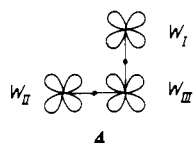


Figure 8. Dispersion relations of the bottom portion of the t_{2g} -block bands calculated for the $W_{12}O_{48}$ lattice of $P_8W_{12}O_{52}$, where the dashed lines refers to the Fermi level, $\Gamma = (0, 0, 0)$, $X = (a^*/2, 0, 0)$, $Y = (0, b^*/2, 0)$, and $Z = (0, 0, c^*/2)$.

substantial dispersions in all three directions. Since the $W_{12}O_{48}$ lattice has two W_6O_{28} chains per unit cell, there are eight d electrons to fill the bands of Figure 8. Consequently, the π -type bands are cut by the Fermi level in all three directions, and $P_8W_{12}O_{52}$ is a 3D metal. It is of interest to examine why the π -type bands show dispersion in all three directions. As shown in Figure 1 and diagram 2, the $W_{III}O_6$ octahedra of one W_6O_{28} chain are linked to the $W_{II}O_6$ octahedra of the neighboring W_6O_{28} chain. Therefore, the π -type orbitals of an $W_{III}O_6$ octahedron provide π -type interactions not only within a W_6O_{28} chain but also between W_6O_{28} chains, as schematically depicted in 4. This



interchain interaction is effective in the low-lying π -type bands of $P_8W_{12}O_{52}$. A $W_{III}O_6$ octahedron of one W_6O_{28} chain is linked in a tilted manner (due to the diphosphate ions) to a $W_{II}O_6$ octahedron of the neighboring W_6O_{28} chain, which leads to a better interaction between the $W_{II}O_6$ and $W_{III}O_6$ octahedra. In addition, the π -type d-block levels of each $W_{III}O_6$ octahedron are somewhat lowered in energy by sharing their two oxygen atoms with the $W_{II}O_6$ octahedron of the neighboring W_6O_{28} chain. This also leads

to a greater participation of the $W_{III}O_6$ character in the low-lying π -type bands of the $W_{12}O_{48}$ lattice. The pseudo-1D bronze $CsP_8W_8O_{40}$ was found to lose its metallic character when more than 3% of W was replaced by Mo.⁹ In contrast, $P_8W_{12}O_{52}$ remains a 3D metal even when 5% of W is replaced by Mo. This is understandable since the $W_{12}O_{48}$ lattice has a 3D connectivity of WO_6 octahedra via the $W_{III}O_6$ octahedra.

According to Figure 8, $P_8W_{12}O_{52}$ will behave like a 1D metal if more electrons are added to its lattice so that the Fermi level lies above the top of the π bands. Our calculations show that this change requires more than four electrons per formula unit $P_8W_{12}O_{52}$. This explains why all the $A_xP_8W_{12}O_{52}$ ($A = Li, Na; x < 1$) bronzes are 3D metals. One might consider the possibility of preparing $Li_xP_8W_{12}O_{52}$ ($x > 4$) to see if it becomes a 1D metal, provided that the pentagonal and hexagonal channels of $P_8W_{12}O_{52}$ can accommodate enough Li atoms.

Concluding Remarks

In summary, we prepared $P_8W_{12}O_{52}$ and its substituted analogues and measured their physical properties. All those bronzes are 3D metals and hence show no resistivity anomalies. Our tight-binding band electronic structure calculations show that this 3D metallic character arises from two factors: (a) The lattice of the $P_8W_{12}O_{52}$ has a 3D connection of WO_6 octahedra, and (b) $P_8W_{12}O_{52}$ has a small number of d electrons so that its 3D bands, occurring near the bottom of the t_{2g} -block bands, become partially filled. Our calculations predict that $A_xP_8W_{12}O_{52}$ ($A = \text{alkali metal}$) would remain a 3D metal unless $x > 4$. Finally, the close relationship between $P_8W_{12}O_{52}$ and $CsP_8W_8O_{40}$ structures was demonstrated by the intergrowth of these two bronzes and the phase transition from $P_8W_{12}O_{52}$ to $CsP_8W_8O_{40}$. Investigation of the phase transition led to a new synthetic route for the preparation of single crystals of Rb and Tl analogues of $CsP_8W_8O_{40}$.

Acknowledgment. Work at Rutgers University was supported in part by the Office of Naval Research, the National Science Foundation-Solid State Chemistry Grants DMR-84-04003 and DMR-87-14072, and the National Science Foundation Materials Research Instrumentation Grants DMR-84-08266 and DMR-87-05620. Work at the Universite de Paris-Sud and North Carolina State University was supported by NATO, Scientific Affairs Division, and also by DOE, Office of Basic Sciences, Division of Materials Science, under Grant DE-FG05-86ER45259.

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Efficient Reduction of Dioxygen with Ferrocene Derivatives, Catalyzed by Metalloporphyrins in the Presence of Perchloric Acid

Shunichi Fukuzumi,^{*,1a} Seiji Mochizuki, and Toshio Tanaka^{1b}

Received November 28, 1988

Reduction of dioxygen with ferrocene derivatives (Fc) is catalyzed by metalloporphyrins (MTPP⁺: M = Co, Fe, Mn; TPP⁺ = tetraphenylporphyrin) or Co(TIM)³⁺ (TIM: a tetraaza macrocyclic ligand) in the presence of HClO₄ in acetonitrile (MeCN). Electron transfer from Fc to MTPP⁺ is the rate-determining step for the MTPP⁺-catalyzed oxidation of Fc by dioxygen, when the rate is independent of the concentration of dioxygen or HClO₄. On the other hand, the rate of electron transfer from Fc to Co(TIM)³⁺ is accelerated by the presence of HClO₄ and dioxygen. The rates of these electron-transfer reactions are discussed in light of the Marcus theory of electron transfer to distinguish between outer-sphere and inner-sphere electron-transfer processes. The strong inner-sphere nature of metalloporphyrins in the electron-transfer reactions with dioxygen in the presence of HClO₄ plays an essential role in the catalytic reduction of dioxygen.

Metalloporphyrin-catalyzed reduction of dioxygen has been extensively studied in the electrochemical system in conjunction

with the search for an inexpensive cathode material for a dioxygen fuel cell,^{2,3} and four-electron reduction of dioxygen to water has

been achieved by using various dimeric metalloporphyrins⁴ as well as monomeric indium porphyrins.⁵ However, very little is known of efficient catalytic reduction of dioxygen by appropriate chemical reductants.

