyzed by a Cu complex with tetrakis(4-*N*-methylpyridyl)porphyrin. Their experimental results suggested the 1e-oxidized species of Cu^{II}-porphyrin triggered the O–O bond formation reaction, and the BHC of the Cu^{III}-OH (better described as Cu^{II}-OH[•]) species was suggested as the O–O bond formation mechanism. This reaction mechanism allowed for this Cu porphyrin to catalyze water oxidation at neutral pH values and very low overpotentials. Furthermore, at acidic pH values, a H₂O₂ intermediate was detected. It is unprecedented that this Cu porphyrin could catalyze the 4e[−] water oxidation to produce O₂ in neutral solutions and catalyze the 2e[−] water oxidation to produce H₂O₂ in acidic solutions.

5.2. IOC mechanism

O–O bond formation could also take place via the direct coupling between two unimolecular metal-oxo species. Smith *et al.* [147] reported a mononuclear *cis*-aqua Mn complex **33** with *t*-Bu-substituted pyridinophane ligands, which could mediate water oxidation and generate O₂. Baik *et al.* [148] proposed that a Mn^V-bis(oxo) species was involved in the O–O bond formation via the IOC mechanism (Scheme 25). The energy barrier differences between the WNA- and IOC-type O–O bond formation pathways were further investigated by Liao *et al.* [149], and the

Scheme 22. Molecular structure of **29**, and proposed mechanism for the formation of H₂ and O₂ from H₂O.

Scheme 24. Molecular structure of **32** and the proposed catalytic cycle of water oxidation.

Scheme 25. Molecular structure of **33** and the two different O–O bond formation mechanisms of WNA and IOC.

calculated results indicated that the energy barrier of the WNA-type O–O bond formation was 0.7 kcal/mol lower than that of IOC mechanism. For the slightly favored WNA pathway, the $\text{Mn}^{\text{V}}=\text{O}$ species was nucleophilically attacked by a H_2O molecule and the other oxo moiety acted as internal base to abstract a proton from the coming H_2O molecule.

Zhang *et al.* [150] reported the electrocatalytic water oxidation using a binuclear naphthyridine-bridged Cu complex **34** in neutral aqueous solution. The initial $\text{H}_2\text{O}-\text{Cu}^{\text{II}}-\text{OH}-\text{Cu}^{\text{II}}$ complex was found to undergo two consecutive PCET processes to generate $\text{HO}-\text{Cu}^{\text{III}}-\text{OH}-\text{Cu}^{\text{III}}$ and $\text{HO}-\text{Cu}^{\text{III}}-\text{O}-\text{Cu}^{\text{III}}$. Subsequently, direct O–O bond formation occurred via the IOC between the $\text{Cu}^{\text{III}}-\text{O}(\text{H})$ species and bridging μ -oxo synchronously with the intramolecular proton transfer from the Cu^{III} -bound hydroxyl to the uncoordinated pyridine moiety (Scheme 26). Conversely, the energy barrier of the conventional WNA-type O–O bond formation triggered by the highly oxidized $\text{Cu}^{\text{IV}}=\text{O}$ intermediate was significantly higher. DFT calculations suggested that the O–O bond formation occurred via a direct IOC mechanism rather than the WNA of the high-valent $\text{Cu}^{\text{IV}}=\text{O}$ moiety.

Recently, Hartzler *et al.* [151] synthesized a $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{bpy}-\text{NO})]^{2+}$ complex and subsequently proposed a new O–O bond formation pathway via the radical coupling of the metal- and ligand-based radicals. The authors calculated that the energy barrier of the intramolecular O–O bond formation between $\text{Ru}^{\text{IV}}-\text{O}^\bullet$ and the ligand based radical ($\text{L}-\text{NO}^{\bullet+}$) was significantly lower than that of WNA pathway triggered by the high-valent $\text{Ru}^{\text{V}}=\text{O}$ intermediate. Computational analysis revealed that the overpotential of the formation of the $\text{Ru}^{\text{IV}}-\text{L}-\text{NO}^{\bullet+}$ radical was lower than that of the formation of the $\text{L}-\text{Ru}^{\text{V}}=\text{O}$ intermediate.

