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On the Chemical Mechanism of O_2-Evolution in Photosystem II

YUZO NISHIDA

Department of Chemistry, Faculty of Science, Yamagata University, Koshirakawa Yamagata 990, Japan

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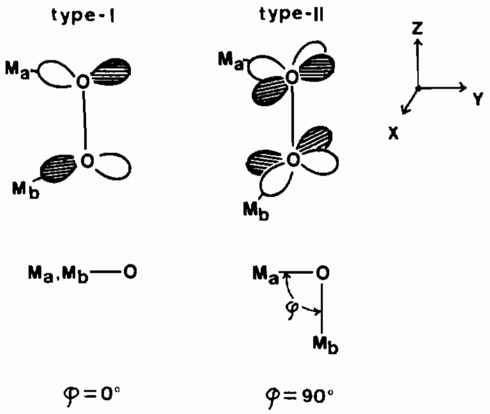
Elucidating the precise structure and mode of action of the Mn aggregate responsible for photosynthetic water oxidation/oxygen evolution represents an area of intense research at present [1–3]. It is generally believed that four Mn atoms are essential for this activity [4]. The Mn aggregate is capable of cycling between five oxidation levels (S_0–S_4) during the catalytic cycle. As shown in several chemical models [1–3, 5], O_2-evolution is assumed to occur through the two-electron oxidation of peroxide ion (transfer from peroxide to two Mn ions), although the exact determination of the oxidation state of Mn atoms remains unsolved [6]. In this step, two configurations are possible for the evolved dioxygen molecule: triplet ($^3\Sigma$) and singlet ($^1\Delta_g$). There are few discussions of this problem [1], however it is very important because the singlet oxygen ($^1\Delta_g$) is very hazardous to life [7].

The electronic structure of peroxide ion is represented by $[\text{----}(1\pi_{g(px)}{}^*)^2(1\pi_{g(py)}{}^*)^2]$, and those of triplet and singlet ($^1\Delta_g$) oxygens, $[\text{----}(1\pi_{g(px)}{}^*)^1(1\pi_{g(py)}{}^*)^1]$ and $[\text{----}(1\pi_{g(px)}{}^*)^2(1\pi_{g(py)}{}^*)^0]$, respectively [8]. Singlet oxygen ($^1\Delta_g$) will form when two electrons in the ($1\pi_{g(py)}{}^*$) orbital of the peroxide ion are transfered to two metal ions through coordination type-I where two lobes of the $1\pi_{g(py)}{}^*$ orbital coordinate to two metal ions, as shown in Scheme 1. On the other hand, the triplet oxygen will evolve if the two-electron transfer reaction proceeds via coordination type-II where two metal atoms are coordinated by two orbitals, ($1\pi_{g(px)}{}^*$) and ($1\pi_{g(py)}{}^*$). These two coordination types are discriminated by the dihedral angle, ϕ defined by the projection of the M–O–O–M bonds along the O–O bond as illustrated above ($\phi = 0$ and $90°$ for type-I and type-II, respectively).

Mononuclear metal–peroxide adducts such as $[PtO_2(PPh_3)_2]$ [9] and $[MoO_2L_2(O_2)]$ [10] may correspond to the coordination type-I complexes. This is supported by the fact that singlet oxygen is produced when the Pt-complex is irradiated by light corresponding to the charge-transfer band ($O_2{}^{2-} \rightarrow Pt$) [9]. Nishida *et al.* [11] pointed out that the peroxide ion in these complexes may contain more or less singlet oxygen character, which was confirmed by the fact that these peroxide adducts show high reactivity with 1,3-diphenylisobenzofuran (DPBF), one of the efficient singlet oxygen scavengers [12]. Similar high reactivities were also observed for the peroxide adduct of a binuclear iron(III) complex [11] and oxyhemocyanin model compounds [13].



Scheme 1.

Some examples belonging to coordination type-II are known for the dioxygen complexes of cobalt(II) [14]. In the case of $[Co_2(L)(O_2)(\text{benzoate})]^{2+}$, ϕ is 51°, the midpoint between type-I and type-II coordination [15]. In this study we have observed that the $[Co_2(L)(O_2)(\text{acetato})]^{2+}$ complex exhibits very low activity for the decomposition of DPBF (in methanol), which is quite different from the cases of peroxide adducts of iron(III) and copper(II) compounds. This fact can be elucidated in terms of Nishida's explanation [11]; i.e., singlet oxygen character in the peroxide ion is greatly reduced for compounds with coordination type-II. This fact supports our proposal that triplet oxygen evolves when two electrons of a peroxide ion are transfered to two metal atoms through coordination type-II.

In previous papers, Nishida *et al.* [16–18] have investigated the two-electron transfer reactions between peroxide ion (or dioxygen molecule) and synthetic binuclear metal complexes, and pointed out that environments around the two metal atoms should be similar for facile electron transfer between them. At present there is no chemical evidence to suggest that the singlet oxygen is formed in the PS II. Thus, we can estimate that O_2-evolution in PS II may occur through the two-electron transfer from peroxide to a special binuclear Mn(III) pair via the coordination type-II. The preparation of peroxide adducts of Mn(III) complexes with coordination type-II is now in progress.

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