We report herein efficient electron-transfer systems for the two-electron and four-electron reduction of dioxygen by ferrocene derivatives using metalloporphyrins or Co(TIM)³⁺ (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) as catalysts in the presence of perchloric acid (HClO₄) in acetonitrile (MeCN).⁶ Mechanisms of the catalytic reduction of dioxygen by ferrocene derivatives in the presence of HClO₄ are discussed on the basis of detailed kinetic studies on the overall catalytic reactions as well as on each redox reaction in the catalytic cycle: the reduction of CoTPP⁺ by ferrocene derivatives and the oxidation of CoTPP by dioxygen in the presence of HClO₄ in MeCN.

Experimental Section

Materials. (Tetraphenylporphinato)iron(III) chloride (FeTPPCL) and (tetraphenylporphinato)manganese(III) chloride (MnTPPCL) were synthesized and purified according to the literature.⁷ Cobalt(II) tetraphenylporphyrin (CoTPP) was prepared as given in the literature.⁸ CoTPP was oxidized by dioxygen in the presence of HCl in methanol to obtain (tetraphenylporphinato)cobalt(III) chloride (CoTPPCL),⁹ which was purified by recrystallization from methanol. The perchlorate salts of FeTPP⁺, MnTPP⁺, and CoTPP⁺ were obtained by the metathesis of the corresponding chloride salts with AgClO₄ and recrystallized from toluene.¹⁰ The macrocyclic ligand TIM (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) and the cobalt(III) complex, (H₂O)Co(TIM)(ClO₄)₃, were prepared according to the procedures described in the literature.¹¹ The purity of the metal complexes was checked by the elementary analyses, which gave satisfactory results. Ferrocene, 1,1'-dimethylferrocene, *n*-butylferrocene, and decamethylferrocene were obtained commercially and purified by sublimation or recrystallization from ethanol. The corresponding ferrocenium ions were prepared by the oxidation of ferrocene derivatives by *p*-benzoquinone in the presence of HClO₄ in MeCN.¹² Perchloric acid

(70%) was obtained from Wako Pure Chemicals. Reagent grade acetonitrile was purified by successive distillation (four times) over P₂O₅ before use.

Spectral Measurements. Electronic absorption spectra were recorded by using a Union SM-401 spectrophotometer with a quartz cell (1-mm or 1-cm i.d.), which was placed in a thermostated compartment at 298 K. The stoichiometry of the catalytic reduction of dioxygen by ferrocene derivatives in the presence of CoTPP⁺ and HClO₄ in MeCN was determined by measuring the absorbances due to the ferrocenium ions with various initial concentrations of ferrocene derivatives and a fixed concentration of dioxygen. It was confirmed that the reaction was completed, since further addition of a catalyst resulted in no further oxidation of the reductant.

The concentration of dioxygen in air-saturated MeCN containing the same concentration of HClO₄ as employed in determining the stoichiometry of the catalytic reduction of dioxygen was determined as 2.6×10^{-3} M from the photooxidation of 10-methylacridin (AcrH₂) by dioxygen in the presence of HClO₄ in MeCN as follows. The photooxidation of AcrH₂ by dioxygen in the presence of an excess amount of HClO₄ is known to yield the equivalent amount of 10-methylacridinium ion (AcrH⁺) relative to dioxygen.¹³ The quartz cell (1-mm i.d.) that was filled with an MeCN solution (6 cm³) containing excess amounts of AcrH₂ and HClO₄ relative to dioxygen was irradiated by using a monochromatized light $\lambda = 300$ nm. After completion of the photooxidation, the concentration of AcrH⁺ was determined by measuring the absorbance at 400 nm due to AcrH⁺ ($\epsilon = 4.0 \times 10^3$ M⁻¹ cm⁻¹). The dioxygen concentration in air-saturated MeCN determined in this manner was in good agreement with those in solvents such as alkanes, acetone, alcohol, and carbon tetrachloride.¹⁴

Kinetic Measurements. Acetonitrile solutions containing various concentrations of dioxygen were prepared by saturating the MeCN solution with a stream of mixture gas (dioxygen and nitrogen) of various partial pressures of dioxygen. The various partial pressures of dioxygen were attained by controlling the flow rates of dioxygen and nitrogen with gas regulators. Kinetic measurements for the fast reactions with half-lives < 10 s were performed by using a Union RA-103 stopped-flow spectrophotometer. Rates of the catalytic oxidation of ferrocene derivatives by dioxygen in the presence of a metalloporphyrin and HClO₄ in MeCN at 298 K were followed by the increase in absorbance due to the corresponding ferrocenium ions in the long-wavelength region (600–700 nm)¹⁵ by using the stopped-flow technique under 4 atm of dioxygen. The stopped-flow measurements were also employed for the oxidation of CoTPP by dioxygen in the presence of HClO₄ in MeCN at 298 K under 4 atm of dioxygen by monitoring the disappearance and rise of the absorption bands at 412 and 434 nm due to the decay of CoTPP and the formation of CoTPP⁺, respectively. When the stopped-flow measurements were carried out under deaerated conditions, deaerated MeCN solutions with a stream of argon were transferred by means of a glass syringe to spectrometer cells that were already purged with a stream of nitrogen. Rates of the oxidation of ferrocene derivatives by CoTPP⁺ in the absence of dioxygen were determined under 4 atm of nitrogen. Blank determinations without added oxidant indicated that the oxidation by dioxygen due to possible leaks did not interfere with this system. All the kinetic measurements were carried out under pseudo-first-order conditions where the concentrations of dioxygen and HClO₄ were maintained at >10-fold excess of the concentration of reductant, which was also maintained at >10-fold excess of the catalyst concentration whenever possible. Pseudo-first-order rate constants $k^{(1)}$ were determined by a least-squares curve fit by using a Union System 77 microcomputer. The pseudo-first-order plots were linear for 3 or more half-lives with the correlation coefficient $\rho > 0.999$. Second-order rate constants were calculated from the slope of $k^{(1)}$ vs the concentration of the catalyst or excess substrate by the least-squares analysis.

