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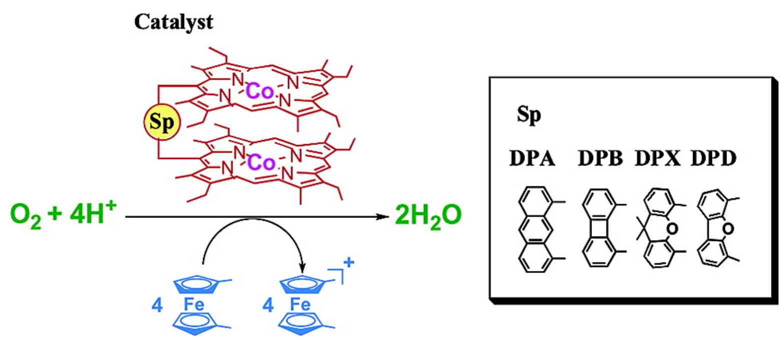

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Mechanism of Four-Electron Reduction of Dioxygen to Water by Ferrocene Derivatives in the Presence of Perchloric Acid in Benzonitrile, Catalyzed by Cofacial Dicobalt Porphyrins

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Abstract: The selective two-electron reduction of dioxygen occurs in the case of a monocobalt porphyrin [Co(OEP)], whereas the selective four-electron reduction of dioxygen occurs in the case of a cofacial dicobalt porphyrin [Co_2(DPX)]. The other cofacial dicobalt porphyrins [Co_2(DPA), Co_2(DPB), and Co_2(DPD)] also catalyze the two-electron reduction of dioxygen, but the four-electron reduction is not as efficient as in the case of Co_2(DPX). The μ-superoxo species of cofacial dicobalt porphyrins were produced by the reactions of cofacial dicobalt(II) porphyrins with dioxygen in the presence of a bulky base and the subsequent one-electron oxidation of the resulting μ-peroxo species by iodine. The superhyperfine structure due to two equivalent cobalt nuclei was observed at room temperature in the ESR spectra of the μ-superoxo species. The superhyperfine coupling constant of the μ-superoxo species of Co_2(DPX) is the largest among those of cofacial dicobalt porphyrins. This indicates that the efficient catalysis by Co_2(DPX) for the four-electron reduction of dioxygen by $Fe(C_5H_4Me)_2$ results from the strong binding of the reduced oxygen with Co_2(DPX) which has a subtle distance between two cobalt nuclei for the oxygen binding. Mechanisms of the catalytic two-electron and four-electron reduction of dioxygen by ferrocene derivatives will be discussed on the basis of detailed kinetics studies on the overall catalytic reactions as well as on each redox reaction in the catalytic cycle. The turnover-determining step in the Co(OEP)-catalyzed two-electron reduction of dioxygen is an electron transfer from ferrocene derivatives to $Co(OEP)^+$, whereas the turnover-determining step in the Co_2(DPX)-catalyzed four-electron reduction of dioxygen changes from the electron transfer to the O−O bond cleavage of the peroxo species of Co_2(DPX), depending on the electron donor ability of ferrocene derivatives.

Introduction

The highly exergonic four-electron reduction of oxygen to water is essential to maintain the life of an aerobic organism by the respiration.[1−3] Cytochrome *c* oxidases (C*c*Os) located in the inner mitochondrial membrane are the terminal enzymes of the respiratory chains, catalyzing the reduction of molecular oxygen to water by the soluble electron carrier, cytochrome *c*.[1−3] 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 *a* and Cu (Fe_{a3}/Cu_B) where the distance between Fe_{a3} and Cu_B has been reported as 4.5 Å in the absence of O_2.[4−6] On the matrix side of the membrane, four protons are consumed for each oxygen molecule reduced, and this is coupled to the intramembrane proton translocation.[6,7] The resulting proton gradient is used as the driving force for generation of ATP as protons flow back through the membrane via the enzyme ATP synthase.[6,7]

A number of synthetic Fe_{a3}/Cu_B analogues have been synthesized to mimic the coordination environment of the Fe/Cu core as well as the catalytic function of the four-electron reduction of O_2.[8−13] Although the four-electron reduction of O_2 is not only of great biological interest[9−13] but also of techno-

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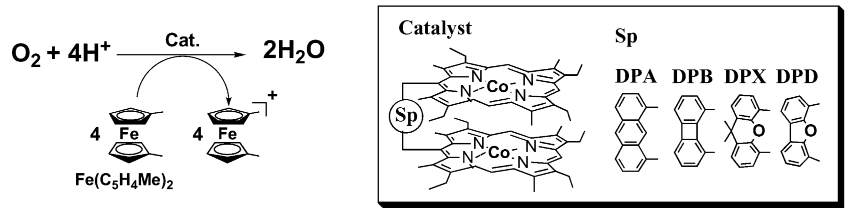
Scheme 1



logical significance such as fuel cells,[14−17] electrocatalytic reduction of O_2 has been the only method to probe the catalytic reactivity of synthetic C*c*O model complexes. The most important question of 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) has yet to be well understood. Comparison of the catalytic reactivities of the biomimetic complexes in the FeCu and Cu-free forms indicate that Cu does not significantly affect the turnover frequency or the stability of the catalyst and do not improve catalysis.[18,19] The O_2 binding to Fe at one end and to Cu at the other is not necessary, and only the iron porphyrin itself has been reported to be essential for the four-electron reduction of O_2.[18−20] In contrast, dicobalt bisporphyrins efficiently electrocatalyze the direct four-electron reduction of O_2 to water,[21−23] whereas single cobalt porphyrins can act as the four-electron reduction catalysts only through self-assembly on the electrode surface.[24] The difficulty in determining the self-assembled structure on the electrode surface has precluded the actual role of the bimetallic systems in the four-electron reduction of O_2. Thus, it is highly desired to study the catalytic four-electron reduction of O_2 vs two-electron reduction of O_2 using a one-electron reductant in a homogeneous solution. Although cytochrome *c* is used as a one-electron reductant in C*c*Os, no catalytic systems of four-electron reduction of O_2 by a one-electron reductant in a homogeneous system has ever been clarified quantitatively.[25,26]

We report herein efficient four-electron reduction of dioxygen by ferrocene derivatives which are one-electron reductants, catalyzed by cofacial dicobalt porphyrins in the presence of perchloric acid ($HClO_4$) in benzonitrile (PhCN) as shown in Scheme 1. The cofacial dicobalt porphyrins are chosen as catalysts for the four-electron reduction of O_2, because the bimetallic system is indispensable for the four-electron reduction of oxygen in the case of cobalt porphyrins, thus allowing for the difference from the single metal system to be clarified. Detailed kinetic comparison of catalytic reactivities of cofacial dicobalt porphyrins and a single cobalt porphyrin and detection of the reactive intermediates by ESR provide valuable insights into the question how the bimetallic system catalyzes the four-electron reduction of O_2 to water without releasing the two-electron reduced species (H_2O_2).

