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Functional Chemical Models of Multielectron Water Oxidation in Photosynthesis

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Abstract—The study of water oxidation by Mn_n^{IV} clusters, which are functional chemical models of the manganese cofactor (enzyme that oxidizes water in photosystem II of natural photosynthesis) has demonstrated that a Mn_2^{IV} cluster oxidizes two water molecules to form one oxygen molecule, Mn_4^{IV} oxidizes four water molecules to form two O_2 molecules, and Mn_8^{IV} oxidizes eight water molecules to form four O_2 molecules. A Mn_6^{IV} cluster oxidizes six water molecules to two ozone molecules, whereas Mn_{12}^{IV} oxidizes twelve water molecules to four ozone molecules. The six-electron oxidation of water to ozone is also observed in photosynthesis in red and brown sea algae under conditions of water deficit. It is hypothesized that, in the case of water deficit in algae, the manganese cofactor with four manganese ions turns into the cofactor with six manganese ions.

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The energy basis of life on the Earth is almost entirely solar energy. The amount of energy delivered to the Earth surface by solar radiation is by several thousands of times greeter than that produced by all existing electric power stations. About half the radiation that arrives at the Earth surface, specifically, visible light can be utilized by photosynthetic organisms [1], which are capable of converting solar energy to the chemical energy of carbohydrates and dioxygen.

Oxygen photosynthesis can be described by the equation given below, where (CH_2O) denotes carbohydrates [1]:

$$CO_2 + 2\,H_2\mathbf{O} \longrightarrow (CH_2O) + \mathbf{O}_2 + H_2O.$$

Both atoms of the resulting oxygen molecule originate from two water molecules, which are oxidized to release, into the medium, four protons on a special enzyme in photosystem II (PS-2) of photosynthesis. In this largest-scale process on the Earth, only flora of the dry land evolves 336 billion tons of dioxygen annually, or about 11000 t of O_2 per second [2]. A little less oxygen (approximately 46% of the total amount) is produced by aquatic photosynthetic organisms [2].

Long before the nature started to use water as an electron donor in photosynthesis (more than 2.3 billion years ago), there was a photosystem capable to produce carbohydrates by the reduction of carbon dioxide using visible light energy and sulfide or other electron donors. To use water as an electron source, the nature had to create a "device" that can perform the noncomplementary [3] oxidation of two water molecules by one-electron oxidizers ("holes" $P680^{+\cdot}$ in the PS-2) to form an oxygen molecule. The catalyst in this noncomplementary four-electron water oxidation to oxygen in PS-2 is the manganese cofactor (Mn-co). This process needs catalysis because, according to the principle of equivalent electron exchange (Shaffer principle [4]), a reaction proceeds freely only when the oxidizer and reducing agent molecules accept and donate, respectively, the same number of electrons.

During photosynthesis, Mn-co is oxidized stepwise by four $P680^{+\cdot}$ holes. After four holes are accumulated, Mn-co returns to the initial state, having oxidized two water molecules to O_2. Water oxidation in PS-2 can be presented by the equation

$$4P680^{+\cdot} + 2H_2O = 4P680 + O_2 + 4H^+.$$

At present, most researchers accept this conception of the concerted formation of an oxygen molecule in natural photosynthesis (see, e.g., [1, 5, 6]). However, there was no consensus until recently and water oxidation was extensively studied by various methods. We attempted to understand the mechanism of Mn-co action by examining the simple functional chemical model "Mn-co–sulfuric acid solution of Mn^{IV} sulfate."

In the simplest chemical model of Mn-co, light irradiation or sufficient heating of the solution results in the reduction of Mn^{IV} accompanied by water oxidation. At low oxidizer concentrations ($[Mn^{IV}] < 0.01$ mol/l) and high temperatures of the reaction mixture (85–100°C), water is oxidized to oxygen in the coordination sphere of the dinuclear manganese

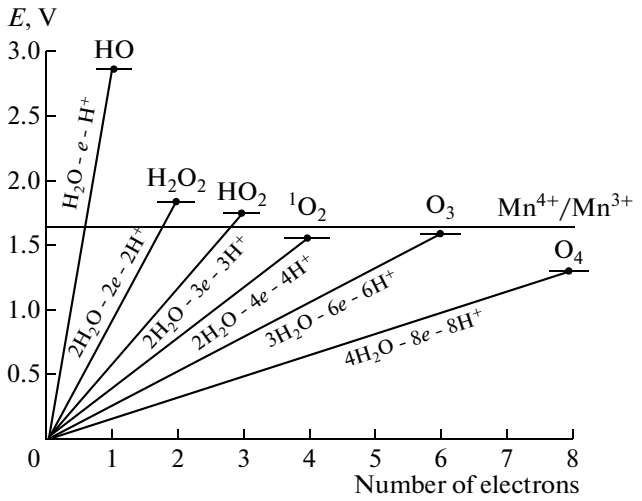

Fig. 1. Shilov's diagram for the multielectron oxidation of water by the Mn^{IV} clusters at pH −1.