Cyclic Voltammetry. One-electron oxidation and reduction potentials of ferrocene derivatives, metalloporphyrins, and Co(TIM)³⁺ were determined by cyclic voltammetry, which was performed on a Hokuto Denko Model HA-301 potentiostat-galvanostat at 298 K in MeCN containing 0.10 M BuⁿNClO₄ as a supporting electrolyte using a saturated calomel electrode (SCE) as a reference under deaerated conditions. The platinum microelectrode used for the measurements in the absence of HClO₄ was routinely cleaned by soaking it in concentrated nitric acid,

- (1) (a) To whom correspondence should be addressed. (b) Current address: Department of Applied Physics and Chemistry, Fukui Institute of Technology, Fukui 910, Japan.
- (2) (a) Jahnke, H.; Schonborn, M.; Zimmerman, G. *Top. Curr. Chem.* **1976**, *61*, 133. (b) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 59. (c) Shigehara, K.; Anson, F. C. *J. Phys. Chem.* **1982**, *86*, 2776. (d) Forshey, P. A.; Kuwana, T.; Kobayashi, N.; Osa, T. *Adv. Chem. Ser.* **1982**, No. 201, 601. (e) Ozer, D.; Parash, R.; Broitman, F.; Mor, U.; Bettelheim, A. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1139. (f) Bettelheim, A.; White, B. A.; Raybuck, S. A.; Murray, R. W. *Inorg. Chem.* **1987**, *26*, 1009. (g) Bettelheim, A.; Ozer, D.; Parash, R. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1555.
- (3) (a) Gorton, L. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1245. (b) Albery, W. J.; Bartlett, P. N. *J. Chem. Soc., Chem. Commun.* **1984**, 234. (c) Jaegfeldt, H.; Kuwana, T.; Johansson, G. *J. Am. Chem. Soc.* **1983**, *105*, 1805. (d) Natsue, T.; Kato, T.; Akiba, U.; Osa, T. *Chem. Lett.* **1986**, 843. (e) Samec, Z.; Elving, P. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *144*, 217. (f) Degrand, C.; Miller, L. *J. Am. Chem. Soc.* **1980**, *102*, 5278.
- (4) (a) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027. (b) Durand, R. R.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *Ibid.* **1983**, *105*, 2710. (c) Liu, H. Y.; Weaver, M. J.; Wang, C.-B.; Chang, C. K. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *145*, 439. (d) Chang, C. K.; Liu, H. Y.; Abdalmuhdi, I. *J. Am. Chem. Soc.* **1984**, *106*, 2725. (e) Liu, H.-Y.; Abdalmuhdi, I.; Chang, C. K.; Anson, F. C. *J. Phys. Chem.* **1985**, *89*, 665. (f) Collman, J. P.; Hendricks, N. H.; Kim, K.; Bencosme, C. S. *J. Chem. Soc., Chem. Commun.* **1987**, 1537.
- (5) Collman, J. P.; Kim, K. *J. Am. Chem. Soc.* **1986**, *108*, 7847.
- (6) A preliminary report has appeared: Fukuzumi, S.; Mochizuki, S.; Tanaka, T. *Chem. Lett.* **1989**, 27.
- (7) (a) Aldler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443. (b) Fleischer, E. B.; Palmer, J. M.; Srivastava, T. S.; Chatterjee, A. *J. Am. Chem. Soc.* **1971**, *93*, 3162. (c) Jones, R. D.; Summerville, D. A.; Basolo, F. *Ibid.* **1978**, *100*, 4416.
- (8) (a) Shirazi, A.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 3420. (b) Aldler, A. D.; Longo, F. R.; Varadi, V. *Inorg. Synth.* **1976**, *16*, 213.
- (9) Sakurai, T.; Yamamoto, K.; Naito, H.; Nakamoto, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3042.
- (10) Reed, C. A.; Mashiko, T.; Bently, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.
- (11) Jackels, S. C.; Farmery, K.; Barefield, E. K.; Rose, N. J.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 2893.

- (12) Fukuzumi, S.; Ishikawa, K.; Hironaka, K.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1987**, 751.
- (13) Fukuzumi, S.; Tanaka, T. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, Chapter 10, pp 578–636.
- (14) Battino, R., Ed. *Solubility Data Series Oxygen and Ozone*; Pergamon Press: Oxford, England, 1981; Vol. 7.
- (15) Yang, E. S.; Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1975**, *79*, 2049.

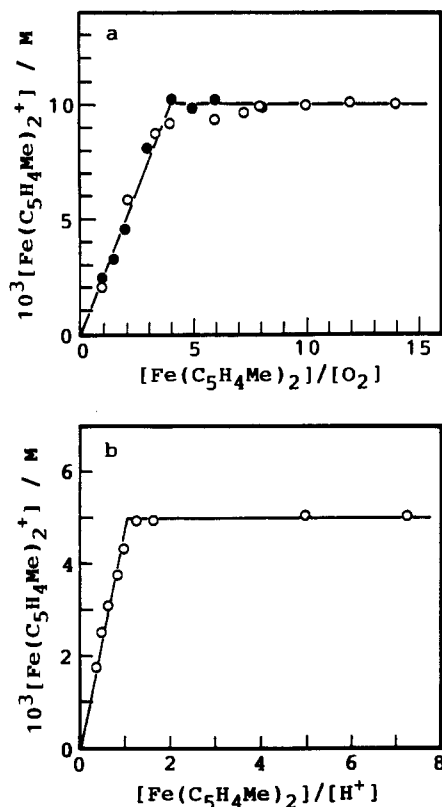
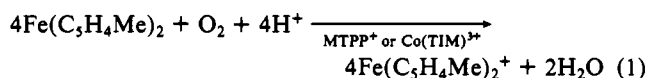


Figure 1. Plots of the concentration of $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2^+$ formed in the oxidation of $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ by dioxygen, catalyzed by $\text{Co}(\text{TIM})^{3+}$ (O) and CoTPP^+ (●), vs (a) the ratio of the $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ concentration to the initial concentration of dioxygen (2.6×10^{-3} M) ($[\text{HClO}_4] = 5.0 \times 10^{-2}$ M; $[\text{Co}(\text{TIM})^{3+}] = 2.4 \times 10^{-4}$ M; $[\text{CoTPP}^+] = 4.8 \times 10^{-5}$ M) and vs (b) the ratio of the $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ concentration to the initial concentration of HClO_4 (5.0×10^{-3} M) ($[\text{O}_2] = 1.3 \times 10^{-2}$ M; $[\text{Co}(\text{TIM})^{3+}] = 5.0 \times 10^{-4}$ M).

followed by repeating rinsing with water and acetone, and drying at 353 K prior to use. For the CV measurements in the presence of HClO_4 , a capillary dropping-mercury electrode was employed.

