Highlight Review

Metal Ion-coupled Electron-transfer Reduction of Dioxygen

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Abstract

Metal ion-coupled and proton-coupled electron-transfer reactions of dioxygen is described for one-electron, two-electron, and four-electron reduction of dioxygen by one-electron reductants such as ferrocene derivatives as well as by two-electron reductants such as NADH analogs. The catalytic mechanism of the four-electron reduction of dioxygen with cofacial dicobalt porphyrins has been clarified based on the detailed kinetic study and the detection of the intermediate.

◆ Introduction

Binding of metal ions to radical anions of electron acceptors results in significant positive shifts of the one-electron reduction potentials of electron acceptors.[1,2] Uphill electron-transfer reactions, which are thermodynamically infeasible to occur, are made possible by the presence of metal ions provided that the strong binding of metal ions to radical anions of electron acceptors changes the energetics of electron transfer from uphill to downhill.[1,2] In such a case metal ions can promote electron-transfer reactions, which would otherwise be impossible to occur.[1–3] This is defined herein as metal ion-coupled electron transfer (MCET) in analogy of proton-coupled electron transfer (PCET), which plays pivotal roles in biological electron-transfer systems such as photosynthesis and respiration.[4,5]

MCET is particularly important for the electron-transfer reduction of dioxygen (O_2), because electron transfer is only the spin-allowed process of the reactions of O_2, which is triplet in the ground state, with singlet molecules. The highly exergonic four-electron reduction of O_2 to water, which is the reverse process of photosynthesis, maintains the life of an aerobic organism by the respiration.[6–8] Cytochrome *c* oxidases (C*c*Os) are responsible for catalyzing the reduction of O_2 to water by the soluble electron carrier, cytochrome *c*.[6–8] The X-ray structures of C*c*Os have revealed that the catalytic site of C*c*Os consists of the bimetallic complex of heme and Cu, where the distance between Fe and Cu has been reported as 4.5 Å in the absence of O_2.[9,10] A number of synthetic analogs of the C*c*O active site have been synthesized to mimic the coordination environment of the Fe/Cu core as well as the catalytic function.[11–13] The four-electron reduction of O_2 is not only of great biological interest but also of technological significance such as fuel cells.[14–16]

The most important question is how the C*c*O enzyme catalyzes the four-electron reduction of O_2 to water without releasing the two-electron-reduced species (H_2O_2). This Highlight Review focuses on the MCET and PCET mechanisms of one-electron, two-electron, and four-electron reduction of O_2 in homogeneous solutions.

◆ One-electron Reduction of O_2 by One-electron Reductants

The promoting effects of metal ions on electron transfer from one-electron reductants to oxygen are certainly related to the Lewis acidity of metal ions.[1] Charges and ion radii are important factors to determine the Lewis acidity of metal ions.[17] The binding energies of a variety of metal ions with superoxide ion ($O_2^{\bullet-}$) can be readily derived from the g_{zz} values of the ESR spectra of the superoxide–metal ion complexes ($O_2^{\bullet-}/M^{n+}$), providing the quantitative measure of Lewis acidity of the metal ions (vide infra).[18]

The $O_2^{\bullet-}/M^{n+}$ complex is produced by the photoinduced electron-transfer reduction of O_2 by a dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$][19] in acetonitrile (MeCN). When an oxygen-saturated MeCN solution containing $(BNA)_2$ was irradiated with a high-pressure mercury lamp, $O_2^{\bullet-}$ formed photochemically is detected by the ESR spectrum in frozen MeCN at 143 K. The ESR spectrum shows a typical anisotropic signal with $g_{//} = 2.090$ and $g_{\perp} = 2.005$.[20] The g_{zz} values of $O_2^{\bullet-}/M^{n+}$ complexes produced in the presence of a variety of closed shell metal ions become significantly smaller than the value of $O_2^{\bullet-}$ due to the binding of metal ions to $O_2^{\bullet-}$ ($O_2^{\bullet-}/M^{n+}$, $n = 1$–3). The deviation of the g_{zz} value from the free spin value ($g_e = 2.0023$) is caused by the spin–orbit interaction as given by eq 1,[21,22] where λ is the spin–orbit coupling constant (0.014 eV),[23] and ΔE is the energy splitting of π_g levels due to the biding of M^{n+} to $O_2^{\bullet-}$.

