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Review

Water exchange in manganese-based water-oxidizing catalysts in photosynthetic systems: From the water-oxidizing complex in photosystem II to nano-sized manganese oxides☆

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ABSTRACT

The water-oxidizing complex (WOC), also known as the oxygen-evolving complex (OEC), of photosystem II in oxygenic photosynthetic organisms efficiently catalyzes water oxidation. It is, therefore, responsible for the presence of oxygen in the Earth's atmosphere. The WOC is a manganese–calcium ($Mn_4CaO_5(H_2O)_4$) cluster housed in a protein complex. In this review, we focus on water exchange chemistry of metal hydrates and discuss the mechanisms and factors affecting this chemical process. Further, water exchange rates for both the biological cofactor and synthetic manganese water splitting are discussed. The importance of fully unveiling the water exchange mechanism to understand the chemistry of water oxidation is also emphasized here. This article is part of a Special Issue entitled: Photosynthesis Research for Sustainability: Keys to Produce Clean Energy.

1. Introduction

Oxygenic photosynthesis is a fundamental biological process by which cyanobacteria, algae, and plants reduce atmospheric CO_2 to energy-rich organic compounds using electrons extracted from water during water-splitting [1]. Photosynthetic water-splitting takes place in the water-oxidizing complex (WOC) of photosystem II (PSII), a large pigment-binding protein complex found in all oxygen-evolving organisms. To understand the mechanism of photoinduced water-splitting in PSII, a large number of studies have been carried out [1,2]. Pirson was the first to discover that Mn is essential for oxygenic photosynthesis [2,3] and extensive research since then has led to the establishment of the PSII pigment–protein complex to be responsible for photosynthetic oxygen evolution [4]. X-ray crystallographic analysis of thermophilic cyanobacterial PSII preparations has provided detailed information on the catalytic center of oxygen evolution [5–8].

The 1.9 Å resolution structural analysis (Fig. 1a) has revealed that the WOC contains five O atoms in addition to Mn_4Ca, forming a Mn_4CaO_5-cluster, and that they are arranged in a distorted chair-like form (Fig. 1a) [8]. In this chair form (Fig. 1a), three Mn (designated Mn1 to Mn3), one Ca, and four O atoms form a cubane-like structure, whereas the fourth Mn (Mn4) is located outside of the cubane and is associated with the cubic structure by μ-oxo-bridges (Fig. 1a). Four water molecules were found to serve as the terminal ligands to the metal cluster,

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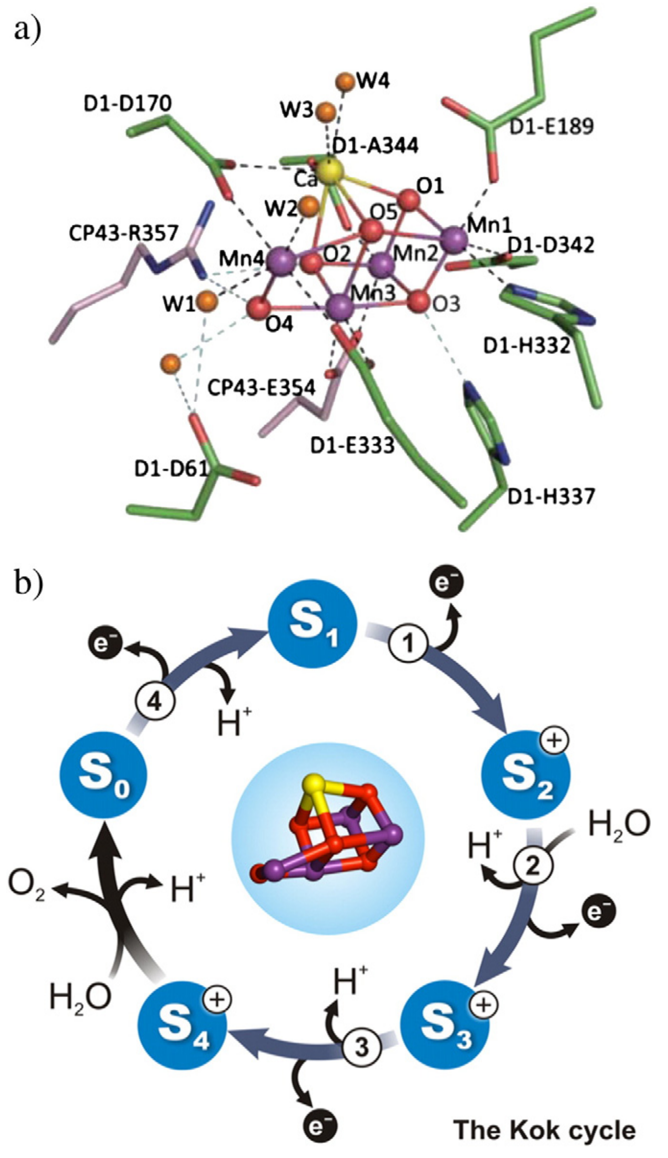