Experimental Section

Materials. All solvents and chemicals were of reagent grade quality, obtained commercially and used without further purification except as noted below. 2,3,7,8,12,13,17,18-Octaethyl-21*H*,23*H*-porphine cobalt(II) [Co(OEP)] was purchased by Aldrich Co., USA. The PhCN solution of Co(III)(OEP) was produced by addition of the trace of perchloric acid. Details on the synthesis and characterization of each cofacial dicobalt porphyrin [Co_2(DPB), Co_2(DPA), Co_2(DPX), and Co_2(DPD)] have been reported elsewhere.[22a,23a,27,28] Preparation of 1-*tert*-butyl-5-phenylimidazole has been described.[29] Benzonitrile (PhCN) was purchased from Tokyo Kasei Organic Chemicals, Japan, and distilled over P_2O_5 prior to use.[30] Ferrocene (Wako Pure Chemicals, Japan), 1,1′-dimethylferrocene (Aldrich Co., USA), and decamethylferrocene

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(Wako Pure Chemicals) were obtained commercially and purified by sublimation or recrystallization from ethanol. Perchloric acid (70%), hydrogen peroxide, and iodine were obtained from Wako Pure Chemicals. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemical Co., twice recrystallized from absolute ethanol and dried in a vacuum at 45 °C prior to use. Tris(2,2′-bipyridyl)-ruthenium(III) hexafluorophosphate [$Ru(bpy)_3(PF_6)_3$] was prepared according to the literature.[31]

Spectral Measurements. The amount of hydrogen peroxide (H_2O_2) was determined by titration by iodide ion.[32] The aliquots of the product mixture in PhCN was treated with excess NaI, and the amount of I_3^- formed was determined by the UV−visible spectrum (λ_{max} = 365 nm, ϵ_{max} = 28 000 M^{-1} cm^{-1})[33] using a Hewlett-Packard 8453 diode array spectrophotometer with a quartz cuvette (path length = 10 mm) at 298 K.

Kinetic Measurements. All kinetic measurements were performed on a UNISOKU RSP-601 stopped-flow spectrophotometer with the MOS-type high selective photodiode array at 298 K using a Unisoku thermostated cell holder. Rates of oxidation of ferrocene derivatives by O_2 in the presence of a catalytic amount of Co(OEP) or cofacial dicobalt porphyrin and $HClO_4$ in aerated PhCN at 298 K were determined by monitoring the appearance of the absorption band due to ferricenium ions ($Fe(C_5H_5)_2^+$: λ_{max} = 620 nm, ϵ_{max} = 330 M^{-1} cm^{-1}. $Fe(C_5H_4Me)_2^+$: λ_{max} = 650 nm, ϵ_{max} = 290 M^{-1} cm^{-1}. $Fe(C_5Me_5)_2^+$: λ_{max} = 700 nm, ϵ_{max} = 240 M^{-1} cm^{-1}). The ϵ_{max} values of ferricenium ions were determined by the electron-transfer oxidation of ferrocene derivatives with $Ru(bpy)_3(PF_6)_3$. At the monitoring wavelengths, there is no spectral overlap with cobalt porphyrins (Co(II)(OEP): λ_{max} = 396 nm (107 000 M^{-1} cm^{-1}), 518 nm (9200 M^{-1} cm^{-1}), 552 nm (15 000 M^{-1} cm^{-1}). $Co(III)(OEP)^+$: λ_{max} = 417 nm (150 000 M^{-1} cm^{-1}), 526 nm (9100 M^{-1} cm^{-1}), 558 nm (10 000 M^{-1} cm^{-1}). Co(II)Co(II)-(DPD): λ_{max} = 397 nm (212 000 M^{-1} cm^{-1}), 526 nm (10 200 M^{-1} cm^{-1}), 555 nm (16 100 M^{-1} cm^{-1}). $Co(III)Co(III)(DPD)^{2+}$: λ_{max} = 420 nm (243 000 M^{-1} cm^{-1}), 533 nm (14 900 M^{-1} cm^{-1}), 563 nm (10 000 M^{-1} cm^{-1})). An air-saturated PhCN solution was used for the catalytic reduction of oxygen by ferrocene derivatives. The O_2 concentration in an air-saturated PhCN solution (1.7 × 10^{-3} M) was determined by the spectroscopic titration for the photooxidation of 10-methyl-9,10-dihydroacridine by O_2 described as reported previously.[34] The concentrations of ferrocene derivatives larger than the O_2 concentration were used for the catalytic reduction of O_2 by ferrocene derivatives, when oxygen is the limiting reagent in the reaction cell which is filled with the reactant solution. In contrast, the concentrations of ferrocene derivatives smaller than the O_2 concentration were used in O_2-saturated PhCN, when ferrocene derivatives are the limiting reagents.

Rates of electron transfer from ferrocene derivatives to Co(III) porphyrins in deaerated PhCN were determined by the decay of the spectrum at 417 nm due to $Co(III)(OEP)^+$ or at 420 nm due to $Co_2(DPX)^+$ using the stopped-flow apparatus mentioned above. A deaerated PhCN solution containing a Co(III) porphyrin and that of a ferrocene derivative was transferred by means of a glass syringe to the reactant reservoirs of the stopped flow apparatus which were already purged with a stream of argon. Co(III) porphyrins were prepared by the oxidation of Co(II) porphyrins by O_2 in the presence of an acid.[35,36] The kinetic measurements of electron transfer were carried out under the pseudo-first-order conditions where concentrations of ferrocene derivatives were maintained at an excess of more than 10 times the Co(III) porphyrin concentration.

ESR Measurements. The ESR spectra of μ-superoxo (Co−O_2−Co) species in $Co_2(DPA)$, $Co_2(DPB)$, $Co_2(DPX)$, and $Co_2(DPD)$ were produced by the chemical oxidation of the dicobalt porphyrins (∼1 × 10^{-3} M) containing the bulky base, i.e., 1-*tert*-butyl-5-phenylimidazole (5 × 10^{-3} M), with a trace of iodine in deaerated PhCN under an atmospheric pressure of oxygen according to the literature procedure.[37] The solution containing the μ-superoxo species was transferred to an ESR tube under an atmospheric pressure of oxygen. The ESR spectra were taken on a JEOL X-band spectrometer (JES-RE1XE) with a quartz ESR tube (1.2 mm i.d.). The ESR spectra were recorded under nonsaturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and the signal-to-noise (*S*/*N*) ratio of the observed spectra. The *g* values were calibrated with a Mn^{2+} marker, and the super hyperfine coupling constants were determined by computer simulation using a Calleo ESR Version 1.2 program coded by Calleo Scientific on a personal computer.

Cyclic Voltammetry. Cyclic voltammetry measurements were performed at 298 K on a BAS 100 W electrochemical analyzer in deaerated PhCN containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm^2) and a platinum wire as the counter electrode. The Pt working electrode (BAS) was routinely polished with a BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/$AgNO_3$ (0.01 M) reference electrode. All potentials (vs Ag/Ag^+) were converted to values vs SCE by adding 0.29 V.[38] All electrochemical measurements were carried out under an atmospheric pressure of argon.

