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Water Oxidation: A Robust All-Inorganic Catalyst

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heterogeneous catalysis · oxidation · polyoxometalates · ruthenium · water

Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

Water is the most abundant molecular compound on Earth: it is omnipresent and essential for life. Water is a very stable compound because of its high formation enthalpy of $-286\,\text{kJ}\,\text{mol}^{-1}$, and thus the splitting of water into dihydrogen and dioxygen is a high-energy process—the thermal splitting of water requires temperatures above 2500 °C, and is still incomplete. Although the electrochemical splitting of water is efficient, it needs large amounts of fuel-consuming electrical energy. An alternative is the photocatalytic splitting of water, with the aim of storing solar energy in the form of high-energy chemicals—this is, however, a challenging problem.[1,2]

The splitting of water into its elements [Eq. (1)] can be divided into two steps: the oxidation of water to give dioxygen [Eq. (2)] and the reduction of water to give dihydrogen [Eq. (3)], with the oxidation potential being −0.82 V for Reaction (2) and the reduction potential being −0.41 V for Reaction (3), both measured at pH 7 versus the standard hydrogen electrode. Although much progress has been made in the reduction of water, the oxidation of water is more difficult because of its implicit complexity, since it requires the loss of four electrons and four protons from two water molecules.[3]

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \quad \Delta H_r^{\,0} = 286\,\text{kJ}\,\text{mol}^{-1} \tag{1}$$

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \quad E = -0.82\,\text{V (pH 7)} \tag{2}$$

$$4\,H_2O + 4\,e^- \rightarrow 2\,H_2 + 4\,OH^- \quad E = -0.41\,\text{V (pH 7)} \tag{3}$$

However, the oxidation of water is accomplished by nature during photosynthesis: this light-powered process takes place in green plants and in certain bacteria and converts carbon dioxide and water into carbon hydrates and dioxygen. In this permanently occurring natural reaction, the oxidation of water is coupled to the reduction of carbon dioxide, with the energy necessary for this process coming from sunlight. The goal of artificial photosynthesis is to mimic the photosynthetic apparatus of green plants to convert solar energy into chemical energy, with the photocatalytic oxidation of water giving dioxygen.[2]

The chemical approach to artificial photosynthesis by using synthetic nonprotein catalysts for the oxidation of water was pioneered by Meyer and co-workers in the early 1980s.[2] The "ruthenium blue dimer" ($[Ru_2(bpy)_4(H_2O)_2(\mu_2\text{-}O)]^{4+}$), an oxo-bridged dinuclear ruthenium complex with 2,2′-bipyridine (bpy) ligands, efficiently catalyzes the oxidation of water with a strong oxidizing agent such as cerium(IV); however, it rapidly loses its catalytic efficiency after just a few cycles.[4,5] A related oxo-bridged diruthenium complex containing 2,2′-bipyridyl-5,5′-dicarboxylic acid (Hbpd) ligands, $[Ru_2(Hbpd)_4(H_2O)_2(\mu_2\text{-}O)]^{2+}$, was found by Grätzel and co-workers to catalyze the oxidation of water with cobalt(III) species.[6]

A new impetus in this field came in 2004, when Llobet and co-workers reported a highly active catalyst that does not contain an oxo bridge, namely $[Ru_2(trpy)_2(H_2O)_2(\mu_2\text{-}bpp)]^{2+}$ (trpy = 2,2′,6,2″-terpyridine, Hbpp = 2,2′,6,2″-bipyridylpyrazol), for the oxidation of water.[7] Instead, the two ruthenium centers had been deliberately placed in proximity and in a appropriate orientation by the bpp bridging ligand. This complex, which is superior to the oxo-bridged diruthenium complexes as a water-splitting catalyst, shows high rates for the oxidation of water with cerium(IV) at pH 1, but eventually also undergoes deactivation—presumably by ligand oxidation.[7] A similar approach was used by Zong and Thummel, who synthesized the cations $[Ru_2(py)_4(\mu\text{-}bnp)(\mu\text{-}Cl)]^{3+}$ containing the bridging pyridazine-based ligand 3,6-bis[6′-(1″,8″-naphthyrid-2″-yl)-pyrid-2′-yl]pyridazine (bnp) and four terminal substituted pyridine ligands (py = NC_5H_4-4-R; R = Me, CF_3, NMe_2).[8] However, the high catalytic turnovers (up to 3200) of these cations claimed for the oxidation of water with cerium(IV) at pH 1 were due to a calibrating error of the oxygen-measuring device and had to be corrected.[9] Earlier this year, Bernhard and co-workers reported cyclometalated phenylpyridine–iridium(III) complexes of the type $[Ir(H_2O)_2(ppy)_2]^+$ (Hppy = 5-R-4-R′-2-phenylpyridine; R = H, Me, R′ = H, Ph, F, Cl), which are highly active as catalysts for the oxidation of water (turnover numbers up to 2760) working in acidic solution (pH 0.7) with cerium(IV),[10] and which are said to be simultaneously simple, robust, and effective despite the organic nature of the ligands.[3]

There is, however, a large body of evidence that likely intermediates in the oxidation of water may degrade organic ligands,[11] thus stimulating the search for catalysts that are solely inorganic in nature. This major problem has now been overcome by a new purely inorganic homogeneous catalyst based on a ruthenium-containing polyoxometalate

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$[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ (**1**) that was independently synthesized and characterized by two research groups.