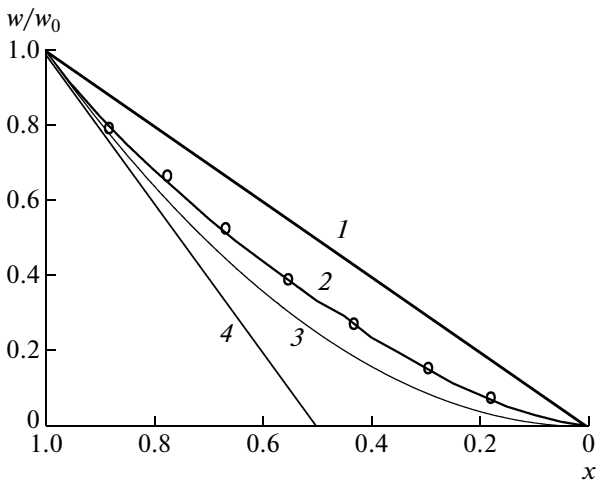

Fig. 2. Phase trajectories of oxidizer disappearance for the concerted process in the coordination sphere of the Mn_2 dimers for the following values of the cluster–cluster equilibrium constant K: (*1*) 0, (*2*) 1, (*3*) 4, and (*4*) 10^4. Points in curve *2* represent the experimental data on Mn^{IV} reduction at $T = 360$ K; $[Mn^{IV}]_0 = 1 \times 10^{-2}$ mol/l; $[H_2SO_4] = 9.3$ mol/l.

complexes Mn_2^{IV} (the entire oxidizer consists of these complexes [7]). In an elementary event, the dinuclear complex is reduced to Mn_2^{II}, which reacts very rapidly with Mn_2^{IV}, turning into Mn_2^{III}. According to the assumed scheme of the process, the initial reaction rate increases linearly with an increase in the oxidizer concentration, whereas the disappearance of the oxidizer in a particular experiment is not described by the kinetic equation of a monomolecular reaction [7]. To explain the observed regularities, it was necessary to consider all possible dinuclear manganese complexes, namely, $Mn^{IV}Mn^{IV}$, $Mn^{IV}Mn^{III}$, and $Mn^{III}Mn^{III}$. Of these complexes, only the first dimer is active, whose number of holes (4 h^+) is sufficient for the oxidation of two water molecules to form an oxygen molecule. The two other clusters cannot oxidize water because of stoichiometric limitations: they do not have the necessary number of holes (four) for oxygen formation, while the oxidation of water to other products ($^{\bullet}OH$, H_2O_2, and $HO_2^{\bullet}$) is thermodynamically unfavorable. The possible reactions of water with the Mn^{IV} clusters can clearly be presented as Shilov's diagram [8], in which the redox potentials of all possible water oxidation processes are compared with the redox potential of the Mn^{4+}/Mn^{3+} pair (Fig. 1). It is seen from Fig. 1 that the one-, two-, and three-electron oxidation of water by Mn^{IV} is thermodynamically unfavorable even if the manganese cluster contains the necessary number of holes. In the cases of four-electron water oxidation to oxygen, six-electron water oxidation to ozone, and eight-electron water oxidation to "oxozone" O_4, no thermodynamic difficulties should appear.