$$\Delta E = (g_{zz} - g_e)/2\lambda \qquad (1)$$

The ΔE value obtained from the deviation of the g_{zz} value from the free spin value increases in order: monovalent cations (M^+) < divalent cations (M^{2+}) < trivalent cations (M^{3+}).[18] The ΔE value also increases with decreasing the ionic radius when the oxidation state of the metal ion is the same. The same trend has been reported for $O_2^{\bullet-}$ adsorbed on the surface of various metal oxides.[24,25] Scandium ion, which has the smallest ionic radius among the trivalent metal cations, gives the largest ΔE value.[18]

The promoting effects of metal ions on electron transfer from Co(TPP) (TPP = tetraphenylporphyrin dianion) to O_2 were examined in the presence of a series of metal ions (M^{n+}, $n = 1$–3) by the UV–vis spectral change for the decay of Co(TPP) ($\lambda_{max} = 411$ nm) and the formation of $[Co(TPP)]^+$ ($\lambda_{max} = 434$ nm) in MeCN at 298 K.[18] No electron transfer from Co(TPP) ($E_{ox} = 0.35$ V vs. SCE in MeCN)[26] to O_2 ($E_{red} = -0.86$ V vs. SCE in MeCN)[27] has occurred in MeCN at 298 K. In the presence of M^{n+}, however, an efficient electron transfer from Co(TPP) to O_2 occurs to yield $[Co(TPP)]^+$ (Scheme 1).[18]

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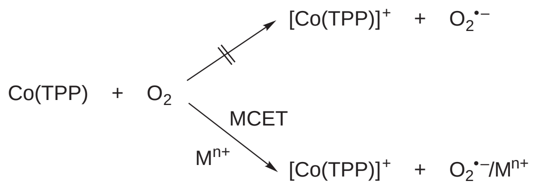

Scheme 1. MCET from Co(TPP) to O_2 in the presence of M^{n+}.[18]

The MCET rates obeyed second-order kinetics, showing a first-order dependence on the concentration of each reactant, O_2 and Co(TPP).[18] The observed second-order rate constant (k_{obs}) increases linearly with increasing metal ion concentration.[18] This confirms that the binding of M^{n+} to $O_2^{\bullet-}$ is indeed coupled with electron transfer (MCET), when MCET occurs in a concerted manner rather than a stepwise manner. If the rate-determining step were a uphill electron transfer from Co(TPP) to O_2, followed by rapid binding of M^{n+} to $O_2^{\bullet-}$, the ET rate would be independent of metal ion concentration.

From the slopes of the linear plots of k_{obs} vs. $[M^{n+}]$ were determined the MCET rate constants (k_{MCET}). There is a striking linear correlation between $\log k_{MCET}$ and the ΔE values of $O_2^{\bullet-}/M^{n+}$ derived from the g_{zz} values as shown in Figure 1, where the data for organotin compounds and scandium complexes acting as Lewis acids are included.[28] The remarkable correlation spans a range of more than 10^7 in the rate constant. The slope of the linear correlation between $\log k_{MCET}$ and ΔE is determined to be 14.0, which is close to the value of $1/2.3k_BT$ ($=16.9$, where k_B is the Boltzmann constant and $T = 298$ K).[28] This means that the variation of ΔE is directly reflected on the difference in the activation free energy for MCET from Co(TPP) to O_2. The stronger the binding of M^{n+} with $O_2^{\bullet-}$, the faster becomes the MCET rate.

◆ Two-electron Reduction of O_2 by One-electron Reductants

No electron transfer occurs from ferrocene derivatives to O_2 in the presence of $HClO_4$ in benzonitrile (PhCN) or MeCN at 298 K.[26,29] The addition of cobalt porphyrin catalysts to an air-saturated PhCN or MeCN solution of ferrocene derivatives with $HClO_4$ results in efficient electron transfer from ferrocene derivatives to O_2.[26,29] The formation of ferricenium ion derivatives was monitored by rise in absorbance at 620–700 nm. As soon as the reaction is started, Co(OEP) (OEP = octaethylporphyrin dianion) is oxidized to $[Co(OEP)]^+$ which remains virtually the same during the reaction.[29] This indicates that the catalytic steady state is established during the reaction. The concentration of ferricenium ion (e.g., $[Fe(C_5H_4Me)_2]^+$) formed in the Co(OEP)-catalyzed reduction of O_2 by $Fe(C_5H_4Me)_2$ is twice that of the O_2 concentration. Thus, only two-electron reduction of O_2 occurs and no further reduction proceeds to produce more than two equivalents of $[Fe(C_5H_4Me)_2]^+$ (eq 2). It was confirmed that H_2O_2 was formed in the two-electron reduction of O_2 by iodometric measurements.[26,29]

