MOLECULAR ORBITAL STUDY OF PHOTOSYNTHETIC WATER DECOMPOSITION

Roles of manganese and proton-accepting site

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1. Introduction

Despite its importance in understanding the conversion of sunlight into useful chemical energy in green plants, the molecular mechanism of oxygen-evolving reaction (1) remains to be elucidated [1,2].

$$2\,H_2O - 4\,e^- \longrightarrow O_2 + 4\,H^+ \qquad (1)$$

A manganese-containing protein has been long regarded as the positive-charge accumulation place in photosystem II (PSII), where the water-splitting reaction (1) is catalyzed [3–6]. It is considered that such PSII reaction center contains possibly 4 Mn atoms as a mixture of Mn(II) and Mn(III) [4–6]. Proton release and change of valence state of Mn are believed to occur asynchronously with O_2 evolution, when being excited by a sequence of short saturation flashes [5–11]. However, no direct information is available concerning the valence state of bound manganese and the nature of the ligands surrounding the manganese.

We have made the first molecular orbital (MO) calculations for water oxidation process:

$$(HOH')^* - e^- \longrightarrow (HO)^* + H'^+ \qquad (2)$$

where H′ stands for a releasing proton. Our principal assumption is that some valence state of manganese works as a catalytic metal cation, which directly decomposes H_2O into H′ and OH^- (or OH radical). In vivo systems must have a proton-accepting site which forms a hydrogen bond with a water molecule to be oxidized by the manganese protein. Whether the proton-accepting site is a water molecule in the second solvation shell [12] or any another kind of proton acceptor in the water-splitting enzyme (WSE) system is entirely unknown. Here we assume the former possibility; as will be shown later, we found that no proton acceptor stronger than neutral water is necessary. Here, using the MO investigation, we aim to answer the following questions:

(1) What valence state of Mn can catalyze water-splitting reactions?
(2) What is the enzymatic effect of another molecule representing the proton-accepting site?
(3) How can the valence state of Mn and the ligands around Mn influence proton transfer?

2. Models and method

We used two kinds of models for calculations: A $Mn^{\nu+}$ cation is surrounded by square planary ligands (with D_{4h} symmetry) of 4 negative point charges of 0.3e placed at 2.0 Å (model A in fig.1), or of 4 water molecules placed at the respective equilibrium points of $R_1 \equiv d$ (Mn–O) (model B in fig.2). One water molecule (HOH′) was found to coordinate to the Mn complex in C_{2v} symmetry at the respective stable point of $R_2 \equiv d$ (Mn–O) (see table 1). Finally, another water molecule as proton acceptor, denoted by (OH_2), we placed to form a hydrogen bond with the bound water HOH′ at the experimental O–O distance of 2.8 Å. All the O–H bond lengths and all the bisected H–O–H bond angles designated by arcs were taken from the experimental data for the free water molecule. We assume that Mn cations are in a high spin state, as is often found for their hydrates [13]. This assumption is not

inconsistent with the findings that Mn in WSE is loosely bound to some protein moieties [4,6].

The IMSPACK program system was used for ab initio LCAO (linear combination of atomic orbital) MO UHF (unrestricted Hartree Fock) calculations. The basic set used for model A was of double zeta quality: the [6s, 4p, 3d] contracted Gaussian set for Mn and the 4–31 G set for water dimer, $HOH'–(OH_2)$. For model B, we used the [4s,3p,2d] contracted set for Mn, the 4–31 G set for the other water molecules, $(H_2O)_4$. The sets for Mn were obtained from the (11s,7p,5d) primitive set modified from the (12s,6p,4d) set [14].

3. Results and discussion

The fractional charge model for ligands (model A) may provide useful information on the ligands and on the charge transfer from the water molecule to the Mn cation. Three curves, A_{II}, A_{III} and without Mn in fig.1 show the relative potential energies for the systems with $(0.3e)_4Mn(II)$, with $(0.3e)_4Mn(III)$ and without Mn, as functions of $R_{OH'}$ (distance between O and the releasing proton H' in HO–H'). The proton transfer energy, defined by the energy difference $\Delta E_{pt} = E(R_{OH'} = 1.82\ Å) - E(R_{OH'} = 0.98$ Å), is considered to be the most direct measure of reactivity in the water-splitting reaction and are listed in table 1. Without Mn, the potential energy for proton transfer is largely repulsive (ΔE_{pt}=88 kcal/mol). In the presence of $(0.3e)_4Mn(II)$, ΔE_{pt} decreases by 48 kcal/mol (curve A_{II} in fig.1), but the potential energy is still repulsive. Repulsive nature of the potential energy is ascribed to the fact that the donation of electron from HO^- to Mn(II) is not sufficient to bring about an attractive energy because of the higher LUMO (lowest unoccupied molecular orbital) of the Mn(II)-complex than the HOMO (highest occupied molecular orbital) of OH^-—H_3^+O. However, when a Mn(III) is involved, it caused substantial decrease of ΔE_{pt}, leading to an attractive double minimum potential (curve A_{III}). This can be traced back to the fact that the energy levels of unoccupied A_{1g} ($3d_z2 + 4s$), $d_{xz\downarrow}$, and $d_{yz\downarrow}$ orbitals in the Mn(III)-complex are much lower than the HOMO of OH^- and comparable to that of H_2O. When Mn(IV) is involved, the SCF (self-consistent field) energy does not converge because of extremely low level of HOMO of Mn(IV) cation.

