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Water Splitting

Water Splitting by Cooperative Catalysis**

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cooperative catalysis · dioxygen · photocatalysis · ruthenium · water splitting

Our current global energy consumption is primarily based on the combustion of fossil fuels,[1] and while supplies are dwindling, global demand is rapidly increasing. Furthermore, pollution and climate change represent undesirable side effects of global concern. The most sustainable alternatives are based on sunlight as an environmentally friendly and practically unlimited energy source. Although the capture of this energy has received a lot of attention and is currently being explored worldwide, the complete transition to such an alternative energy source also implies proper storage of energy, as production and consumption generally do not match. The direct conversion of sunlight into chemical energy, preferably hydrogen, constitutes breakthrough technology and as such is one of the most important challenges that scientists need to address within the next few decades. Ultimately, efficient water splitting is the key process to be developed, because water is the most abundant, cheap, and sustainable source of electrons available, and it is also the sole product during consumption of H_2 as a fuel. The overall water-splitting redox reaction can be described as a hydrogen-evolving half-reaction and a dioxygen-producing half-reaction occurring at the cathode and anode, respectively, of an electrochemical cell. The latter half-reaction, that is, $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$, has a redox potential $E_{anode} = +1.23-(0.059*pH)$ V (thermodynamic factor). This deceptively simple process comprises a complicated multielectron, multiparticle reaction, and generally kinetic limitations against oxidation of water are encountered. As a rule of thumb, in order for oxidation of H_2O to O_2 to take place at observable rates, an overpotential of approximately 0.6 V is required (this holds for both electrochemical and chemical oxidation of water). This situation is also clear from the redox potentials of Ce^{IV} ($E^o = +1.67$ V) and MnO_4^- ($E^o = +1.51$ V at pH 0), which are thermodynamically able to oxidize water. However, owing to the large activation barriers, water is practically inert to both reagents. A proper water oxidation catalyst should lower these kinetic barriers (Figure 1).

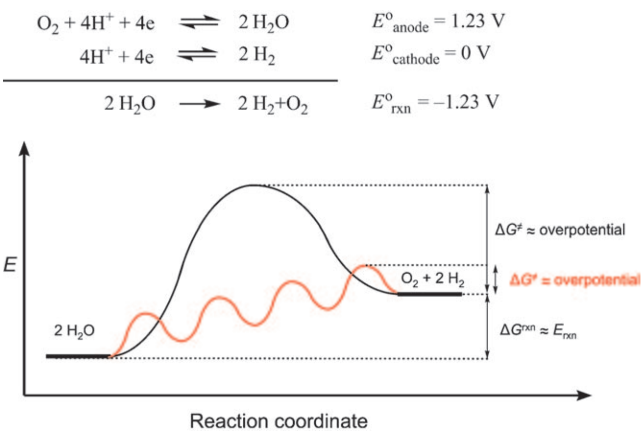

Figure 1. Half-reactions for the electrolysis of water and an energy diagram for uncatalyzed (black) and catalyzed (red) water oxidation.

The active site of the oxygen-evolving complex (OEC) of photosystem II, the natural enzyme that converts water into dioxygen using sunlight, consists of a cooperative Mn_4O_4Ca cluster. The Ca center actively participates in the formation of dioxygen.[2] It was generally believed that a multinuclear cluster is required, as water oxidation involves a multielectron process. As such, it has been a source of inspiration for the development of several Mn-based model complexes to mimic natural water oxidation catalysis.[3] Some truly functional systems are known,[4] but to date none have achieved the level required to produce hydrogen from water efficiently.[5] Besides manganese, multinuclear ruthenium complexes have also received a lot of attention since the mid 1980s, especially after the first functional Ru-based water oxidation catalyst, the "blue dimer", was reported by Meyer and co-workers (see Scheme 1 for some examples).[6,7] Interestingly, poorly defined, heterogeneous catalysts tend to outperform their well-defined homogeneous counterparts. Significant results have been reported with iridium colloids[8] and a heterogenized cobalt phosphate system.[9]