The concentrations of the dinuclear complexes Mn_2 are interrelated by the redox equilibrium $Mn^{IV}Mn^{IV} + Mn^{III}Mn^{III} \rightleftharpoons 2\ Mn^{IV}Mn^{III}$, whose equilibrium constant (K) determines the kinetics of oxidizer disappearance in a given experiment. If $K = 0$ (in the absence of a negative feedback [9]), the kinetic curve of disappearance of the Mn^{IV} oxidizer is described by an exponential equation represented as a straight line in the phase plane in the dimensionless rate w/w_0—conversion $(1 - x)$ coordinates, where $x = [Mn^{IV}]/([Mn^{IV}] + [Mn^{III}])$ is the mole fraction of the oxidizer Mn^{IV} in the $Mn^{IV} + Mn^{III}$ mixture [10] (Fig. 2, line *1*). In the other limiting case, $K \longrightarrow \infty$ (very strong negative feedback), the Mn^{IV} reduction kinetics is also described by an exponential equation (Fig. 2, straight line *4*). However, the process ceases after the reduction of half the oxidizer (at $x \geq 0.5$, $w = 0$). At $K = 4$ the phase trajectory of Mn^{IV} disappearance is described by curve *3* in Fig. 2. This is true for any bimolecular reaction $A + A \longrightarrow$ products. At low concentrations of manganese(IV) and high temperatures, the process is described by phase trajectory *2* (in this case, the calculation was performed for $K = 1$). If $K = 1$, this means that the redox potentials of the $Mn^{IV}Mn^{IV}/Mn^{IV}Mn^{III}$ and $Mn^{IV}Mn^{III}/Mn^{III}Mn^{III}$ pairs are equal. Let us turn from the kinematic solution of the autonomous differential equation $-d[Mn^{IV}]/dt = k[Mn_2^{IV}]$ on the phase plane to the geometric representation of $[Mn^{IV}] = f(t)$ [10]. In the particular case of $K = 1$, the linear anamorphosis of the Mn^{IV} disappearance curve will be described by the following equation [11]:

$$\varphi(x) = k_0 t + 11.932,$$

where $\varphi(x) = x^{-1}\{1 + 4(\alpha - \beta)^{-1}[(\alpha - x)(x - \beta)]^{1/2}\} + 8(\alpha - \beta)^{-1}\arctan[(x - \beta)/(\alpha - x)]^{1/2} + 6\ln\{(x - \beta)^{1/2} +$

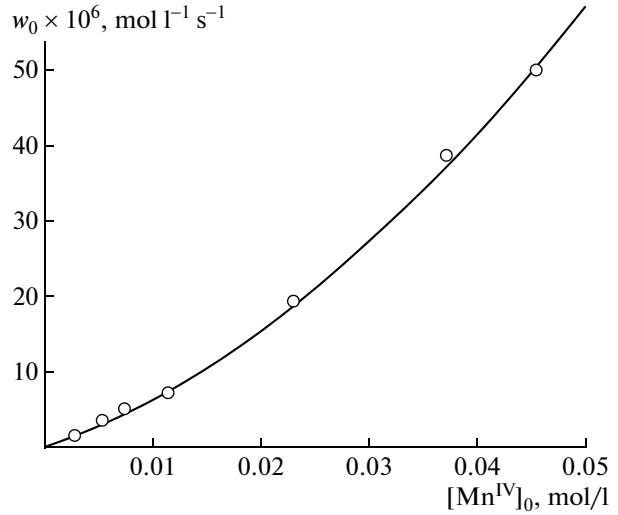

Fig. 3. Initial rate of oxygen formation versus the oxidizer concentration; $T = 367$ K, $[H_2SO_4] = 9.3$ mol/l.

$[\beta(\alpha - x)/\alpha]^{1/2}\} - 6\ln x\{(x - \beta)^{1/2} - [\beta(\alpha - x)/\alpha]^{1/2}\}$. In this expression, $\alpha = 1.07735$, $\beta = -0.07735$, and k_0 is the rate constant for the decomposition of the activated complex, which consists of two water molecules and the Mn_2^{IV} complex, to Mn_2^{II}, one oxygen molecule, and $4H^+$. One O_2 molecule is formed in this event, which is confirmed by the phase trajectory derived from the O_2 formation kinetics. The Mn^{IV} disappearance curve, from which the data points on phase trajectory *2* were obtained (Fig. 2), becomes rectilinear in the coordinates of the equation $\varphi(x) = k_0 t + 11.932$.

