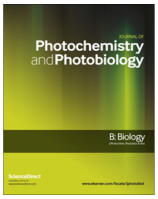
Journal of Photochemistry and Photobiology B: Biology 152 (2015) 162–172

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology B: Biology

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



Mechanism for O—O bond formation in a biomimetic tetranuclear manganese cluster – A density functional theory study

Rong-Zhen Liao *, Per E.M. Siegbahn *

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-10691 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 28 October 2014
Received in revised form 25 November 2014
Accepted 1 December 2014
Available online 11 December 2014

ABSTRACT

Density functional theory calculations have been used to study the reaction mechanism of water oxidation catalyzed by a tetranuclear Mn-oxo cluster $Mn_4O_4L_6$ ($L = (C_6H_4)_2PO_4^-$). It is proposed that the O—O bond formation mechanism is different in the gas phase and in a water solution. In the gas phase, upon phosphate ligand dissociation triggered by light absorption, the O—O bond formation starting with both the Mn_4(III,III,IV,IV) and Mn_4(III,IV,IV,IV) oxidation states has to take place via direct coupling of two bridging oxo groups. The calculated barriers are 42.3 and 37.1 kcal/mol, respectively, and there is an endergonicity of more than 10 kcal/mol. Additional photons are needed to overcome these large barriers. In water solution, water binding to the two vacant sites of the Mn ions, again after phosphate dissociation triggered by light absorption, is thermodynamically and kinetically very favorable. The catalytic cycle is suggested to start from the Mn_4(III,III,III,IV) oxidation state. The removal of three electrons and three protons leads to the formation of a Mn_4(III,IV,IV,IV)-oxyl radical complex. The O—O bond formation then proceeds via a nucleophilic attack of water on the Mn^{IV}-oxyl radical assisted by a Mn-bound hydroxide that abstracts a proton during the attack. This step was calculated to be rate-limiting with a total barrier of 29.2 kcal/mol. This is followed by proton-coupled electron transfer, O_2 release, and water binding to start the next catalytic cycle.

1. Introduction

The development and production of clean and sustainable fuels is one of the most challenging tasks facing scientists in this century. One attractive solution would be to design artificial leaves that utilize solar energy to split water into O_2 and H_2. About 3 billion years ago, nature developed a delicate photosynthetic system that can capture sunlight and convert it into chemical energy to oxidize water into O_2 and to reduce CO_2 into biomass [1–4]. In this process, the oxidation of water is catalyzed by the Mn_4Ca cluster in the oxygen evolving complex (OEC) of photosystem II (PSII). Considerable efforts have been dedicated to the synthesis of Mn-based multinuclear complexes that mimic the structure and function of OEC [5–14].

Dismukes and co-workers have reported the synthesis of a series of tetranuclear Mn-oxo cluster [15–28], $Mn_4O_4L_6$ ($L = (p\text{-}R\text{-}C_6H_4)_2PO_4^-$, R = H, CH_3, OCH_3), which catalyzes photochemical water oxidation utilizing a TiO_2-supported $[Ru^{II}(bipy)_2(bipy(COO)_2)]$-type photosensitizer. They investigated the process both in water solution [28] and in gas phase [18,19]. In the catalytic process in water, the Mn_4 cluster was immobilized on a Nafion membrane-coated conductive electrode and immersed in an aqueous solution (pH = 6.5). Kinetic investigations showed a turnover number (TON; defined as moles of O_2 produced per mole catalyst) of more than 1000 and a turnover frequency (TOF; defined as moles of O_2 produced per mole catalyst per unit time) of 47 h^{-1}, which can be translated into a barrier of about 20 kcal/mol, using classical transition state theory. Upon light excitation, the Ru^{II} dye donates one electron to the TiO_2 band and a one-electron oxidant $[Ru^{III}(bipy)_2(bipy(COO)_2)]^+$ is generated with a reduction potential of 1.4 V. This Ru^{III} complex is capable of oxidizing the Mn_4 cluster from Mn_4(II,II,III,III) (**1**) to Mn_4(III,III,IV,IV) (**5**) via four sequential proton-coupled electron transfer (PCET) steps (Scheme 1) [25]. From **5**, the O—O bond formation takes place upon excitation by a second beam of light [28]. Very importantly, the excitation process involves the dissociation of one phosphate ligand to generate **6**, which was found to be required for the O—O bond formation [18].

