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PHOTOCHEMISTRY
AND MAGNETOCHEMISTRY

Many-Electron Oxidation of Water as Treated within the Framework of a Functional Chemical Model of the Manganese Cofactor of Oxidase in Photosystem II of Natural Photosynthesis

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Abstract—The kinetics and products of the oxidation of water by Mn^{IV} clusters in a 12 M sulfuric acid solution, a functional chemical model of the manganese cofactor of the oxidase in photosystem **II** of natural photosynthesis, were studied. It was demonstrated that, depending of the conditions, water can be oxidized to either oxygen or ozone. In the reaction mixture, ozone is rapidly and almost completely converted into oxygen. The results obtained were compared to the data on the photosynthetic oxidation of water in red seaweeds.

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An effective tool for studying the complex mechanism of the operation of enzymes is their functional chemical models that imitate the main reactions on natural catalysts under more strictly controlled conditions [1]. In this report, we presented data on the kinetic characteristics and the composition of the products of the many-electron oxidation of water by Mn^{IV} compounds in sulfuric acid solutions, a chemical model of the manganese cofactor of the oxidase, which oxidates water in photosystem **II** (PS-2) of natural photosynthesis. Along with providing insights into some details of the mechanism of operation of PS-2 in nature, such models play an important role in creating artificial photocatalytic converters of light energy into the potential energy of chemical bonds on the basis of the reaction of decomposition of water into hydrogen and oxygen [2]. Interest in artificial photosynthesis is not expected to slacken over time because of the inevitable exhaustion of fossil fuel in the foreseeable future, which should be replaced by renewable sources of energy.

Since light irradiation normally produces one-electron oxidizers and reducers (for example, in semiconductor solar cells, electrons and holes are generated), the many-electron oxidation of water to oxygen and other product can only be accomplished by using effective catalysts capable of accumulating several one-electron oxidizers and, then, converting several water molecules into O_2 and other product in a single elementary event [3]. Studies of the oxidation of water to oxygen by Mn^{IV} sulfate in sulfuric acid solutions [4–6] demonstrated that this complex process occurs in the coordination spheres of bi- or tetranuclear complexes of Mn^{IV} without releasing the intermediate products of water oxidation (H_2O_2, HO, HO_2) into the solution. The kinetic behavior of the process under certain experimental conditions led the author of [7] to conclude that water experiences six-electron oxidation to ozone; no direct evidence of ozone formation has been obtained, however. In addition, no mechanism of the possible eight-electron oxidation of water to oxozone has been put forward, although the kinetic data obtained clearly suggested that it occurred [7] (the formation of two O_2 molecules from four H_2O molecules was observed experimentally). This prompted us to perform additional studies of the oxidation of water by Mn^{IV} clusters.

The aim of the present work was to elucidate the mechanism of the formation of ozone and the other products of the oxidation of water by Mn^{IV} clusters in sulfuric acid solutions and to compare the mechanisms of the operation of the model system and the active sites of the PS-2 in red seaweeds.

EXPERIMENTAL

The reagents were analytical-grade $KMnO_4$, reagent-grade 18 M (96%) sulfuric acid ($\rho = 1.84$ g/cm^3 at 20°C), and distilled water. Mn^{IV} was obtained either by the spontaneous reduction of $KMnO_4$ sulfuric acid solutions for 10 h at 20°C or by mixing a $KMnO_4$ aqueous solution with the required amount of a $MnSO_4$ solution. The reduction of Mn^{IV} in sulfuric acid solutions was studied in a thermostatically controlled glass reactor, which was blown with argon passing at a volumetric flow rate of 0.2 l/min. The flow of argon and the gaseous reaction products formed passed through a layer of water to trap volatile $HMnO_4$ acid, which is formed during the oxidation of Mn^{III} by ozone. Upon leaving the water-filled trap, the flow of argon carrying the water oxidation products (oxygen and ozone) passed through a KI aqueous solution, used to quantitatively determine the ozone concentration [8]. The concentration of iodine formed during the oxidation of KI by ozone was determined spectrophotometrically by measuring the optical absorption of I_3^- at 350 nm [9]. The measurements were performed on a Specord UV-VIS spectrophotometer fitted with a thermostatically controlled quartz cell. The Mn^{III} concentration was calculated by the formula $D_{556} = \varepsilon^{III} l[Mn^{III}] + \varepsilon^{IV} l(c_0 - [Mn^{III}])$, where D_{556} is the optical density of the reaction medium at 556 nm (a wavelength located between two isobestic points, $\lambda = 510$ and 645 nm) and c_0 is the Mn^{IV} concentration at the beginning of the process. The cell's optical path was $l = 0.073$ cm; the molar extinction coefficients of Mn^{III} and Mn^{IV} at 556 nm under our experimental conditions were set equal to $\varepsilon^{III} = 146$ l/(mol cm) and $\varepsilon^{IV} = 68$ l/(mol cm), respectively. The kinetics of the formation of O_2 was studied using a glass setup. The amount of O_2 was determined volumetrically. When necessary, the degree of reduction of manganese at various stages of the reaction was determined by titration of the reaction mixture with a Mohr salt solution ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$). The reaction rate was numerically calculated by the Gregory–Newton formula [10].

