Chapter 25

Mechanism of Photosynthetic Oxygen Production

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Summary

This chapter deals with the mechanism of photosynthetic water oxidation that leads to O₂ formation in Photosystem II (PS II). After a brief introduction to the structure and function of the PS II complex, the S-state cycle (Kok model) is outlined and the structure and oxidation states of the catalytic Mn₄O₃Ca complex are summarized. We then cover in detail the current information concerning substrate water binding and consider energetic and kinetic aspects of photosynthetic water oxidation. On that basis, we discuss several recent mechanistic proposals for O-O bond formation in PS II and summarize our current perceptions in a novel mechanistic proposal for photosynthetic water oxidation.

I. Introduction

Photosynthesis describes the complex biological processes by which solar energy is converted into chemical energy. This energy conversion is performed by so-called photosystems. Photosystem II (PS II) is of pivotal importance to life on earth because it is the principle means by which molecular oxygen is generated. The light-induced formation of O₂ in PS II can be summarized as follows:

\[
2 \text{H}_2\text{O} + 4 \text{hv} \rightarrow \text{O}_2 \uparrow + 4 \text{H}^+ + 4 \text{e}^- \quad (1)
\]

PS II is distributed throughout all higher plants; the aquatic green, red and brown algae (Chlorophyta, Rhodophyta, Phaeophyta); cyanobacteria and diatoms (Chrysophyta). Common to all PS II complexes is the presence of chlorophyll (Chl) α pigments. Structurally, PS II is a multi-subunit Chl/protein complex that consists of close to 30 polypeptides (Hankamer et al., 2001; Shi and Schroder, 2004; Chapter 6, Thornton et al.; Chapter 18, Hankamer et al.). It is located within the thylakoid membrane. With the exception of the light-harvesting antenna system and a number of extrinsic proteins, only minor structural/functional differences have been reported between PS II complexes from these different species. The origin of PS II is unclear and extensive lateral gene transfer is likely involved between different reaction centers (Chapter 30, Dismukes and Blankenship).

Figure 1 presents a schematic overview of the arrangement of the co-factors in PS II (a more detailed picture is given in Chapters 19 (Witt), 20 (Shen and Kamiya), 21 (Harber and Iwata)). The catalytic center of water oxidation, the Mn₄O₃Ca complex (see Fig. 1), is located on the lumenal side of PS II. However, due to large luminal extensions of the inner antenna proteins CP43 and CP47 (Chapter 3, Eaton-Kaye and Putnam-Evans) and the presence of three extrinsic proteins (Chapter 5, Bricker and Burnap), the Mn₄O₃Ca complex is actually situated not far from the center of PS II, where it is apparently well shielded from the aqueous phase. In the case of higher plants, the extrinsic proteins have molecular weights of about 33 kDa, 23 kDa, and 17 kDa; while in cyanobacteria, the two smaller proteins are substituted by cytochrome c₅₅₉ and a 12 kDa extrinsic protein (Shen et al., 1992; Seidler, 1996; Chapter 5, Bricker and Burnap).

The secluded position of the Mn₄O₃Ca complex within the PS II structure suggests that the protein matrix is important for the proper function of the oxygen-evolving complex (OEC). In the absence of the extrinsic proteins, for example, nonphysiological

Abbreviations: Kβ XES - Kβ X-ray emission spectroscopy; Chl - chlorophyll; EPR – electron paramagnetic resonance; ENDOR – electron nuclear double resonance; ESEEM – electron spin echo envelope modulation; ET – electron transfer; ELEXAFS – extended X-ray absorption fine structure; NMR – nuclear magnetic resonance; OEC – oxygen-evolving complex; Pheo – pheophytin; PT – proton transfer; PCET – proton coupled electron transfer; PRE – proton-relaxation rate enhancement; P680 – the primary electron donor in PS II; Sₙ states (n = –5, ..., 4) – formal notation for the oxidation states of the OEC; XANES – X-ray absorption near edge structure; Q₁, Q₂, plastoquinone molecules that act as one and two electron acceptors in PS II, respectively; Y₁ – redox active tyrosine D2-Y160; Y₂ – redox-active tyrosine D1-Y161