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ON THE FORMATION OF DIOXYGEN FROM WATER

by

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SUMMARY Water may be oxidized to dioxygen (O_2) by a variety of chemical processes including electrolysis, acidic cobaltic ion, hypochlorite, complexed ferric or ruthenium ions, etc., and also by natural photosynthesis. Usually the high energy intermediate chemical species appear to be higher oxides, or peroxide-like compounds, and the dioxygen produced is poorer in ^{18}O than the original water. In natural photosynthesis the intermediate chemical species involve manganese and the dioxygen produced is enriched in ^{18}O. The formation of dioxygen from water might be facilitated by special large catalytic molecules which help to bring two O atoms together from two water molecules while four electrons are withdrawn from the system.

KEY WORDS

water oxidation, oxidizing agents, peroxide, superoxide, oxygen

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ON THE FORMATION OF DIOXYGEN FROM WATER

R. H. Wentorf, Jr.

I. Introduction

The formation of dioxygen (O_2) from water is an important step in natural photosynthesis and also in the electrolysis of water. The details of the chemical steps involved in these important processes are not yet thoroughly understood. Several other chemical processes are known in which dioxygen is formed from water or hydorxyl ions. Consideration of these various processes in the light of current chemical knowledge may indicate new approaches to the problem of facilitating the formation of dioxygen from water. The basic problem is to combine the separate O atoms of water molecules into the joined O atoms of O_2 while transferring 4 electrons.

II. General Considerations

The overall chemical reaction involved is

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

for which the net free energy change at 25°C, and one atmosphere is about 56.7 kcal, corresponding to an electrode potential difference of 1.23 volt for the reversible reaction. The reversible reaction can occur on carefully prepared (oxidized) Pt electrodes at low current densities ($<40\ \mu A\ cm^{-2}$) (Ref. 1, p. 715). With most other electrode surfaces the voltage required to liberate O_2 is higher, owing to the formation of intermediate chemical species of higher free energy content. Such species include peroxides ($O_2^=$, HO_2^-, H_2O_2), superperoxides (O_2^-, HO_2), the superperoxide radical (HO_2^-), the hydroxyl radical (OH), etc.

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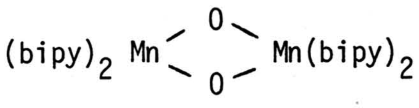
Various chemical (non-electrolytic) reactions are known by which strong oxidizing agents cause the formation of dioxygen from water. These will be discussed more fully below. It is interesting to consider some of the O-O separation distances in various compounds:

TABLE I

Compound	O-O Distance, Å	Reference
O_2	1.21	(1)
O_2^-, HO_2	1.28-1.35	(1)
HO_2'	1.30-1.35	(1)
$O_2^{=}$, H_2O_2	1.48-1.50	(1)
O_3	1.28	(1)
H_2O ice	2.76	(1)
$O^{=}$ oxides	2.7-2.8	(1)
Hemoglobin	1.30	(2)
$O_2Ir(CO)Cl(P\phi_3)_2$	1.30	(2)
$O_2Ir(CO)I(P\phi_3)_2$	1.50	(2)
$[(HN_3)_5CoO_2Co(NH_3)_5]^{4+}$	1.45	(3)
$O_2Pt(P\phi_3)_2$	1.45	(2)
	2.43	(4)

One notes that for O-O separations of about 1.35Å or less, O_2 formation is not particularly difficult. For example, hemoglobin, an iron porphyrin, absorbs and desorbs O_2 relatively easily, the O-O distance thereby changing between 1.21 and 1.30Å.

The estimated free energy changes for the following reactions are also worth noting:

TABLE II

Reaction	ΔG, kcal
$H_2O \rightarrow H_2 + \frac{1}{2} O_2$	56.7
$H_2O \rightarrow H_2 + O$	118
$H_2O \rightarrow HO + H$	120
$HO \rightarrow O + H$	102
$O_2 \rightarrow 2O$	119
$HOOH \rightarrow 2H + O_2$	136
$HOOH \rightarrow 2OH$	52
$HOOH \rightarrow H_2 + O_2$	32
$HOOH + H_2O \rightarrow HO_2^- + H_3O^+$	0
$HO_2^- + OH^- \rightarrow H_2O + O_2 + 2e^-$	-4
$3OH^- \rightarrow H_2O + HO_2^- + 2e^-$	40
$H_2O + \frac{1}{2} O_2 \rightarrow HOOH$	28
$2H_2O \rightarrow 2HOOH + 2H^+ + 2e^-$	81

The values in Table II indicate that the lowest energy requirement for forming O_2 from H_2O is the four-electron transfer reaction

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \rightarrow O_2 + 2H_2.$$

However, the simultaneous transfer of 4 electrons is a relatively unlikely event. One or two-electron transfers are more likely, but then the intermediate species such as O or HO require considerable energy to form unless they are in effect stabilized by association with other chemical species which would function as catalysts. In the absence of such species, a compromise may be reached in the two-electron transfer formation of peroxide, HOOH, with an energy requirement of 81 kcal, followed by the relatively easy decomposition of peroxide, another two-electron process.