RESULTS AND DISCUSSION

At low Mn^{IV} concentration (<3 mmol/l) and elevated temperatures (85–100°C), the oxidation of water occurs in the coordination sphere of a binuclear complex: $Mn_2^{IV} \cdot 2H_2O \longrightarrow 2Mn^{II} + O_2 + 4H^+$ [4]. In this case, each Mn^{IV} ion acts as a two-electron oxidizer ($Mn^{IV} \longrightarrow Mn^{II}$), while the binuclear complex as a whole acts as a four-electron oxidizer. The Mn^{II} compounds formed by the reaction are rapidly oxidized by Mn^{IV} to produce Mn^{III}, since the existence of two isobestic points, at 510 and 645 nm, is indicative of the absence of appreciable concentrations of manganese compounds other than Mn^{IV} and Mn^{III}. Clearly, the Mn_2^{IV} binuclear complex, a four-electron oxidizer, is incapable of generating ozone, a product of the six-electron oxidation of water. To produce ozone, it is necessary to use higher concentrations of Mn^{IV}, so as to obtain manganese clusters larger than the Mn_2^{IV} binuclear complex. Products of water oxidation other than oxygen were sought for in a 12 M sulfuric acid solution.

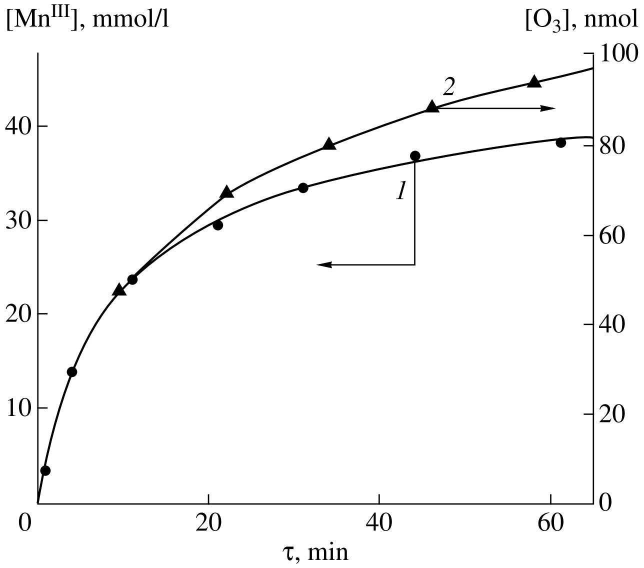

Fig. 1. Kinetics of the formation of (*1*) Mn^{III} and (*2*) ozone during the oxidation of water by Mn^{IV} compounds in a sulfuric acid solution (0.05 M Mn^{IV} in 12 M H_2SO_4) at 82°C. The volume of the reaction mixture producing ozone was 13 ml.

Figure 1 shows typical kinetic curves of Mn^{III} accumulation during Mn^{IV} reduction (curve *1*) and ozone formation (curve *2*) at a high manganese concentration (0.05 mol/l) and an elevated temperature (82°C). An analysis of the curve of consumption of the oxidizer (Mn^{IV}) plotted in the phase plane demonstrated that the reactive cluster is a trimer composed of kinetically independent oxidizer (Ox) molecules [11]. Note that Ox is the Mn_2^{IV} dimers [4] even at the lowest concentrations of Mn^{IV}—there are no Mn^{IV} monomers in the solution.

