Journal of Catalysis 354 (2017) 169–181

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Possible water association and oxidation mechanisms for a recently synthesized Mn_4Ca-complex

Rong-Zhen Liao [a],*, Per E.M. Siegbahn [b]

[a] Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Key Laboratory of Materials Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
[b] Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-10691 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 31 May 2017
Revised 17 July 2017
Accepted 18 July 2017
Available online 9 September 2017

Keywords:
DFT
Water oxidation
Reaction mechanism
Mn_4Ca complex
Electrocatalysis

ABSTRACT

The laboratory synthesis of complexes to mimic the structure of the Mn_4Ca cluster in the oxygen-evolving complex (OEC) of photosystem II is a very challenging task to accomplish. The most encouraging breakthrough in this field was recently achieved with the synthesis of a Mn_4Ca complex (Zhang et al., 2015) that shows a very similar core structure to the OEC. On the basis of density functional calculations, the structure and the redox potentials of this Mn_4Ca complex in acetonitrile are obtained with very good agreement to experiments. A possible mechanism for water oxidation is more problematic. If only the thermodynamics is considered and assuming a standard state of 1 mol/L, it turns out that up to five water molecules can be inserted into the complex with only a small cost. This leads to a barrier for O—O bond formation which is 22.8 kcal/mol with an applied potential of 1.3 V. However, a study of the kinetics for the insertion of the critical water bridge between Mn3 and Mn4 indicates that the barrier for that process is quite high with 24.6 kcal/mol. A model where this water is not inserted also led to a rather high barrier for O—O bond formation with 31.7 kcal/mol with an applied potential of 1.3 V. However, the barrier decreases significantly to only 13.4 kcal/mol with an applied potential of 1.7 V. The different barrier originates from the different energetic penalty for the formation of the catalytic competent $\mathbf{S_4}$ state. A major experimental problem discussed below, is the instability of the complex, which does not allow a high water concentration. The best calculated overall mechanism obtained is essentially the same as the leading suggestion for the OEC, where the critical O—O bond formation takes place at the S_4 state (formally $Mn_4^{IV,IV,IV,V}$) via direct coupling of a Mn^{IV}-oxyl radical and a di-Mn bridging oxo group.

1. Introduction

Photosystem II is the only enzyme in nature that can perform water oxidation. The oxygen evolving catalyst (OEC) is situated close to the lumenal side and is an Mn_4Ca complex in which the metals are connected by oxo bridges. O_2 is formed from two water molecules bound to the complex in a process with four sequential oxidation steps, termed S_0 to S_4, each one initiated by a photon absorption [1]. One electron is removed from the OEC in each oxidation step, and is transferred to the P_{680} porphyrin complex in the reaction center, passing over a redox active tyrosine Tyr_Z. At the same time, protons are sent to the luminal side. These oxidations lead to four Mn(IV) centers in the S_3 state. In the subsequent S_4 state, the O—O bond is suggested to be formed between an oxygen radical and a bridging oxo ligand [2–5]. The model calculations leading to this mechanism were initiated using the first low-resolution X-ray structures of PSII [6,7]. Very strong support for the suggested mechanism has been given by X-ray structures [8,9] and spectroscopic measurements the past five years [10–12].

Synthetic work trying to mimic the OEC complex has been going on for nearly two decades [13,14]. The survey given here will only concern complexes built on manganese. The first water oxidation active complex was an Mn_2-complex [15], synthesized by Crabtree et al, shown at the top left in Fig. 1. A mechanism has been suggested based on density functional theory (DFT) with an O—O bond formation using a nucleophilic attack by an outside water on an oxygen radical [16]. Another one was a cubic Mn_4-complex [17], synthesized by Dismukes et al, shown in top right in Fig. 1. It was shown that phosphate ligand dissociation trigged by photon excitation is needed for the following oxygen evolution [18]. A mechanism for this complex has recently been suggested based on DFT [19]. Again, a nucleophilic attack by a water on an oxyl radical had the lowest barrier. However, photons appear to be needed

---

* Corresponding author.
E-mail address: rongzhen@hust.edu.cn (R.-Z. Liao).