Hill and co-workers synthesized **1** from potassium γ-decatungstosilicate and ruthenium(III) chloride in acidic aqueous solution in the presence of air according to Equation (4); after addition of rubidium chloride, the mixed rubidium potassium salt $Rb_8K_2[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]\cdot 25\,H_2O$ (Rb_8K_2[**1**]$\cdot 25\,H_2O$) was obtained in 40% yield.[12] Bonchio and co-workers assembled **1** in a "Lego-type" approach by combining directly the tetraruthenium(IV) complex $[Ru_4O_6(H_2O)_n]^{4+}$,[13] prepared in situ from $[Ru_2Cl_{10}(\mu\text{-}O)]^{4-}$, with two lacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ ions according to Equation (5); in addition to the water-soluble lithium salt $Li_{10}[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]$ (Li_{10}[**1**]), the cesium salt $Cs_{10}[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]$ (Cs_{10}[**1**]) was also isolated (for X-ray analysis) in 85% yield.[14]

$$\begin{aligned}&2\,[SiW_{10}O_{36})_2]^{8-} + 4\,[Ru(H_2O)_6]^{3+}\\&\rightarrow [\{Ru_4O_4(OH)_2(H_2O)_4\}(SiW_{10}O_{36})_2]^{10-} + 6\,H^+ + 18\,H_2O\end{aligned} \tag{4}$$

$$\begin{aligned}&2\,[SiW_{10}O_{36})_2]^{8-} + [Ru_4O_6(H_2O)_n]^{4+} + O_2\\&\rightarrow [\{Ru_4O_4(OH)_2(H_2O)_4\}(SiW_{10}O_{36})_2]^{10-} + 2\,OH^- + (n{-}6)\,H_2O\end{aligned} \tag{5}$$

Given the known catalytic activity of diruthenium complexes for the oxidation of water,[4–9] and the well-documented ability of polyoxometalates to stabilize high-valent intermediates by their electron-withdrawing nature,[15,16] the synthesis of **1** was not based on serendipity but on design, despite the complexity of this tetraruthenium polyoxometalate. With anion **1**, the authors succeeded in the synthesis of an oxidatively and hydrolytically stable complex that indeed catalyzes the rapid oxidation of H_2O to O_2 in aqueous solution, thus addressing the core challenges of this research field.

The four ruthenium centers in **1** (Figure 1) are in the oxidation state +IV, which is not only consistent with elemental analysis and bond valence sum considerations, but is also evident from the magnetic properties (d^4-Ru^{IV} centers are diamagnetic, while d^5-Ru^{III} centers are paramagnetic) and electrochemical measurements on **1**.[12] It was also shown by spectrophotometric titration that **1** undergoes a reversible monoprotonation in aqueous solution, with the acid–base equilibrium being concentration-independent, thus ruling out dissociation or aggregation of the polyoxometalate framework.[14]

Bonchio and co-workers demonstrated the catalytic potential of Li_{10}[**1**] for the oxidation of water in acidic solution (pH 0.6) at 20 °C by using the cerium(IV) salt $(NH_4)_2Ce(NO_3)_6$ as the oxidant, and obtained up to 500 turnovers within two hours (based on the evolved oxygen), with an overall yield of 90% with respect to the oxidant added. The maximum turnover frequency was $450\,h^{-1}$; further addition of cerium(IV) induced an equivalent evolution of oxygen.[14] As the electrochemical results for **1** pointed to an electrocatalytic oxidation of water at low potentials (950–1050 mV) at pH 7, Hill and co-workers evaluated the use of Rb_8K_2[**1**]$\cdot 25\,H_2O$ as a homogeneous catalyst for the oxidation of water in neutral aqueous solution by using $[Ru(bpy)_3]^{3+}$ as an oxidizing agent.