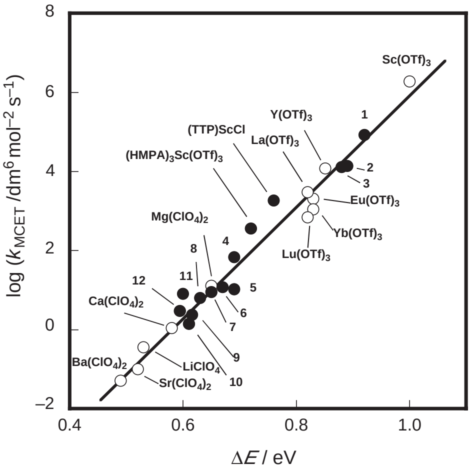

Figure 1. Plot of $\log k_{et}$ vs. ΔE in MCET from Co(TPP) to O_2 in the presence of metal ions (triflate or perchlorate salts) (○) and organotin compounds and scandium complexes (●) in MeCN at 298 K. Numbers refer to a variety of organotin compounds in ref 28.

$$2Fe(C_5H_4Me)_2 + O_2 + 2H^+ \xrightarrow[Co(OEP)]{} 2[Fe(C_5H_4Me)_2]^+ + H_2O_2 \qquad (2)$$

The rate of formation of $[Fe(C_5H_5)_2]^+$ in Co(OEP)-catalyzed two-electron reduction of O_2 by $Fe(C_5H_5)_2$ in the presence of $HClO_4$ in O_2-saturated PhCN at 298 K obeyed pseudo-first-order kinetics. The pseudo-first-order rate constant (k_{obs}) increases linearly with an increase in the catalyst concentration (Figure 2a). The second-order catalytic rate constant (k_{cat}) remains constant with the change in O_2 and $HClO_4$ concentrations (Figures 2b and 2c).[29] The k_{cat} values determined from formation of $[Fe(C_5H_5)_2]^+$ and $[Fe(C_5H_4Me)_2]^+$ in the Co(OEP)-catalyzed reduction of O_2 by $Fe(C_5H_5)_2$ and $Fe(C_5H_4Me)_2$ are twice of the k_{et} values of electron transfer from $Fe(C_5H_5)_2$ and $Fe(C_5H_4Me)_2$ to $[Co^{III}(OEP)]^+$ in the absence of O_2, respectively.[29] This indicates that the turnover-determining step (t.d.s.) for the catalytic two-electron reduction of O_2 is the electron-transfer step from

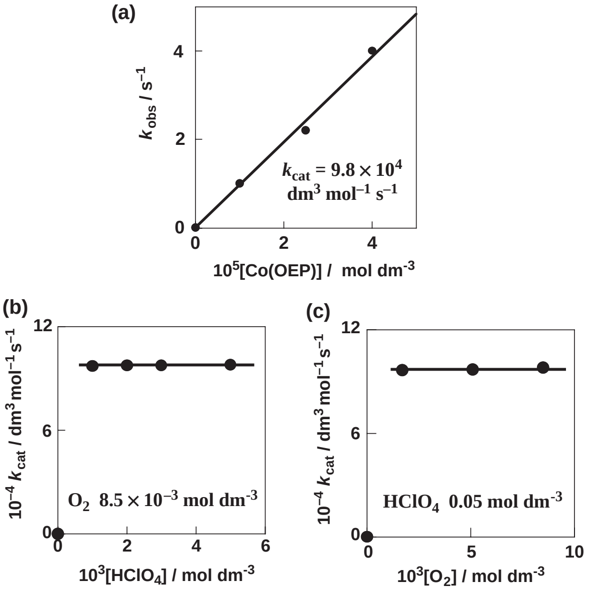

Figure 2. (a) Plot of k_{obs} vs. [Co(OEP)] for the Co(OEP)-catalyzed two-electron reduction of O_2 by $Fe(C_5H_5)_2$ in the presence of $HClO_4$ in PhCN at 298 K.[29] (b) Plot of k_{cat} vs. $[HClO_4]$.[29] (c) Plot of k_{cat} vs. $[O_2]$.[29]

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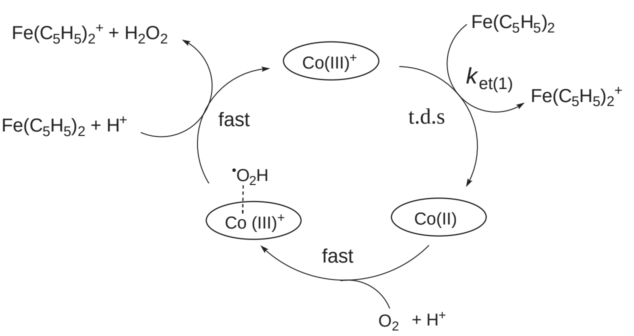


Scheme 2. Co(OEP)-catalyzed two-electron reduction of O_2 in the presence of $HClO_4$.[29]

ferrocene derivatives to $[Co^{III}(OEP)]^+$ as shown in Scheme 2. In such a case the rate of formation of ferricenium ions is given by eq 3, where the catalytic rate constant (k_{cat}) corresponds to $2k_{et}$.