To elucidate the kinetic behavior of the collective many-electron process occurring in the coordination sphere of the Ox_3 trimer, we considered an idealized scheme of the process. Let nearly all available oxidizer exists in the form of trimer clusters. In the course of the process, active clusters Ox_3 can incorporate Ox reduction products, designated as Red. Then, at a certain instant of time, the reaction mixture will be composed of a mixture of trimers, Ox_3, Ox_2Red, $OxRed_2$, and Red_3, with the only species at the beginning and end of the reaction being active (Ox_3) and inactive clusters, respectively. The Ox_3 concentration changes with the extent of conversion (according to our scheme, the rest of the trimers, containing at least one Red molecule, cannot participate in the many-electron process under consideration because of lacking the required number of oxidative equivalents, i.e., three Ox species).

To determine the Ox_3 concentration at a preset duration of the reaction, we derived the corresponding system of equations. Let the mole fraction of Ox be x ($x = [Ox]/([Ox] + [Red])$), then the mole fraction of the Ox reduction product will be $(1 - x) = [Red]/([Ox] + [Red]$. We assumed that the reaction mixture contains manganese only in two degrees of oxidation, Mn^{IV} and Mn^{III}. At every instant t of the reaction, the mole fractions of the oxidizer and reducer obey the balance equations:

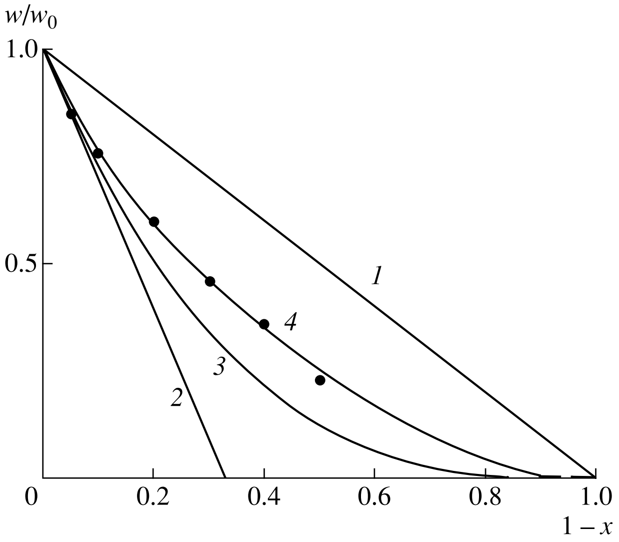

Fig. 2. Phase trajectories for the collective processes in the coordination sphere of the Ox_3 trimer cluster at various values of the constants of equilibrium between the clusters. The experimental points were obtained from kinetic curve *1* in Fig. 1. For the notations, see the text.

$ax = 3[\mathrm{Ox}_3] + 2[\mathrm{Ox}_2\mathrm{Red}] + [\mathrm{OxRed}_2]$ and $a(1 - x) = 3[\mathrm{Red}_3] + 2[\mathrm{OxRed}_2] + [\mathrm{Ox}_2\mathrm{Red}]$, where a is the total concentration of trimers of all kinds, a quantity three times lower than the initial concentration of $[\mathrm{Mn}_2^{\mathrm{IV}}]_0$ in the idealized scheme. Along with these equations, it is necessary to take into account the rapidly established redox equilibria within the ensemble of trimers, referred to as internal equilibria [11]: $\mathrm{Ox}_3 + \mathrm{OxRed}_2 \Leftrightarrow 2\mathrm{Ox}_2\mathrm{Red}$ (equilibrium constant K_{31}), $\mathrm{Ox}_3 + \mathrm{Red}_3 \Leftrightarrow \mathrm{Ox}_2\mathrm{Red} + \mathrm{OxRed}_2$ (K_{30}), $\mathrm{Ox}_2\mathrm{Red} + \mathrm{Red}_3 \Leftrightarrow 2\mathrm{OxRed}_2$ (equilibrium constant K_{20}). These set of equations is more than sufficient to calculate the concentrations of all types of trimers at any extent of conversion $(1 - x)$ for the oxidation of water by $\mathrm{Mn}^{\mathrm{IV}}$ compounds in the coordination sphere of Ox_3 (a hexanuclear cluster). If $[\mathrm{Ox}_3]$ is known, it is easy to determine the rate of the entire process, which can be thought of as the decay of the complex composed of the Ox_3 active cluster and water molecules coordinated to it to Red_3 and water oxidation products. If the trimer contain only part of the available oxidizer, the value of a will be smaller than one-third of the initial concentration of $\mathrm{Mn}_2^{\mathrm{IV}}$; nevertheless, the above argumentation still stands. Naturally, the internal equilibria between the trimers will be substantially affected by the environment, which will act so as to establish a certain distribution of trimers. In particular, when the internal equilibria between the trimers are replaced by the external equilibria with all species except for the trimers themselves, a binominal distribution of Ox and Red over the trimer clusters is observed. In this case, the intercluster collective process will imitate the classical trimolecular reaction of Ox consumption [11].

