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Article

Forum

Preface on Making Oxygen

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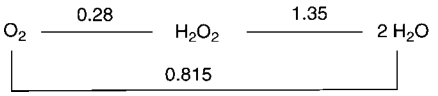
Imagine a planet whose atmosphere is irreversibly changed by the dominant lifeform inhabiting it. The lifeform releases a gas—a waste gas—trillions and trillions of tons of it. The atmosphere becomes so altered that evolution on the planet is forever changed. Science fiction? Not at all! The planet is Earth, but the waste gas is not carbon dioxide and the time is not now. Instead, the unwanted gas is oxygen, the subject of this issue's Forum, and the time is long, long ago. On primordial Earth, the atmosphere was reducing, most likely made up mainly of nitrogen, methane, ammonia, and water vapor. While oxygen is the most abundant element in the Earth's crust, it did not exist in the atmosphere in primordial times to even a small fraction of the extent that it does today.

What happened to cause such a change was the appearance of cyanobacteria that carried out photosynthesis for storing chemical energy in carbohydrate molecules. In this remarkable process, solar photons drive the reduction of oxidized or metabolized carbon by water in a reaction in which molecular oxygen is the oxidation product. More than two billion years ago, photosynthesis transformed Earth's environment from reducing to oxidizing, with the result that today a powerful—and very essential—diatomic oxidant makes up one-fifth of the air we breathe.

The Forum on Making Oxygen focuses on the oxidation of water in both biological and abiological systems. Understanding the fundamental factors that control this complex four-electron, four-proton reaction is one of science's grand challenges because research progress in this area is absolutely essential for the development of efficient artificial photosynthetic machines to convert sunlight into stored chemical energy on an enormous scale. The main goal is the light-driven splitting of water to generate hydrogen, but other solar fuels could be produced with protons and electrons extracted from water. (The solar-driven reduction of carbon dioxide to methanol is one very attractive target.) However, first we must learn how to make oxygen!

Molecular oxygen played a leading role in the birth of modern chemistry, when Priestley and Scheele first described making it and Lavoisier made it famous through his brilliant investigations of its properties. Some say that the Lewis structure of oxygen (which students write every day) is wrong because it shows only paired electrons, and we all know that the molecule is paramagnetic. Seeing blue liquid oxygen trapped between the poles of a magnet demonstrates in spectacular fashion the molecule's paramagnetism. Indeed, an early success of molecular orbital theory was the prediction that the diatomic molecule should be paramagnetic, with a spin-triplet ground state. The triplet spin of oxygen confers on it a sluggishness in terms of its reactivity in the absence of a catalyst. This sluggishness is a good property because if oxygen could react rapidly with proteins and nucleic acids without a catalyst present, we would not be here at all and life on Earth would have taken a far different turn.

One might think that the total synthesis of a diatomic molecule should not be that complicated, but the problem is fraught with many twists and turns. An analysis of the challenge of making oxygen from water logically begins with thermodynamic considerations. In our world, water and carbon dioxide occupy unique positions as the thermodynamic sinks for the oxidation of hydrogen and carbon in organic compounds. Consider first the reduction potentials for dioxygen species in the simplified Latimer diagram below:



Each number corresponds to the standard reduction potential *adjusted to pH 7* connecting the two species linked by the line. To adjust to standard conditions with 1 M acid,

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each value should be incremented by 0.415 V. Even at pH 7, however, ΔE for the *overall* water-splitting reaction remains the same because it is under standard 1 M acid conditions at -1.23 V. The diagram also reveals that if the oxidation of water to oxygen were done via intermediate formation of free hydrogen peroxide, then the initial two-electron oxidation would be an additional 0.53 V less favorable than the overall four-electron transformation. Thus, to avoid prohibitively high-energy barriers, the four electrons must be extracted from two water molecules in a highly choreographed manner that may involve multielectron processes and will allow stabilization of oxidized intermediates. Additionally, the extraction of electrons must be balanced with the removal of protons (though not necessarily to the same place) to avoid a buildup of excess charge that would otherwise unfavorably impact subsequent reduction potentials. Also, all of these processes must be done in a way that the catalyst itself is not irreversibly degraded. Suddenly the seemingly simple synthesis of a diatomic molecule has become a staggering problem!

