

Surprising glycerol effect on the activation enthalpy of water oxidation in photosystem II

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Water oxidation in Photosystem II (PSII) is a process of fundamental importance for life on our planet. Moreover, it is a key reaction in future technological systems for production of solar fuel, where the biological process represents an important source of inspiration. Tremendous progress has been obtained, especially in structural characterization of photosystem II. However, mechanistically water oxidation still is insufficiently understood. Knowledge gaps relate not only to the local redox chemistry at the Mn₄Ca complex of PSII, but also to the pivotal coupling to protonation and protein dynamics at various time and length scales.

In protein crystallography, glycerol is often used as a cryoprotectant. In the ground-breaking PSII model of Shen and coworkers, several protein-internal glycerol molecules are resolved. Now we have investigated how glycerol affects individual reaction steps in PSII employing analysis of time courses (after laser-flash excitation) of delayed Chl fluorescence (10 μ s - 10 ms) and of the variable Chl fluorescence yield (100 μ s - 500 ms). We used PSII membrane particles from spinach and focused on (i) analysis of the oxygen evolution step (S₃→S₄→S₀ + O₂) and (ii) the quinone electron transfer at the acceptor side of PSII.

The deprotonation step before O-O bond formation is found to be strongly affected by glycerol in the aqueous buffer, even at relatively low concentration, while the rate constant of oxygen evolution and the quantum efficiency of S-state transitions is affected only at high glycerol concentration (above 30% volume percent). An Arrhenius analysis reveals that, surprisingly, the activation enthalpy of oxygen evolution is strongly affected (decreased) by using a buffer system with 30% glycerol, whereas the influence on the rate constant at room temperature is negligibly small. With and without glycerol, the activation enthalpies are significantly lower than the energetic barriers obtained by quantum chemical calculations of (e.g.) Siegbahn.

We conclude that the rate of O-O bond formation is determined, inter alia, by the coupling of the local redox chemistry to protonation and/or protein dynamics. The glycerol influence may result from an influence of the protein dynamics relating to increased solvent viscosity or from disturbed protonation dynamics by specific binding of glycerol molecules within PSII.

figure 1

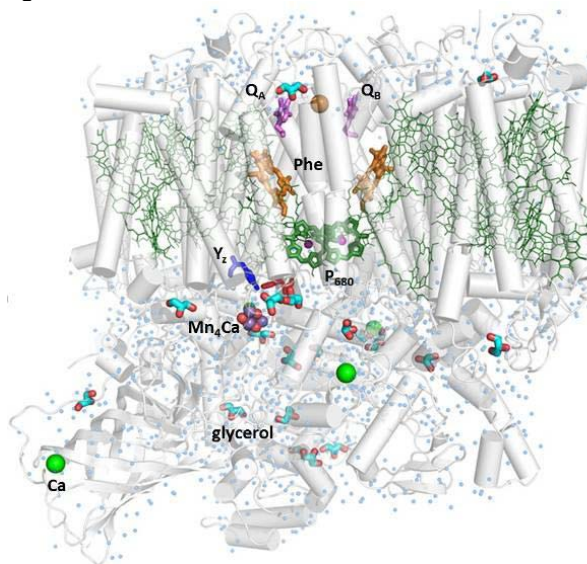


figure 2