http://dx.doi.org/10.1016/j.jcat.2017.07.016
0021-9517/

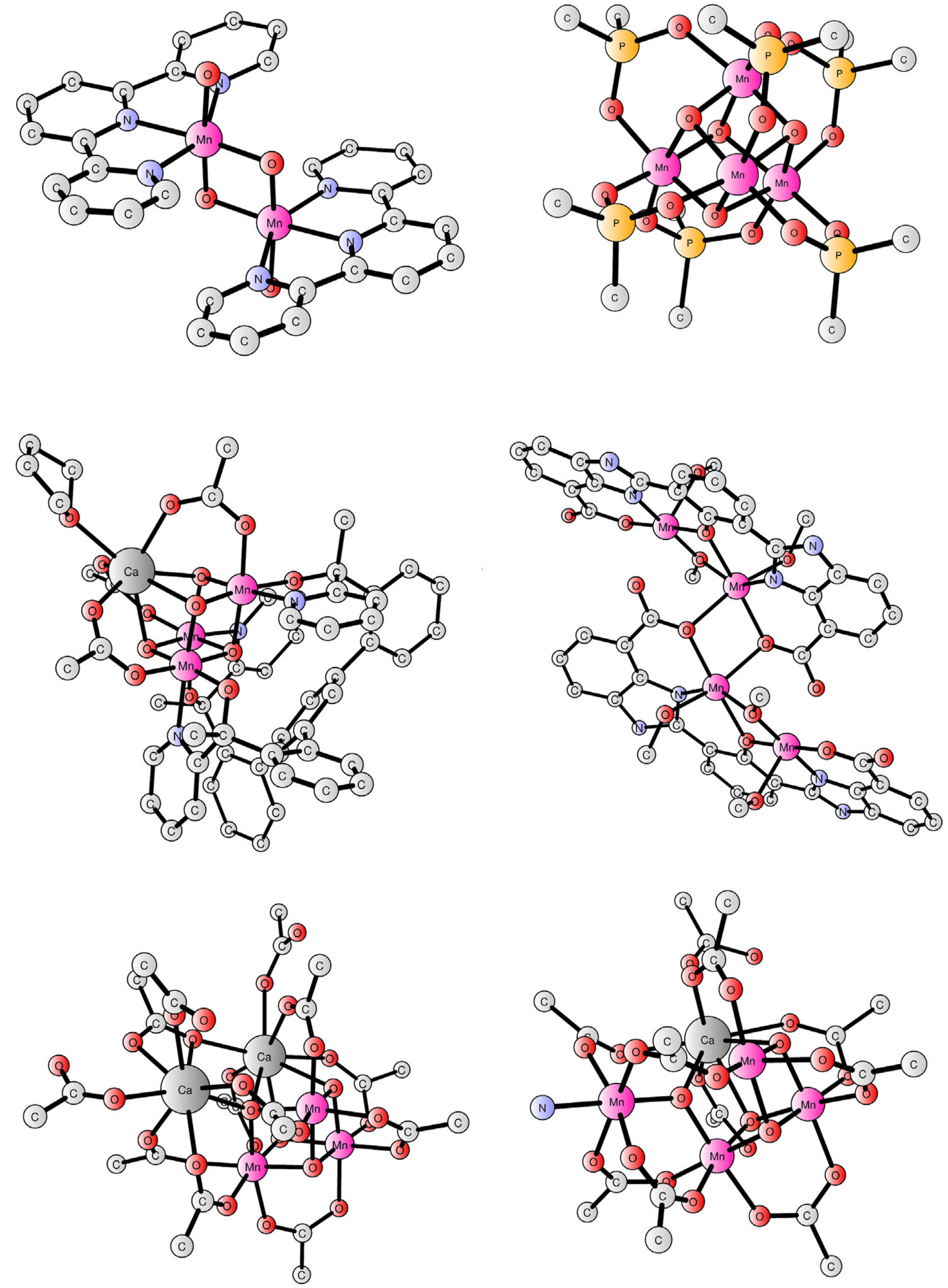

Fig. 1. The development of synthetic mimics to the oxygen evolving complex of Photosystem II. Top row: Mn_2 complex of Crabtree et al. [15], and Mn_4 complex of Dismukes et al. [17] Middle row: Mn_3Ca complex of Agapie et al. [20], and Mn_4 complex of Åkermark et al. [21] Bottom row: Mn_3Ca_2 complex of Christou et al. [23] and Mn_4Ca complex of Zhang et al. [25]. For clarity, hydrogen atoms are not shown, the phenyl groups in the Dismukes Mn_4 complex, the pyridyl groups in the Agapie Mn_3Ca complex, as well as the ter-butyl groups in both the Christou Mn_3Ca_2 complex and the Zhang Mn_4Ca complex are all represented by carbon atoms.

to overcome the very large barrier. Both these complexes were synthesized before the structure of the OEC was presented. After the first structure came, Agapie and coworkers have made a series of complexes more and more resembling the OEC. One of them is an Mn_3Ca-complex [20] shown at the middle left in Fig. 1. Åkermark et al. [21] recently synthesized the Mn_4-complex shown at the middle right in Fig. 1. The origin of this complex was an Mn_2-complex, which turned out to dimerize in solution. The mechanism for this complex has been studied by similar methods as the ones used here [22]. Interestingly, the suggested mechanism is quite similar to the one for PSII, with an O—O bond formed between an oxyl radical and a bridging oxo-ligand. However, the catalytic rate is much lower than for the OEC and the complex is quite unstable. Christou et al have also synthesized a number of OEC-mimics, the most recent one is an Mn_3Ca_2 –complex shown at the bottom left in Fig. 1 [23].

In order to investigate the minimum requirement for a low-barrier formation of O_2, a DFT study was previously performed by Li and Siegbahn on small hypothetical models containing the same Mn_4CaO_5 core as in the OEC [24]. The results were very encouraging for the possibility to construct small active model complexes. Some minor requirements were found for the ligands, which help the complex open up for water binding.

The final complex shown in Fig. 1 (bottom right) is an Mn_4Ca-complex synthesized recently by Zhang et al. [25]. The core structure is remarkably similar to the OEC in PSII, in fact, it is nearly