If system has no negative feedbacks [12], i.e., all K_{ij} values are equal to zero, the phase trajectory of the collective intercluster process (the dependence of the dimensionless rate w/w_0 of the process on the extent of reaction $(1 - x)$ [11]) will appear as straight line *1* in Fig. 2. This straight line is the universal phase trajectory of unimolecular reactions. In the opposite case, when the feedback is very strong [12] ($K_{ij} \longrightarrow \infty$), once formed, Red immediately reacts with an Ox_3 active cluster to form an $\mathrm{Ox}_2\mathrm{Red}$ inactive cluster. This behavior is represented by straight line *2* in Fig. 2. In this case, the kinetics of Ox consumption also obeys the first-order-reaction law; the process comes to an end, however, after one-third of the initial amount of Ox has been consumed, with the rest of the oxidizer remaining in the solution (curve *2* in Fig. 2). The phase trajectory of a classical trimolecular reaction is described by curve *3* in Fig. 2. This corresponds to the binominal distribution of Ox and Red over the trimers according to the Bernoulli scheme [13], when $K_{31} = 3$, $K_{30} = 9$, and $K_{20} = 3$. Given this distribution is formed, the unimolecular decay of Ox_3 into products will imitate a classical trimolecular reaction of consumption of Ox: $-d[\mathrm{Ox}]/dt = k[\mathrm{Ox}]^3$. Note that not all K_{ij} constant are independent; in all cases, $K_{30} = K_{20}K_{31}$.

For the oxidation of water in the coordination sphere of the $\mathrm{Mn}_2^{\mathrm{IV}}$ binuclear complex, we previously found that the equilibrium constant of the redox reaction $\mathrm{Mn}_2^{\mathrm{IV}} + \mathrm{Mn}_2^{\mathrm{III}} \Leftrightarrow 2\mathrm{Mn}^{\mathrm{IV}}\mathrm{Mn}^{\mathrm{III}}$ is $K = 1$ [4]. This means that the redox potentials of the $\mathrm{Mn}_2^{\mathrm{IV}}/\mathrm{Mn}^{\mathrm{IV}}\mathrm{Mn}^{\mathrm{III}}$ and $\mathrm{Mn}^{\mathrm{IV}}\mathrm{Mn}^{\mathrm{III}}/\mathrm{Mn}_2^{\mathrm{III}}$ pairs, E_1 and E_2, are equal to each other, since $K = \exp(-\Delta G°/RT) = 1$, i.e., $\Delta G° = -nF(E_1 - E_2) = 0$ (n is the number of electrons transferred and $F = 23.06$ kcal/(mol V)) [14]. Note that, for similar model Mn_2 dimers, the redox potentials of the $\mathrm{Mn}_2^{\mathrm{III}}/\mathrm{Mn}^{\mathrm{III}}\mathrm{Mn}^{\mathrm{II}}$ and $\mathrm{Mn}^{\mathrm{III}}\mathrm{Mn}^{\mathrm{II}}/\mathrm{Mn}_2^{\mathrm{III}}$ are also equal to each other [15], although they can differ markedly in the presence of organic ligands capable of stabilizing one or another oxidation state of the metal ion.