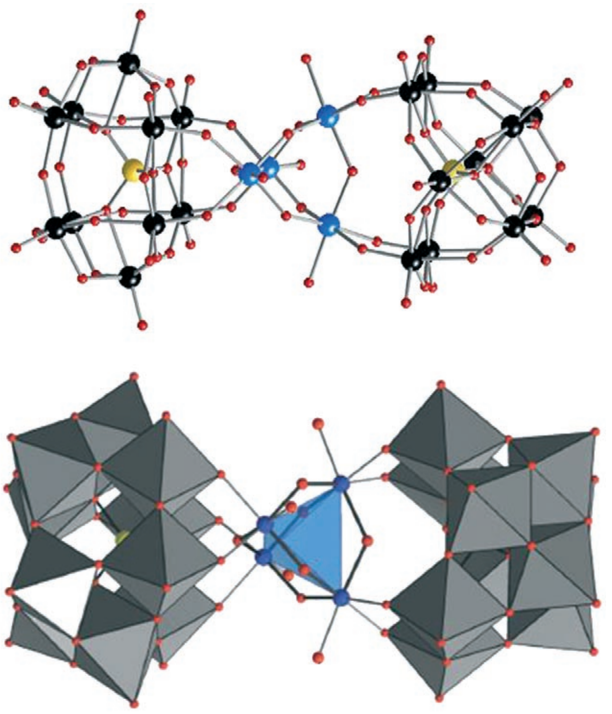

Figure 1. Molecular structure of the anion $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ (**1**), with the central $\{Ru_4O_4(OH)_2(H_2O)_4\}$ core highlighted (the ruthenium atoms spanning a slightly distorted tetrahedron are in blue) and the two (γ-$SiW_{10}O_{36}$) units shown in ball and stick representations (top) or as gray polyhedra (bottom). Yellow Si, black W, red O. Reproduced from Ref. [12].

Rb_8K_2[**1**]$\cdot 25\,H_2O$ catalyzes Reaction (6) under ambient conditions at pH 7 (phosphate buffer), giving 18 turnovers after 30 to 40 s; the catalyst is reported to be highly active and stable under turnover conditions. The catalytic activity is, unfortunately, not unambiguously described in Ref. [12]: It is said that the "highly active" water oxidation catalyst **1** gives a turnover number of 18 moles of O_2 per mole of **1**, the reaction being complete after 30 to 40 seconds. However, nothing is said about a possible continuation of the catalytic reaction on further addition of $[Ru(bpy)_3]^{3+}$, **1** is only said to be "quite stable under turnover conditions".[12] Since **1** continues to reproduce oxygen from water under acidic conditions after further addition of cerium(IV),[14] it may also continue to be active under neutral conditions. Catalysis by RuO_2, a conceivable decomposition product of **1**, was ruled out, since carrying out the catalytic reaction in the presence of $RuCl_3$ under otherwise identical conditions had only a minor effect. Finally, the oxidation of H_2O, catalyzed by **1** using ^{18}O isotopically labeled water, proves the two oxygen atoms in O_2 are indeed derived from H_2O.[12]

$$4\,[Ru(bpy)_3]^{3+} + 2\,H_2O \xrightarrow{\mathbf{1}} 4\,[Ru(bpy)_3]^{2+} + O_2 + 4\,H^+ \tag{6}$$

An interesting experiment to be done in this context would be the photochemical regeneration of $[Ru(bpy)_3]^{3+}$ from its reduced form $[Ru(bpy)_3]^{2+}$. It is well documented that the ruthenium(II) complex $[Ru(bpy)_3]^{2+}$ is susceptible to the absorption of light in the near –UV/Vis region as a result of metal-to-ligand charge-transfer transitions,[17] in which an electron is promoted from a metal-based t_{2g} orbital to a low-lying π* orbital of the bipyridine ligand, thus converting $[Ru^{II}(bpy)_3]^{2+}$ into $[Ru^{III}(bpy)_2(bpy^{\bullet -})]^{2+}$. The excited state $[Ru^{III}(bpy)_2(bpy^{\bullet -})]^{2+}$ may undergo quenching before it can decay by $\pi^*\text{–}e_g$ transitions. Such a quenching reaction could be an oxidation with a sacrificial oxidant such as the paraquat dication (1,1′-dimethyl-4,4′-bipyridinium, paq^{2+}) as shown in Equation (7), thus closing the light-harvesting cycle.[2]

$$[Ru^{III}(bpy)_2(bpy^{\bullet -})]^{2+} + paq^{2+} \rightarrow [Ru(bpy)_3]^{3+} + paq^{+} \quad (7)$$

The design of a highly active, totally inorganic catalyst for the oxidation of water that is stable under turnover conditions may be considered as a breakthrough for this difficult reaction, since for the first time one of the major problems, the oxidative degradation of the catalyst by the intermediates, has been overcome. There is, however, still a long way to go before a better understanding of the functioning of this new all-inorganic material will offer the real prospect of a tunable catalyst.

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