Results

Catalytic Reduction of Dioxygen by Ferrocene Derivatives. No oxidation of ferrocene or 1,1'-dimethylferrocene by dioxygen has been observed in MeCN at 298 K, although the much stronger reductant, decamethylferrocene, was gradually oxidized by dioxygen in MeCN at 298 K. The addition of HClO_4 to MeCN solutions of the ferrocene derivative in the presence of dioxygen is known to result in the oxidation of the ferrocene derivative to yield the corresponding ferrocenium ion.¹⁶ The rates of oxidation of ferrocene derivatives by dioxygen in the presence of HClO_4 in MeCN were enhanced significantly by the addition of catalytic amounts of metalloporphyrins (MTPP⁺: M = Co, Fe, Mn) or $\text{Co}(\text{TIM})^{3+}$. The stoichiometry of the catalytic reduction of dioxygen by 1,1'-dimethylferrocene ($\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$) using CoTPP^+ or $\text{Co}(\text{TIM})^{3+}$ as a catalyst is determined from the spectral titration. As shown in Figure 1, four molecules of $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ are consumed in the reduction of one molecule of dioxygen (Figure 1a) when the equivalent proton to $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ amount (Figure 1b) is consumed (eq 1).



A typical time course of the catalytic four-electron reduction of dioxygen by an excess amount of $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ in the presence of CoTPP^+ is shown in Figure 2. Upon the mixing of $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ and CoTPP^+ in the presence of HClO_4 in air-saturated

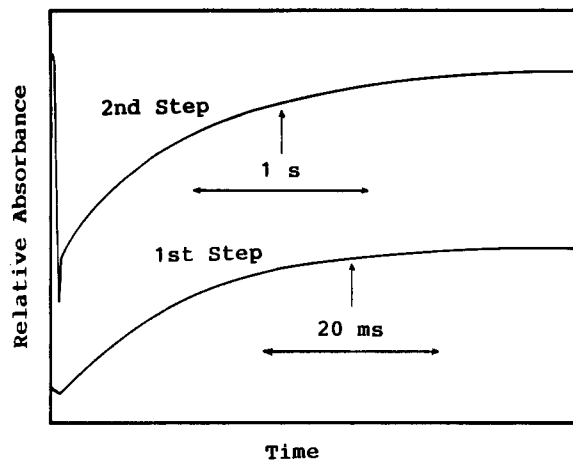


Figure 2. Kinetic curves for two-step oxidation of $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ (2.0×10^{-2} M) by dioxygen (2.6×10^{-3} M), catalyzed by CoTPP^+ (2.0×10^{-4} M) in the presence of HClO_4 (2.0×10^{-2} M) in MeCN, followed by the increase in absorbance at 690 nm due to $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2^+$.

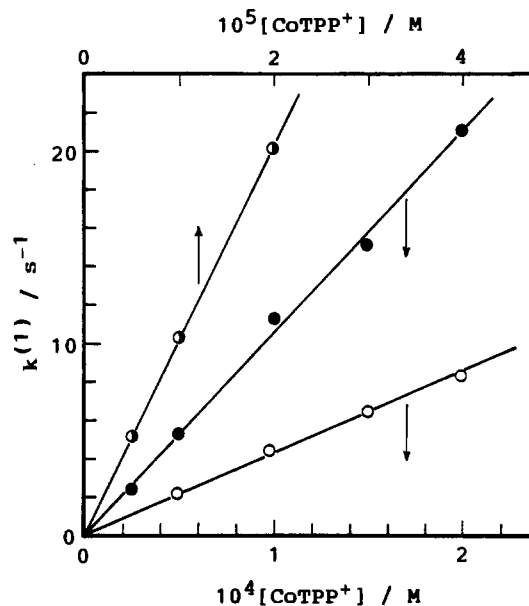
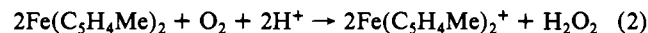
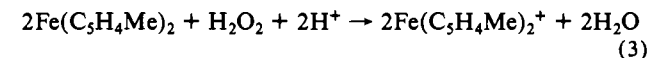


Figure 3. Plots of pseudo-first-order rate constants $k^{(1)}$ vs the CoTPP^+ concentration for the oxidation of $\text{Fe}(\text{C}_5\text{H}_5)_2$ (O), $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ (●), and $\text{Fe}(\text{C}_5\text{Me}_5)_2$ (◐) with dioxygen, catalyzed by CoTPP^+ in the presence of HClO_4 (3.0×10^{-3} – 2.0×10^{-2} M) in MeCN at 298 K.

MeCN at 298 K, the rise of an absorption band at 690 nm due to $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2^+$ was immediately observed within 0.1 s, followed by an additional slower increase in the absorbance with a much longer reaction time (Figure 2). The first step in Figure 2 corresponds to the initial two-electron reduction of dioxygen with $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$, catalyzed by CoTPP^+ in the presence of HClO_4 in MeCN, yielding H_2O_2 (eq 2). The slower second step in Figure



2 may be ascribed to the further two-electron reduction of H_2O_2 by $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ (eq 3). In consequence, the oxidation of Fe



($\text{C}_5\text{H}_4\text{Me})_2$ with an excess amount of dioxygen, catalyzed by CoTPP^+ in the presence of HClO_4 , results in only the two-electron reduction of dioxygen to hydrogen peroxide (eq 2).

Rates of the oxidation of ferrocene derivatives (Fc: $\text{Fe}(\text{C}_5\text{H}_5)_2$, $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$, $\text{Fe}(\text{C}_5\text{Me}_5)_2$) with an excess amount of dioxygen, catalyzed by metalloporphyrins (MTPP⁺: M = Co, Fe, Mn) or $\text{Co}(\text{TIM})^{3+}$ in the presence of HClO_4 in MeCN, obeyed pseudo-first-order kinetics. The pseudo-first-order rate constants $k^{(1)}$