By the next calculation on model B, it is intended

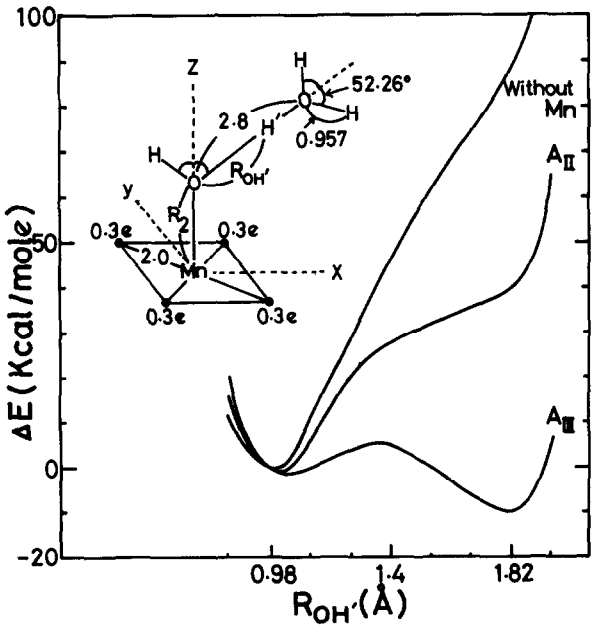

Fig.1. The potential energy curves for various systems in model A. For details of the systems, see table 1.

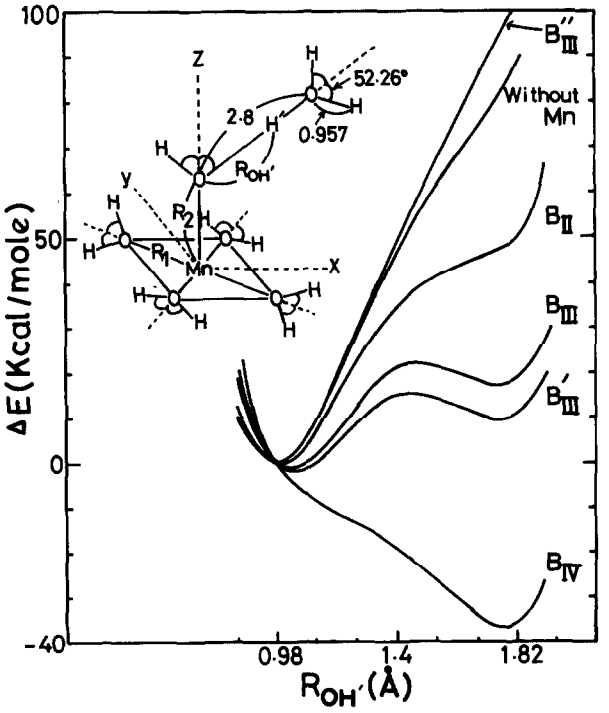

Fig.2. The potential energy curves for various systems in model B. For details of the system, see table 1.

Table 1
The proton transfer energy (ΔE_{pt}) as a function of the induced charge transfer (δ) from the water molecules to the catalytic Mn-complex

System [R_1(A), R_2 (A)]	LUMO (A_{1g}) of Mn-complex (eV)	ΔE_{pt} (kcal/mol)	$\delta \equiv -\Delta$ (HOH 'OH$_2$) $= \Delta$ (Mn-complex)
A_{II} [----, 2.069*]	−3.29	39.4	0.087
A_{III} [----, 2.069]	−17.03	−9.8	0.228
B_{II} [2.0*, 2.0*]	−1.80	48.9	0.068
B_{III} [1.86*, 1.95*]	−12.19	18.9	0.121
B'_{III} [2.2, 1.95*]	−12.67	10.7	0.160
B_{IV} [1.8*, 1.9*]	−21.96	−35.5	0.472
Without Mn	–	88.0	0

A and B designate the models A and B, respectively. For R_1 and R_2, see fig.2. The values denoted by asterisk were optimized by the calculation for respective fragments as mentioned in text (section 2). Suffixes, II, III and IV correspond to Mn(II), Mn(III), and Mn(IV), respectively

to take into account the effect of charge transfer from the surrounding to the central Mn atom. We found that this approach gave rise to a qualitatively similar result with the case of model A. Thus, the double minima are obtained for B_{III} and B'_{III} (fig.2). For these cases the potential energies at $R_{OH'}$=1.82 Å are not attractive in disagreement with the A_{III} system in model A. For model B, a less sophisticated basis set of Mn was used than for model A because of computational limitations (see section 2), and this is the reason for the different behavior between A_{III} and B_{III} (or B'_{III}). In fact, we ascertained that the ΔE_{pt} in the A_{II} system increases by 16 kcal/mol when the [4s,3p,2d] set of double zeta quality is used for Mn instead of the [6s,4p,3d] set of triple zeta quality. Further, decrease of ΔE_{pt} is expected by the conformational reorientation induced by the proton transfer. Taking into account these facts, ΔE_{pt} in the B_{III} or B'_{III} is considered to be decreased, resulting in the attractive potential curve. For Mn(IV)-complex, the potential curve is extremely attractive having no double minima (fig.2). This tendency will be strengthened by taking into account the above-stated facts, excluding possible involvement of Mn(IV). Thus, it is highly probable that Mn(III) ion is utilized in the water-splitting reaction in agreement with experimental proposition [6].