It is against this backdrop that the Forum on Making Oxygen is presented. The Forum opens with a contribution from Jim Barber revealing details of the structure of the natural photosynthetic apparatus known as photosystem II (PSII) that is embedded in the thylakoid membranes of plants, algae, and cyanobacteria. The site where water is oxidized is an oxo-bridged cluster of four Mn ions and one Ca^{2+} that is linked to the protein by a number of amino acid side chains. Crystallographic results for PSII yield information on the structure of the oxygen-evolving complex (OEC), although at current resolution, there is uncertainty in aspects of the detailed bonding arrangement. Barber and others subsequently discuss how charge separation is achieved in PSII as the system cycles through five states, designated as S_0-S_4, that differ in metal valence, proton content, and overall charge. In another OEC paper, Junko Yano and Vittal Yachandra report a model of the structure of the oxo-bridged Mn_4Ca cluster based on X-ray absorption and emission spectroscopic experiments that reveal features different from those found by crystallography. The authors also discuss the structures of the OEC catalytic center as it cycles through the four S states originally proposed by Bessel Kok. A different experimental perspective is provided by Dave Britt and co-workers using pulsed electron paramagnetic resonance methods and, in particular, multifrequency electron spin–echo envelope modulation spectroscopy. From their data, detailed information about the structure and coordination geometry of the S_2 state can be extracted, including the latest picture of the so-called ”dangler” model of the Mn_4Ca cluster.

Per Siegbahn reports theoretical and computational investigations of arguably the most critical step in the catalysis of oxygen evolution, namely, O–O bond formation. His article highlights the interplay of theory and experiment in elucidating the mechanism of the reaction. A different approach to the challenge of O–O bond formation is taken by Ted Betley and Dan Nocera in an article that focuses on the basis of metal−oxo bonding and its implication for O–O coupling through either an ”even electron” acid–base mechanism or a radical coupling model. Their article also reports new ligand scaffolds that test the viability of O–O bond-forming proposals.

Two papers address the issue of metal complex models for the OEC from structural and functional viewpoints. One, by Vince Pecoraro and co-workers, places efforts in their laboratory over the last 2 decades firmly in the context of developments regarding the structure and spectroscopy of the PSII OEC. Their work serves to guide the design and study of new model compounds for different OEC intermediate states that to date have been very difficult to investigate. The other paper, coauthored by Ranit Tagore, Bob Crabtree, and Gary Brudvig, deals with a dinuclear manganese μ-oxo *functional* model of the OEC with oxygen evolution obtained using HSO_5^- as the oxidant. By monitoring of the reaction by UV–vis spectroscopy, the oxidation states of manganese in the model complexes were probed under catalytic conditions.

While manganese is the redox-active metal in the OEC, inorganic chemists pursuing an artificial photosynthetic system for water splitting have enjoyed success in the design and development of catalysts based on ruthenium for oxygen evolution. This work began nearly 30 years ago when Tom Meyer and his group discovered an oxo-bridged dinuclear complex that in its resting state became known as the “blue dimer”. The origin of this research had its roots in the realization that the lowest electronic excited states of $Ru(bpy)_3^{2+}$ and related complexes possess reduction potentials that, in principle, could drive water splitting. The contribution by Meyer and co-workers recounts the story of this work and why the blue dimer is special in catalyzing water oxidation. The article also includes an instructive section on proton and charge management in water oxidation catalysis with a discussion of proton-coupled electron transfer and an analysis relating the mechanism proposed for oxygen formation by the blue dimer with that in the OEC. Some of the complexities of water oxidation by the blue dimer and related oxo-bridged ruthenium bipyridine dinuclear complexes are revealed in another Forum contribution by Jim Hurst and co-workers using ^{18}O isotope labeling studies, and a more efficient catalyst system that functions under neutral and alkaline conditions rather than the acidic media used by others is also presented.

The design and synthesis of new ruthenium dinuclear systems for water oxidation are reported in other Forum contributions. An article by Randy Thummel and co-workers outlines an approach in which new bridging ligands are created that will hold the metal ion assembly intact throughout the full water oxidation redox cycle. Several resultant complexes incorporating these ligands catalyze water oxidation using ceric ion as the oxidant. A contribution by Jim Muckerman, Etsuko Fujita, and Koji Tanaka focuses on a related dinuclear system reported by Tanaka that exhibits excellent electrocatalytic activity for oxygen generation. This system features a redox-active quinone/catecholate ligand attached to each ruthenium center. On the basis of density functional theory calculations, it is proposed that the ruthenium centers are redox-inactive during reactions in which oxidizing equivalents are generated via catecholate-to-quinone conversions. Yet another perspective is offered in the final Forum paper by Antoni Llobet highlighting distinctive features of ruthenium-based oxidation catalysts.

We know that you will find the articles in our Forum interesting and stimulating, as they show vividly how fundamental research in inorganic chemistry is central to the development of viable systems for the oxidation of water to oxygen. From a practical standpoint, we must learn how to run this reaction efficiently if we ever are to realize the dream of obtaining clean fuel from sunlight and water on a scale that would provide enough energy to power our planet.

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