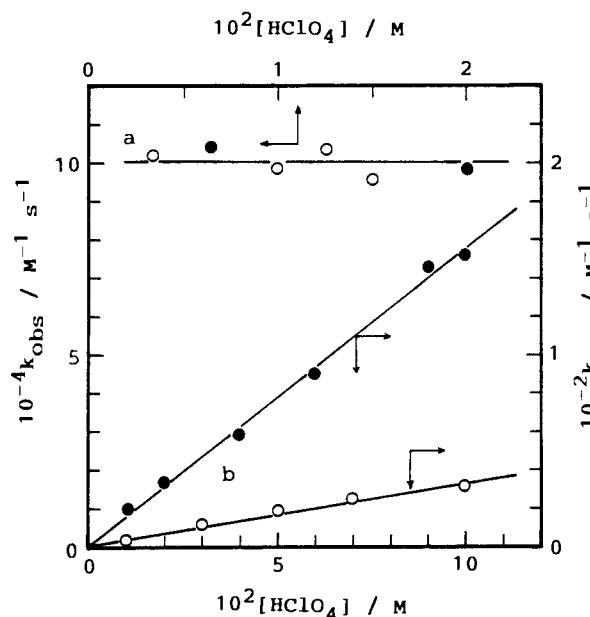


Figure 4. Plots of observed second-order rate constants k_{obs} (eq 4) vs the HClO_4 concentration for the oxidation of $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ with dioxygen, catalyzed by (a) CoTPP^+ and (b) $\text{Co}(\text{TIM})^{3+}$ in the presence of HClO_4 in MeCN at 298 K ($[\text{O}_2] = 2.6 \times 10^{-3} \text{ M}$ (O), $1.3 \times 10^{-2} \text{ M}$ (●)).

Table I. Rate Constants (k_{obs}) for the MTPP⁺-Catalyzed Oxidation of Ferrocene Derivatives by Dioxygen ($5.0 \times 10^{-2} \text{ M}$) in the Presence of HClO_4 (3.0×10^{-3} – $2.0 \times 10^{-2} \text{ M}$) in MeCN at 298 K and the One-Electron Reduction Potentials (E_{red}° vs SCE) of MTPP⁺ in MeCN

| MTPP ⁺ | $E_{\text{red}}^\circ/\text{V}$ | $k_{\text{obs}}/\text{M}^{-1} \text{ s}^{-1, a, b}$ | | |
|-------------------|---------------------------------|---|--|--|
| | | $\text{Fe}(\text{C}_5\text{H}_5)_2$ | $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ | $\text{Fe}(\text{C}_5\text{Me}_5)_2$ |
| CoTPP^+ | 0.35 | 4.2×10^4 (2.1×10^4) | 1.0×10^5 (4.6×10^4) | 1.1×10^6 (6.0×10^5) |
| FeTPP^+ | 0.14 | 2.9×10^6 | 1.2×10^7 | ^c |
| MnTPP^+ | -0.15 | ^d | 2.6×10^2 | 1.4×10^5 |

^aThe values in parentheses are the k_{obs} values for electron transfer from ferrocene derivatives to CoTPP^+ in the absence of dioxygen in MeCN at 298 K. ^bThe experimental errors are within $\pm 10\%$. ^cToo fast to be determined accurately. ^dToo slow to be determined accurately because of the competing demetalation reaction of MnTPP^+ .

increase linearly with an increase in the catalyst concentration, as shown in Figure 3. Thus, the rate of formation of Fc^+ is given by eq 4, where [cat] is the concentration of catalyst, MTPP⁺ or

$$d[\text{Fc}^+]/dt = k_{\text{obs}}[\text{Fc}][\text{cat}] \quad (4)$$

$\text{Co}(\text{TIM})^{3+}$. The observed second-order rate constant k_{obs} of the CoTPP^+ -catalyzed reaction remained constant with the change in the dioxygen or HClO_4 concentration, as shown in Figure 4a. The k_{obs} values for other MTPP⁺ (M = Fe, Mn) were also independent of the concentration of dioxygen or HClO_4 . The k_{obs} values are listed in Table I, together with the one-electron reduction potentials (E_{red}°) of MTPP⁺ in MeCN.

In the absence of dioxygen as well, electron transfer from ferrocene derivatives to CoTPP^+ occurs and the rate also obeyed the second-order kinetics (eq 4) where [cat] is $[\text{CoTPP}^+]$. The k_{obs} values in the absence of dioxygen are also listed in Table I (the values in parentheses).

In contrast with the case of MTPP⁺, the k_{obs} value of the $\text{Co}(\text{TIM})^{3+}$ -catalyzed reduction of dioxygen by $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ increases linearly with the concentrations of HClO_4 and O_2 , as shown in Figure 4b,c. The k_{obs} values of the $\text{Co}(\text{TIM})^{3+}$ -catalyzed oxidation of various ferrocene derivatives by dioxygen ($1.3 \times 10^{-2} \text{ M}$) in the presence of HClO_4 ($1.0 \times 10^{-2} \text{ M}$) in MeCN at 298 K are listed in Table II, together with the one-electron oxidation potentials (E_{ox}°) of ferrocene derivatives.

Oxidation of CoTPP by Dioxygen in the Presence of HClO_4 . In the absence of HClO_4 , CoTPP is stable toward dioxygen. Upon

Table II. Rate Constants (k_{obs}) for the $\text{Co}(\text{TIM})^{3+}$ -Catalyzed Oxidation of Ferrocene Derivatives by Dioxygen ($1.3 \times 10^{-2} \text{ M}$) in the Presence of HClO_4 ($1.0 \times 10^{-2} \text{ M}$) in MeCN at 298 K and the One-Electron Oxidation Potentials of Ferrocene Derivatives (E_{ox}° vs SCE)

| no. | ferrocene derivative | E_{ox}° vs SCE ^a /V | $k_{\text{obs}}/\text{M}^{-1} \text{ s}^{-1}$ |
|-----|--|--|---|
| 1 | $\text{Fe}(\text{C}_5\text{Me}_5)_2$ | -0.08 | 2.4×10^4 |
| 2 | $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ | 0.26 | 1.0×10^4 |
| 3 | $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{-}n\text{-Bu})$ | 0.31 | 6.5 |
| 4 | $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{-}n\text{-Amyl})$ | 0.31 | 6.0 |
| 5 | $\text{Fe}(\text{C}_5\text{H}_5)_2$ | 0.37 | 2.1 |

^aThe one-electron reduction potential of $\text{Co}(\text{TIM})^{3+}$ in MeCN E_{red}° (vs SCE) = -0.12 V. ^bThe experimental errors are within $\pm 10\%$.

