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Metalloporphyrin-Catalyzed Reduction of Dioxygen by Ferrocene Derivatives

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Metalloporphyrin-catalyzed reduction of dioxygen by ferrocene derivatives occurs efficiently *via* outer-sphere electron transfer from ferrocene derivatives to metalloporphyrins ($MTPP^+$), followed by acid-catalyzed reduction of dioxygen by MTPP in the presence of perchloric acid in acetonitrile.

Metalloporphyrin-catalyzed reduction of dioxygen has been extensively studied in the electrochemical systems,1) and four-electron reduction of dioxygen to water has been achieved by using various dimeric metalloporphyrins2) as well as monomeric indium porphyrins.3) However, little is known of catalytic four-electron reduction of dioxygen by mild chemical reductants. We wish to report herein an efficient electron-transfer catalytic system for two-electron and four-electron reduction of dioxygen by ferrocene derivatives (Fc) in the presence of perchloric acid ($HClO_4$) in acetonitrile (MeCN) at 298 K. The catalytic mechanism will be elucidated by the kinetic study on the catalytic reactions as well as on the elementary reactions; the reduction of metalloporphyrins by Fc and the oxidation of the reduced metalloporphyrins by dioxygen in the presence of $HClO_4$ in MeCN, using the Marcus theory of electron transfer.4)

No oxidation of Fc (ferrocene $[Fe(C_5H_5)_2]$ and 1,1'-dimethylferrocene $[Fe(C_5H_4Me)_2]$), has occurred in MeCN at 298 K, although the much stronger reductant, decamethylferrocene $[Fe(C_5Me_5)_2]$, was gradually oxidized by dioxygen. The addition of $HClO_4$ to the Fc-O_2 system results in the sluggish oxidation of Fc to yield the corresponding ferricenium ion (Fc^+).5) The rates of oxidation of Fc by dioxygen in the presence of $HClO_4$ were enhanced significantly by the addition of catalytic amounts of metalloporphyrins ($MTPPClO_4$: M = Co, Fe, Mn; TPP = tetraphenylporphyrin). The stoichiometry of the $MTPP^+$-catalyzed reduction of dioxygen by Fc was determined from the spectral titration in Fig. 1, which shows that four equivalent $[Fe(C_5H_4Me)_2]$ and $HClO_4$ are consumed in the reduction of dioxygen to yield four-equivalent $[Fe(C_5H_4Me)_2]^+$, Eq. 1. When the $CoTPP^+$-catalyzed four-electron reduction of dioxygen by an excess amount of $[Fe(C_5H_4Me)_2]$ was monitored by the increase in absrobance due to $[Fe(C_5H_4Me)_2]^+$, the formation of $[Fe(C_5H_4Me)_2]^+$ was separated in two steps; the first step corresponds to the initial

$$4[Fe(C_5H_4Me)_2] + O_2 + 4H^+ \xrightarrow[MTPP^+]{} 4[Fe(C_5H_4Me)_2]^+ + 2H_2O \qquad (1)$$

two-electron reduction of dioxygen by $[Fe(C_5H_4Me)_2]$ to yield $[Fe(C_5H_4Me)_2]^+$ and H_2O_2, which was followed by the further reduction of H_2O_2 by $[Fe(C_5H_4Me)_2]$ with a 10^2-fold slower rate than the first step. Thus, the catalytic oxidation of Fc with an excess amount of dioxygen may result only in the two-electron reduction of dioxygen to H_2O_2 and no further reduction of H_2O_2 to H_2O has occurred.