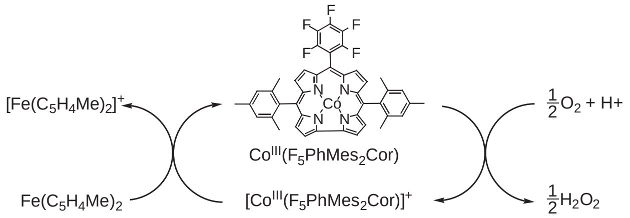
$$d[Fe(C_5H_5)_2{}^+]/dt = 2k_{et}[Fe(C_5H_5)_2][Co(OEP)] \qquad (3)$$

Electron transfer from $Fe(C_5H_5)_2$ to $[Co^{III}(OEP)]^+$ occurs, followed by fast electron transfer from $Co^{II}(OEP)$ to O_2 in the presence of an acid to produce the $[Co^{III}(OEP)O_2H]^+$, which is further reduced by $Fe(C_5H_5)_2$ in the presence of $HClO_4$ to produce H_2O_2, accompanied by regeneration of $[Co^{III}(OEP)]^+$. The catalytic mechanism of two-electron reduction of O_2 in Scheme 2 is virtually the same as that reported for Co(TPP)-catalyzed two-electron reduction of O_2 by ferrocene derivatives.[26]

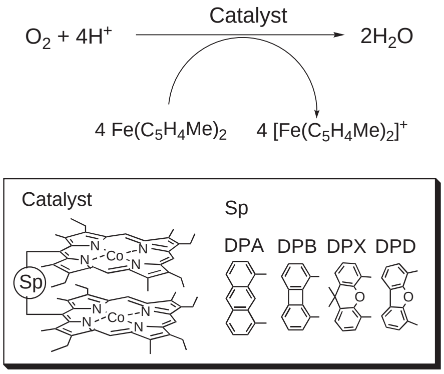
The catalytic two-electron reduction of O_2 also occurs with cobalt corroles as well as cobalt porphyrins in PhCN.[30] The addition of [10-pentafluorophenyl-5,15-dimesitylcorrole]-cobalt [(F_5PhMes_2Cor)Co] to an air-saturated PhCN solution of $Fe(C_5H_4Me)_2$ and $HClO_4$ resulted in efficient oxidation of ferrocene by O_2. Only the two-electron reduction of O_2 occurs and there is no further reduction to produce more than two equivalents of $[Fe(C_5H_4Me)_2]^+$ (Scheme 3).[31] Electron transfer from $Fe(C_5H_4Me)_2$ ($E_{ox} = 0.29$ V vs. SCE)[26] to $[(F_5PhMes_2Cor)Co]^+$ ($E_{red} = 0.38$ V)[30] occurs efficiently to produce $[Fe(C_5H_4Me)_2]^+$ and (F_5PhMes_2Cor)Co.[31] The cobalt(III) corrole complex [(F_5PhMes_2Cor)Co] can reduce O_2 in the presence of $HClO_4$. The site of electron transfer was examined by ESR characterization of the singly oxidized cobalt corrole.[31] The observed g value (2.0032) of the singly oxidized cobalt corrole, obtained by the chemical oxidation of (F_5PhMes_2Cor)Co with one equivalent of $[Fe(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine), is characteristic of an organic radical; it is quite different from the large g value (2.037) observed for cobalt(IV) porphyrin complexes.[32] Thus, the singly oxidized species is assigned as cobalt(III) corrole radical cation rather than cobalt(IV) corrole. In contrast to the case of cobalt porphyrins (Scheme 2), cobalt corroles act as effective catalysts in the reduction of O_2 with $HClO_4$ via the redox couple between cobalt(III) corroles and cobalt(III) corrole radical cations (Scheme 3).[31]

Four-electron Reduction of O_2 by One-electron Reductants

When monomeric cobalt porphyrins are replaced by cofacial dicobalt porphyrins, the four-electron reduction of O_2 by ferrocene derivatives occurs efficiently in the presence of $HClO_4$ in PhCN as shown in Scheme 4.[29]



Scheme 3. (F_5PhMes_2Cor)Co-catalyzed two-electron reduction of O_2 in the presence of $HClO_4$.[31]