Table III. Rate Constants (k_{obs}) for the Acid-Catalyzed Electron Transfer from CoTPP ($2.7 \times 10^{-6} \text{ M}$) to Dioxygen ($5.0 \times 10^{-2} \text{ M}$) in MeCN at 298 K

| $[\text{HClO}_4]/\text{M}$ | $k_{\text{obs}}/\text{M}^{-1} \text{ s}^{-1}$ | $[\text{HClO}_4]/\text{M}$ | $k_{\text{obs}}/\text{M}^{-1} \text{ s}^{-1}$ |
|----------------------------|---|----------------------------|---|
| 0 | ^b | 1.1×10^{-4} | 4.6×10^3 |
| 3.9×10^{-5} | 9.6×10^2 | 1.8×10^{-4} | 7.0×10^3 |
| 6.5×10^{-5} | 2.3×10^3 | 3.0×10^{-4} | 1.0×10^4 |

^aThe experimental errors are within $\pm 10\%$. ^bNo reaction.

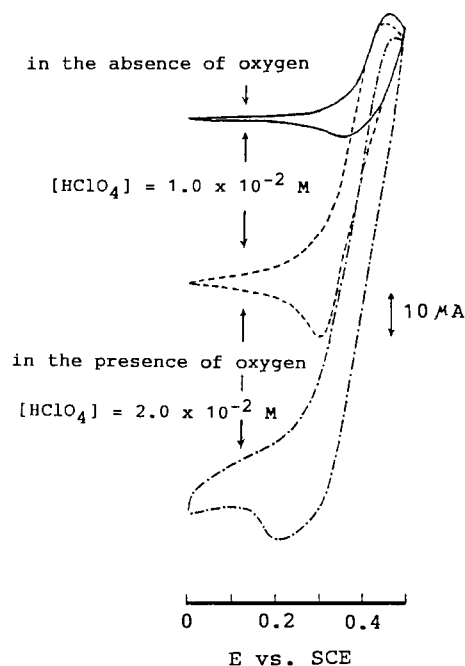


Figure 5. Cyclic voltammograms of CoTPP^+ ($2.0 \times 10^{-3} \text{ M}$) in the absence and presence of dioxygen in MeCN containing different concentrations of HClO_4 .

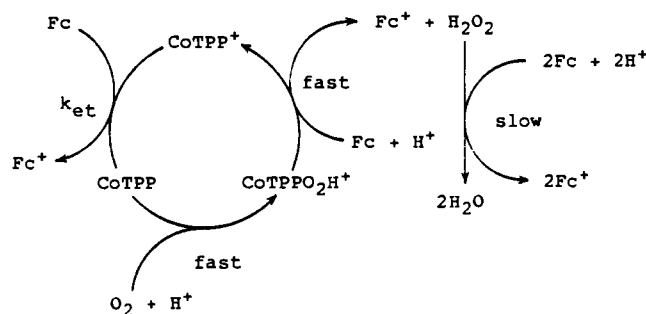
the addition of HClO_4 to a dioxygen-saturated MeCN solution of CoTPP , however, CoTPP was instantly oxidized to yield CoTPP^+ . Rates of the oxidation of CoTPP by an excess amount of dioxygen in the presence of HClO_4 in MeCN were determined by using a stopped-flow technique (see Experimental Section). The rate of formation of CoTPP^+ is given by eq 5. The sec-

$$d[\text{CoTPP}^+]/dt = k_{\text{obs}}[\text{CoTPP}][\text{O}_2] \quad (5)$$

ond-order rate constant (k_{obs}) under 4 atm of dioxygen increases linearly with an increase in the HClO_4 concentration, as shown in Table III.

The facile oxidation of CoTPP by dioxygen in the presence of HClO_4 in MeCN has been confirmed also by the voltammetric study. The cyclic voltammogram (CV) of CoTPPClO_4 in the absence of dioxygen shows the quasi-reversible redox couple of $\text{CoTPP}^{+/0}$ at 0.35 V vs SCE unaffected by the presence of HClO_4 (Figure 5a). In the presence of dioxygen, however, the catalytic reduction of dioxygen is observed at the reduction potential of CoTPP^+ , and the reduction current increases with an increase in

Scheme I



the HClO₄ concentration (Figure 5b,c). No reduction of dioxygen has been observed in the absence of CoTPP⁺ under otherwise the same conditions.

Discussion

Mechanism of the Catalytic Reduction of Dioxygen by Ferrocene Derivatives. As shown in Table I, the k_{obs} values for the oxidation of ferrocene derivatives (Fc) with an excess amount of dioxygen, catalyzed by CoTPP⁺ in the presence of HClO₄ in MeCN, are approximately 2-fold larger than those for the oxidation of Fc with CoTPP⁺ in the absence of dioxygen. 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⁺, as shown in Scheme I. According to Scheme I, the rates of oxidation of Fc in the absence and presence of dioxygen are given by eq 6 and 7, respectively, where k_{et} is the second-order rate constant of the electron transfer from Fc to CoTPP⁺.

$$d[\text{Fc}^+]/dt = k_{\text{et}}[\text{Fc}][\text{CoTPP}^+] \text{ in the absence of O}_2 \quad (6)$$

$$d[\text{Fc}^+]/dt = 2k_{\text{et}}[\text{Fc}][\text{CoTPP}^+] \text{ in the presence of O}_2 \quad (7)$$

The Gibbs energy change of electron transfer $\Delta G_{\text{et}}^\circ$ is given by eq 8, where F is the Faraday constant and E_{ox}° and E_{red}° are the one-electron oxidation potential of the reductant (Fc) and the one-electron reduction potential of the oxidant (MTPP⁺), respectively. According to eq 8, the electron transfer from Fc to

$$\Delta G_{\text{et}}^\circ = F(E_{\text{ox}}^\circ - E_{\text{red}}^\circ) \quad (8)$$

CoTPP⁺ is exothermic or slightly endothermic, judging from the one-electron reduction and oxidation potentials of CoTPP⁺ and Fc (Tables I and II, respectively). In fact, the electron transfer from Fc to CoTPP⁺ under the pseudo-first-order conditions, where the Fc concentrations were maintained at a large excess over the CoTPP⁺ concentration, goes to completion, yielding Fc⁺ and CoTPP. Under the experimental conditions employed in determining the rates of the CoTPP⁺-catalyzed oxidation of Fc by dioxygen ([HClO₄] > 3.0 × 10⁻³ M; Figure 3), the pseudo-first-order rate constants of the oxidation of CoTPP by dioxygen (>5.0 × 10³ s⁻¹ at [HClO₄] > 3.0 × 10⁻³ M), estimated from the observed dependence of the rate constant on the HClO₄ concentration (eq 5, Table III), are much faster than the pseudo-first-order rate constants in Figure 3 (<21 s⁻¹). This may be the reason that the rates of the CoTPP⁺-catalyzed oxidation of Fc by dioxygen in the presence of HClO₄ are independent of the dioxygen or HClO₄ concentration (Figure 4a).

