Theory of chemical bonds in metalloenzymes XVI. Oxygen activation by high-valent transition metal ions in native and artificial systems

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ABSTRACT

Activation mechanisms of oxygen dianion and hydroxide by high-valent transition metal ions for the oxygen–oxygen (O–O) bond formation of water splitting reaction have been investigated on the theoretical grounds, together with experimental results. First of all, broken-symmetry MO formulations are revisited to elucidate the instability of the $d\pi$–$p\pi$ bond in high-valent metal–oxo M(X)=O (M = Mn, Fe, Ru, etc.; X = IV, V) systems that react with hydroxide anion (or radical) or water to afford hydroperoxide anion (or peroxide). The triplet instability of these bonds entails strong or intermediate diradical characters: •M(X−1)=O• and ••M(X−2)=O••; the broken-symmetry (BS) molecular orbitals (MO) resulted from strong electron correlation, leading to the concept of electron localizations and local spins. As a continuation of these theoretical results, the BS MO interaction diagrams, namely orbital and spin correlation diagrams, for one-electron and electron-pair transfer mechanisms for the O–O bond formation have been depicted to reveal scope and applicability of local singlet diradical (LSD) and local triplet diradical (LTD) mechanisms that have been successfully utilized for theoretical understanding of mechanisms of oxygenation reactions by p450, methane mono- oxygenase (MMO) and homolytic radical coupling mechanisms by oxygen evolving complex (OEC) of PSII. The spin alignments in high-valent M(X)=O systems are found directly corresponding to possible mechanisms of the O–O bond formation between Mn(X)=O and hydroxide (OH) anion via one-electron, electron-pair transfer and their superposed (chameleon) processes. The broken-symmetry (BS) UB3LYP calculations of the model systems have been performed to confirm these mechanisms for oxygen evolution; charge and spin densities by BS UB3LYP are utilized for elucidation and confirmation of the LSD and LTD mechanisms and orbital and spin correlation diagrams. Implications of the theoretical results are discussed in relation to three scenarios of the O–O bond formation for water oxidation: (a) HO–OH, (b) OOH and (c) O–O, and water oxidation of OEC of PSII.
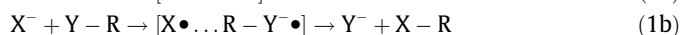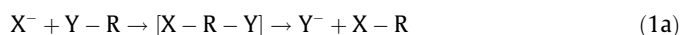
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1. Introduction

Past decades molecular mechanisms of oxygen evolution at the oxygen-evolving complex (OEC) of photosystem II (PSII) have been receiving great interest. The nucleophilic attack of hydroxide or water to electrophilic oxygen site in high-valent manganese oxides has been proposed for the oxygen–oxygen (O–O) bond formation in water splitting reaction at OEC of PSII and its model systems: this is often regarded as acid–base mechanism. However, electronic mechanisms of the O–O bond formation are not so simple because both one-electron transfer (OET) and electron-pair transfer (EPT) processes are conceivable for the process [1–25]. Open-shell formulations are necessary for theoretical description of electron-transfer (ET) diradical in the OET reaction, whereas the closed-shell description is feasible for EPT. Therefore suppression of generations of discrete active oxygens and oxy radicals [24,25] becomes crucial for water oxidation in biological systems. In the part XVI of this series broken-symmetry (BS) open-shell approaches to OET are thoroughly examined in relation to the O–O bond formation in water oxidation.

The theoretical distinction between OET and EPT mechanisms goes back to a classic problem: nucleophilic substitution of aromatic halogen compounds (Y–R) with anionic species (X⁻) proceeds through EPT and/or OET mechanism(s) [1–25].

$$X^- + Y - R \rightarrow [X - R - Y] \rightarrow Y^- + X - R \tag{1a}$$

$$X^- + Y - R \rightarrow [X\bullet \ldots R - Y^-\bullet] \rightarrow Y^- + X - R \tag{1b}$$