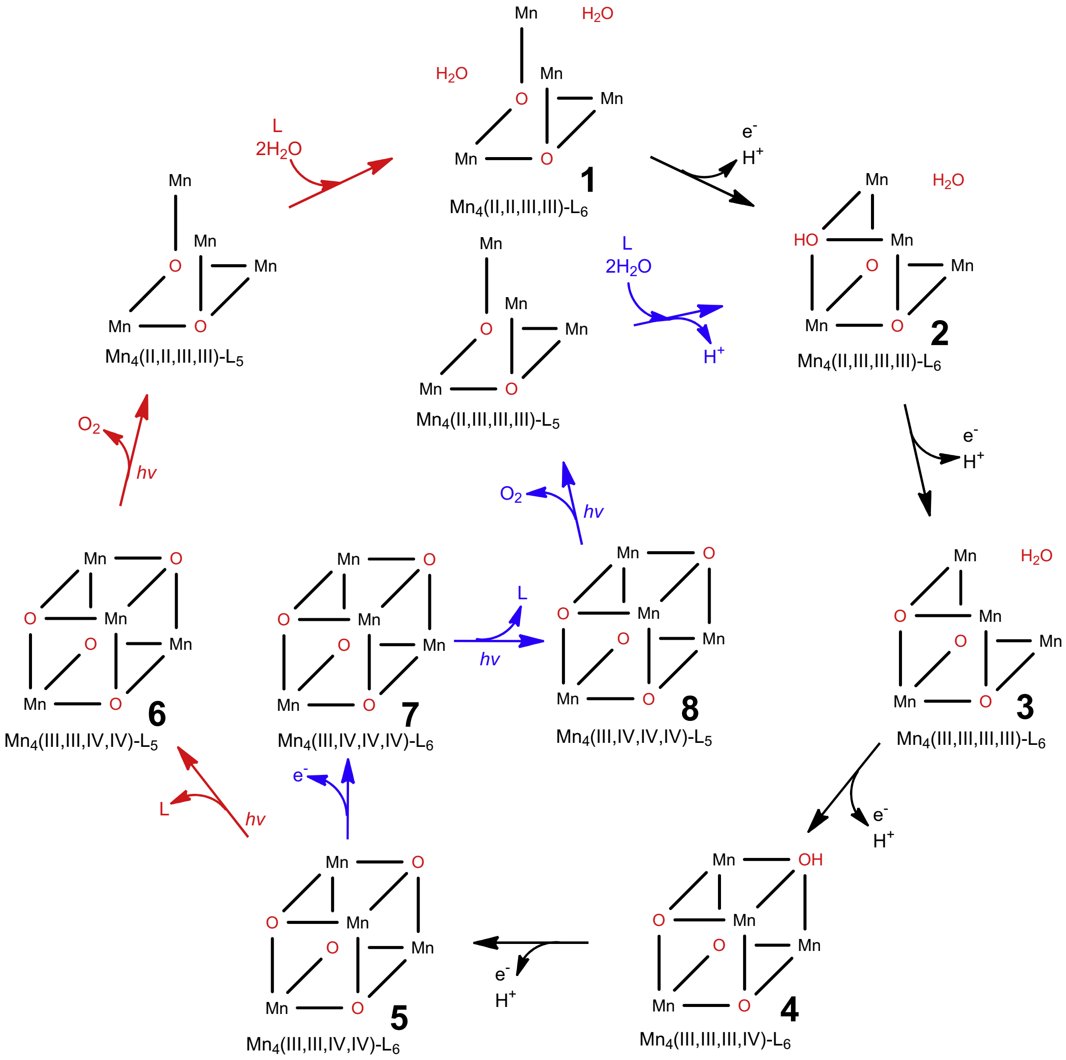
In gas phase, photo-excitation of **5** at 337 nm (Mn—O charge transfer excitation) followed by a laser desorption/ionization mass spectrometry (LDI-MS) analysis showed that the formation of O_2 is associated with the dissociation of one phosphate ligand [18]. Further an ^{18}O isotope labeling study confirmed that both oxygen atoms in O_2 came from the parent complex **5** [19]. When only *d*–*d* ligand field excitation (532 nm) was involved, no product

