The Manganese Center in Photosynthetic Oxygen Evolution

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Photosynthetic oxidation of water to dioxygen is a process essential for the maintenance of life. The structure and mechanism of the enzyme which catalyzes the four-electron oxidation of two water molecules to dioxygen by photooxidation is being pursued in several laboratories.

For many years it has been known that manganese ions are required in oxygen-evolving photosynthesis organisms [1]. Removal of manganese from chloroplasts invariably results in the loss of their oxygen-evolving capacity. Manganese is attractive as an element in the water splitting reactions of photosynthesis because it has several stable oxidation states which encompass a wide range of redox potentials. However, the details of its participation have not yet been well established. It is generally agreed that "pools" of manganese exist in chloroplasts. These pools have been classified into three groups [2] only two-thirds of which are involved in O_2-evolution.

In 1970 Kok et al. [3] proposed the first detailed scheme for the evolution of O_2 in photosystem II (PSII). In this scheme, the reaction center of PSII goes through four consecutive photoactive states (S_0, S_1,..., S_4), which are related by one electron oxidation (Figure 1). Oxygen is released at the decay of a final state

$$S_0 \xrightarrow{h\nu} S_1^{+} \xrightarrow{h\nu} S_2^{2+} \xrightarrow{h\nu} S_3^{3+} \xrightarrow{h\nu} S_4^{4+} \longrightarrow S_0 + O_2$$

Figure 1

(S_4) to the initial state (S_0). The deduction that there is an accumulation of oxidizing equivalents at the poly-manganese site in the oxygen-evolving system has initiated several attempts to demonstrate experimentally changes in the oxidation state of manganese. The dependence of the NMR relaxation times of water protons on the number of light flashes given to chloroplasts was taken by Whydrzynski et al. [4] as evidence for changes in the oxidation state of photosynthetic manganese. Support for the oxidation state changes has also been obtained by Sauer et al. [5,6]. In their work, the amount of manganese released after heat-treatment of flash-illuminated chloroplasts was estimated. Recently, Dismukes et al. [7,8] have been able to observe a multi-line EPR signal due to hyperfine structure from two or more manganese ions by a freeze-trapping technique. This signal is similar to that seen [7,8] for the $Mn^{III}Mn^{IV}$ complex $(bpy)_2Mn\langle O \rangle_O Mn(bpy)_2^{3+}$. EXAFS studies of the manganese ions in PSII further suggest a Mn-Mn separation of 2.7 Å and an inner coordination sphere for the metal ions consisting of "light" donor atoms (O and N) [9,10]. Several mechanisms have been proposed for the oxygen evolution reaction in the Mn center of PSII. One of the mechanisms is shown in Figure 2.

Recent studies of a Mn(III)-catechol-semiquinone chelate system (i.e., Figure 3) suggest that system may serve as an important model for the O-O bond formation during the oxidation of water. The existence of the "quinoid" species has also been supported by Sauer's observation of a rapidly decaying (τ = 400-900 μs) radical species in spinach chloroplasts [11]. Recent work of Pierpont, Hendrickson and coworkers has demonstrated that quinone ligands are capable of functioning as multielectron storage sites during the process of producing oxygen from two coordinated water molecules [12].

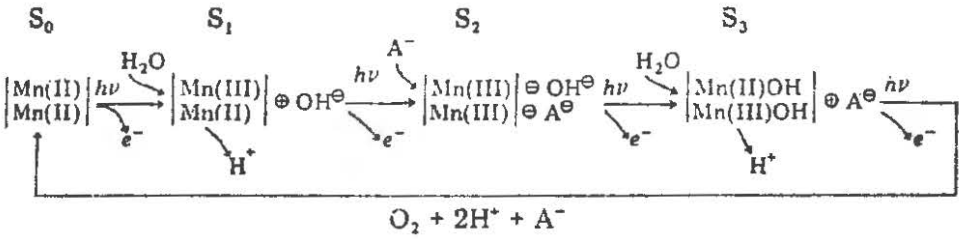

Figure 2

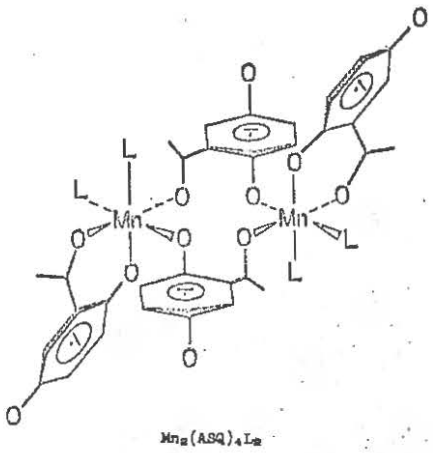

Figure 3

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