Necessity of structural rearrangements for O—O bond formation between O5 and W2 in photosystem II

Yu Guo a,1, Biaobiao Zhang a, Lars Klooa,*, Licheng Sun a,b,c,*

a Department of Chemistry, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden
b State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Dalian 116024, Liaoning, China
c Center of Artificial Photosynthesis for Solar Fuels, School of Science, Westlake University, Hangzhou 310024, Zhejiang, China

ABSTRACT

Numerous aspects of the water oxidation mechanism in photosystem II have not been fully elucidated, especially the O—O bond formation pathway. However, a body of experimental evidence has identified the O5 and W2 ligands of the oxygen-evolving complex as the highly probable substrate candidates. In this study, we investigated O—O bond formation between O5 and W2 based on the native Mn4Ca cluster by density functional calculations. Structural rearrangements before the formation of the S4 state were found as a prerequisite for O—O bond formation between O5 and W2, regardless of the suggested pathways involving the typical Mn1(IV)-O species or the recently proposed Mn4(VII)(O) species. Possible alternatives for the S4 state include the S3 → S4 and S2 → S4 transitions, accounting for structural rearrangements during the catalytic cycle. © 2020 The Authors. Published by ELSEVIER B.V. and Science Press on behalf of Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

1. Introduction

Water is oxidized to molecular oxygen by the oxygen-evolving complex (OEC) in photosystem II (PSII) through a catalytic ‘S-state cycle’ (i = 0 to 4) fueled by light absorption, as proposed by Kok [1]. Among the intermediate states in the Kok cycle, the most critical one is the S4 state involving O—O bond formation. However, the S4 state has not been experimentally identified yet, and its structural details remain elusive [2–5]. At present, few proposals for the S4 state involving the O—O bond formation mechanism have been proposed, providing both insights as well as raising controversial hypotheses [6–12]. Revelation of the operation mechanism in nature is pending further research, which is also helpful for the design of water oxidation catalysts in artificial photosynthesis [13–15].

Over the past five years, femtosecond X-ray free electron laser (XFEL) techniques have been developed to resolve ‘radiation-damaged’ crystal structures of the PSII system [16–19]. Up to now, four of the (meta)stable intermediates (S0, S1, S2, and S3) have been visualized, and the most remarkable observation is that an additional oxygen ligand linking Mn1 and Ca in the OEC is only now, four of the (meta)stable intermediates (S0, S1, S2, and S3) have been visualized, and the most remarkable observation is that an additional oxygen ligand linking Mn1 and Ca in the OEC is only visible when the S3 state is involved [18]. This discovery narrows down the possible pathways of O—O bond formation during the S3 → S4 transition, with the remaining possible pathways including O5-Ox, O5-W2, and O5-W3 (Fig. 1) [18].

In parallel to structural crystallography, substrate water exchange investigations combined with spectroscopic results also offer important mechanistic information [20–22]. It is suggested that O5 and W2 are the best options for the identified slowly exchanging substrate water (Wf) and fast exchanging substrate water (Ws), respectively [22–25], although definitive assignments would require further studies scrutinizing other factors, such as the actual conformation of a high-spin S2 state and the diffusion of water through protein channels [25]. The available kinetic data show obvious preference for O5 and W2 to be involved in the dioxygen generation, which is also supported by the results from the recent XFEL experiment [18].

This work tentatively identifies O5 and W2 as the substrates, and explores more details of this indicated O—O bond formation pathway by extensive density functional theory (DFT) calculations.
The main goal is to check the feasibility with their native positions in a non-rearranged OEC cluster, for which situation as we found would generate high reaction barriers. Consequently, structural rearrangements will be necessary for the realistic pathway of O–O bond formation based on the substrates OS and W2.