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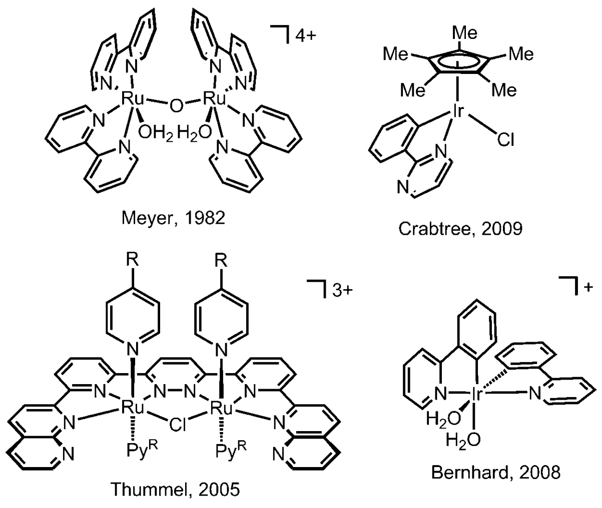
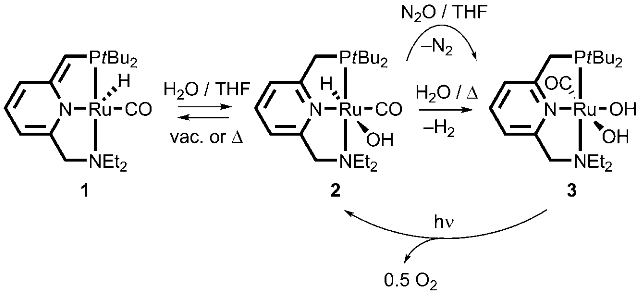


Scheme 1. Representative contributions to splitting of H_2O using homogeneous catalysts (Py^R = *p*-R-substituted pyridine).[6,7,11,12]

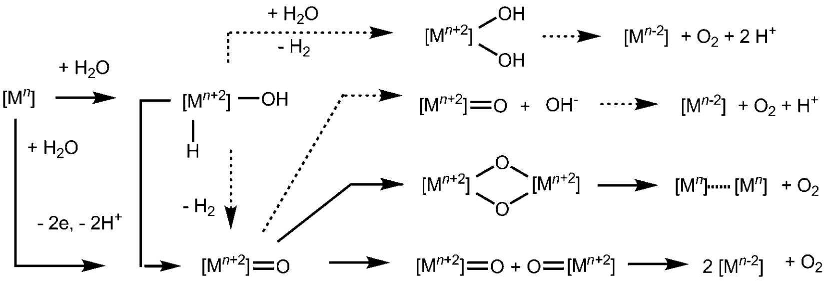
Neither in the natural OEC nor in the synthetic homogeneous systems is the exact mechanism for O_2 formation known. It is commonly assumed that high-valent oxo species are involved. External attack of water or OH^- at such oxo species as well as a variety of binuclear pathways have been proposed as the key steps in the observed O_2 evolution (Scheme 2). These high-valent oxo species are strong oxidants that can easily oxidize organic ligands. This property is a major problem in most current synthetic water-splitting catalysts, thus limiting their lifetimes.

Interesting recent breakthroughs in that respect are the use of polyoxometallates as ligands, which are stable under these conditions, but structural diversity is limited for such systems.[10] In principle, alternative mechanisms can be envisaged in which both oxygen and hydrogen evolve in a single catalytic cycle.[1] This approach seems most easily achievable with multinuclear species, which would allow reductive elimination of O_2 from a binuclear species as the key step (Scheme 2). Pathways via mononuclear species are rarely proposed[11,12] but could be envisioned. Double oxidative addition of water at a single metal center and subsequent reductive or α-H elimination processes, deprotonation, or nucleophilic attack of OH^- on a high-valent oxo species are all elementary steps that could potentially lead to formation of H_2 and O_2 mediated by a single metal site. Although some examples of oxidative addition of water to transition metals have been reported,[13] there are no examples of subsequent formation of H_2 or O_2 from such species.