With these thoughts in mind, it seems appropriate next to examine the various chemical reactions which are known to produce oxygen in aqueous systems.

III. Chemical Reactions Which Produce Dioxygen in Aqueous Systems

1. Electrolysis. Although this method is widely used, the mechanisms of oxygen formation are not clear in most cases. With the exception of O_2 formation on an oxidized Pt anode at low current densities, most electrolytic O_2 formation involves an extra potential drop known as "oxygen overvoltage". This overvoltage usually depends on the current density and the anode material, and is lowest for Group VIII metals such as Ni, Co, Pt, etc. Peroxide, OOH^-, is believed to be an intermediate in many cases, and oxide on the anode often is found to exchange oxygen with water. The dioxygen involved is usually depleted in ^{18}O from a wide variety of anode materials and over a wide pH range (Ref. 5) (For a brief discussion of isotope effects, see the Appendix to this paper. A general rule is: "At equilibrium, the heavier isotope is more firmly bound.")

2. $F_2 + H_2O \rightarrow HF + O_2 + O_3 + H_2O_2$, etc. Fluorine (itself prepared by

electrolysis) is a powerful oxidizing agent. Several oxygen-fluorine compounts (OF_2, O_2F_2, O_2F, etc.) exist (Ref. 1). OF_2 is prepared from F_2 and dilute NaOH solution. Because our aim is to produce oxygen with as little driving force as possible, high energy processes such as those using F_2 do not seem worth studying in detail here.

3. $2ClO^-$ or $2BrO^- \xrightarrow[OH^-]{CAT} O_2 + 2Cl^-$ or $2\ Br^-$

In acidic solutions the product also contains dihalogen. Effective catalysts are the higher hydrated oxides of Co, Ni, Cu; the O_2 bubbles from the solid surface. Oxides of Fe or Mn are ineffective, presumably because they can form soluble ferrates, manganates, etc. Isotope studies with ^{18}O (Ref. 6) show that the O of ClO^- exchanges easily with the O of H_2O; perhaps there is present in solution $[ClO(H_2O)_3]^-$ ion as one member of the family extending from ClO_4^- to $[Cl(H_2O)_4]^-$, all of which have 4 O atoms about a central halogen. In this reaction the intermediate compounds which are the precursors of dioxygen appear to be unstable oxides involving the higher oxidation states of the active metal. Experiments here with alkaline chlorate and cobalt ion produced no black active oxide and no oxygen. Experiments with alkaline chlorite and cobalt produced the black oxide but no oxygen, so the intermediates on the way to dioxygen are not chlorite or chlorate.

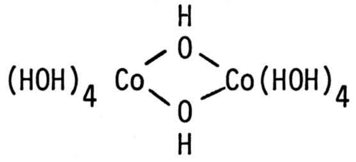
Isotope studies on the oxygen produced by this reaction show an enrichment in ^{16}O relative to ^{18}O (Ref. 7). This suggests that the dioxygen precursors involved a large number of O atoms and the process was thermally activated. (The rate of dioxygen evolution is observed to increase with temperature).

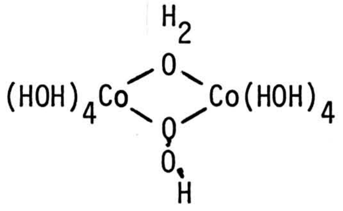
4. $S_2O_8^{=} + 2OH^{-} \xrightarrow{Cat} 2SO_4^{=} + H_2O + \frac{1}{2}O_2$

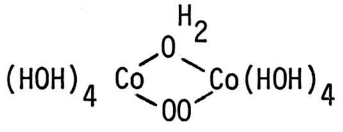
The catalysts are, as with hypochlorite, the hydrated higher oxides of Ni, Co, and Cu. The oxygen evolved is enriched in ^{16}O relative to the starting water with ratios about the same as with hypochlorite (Ref. 7), and the oxygen bubbles form on the solid oxide. The $S_2O_8^{=}$ ion has an O-O group with the O-O distance only 1.31Å, but evidently this group does not remain intact.