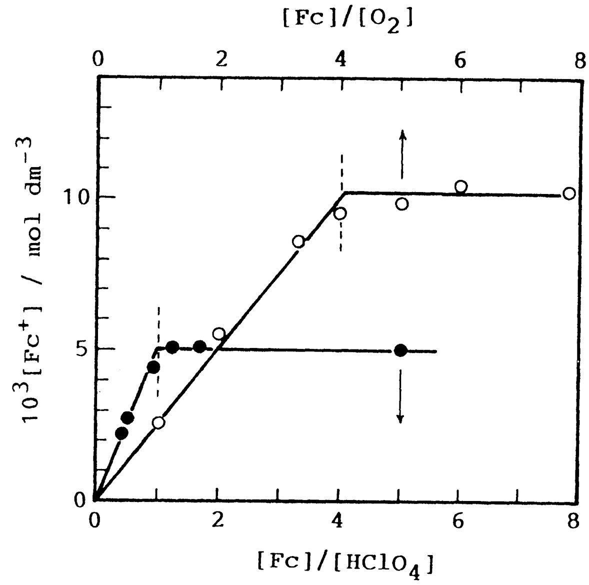


Fig. 1. Plots of the concentration of $[Fe(C_5H_4Me)_2]^+$ formed in the $CoTPP^+$-catalyzed oxidation of $[Fe(C_5H_4Me)_2]$ by dioxygen in the presence of $HClO_4$ in MeCN vs. the ratio of $[Fe(C_5H_4Me)_2]$ to $[O_2]$ (○); $[O_2] = 2.6 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 5.0 \times 10^{-2}$ mol dm^{-3}, and vs. the ratio of $[Fe(C_5H_4Me)_2]$ to $[HClO_4]$ (●); $[O_2] = 1.3 \times 10^{-2}$ mol dm^{-3}, $[HClO_4] = 5.0 \times 10^{-3}$ mol dm^{-3}.

Rates of oxidation of ferrocene derivatives by excess dioxygen, catalyzed by $MTPPClO_4$ (M = Co, Fe, Mn) in the presence of $HClO_4$ were determined by the increase in the absorbance due to Fc^+ in the long-wavelength region (600-700 nm).[6] The rate was expressed by second-order kinetics, showing first-order dependence on the concentrations of Fc and the catalyst $MTPP^+$, Eq. 2.

$$d[Fc^+]/dt = k_{obsd}[Fc][MTPP^+] \qquad (2)$$

The observed second-order rate constant k_{obsd} remained constant with the change in the dioxygen or $HClO_4$ concentration. The k_{obsd} values are listed in Table 1, together with the one-electron reduction potential (E^0_{red}) of $MTPP^+$ and the one-electron oxidation potentials (E^0_{ox}) of ferrocene derivatives, determined by the cyclic voltammograms in MeCN.

Electron transfer from Fc to $CoTPP^+$ is exothermic based on the redox potentials (Table 1), and thus the electron transfer occurs readily in the absence of dioxygen to yield Fc^+ and CoTPP, Eq. 3. The rates of electron transfer also

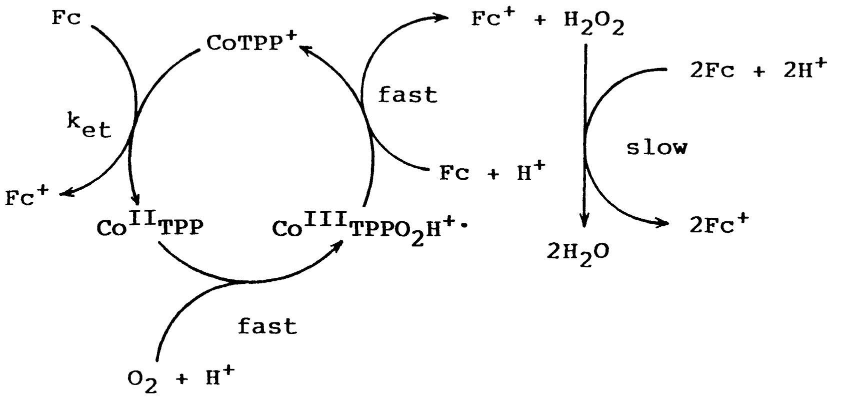
$$\mathbf{Fc + CoTPP^+ \xrightarrow{k_{et}} Fc^+ + CoTPP} \qquad (3)$$

obeyed the second-order kinetics (Eq. 2), and the k_{obsd} values in the absence of dioxygen are also listed in Table 1 (the values in parentheses). The k_{obsd} values for the $CoTPP^+$-catalyzed oxidation of Fc by dioxygen in the presence of $HClO_4$ are approximately 2-fold larger than those for the electron transfer from Fc to $CoTPP^+$ in the absence of dioxygen (Table 1). Such a 2-fold difference indicates that the catalytic oxidation of Fc by dioxygen proceeds via the rate-determining electron transfer from Fc to $CoTPP^+$, followed by the facile oxidation of $Co^{II}TPP$ by dioxygen in the presence of $HClO_4$ to give $Co^{III}TPPO_2H^{+\cdot}$ and the subsequent reduction of $Co^{III}TPPO_2H^{+\cdot}$ by Fc to yield Fc^+ and H_2O_2, accompanied by regeneration of $CoTPP^+$ (Scheme 1). In fact, the electronic spectrum of $CoTPP^+$ remained unchanged during

Table 1. Observed Second-Order Rate Constants (k_{obsd}) for $MTPP^+$-Catalyzed Oxidation of Ferrocene Derivatives (Fc) by Dioxygen in the Presence of $HClO_4$ and k_{obsd} for Electron Transfer from Fc to $CoTPP^+$ in MeCN at 298 K, One-Electron Reduction Potentials (E^0_{red} vs. SCE) of $MTPP^+$ and One-Electron Oxidation Potentials (E^0_{ox} vs. SCE) of Ferrocene Derivatives, and the Calculated Electron Transfer Rate Constants Based on the Marcus Theory