2. Experimental

2.1. Model construction

The S3 structure was taken from the recent high-resolution (2.07 Å) XFEL structure (PDB:6DHO, monomer A, after deletion of the mixed S2 state) [18]. The truncated OEC model contains the Mn4CaO6 core, the first-sphere ligands W1, W2, W3, W4, D1-Asp170, D1-Glu189, D1-His332, D1-Glu333, D1-Asp342, D1-Glu190, and the nearby crystal waters HOH513, HOH534, HOH597, HOH562, HOH617, HOH622. The α-carbon atoms where the peptide chains were cut off were capped by methyl groups. The initial protonation states of the S3Yz state were decided according to current literatures [26–30], importantly, O1 being oxidized. The protonation arrangements of this S3 model is different from that of the O5-Ox coupling mechanism which had been deeply studied [37,38], where W1 was designed as HO· and Ox was fully deprotonated because the deprotonated W1 (OH−) was considered to accept H+ from Ox (mediated by waters) before Ox being oxidized.

2.2. Spin state definition

As the ground state for S3 is septet/αββ (α/β denotes spin up/down for Mn1, Mn2, Mn3, Mn4) (S = 3) [39], two spin states octet/ααααα and sextet/ααβββ (the last spin center referring to Yz) were adopted for W1 deprotonation in the S3Yz state. Given the spin-crossover effect induced by strong spin–orbit coupling in transition metal chemistry [40,41], all the 16 possible spin states were considered for each case of the S4 state (with reduced Yz): 14-et/ααααα, 12-et/αααββ, octet/αααααα, sextet/ααββββ, 12-et/αααααβ, 10-et/ααααββ, 8-et/ααβββα, 6-et/ααββββ). The last electron hole is supposed to come from Yz oxidation during the S3Yz → S4 transition.

2.3. Computational details

All the DFT calculations were executed by Gaussian 16 (version C. 01) [42]. Geometry optimizations were performed using the unrestricted hybrid functional B3LYP (15% Hartree-Fock (HF) exact exchange), which shows the most reliable energetics compared with experimental results for the OEC system [43]. The effective core potential (ECP) basis set LanL2DZ was employed for Mn, a full electron basis set 6-31G* for the rest C, N, O, H atoms. During geometry optimizations, Grimme’s empirical formula DFT-D3 (Bj-damping) was used for dispersion correction [44]; SMD continuum solvation model (ε = 6.0, solvent-accessible surface (SAS)) was also added to mimic the surrounding protein medium [45]. All the local minima were verified by analytic frequency calculations on the entire models at the same level as geometry optimizations. Zero point energies (ZPE) and thermal frequency calculations on the entire models at the same level as geometry optimizations. Zero point energies (ZPE) and thermal effects (298.15 K, 1 atm) were also obtained in the form of Gibbs free energies corrections. For each transition state (TS) stucture, intrinsic reaction coordinate (IRC) analysis was done to confirm its relationship with the reactant (Rea) and product (Pro). More accurate single point energies were then computed with a larger basis set: SDD for Mn, Ca, and cc-pvTZ for the rest H, C, N, O atoms, with inclusion of Grimme’s DFT-D3 (Bj-damping) and SMD (ε = 6.0, solvent-accessible surface (SAS)).
3. Results and discussion

The O—O bond formation between O5 and W2 was first investigated using the structural model based on the crystal structure of the S3 states [18], i.e., O5 and W2 are at their native positions in a non-rearranged OEC cluster. Assuming a proton loss from W1 during transformation of S3Yz to S4 (Section I in the SM), all the 6 protonation forms of the substrates were considered (Section II in the SM), among which only the two cases of W1H2W2H_O5 and W1H2W2_O5 are worth deeper investigations based on the minimum energy paths (MEP) of O—O bond formation. For simplicity, these pathways are denoted as O5-W2H and O5-W2 coupling, respectively.

In contrast to W1 deprotonation, which is basically spin-insensitive, the O5-W2H and O5-W2 couplings in the S4 state are highly affected by the nature of spin state from aspects of geometric/electronic configurations, energetics, and mechanistic details. Furthermore, the two scenarios of O—O bond formation differ on account of the different protonation states of W2. These demonstrate the necessity to involve multiple spin states and inspection of the substrate protonation states. In the following, we will describe their reaction characteristics along their respective MEPs regarding spin, valence, structure, and above all, thermodynamics/kinetics which determine the feasibility of the different pathways. The upper and lower limits for the overall barriers were calculated by taking into account the spin-transition energy from the 6 protonation forms of the substrates were considered (Sections I and II in the SM), offers another scenario for O—O bond formation from fully deprotonated O5 and W2. Different from the O5-W2H coupling, the electron hole in the S4 reactants for the O5-W2 coupling is located on W2 instead of Asp61. This is attributed to the spontaneous W1H2 deprotonation to Asp61 that retrieves an electron from W2 to fill its hole via a PCET process. Accordingly, O5-W2 coupling can be seen as an oxo—oxyl gain coupling due to the radical nature of W2 already from the start, and it creates a deprotonated peroxide group (−O2H−) bound to Mn4 with Mn3-O5 bond cleavage (Fig. 3).

