A Molecular 'Double-pivot' Mechanism for Water Oxidation

JOHN B. VINCENT and GEORGE CHRISTOU*
Department of Chemistry, Indiana University, Bloomington, Ind. 47405, U.S.A.
(Received January 21, 1987)

In spite of efforts to elucidate the structure and properties of the Mn center operating in the photosynthetic apparatus of green plants and catalyzing the water oxidation reaction of eqn. (1), little is known about

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

the arrangement of the metal atoms, their ligation or their precise mode of action. A number of mechanistic proposals have been presented e.g. [1-4], but none have been able to satisfactorily account for all the available EXAFS [5,6], EPR [7,8] and UV–Vis data [9,10]. Recent reviews of this area are available [11,12].

The photosynthetic Mn center is capable of cycling between five distinct oxidation levels, labelled S0 to S5, with oxygen evolution occurring during the S4 → S0 transition (eqn. (2)) [13]. It is believed that four Mn atoms per photosystem II (PSII) reaction center are essential for oxygen evolution [14]. The four Mn are apparently composed of two pools of two similar atoms [15]. EXAFS results on S1 suggest two Mn occur in a binuclear site (Mn–Mn = 2.69(3) Å), with bridging oxide and terminal O and/or N ligands [5]. The EXAFS data can also accommodate two other Mn atoms at distances of approximately 3.3 Å from the binuclear center [5]. X-ray absorption edge studies show the edge position of the Mn in dark-adapted PSI1 particles (S1, S2) to be between those of Mn(II) and Mn(III) model complexes [6]. Wells has shown that the equilibrium constant for the reaction of eqn. (3) is at least two orders of magnitude greater for Mn(II) than for any other trivalent first row transition metal [17].

\[ \text{Mn(III)-OH} \rightarrow \text{H}_2\text{O} + \text{Mn(III)-OH} \rightarrow \text{H}_2\text{O}^+ + \text{Mn(III)} \quad (3) \]

Recently, we discovered that reaction of trinuclear \([\text{Mn}_3\text{O}(\text{O}_2\text{CR})_6\text{L}_3]^0\) with bipyridine (bipy) yields tetranuclear \([\text{Mn}_4\text{O}_2(\text{O}_2\text{CR})_4(\text{bipy})_2]^+\) (R = Ph, \(\alpha = 0\); R = Me, \(\alpha = 1\)). The structure of R = Me complex has been determined and is shown in Fig. 1. Pertinent bond distances and angles are given in the figure legend. The complex possesses several features which are very similar to the water oxidation Mn complex: (a) a metal nuclearity of four; (b) oxide bridges between the metal centers; (c) O- and N-based ligation; (d) two pairs of inequivalent Mn atoms; and (e) metric parameters which are reasonably consistent with the EXAFS data on the native site. We thus consider the above evidence spectra of model complexes by Dekker et al. [9] and ourselves [16] indicate that individual metal oxidation state changes of Mn(II) → Mn(III) and Mn(III) → Mn(IV) could both be involved during this cycle.

The Mn4 center is obviously able to perform the three main functions associated with facile conversion of two molecules of H2O to one molecule of O2: (i) stabilization and storage of oxidizing equivalents; (ii) formation of a template to hold two molecules of H2O in close proximity to facilitate oxygen–oxygen bond formation; and (iii) making the bound H2O molecules more acidic to facilitate II1 loss.
two complexes as potential models for the S₀ and S₁ states of the water oxidation center.

Entertaining further the possibility that models of the S₀ and S₁ states are at hand, we have sought to encompass them into a mechanistic scheme for how the water oxidation reaction is carried out, incorporating also the available biochemical data described above, and have arrived at a mechanistic scheme consistent with EXAFS, EPR and UV-Vis difference data on the native site.

The mechanism for the water oxidation cycle is depicted in schematic form in Fig. 2. For clarity, we have not shown the O- and N-based peripheral ligation, only the structural rearrangements of the core. The S₀ (Mn(II) + 3Mn(III)) and S₁ (4Mn(III)) states possess the Mn₄O₂ structure established in the model complexes, the S₁ state being obtained from S₀ by a one-electron oxidation step. On oxidation of S₁ to S₂ (3Mn(III) + Mn(IV)), the unit is EPR active and two H₂O molecules are now bound, in accord with NMR and EPR results [18–20]. Although no model complex has yet been synthesized with a structure and oxidation level analogous to that shown for S₂, it is nevertheless found as a sub-structure of a dodecanuclear mixed-valence Mn(III, IV) complex, Mn₁₂O₁₂(O₂CMe)₁₆(H₂O)₄ [21]. This sub-structure possesses an Mn₄O₂ unit with the same type of butterfly arrangement as seen in Fig. 1. The two ‘wing-tip’ Mn atoms possess bound H₂O molecules and the (IV) center occupies one of the ‘hinge’ sites. This arrangement thus lends some feasibility to the proposed S₂ structure.