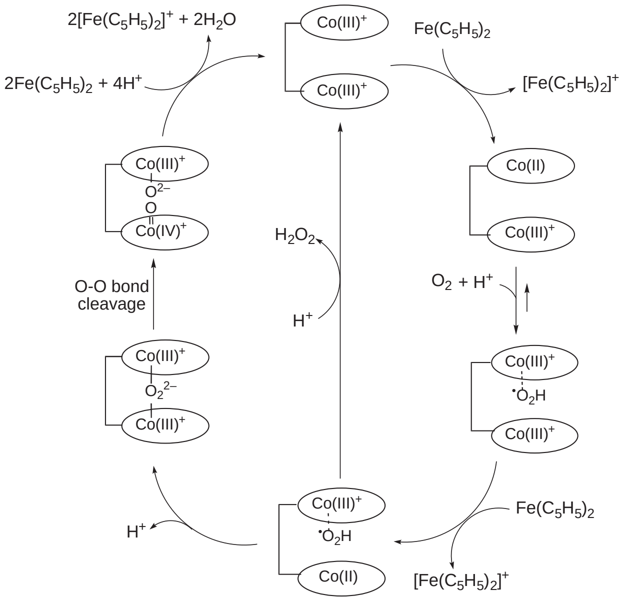
Scheme 4. Catalytic four-electron reduction of O_2 by a ferrocene derivative with cofacial dicobalt porphyrins.[29]

When a cofacial dicobalt porphyrin $[Co_2(DPX)]$ is used as a catalyst instead of a monomeric cobalt porphyrin Co(OEP), the concentration of $[Fe(C_5H_4Me)_2]^+$ formed in the $Co_2(DPX)$-catalyzed reduction of O_2 by $Fe(C_5H_4Me)_2$ is four times of O_2 concentration.[29] Thus, the four-electron reduction of O_2 by $Fe(C_5H_4Me)_2$ occurs efficiently in the presence of a catalytic amount of $Co_2(DPX)$ and $HClO_4$ in PhCN (eq 4). It was confirmed that no H_2O_2 was formed in the catalytic reduction of O_2 by $Fe(C_5H_4Me)_2$.[29]

$$\begin{aligned}&4Fe(C_5H_4Me)_2 + O_2 + 4H^+\\&\xrightarrow[Co_2(DPX)]{} 4[Fe(C_5H_4Me)_2]^+ + 2H_2O \qquad (4)\end{aligned}$$

The other cofacial dicobalt porphyrins [$Co_2(DPA)$, $Co_2(DPB)$, and $Co_2(DPD)$] also catalyze the reduction of O_2 by $Fe(C_5H_4Me)_2$, but the amount of $[Fe(C_5H_4Me)_2]^+$ formed was less than four equivalents of O_2.[29] Thus, the clean four-electron reduction of O_2 by $Fe(C_5H_4Me)_2$ occurs only in the case of $Co_2(DPX)$ used as a catalyst.

Based on the detailed kinetic comparison of the catalytic reactivities of cofacial dicobalt porphyrins and a monomeric cobalt porphyrin together with the detection of the reactive intermediates by ESR, the catalytic mechanism of four-electron reduction of O_2 by ferrocene derivatives is summarized as shown in Scheme 5. The initial electron transfer from ferrocene derivatives to the Co^{III}–Co^{III} complex gives the Co^{II}–Co^{III} complex, which reacts with O_2, accompanied by the reduction by ferrocene derivatives, to produce the Co^{III}–O_2–Co^{III} complex. The heterolytic O–O bond cleavage of the Co^{III}–O_2–Co^{III} complex affords the high-valent cobalt(IV)oxo porphyrin π-radical cation, which is further reduced by ferrocene derivatives in the pres-



Scheme 5. The catalytic mechanism of four-electron reduction of O_2 by ferrocene with a cofacial cobalt porphyrin.[29]

ence of proton to yield H_2O (Scheme 5).[29] The critical point to distinguish between the two-electron and four-electron reduction pathways is formation of the μ-peroxo Co^{III}–O_2–Co^{III} complex, which requires an appropriate Co–Co distance in the cofacial dicobalt complex. The Co–Co distance in Co_2(DPX) is best suited for formation of the μ-peroxo Co^{III}–O_2–Co^{III} complex, resulting in the catalytic four-electron reduction of O_2.[29] In the case of monomeric cobalt porphyrins such as Co(TPP) and Co(OEP), there is no way to form the μ-peroxo Co^{III}–O_2–Co^{III} complex, resulting in only the two-electron reduction of O_2.[29]

