

Chemical Scheme of Water-Splitting Process during Photosynthesis by the Way of Experimental Analysis

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Abstract: Different water oxidation schemes during photosynthesis are developed from different view-point by analysis of different experimental data. In this paper, an approach will be done to create a symmetrical opinion among all of the opinions of water oxidation by perfect analysis of experimental data. However it is an important guide-line to explain the chemical changes in S-state mechanism during water oxidation process.

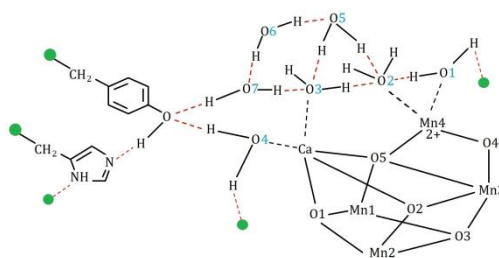
Keywords: S-state Mechanism, Bonding Chemistry, Photochemical Effect, Oxide Reaction.

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I. Introduction

It is already known that the arrangement of hydrogen-bonding network among oxygen-evolving complex (OEC), water molecules (H_2O), tyrosine D1-Y161 and D1-His190 in PS II can play an important role in water oxidation process during photosynthesis. The hydrogen-bonding network which is placed at normal situation of water-splitting procedure in PS II is denoted by red dot lines below:



Water-splitting is occurred obviously in between the first and second water molecules (marked as blue numbers in the above figure) attached with Ca^{2+} and Mn^{4+} of Mn_4CaO_5 cluster by coordinate covalent bonding (shown as black dot lines above). The reaction of water oxidation is proceeded through absorption of photon ($h\nu$) by Mn4 whose oxidation states ranging from +2 to +3 & +4 and finally rearrangement of hydrogen-bonding network will be happened by accepting two water molecules ($2H_2O$) from outside to comeback at normal situation (preliminary figure) of water-splitting procedure.

II. Water-Splitting

At first in the water oxidation process, Mn^{4+} absorbs a photon ($h\nu$) from light and releases an active electron (e) which attacks tyrosine D1- Y161 to produce phenoxide ion of D1-Y161, H^+ and an electron (e). This electron can stabilize photoactive ionized accessory-chlorophyll (P_A^+) into stable accessory-chlorophyll (P_A) [1]. H^+ is accepted by D1-His190 to form ionized D1-His190. As a result, the metallo-oxo cluster (Mn_4CaO_5) is transferred into a state of ionized metallo-oxo cluster ($[Mn_4CaO_5]^+$).

To stabilize the ionized cluster, H^+ ion will be released from second water molecule and a new bond will be formed in between oxygen atom of the water molecule and Mn4 atom (now its oxidation state is +3). That H^+ can be accepted by phenoxide ion of D1-Y161 to generate normal D1-Y161 again. In this situation, ionized D1-His190 can release its previous accepted H^+ to develop normal D1-His190. Here stable metallo-oxo cluster will be created with hydroxide formation from second water molecule at period-one in S-state mechanism [2].

In this way, stable metallo-oxo cluster with peroxide, super oxide and dioxygen [3] (also intermediate S-states [4]) will be formed at period-two, period-three and period-four [5] respectively in S-state mechanism. As well as the oxidation states of Mn4 (+2 in preliminary state) are transferred into +3, (+4 to +2), +3 & (+4 to

+2) respectively in the all periods of S-state mechanism. At final level, two new water molecules ($2\text{H}_2\text{O}$) are accepted to regenerate normal metallo-oxo cluster with its preliminary form.

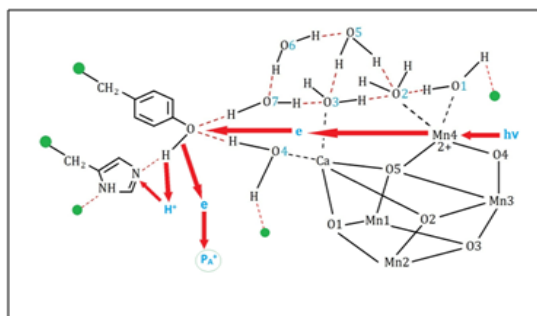


Figure- 1: S_0 (monoxide)

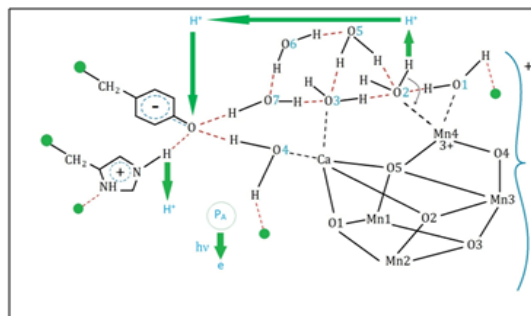


Figure- 2: S_0^* ($[Y_2S_0]$)

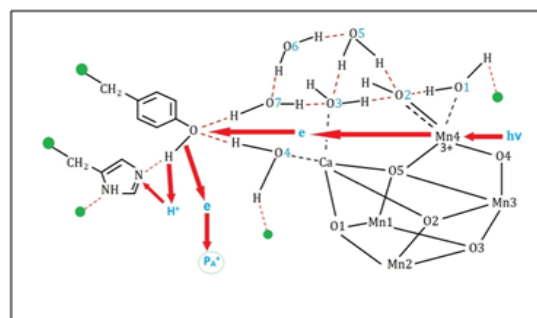


Figure- 3: S_1 (hydroxide)