An analysis of the variation of the initial rates of oxidizer disappearance with an increase in the oxidizer concentration ($[Mn_2^{IV}] \geq 0.01$ mol/l) shows that a second channel is added to the Mn_2^{IV} complex reduction process. The reaction rate for the second channel is proportional to the squared oxidizer concentration: $w_0 \sim [Mn^{IV}]^2$. This behavior is due to the fact that, with an increase in the oxidizer concentration, part of the Mn_2^{IV} complexes dimerize into tetranuclear clusters Mn_4^{IV}, whose rate constant for water oxidation (k_0) exceeds the corresponding value found for Mn_2^{IV} by more than one order of magnitude. Under these conditions, both the rate of oxidizer disappearance and the oxygen formation rate w_0 are described by a binomial including linear and quadratic components: $w_0 = k_1[Mn^{IV}] + k_2[Mn^{IV}]^2$ (Fig. 3). The experiments were carried out in a 9.3 M solution of sulfuric acid at 94°C using known procedures [7, 11]. The rate of oxygen formation is described well by the binomial $w_0(O_2) = (5.2 \times 10^{-4})[O_2] + 0.013[O_2]^2$ (Fig. 3). The linear term of the binomial corresponds to the formation of one O_2 molecule in the coordination sphere of Mn_2^{IV} (see above), whereas the quadratic term indicates the concerted formation of two O_2 molecules from four H_2O molecules in the coordination sphere of Mn_4^{IV}. It is likely that a molecule of "oxozone" O_4 is formed in the elementary event and turns into two O_2 molecules within 10^{-12} s [12], so the kinetics of O_2 formation is actually observed.

To explain the above facts, let us consider the general case of the equilibrium formation of a highly reactive Ox_n cluster from kinetically independent oxidizers Ox: $n\text{Ox} \rightleftharpoons \text{Ox}_n$ (equilibrium constant K). The rate of this process is proportional to $[Ox]^n$: $w = k[Ox_n] = kK[Ox]^n$. To determine the degree of aggregation of Ox (n) with the formation of the active cluster Ox_n, let us take the logarithm of this equation and differentiate $\ln w$ with respect to the Ox concentration:

$$n = d\ln w/d\ln[Ox] = [Ox]dw/wd[Ox].$$

At the very beginning of the process ($t = 0$), $[Ox] = [Ox]_0$ and $w = w_0$. Thus, $n = d(w/w_0)/dx$, where $x = [Ox]/[Ox]_0$ is the mole fraction of Ox, and the degree of aggregation n of the highly active cluster Ox_n is determined by the first derivative of the phase trajectory of the process in the dimensionless rate–conversion coordinates at $x = 1$ ($t = 0$). Similar reasoning is applicable to the process $Ox_m + 2mH_2O = Red_m + mO_2 + 4mH^+$; i.e., the reaction order m (according to which oxygen forms) is equal to the number m of O_2 molecules generated in the coordination sphere of the Ox_m cluster upon the concerted oxidation of $2m$ water molecules. Thus, the phase trajectories of the oxidizer disappearance and reaction product formation processes make it possible to easily determine their stoichiometric coefficients in the equation describing the elementary inner-cluster event.

It might be expected that, with further aggregation of Mn_2^{IV} to Mn_6^{IV} (trimerization of Mn_2^{IV}), six water molecules will be oxidized to form three O_2 molecules. However, the Mn_6^{IV} clusters produce two ozone molecules instead of three O_2 molecules. As in the case of finer clusters (Mn_2^{IV} and Mn_4^{IV}), when six water molecules are oxidized, the Mn_6^{IV} cluster spends all of its 12 holes in the elementary event, turning to Mn_6^{II}. When interacting with the Mn^{IV} compounds, the Mn_6^{II} cluster is rapidly oxidized to Mn_6^{III}, as in the case of the finer clusters. The oxidation of water to ozone by the Mn_6^{IV} is described by the equation

$$Mn_6^{IV} + 6H_2O = Mn_6^{II} + 2O_3 + 12H^+.$$

It is interesting that the Mn_{12}^{IV} cluster, which is twice as large, also oxidizes water to ozone; more exactly, 12 water molecules give 4 ozone molecules. However, the Mn_8^{IV} cluster, next to the Mn_6^{IV} cluster in

size, oxidizes water not to ozone, but to oxygen, just as its "half" (Mn_4^{IV} cluster). Although the reduction of the Mn_8^{IV} cluster yields four O_2 molecules per elementary inner-cluster event (as is shown by the phase trajectory of O_2 evolution), it can be assumed that two O_4 "oxozone" molecules are evolved first and then, within about 10^{-12} s, they turn into four oxygen molecules [12], whose formation kinetics is actually monitored. Ozone molecules are formed in the coordination spheres of the Mn_6^{IV}, Mn_{12}^{IV}, and Mn_{18}^{IV} clusters, which are likely hexagonal, whereas oxygen is produced by the cubic clusters: Mn_4^{IV} (cubane), Mn_8^{IV} (cubane dimer), Mn_{16}^{IV} (cubane tetramer), Mn_6^{IV} (trihedral prism having three Mn ions in the base and three Mn ions at the top and resembling prismane, one of the benzene isomers), Mn_{12}^{IV} (six Mn ions at the bottom and six Mn ions at the top), and Mn_{18}^{IV} (two-decked analogue evolving 6 ozone molecules in the oxidation of 18 water molecules).