Results and Discussion

Catalytic Two-Electron vs Four-Electron Reduction of O_2 by Ferrocene Derivatives. No oxidation of ferrocene derivatives occurs by O_2 in the presence of $HClO_4$ in benzonitrile (PhCN) at 298 K. The addition of cobalt porphyrin catalysts and $HClO_4$ to air-saturated PhCN solutions of ferrocene derivatives results in efficient oxidation of ferrocene derivatives by O_2. The formation of ferrocene derivatives was monitored by a rise in absorbance at 620−700 nm due to ferricenium ions (see Experimental Section, e.g., ϵ(650 nm) = 290 M^{-1} cm^{-1} for $Fe(C_5H_4Me)_2^+$). Figure 1a shows the time course of formation of 1,1′-dimethylferricenium ion $Fe(C_5H_4Me)_2^+$ in the reduction of O_2 (1.7 × 10^{-3} M)[34] by a large excess of 1,1′-dimethylferrocene [$Fe(C_5H_4Me)_2$] (0.10 M) in the presence of catalytic amounts of Co(OEP) (7.2 × 10^{-6}−1.7 × 10^{-5} M) and

(26) Redox titrations with O_2 and cobaltocene were reported using a cobalt(II) porphyrin with a copper(I) triazacyclononane macrocycle as a cytochrome *c* oxidase model, and the O_2 adduct was fully reduced to the deoxygenated form with 4 equiv of cobaltocene.[10a] See also: Collman, J. P.; Herrmann, P. C.; Boitrel, B.; Zhang, X.; Eberspacher, T. A.; Fu, L.; Wang, J. L.; Rousseau, D. L.; Williams, E. R. *J. Am. Chem. Soc.* **1994**, *116*, 9783.
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(35) Formation of $Co(III)(OEP)^+$ was confirmed by the appearance of $Co(III)(OEP)^+$ (λ_{max} = 417 nm) together with the disappearance of Co(II)(OEP) (λ_{max} = 395 nm) upon addition of 5.0 × 10^{-3} M $HClO_4$ to a air-saturated PhCN solution of Co(II)(OEP). See: Setsune, J.; Saito, Y.; Ishimaru, M.; Ikeda, M.; Kitao, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 639.
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(37) (a) Chang, C. K. *J. Chem. Soc., Chem. Commun.* **1977**, 800. (b) Le Mest, Y.; L'Her, M.; Courtot-Coupez, J.; Collman, J. P.; Evitt, E. R.; Bencosme, C. S. *J. Chem. Soc., Chem. Commun.* **1983**, 1286. (c) Guilard, R.; Jérôme, F.; Gros, C. P.; Barbe, J.-M.; Ou, Z.; Shao, J.; Kadish, K. M. *C. R. Acad. Sci., Ser. IIc: Chim.* **2001**, *4*, 245.
(38) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1990.

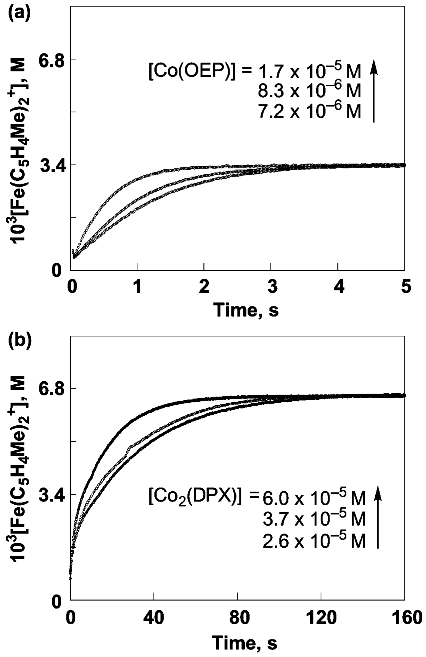


Figure 1. Time profiles of formation of $Fe(C_5H_4Me)_2^+$ monitored at 650 nm ($\epsilon = 290$ M^{-1} cm^{-1}) in electron-transfer oxidation of $Fe(C_5H_4Me)_2$ (1.0×10^{-1} M) by O_2 (1.7×10^{-3} M), catalyzed by (a) Co(OEP) and (b) Co_2(DPX) in the presence of $HClO_4$ (2.0×10^{-2} M) in PhCN at 298 K.

$HClO_4$ (2.0×10^{-2} M). As soon as the reaction is started, Co(OEP) is oxidized to Co(III)(OEP)$^+$ which remains virtually the same during the reaction. This indicates that the catalytic steady state is established during the reaction. The concentration of $Fe(C_5H_4Me)_2^+$ (3.4×10^{-3} M) formed in the Co(OEP)-catalyzed reduction of O_2 by $Fe(C_5H_4Me)_2$ is twice that of the O_2 concentration (1.7×10^{-3} M). Thus, only two-electron reduction of O_2 occurs and no further reduction occurs to produce more than 2 equiv of $Fe(C_5H_4Me)_2^+$ (eq 1).

$$2Fe(C_5H_4Me)_2 + O_2 + 2H^+ \xrightarrow{Co(OEP)} 2Fe(C_5H_4Me)_2^+ + H_2O_2 \quad (1)$$

It was confirmed that H_2O_2 (1.6×10^{-3} M) is formed in the two-electron reduction of O_2 by iodometric measurements (see Experimental Section).

When a cofacial dicobalt porphyrin [Co_2(DPX)] is used as a catalyst instead of a single cobalt porphyrin Co(OEP), the concentration of $Fe(C_5H_4Me)_2^+$ formed in the Co_2(DPX)-catalyzed reduction of O_2 by $Fe(C_5H_4Me)_2$ (6.8×10^{-3} M in the case of Co_2(DPX) compared to 3.4×10^{-3} M in the case of Co(OEP)) is 4 times the O_2 concentration (1.7×10^{-3} M) as shown in Figure 1b. 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 $HClO_4$ (2.0×10^{-2} M) in PhCN (eq 2).

$$4Fe(C_5H_4Me)_2 + O_2 + 4H^+ \xrightarrow{Co_2(DPX)} 4Fe(C_5H_4Me)_2^+ + 2H_2O \quad (2)$$

It was confirmed that no H_2O_2 was formed in the catalytic reduction of O_2 by $Fe(C_5H_4Me)_2$. The rate of four-electron reduction of O_2 increases with increasing the catalyst concentration (Figure 1b).

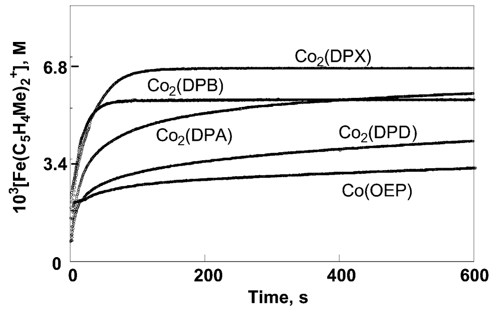


Figure 2. Time profiles of formation of $Fe(C_5H_4Me)_2^+$ monitored at 650 nm ($\epsilon = 290$ M^{-1} cm^{-1}) in electron-transfer oxidation of $Fe(C_5H_4Me)_2$ (1.0×10^{-1} M) by O_2 (1.7×10^{-3} M), catalyzed by Co_2(DPX) (2.0×10^{-5} M), Co_2(DPA) (2.0×10^{-5} M), Co_2(DPB) (2.0×10^{-5} M), Co_2(DPD) (2.0×10^{-5} M), and Co(OEP) (3.0×10^{-5} M) in the presence of $HClO_4$ (2.0×10^{-2} M) in PhCN at 298 K.