5.3. RI mechanism

Tolman *et al.* [152] observed the reversible O–O bond formation between $\text{Cu}_2^{\text{III,III}}-\text{bis}(\mu\text{-oxo})$ and $\text{Cu}_2^{\text{II,II}}-(\mu\text{-O}_2)$ species,

Scheme 26. Molecular structure of **34** and the proposed O–O bond formation mechanism via an IOC mechanism.

which elucidated the O–O bond formation mechanism via the RI pathway. Emmons *et al.* [153] reported a Cu dimer bearing two μ -hydroxyl bridges, which mediated electrocatalytic water oxidation. The O–O bond formation mechanism disfavored single-site pathways. A large kinetic isotope value suggests that the PCET during the initial oxidation was the rate-determining step. The oxidation of the $\text{Cu}_2^{\text{II,II}}-(\mu\text{-OH})_2$ generated μ -oxo-bridged $\text{Cu}_2^{\text{III,III}}$ species without the formation of $\text{Cu}^{\text{III}}-\text{O}^\bullet$ or $\text{Cu}^{\text{IV}}=\text{O}$ species. Subsequently, the O–O bond formation mechanisms were investigated, and DFT calculations revealed that energy barrier of the O–O bond formation via the RI mechanism was similar to that of the O–O formation process that occurred via the nucleophilic attack of a H_2O molecule on the μ -oxo bridge (Scheme 27). Thus, the RI O–O bond formation pathway was demonstrated to be feasible particularly for redox-active metal complex dimers with fragile facial bis(μ -oxo) linkages between bimetallic centers.

6. Concluding remarks

In this study, two popular O–O bond formation mechanisms: WNA and I2M, and four other mechanisms, viz. BHC, IHC, IOC, and RI, were reviewed.

The sequence of oxidations and/or PCET processes occurred to form high-valent metal-oxo intermediates, which triggered the WNA to form metal-hydroperoxide species while undergoing the typical $2e^-$ reduction of the metal center. In addition, the O–O bond formation could occur via the two-step consecutive $1e^-$ transfers to generate metal-hydroperoxide species. The traditional nucleophile species for WNA is a H_2O molecule, but hydroxide anions and other dissociative anions could also serve as nucleophile species. For the WNA-type O–O bond formation process, APT with O-atom transfer to the oxo terminal occurs together with proton transfer to the base. The base species could be intramolecular metal-oxo species, H_2O cluster, anions in the solution, or added buffer base. The base species involved in the APT process significantly affect the en-

Scheme 27. Molecular structure of **35** and the proposed O–O bond formation mechanism via either a RI or a WNA strategy.

energy barrier of the O–O bond formation process. Typically, more basic proton acceptors decrease the energy barrier of O–O bond formation. Ligands with more pronounced σ -donating nature or anionic origin decrease the redox potentials of metal-oxygen species, which is beneficial for the generation of high-valent metal-oxo intermediates. The highly oxidized metal-oxo species were typically better described as radicaloids during DFT calculation studies. Despite of extensive experimental and theoretical studies, many uncertainties remain in the identification of the key metal-oxo intermediates, and determination of base species during the APT process of O–O bond formation, which require further systematic mechanistic investigations.

For the I2M mechanism, the intermolecular coupling between two metal-oxo radicals requires that the head-to-head radicals converge and feature small bimetallic distance and strong through-space interaction. The O–O bond formation mechanism of metal complexes with flexible equatorial coordination planar for seven-coordination and small steric hindrance between mononuclear halves was estimated to be I2M. The confinement and collisions of ligands were found to change the bimetallic distance, which consequently altered the O–O bond formation mechanisms.

metal-hydroxyl coupling also resulted in O–O bond formation. Typically, IHC and BHC processes do not generate highly oxidized metal-oxo species, which consequently results in the relatively lower O–O bond formation barrier than that of the WNA mechanism. Experimental evidence of O–O bond formation via IOC and RI was scarce, and both mechanisms were estimated to be feasible when the intramolecular metal-oxo terminals were in close proximity, and more importantly, the O–M–O angles were small (here M denotes the metal center).