$MTPP^+$	E^0_{red} / V	Fc	E^0_{ox} / V	k_{obsd}[a] / $dm^3\ mol^{-1}\ s^{-1}$	k_{calcd}[b] / $dm^3\ mol^{-1}\ s^{-1}$
$CoTPP^+$	0.35	$[Fe(C_5H_5)_2]$	0.37	4.2×10^4	1×10^4
				(2.1×10^4)	
		$[Fe(C_5H_4Me)_2]$	0.26	1.0×10^5	1×10^5
				(4.6×10^4)	
		$[Fe(C_5Me_5)_2]$	-0.08	1.1×10^6	3×10^7
				(6.0×10^5)	
$FeTPP^+$	0.14	$[Fe(C_5H_5)_2]$	0.37	2.9×10^6	1×10^6
		$[Fe(C_5H_4Me)_2]$	0.26	1.2×10^7	1×10^7
$MnTPP^+$	-0.15	$[Fe(C_5H_4Me)_2]$	0.26	2.6×10^2	3×10
		$[Fe(C_5Me_5)_2]$	-0.08	1.4×10^5	1×10^5

[a] The values in parentheses are the k_{obsd} values of electron transfer from Fc to $CoTPP^+$ in the absence of dioxygen in MeCN at 298 K. [b] Calculated based on the Marcus theory (Ref. 4) of outer-sphere electron transfer, see text.



Scheme 1.

the catalytic oxidation of Fc by dioxygen in the presence of $HClO_4$ in MeCN. According to Scheme 1, the observed rate constant in the presence of dioxygen k_{obsd} should correspond to $2k_{et}$. The facile oxidation of CoTPP by dioxygen in the presence of $HClO_4$ was confirmed independently by measuring the rise and decay of the absorption bands due to CoTPP (λ_{max} 412 nm) or $CoTPP^+$ (λ_{max} 434 nm), respectively. The second-order rate constant was determined as $1.0 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$ in the presence of $HClO_4$ ($3.0 \times 10^{-4}\ mol\ dm^{-3}$), and the value increased linearly with an increase in the $HClO_4$ concentration.[7]

The reported values of self-exchange rate constants for ferrocene derivatives

(5.3×10^6 dm^3 mol^{-1} s^{-1})[8] and metalloporphyrins (20, 1×10^9, and 3.2×10^3, for Co,[9] Fe,[10] and Mn,[11] respectively) together with the one-electron redox potentials in Table 1 constitute a satisfactory basis for accounting for the experimental kinetic data when considered in light of the Marcus theory of outer-sphere electron transfer.[4,12] The calculated values ($k_{calcd} = 2k_{et}$) are also listed in Table 1, where the observed rate constants k_{obsd} agree with the calculated values within ± 1 in the logarithm unit, except for the $[Fe(C_5Me_5)_2]$-$CoTPP^+$ system.[13] Taking account for uncertainties in the estimates of the self-exchange rates, the agreement between the observed and calculated rate constants demonstrates that the electron transfer from Fc to $MTPP^+$ in Scheme 1 proceeds by an outer-sphere mechanism.

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7) Under the experimental conditions to determine the k_{obsd} values for the $CoTPP^+$-catalyzed oxidation of Fc, the rate of electron transfer from Fc to $CoTPP^+$ is much slower than the rate of oxidation of CoTPP by dioxygen in the presence of $HClO_4$ ($> 1 \times 10^{-2}$ mol dm^{-3}).

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12) The k_{calcd} ($= 2k_{et}$) value was calculated by the relation, $k_{et} = (k_{11}k_{22}K_{12}f)^{1/2}$ and $\log f = (\log K_{12})^2/[4\log(k_{11}k_{22}/Z^2)]$, where k_{11} and k_{22} are the self-exchange rate constants of Fc and $MTPP^+$ (Refs. 8-11), K_{12} is the equilibrium constant of electron transfer, which is obtained from E^0_{ox} and E^0_{red} values in Table 1 by using the relation, $\log K_{12} = (-2.3RT/F)(E^0_{ox} - E^0_{red})$, and Z is the frequency factor, taken as 1×10^{11} dm^3 mol^{-1} s^{-1} (Ref. 4). The work terms were neglected since the reactants and products include neutral species.

13) The smaller k_{obsd} value than the k_{calcd} value may be suggestive of nonadiabatic behavior of the system, see: R. M. Nielson, M. N. Golovin, G. E. McManis, and M. J. Weaver, J. Am. Chem. Soc., 110, 1745 (1988).

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