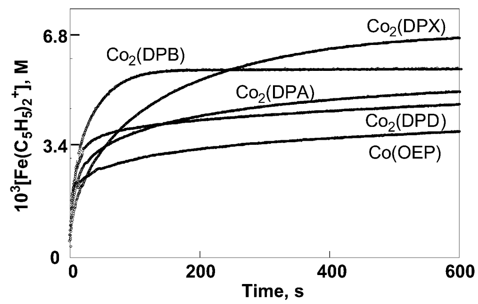


Figure 3. Time profiles of formation of $Fe(C_5H_5)_2^+$ monitored by absorbance at 620 nm ($\epsilon = 330$ M^{-1} cm^{-1}) in electron-transfer oxidation of $Fe(C_5H_5)_2$ (1.0×10^{-1} M) by O_2 (1.7×10^{-3} M), catalyzed by Co_2(DPX) (2.0×10^{-5} M), Co_2(DPA) (2.0×10^{-5} M), Co_2(DPB) (2.0×10^{-5} M), Co_2(DPD) (2.0×10^{-5} M), and Co(OEP) (3.0×10^{-5} M), in the presence of $HClO_4$ (2.0×10^{-2} M) in PhCN at 298 K.

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 is less than 4 equiv of O_2 (Figure 2). 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.

When $Fe(C_5H_4Me)_2$ ($E°_{ox} = 0.26$ V vs SCE) is replaced by a weaker one-electron reductant, $Fe(C_5H_5)_2$ ($E°_{ox} = 0.37$ V), and a stronger one-electron reductant, $Fe(C_5Me_5)_2$ ($E°_{ox} = -0.08$ V), the clean four-electron reduction of O_2 also occurs only in the case of Co_2(DPX) used as a catalyst as shown in Figure 3. It was confirmed that no H_2O_2 was formed in the Co_2(DPX)-catalyzed reduction of O_2 and that the rate of reduction of H_2O_2 is much slower than the rate of reduction of O_2. This indicates that H_2O_2 is not an intermediate for the Co_2(DPX)-catalyzed four-electron reduction of O_2 by ferrocene derivatives.

Electron Transfer from Ferrocene Derivatives to Catalysts. As described above, electron transfer from ferrocene derivatives to the oxidized form of the catalyst is the key step in the catalytic reduction of O_2 by ferrocene derivatives. To determine the free energy change of electron transfer, the one-electron reduction potentials ($E°_{red}$ vs SCE) of Co(OEP) are determined by the cyclic voltammetry measurements as shown in Figure 4.[39] The $E°_{red}$ value of Co(OEP) is determined at 0.31 V which corresponds to the Co(II)/Co(III) couple.[40,41] In the

(39) Cyclic voltammograms for Co_2(DPB), Co_2(DPA), Co_2(DPX), and Co_2(DPD) have been reported previously in different conditions. See: ref 23b and c.
(40) (a) Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J.; Felton, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 614. (b) Felton, R. H.; Dolphin, D.; Borg, D. C.; Fajer, J. *J. Am. Chem. Soc.* **1969**, *91*, 196.

Table 1. Free Energy Change ($\Delta G°_{et}$) and Rate Constants (k_{et}) of Electron Transfer from Ferrocene Derivatives to Co(III) Porphyrins in Deaerated PhCN at 298 K and Rate Constants (k_{cat}) of Co(III) Porphyrin-Catalyzed Reduction of O_2 (8.5×10^{-3} M) by Ferrocene Derrivatives in the Presence of $HClO_4$ (5.0×10^{-2} M)

cobalt porphyrin	ferrocene	$\Delta G°_{et(1)}$, eV	$k_{et(1)}$, M^{-1} s^{-1}	$\Delta G°_{et(2)}$, eV	$k_{et(2)}$, M^{-1} s^{-1}	k_{cat}, M^{-1} s^{-1}
Co_2(DPX)	$Fe(C_5H_5)_2$	−0.16	4.0×10^6	−0.02	2.8×10^5	3.6×10^5 [b]
	$Fe(C_5H_4Me)_2$	−0.27	*a*	−0.13	1.0×10^6	8.0×10^5 [b]
	$Fe(C_5Me_5)_2$	−0.61	*a*	−0.47	*a*	320 s^{-1} [c]
Co(OEP)	$Fe(C_5H_5)_2$	0.06	4.8×10^4			9.8×10^4
	$Fe(C_5H_4Me)_2$	−0.05	1.0×10^5			2.1×10^5
	$Fe(C_5Me_5)_2$	−0.39	*a*			*a*

[a] Too fast to be determined accurately. [b] In the case of 0.05 M $HClO_4$ and 8.5×10^{-3} M O_2. [c] k_{cat} determined from (zero-order rate)/[Co_2(DPX)] in Figure 10, which corresponds to the rate of O−O bond cleavage.

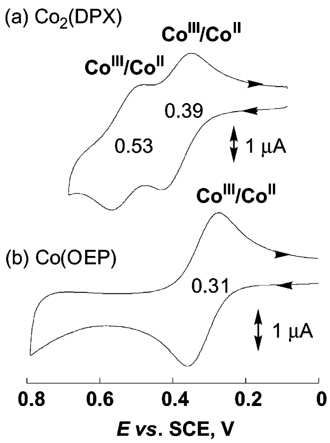


Figure 4. Cyclic voltammograms of (a) Co_2(DPX) and (b) Co(OEP) (1.0×10^{-3} M) in PhCN containing 0.1 M TBAP; scan rate 100 mV s^{-1}.

case of cofacial dicobalt porphyrins [Co_2(DPX)], two reversible redox waves ($E°_{red}$) are observed at 0.53 and 0.39 V (vs SCE) (Figure 4). The two reversible waves correspond to the first and second one-electron reduction potentials of two Co(III) moieties.[42]

The free energy change ($\Delta G°_{et}$ in eV) of electron transfer from $Fe(C_5H_5)_2$ ($E°_{ox} = 0.37$ V), $Fe(C_5H_4Me)_2$ ($E°_{ox} = 0.26$ V), or $Fe(C_5Me_5)_2$ ($E^0_{ox} = -0.08$ V) to $Co(III)(OEP)^+$ ($E°_{red} = 0.31$ V) or $Co(III)_2(DPX)^{2+}$ ($E°_{red} = 0.53, 0.39$ V) is obtained from the $E°_{ox}$ values of $Fe(C_5H_5)_2$ and the $E°_{red}$ values of Co(III) porphyrins using eq 3, where e is elementary charge.

$$\Delta G°_{et} = e(E°_{ox} - E°_{red}) \quad (3)$$

The $\Delta G°_{et}$ values are described in Table 1. In most cases, the free energy change of electron transfer is negative (exergonic), and thereby the electron transfer is expected to occur thermally.