The phase trajectory of the consumption of $\mathrm{Mn}^{\mathrm{IV}}$ (or the accumulation of the product of its reduction, $\mathrm{Mn}^{\mathrm{III}}$) plotted based on kinetic curve *1* is displayed in Fig. 2 (circles). As can be seen, the experimental points are closely described by curve *4*, which was calculated for the collective process in the coordination sphere of the trimer cluster at $K_{ij} = 1$ for all internal equilibria involved. The first derivative of trajectory *4* at the beginning of the process is equal to 3 (straight line *2* in Fig. 2 is the tangent to the initial segment of curve *4*, the slope of which is identical to the derivative of curve *4* at the beginning of the reaction), the value that corresponds to the number of kinetically independent oxidizers in the medium that enter into the composition of the reactive cluster [11]. At low values of [Mn], nearly all Mn^{IV} exists in the form of Mn_2^{IV} binuclear complexes [4]. Therefore, the role of a kinetically independent oxidizer is played by the Mn_2^{IV} complex, capable only of producing the four-electron oxidation of water to oxygen. The standard redox potentials of the Mn^{IV}/Mn^{I} and Mn^{IV}/Mn^{0} pairs are too low to oxidize water, a factor that makes both the six- ($Mn_2^{IV} \longrightarrow Mn_2^{I}$) and eight-electron ($Mn_2^{IV} \longrightarrow Mn_2^{0}$) processes unfeasible. An analysis of the Frost diagram [16] shows that the redox potentials for the first and second of the above two pairs do not exceed +0.7 and +0.2 V, respectively. The oxidation of water can involve only the $Mn^{IV} \longrightarrow Mn^{II}$ and $Mn^{IV} \longrightarrow Mn^{III}$ transitions, while the active trimer cluster Ox_3 (as the derivative of trajectory *4* in Fig. 2 suggests) is a hexanuclear cluster, $(Mn_2^{IV})_3$, since Ox designates Mn_2^{IV}. In contrast to Mn_2^{IV}, the hexanuclear cluster contains a sufficient number of holes to be able to oxidize water to ozone. The formation of ozone was observed experimentally (curve *2* in Fig. 1). That the amount of ozone is much smaller than that expected based on the kinetic data (a fraction of a percent of the amount of Mn^{III} formed; Fig. 1) is difficult to explain. We know, however, that the major part of the ozone formed decomposes catalytically in the reaction mixture in the presence of Mn^{IV} compounds, a process accompanied by the oxidation of Mn^{III} to Mn^{VII} [8]. The consumption of ozone in the reaction mixture is accompanied by the reduction of Mn^{IV} with the formation of small amounts of Mn^{VII} [5, 6], an observation that we previously erroneously explained by the disproportionation of four Mn^{IV} ions into three Mn^{III} ions and one Mn^{VII} ion.

If the reaction mixture contains no catalysts of ozone decomposition or easily oxidizeable substances, chemical methods of ozone production are characterized by significant yields of the target product. For example, the thermal decomposition of the peroxocomplex of sulfuric acid, which is formed in a sulfuric acid solution of hydrogen peroxide [17], is characterized by an ozone yield that can exceed 30% [18]. For the oxidation of water by the reaction $2O_2^{+}AsF_6^{-} + 3H_2O \longrightarrow O_3 + O_2 + 2H_3O^{+}AsF_6^{-}$ in HF solutions, the ozone yield is as high as 83% [18].

The formation of ozone during the electrolysis of water was first detected as long ago as 1801 due to its specific order, but it was not until 1840 that it was identified as a new compounds by C.F. Schonbein, who called it ozone (after Greek ozein, “to smell”) [19]. Since ozone is considered a promising disinfecting agent [20], an intense search for stable electrodes for its industrial production by means of the $3H_2O - 6e^{-} \longrightarrow O_3 + 6H^{+}$ electrolysis reaction is under way. Therefore, it is small wonder that ozone is produced on so-called nanoelectrodes, Mn_k^{IV} clusters existing in electrochemical equilibrium with the medium [21].