3.1. O5-W2H coupling

After one proton release from W1 in the S2Yz state, W1H2W2H_O5 represents the most straightforward proton distribution in the S4 state. For the S2Yz to S4 transition in this case, the electron hole initially localized at Yz was observed to emerge on the carboxylate oxygen atoms of Asp61 in S4 prior to the O—O bond formation. This hole relocation is not surprising considering of a proton-coupled electron transfer (PCET) process involving Asp61, which serves as the proton channel gate following one proton removal [48–51]. Focusing on the O5-W2H coupling, it is actually nucleophilic attack of the terminal ligand W2H (hydroxide) onto the electron-deficient bridged group μ-O5 (oxo), and finally produces a protonated peroxide group (−O2H−) bound to Mn4. In the early stage, W2H (OH−) fills the electron hole on Asp61 and thus becomes an active but transient OH species which then immediately approaches O5. Their interaction leads to O—O bond formation accompanied by an electron transfer (ET) to Mn3 causing the Mn3-O5 bond cleavage.

The S4 reactants are almost spin-insensitive regarding energetics (maximum 2.1 kcal/mol difference, Table S5 in the SM), however, the reaction paths of O—O bond formation are diverse and can be classified in three spin groups depending on the spin selectivity: (1) 14/ababaa, octet/τxαβγ/τxαβγ/τxαβγ, sexet/τxαβγ, and doublet/τxαβγ/τxαβγ/τxαβγ; (2) 12-et/ababaa, sexet/τxαβγ β/τxαβγ and doublet/τxαβγ/τxαβγ; (3) octet/τxαβγ, sexet/τxαβγ, and doublet/τxαβγ/τxαβγ. The different spin-channel groups share common features regarding electron/charge transfer, spin/valence variations, structural changes and reaction energetics within each group, but they differ considerably between groups. These different reaction paths for O5-W2H coupling are graphically depicted in Fig. 2.

Transition states lie near midway with respect to Mn3 reduction: spin groups (2) and (3) show very high barriers (over 50 kcal/mol) because of the generation of the spin-antiparallel OH causing a low-spin Mn3. This is also the reason why the S4 products in spin group (2) are in much higher energy than group (3). An interesting phenomenon for spin group (3) is that after TS, the portion of electron addition to Mn3 with the opposite spin orientation would hop to Mn4, thus avoiding electron-pairing on Mn3 and stabilizing the S4′ products to some extent. This does not take place in spin group (2) because neither Mn3 nor Mn4 is ferromagnetically coupled to .OH. In contrast, the unstable, low-spin electronic configurations do not appear along the MEPs of spin group (1), however, the activation free energies all exceed 30 kcal/mol, indicating the impossibility that a mechanism involving W2H as the nucleophile attacking O5. Counting from the most stable spin form of the S4 reactants, O5-W2H coupling has to overcome a barrier as high as 34.8–50.6 kcal/mol, which is prohibitively difficult.

3.2. O5-W2 coupling

The proton arrangement of W1H2W2_O5, which is energetically close to the previous scheme (Table S7 versus Table S4 in the SM), offers another scenario for O—O bond formation from fully deprotonated O5 and W2. Different from the O5-W2H coupling, the electron hole in the S4 reactants for the O5-W2 coupling is located on W2 instead of Asp61. This is attributed to the spontaneous W1H2 deprotonation to Asp61 that retrieves an electron from W2 to fill its hole via a PCET process. Accordingly, O5-W2 coupling can be seen as an oxo—oxyl gain coupling due to the radical nature of W2 already from the start, and it creates a deprotonated peroxide group (−O2H−) bound to Mn4 with Mn3-O5 bond cleavage (Fig. 3).