In the absence of O_2, efficient electron transfer from ferrocene to $Co(III)(OEP)^+$ occurs under pseudo-first-order conditions (large excess ferrocene derivatives). The rates obeyed pseudo-first-order kinetics, and the observed pseudo-first-order rate constant increased linearly with increasing the [$Fe(C_5H_5)_2$] (eq 4).

(41) The first oxidation of a Co(II) porphyrin in a noncoordinating solvent involves formation of a Co(II) porphyrin radical cation, whereas the first oxidation in potentially coordinating solvents invariably involves the metal-centered oxidation to produce a Co(III) porphyrin. See: (a) Salehi, A.; Oertling, W. A.; Babcock, G. T.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 5630. (b) Kadish, K. M.; Lin, X. Q.; Han, B. C. *Inorg. Chem.* **1987**, *26*, 4161.

(42) (a) Le Mest, Y.; L'Her, M.; Collman, J. P.; Kim, K.; Hendricks, N. H.; Helm, S. *J. Electroanal. Chem.* **1987**, *234*, 277. (b) Kadish, K. M.; Guo, N.; Van Caemelbecke, E.; Paolesse, R.; Monti, D.; Tagliatesta, P. *J. Porphyrins Phthalocyanines* **1998**, *2*, 439.

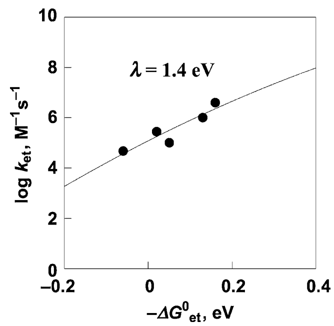


Figure 5. Plots of log k_{et} vs $-\Delta G°_{et}$ in electron transfer from ferrocene derivatives [$Fe(C_5H_5)_2$, $Fe(C_5H_4Me)_2$, and $Fe(C_5Me_5)_2$] to Co(III) porphyrins [Co_2(DPX) and Co(OEP)] in deaerated PhCN at 298 K.

$$d[Fe(C_5H_5)_2^+]/dt = k_{et(1)}[Fe(C_5H_5)_2][Co(III)(OEP)^+] \text{ in the absence of } O_2 \quad (4)$$

From the slope is determined the second-order rate constant of electron transfer ($k_{et(1)}$). The $k_{et(1)}$ values of ferrocene and other ferrocene derivatives are listed in Table 1.

Electron transfer from ferrocene derivatives to $Co(III)_2(DPX)^{2+}$ occurs via two step processes which correspond to electron transfer from ferrocene derivatives to $Co(III)_2(DPX)^{2+}$ and the subsequent electron transfer from ferrocene derivatives to $Co(III)Co(II)(DPX)^+$. Both the first and second steps obeyed pseudo-first-order kinetics. The pseudo-first-order rate constants increased linearly with increasing concentrations of $Co(III)_2(DPX)^{2+}$. Thus, the kinetic formulation is given by eq 5.

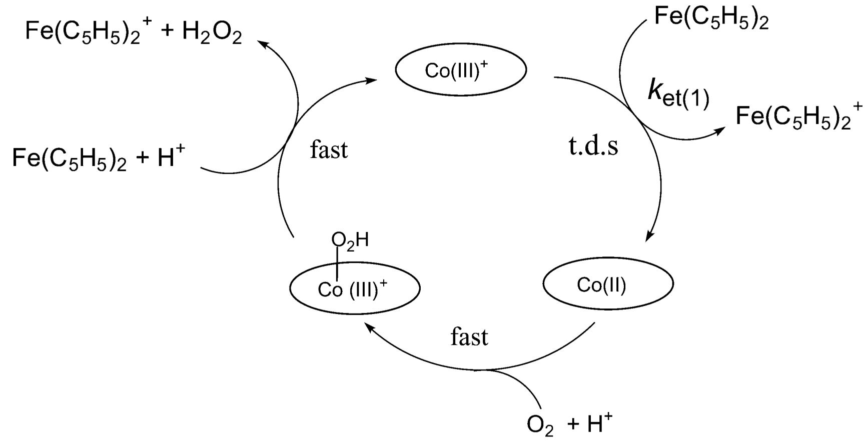
$$d[Fe(C_5H_5)_2^+]/dt = k_{et(1)}[Fe(C_5H_5)_2][Co(III)_2] + k_{et(2)}[Fe(C_5H_5)_2][Co(III)Co(II)] \quad (5)$$

The second-order rate constants of the first-step and second-step electron transfer ($k_{et(1)}$ and $k_{et(2)}$, respectively) were determined from the slopes of linear plots of the pseudo-first-order rate constant vs [$Fe(C_5H_5)_2$], and the results are summarized in Table 1.

The $k_{et(1)}$ values of electron transfer from ferrocene derivatives to $Co(III)_2(DPX)^{2+}$ are larger than the $k_{et(2)}$ values of the subsequent electron transfer to $Co(III)Co(II)(DPX)^+$ because of the more positive one-electron reduction potential of $Co(III)_2(DPX)^{2+}$ than that of $Co(III)Co(II)(DPX)^+$. In the case of electron transfer from $Fe(C_5Me_5)_2$ to $Co(III)Co(II)(DPX)^+$, the initial electron transfer was too fast to determine the rate constant accurately.

The driving force dependence of the $k_{et(1)}$ and $k_{et(2)}$ values in Table 1 is shown in Figure 5, where the k_{et} values increase with increasing the driving force of electron transfer ($-\Delta G°_{et}$). The

Scheme 2



driving force dependence of k_{et} is evaluated in light of the Marcus theory of adiabatic outersphere electron transfer (eq 6),[43]

$$k_{et} = Z \exp[-(\lambda/4k_BT)(1 + \Delta G^\circ_{et}/\lambda)^2] \quad (6)$$

where Z is the frequency factor (1×10^{11} M^{-1} s^{-1}), λ is the reorganization energy of electron transfer, and k_B is the Boltzmann constant. The best fit of the data to eq 6 (the solid line in Figure 5) affords the λ value 1.4 eV.