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The former process can be followed by the closed-shell Hartree–Fock (RHF) [9] and density functional theory (RDFT) [11], but the latter process entails the break down of the RHF and RDFT treatments because the closed-shell pair bifurcates into electron-transfer diradical pair in the transition state region, leading to the necessity of the different orbitals for different spins (DODS) or broken-symmetry (BS) theoretical approaches [9–11] for theoretical description of the process (1b) [4–7]. Historically, Mulliken [3] has proposed the charge-transfer (CT) theory for colored molecular complexes formed between donor (D) and acceptor (A), and Nagakura and his collaborators [5,6] have presented the charge-transfer (CT) theory for the (1b) process [16–23]. On the other hand, we have applied the DODS BS molecular orbital (MO) methods for (1b) [12,13] that require the mixing of HOMO of D and LUMO of A as shown in section II. Under the approximate spin projection (AP) procedure [24], the pure CT singlet state can be given by superposition of the ground (DA) and one electron-transfer (ET) configurations, respectively [24]. The configuration mixing coefficients are given by the orbital mixing parameters [14,15,24]. Thus the CT (intermolecular CI) and AP BS theories for one ET process are closely related each other. The AP BS theory has been successfully applied to theoretical illumination of CT-induced luminescence (CTIL) reactions of peroxide species [24].

The one-electron transfer (OET) and electron-pair transfer (EPT) mechanisms play important roles for base-catalyzed dioxygenation reactions of phenol, indole and flavin derivatives [16–23] that have been investigated by the BS methods [24,25]. Past decades Russel et al. [18,19] and Walling et al. [20,21] have intensively investigated the base-promoted oxygenation of organic compounds, resulting in dioxygen incorporation into a carbanion (R^-), proposing the so-called autoxidation mechanism, which involves substrate radicals $(R\bullet)$ produced by a one ET from carbanions to triplet molecular oxygen.

$$R^- + {}^3O{-}O \rightarrow R\bullet + {}^2O{-}O^-\bullet \qquad (2a)$$

$$R\bullet + {}^2O{-}O^-\bullet \rightarrow RO{-}O^- \qquad (2b)$$

$$R\bullet + {}^3O{-}O \rightarrow RO{-}O\bullet \qquad (2c)$$

$$RO{-}O\bullet + R^- \rightarrow RO{-}O^- + R\bullet(\text{chain}) \qquad (2d)$$

However, the oxygenation of this type usually includes a radical chain process, the control of which is quite difficult for selective oxygenations, giving rise to crucial by products, which seem not to be involved in biological dioxygenations.

On the other hand, our previous BS computations have elucidated that a CT complex formation followed by the spin inversion (CTSI) mechanism is feasible for oxygenations of phenol, indole and flavin derivatives in well-organized systems; namely the electronic properties of the CT intermediates $^{1,3}[R\delta\bullet\ldots\bullet\delta O{-}O]^-$ in the oxygenation reactions of anionic species could be variables within the discrete extremes: a closed-shell (nonradical) organodioxide anion $(^1DOO^-)$ and a complete one ET diradicals $^{1,3}[^2R\bullet\ldots\bullet^2O{-}O^-]$: this mechanism is referred to as the "chameleon" mechanism because of the labile nature with environmental effects [25]. The CT complex (chameleonic) mechanism does not afford free radicals, leading to a diradicaloid transition structures that are consistent with a lot of experimental results by Nishinaga et al. [25]. Thus the base-catalyzed dioxygenations of phenol, indole and flavin derivatives are highly dependent on three important factors: (1) proton transfer (deprotonation of OH and NH groups), (2) electron transfer and (3) spin inversion (SI). The BS theoretical treatments including spin–orbit interaction are essential in the CT-induced spin inversion (SI) mechanism that involves both singlet and triplet ET diradicals (not free radicals) as shown previously [24,25].
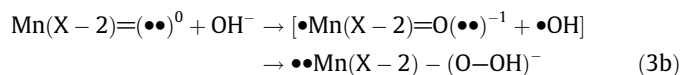
The spin degree of freedom is indeed a third important factor for the proton-coupled electron transfer (PCET) process in various oxygenations since molecular oxygen is the ground triplet species.