5. $4Co^{III}(aq) + 2H_2O \xrightarrow{H^+} 4Co^{II}(aq) + 4H^+ + O_2$

Although cobaltic ion is very stable when coordinated to N in basic or neutral solutions, in acid solutions cobaltic ion is a strong oxidant. Possible intermediate forms for Co^{III} in acid are:





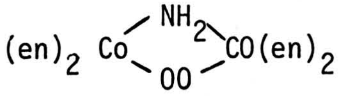


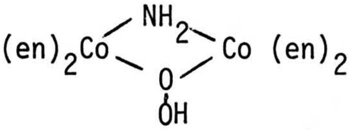
and

$$(H_2O)_5\ Co{-}O{-}O{-}Co(H_2O)_5$$

in analogy with the nitrogen-coordinated complexes

$[(NH_3)_5Co\text{-}O\text{-}O\text{-}Co(NH_3)_5]^{+5}$, $[(NH_3)_5Co\text{-}O\text{-}O\text{-}Co(NH_3)_5]^{+4}$,





In the pentavalent decamino complex the O-O distance is only 1.31Å, as in HO_2; in the quadrivalent decamino complex the O-O distance is about 1.47Å as in HOOH. (Ref. 1, p. 781).

The oxidation of water by Co^{III} has been extensively studied by Anbar and Pecht(Ref. 8). The dioxygen produced is enriched in ^{16}O. The evidence favors a peroxide intermediate, with perhaps Co^{III} oxidizing a double hydroxy bridged binuclear Co^{III} complex to form a peroxide bridge which then loses O_2.

6. $\underline{2Ni[O_2\ Te(OH)_4]_2 + 2H_2O \xrightarrow{H^+} 2NiO_2Te(OH)_4 + O_2 + 2Te(OH)_6}$

Here the Ni begins with a formal charge of +4, but part of the oxidizing power may lie on the tellurate ion also. The solid reactant is prepared by oxidation with $S_2O_8^{=}$. The dioxygen evolved from acid solution is enriched in ^{16}O relative to the water (Ref. 7).

7. $\underline{Na_7[Cu(HTeO_6)_2] + H_2O \xrightarrow{H^+} O_2 + \text{etc.}}$

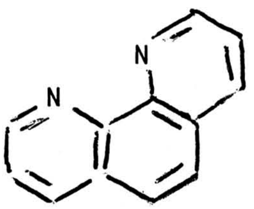
Here again the dioxygen is enriched in ^{16}O. OH radicals are presumed intermediates (Ref. 7).

8. $4KCuO_2 + 12H_3O^+ \rightarrow 4Cu^{++} + 4K^+ + O_2 + 12H_2O$

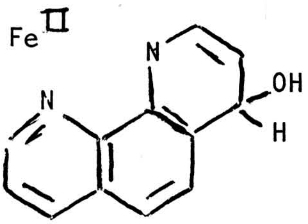
This is a liquid-solid heterogeneous reaction. The Cu is formally in the +3 state although the compound $KCuO_2$ is made from KO_2 and CuO. Presumably the H_2O coordinated to Cu supplies some of the evolved dioxygen. The enrichment in ^{16}O is very small (Ref. 7).

9. $4Fe^{III}(phen)_3 + 4OH^- \rightarrow O_2 + 4Fe^{II}(phen)_3 + H_2O$

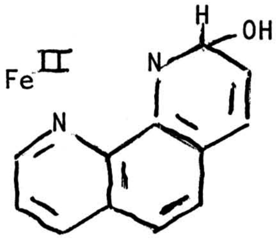
Here "phen" = 1, 10 phenathroline:



The iron atom is coordinated with the 2N atoms to form a fairly stable 6-membered ring. The reaction has been studied by Nord and Wernberg (Ref. 9). Presumably the first step in dioxygen evolution is the oxidation-attachment of OH^- to form a hydroxyl-bearing quinonoid structure coordinated to Fe^{II}:



or



This intermediate might then be re-oxidized by another Fe^{III} ion to a Fe^{III} hydroxylated complex which could oxidize another OH^- ion and immediately split off H_2O_2, leaving the Fe^{II} complex. H_2O_2 or HO_2^- has been detected in the reacting mixture. Attachment of OH to Fe is considered unlikely because the bulkier phenanthroline complex reacts faster than the slightly more open bipyridyl complex. (see reaction group 10, below). The Fe^{III} complex is known to oxidize HO_2^- rapidly to HO_2 radical, perhaps by reacting with a hydroxylated Fe^{III} complex to form O_2, H_2O and the Fe^{II} complex.

