Unique Reactivity of Peroxide Ion Trapped by Binuclear Iron(III) Complex

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Binuclear Iron(III) Complex, Peroxide Ion

The (1:1) peroxide adduct of the binuclear iron(III) complex exhibited high reactivity towards 1,3-diphenylisobenzofuran, one of the efficient singlet oxygen (\(\Delta g\)) quencher. The activation of the peroxide ion in this molecule was discussed in relation to the monooxygenase function of this compound.

1. Introduction

Metalloproteins that catalyse the incorporation of oxygen atom derived from dioxygen into organic substrates usually contain either iron or copper. Our understanding of the mechanism involved in the reaction of the iron-containing heme oxygenases has been substantially advanced by the characterization of high-valent iron porphyrin oxo-complexes capable of epoxidation or hydroxylation of organic substrates [1–4]. In the case of copper enzymes e.g., tyrosinase [5] or dopamin-\(\beta\)-hydroxylase [6], our understanding is much limited, and no suitable model has been reported for tyrosinase reaction.

In the preceding paper, Nishida et al. [7] showed that the binuclear iron(III) complex with \(\mu\)-alkoxo bridge, \(\text{Fe}_2(L)(\text{NO}_3)_5\), reacts with \(\text{H}_2\text{O}_2\) to yield a blue species 1, where \(H(L)\) denotes 1,3-bis[N,N-bis(2-benzimidazolylmethyl)aminomethyl]-2-hydroxypropane.

![Fig. 1. Assumed structure for “blue species” obtained from \(\text{H}_2\text{O}_2\) and \(\text{Fe}_2(L)^{3+}\) complex [7].](image)

Based on the spectroscopic studies (absorption and resonance Raman [8]), 1 was confirmed to be (1:1) peroxide adduct of the binuclear iron(III) complex (cf. Fig. 1), and to catalyse the transformation of phenol to catechol. Thus, blue species 1 is the first oxy-tyrosinase model compound, e.g., the peroxide adduct of binuclear metal complex catalyses the hydroxylation of phenol ring [9]. These facts clearly indicate that the peroxide ion trapped in the binuclear metal complexes exhibits unique reactivity different from that of free \(\text{H}_2\text{O}_2\) molecule. In this study we have investigated the reaction between 1 and 1,3-diphenylisobenzofuran (hereafter abbreviated as DPBF), one of the efficient quenchers of singlet oxygen (\(\Delta g\)) in order to attempt to elucidate the reaction mechanism of hydroxylation of phenol ring catalyzed by peroxide ion in binuclear metal complexes.

2. Materials and Methods

DPBF was obtained commercially (Tokyo Kasei Co. Ltd.), and its purity was checked by the absorbance at 414 nm (\(\varepsilon = 24,700 \text{ M}^{-1}\text{cm}^{-1}\)) [10]. Iron(III) complex and blue species 1 were prepared by the Nishida’s method [7]. The decomposition of DPBF was monitored by measuring the decrease of absorbance at 414 nm of the reaction mixture. The absorption spectra were obtained with a Shimadzu Spectrophotometer model UV-240 at 288 K.

**Abbreviations:** DPBF; 1,3-diphenylisobenzofuran.

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The time course of the decomposition of DPBF in the presence of (A) H$_2$O$_2$ and (B) blue species 1 were shown in Fig. 2. It is well known that DPBF exhibits low reactivity towards O$_2$, H$_2$O$_2$, and O$_2$••• [10]. Fig. 2 shows that little decomposition of DPBF occurred for one hour in the presence of H$_2$O$_2$ under an aerobic condition. In contrast to this, the presence of 1 accelerated notably the decomposition of DPBF, as shown in Fig. 2. The similar decomposition of DPBF was also observed in the dimethylsulfoxide (dms) solution. This is suggesting that the decomposition of DPBF was not caused by the hydroxyl radical, because dms is known as one of the quencher of hydroxyl radical [11]. The addition of DPBF to the solution of 1 caused the remarkable decrease of the absorbance at 600 nm [7]. These results indicate that DPBF exhibits high reactivity towards 1 (undoubtedly towards peroxide ion trapped in the binuclear complex), and the reactivity of peroxide ion in the binuclear metal complex is quite different from that of free H$_2$O$_2$ molecule.

In 1970, Chan et al. showed that Cr(VI) complex with peroxide ion of side-on type coordination mode (see below) reacts with DPBF readily [12]. In this study we also found that monomeric metal complexes containing peroxide ion of side-on coordination type, Mo(VI) [13] and V(V) [14] (see above, all these compounds are diamagnetic) show high reactivity towards DPBF, similar to 1 and Cr(VI) complex. According to the simple molecular orbital considerations [15, 16], the interaction between $\pi^*_n$ and $\pi^*_v$ of peroxide ion and d-orbitals can be illustrated as in Fig. 3. There should be considerable difference in bond strength between $\sigma$-bonding ($d_{x^2-y^2}$ and $\pi^*_n$) and $\pi$-bonding ($d_{yz}$ and $\pi^*_v$), and thus it is expected that the peroxide ion in these complexes contains some degree of singlet oxygen ($^1\Delta_g$) character, because the peroxide ion contains more or less $\left[\cdots-d^+_{x^2-y^2}d_{yz}\cdots\right]^2$ electronic configuration which originates from the difference in the coefficients for $\pi^*_n$ and $\pi^*_v$ orbitals in two doubly occupied molecular orbitals (cf. Fig. 3). This may be the main reason for the fact that DPBF reacts with the peroxide adducts of Mo(VI), V(V), Cr(VI), and also 1. According to Mimoun et al., the peroxide adducts of V(V) and Cr(VI) complexes can catalyse the hydroxylation of benzene ring to yield phenol [14, 17]. Thus, the function of the hydroxylation of 1 and also that of oxytyrosinase may be closely related to the high reactivity of the peroxide ion trapped in the binuclear metal complexes.


[8] Resonance Raman spectra of I were measured by Prof. K. Nakamoto at Marquette University (Milwaukee, USA). New bands appeared at 890 and 495 cm\(^{-1}\) by the 590 nm light irradiation, and these bands are assigned to \(\nu(O=O)\) and \(\nu(Fe=O)\), respectively.