The same situation appears in the nucleophilic attack of hydroxide (OH) to atomic oxygen (O or O=(M)) that is also a ground triplet species, for which the CT complex formation has been introduced for lucid explanation. The spin inversion (SI) is often necessary for the radical coupling to afford singlet hydroperoxide anion $(HO{-}O^-)$. On the other hand, the one ET followed by the facile radical coupling is feasible in the case of singlet excited state (the Dxy configuration of O) [24]. Moreover, the electron-pair transfer (EPT) is feasible to vacant p-orbital of singlet O-atom (the Dxx configuration of O) [24]. The singlet and triplet O models have been proposed for theoretical understanding of metal-oxo species with oxygen site, though the oxygen site of metal oxo species such as manganese oxides [26–29] is usually regarded as oxygen dianion without vacant orbitals $[Mn(X)=O^{2-}]^0$ as illustrated in Fig. 1. However, the back CT from oxygen dianion to metal site occurs in high-valent manganese oxides, providing the oxygen radical anion site $[Mn(X-1)=(\bullet)^{1-}O]^0$ [26]. Moreover, one more back CT to metal site is feasible to afford formal atomic oxygen site: $[Mn(X-2)=(\bullet)^0]^0$ or $[Mn(X-2)=O^0]^0$ (see Fig. 1). Therefore OET and EPT processes are conceivable for high-valent Mn–oxo species. The spin degree of freedom plays an important role in these processes since the local spin configurations of manganese ions are usually maintained to be high spin in oxygenation reactions in biological systems [27–29].

The one-electron transfer (OET) and EPT mechanisms may be operative for water oxidation reaction in biological systems [30–44]. The OET mechanism followed by the radical coupling (RC) mechanism for the high-valent manganese–oxo species is expressed by

$$[Mn(X-1)=(\bullet)^{1-}O]^0 + OH^- \rightarrow [\bullet Mn(X-2)=O(\bullet)^{1-} + \bullet OH]$$
$$\rightarrow \bullet Mn(X-2) - (O{-}OH)^- \qquad (3a)$$
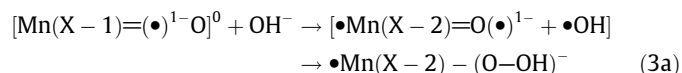
The former one-electron transfer (OET) step is independent of the spin alignment but the local singlet (LSD) or local triplet diradical (LTD) mechanism is feasible for the latter radical coupling (RC) step for the O–O bond formation. The generation of local spins is a direct indication of strong electron correlation effects in the Mn-oxide species related to OEC of PSII and related systems [30–100]. In fact, on theoretical grounds, these effects inevitably entail several kinds of instabilities of spin-restricted Hartree–Fock (RHF) and density functional (RDFT) solutions; they are therefore reorganized into the corresponding spin-polarized broken-symmetry (BS) solutions within single-reference MO-theoretical framework [8–15,101–119]. Similarly the OET process is conceivable for the triplet oxygen site (triplet O model) as follows [26]:

$$Mn(X-2)=(\bullet\bullet)^0 + OH^- \rightarrow [\bullet Mn(X-2)=O(\bullet\bullet)^{-1} + \bullet OH]$$
$$\rightarrow \bullet\bullet Mn(X-2) - (O{-}OH)^- \qquad (3b)$$

On the other hand, the electron-pair transfer (EPT) (acid–base) mechanism is feasible for the O–O bond formation process for the singlet oxygen site (singlet O(Dxx) model) of the metal–oxo species [26–29].

$$Mn(X-2)=O^0 + OH^- \rightarrow Mn(X-2) - (O{-}OH)^- \qquad (4)$$
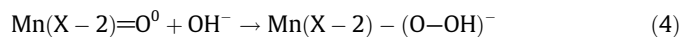
Thus spin-coupling modes at reaction sites are directly related to possible mechanisms for the O–O bond formation process that is a key step of water splitting reaction at OEC of PSII [30–100].

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (5)$$

where the deprotonation of water molecules in Eq. (5) occurs to afford molecular oxygen without generation of discrete active oxygens such as OH and OOH radicals.

Here (part XVI), as a continuation of previous theoretical studies [120–132] on oxygenations of p450 (part XIII [133–135]), methane