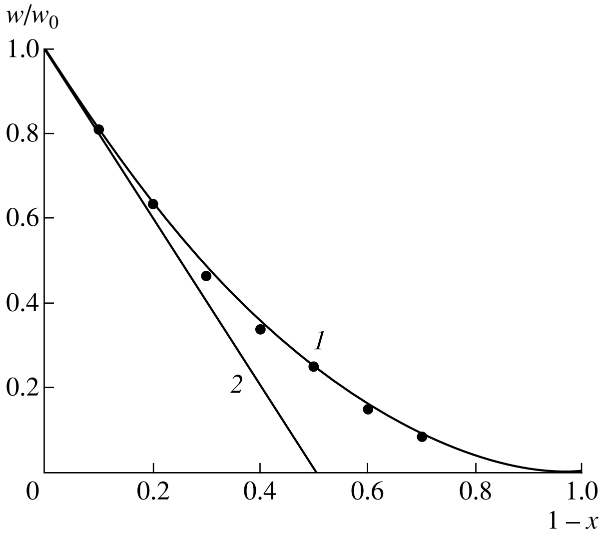

Fig. 3. Phase trajectories for the formation of ozone during the oxidation of water by Mn^{IV} hexanuclear clusters. The experimental points were obtained from kinetic curve *2* in Fig. 1. For the notations, see the text.

By analogy with the evaluation of the number of the oxidizing species in the active cluster on the basis of the Ox consumption trajectory [11], one can determine the number of product molecules per elementary event of the intercluster collective reaction. Figure 3 shows the phase trajectory of the ozone formation reaction (curve *1*) and the tangent to it at the beginning of the process, the slope of which is the first derivative $n = dw/dx$. These data, obtained from curve *2* in Fig. 1, are indicative of the formation of two ozone molecule in the elementary event of decay of the Ox_3 hexanuclear cluster. Thus, at 82°C and a manganese concentration in the reaction mixture of $[Mn]_0 = 0.05$ mol/l, the major part of ozone is produced by Ox_3, in the coordination sphere of which six water molecules are concurrently oxidized to yield two ozone molecules: $Mn_6^{IV} \cdot 6H_2O \longrightarrow Mn_6^{II} + 2O_3 + 12H^{+}$.

As during the formation of an oxygen molecule in the coordination sphere of Mn_2^{IV} [4], Mn^{II} formed interacts with Mn^{IV} to produce Mn^{III}, so that the reaction mixture contains no other manganese-bearing complexes in appreciable concentrations except for Mn^{IV} and Mn^{III} clusters.

At a lower temperature, 75°C, the concentration of Ox_3 is higher, as is the rate of the formation of ozone at the expense of the other reaction products. Note, how-

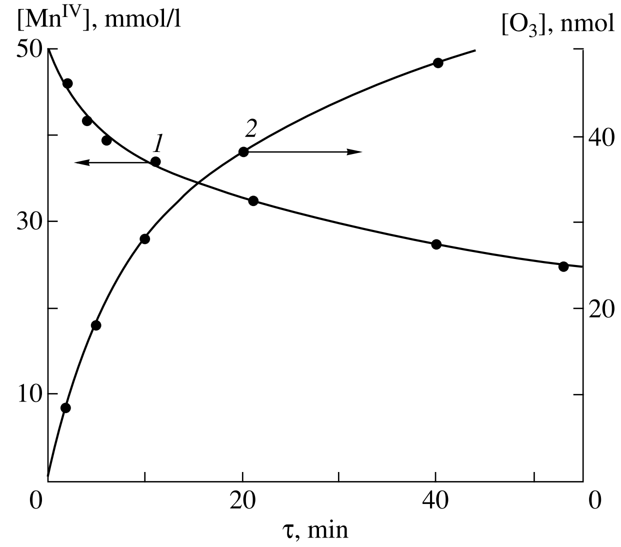

Fig. 4. Kinetics of (*1*) Mn^{IV} consumption and (*2*) ozone formation during the oxidation of water by Mn^{IV} clusters at 61°C. The rest of the experimental conditions are specifies in the caption of Fig. 1.