Catalytic Mechanism of Two-Electron Reduction of O_2. The rate of formation of $Fe(C_5H_5)_2^+$ in the Co(OEP)-catalyzed electron-transfer oxidation of $Fe(C_5H_5)_2$ by O_2 (8.5×10^{-3} M) in the presence of 0.05 M $HClO_4$ in O_2-saturated PhCN at 298 K obeyed pseudo-first-order kinetics. A typical time course is shown in Figure 6a with the pseudo-first-order plot (inset of Figure 6a). The pseudo-first-order rate constant (k_{obs}) increases linearly with an increase in the catalyst concentration (Figure 6b). From the slope is determined the second-order rate constant of the catalytic electron transfer (k_{cat}). The k_{cat} values remain constant with the change in O_2 and $HClO_4$ concentrations as shown in Figure 6c and d, respectively. The k_{cat} values thus determined are also listed in Table 1. The k_{cat} values determined from formation of $Fe(C_5H_5)_2^+$ and $Fe(C_5H_4Me)_2^+$ in the Co(OEP)-catalyzed electron-transfer oxidation of $Fe(C_5H_5)_2$ and $Fe(C_5H_4Me)_2$ by O_2 are approximately 2 times 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 (Table 1). 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 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 7, where the catalytic rate constant (k_{cat}) corresponds to $2k_{et}$.

$$d[Fe(C_5H_5)_2^+]/dt = 2k_{et}[Fe(C_5H_5)_2][Co(OEP)] \text{ in the presence of } O_2 \quad (7)$$

The initial fast electron transfer from $Fe(C_5H_5)_2$ to Co(III)(OEP)$^+$ is followed by the 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 an acid 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) (TPP = tetraphenylporphyrin dianion)-catalyzed two-electron reduction of O_2 by ferrocene derivatives.[25a]

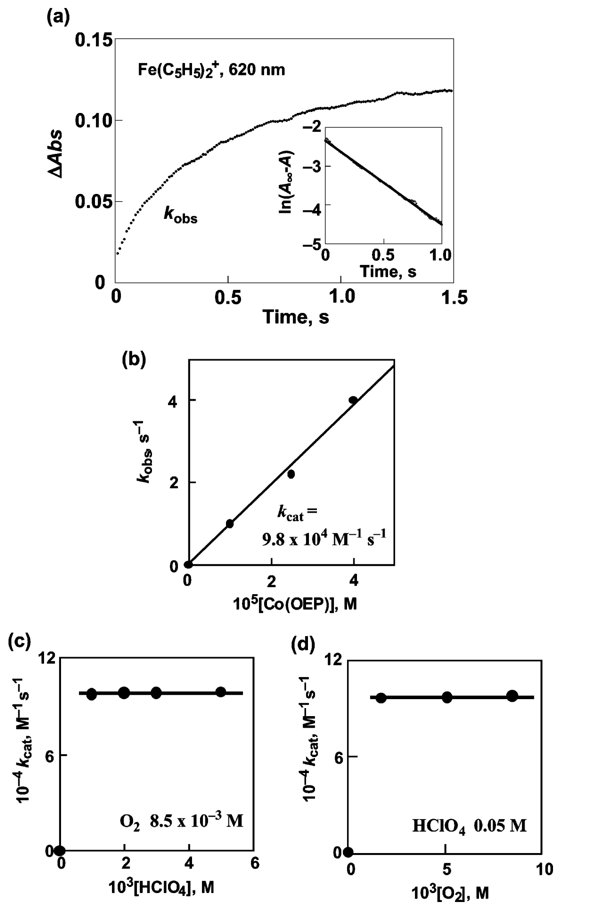


Figure 6. (a) Time profile of formation of $Fe(C_5H_5)_2^+$ monitored by absorbance at 620 nm (ϵ = 330 M^{-1} cm^{-1}) in electron-transfer oxidation of $Fe(C_5H_5)_2$ (3.0×10^{-4} M) by O_2 (8.5×10^{-3} M), catalyzed by Co(OEP) (2.5×10^{-5} M) in the presence of 0.05 M $HClO_4$ in PhCN at 298 K. Inset: First-order plots. (b) Plot of k_{obs} vs [Co(OEP)]. (c) Plot of k_{cat} vs [$HClO_4$] in the presence of 8.5×10^{-3} M O_2. (d) Plot of k_{cat} vs [O_2] in the presence of 0.05 M $HClO_4$.

Catalytic Mechanism of Four-Electron Reduction of O_2. Monomeric cobalt porphyrin catalyzes only two-electron reduction of O_2 by ferrocene derivatives (eq 1) and a cofacial dicobalt porphyrin is required for the four-electron reduction of O_2 by ferrocene derivatives (eq 2). Thus, the interaction of two cobalt nuclei with an active form of oxygen seems essential for the

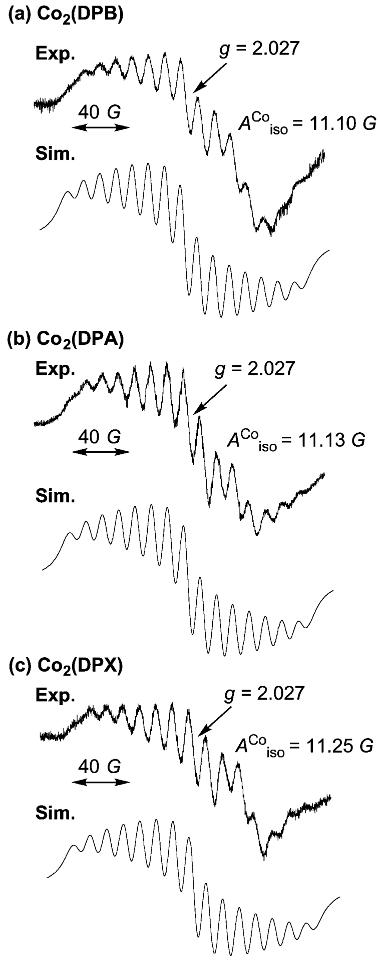


Figure 7. ESR spectra of the μ-superoxo complex ($\sim 10^{-3}$ M) produced by adding iodine ($\sim 10^{-3}$ M) to an air-saturated PhCN solution and ESR simulation of (a) Co_2(DPB), (b) Co_2(DPA), and (c) Co_2(DPX) in the presence of 1-*tert*-butyl-5-phenylimidazole (5×10^{-3} M) at 298 K.

four-electron reduction of O_2. In fact, 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 (see Experimental Section).[37] The superhyperfine structure due to two equivalent cobalt nuclei is observed at room temperature in the ESR spectra of the μ-superoxo species as shown in Figure 7.[44] The superhyperfine coupling constant of the μ-superoxo species of Co_2(DPX) determined from the computer simulation (Figure 7) is the largest among those of cofacial dicobalt porphyrins. This suggests that the efficient catalysis of Co_2(DPX) for the four-electron reduction of O_2 by $Fe(C_5H_4Me)_2$ (Figure 1b) results from the strong binding of the reduced oxygen with Co_2(DPX) which may have the most suitable distance between two cobalt nuclei for the oxygen binding.[45]

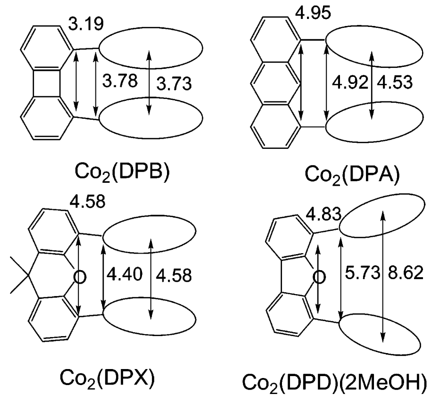


Figure 8. Selected distance (Å) in Co_2(DPB),[22a] Co_2(DPA),[46] Co_2(DPX),[23b,47] and Co_2(DPD)(2MeOH).[23b,47]