Cobalt(II) tetraphenylporphyrin, CoTPP, is known to exist in the low-spin square-planar configuration in noncoordinating solvents¹⁷ and is stable toward dioxygen.¹⁸ A single axial coordination of electron-donating ligand such as pyridine to CoTPP increases significantly the affinity of CoTPP to dioxygen, yielding the dioxygen adduct.¹⁷ In fact, the reducing power of CoTPP is

enhanced by the axial coordination, as indicated by a large negative shift of the one-electron oxidation potential in coordinating solvents such as pyridine.¹⁹ Then, CoTPP may be readily oxidized by oxygen in the presence of acid, since the presence of acid is known to enhance the oxidizing power of dioxygen significantly.^{16,20,21} Thus, an increase in the coordinating ability of the solvent enhances the rate of oxidation of CoTPP by dioxygen but at the same time decreases the oxidizing power of CoTPP⁺. In order to achieve the efficient CoTPP⁺-catalyzed oxidation of Fc by dioxygen, however, the coordinating ability of the solvent should be weak enough to make the electron transfer from Fc to CoTPP⁺ exothermic. Acetonitrile used as a solvent in this study may be a good choice, since the coordinating ability is weak enough to keep the reduction potential of CoTPP⁺ more positive than the one-electron oxidation potentials of Fc when electron transfer from Fc to CoTPP⁺ is exothermic but strong enough to accelerate the rate of oxidation of CoTPP by dioxygen in the presence of HClO₄.²²

Although the electron-transfer reactions from Fc to FeTPP⁺ and MnTPP⁺ in MeCN are endothermic on the basis of the reduction potentials of FeTPP⁺ and MnTPP⁺ and the oxidation potentials of Fc (Tables I and II, respectively), the facile oxidation of FeTPP²³ and MnTPP²⁴ by dioxygen in the presence of HClO₄ in MeCN may make the initial electron transfer from Fc to FeTPP⁺ or MnTPP⁺ the rate-determining step. Thus, the rates of the FeTPP⁺- and MnTPP⁺-catalyzed oxidation of Fc by dioxygen in the presence of HClO₄ in MeCN are also determined solely by the rates of electron transfer from Fc to FeTPP⁺ and MnTPP⁺ and thereby become independent of the dioxygen or HClO₄ concentration.

Outer-Sphere Electron-Transfer Pathways. Ferrocene derivatives are known to react by outer-sphere mechanisms in a variety of electron-transfer processes especially with inorganic oxidants.²⁵ On the other hand, metal porphyrins that have axial coordination sites left open to interact with redox partners can undergo both outer-sphere²⁶ and inner-sphere²⁷ electron-transfer pathways. In the present study, rates of electron transfer from ferrocene derivatives, Fe(C₅H₅)₂, Fe(C₅H₄Me)₂, and Fe(C₅Me₅)₂, to metal porphyrins, CoTPP⁺, FeTPP⁺, and MnTPP⁺, were determined as shown in Table I. The electron-transfer rate constant k_{et} ²⁸ with a fixed metal porphyrin increases in the order Fe(C₅H₅)₂ < Fe(C₅H₄Me)₂ < Fe(C₅Me₅)₂ in accordance with the negative shift of the one-electron oxidation potentials of ferrocene derivatives when the electron transfer becomes energetically more favorable. With a fixed ferrocene derivative, the k_{et} value increases in the order MnTPP⁺ < CoTPP⁺ < FeTPP⁺, although the reduction potentials of metal porphyrins (Table I) indicate that the electron

(17) La Mar, G. N.; Walker, F. A. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 61-157.
 (18) Dokuzović, Z.; Ahmeti, Xh.; Paulović, D.; Murati, I.; Ašperger, S. *Inorg. Chem.* **1982**, *21*, 1576.

(19) (a) Walker, F. A.; Beroiz, D.; Kadish, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 3484. (b) Lin, X. Q.; Boisselier-Cocolios, B.; Kadish, K. M. *Inorg. Chem.* **1986**, *25*, 3242.
 (20) (a) Pavlović, D.; Ašperger, S.; Dokuzović, Z.; Jurišić, B.; Ahmeti, X.; Sertić, M.; Murati, I. *J. Chem. Soc., Dalton Trans.* **1985**, 1095. (b) Pavlović, D.; Ašperger, S.; Domi, B. *Ibid.* **1986**, 2535.
 (21) (a) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393. (b) Bockrath, B.; Dorfman, L. M. *J. Phys. Chem.* **1975**, *79*, 1509.
 (22) (a) Kadish, K. M.; Lin, X. Q.; Han, B. C. *Inorg. Chem.* **1987**, *26*, 4161. (b) Truxillo, L. A.; Davis, D. G. *Anal. Chem.* **1975**, *47*, 2260.
 (23) (a) James, B. R. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; pp 153-203. Chin, D.-H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 4344. (b) Chin, D.-H.; Graudio, J. D.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5486. (c) Thompson, A. N.; Krishnamurthy, M. *Inorg. Chim. Acta* **1979**, *34*, 145. (d) Ostfeld, D.; Colfax, J. A. *Inorg. Chem.* **1978**, *17*, 1796.
 (24) (a) VanAtta, R. B.; Strouse, C. E.; Hanson, L. K.; Valentine, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 1425. (b) Creager, S. E.; Murray, R. W. *Inorg. Chem.* **1987**, *26*, 2612.
 (25) (a) Pladziewicz, J. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 56. (b) Pelizzetti, E. *Inorg. Chem.* **1979**, *18*, 1386. (c) Borchardt, D.; Pool, K.; Wherland, S. *Ibid.* **1982**, *21*, 93. (d) Borchardt, D.; Wherland, S. *Ibid.* **1986**, *25*, 901.
 (26) Chapman, R. D.; Fleischer, E. B. *J. Am. Chem. Soc.* **1982**, *104*, 1575.
 (27) Chapman, R. D.; Fleischer, E. B. *J. Am. Chem. Soc.* **1982**, *104*, 1582.
 (28) The k_{et} values are obtained from the observed second-order rate constants k_{obs} for electron transfer from ferrocene derivatives to metalloporphyrins in the presence of dioxygen by using the relation $k_{\text{obs}} = 2k_{\text{et}}$ (see eq 7).