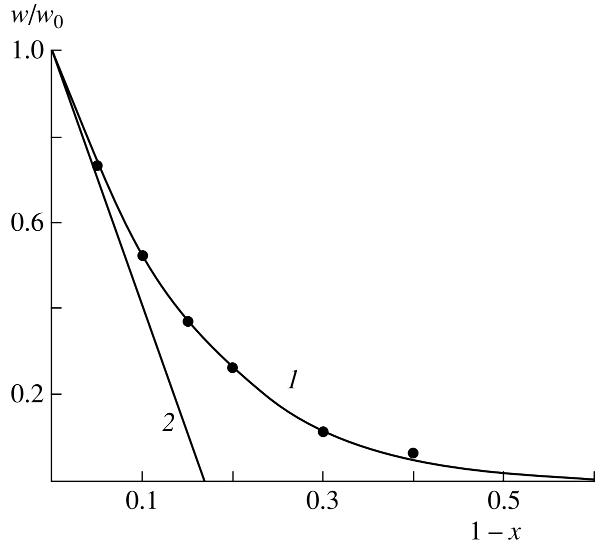

Fig. 5. Phase trajectory for the reduction of Mn^{IV} at 61°C. The rest of the experimental conditions are specifies in the caption of Fig. 1.

ever, that, at 69°C, the formation of ozone virtually stops, although the oxidation of water proceeds at a sufficiently high rate, as can be seen from the rate of the consumption of the oxidizer (Mn^{IV}). In this case, the phase trajectory shows that Ox_4, not Ox_3, exhibits high activity. The decay of Ox_4 yields four oxygen molecules rather than two ozone molecules. We believe that, in this case, the primary products are two oxoozone molecules (O_4), which decompose to give four oxygen molecules within 10^{-12} s [22]. The lifetime of O_4 is too short, however, to detect it; probably femtosecond flash photolysis would be helpful in identifying O_4 during photochemically stimulated water decomposition. At present, whether O_4 is formed remains unclear.

Typical kinetic curves of the consumption of Mn^{IV} and formation of ozone at 61°C are displayed in Fig. 4. The phase trajectory of the reduction of Mn^{IV} (Fig. 5) plotted based on curve *1* in Fig. 4 shows that, at this temperature, the main contribution to water oxidation comes from Ox_6, a hexamer cluster ($dw/dx = 6$) containing 12 Mn^{IV} nucleus; as a result, four ozone molecules are formed (Fig. 6); i.e., all 24 hole available in the Mn_{12}^{IV} dodecanuclear cluster are involved. At a lower temperature, 58°C, clusters larger than Ox_6 appear. Correspondingly, the number of electrons transferred becomes larger, so that six ozone molecules are concurrently formed. Naturally, at still lower temperatures, $T < 50$°C, Mn^{IV} solutions are stable and do not oxidize water.

The structure of clusters formed under various experimental conditions is unknown. Previously, it was assumed that $L_4Mn(\mu\text{-}O)_2MnL_4$ binuclear complexes dimerize to form Mn_4 tetranuclear clusters with cubane structure [6]. Such structures were later observed for cobalt clusters and postulated to exist in the manganese cofactor of the active site of the PS-2 [23]. We believe that the enlargement of clusters (through the consecutive addition of binuclear complexes) results in the formation of hexa- (Ox_3), octa- (Ox_4), and bigger clusters, up to the formation of a solid phase.

The rate of reduction of Mn^{IV} increases with the temperature up to 80°C, remaining constant at higher temperatures. Despite the fact that the composition of the active cluster changes (from Ox_6 to Ox_3), as does that of the products (ozone, oxygen), with increasing temperature, the temperature dependence of the rate of reduction of Mn^{IV} (at $t < 80$°C) obeys the Arrhenius law with an activation energy of 10 ± 1.5 kcal/mol. The activation barrier for the formation of O_3 coincides with this value within the error limits if the experimental points near 70°C are excluded from consideration, a temperature range within which water is oxidized to oxygen rather than to ozone.

It is understandable why all accessible holes of clusters with various compositions participate in the oxidation of water (the larger the number of electrons transferred, the lower the Gibbs energy of the process). It is more difficult to understand how these clusters decide what product should be formed from the substrate undergoing oxidation (oxygen or ozone). It is quite clear that the Mn_2^{IV} clusters can yield only one oxygen molecule; but it is not quite clear why Ox_3, which could yield six oxygen molecules, produces two ozone molecules instead. This problem calls for further studies.