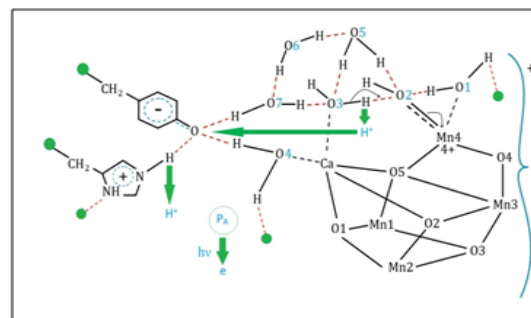


Figure- 4: S_1^* ($[Y_2S_1]$)

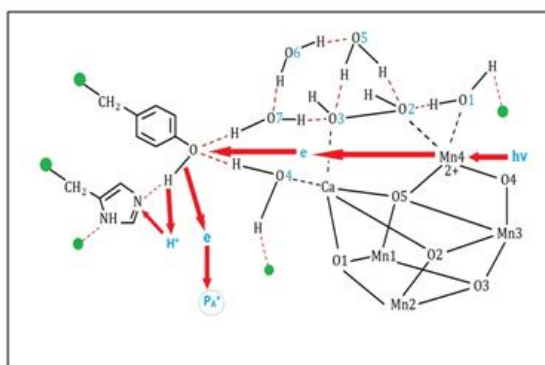


Figure- 5: S_2 (peroxide)

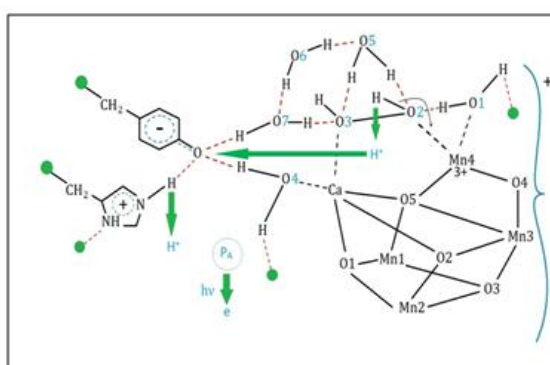


Figure- 6: S_2^* ($[Y_2S_2]$)

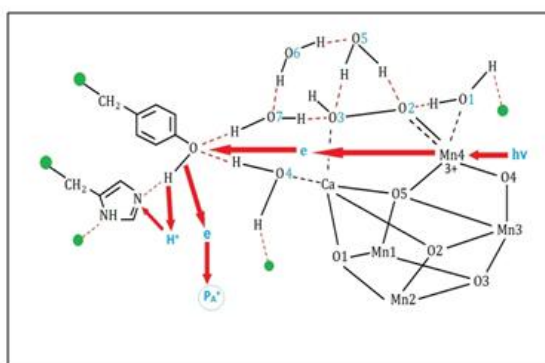


Figure- 7: S_3 (super oxide)

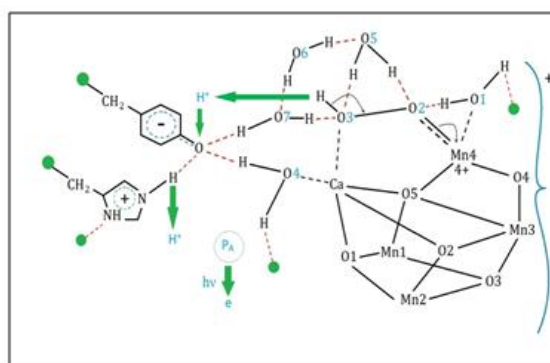


Figure- 8: S_3^* ($[Y_2S_3]$)

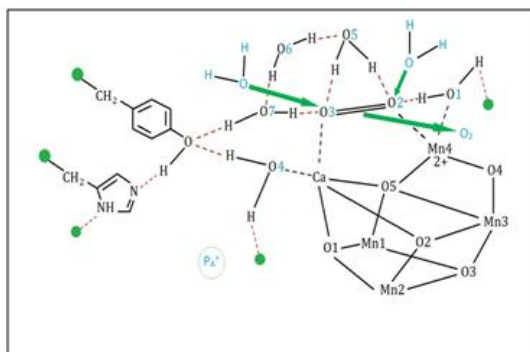


Figure- 9: S_4 (di-oxygen)

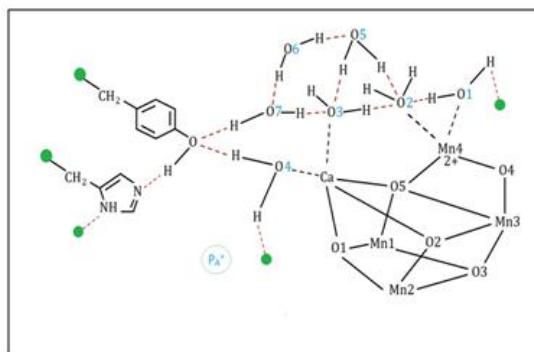


Figure- 10: S_0 (monoxide)

The above figures are considered according to modern introduced S-states (S_0 , S_1 , S_2 & S_3) and intermediate S-states (S_0^* , S_1^* , S_2^* , S_3^* & S_4) [3, 4]. However the discussed scheme successfully explains actual nature of all S-states and the reality of chemical changes in S-state mechanism side by side.

III. Summary

The period-one, two, three and four of S-state mechanism are expressed in figures: 1-3, 3-5, 5-7 & 7-10 respectively. Here the figures of reaction to split water (H_2O) during photosynthesis are developed by perfect analysis of experimental data. All of the possible ways from the data are maintained as a sufficient manner of accuracy (data not shown).

References

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