All the above calculations were performed in the presence of proton-accepting site. In the absence of this site, the potential energy curve changes drastically from B'_{III} to B''_{III} (fig.2). This can be easily understood by the fact that the increase of the energy of the HOMO in HO–H'––(OH$_2$) induced by the proton transfer (4. 1 eV) is much larger than that in HO–H' (1.6 eV). The increase of ΔE_{pt} is 86 kcal/mol and this is sufficiently large to give a strong repulsive potential even for Mn(IV). Therefore, it is concluded that the existence of proton-accepting site is essential for the occurrence of water-splitting reaction. Our calculation shows that there may be in fact another water molecule representing the second solvation shell. Thus, it is not appropriate to consider the

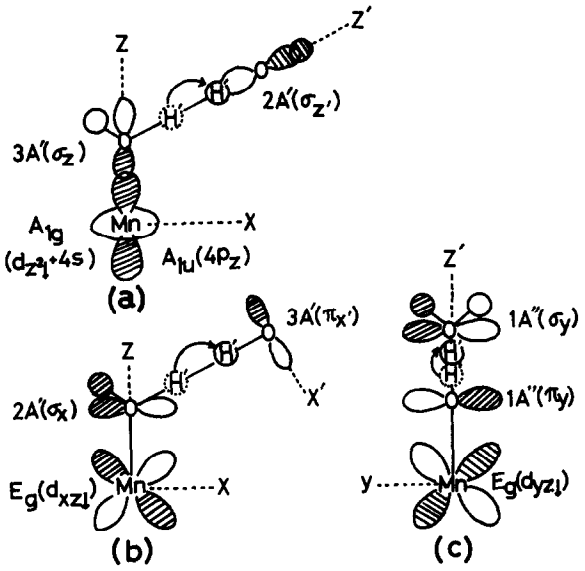

Fig.3. Bonding schemes of interactions among Mn, water and proton acceptor which contribute to the charge transfer from the water molecules to Mn-complex.

acceptor with larger proton affinity such as amines, carboxyl anion and imidazole anion.

As seen in table 1, the total charge transfer from the water molecules to the Mn-complex induced by proton transfer (denoted by δ) was found to be the most important index for predicting the different potentials towards different Mn-valencies and different ligands. Thus, ΔE_{pt} is a monotonically decreasing function of δ which in turn increases as the LUMO (A_{1g}) energy of a Mn-complex is lowered. But this correlation does not mean that the electron donation to the lowest unoccupied A_{1g} orbital alone dominantly contributes to δ. In fig.3 the bonding schemes of interactions among Mn, water and proton acceptor which are characteristics of the high spin $Mn^{\nu+}$ cation are indicated. In the case of Mn(III), the induced charge transfers to the $d_{xz\downarrow}$ and $d_{yz\downarrow}$ orbitals, which nearly degenerate to the $d_{z^2\downarrow}$ orbital but have smaller overlap integrals, are also important (18% and 18%, respectively), although the charge transfer to the A_{1g} orbital is predominant (51%).

The most widely accepted hypothesis explaining the oscillatory phenomena in PSII [5,7–11,15] was proposed [8], in which photochemically activated intermediates of the WSE system accumulate sequentially to produce 4 oxidizing equivalents (i.e., $S_0 \rightarrow S_1^+ \rightarrow S_2^{2+} \rightarrow S_3^{3+} \rightarrow S_4^{4+}$) until 1 molecular oxygen and 4 protons can be evolved ($S_4^{4+} \rightarrow S_0 + O_2 + 4\,H^+$). As regards the nature of each S state, some conflicting models have been proposed [9–11, 16]. Our calculation strongly suggests that, in the above cycle, Mn(IV) ion or higher oxidation states is not included but the oxidation product of $[(Mn{-}HO)^{2+}{-}(H'OH_2)^+]$ is an intermediate between $[Mn(II){-}HO{-}(H'OH_2)^+]$ and $(Mn(III){-}{-}HO^-{-}(H'OH_2)^+]$. This agrees with the observation that a mixture of Mn(II) and Mn(III) in dark-adapted algae and chloroplasts is involved as far as this species is involved in S_0 and/or S_1 states. If the oxidation product is involved only in S_1, a proton must be released just after the flash-induced transition of $S_0 \rightarrow S_1$, preferring to the proton release scheme (1:0:1:2) proposed [9,10] rather than the scheme (0:1:1:2) [11,16].

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