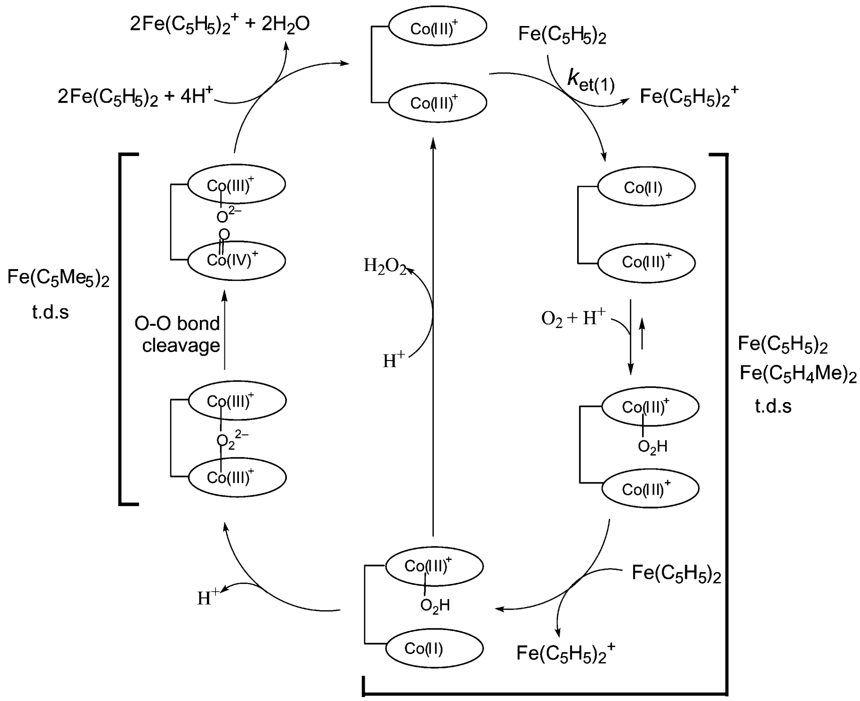
The reported crystal structures of Co_2(DPB),[22a] Co_2(DPA),[46] Co_2(DPX),[23b,47] and Co_2(DPD)(2MeOH)[23b,47] indicate that the lengths between cofacial porphyrins are quite different depending on the spacer as shown in Figure 8. The metal−metal separations in Co_2(DPA) (4.53 Å) and Co_2(DPX) (4.58 Å) are virtually the same. Flexibility by itself would not favor stronger binding; it may accommodate a shorter Co−Co distance that favors O_2 binding. The metal−metal separation in Co_2(DPB) (3.73 Å) may be too short, whereas the separation in Co_2(DPD)-(2MeOH) (8.62 Å) is too long to achieve efficient four-electron reduction of O_2 by ferrocene derivatives. The metal−metal separation in Zn_2(DPD) is also too long (7.78 Å).[47,48] However, the definitive structures of the μ-superoxo species of cofacial dicobalt porphyrins in solution have yet to be determined.

This suitable metal−metal separation may be the reason Co_2(DPX), which has the largest superhyperfine coupling constant of the μ-superoxo species (Figure 7), acts as the most efficient catalyst for the selective four-electron reduction of O_2 by ferrocene derivatives (Figure 2,3).

The proposed mechanism of four-electron reduction of O_2 by ferrocene derivatives is summarized as shown in Scheme 3 by combining with the mechanism of the two-electron reduction of O_2 in Scheme 2. The initial two-electron reduction of the $Co(III)_2$ complex by ferrocene derivatives gives the $Co(II)_2$ complex, which reacts with O_2 to produce the μ-peroxo 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 Co(IV)oxo species which is reduced by ferrocene derivatives in the presence of proton to yield H_2O (Scheme 3).[49] Alternatively the homolytic O−O bond cleavage affords two Co(III)-oxyl species which are reduced by ferrocene derivatives to H_2O in the presence of proton. The critical point to distinguish between the two-electron and four- electron reduction pathways is the competition between the O−O bond cleavage and the protonation of the Co(III)−O_2−Co(III) complex. The O−O bond cleavage of the Co(III)−O_2−Co(III) complex leads to the four-electron reduction of O_2, whereas the protonation leads to

(43) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1111. (c) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.
(44) The ESR spectra of μ-superoxo species in the case of Co_2(DPD) and Co(OEP) was not observed at room temperature due to less stability as compared with those in the case of Co_2(DPB), Co_2(DPA), and Co_2(DPX). Without a bulky base (1-*tert*-butyl-5-phenylimidazole), the μ-superoxo species could not be detected either. This indicates that the detected μ-superoxo species are formed by the intramolecular binding of O_2 between the two cobalt atoms of cofacial dicobalt porphyrins with an appropriate cobalt−cobalt separation.
(45) However, it should be noted that the thermodynamic stability is not necessarily related directly with the kinetic reactivity.
(46) Bolze, F.; Gros, C. P.; Drouin, M.; Espinosa, E.; Harvey, P. D.; Guilard, R. *J. Organomet. Chem.* **2002**, *643*−*644*, 89.
(47) Chang, C. J.; Baker, E. A.; Pistorio, B. J.; Deng, Y.; Loh, Z.-H.; Miller, S. E.; Carpenter, S. D.; Nocera, D. G. *Inorg. Chem.* **2002**, *41*, 3102.
(48) The flexibility of the DPD spacer allows us to shorten the metal−metal separation, resulting in forming the μ-oxo species; see ref 47.
(49) Although the formation of the Co(III)−Co(IV) intermediate is energetically uphill, the followup rapid electron transfer from ferrocene derivatives makes the process energetically feasible. Formation of a high-valent cobalt-oxo complex has been suggested. See: Nam, W.; Kim, I.; Kim, Y.; Kim, C. *Chem. Commun.* **2001**, 1296.

Scheme 3



the two-electron reduction of O_2 to produce H_2O_2 which is not reduced further under the present experimental conditions (Scheme 3).

The rate of formation of $Fe(C_5H_5)_2^+$ in Co_2(DPX)-catalyzed electron-transfer oxidation of $Fe(C_5H_5)_2$ by O_2 (8.5×10^{-3} M) 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) (Figure 9b). The k_{cat} values increase linearly with increasing concentrations of $HClO_4$ and O_2 as shown in Figure 9c and d, respectively. 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 6 where the k_{cat} values remain constant irrespective of $HClO_4$ or O_2 concentration. The k_{cat} values of the Co_2(DPX)-catalyzed four-electron reduction of O_2 by $Fe(C_5H_4Me)_2$ also increase linearly with increasing concentrations of $HClO_4$ and O_2. This indicates that the proton-coupled electron transfer from Co(III)Co(II)(DPX)$^+$, which is produced in the initial electron transfer from $Fe(C_5H_5)_2$ and $Fe(C_5H_4Me)_2$ 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 3.