Valence alterations and ET routes in this situation were found to follow similar patterns in the three spin groups as observed in the O5-W2H case: (1) ET to Mn3(IV) for high-spin Mn3(III); (2) ET to Mn3(IV) for low-spin Mn3(III); (3) ET to Mn3(IV) and then to Mn4(IV) for high-spin Mn4(III). An additional structural character was revealed in the S4 products: while the spin groups (2) and (3) retain the original open-cubane conformation, the spin group (1) is instead dominated by closed cubane-like structures as the lowest energy conformations. This open-to-closed cubane conversion essentially consists of a ligand exchange on Mn3, more specifically O5 substitution by Ox taking place automatically in the late stage of O—O bond formation. This process may be driven by a repulsive electrostatic effect between the doubly Mn4-coordinated O2− group and other oxygen-containing ligands. This effect is significantly weaker in the above O5-W2H case because the protonation electrostatically neutralizes the negative charge on W2 and eliminates its bonding to Mn4. Besides, the spin discrimination can be explained by invoking the theoretical rationalization of the substrate water exchange, i.e. a high-spin Mn3(III), only existing in the spin group (1), has to be present for such a structural transformation [52]. Finally, this pathway is also infeasible as judged from the energetics of O5-W2 coupling, whose overall barrier reaches 25.3–41.0 kcal/mol.

3.3. Implications for water oxidation mechanism in PSII

Since O5 and W2 have been identified as the preferred candidates for O—O bond formation [22–23], and at the same time O5 and W2 coupling in their native positions in a non-rearranged OEC cluster appears energetically unrealistic, it is rational to consider relaxations of O5 and W2 into more favorable positions prior to O—O bond formation. Although compelling evidences on the specific ways are scarce, it has been suggested that either S2 → S3 or S3 → S4 transition should be responsible for such
structural rearrangements throughout the catalytic cycle, because of the relatively large activation/reorganization energies [34, 53–58]. So far two mechanisms of O–O bond formation with O5 and W2 as substrates have been reported involving significant structural rearrangements during either $S_2 \rightarrow S_3$ or $S_3 \rightarrow S_4$ transition, i.e. the oxo–oxyl (W2-O5) coupling pathway suggested by Cox and Pantazis [59, 60], and the dangling Mn4(VII)–dioxo involved pathway proposed by Zhang and Sun [11, 61], respectively (Fig. 4).

Fig. 2. Schematics of the spin, valence and structural changes and reaction energetics for the different spin-channel MEPs of O5-W2H coupling. One representative spin state is shown for each spin group; spin up/down are marked in green/purple at atomic regions (the isovalue for the spin density is set to 0.04). The same formalism will be used hereafter.

Fig. 3. Schematics of the spin, valence and structural changes and reaction energetics for the different spin-channel MEPs of O5-W2 coupling.
3.3.1. The possible pathway with structural rearrangements in $S_2 \rightarrow S_3$

For the structural rearrangement in the $S_2 \rightarrow S_3$ transition, results from quantum chemical simulation and electron paramagnetic resonance (EPR) spectroscopy [59,60] have suggested the existence of a five-coordinate Mn(IV) intermediate involving major conformational changes of the OEC cluster during the transition, including an open-to-closed isomerization ($S_2$-A to $S_2$-B) by O5 movement [62,63], water binding to Mn4(IV) of $S_3$-B by a pivot mechanism [59,64], followed by a closed-to-open reorganization ($S_3$-B to $S_3$-A) by Mn3 ligand exchange [65]. In this way, the newly inserted 'Ox' in the $S_3$ state observed by XFEL is derived from O5. Although W2-O5 is subject to oxo-oxyl coupling in the $S_4$ state, the sources of substrates and mechanism of the $S_2 \rightarrow S_3$ transition are inherently different from Siegbahn’s theory, where the high-spin, closed-cubane structure is not introduced in the $S_2 \rightarrow S_3$ transition [33,37]. Notably, some new studies favor the high-spin $S_2$ state being represented by an open-cubane structure, either with OH$^-$ binding to Mn1(IV) [25,66–68] or with proton isomerization between W1 and O4 [69]. This highlights the present inconsistencies between the results from EPR and X-ray crystallography regarding structural heterogeneity for the $S_2$ state at cryogenic temperatures [70]. In a very recent study by Ibrahim et al. using combined X-ray crystallography and emission spectroscopy, a closed-cubane structure is never observed during the dynamically refined $S_2 \rightarrow S_3$ transition [71], which, as a consequence, challenges the occurrence of structural rearrangement in the $S_2 \rightarrow S_3$ transition.