The O–O bond formation mechanisms have not been completely elucidated. For example, the identifications of the metal oxidation states of the key metal-oxygen species and the origins triggered different O–O bond formation mechanisms. In addition, the lack of direct experimental evidences rendered the mechanistic investigations more difficult but meaningful. The elucidation of the key O–O bond formation process is beneficial

for the practical applications of industrial water splitting, and use of clean energy.

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Graphical Abstract

Chin. J. Catal., 2021, 42: 1253–1268 doi: 10.1016/S1872-2067(20)63681-6

O–O bond formation mechanisms during the oxygen evolution reaction over synthetic molecular catalysts

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The O–O bond formation mechanisms for water oxidation catalyzed by molecular transition metal catalysts are reviewed. The evolutions of metal-oxo species, water nucleophilic attack and metal-oxo radical couplings of O–O bond formation mechanisms are focused.

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分子催化剂催化水氧化过程及其O–O成键机理

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摘要: 随着化石燃料的不断消耗和生存环境的日益恶化, 可再生、清洁且环境友好的新能源逐渐受到广泛关注与利用. 太阳能作为一种洁净的可再生能源, 在自然界中, 植物可以通过光合作用将太阳能转换成化学能. 在该过程中, 水分子在光系统II中被氧化而释放出氧气, 伴随生成的质子和电子进一步将二氧化碳转化为蕴含生物质能的碳水化合物.

在光系统II中, 叶绿素P680被光照激发生成阳离子自由基P680⁺, 其具有很强的氧化能力, 可以从附近的析氧中心中夺取电子. 析氧中心通过这一过程失去4个电子, 可以将两分子水氧化生成一分子氧气和4个质子. 作为水裂解的半反应之一, 水氧化在热力学方面需要很多能量来断裂4个O–H键($\Delta E = 1.23 \text{ V vs. NHE}$), 在动力学方面涉及4个氢原子与2个氧原子的重组以及氧气的释放, 因而水氧化析氧是一个非常缓慢的过程, 如何高效稳定地催化水氧化一直是人们研究的热点和难点. 研究发现, 自然界中存在的析氧中心为Mn₄CaO_x的钙锰簇合物, 在水氧化过程中生成的Mn=O物种可以被游离的水分子亲核进攻形成O–O键, 也可以与桥连 $\mu\text{-O(H)}$ 反应生成O–O键. 通过对析氧中心持续的研究, 在过去几十年中设计合成了一系列具有水氧化催化活性的基于金属配合物的分子催化剂.

分子催化剂催化水氧化一般主要分为金属-氧物种的演化过程以及O–O成键过程. 通常, 金属-氧物种可以通过失电子或质子耦合的失电子过程逐步生成高价态的金属-氧物种, 其引发的O–O成键过程通常是水氧化催化循环的决速步骤. 基于之前的研究成果, 目前主要报道了五种不同的O–O成键机理: (1)水亲核进攻金属-氧物种的WNA机理, (2)金属-氧自由基耦合的I2M机理, (3)金属-羟基自由基耦合的HC机理, (4)分子内进攻桥连氧的IOC机理以及(5)氧化还原异构的RI机理.

本文综述了过去几十年水氧化分子催化剂的发展, 总结了贵金属钌和铱配合物到第一过渡金属锰、铁、钴、镍和铜配合物催化水氧化过程中金属-氧物种的生成与演化, 重点阐述了引发O–O成键过程的高价态金属-氧物种的种类及其不同的O–O成键机理. 重点总结了O–O成键中WNA机理与I2M机理的异同, 并阐述了催化剂设计对WNA与I2M机理选择性的影响. 通过对金属-氧物种种类和O–O成键机理的总结, 将有助于进一步设计合成高效稳定的水氧化分子催化剂.

关键词: 产氧反应; 水氧化; O–O成键; 过渡金属配合物; 分子电催化; 反应机理

收稿日期: 2020-08-11. 接受日期: 2020-09-22. 上网时间: 2021-04-05.

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基金来源: 国家自然科学基金(21101170, 21573139, 21773146); 霍英东青年教师基金; 中央高校基本科研基金; 陕西师范大学研究经费.

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/journal/chinese-journal-of-catalysis>).