Consecutive Thermal H₂ and Light-Induced O₂ Evolution from Water Promoted by a Metal Complex

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Discovery of an efficient artificial catalyst for the sunlight-driven splitting of water into oxygen and dihydrogen is a major goal of renewable energy research. We describe a solution-phase reaction scheme that leads to the stoichiometric liberation of dihydrogen and dioxygen in consecutive thermal- and light-driven steps mediated by mononuclear, well-defined ruthenium complexes. The initial reaction of water at 25°C with a deamidated ruthenium (II) [Ru(II)] pincer complex yields a monomeric aromatic Ru(II) hydrido-hydroxo complex that, on further reaction with water at 100°C, releases H₂ and forms a cis dihydroxo complex. Irradiation of this complex in the 320-to-420-nanometer range liberates oxygen and regenerates the starting hydrido-hydroxo Ru(II) complex, probably by elimination of hydrogen peroxide, which rapidly disproportionates. Isotopic labeling experiments with H₂¹⁸O and H₂¹⁷O show unequivocally that the process of oxygen–oxygen bond formation is intramolecular, establishing a previously elusive fundamental step toward oxygen-generating homogeneous catalysis.

The design of efficient catalytic systems for splitting water into H₂ and O₂, driven by sunlight without the use of sacrificial reductants or oxidants, is among the most important challenges facing science today, underpinning the long-term potential of hydrogen as a clean, sustainable fuel (1, 2). In this context, it is essential to enhance our basic understanding of the fundamental chemical steps involved in such processes (3–17). Of the two parts of the water-splitting cycle, the oxidation half-cycle to form O₂ presents the greatest challenge. Well-defined metal complexes that catalyze water oxidation to oxygen bond formation remains a considerable challenge. In addition, a major challenge faced by hydrogen and oxygen photogeneration systems based on soluble metal complexes is that for a viable system, the two half-cycles must be combined, avoiding the use of sacrificial oxidants and reductants. We present here a ruthenium-mediated reaction sequence that, in a stepwise stoichiometric manner, generates hydrogen thermally and oxygen photochemically, involves well-defined complexes, and demonstrates the feasibility of unimolecular O–O bond formation at a single metal center.

References and Notes
26. See supporting material on Science Online.
31. Although detailed cost analysis of these Fe-based electrocatalysts was not performed, their principal elements are carbon, nitrogen, and iron and they require no expensive precursors or processing steps. Their manufacturing cost is conservatively estimated to be at least two orders of magnitude lower than that of current Pt-based ORR catalysts for PEMFCs.
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Supporting Online Material
www.sciencemag.org/cgi/content/full/324/5923/71/DC1
Materials and Methods
SOM Text
Figs. S1 to S4
Tables S1 and S2
References
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We have previously reported that the non-aromatic pincer Ru(II) complex 1 (Fig. 1) is a powerful catalyst for the coupling of alcohols to form esters with the liberation of H₂ (18) and for the dehydrogenative coupling of alcohols with amines to produce amides (19). We have now studied the reactivity of this complex with water. The addition of one equivalent of water to a solution of 1 in tetrahydrofuran (THF) at room temperature immediately led to ligand aromatization with quantitative formation of the trans hydrido-hydroxo complex 2 (Fig. 1), which we isolated and fully characterized (20). This compound is probably formed by a mechanism involving coordination of water at the vacant coordination site trans to the hydride ligand, followed by proton migration to the side arm. This unique water activation process involves cooperation between the metal and the ligand and no change in the metal oxidation state (21).