Fig. 1. There are only a small fraction of the residues that come in direct contact with the Mn–Ca cluster (image was modified from [8]) (a). Kinetic scheme (Kok cycle) describing the S_i state advancement by electron and proton removals from the WOC during water-splitting in PSII. Water-binding within the cycle is based on FTIR data by Noguchi [42,87]. Both waters likely represent ones that become substrates in the next cycle. Image is from [68] (b).

among which, two are ligated to Mn4 and the other two to the Ca ion. Some of these water molecules may serve as the substrate for water-splitting. For available kinetic, energetic, biochemical and structural information on the WOC see Refs. [9–11].

2. Flash-induced oxygen evolution pattern — the Joliot experiment and the Kok cycle

A first understanding of steps involved in oxygen evolution in photosynthesis became possible when short and intense light flashes, with appropriate dark periods, were used and oxygen evolution was measured per flash in a sequence of flashes. Experiments by Joliot in 1969 showed that flash illumination produced an oscillating pattern in the oxygen evolution and a maximum occurred on every *fourth* flash [12]. Water oxidation to produce one oxygen molecule requires the removal of four electrons, and Kok et al. [13] proposed an explanation for the observed oscillation of the oxygen evolution pattern. Kok's hypothesis was that in a cycle of water oxidation, a succession of oxidizing equivalents is stored at the WOC, and when four oxidizing equivalents have accumulated one by one, an oxygen molecule is spontaneously evolved [14]. Each oxidation state of the WOC is known as an "S-state", with S_0 being the most reduced state and S_4 the most oxidized state in the catalytic cycle (Fig. 1b) [13]. However, a tyrosine (Y_D) in PSII slowly oxidizes the WOC from S_0 to S_1 in the dark. States that are more reduced than S_0, such as S_{-1} and S_{-2}, are also possible [15].

In order to explain the fact that the first maximum of oxygen evolution is after the 3rd flash, and then after the 7th and the 11th flash, the S_1 state was concluded to be dark-stable. The $S_4 \rightarrow S_0$ transition is light independent and in this state oxygen is evolved. All other S-state transitions are initiated after photochemical oxidation of P_{680} at the PSII reaction center [13].

Even after the availability of 1.9 Å atomic structure of WOC [8], relatively little is known about the molecular mechanism of water oxidation. In this context, information on when the substrate water molecules bind to the catalytic site during the S_i state cycle of the photosynthetic oxygen evolution would be of significant value because it can provide a deeper insight into the mechanism of water oxidation. In addition, mimicking this reaction with synthetic analogs is expected to be of fundamental importance for bioinorganic chemistry of this system [16–31]. Additionally, Mn based water oxidation catalysts are important candidates for the development of artificial photosynthetic devices, i.e., systems for the synthesis of fuels such as hydrogen or methanol using solar energy [16–31]. In this review, we will focus on water exchange chemistry and explain different mechanisms and different factors in water exchange by metal ions. Then, we will consider water exchange for the Mn compounds as water-oxidizing catalysts in both artificial and natural photosynthetic systems.

3. Ion hydration/solvation

Many physico- and bio-chemical processes are directly controlled, or indirectly conditioned by metal ions [32]. In aqueous solution, metal ions are coordinated by water molecules, and, in addition to the first coordinated group, there are some water molecules in the second shell around the ions. The first solvation number, n, in $M(H_2O)_n$ of many metal ions has been determined directly by X-ray or neutron diffraction. Regarding the first shell, if $M(H_2O)_n$ exchanged water molecules rapidly (within a matter of seconds) it would be considered labile, whereas if it substituted slowly, it would be considered inert. The rate of exchange depends on the properties of the metal ion, the oxidation state, the ratio of the charge to the radius of metal ions and many other factors (Fig. 2) [13,33–35].

The water exchange is a substitution reaction. In a substitution reaction, also known as single displacement reaction or single replacement reaction, a group in a compound is replaced by another group [36,37]. For substitution reaction of metal complexes, Langford and Gray (1965) proposed three different mechanisms [38] (see Fig. 3 [39]):

a) A dissociative (D) reaction with an identifiable intermediate of low coordination number; it is called the D mechanism.
b) An associative (A) reaction with an identifiable intermediate of higher coordination number; it is called the A mechanism.
c) An interchange (I) reaction where the bond making and breaking were either synchronous or else took place within the pre-formed aggregate; it is called the I mechanism which is subdivided into dissociative-like (I_d) or associative-like (I_a) mechanism. Thus, the identification of an intermediate species is essential for the determination of the mechanism of reaction.

4. Activation parameters

By studying the effect of temperature or pressure on the water exchange rate, we expect to obtain useful information on the activation parameters of these reactions [35].