When $Fe(C_5H_5)_2$ is replaced by a much stronger reductant than $Fe(C_5H_5)_2$ or $Fe(C_5H_4Me)_2$, 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 $Fe(C_5H_5)_2$ (Figure 6a) to zero-order kinetics as shown in Figure 10a, where the rate remains constant irrespective of concentration of $Fe(C_5Me_5)_2$. Furthermore the zero-order rate constant in the case of $Fe(C_5Me_5)_2$ remains constant with variation of concentrations of $HClO_4$ and O_2 as shown in Figure 10c and d, respectively. In contrast, the k_{cat} values in the case of $Fe(C_5H_5)_2$ increase linearly with increasing concentrations of $HClO_4$ and O_2 (Figure 9b and c, respectively). 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 $Fe(C_5H_5)_2$ or $Fe(C_5H_4Me)_2$

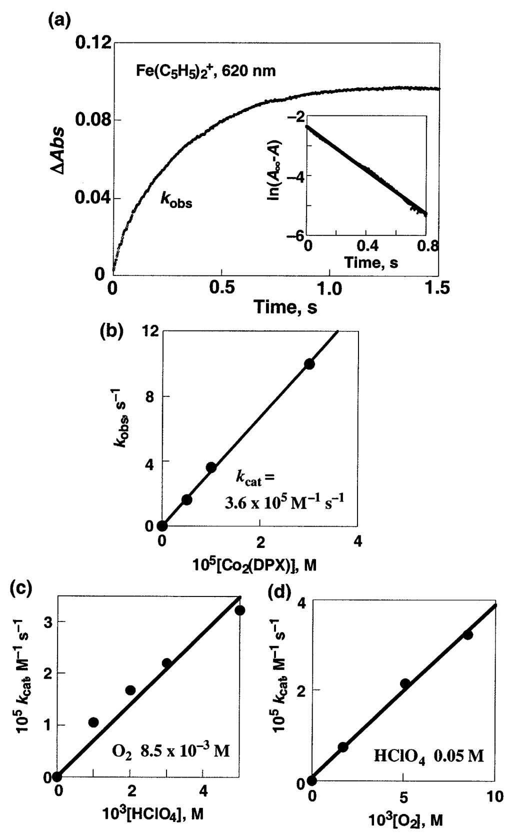


Figure 9. (a) Time profile of formation of $Fe(C_5H_5)_2^+$ monitored by absorbance at 620 nm ($\epsilon = 330$ M^{-1} cm^{-1}) in electron-transfer oxidation of $Fe(C_5H_5)_2$ (3.0×10^{-4} M) by catalytic dioxygen (8.5×10^{-3} M) reduction, catalyzed by Co_2(DPX) (1.0×10^{-5} M) in the presence of 0.05 M $HClO_4$ in PhCN at 298 K. Inset: First-order plots. (b) Plot of k_{obs} vs [Co_2(DPX)]. (c) Plot of k_{cat} vs [$HClO_4$] in the presence of 8.5×10^{-3} M O_2. (d) Plot of k_{cat} vs [O_2] in the presence of 0.05 M $HClO_4$.

to the reaction step which has nothing to do with $Fe(C_5Me_5)_2$, $HClO_4$, or O_2. Such a process which does not involve any intermolecular electron transfer step is most likely to be O−O

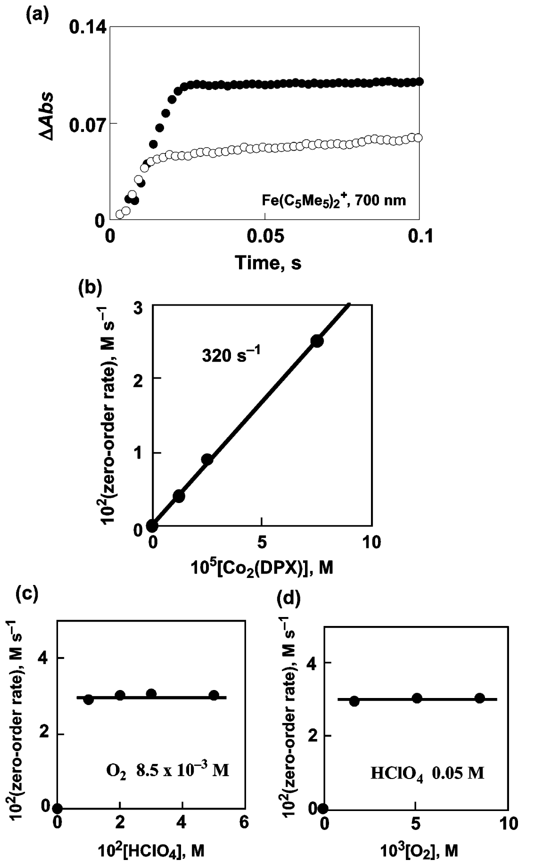


Figure 10. (a) Time profiles of formation of $Fe(C_5Me_5)_2^+$ monitored by absorbance at 700 nm ($\epsilon = 240$ M^{-1} cm^{-1}) in electron-transfer oxidation of $Fe(C_5Me_5)_2$ [2.5×10^{-4} M (○), 4.0×10^{-4} M (●)] by O_2 (8.5×10^{-3} M), catalyzed by Co_2(DPX) (8.0×10^{-5} M) in the presence of 0.05 M $HClO_4$ in PhCN at 298 K. (b) Plot of the zero-order rate constant vs [Co_2(DPX)]. (c) Plot of the zero-order rate vs [$HClO_4$] in the presence of 8.5×10^{-3} M O_2. (d) Plot of the zero-order rate vs [O_2] in the presence of 0.05 M $HClO_4$.

bond cleavage of the Co(III)−O_2−Co(III) complex in Scheme 3. The O−O bond cleavage rate has been determined as 320 s^{-1} from the slope in Figure 10b.

Summary and Conclusions

The present study has demonstrated that the O−O bond cleavage of the Co(III)−O_2−Co(III) complex plays a critical role for the four-electron reduction of O_2 by strong one-electron reductants ($Fe(C_5Me_5)_2$). No such a pathway is available for the monomeric cobalt(III) porphyrin which catalyzes only the two-electron reduction of O_2 (Figure 1a). In the case of iron porphyrins, however, monomeric iron porphyrins act efficiently in the electrochemical four-electron reduction of O_2.[18−20] This indicates that the formation of μ-peroxo derivative (Fe−O_2−Fe) is not necessary for the four-electron reduction of O_2 in contrast to the case of cobalt porphyrins demonstrated herein. In the case of iron porphyrins, the heterolytic O−O bond cleavage of the hydroperoxo species (Fe−OOH), in which the proton acts as an acid instead of a metal Lewis acid in Fe−O_2−Fe, may be essential for the four-electron reduction of O_2 as the case of the Co−O_2−Co complex in which two Co(III) nuclei act as Lewis acids to bind O_2. Even though its catalytic site is bimetallic, the four-electron reduction of O_2 by cytochrome *c* oxidase has been indicated to proceed via intermediates that are similar, with respect to the binding modes of O_2, to those observed in monometallic heme enzymes such as oxygenases, peroxidases, and catalases.[50−53] However, the actual role of ferric hydroperoxo species for the four-electron reduction of O_2 has yet to be clarified.

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