Thus, the interaction of two cobalt nuclei with an active form of oxygen is essential for the four-electron reduction of O_2. The μ-superoxo species of cofacial dicobalt porphyrins are produced by the reactions of cofacial dicobalt(II) porphyrins with O_2 in the presence of a bulky base (1-*tert*-butyl-5-phenylimidazole) and the subsequent one-electron oxidation of the resulting peroxo species by iodine.[29] The superhyperfine structure due to two equivalent cobalt nuclei is observed at room temperature in the ESR spectrum of the μ-superoxo species as shown in Figure 3.[29] The superhyperfine coupling constant of the μ-superoxo species of Co_2(DPX) determined from the computer simulation (Figure 3) is the largest among those of cofacial dicobalt porphyrins.[29] This suggests that the efficient catalysis of Co_2(DPX) for the four-electron reduction of O_2 by ferrocene derivatives results from the strong binding of the reduced oxygen with Co_2(DPX) which has the most suitable distance between two cobalt nuclei for the oxygen binding.[29]

The rate of formation of $[Fe(C_5H_5)_2]^+$ in Co_2(DPX)-catalyzed four-electron reduction of O_2 by $Fe(C_5H_5)_2$ in the presence of 0.05 M $HClO_4$ in O_2-saturated PhCN at 298 K also obeyed pseudo-first-order kinetics. The pseudo-first-order rate constant (k_{obs}) increases with increasing the catalyst concentration of Co_2(DPX).[29] The k_{cat} values increase linearly with increasing concentrations of $HClO_4$ and O_2.[29] Such a linear dependence of k_{cat} on [$HClO_4$] and [O_2] shows sharp contrast with the case of the Co(OEP)-catalyzed two-electron reduction of O_2 by $Fe(C_5H_5)_2$ in Figure 2, where the k_{cat} values remain constant irrespective of $HClO_4$ or O_2 concentration. This indicates that the PCET from $Co^{III}Co^{II}(DPX)^+$, which is produced in the initial electron transfer from $Fe(C_5H_5)_2$ and to $Co^{III}{}_2(DPX)_2{}^+$, to O_2 is the turnover-determining step (t.d.s.) in the catalytic four-electron reduction of O_2 in Scheme 5.

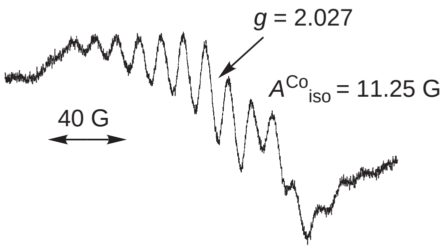


Figure 3. ESR spectrum of the μ-superoxo complex (ca. 10^{-3} mol dm^{-3}) produced by adding iodine (ca. 10^{-3} mol dm^{-3}) to an air-saturated PhCN solution of Co_2(DPX) (5×10^{-3} mol dm^{-3}) in the presence of 1-*tert*-butyl-5-phenylimidazole (5×10^{-3} mol dm^{-3}) at 298 K.[29]

When $Fe(C_5H_5)_2$ is replaced by a much stronger reductant, that is $Fe(C_5Me_5)_2$, the kinetics of formation of $[Fe(C_5Me_5)_2]^+$ changes drastically from pseudo-first-order kinetics in the case of $Fe(C_5H_5)_2$ to zero-order kinetics as shown in Figure 4a, where the rate remains constant irrespective of concentration of $Fe(C_5Me_5)_2$.[29] The zero-order rate constant increases linearly with increasing the catalyst concentration (Figure 4b), but remains constant with variation of concentrations of $HClO_4$ and O_2 as shown in Figures 4c and 4d, respectively.[29] This indicates that the turnover-determining step changes from the proton-coupled electron transfer from $Co^{III}Co^{II}(DPX)^+$ to O_2 in the case of $Fe(C_5H_5)_2$ to the reaction step which has nothing to do with $Fe(C_5Me_5)_2$, $HClO_4$ or O_2. Such a process in which no electron-transfer process is involved is most likely to be O–O bond cleavage of the Co^{III}–O_2–Co^{III} complex in Scheme 5. The O–O bond cleavage rate is determined to be 320 s^{-1} from the slope in Figure 4b.[29]

◆ Two-electron Reduction vs. Four-electron Reduction of Dioxygen by Two-electron Reductants