Kinetic data shows that the reaction rate is proportional to both Fe^{III} complex and OH^- concentrations. The G* of activation is about 14 kcal with H* 11 kcal; and S* -10 cal/°K (Ref. 9). Isotope studies (Ref. 7) show the dioxygen produced is enriched in ^{16}O.

From standard electrode potentials (1N solutions);

$$\begin{aligned}
Fe^{++} &= Fe^{+++} + e^- && -0.74v \\
4OH^- &= O_2 + H_2O + 4e^- && -0.40v \\
3OH^- &= HO_2^- + H_2O + 2e^- && -0.87v \\
2H_2O &= O_2 + 4H^+ + 4e^- && -1.23v
\end{aligned}$$

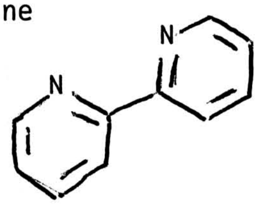
Thus Fe^{+++} should be able to oxidize OH^- to O_2 with 0.74-0.40 = 0.34 volts to spare at pH 14, and equilibrium should be reached at pH 8.2, except that Fe^{+++} as a "bare" ion is not soluble to 1N concentration at pH14 or pH 8.2. However, if Fe^{+++} ion is made sufficiently soluble by complex formation, oxidation of OH^- may occur. The formation of HO_2^- ion in small concentrations may then even be possible, and it would serve as an intermediate species on the way to dioxygen.

10. $\underline{4M^{III}(LL)_3 + 4OH^- \rightarrow 4M^{II}(LL)_3 + O_2 + H_2O}$

This group of reactions consists of the family of which the Fe-phenanthroline complex described in group 9 is a well-studied member. The dioxygen is evolved from basic aqueous solutions. As metallic central ions M one may have Fe^{III}, Os^{III} or Ru^{III}. As complexing ligands LL

(3 about each metal atom), one may have the 1,10 phenanthroline described earlier, or its structurally similar relatives:

5-methyl 1,10 phenanthroline
5,6 dimethyl phenanthroline
4,7 dimethyl phenanthroline
3,4,7,8 tetramethyl phenanthroline
2,2' bipyridyl:



4,4' dimethyl 2,2' bipyridyl

These combinations have been studied kinetically (Ref. 9) in order to shed more light on the nature of the oxygen-evolving reaction, which nevertheless is still somewhat obscure although the kinetic and energetic evidence favors the attachment of OH^- to the aromatic ring as the first step in the reaction. In this way a fairly active OH group might be held until peroxide could form.

The $Ru^{III}(bipyridyl)_3$ system has been studied in some detail by Creutz and Sutin (Ref. 10). They found O_2 production to peak sharply at pH 9. Presumably at lower pH the OH^- ion concentration was too low to be effective and at higher pH destructive oxidation of the bipyridyl became excessive.

The $Ru(bipyr)_3$ system is also of interest in connection with photochemical production of H_2 and O_2 from water by means of thin layers of this complex deposited on glass surfaces, as reported by Whitten, et.al.(Ref 11).

11. Photosynthesis

The overall reaction driven by light is approximately:

$$CO_2 + H_2O \rightarrow O_2 + (CH_2O)_n$$

The dioxygen produced is enriched in ^{18}O in contrast with all the other systems studied (Ref. 7). This finding suggests that the oxygen precursors reside for some time long enough to approach thermodynamic equilibrium on special sites before they are liberated en masse as dioxygen. The most likely sites are those containing complex Mn atoms, for a variety of reasons (Ref 12), especially because green plants deprived of Mn produce no dioxygen. Mn is also attractive because its oxidation states of +2, +3, and +4 permit the transfer of 4 electrons using only 2 Mn atoms.

IV. Search for New Chemical Systems

With the possible exception of natural photosynthesis, most of the reactions which liberate dioxygen from water appear to involve a peroxide or an unstable highly oxidized metal ion as intermediates, and hence demand an extra 0.2 to 0.5 volt of potential above that theoretically required. The oxidation of hydroxyl ion is of course easier than that of water but part of the energy requirement has been prepaid in increasing the hydroxyl concentration above pH 7.

As mentioned earlier, the problem is to move the oxygen atoms from far apart, as in water, to close together, as in dioxygen, while removing

4 electrons. In reversibly dioxygenated materials such as hemoglobin the 0-0 distance is about 1.30Å so that once this closeness has been achieved, liberation of dioxygen should be easy. This closeness implies a minimum amount of electron donation to the oxygen from the non-oxygen atoms that oxygen is bonded to or sharing its electrons with.

One can imagine some ideal systems in which the oxygen atoms first join a large molecule as adjacent H_2O or hydroxyl ions, and then, as electrons are withdrawn from the system, the oxygen atoms move closer together so as to form a direct 0-0 bond without the need for forming high energy intermediate states such as peroxide.