As was indicated above, on passing from the smallest-size oxidizer of water, Mn_2^{IV}, to Mn_4^{IV}, the rate constants of Mn^{IV} reduction and oxygen formation increase by more than one order of magnitude. It would be interesting to observe a similar effect for water oxidation with ozone formation. Selecting experimental conditions, we were able to measure the activation energies of the reduction of the Mn_6^{IV} and Mn_{12}^{IV} clusters, which oxidize 6 and 12 water molecules to form two and four ozone molecules, respectively. For the Mn_{12}^{IV} cluster, the activation energy is $E_{12} =$ 68 kJ/mol; i.e., it is noticeably lower than that for the Mn_6^{IV} cluster ($E_6 = 98$ kJ/mol) [13].

Thus, the manganese clusters can catalyze noncomplementary chemical processes (making it possible to circumvent Shaffer's forbidding principle) and can also perform concerted multisubstrate reactions. For exoergonic processes, an increase in the number of activated substrates decreases the activation energy of the reaction [13]. This is easily explainable. Suppose that the Mn_4^{IV} cluster coordinates and oxidizes two water molecules to O_2 for some reasons (for example, if the coordination sites of the cluster are occupied by inert molecules). The Gibbs energy of this process is $-\Delta G = nF(E_1 - E_2) = -4 \times 96500(1.57 - 1.23) =$ -131.2 kJ/mol, where $E_1 = 1.57$ V and $E_2 = 1.23$ V are the standard redox potential of the Mn^{IV}/Mn^{II} and O_2/H_2O pairs, respectively; n is the number of transferred electrons; and $F = 96500$ J/V is Faraday's constant [14]. If four water molecules are oxidized via the concerted mechanism in the coordination sphere of the Mn_4^{IV} cluster, then $\Delta G = -262.4$ kJ/mol, because eight (two times more) electrons are transferred in this process. According to the Brønsted–Polanyi–Semenov rule, a decrease in the activation energy of the process should be expected in the second case [15], and is actually observed experimentally.

After we had discovered that water can be oxidized to ozone in the functional chemical model of Mn-co, we attempted to find evidence for the same process to occur in photosynthetic organisms. We successfully demonstrated that water is oxidized to O_3 in some sea red (*Phyllophora nervosa, Polysiphonia elongata*, and *Callithamnion corymbosum*) [16, 17] and brown (*Cystoseira barbata*) [17] algae under conditions of water deficit. We attribute this reaction to the fact that the hexanuclear (not tetranuclear) manganese cofactors appear in the anhydrous sea algae, and this makes it possible to oxidize three water molecules to ozone. The following question arises here: Why two O_2 molecules result from water oxidation in the Mn_4^{IV} model of Mn-co, whereas only one oxygen molecule forms in the natural cofactor, as judged from the data on the mechanism of functioning of Mn-co [1, 5, 6]? Evidently, this is due to the necessity of chemical binding between Mn-co and a protein apoenzyme, which occupies some coordination sites of Mn-co. Six amino acid residues of the protein globule D1 are immediate ligands of Mn-co in the PS-2 [18]. The chemical model system (Mn_4^{IV}) has no occupied coordination sites, and, accordingly, it activates twice more (four) water molecules. The doubled yield of O_3 in the case of the Mn_6^{IV} cluster (compared to that in algae) can be explained similarly. Note that neither higher plants (more than ten species were tested) nor freshwater algae or lichen, which is a symbiosis of algae and fungi, can oxidize water to ozone.

The noncomplementary oxidation of water by a one-electron oxidizer needs a catalyst converting one-electron steps to a concerted multielectron step, ensuring the simultaneous oxidation of several water molecules in the coordination sphere of the cluster. The cluster is never limited to the activation of the minimum number of substrate molecules (two water molecules); on the contrary, in all cases studied, the highly organized catalyst activates the maximum possible number of substrate molecules (in our experiments, up to 18 water molecules). Such an unusual, "provident" behavior of the clusters is due to the lower activation energy of the concerted multisubstrate inner-cluster process.

Thus, the study of the functional chemical model of Mn-co shows that the polynuclear character of the metallic cofactor is necessary to circumvent Shaffer's forbidding principle and to perform concerted multisubstrate processes, whose activation energy decreases with an increase in the number of activated substrates.

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