A recent paper by Milstein and co-workers[14] offers a welcome alternative pathway for water-splitting systems via a mononuclear species using the ruthenium PNN metal complex **1** (Scheme 3). In contrast to all previous approaches, it does not rely on the use of high-valent oxo species for water oxidation, but O_2 evolves through light-induced reductive elimination of hydrogen peroxide from a mononuclear low-valent $\{Ru^{II}(OH)_2\}$ species. Although still only stoichiometric, this report clearly shows that water splitting does not necessarily involve formation of highly reactive, potentially even destructive high-valent Ru oxo species. The typical non-innocent behavior of the ligand used in complex **1** plays a crucial role in the new mechanism. Ruthenium complex **1** was previously applied in the Ru-catalyzed dehydrogenative homocoupling of alcohols to form esters, with concomitant release of H_2.[15] The reverse reaction, that is, the catalytic hydrogenation of non-activated esters to alcohols, was also discussed.[16] Most notably, the same complex also catalyzes the coupling of alcohols and amines to form amides, with extrusion of H_2.[17] The efficiency of the Ru complex relates in large part to the non-innocent, cooperative behavior of the lutidine skeleton, which undergoes facile dearomatization of the heterocycle by deprotonation of one of the methylene groups, thus resulting in a formally monoanionic amide.[18]



Scheme 3. Formation of hydroxo complex **2** from dearomatized **1** and water, and subsequent thermal formation of species **3** and H_2 through activation of a second equivalent of water. Photolysis of **3** results in regeneration of **2** and formation of dioxygen.



Scheme 2. Generally considered pathways via dinuclear species (solid lines) and hypothetical strategies via mononuclear species (dashed lines) for evolution of O_2 (and H_2) from water.

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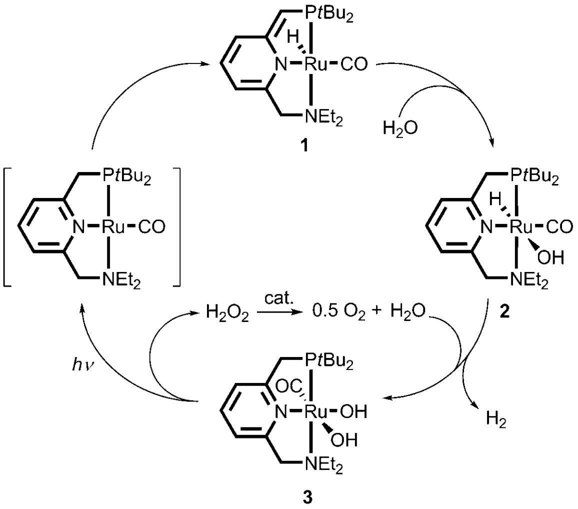
Milstein and co-workers now report that, akin to aliphatic alcohols, water can also be activated using complex **1** with the dearomatized PNN backbone.[14] It was shown that its reaction with water (or isotopically labeled derivatives thereof) led to reprotonation of the PNN backbone after heating at reflux for three days, concomitant with formation of Ru hydroxo complex **2** in moderate yield (Scheme 3).

Thermal activation of a second water molecule led to formation of molecular hydrogen and Ru dihydroxo species **3**. The same product formed more rapidly and cleanly by O-atom transfer using N_2O as reagent. Remarkably, irradiation of **3** led to the regeneration of compound **2** concomitant with evolution of O_2, although not quantitatively. The proposed mechanism for this sequence involves a photochemically induced reductive elimination of H_2O_2 from the two hydroxo ligands, thereby generating a non-observable Ru^0 intermediate that quickly undergoes intramolecular proton transfer to regenerate the starting compound. This hypothesis is supported by elegant isotopic labeling studies employing, for example, $H_2{}^{17}O$, $H_2{}^{18}O$, and $N_2{}^{16}O$ as sources for selective incorporation of labeled oxygen atoms (Scheme 4). Experiments with [^{18}O,^{16}O]**3** resulted only in the formation of ^{18}O–^{16}O, thus demonstrating that both OH groups of complex **3** end up in the initially formed hydrogen peroxide molecule. These results are in line with a reductive elimination and subsequent disproportionation of H_2O_2 in which the O–O bond remains intact. Furthermore, an intermolecular pathway via a dinuclear intermediate for H_2O_2 formation can be dismissed on the basis of these results, and mechanisms involving radicals were discarded on the basis of several experiments with radical traps and the use of the enzyme catalase.