Further oxidation from S₂ to S₃ (2Mn(III) + 2Mn(IV)) now results in the structural rearrangement suggested by X-ray absorption edge studies [6]. Movement of the two ‘wing-tip’ Mn atoms towards each other can be accomplished by pivoting of the two Mn–O vectors about the μ₃-O atoms; this ‘double-pivot’ maneuver requires no movement in the Mn₃O₂ base, but merely an increase in the ‘pyramidality’ of the μ₃-O atoms. The two H₂O molecules will also be brought closer together, of course, and in the extreme this motion and concomitant deprotonation of H₂O molecules to OH⁻ allows the unit to convert into a compact cubane-like structure, possessing two μ₃-O⁻ and two μ₃-OH⁻ bridges. Cubane-like Mn₄O₄ units exist as sub-structures in Mn₁₂O₁₂(O₂CMe)₁₆(H₂O)₄ [21], and Mn₄(OH)₄ cubanes are thought to be occurring in Mn₄(OH)₄(CO)₁₂ [22]. Further, a Mn₄ cubane with two different types of μ₃-bridging atoms has been established in [Mn₄(CO)₁₂F₆(OH)₄₋ₓ] [23]. The proposed structure of S₃, therefore, does have indirect support and precedence.

The structural conversion of S₂ to S₃ has attractive consequences for the overall water oxidation cycle, for examination of [Mn₄O₂(O₂CMe)₁(bipy)₂]⁺ and Mn₁₂O₁₂(O₂CMe)₁₆(H₂O)₄ shows that the H₂O molecules of S₂ will have a (H)O...O(H) distance of approximately 4.5–5.0 Å, whereas in S₃ the (H)O...O(H) distance will be approximately 2.5 Å. The OH groups have thus been brought significantly closer together, and this can facilitate oxygen–oxygen bond formation on subsequent oxidation of S₃. Note also that Krishtalik has shown that ionization of water molecules preceding their oxidation facilitates the enzyme-catalyzed reaction [24], and we suggest that this may assist the described structural rearrangement between S₂ and S₃.

Oxidation of S₃ to S₄ (Mn(II) + 3Mn(IV)) now triggers the substrate oxidation process. The O atoms move towards each other initiating bond formation, and there is concomitant movement apart of the two Mn atoms, transfer of electrons from oxygen to Mn, and loss of the remaining two H⁺. An intermediate in this concerted reaction might be a peroxide-bound form as shown in the scheme, at which point the O–O distance should be approximately 1.5–1.6 Å and a net of two electrons having been transferred to the Mn atoms. Continued approach of the O atoms, transfer of two more electrons to the Mn atoms and further movement apart of the latter by pivoting about the μ₃-O atoms leads, in the limit, to formation (and evolution) of O₂ and return of the remaining Mn₃O₂ unit to the S₀ structure and oxidation level. An attractive aspect of a peroxide-bound intermediate is that the total transfer of four electrons from 2OH groups to the Mn atoms need occur in two two-electron steps, rather than one four-electron step. Note also that structural conversion of S₃ to S₀ is a natural consequence of the approach of the O atoms so that no additional movement is necessary after O₂ evolution to return the Mn₄ unit to its initial conformation ready for recycling. The proposed scheme assumes all water oxidation takes place between S₂ and S₃,...
and this is supported by mass spectral studies which indicate that no intermediates in the oxidation of H₂O to O₂ are bound to S₂ or prior S₃ states [25]. Also, thermoluminescence studies on PSII particles indicate a structural change to accompany conversion of S₃ to S₄; when this change is prevented, S₅ level advancement ceases and O₂ evolution is terminated [26].

Finally, we address the question of the H⁺ release pattern, which is generally believed to be 1:0:1:2 during the S₃ changes S₀ → S₁ → S₂ → S₃ → S₄ [27]. The two H⁺ lost during S₃ conversion to S₀ are already in accord with our proposed scheme. To rationalize the remaining H⁺ release pattern, we invoke involvement of an amino acid side chain function such as a histidine residue and, indeed, there is evidence available to support this. Homann has shown that reactivation of Cl⁻-depleted particles by added anions is contingent upon protonation of membrane-bound buffering groups with apparent pKₐ of approximately 6 [28], indicative of the imidazole ring of a histidine residue. Indirect evidence for the association of histidine with the Mn assembly is also mounting [29]. Thus, we depict in the scheme that the released H⁺ in the S₃ to S₁ conversion originates from a protonated imidazole (imidazolium) group. This may be necessary, for instance, if the imidazole group now becomes bound to a Mn in S₁, although this is not itself essential to the proposal. The S₂ → S₃ conversion of the scheme requires liberation of two H⁺, one which is released and detected and the other becoming re-associated to an imidazole group. Thus, the overall pattern of H⁺ release to the medium is now 1:0:1:2, perfectly in accord with experimental evidence. It should also be added, in conclusion, that the resulting changes in charges of the S₅ states of the scheme are consistent with the experimental changes in charges measured by Saygin and Witt [30].

In summary, a scheme is described that is consistent with available data on the water oxidation site. The scheme has many attractive features, not least of which is the precedence provided by characterization of the Mn₄O₂ unit in [Mn₄O₂(O₂CMe)₇(bipy)₂]⁺. To further assess the viability of this mechanism, synthetic efforts are now being directed to isolation of species having the increased oxidation level of S₃, and species containing the cubane-like structure proposed for S₄. Their isolation may even allow us to reproduce the final oxygen evolution step under laboratory conditions.

Acknowledgement

Research in this area is supported by the National Science Foundation (Grant CHE 8507748).

References