

**MECHANISTIC CONSIDERATIONS ON COUPLING OF ELECTRON
AND PROTON TRANSFER REACTIONS AND THE ACTIVE ROLE
OF THE PROTEIN MATRIX IN PHOTOSYNTHETIC OXIDATIVE
WATER CLEAVAGE**

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Oxidative photosynthetic water cleavage into molecular oxygen and four protons occurs via a sequence of redox steps that are energetically driven by the strongly oxidizing cation radical P^+ . This species formed as a result of light-induced charge separation in Photosystem II becomes reduced by Y_Z thus generating Y_Z^{ox} that in turn oxidizes stepwise the catalytic site of the water-oxidizing complex (WOC).

Thermodynamic and kinetic constraints of this process require a balanced fine tuning of the reaction coordinates that depends on the mode of coupling between electron (ET) and proton (PT) transfer of each individual redox reaction. Mechanistically the formation of the O-O bond is the most critical step of the overall process.

In this communication four topics will be discussed:

1. *Multiphasic kinetics of P^+ reduction by Y_Z .* This characteristic feature is shown to reflect a sequence of three different types of rate limitation: (i) nonadiabatic electron transfer ("fast" ns reaction), (ii) local "dielectric" relaxation ("slow" ns reaction), and (iii) "large scale" proton shift (μ s kinetics).
2. *ET/PT coupling mode of the individual oxidation steps within the WOC.* The coupling mechanism is assumed to depend on the redox state S_i of the WOC: S_0 and S_1 oxidation comprises separate ET and PT pathways while S_2 and S_3 undergo PCET (proton coupled electron transfer) redox reactions analogous to Babcock's hydrogen atom abstractor model [1].
3. *Postulation of S_3 as to be a multistate redox level of the WOC with a fast dynamic equilibrium that comprises both redox isomerism and proton tautomerism.* The primary event in the essential O-O bond formation is the population of a state $S_3(P)$ characterized by an electronic configuration and nuclear geometry that corresponds with a complexed hydrogen peroxide [2]. This peroxidic type $S_3(P)$ is the *entatic* state for the generation of complexed molecular oxygen through $S_3(P)$ oxidation by Y_Z^{ox} [2].
4. *Active role of the protein matrix itself.* It is proposed that the protein matrix exerts catalytic activity by functioning as "PCET director". The WOC is envisaged as a large supermolecule that is especially tailored for oxidative water cleavage [3].

REFERENCES

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3. Renger, G. Coupling of electron and proton transfer in oxidative water cleavage in photosynthesis. **Biochim. Biophys. Acta** 1655 (2004) 195-204.