Throughout this process of electron withdrawal the large molecule should remain fairly stable. This suggests that a transition metal capable of assuming several oxidation states should be a part of this molecule, thereby permitting changes in the oxidation state or electron population of the molecule to proceed one electron at a time. In the absence of such a transition metal atom, a change of one in the electron population implies the temporary existence of higher energy intermediates such as a free radical or half a covalent bond, since a covalent bond involves two electrons. In view of the multi-valent nature of manganese and its known involvement in natural photosynthetic dioxygen evolution, it would be a good choice for a transition metal atom for the large molecule.

In addition to containing manganese, the large molecule should also be fairly resistant to oxidation. This requirement is not so stringent if the intermediate species on the way to oxygen such as peroxide, superoxide, OH radical, etc. are bound to the molecule at insensitive sites and are not allowed to roam about and attack the molecule at sensitive sites. In this way the only free oxidizing species would be dixoygen, which in its ground state at ordinary temperatures is not a very aggressive oxidizing agent.

According to the foregoing criteria such a large molecule in operation would presumably tend to accumulate oxygen-containing species such as hydroxyl ion or water molecules on certain sites for long enough times to approach thermodynamic equilibrium as far as the ^{18}O-^{16}O isotope ratio is concerned. Then after the necessary electron transfers had been completed, dioxygen would be formed from all the visiting oxygen-bearing species and in this way the enrichment of ^{18}O observed in plant photosynthesis would be a natural consequence, although such a mechanism has not been proven for plant photosynthetic oxygen evolution.

The criteria described above put certain limits on suitable large molecules to assist dioxygen production. In the natural system, such molecules are probably special proteins or enzymes. Such large molecules are not practical to synthesize in the laboratory, and instead smaller molecules containing Mn atoms and having the desired functions will be sought. Several different kinds of these molecules have been selected as candidates and work is proceeding on their attempted synthesis.

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Appendix

ISOTOPE EFFECTS

If a system containing two or more isotopes undergoes an incomplete chemical reaction, so that not all the reactants are used up, the isotope ratio of the first products of the reaction may be different from that of the remaining reactants. The change in isotope ratio would probably be a function of the reaction pathway.

At equilibrium one may estimate the magnitude of isotope effects from the classical partition function. The contribution to the Gibbs free energy, G, for particles of mass m, considering only translation and vibration, is:

$$G = NkT\left[\ell n \left(\frac{h^2}{2\pi mkT}\right)^{3/2} \frac{N}{V} + \ell n(1-e^{-u})\right]$$

where h = Planck's constant

k = Boltzmann's constant

N = Avogadro's constant

T = absolute temperature

u = hv/kT where v = vibration frequency.

V = volume available to the particles

We note that $v = (s/m)^{1/2}$ where s = "spring constant", newtons/km.

Thus as m increases, G decreases. For example, the heavier isotope has a lower fugacity or is more firmly bound, or is less likely to escape.

The same result is arrived at in a qualitative fashion by considering the dislodging of a bound atom as a result of collisions. We suppose that the bond is broken if the bond is stretched beyond a critical distance as the result of bombardment by other atoms. If the bound atom has mass m_2 and the bombarding particle has mass m_1, then by conservation of momentum, $m_1v_1 = m_2v_2$, where v is velocity. The maximum displacement, x, of a simple harmonic oscillator is related to its maximum velocity by $x = v(m/s)^{1/2}$.

If the vibration is driven by collisions with momentum transfer $m_1v_1 = m_2v_2$, then

$$x_2 = v_2(m_2/s)^{1/2} = m_1v_1 \ (m_2s)^{-1/2}.$$

So the larger is m_2, the smaller is x_2, and the less likely is the bond breaking as a result of bombardment by the "outside world" particles m_1 in thermal equilibrium.

The kinetic isotope ratio changes depend on the reaction pathways. If the reaction proceeds on a statistical thermal basis, ordinary reaction rate theory, using the form exp(-G*/RT), where G* is the free energy of the activated transition state (which is presumably not very sensitive to isotope masses but depends mostly on electronic configurations, chemical bonds, etc.), would predict that the heavier isotope would react more slowly at the same concentration because more energy is required to reach G* from the heavier isotope "ground state" G, which is lower than that of the lighter isotope.

On the other hand, if the reaction proceeds by a forced decomposition of all of a small number of molecules on a special site after the site has come to thermal equilibrium, then the products would be expected to be richer in the heavier isotope. This kind of phenomenon may explain the enrichment of ^{18}O in the dioxygen produced by natural photosynthesis.

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