When one-electron reductants (ferrocene derivatives) are replaced by two-electron reductants such as NADH analogs, 9-alkyl-10-methyl-9,10-dihydroacridines (AcrHR: R = Me, Et, and CH_2COOEt), the four-electron reduction of O_2 is catalyzed by Co_2(DPA) to yield 9-alkyl-10-methylacridinium ion ($AcrR^+$) and H_2O (Scheme 6).[32] In the case of R = Bu^t and CMe_2-COOMe, however, the catalytic reduction of O_2 by AcrHR results in oxygenation of the alkyl group of AcrHR rather than the dehydrogenation to yield 10-methylacridinium ion ($AcrH^+$) and ROH (Scheme 6).[32]

In the case of $AcrH_2$, the initial slow electron transfer from $AcrH_2$ to the Co^{III}–Co^{III} complex is followed by the C(9)–H cleavage to produce $AcrH^•$ in competition with the back electron transfer from the Co^{III}–Co^{II} complex to $AcrH_2{}^{•+}$.[32,33] The catalytic rate-determining step is deprotonation of $AcrH_2{}^{•+}$. Thus, the Co^{III}–Co^{II} complex reacts rapidly with O_2 and H^+ to give the $Co^{III}Co^{III}(^•O_2H)$ complex, and this is followed by rapid electron transfer from $AcrH^•$ to the $Co^{III}Co^{III}(^•O_2H)$ complex to

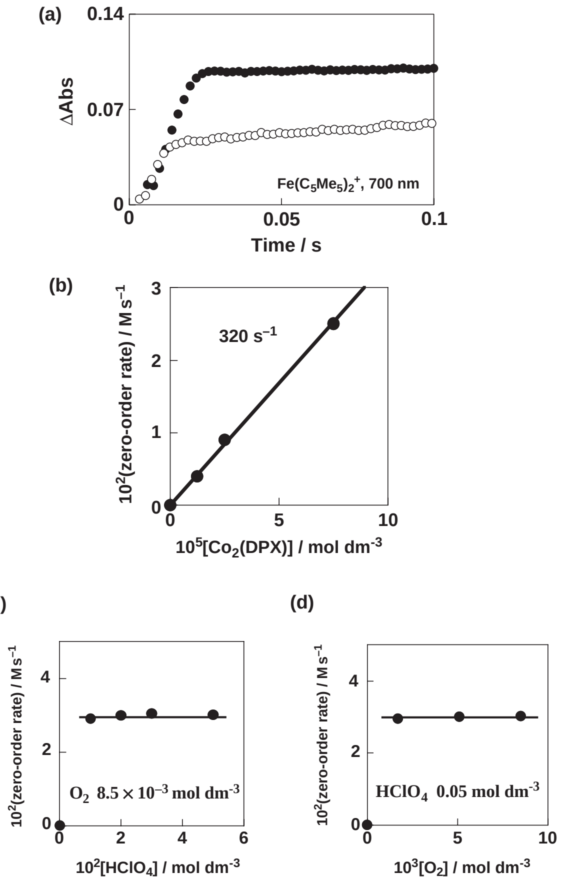
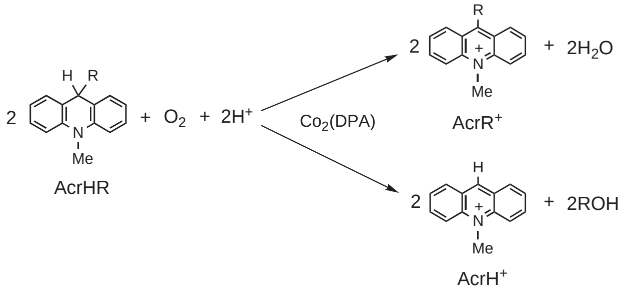
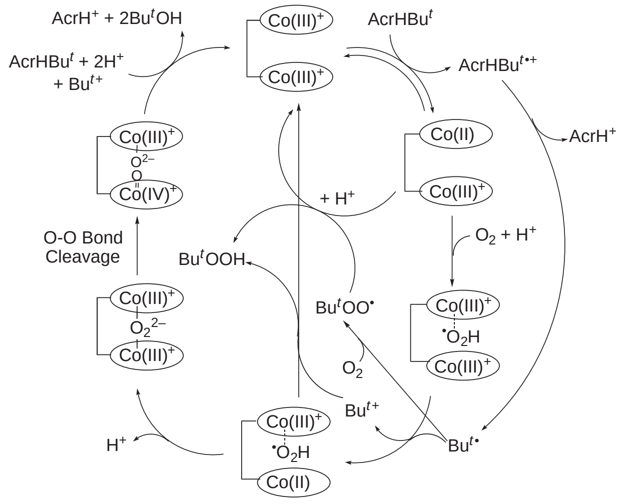