Scheme 4. Proposed reaction mechanism for the Ru-mediated oxidation of H_2O to O_2 and H_2 by Ru complex **1**.

The newly reported system is noteworthy for a number of reasons. Firstly, it is the first time that molecular oxygen and molecular hydrogen have been formed in one catalytic cycle and from a single metal site. Secondly, the reaction consists of a heat-driven and a light-driven step. Thirdly, it is the first time that a non-innocent ligand system is effectively used in a water-splitting reaction. Fourthly, it is the first report of a water oxidation reaction that does not involve high-valent oxo species (e.g. Ru=O), which are generally very reactive and can lead to catalyst or ligand degradation. And finally, this is the first example of photoinduced reductive elimination of hydrogen peroxide from a dihydroxo metal complex.

These findings could well mark the onset of a new paradigm in the area of water splitting. The proposed intramolecular mechanism and mononuclear nature of the metal complex capable of combining two oxygen fragments is a very rare feat. Some precedent for iridium[11] and ruthenium[12] exists, but in these cases strong oxidants (e.g. Ce^{IV}) were employed and the intermediacy of metal oxo species is inferred. There is no reason why this reaction should be specific to the current complex, and optimization of the current process by using Ru complexes of the analogous cooperative PNP and sulfoxide-based SNN ligands or even non-innocent all-nitrogen-based ligands seems logical. The latter ligands might also offer enhanced stability against H_2O_2 and O_2, which could ultimately translate into an actual longevous catalytic system. Another interesting question to be addressed is if this reaction could be extended to other metals such as Ir, Fe, and Co.

The energy profile of the conversion of **1** to the dihydroxide species **3** has been investigated by DFT calculations.[19] It was shown that this overall transformation is only slightly endergonic by roughly 1 $\text{kcal}\,\text{mol}^{-1}$. This result suggests that the light-driven reductive elimination of H_2O_2 must be an endothermic reaction, with the subsequent disproportionation of H_2O_2 obviously being exothermic.[20] As a result, a system such as that described by Milstein and co-workers can in principle function with sunlight as the only energy input, thus allowing for a successful conversion of solar to chemical energy. However, a major drawback is the excess solar energy required for the synthesis of H_2O_2. This energy is subsequently is lost as heat upon disproportionation of H_2O_2, therefore rendering a lower overall efficiency.

Overall, the current system is a first significant contribution to perhaps a new type of water-splitting catalyst, actively utilizing the non-innocent, cooperative effect of the ligand scaffold. Furthermore, reductive elimination of hydrogen peroxide[21] is a remarkable new fundamental step in water oxidation catalysis, and effectively avoids formation of reactive metal oxo species. Both of these new tools may be combined with elementary steps from traditional 'redox' water oxidation pathways. It remains to be seen if these promising results will lead to the breakthrough technology required for the large-scale production of renewable energy.

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[1] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729.

[2] a) J. Yano, J. Kern, K. Sauer, M. J. Latimer, Y. Pushkar, J. Biesiadka, B. Loll, W. Saenger, J. Messinger, A. Zouni, V. K. Yachandra, *Science* **2006**, *314*, 821; b) T. J. Meyer, M. H. V. Huynh, H. H. Thorp, *Angew. Chem.* **2007**, *119*, 5378; *Angew.*

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Chem. Int. Ed. **2007**, *46*, 5284; c) J. Dasgupta, G. M. Ananyev, G. C. Dismukes, *Coord. Chem. Rev.* **2008**, *252*, 347; d) J. Barber, *Chem. Soc. Rev.* **2009**, *38*, 185.