Characteristic spectroscopic features in the ^1H nuclear magnetic resonance (NMR) spectrum of 2 are the large downfield shift of the hydride ligand resonance from –26.5 parts per million (ppm) (d, J^hed = 25.5 Hz) in 1 to –14.9 ppm (d, J^hed = 27.5 Hz) and a doublet at –1.4 ppm (J^hed = 2.3 Hz) assigned to the hydroxo ligand. If one equivalent of D₂O is used instead of H₂O, one deuterium atom is incorporated at the side-arm benzyllic carbon, leading to a broad peak (because of unresolved small J^hed and J^hed) at 2.8 ppm in the ^1H NMR spectrum; the OD group gives rise to a signal at –1.2 ppm (complex 2-D₂, Fig. 1). These reactions are reversible. Placing the solid under vacuum or heating it in benzene solution at 65°C resulted in water elimination to quantitatively yield the starting complex 1. Direct spectroscopic evidence for coordination of the hydroxo group to the metal center was obtained by adding one equivalent of H₂O to 1 in THF. The oxygen atom in the labeled complex 2-HO exhibits a singlet at 32.43 ppm in the ^17O NMR spectrum (in THF). Coupling (J^O,P, 2^O,P) of the ^17O atom (S = 5/2) with the adjacent ligands leads to broadening of the signal in the ^31P NMR spectrum at 112.14 ppm and the appearance of a more complicated signal for the carbonyl ligand in the ^13C[^1H] NMR spectrum (δ = 209.27 ppm). The doublet in the ^1H NMR spectrum (δ = 14.78 ppm) assigned to the hydride ligand in the trans position is not affected.

Repeating the reaction in benzene by adding an excess of water to 1 resulted in formation of colorless crystals at the interface between the water and benzene layers. X-ray diffraction analysis of the isolated solid (2nH₂O) shows a distorted octahedral coordination geometry at ruthenium (Fig. 2). The Ru–O–H non-linear angle [103(3)] indicates repulsion between the oxygen lone pairs and d electrons of the complex (22, 23). The crystals are composed of alternating layers of the metal complex, benzene, and water. The hydroxo groups of the complex are involved in hydrogen bonding with the water layer (Figs. S4 to S6). These crystals are stable below 10°C and release the solvated water at room temperature.

Heating complex 2 (or 2nH₂O) in refluxing water for 3 days resulted in evolution of H₂ with concomitant formation of the green dihydroxo complex 3 (Fig. 3). The gas was collected in a burette, and hydrogen was detected by the reaction of a sample of the gas phase with (PEt₃)₃IrCl to form mer-cis-(PEt₃)₃Ir(H₂)Cl (24). H₂ was quantified with gas chromatography (GC) (yield: 37%). The NMR yield of the complex 3 was 45%. Some unreacted 2nH₂O (25%) remained, the rest being unidentified products. This reaction may proceed by electrophilic attack by water on the hydride ligand. Pure 3 was independently prepared by reaction of 2nH₂O with N₂O (25, 26); N₂O was bubbled into a THF solution of 2nH₂O for 10 min at room temperature, after which the solution was stirred overnight and turned green. We isolated and fully characterized the result-
ant green microcrystalline solid 3 (60% yield). It is stable in a THF solution up to 65°C but decomposes into unidentified products at 102°C in dioxane. The 31P{1H} NMR spectrum of 3 shows a singlet at 94.0 ppm, representing an upfield shift of 14 ppm relative to the corresponding singlet of complex 2. The two tert-butyl (tBu) groups of PtBu2 give rise to different signals in both the 1H and 13C{1H} NMR spectra, and the ethyl groups of NEt2 are also non-equivalent, indicating C1 symmetry and a cis dihydroxo arrangement. The hydroxo ligands give rise to a broad signal at –7.4 ppm in the 1H NMR spectrum and absorb at 3413 cm⁻¹ in the infrared (IR) spectrum. The carbonyl ligand exhibits a doublet at 207.4 ppm (2JPC = 16.1 Hz) in the 13C{1H} NMR spectrum and absorbs at 1923 cm⁻¹ in the IR spectrum. The main peak in the mass spectrum (electrospray ionization) at mass/charge ratio (m/z) = 453 (100) can be assigned to the cation [M – OOH]⁺ and the peak at m/z = 469 (18) is characteristic for [M – OH]⁺. Elemental analysis agrees with the calculated values for our posited structure.