Figure 4. (a) Time profiles of formation of $[Fe(C_5Me_5)_2]^+$ monitored by absorbance at 700 nm in the four-electron reduction of O_2 by $Fe(C_5Me_5)_2$ [2.5×10^{-4} mol dm^{-3} (○), 4.0×10^{-4} mol dm^{-3} (●)], catalyzed by Co_2(DPX) (8.0×10^{-5} mol dm^{-3}) in the presence of 0.05 mol dm^{-3} $HClO_4$ in PhCN at 298 K.[29] (b) Plot of the zero-order rate constant vs. [Co_2(DPX)].[29] (c) Plot of the zero-order rate vs. [$HClO_4$].[29] (d) Plot of the zero-order rate vs. [O_2].[29]



Scheme 6. Catalytic dehydration vs. oxygenation of the R group of AcrHR with Co_2(DPA).[32]

produce $AcrH^+$ and the $Co^{III}Co^{III}(^\bullet O_2H)$ complex. After deprotonation, the μ-peroxo Co^{III}–O_2–Co^{III} complex is formed as the case of the catalytic four-electron reduction of O_2 by ferrocene derivatives.[29] The heterolytic O–O bond cleavage of the Co^{III}–O_2–Co^{III} complex affords the high-valent cobalt(IV)oxo porphyrin π-radical cation, which is readily reduced by $AcrH_2$ in the presence of proton to yield H_2O, accompanied by formation of $AcrH^+$.



Scheme 7. Mechanism of the catalytic oxygenation of the R group of AcrHR by O_2 with a cofacial cobalt porphyrin.[32]

As the case of the catalytic reduction of O_2 by ferrocene derivatives, monomeric cobalt porphyrins catalyze only the two-electron reduction of oxygen by $AcrH_2$ in the presence of H^+.[34]

In the case of $AcrHBu^t$, the mechanism of the catalytic four-electron reduction of O_2, accompanied by the oxygenation of Bu^t, is modified as shown in Scheme 7.[32] The initial electron transfer from $AcrHBu^t$ to the Co^{III}–Co^{III} complex results in the homolytic C(9)–C bond cleavage to produce $Bu^{t\bullet}$ and $AcrH^+$.[35,36] Since the homolytic C(9)–C bond cleavage is also the catalytic rate-determining step, the $Co^{III}Co^{III}(^\bullet O_2H)$ complex is formed by the reaction of O_2 and H^+, followed by electron transfer from $Bu^{t\bullet}$ to the $Co^{III}Co^{III}(^\bullet O_2H)$ complex to produce Bu^{t+} and the $Co^{III}Co^{III}(^\bullet O_2H)$ complex. The subsequent step may be the same as the case of the four-electron reduction of O_2 by $AcrH_2$. The high-valent cobalt(IV)oxo porphyrin π-radical cation is formed by the heterolytic O–O bond cleavage of the Co^{III}–O_2–Co^{III} complex, being reduced by $AcrHBu^t$ in the presence of H^+ to yield Bu^tOH, accompanied by formation of $AcrH^+$ (Scheme 7). However, $Bu^{t\bullet}$ produced in the initial electron transfer from $AcrHBu^t$ to the Co^{III}–Co^{III} complex is readily trapped by O_2 to give the peroxyl radical $Bu^tOO^\bullet$. Such alkylperoxyl radicals ($ROO^\bullet$) are regarded as rather strong one-electron oxidants judging from the highly positive one-electron reduction potentials.[37] Thus, the initial electron transfer from $AcrHBu^t$ to the Co^{III}–Co^{III} complex is followed by the subsequent electron transfer from the Co^{III}–Co^{II} complex to $Bu^tOO^\bullet$ to produce Bu^tOOH after protonation, accompanied by regeneration of the Co^{III}–Co^{III} complex (Scheme 7).

◆ *Summary*

The combination of metal ion-coupled electron transfer (MCET) and proton-coupled electron transfer (PCET) plays an essential role in the catalytic reduction of oxygen. The selective two-electron reduction of O_2 by ferrocene derivatives occurs with a monomeric cobalt porphyrin, whereas the selective four-electron reduction of O_2 occurs with a cofacial dicobalt porphyrin. The four-electron reduction of O_2 by AcrHR is also catalyzed by a cofacial dicobalt porphyrin efficiently via electron transfer from AcrHR to cofacial dicobalt porphyrins, followed by the C(9)–H and C(9)–C bond cleavage of $AcrHR^{\bullet+}$ depending on the type of R, leading to the dehydration and oxygenation of AcrHR, respectively. In each case, the formation of the μ-peroxo $Co^{III}–O_2–Co^{III}$ complex via MCET is crucial for the four-electron reduction of O_2.

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