[3] C. S. Mullins, V. L. Pecoraro, *Coord. Chem. Rev.* **2008**, *252*, 416.

[4] C. W. Cady, R. H. Crabtree, G. W. Brudvig, *Coord. Chem. Rev.* **2008**, *252*, 444.

[5] Storing the equivalent of today's energy consumption would require splitting 10^{15} mol water per year. This is about 100 times the scale of the Haber–Bosch reaction. The TON required depends on the abundance of the catalyst. See reference [9].

[6] a) S. W. Gersten, G. J. Samuels, T. J. Meyer, *J. Am. Chem. Soc.* **1982**, *104*, 4029; b) T. J. Meyer, *Acc. Chem. Res.* **1989**, *22*, 163.

[7] X. Sala, I. Romero, M. Rodríguez, L. Escriche, A. Llobet, *Angew. Chem.* **2009**, *121*, 2882; *Angew. Chem. Int. Ed.* **2009**, *48*, 2842.

[8] a) M. Hara, T. E. Mallouk, *Chem. Commun.* **2000**, 1903; b) H. Han, H. Frei, *J. Phys. Chem. C* **2008**, *112*, 16156.

[9] M. W. Kanan, D. G. Nocera, *Science* **2008**, *321*, 1072.

[10] a) Y. V. Geletii, B. Botar, P. Kögerler, D. A. Hillesheim, D. G. Musaev, C. L. Hill, *Angew. Chem.* **2008**, *120*, 3960; *Angew. Chem. Int. Ed.* **2008**, *47*, 3896; b) A. Sartorel, M. Carraro, G. Scorrano, R. De Zorzi, S. Geremia, N. D. McDaniel, S. Bernhard, M. Bonchio, *J. Am. Chem. Soc.* **2008**, *130*, 5006.

[11] a) N. D. McDaniel, F. J. Coughlin, L. L. Tinker, S. Bernhard, *J. Am. Chem. Soc.* **2008**, *130*, 210; b) J. F. Hull, D. Balcells, J. D. Blakemore, C. D. Incarvito, O. Eisenstein, G. W. Brudvig, R. H. Crabtree, *J. Am. Chem. Soc.* **2009**, *131*, 8730.

[12] R. Zong, R. P. Thummel, *J. Am. Chem. Soc.* **2005**, *127*, 12802.

[13] O. V. Ozerov, *Chem. Soc. Rev.* **2009**, *38*, 83.

[14] S. W. Kohl, L. Weiner, L. Schwartsburd, L. Konstantinovski, L. J. W. Shimon, Y. Ben-David, M. A. Iron, D. Milstein, *Science* **2009**, *324*, 74.

[15] J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840.

[16] J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2006**, *118*, 1131; *Angew. Chem. Int. Ed.* **2006**, *45*, 1113.

[17] C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790.

[18] For a recent overview of the cooperative chemistry of lutidine-based pincer systems, see: J. I. van der Vlugt, J. N. H. Reek, *Angew. Chem.* **2009**, *121*, DOI: 10.1002/ange.200903193; *Angew. Chem. Int. Ed.* **2009**, *48*, DOI: 10.1002/anie.200903193.

[19] J. Li, Y. Shiota, K. Yoshizawa, *J. Am. Chem. Soc.* **2009**, *131*, DOI: 10.1021/ja905073s.

[20] Water splitting is endothermic by 56.7 kcal mol^{-1}, disproportionation of H_2O_2 is exothermic by 27.9 kcal mol^{-1}, see: D. R. Lide, CRC Handbook of Chemistry and Physics, 83. Aufl., CRC Press LLC, London, **2002**.

[21] Reductive elimination of H_2O_2 from dihydroxytelluranes has been reported: M. R. Detty, *Organometallics* **1991**, *10*, 702.

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