3.3.2. The possible pathway with structural rearrangements in $S_3 \rightarrow S_4$

The $S_3 \rightarrow S_4$ transition represents an alternative for large structural rearrangements, as inferred from the kinetics of the ‘slow phase’ preceding oxygen release [31,34,35,57,72–79]. However, the chemical essence of the possible rearrangements remains unclear, which might include proton tautomerization, ligand reorganization and/or structural isomerization [34,80]. Based on the experimental findings that Mn(VII) is highly active regarding O2 evolution in manganese model chemistry [81], Zhang and Sun recently proposed a fundamentally new mechanism for O–O bond formation in PSII involving a dangling Mn4(VII)-dioxo site in the open-cubane structure of the $S_4$ state [11,61]. It is noted that the active species may be its isoelectronic form Mn4(VI)-O/C5 with radi cal feature on the oxygen atoms. This high-valent Mn4 is suggested to generate from charge disproportionation of the four Mn centers launched by multiple intramolecular PCETs after proton release in the $S_3$ state. Especially, the increased Mn4 valence would cause its coordination change from octahedron to tetrahedron (then to trigonal bipyramid after Ox binding), before Yz being reduced for the $S_4$ formation. These significant structural changes during $S_3 \rightarrow S_4$ may account for the slow kinetics observed experimentally and may thus constitute the rate-limiting step of the catalytic cycle. During the structural rearrangements ‘Ox’ is relocated to the original O5 position after the O2 release and behaves as the precursor of O5 in the next catalytic cycle. This is consistent with one of the three models suggested by Kern et al. based on their in-situ XFEL studies [18].

Fig. 4. Two alternative mechanisms involving significant structural rearrangements during the $S_2 \rightarrow S_3$ (upper) or $S_3 \rightarrow S_4$ (lower) transitions. The red shadows denote O–O bond formation in the subsequent $S_4$ state. The carboxyl ligands are not shown here for clarity.
3.3. Comparison of the two possible pathways

The above discussion identifies two possible mechanisms for O–O bond formation between O5 and W2 with significant structural rearrangement within the catalytic cycle. So far, there is no experimental evidence to distinguish between the proposed structural changes in these transitions and quantum chemical calculation can be useful. The advantages of the S2 → S3 pathway is the theoretical feasibility [59,62,64,65] (rate-limiting barrier ~12 [65] or ~17 kcal/mol [25]) and the EPR clue for the S5-coordinate Mn4 (IV) intermediate [60], however, the XFEI-based crystallography disfavors appearance of the closed-cube structure during the transition [18,19,70,71]. The novel S5 → S6 pathway has not been studied in theory but it is consistent with the observed kinetics [31,34,35,57,72–79]. Since crystallizing any intermediate of S2Y•- → S6 is technically difficult at the moment, DFT methodology would provide an important role to test its possibility. The two alternatives are highly related to the water binding pathway during the S5 → S6 transition, and untangling how water inserts to the OEC cluster would be adequate for a judgement. Besides, an unambiguous identification for the high-spin S2 state (open or closed structure) is also helpful.

4. Conclusions

In summary, we have modelled O–O bond formation between O5 and W2 in a non-rearranged OEC cluster, which was derived from the crystal structure of the S3 state. For both the O5–W2H coupling and O5–W2 coupling schemes, the optimized overall barriers are very high, 34.8–50.6 kcal/mol and 25.3–41.0 kcal/mol, respectively. These results in essence rule out the possibility of O–O bond formation between O5 and W2 from their original position of the OEC cluster. Therefore, we draw the conclusion that O5 and W2 are highly probable substrates according to the substrate water exchange studies, and significant structural rearrangements to form the S5 state must be involved, either during the S5 → S6 or S5 → S7 transition. The significant structural changes involved in the two possible mechanisms are essential but require further experimental and theoretical verification.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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