We next studied the stability of complex 3 on exposure to light. Irradiation of THF or aqueous solutions of 3 under N₂ or Ar with a 300-W halogen lamp filtered through perspex (27) over 2 days resulted in a color change from green to greenish-yellow, accompanied by O₂ evolution. NMR of the solution showed that besides unreacted 3 (33%), the hydrido-hydroxo complex 2·nH₂O (45%) was formed, in addition to some unidentified by-products (22%), most probably phosphine oxides (Fig. 3). The liberated gas was identified as dioxygen by GC–mass spectrometry (GC-MS) and by the reaction with (PEt₃)₃IrCl to form the dioxygen complex (PEt₃)₃Ir(O₂)Cl (20). This specific and very sensitive reaction was also used for quantification (20). The yield of the detected dioxygen formed from the reaction in water was 23% (34% based on reacted 3). When irradiation of aqueous solutions of 3 was performed under argon flow to remove the generated O₂, clean conversion of 3 (49%) to 2·nH₂O (49%) was observed, with no by-products being formed, indicating that the unidentified by-products are a result of reaction with the generated dioxygen.

To verify that O₂ was released from the dihydroxo complex, a labeled complex bearing two 18O groups (3-18O18O) was prepared using H₂18O (Fig. 4). The 18O–H stretching vibration is shifted in the IR spectrum to lower energy by 14 wavenumbers, to 3399 cm⁻¹, whereas all NMR spectra are identical to those of 3. Upon irradiation (27) of 3-18O18O in H₂O, 36O₂ was formed as the major dioxygen product, as confirmed by GC-MS (Fig. 4A and fig. S3A). No exchange between 3-18O18O and H₂16O was observed, indicating that no substantial Ru-OH dissociation took place.

An important question is whether the O–O bond formation process is intra- or intermolecular. To address this issue, we prepared the isotopically mixed-labeled dihydroxo complex 3-18O16O by treatment of 2-18O with N₂16O (Fig. 4A). Upon photolysis, 34O₂ was formed predominantly with only small amounts of 32O₂ and 36O₂ observed (observed ratio 32O₂:34O₂:36O₂, 3.8:16.2:1) (fig S3B) (20). Moreover, we performed a crossover experiment involving photolysis of equimolar amounts of complexes 3-18O18O and 3-16O16O, resulting in formation of 36O₂ and 32O₂ with only a small amount of 34O₂ (observed ratio 32O₂:34O₂:36O₂, 13.1:1:15.6) (Fig. 4B). Thus, our results unambiguously show that the O-O

Fig. 4. Photolysis of isotopically labeled dihydroxo complexes. (A) Synthesis and photolysis of complexes 3-18O18O and 3-18O16O. (B) Mass spectrum of a gaseous extract from the photolytic reaction of equimolar amounts of 3-18O18O and 3-18O16O, showing virtually no crossover.

Fig. 5. Proposed mechanism for the formation of H₂ and O₂ from water.
forms photolitically from 3 and undergoes disproportionation to O2 and water, with only a marginal amount of it forming hydroxyl radicals, perhaps by a Fenton-type reaction. As expected, no OH radicals were detected when the hydroxido-hydroxyl complex 2nH2O was irradiated.

Combining the separate stoichiometric reactions presented here gives rise to a stepwise cycle in which H2 and O2 are released in consecutive steps, and the starting Ru complex is regenerated (Fig. 5). The cycle starts with the trans hydroxydihydroxyl complex 2nH2O that reacts with water under refluxing conditions, evolving H2 and forming the cis dihydroxy complex 3. The second step is light-induced. Irradiating 3 may release hydrogen peroxide by reductive elimination, probably forming a Ru(0) intermediate, which converts to 1 by migration of a proton from the methylene group of the phosphorus side arm to the ruthenium center to form a hydride ligand with coincident dearomatization of the pyridine ring (34, 35). The liberated hydrogen peroxide is then rapidly catalytically decomposed into dioxygen and water. A possible catalyst for this latter reaction is complex 1. The addition of a very dilute THF solution of 1 to a THF solution of hydrogen peroxide at room temperature resulted in immediate O2 evolution, as detected by GC-MS and by reaction with (PMe2)3Cl (20). In the last step of the cycle, the water reacts readily with 1 to form the starting complex 2.

We believe that our studies indicate a distinct approach toward a complete cycle for the generation of dihydrogen and dioxygen from water catalyzed by metal complexes and show that light-induced O–O bond formation can be intramolecular and need not necessarily involve bimolecular mechanisms, dinuclear complexes, and metal oxo intermediates.

References and Notes