Note that the four-electron oxidation of water to O_2 by the Mn_2^{IV} complex is characterized by an activation energy (24.5 kcal/mol [4]) substantially higher than that observed for the oxidation of water by larger clusters (~10 kcal/mol; see above). This is probably associated with the fact that the formation of a ground-state (triplet) oxygen molecule from two ground-state (singlet) water molecules in the coordination sphere of Mn_2^{IV} is a spin-forbidden process while the formations of the other products (two ozone or four oxygen molecules) are spin-allowed processes (the ground state of ozone is singlet one, as that of the water molecule).

Thus, the functional chemical model of the manganese cofactor of the oxidase in the PS-2 of natural photosynthesis suggests that water can be oxidized not only to oxygen but also to ozone and, probably, to oxozone. It is difficult to overestimate the importance of many-electron collective processes for inorganic chemistry. Given that the number of such processes will increase (recently, the eight-electron reduction of nitrogen to ammonia was described within the framework of a functional chemical model of the iron–molybdenum cofactor of nitrogenase [24]), it is important to analyze the kinetic behavior of collective processes. Since the traditional methods of chemical kinetics are of little value in this case, the development of kinetic methods for describing collective processes, in particular an analysis of the phase trajectories of many-molecular reactions in the coordination sphere of the cluster, is a promising avenue of research.

Of course, the simulation of many-electron processes (with transfer of 24 (or more) electrons per elementary event) in models of the cofactors of active sites in metalloenzymes produces a strong impression, but the question arises whether such processes are realized in nature. At present, it is firmly established that the manganese cofactor of the oxidase in photosystem **II** of natural photosynthesis is a tetranuclear cluster and that each manganese ion in it is oxidized to Mn^{IV} after which a concert reaction produces an oxygen molecule [25]. Upon receiving new interesting results on many-electron reactions within the framework of the functional model of the manganese cofactor of the oxidase in the PS-2 (ozone formation), we searched for biological photosynthesizing organisms in which such processes, for example, the six-electron oxidation of water to ozone, occur. We managed to detect the release of small amounts of ozone during irradiation of *Phyllophora nervosa* and *Polysiphonia elongate* red seaweeds [26] with visible light. We explained this observation by the presence of small amounts of 6Mn-co hexanuclear manganese cofactors, along with the 4Mn-co normal tetranuclear cofactor. The 6Mn-co cofactors oxidize water to ozone, as in the chemical model under consideration. We cannot exclude the formation of oxozone, both in nature and model systems; however, this hypothesis needs experimental confirmation.

As far as we know, it was for the first time that a new reaction (the oxidation of water to ozone) was first revealed by means of a functional chemical model and then in a natural object (the manganese cofactor of the oxidase in the PS-2 of red seaweeds).

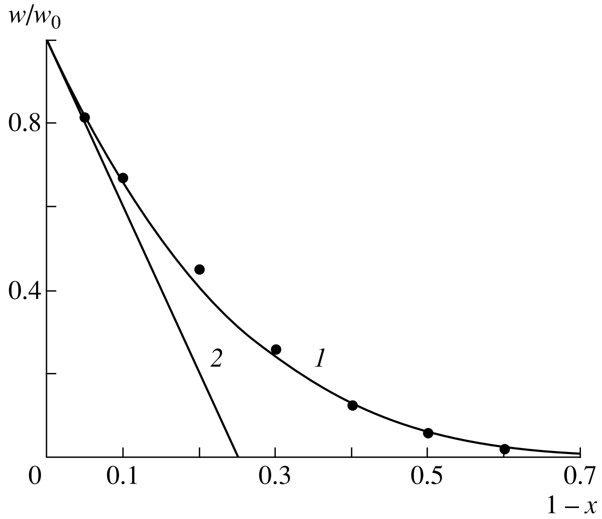

Fig. 6. Phase trajectory for the formation of ozone at 61°C. The rest of the experimental conditions are specified in the caption of Fig. 1.

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