---

* Tel.: +46 162616.

E-mail addresses: rongzhen@organ.su.se (R.-Z. Liao), ps@organ.su.se (P.E.M. Siegbahn).

http://dx.doi.org/10.1016/j.jphotobiol.2014.12.005



Scheme 1. Proposed photocatalytic cycle of water oxidation catalyzed by the Dismukes Mn_4 complex [25].

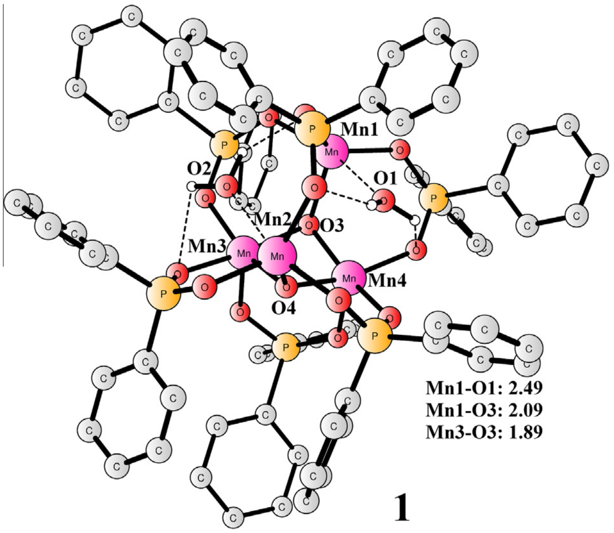


Fig. 1. Optimized structure of **1**(Mn_4(II,II,III,III)). Distances are given in Angstrom. For clarity, hydrogen atoms on phenyl rings are not shown.

Table 1
Spin density on Mn and Mn–Mn distances (in Angstrom) of structures **1–8**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**5**(**exp**)	**7**(**exp**)
Spin density										
Mn1	4.83	3.96	3.95	3.93	3.91	3.89	3.89	3.89	–	–
Mn2	4.83	4.84	3.95	3.93	3.91	3.89	3.04	3.89		
Mn3	3.97	3.94	3.94	3.93	3.11	3.06	3.05	3.06		
Mn4	3.97	3.94	3.93	3.14	3.10	3.06	3.05	3.06		
Distances										
Mn1–Mn2	4.24	3.48	3.20	3.18	3.12	2.93	2.91	2.92	2.9826	2.904
Mn1–Mn3	3.46	3.19	3.10	3.17	2.84	2.91	3.02	2.91	2.9038	~
Mn1–Mn4	3.29	3.08	3.01	2.92	3.03	2.91	3.01	2.92	2.9126	2.954
Mn2–Mn3	3.29	3.42	3.18	3.17	3.03	2.90	2.86	2.92	2.8341	
Mn2–Mn4	3.46	3.31	2.88	2.91	2.86	2.90	2.86	2.91	2.8377	
Mn3–Mn4	2.81	2.84	3.00	2.93	2.83	2.80	2.81	2.79	2.8588	

could be detected [19]. It was shown that **5** can undergo one electron oxidation to generate Mn_4(III,IV,IV,IV) (**7**), in which ligand dissociation can form **8** and then release O_2 with a similar mechanism as **6** [24].

The mechanism of the O—O bond formation in Mn_4(III,III,IV,IV)-L_5 has previously been investigated using density functional calcu-