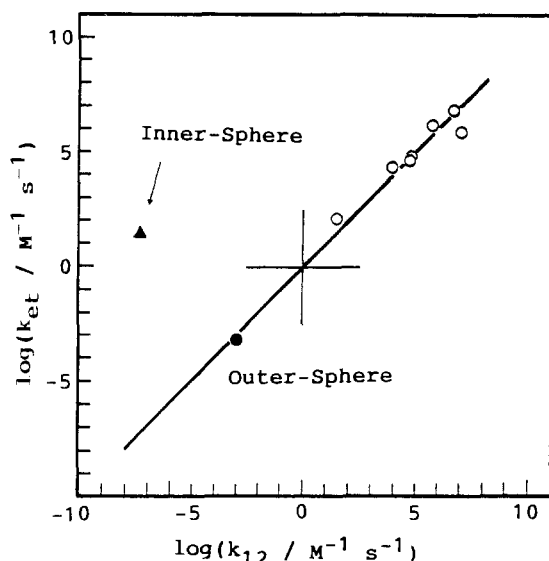


Figure 6. Comparison of the electron-transfer rate constants ($\log k_{et}$) with the calculated rate constants ($\log k_{12}$) for electron transfer from ferrocene derivatives to metalloporphyrins MTPP^+ (O), from $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ to dioxygen in the presence of 0.10 M HClO_4 (●), and from CoTPP to dioxygen in the presence of 3.0×10^{-4} M HClO_4 (▲) in MeCN at 298 K by using eq 9–11 (see text).

transfer becomes energetically more favorable in the order $\text{MnTPP}^+ < \text{FeTPP}^+ < \text{CoTPP}^+$.

A quantitative discussion on the reactivity of metalloporphyrins in the electron-transfer reactions with the ferrocene derivatives can be achieved by comparing the observed rates of the electron transfer to those predicted by the Marcus theory for the rates of outer-sphere electron-transfer reactions.²⁹ The Marcus relation for the rate constant of the electron transfer from the reductant (1) to the oxidant (2), k_{12} , is given by eq 9,²⁹ where k_{11} and k_{22}

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \quad (9)$$

are the rate constants of the corresponding self-exchanges and K_{12} is the equilibrium constant for the electron-transfer reaction. The K_{12} value is obtained from the oxidation potential of the reductant, E_{ox}° , and the reduction potential of the oxidant, E_{red}° , by using eq 10.³⁰ The parameter f in eq 9 is given by eq 11, in

$$\log K_{12} = (-2.3RT/F)(E_{ox}^\circ - E_{red}^\circ) \quad (10)$$

$$\log f = (\log K_{12})^2 / [4 \log (k_{11}k_{22}/Z^2)] \quad (11)$$

which Z , the frequency factor, is taken to be $10^{11} \text{ M}^{-1} \text{ s}^{-1}$.²⁹ The reported values of self-exchange rate constants for ferrocene derivatives ($k_{11} = 5.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$)³¹ and metal porphyrins ($k_{22} = 20, 1 \times 10^9$, and $3.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for Co,³² Fe,³³ and Mn³⁴) together with the oxidation and reduction potentials of ferrocene derivatives and metal porphyrins (Tables I and II, respectively) constitute a satisfactory basis for accounting for the experimental kinetic data when considered in light of the Marcus relation (eq 9–11). The comparison between the calculated rate constants ($\log k_{12}$) and the observed rate constants ($\log k_{obs}$) is shown in Figure 6. If uncertainties in the estimates of k_{11} and k_{22} are taken into account, the agreement between the observed and calculated rate constants demonstrates clearly that the electron transfer from

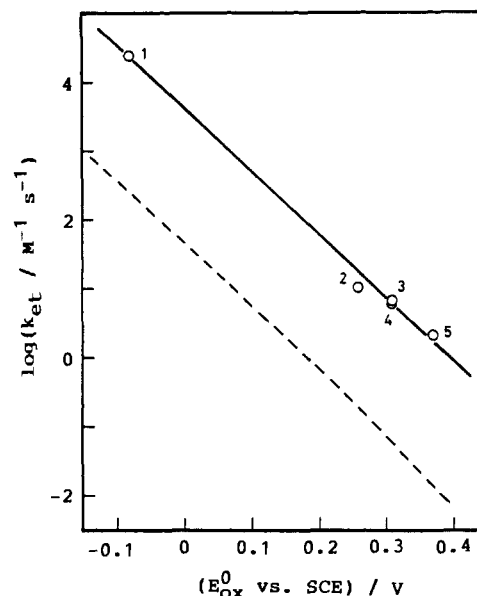


Figure 7. Dependence of $\log k_{et}$ on the one-electron oxidation potentials (E_{ox}°) of ferrocene derivatives for the oxidation of ferrocene derivatives with dioxygen ($1.3 \times 10^{-2} \text{ M}$), catalyzed by $\text{Co}(\text{TIM})^{3+}$ in the presence of HClO_4 ($1.0 \times 10^{-2} \text{ M}$) in MeCN at 298 K. Numbers refer to the ferrocene derivatives in Table II. The dotted line shows the calculated dependence of the rate constant ($\log k_{12}$) for outer-sphere electron transfer from ferrocene derivatives to $\text{Co}(\text{TIM})^{3+}$ in MeCN at 298 K on E_{ox}° , by using eq 9–11 (see text).

ferrocene derivatives to metal porphyrins proceeds by an outer-sphere mechanism.³⁵

The Marcus relation (eq 9 and 11) can also account for the rate constant of electron transfer from $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ to dioxygen in the presence of HClO_4 (0.10 M) in MeCN ($k_{et} = 1.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$)¹⁶ as follows. The one-electron reduction potential of dioxygen ($E(\text{O}_2/\text{HO}_2^*)$) in the presence of 0.10 M HClO_4 in MeCN can be estimated as -0.21 V (vs SCE) from the reduction potential in MeCN ($E_{red}^\circ = -0.86 \text{ V}$ vs SCE)³⁶ and the $\text{p}K_a$ value of HO_2^* in an aprotic solvent ($\text{p}K_a = 12$)^{21a} by using eq 12.²¹ Then, the $E(\text{O}_2/\text{HO}_2^*) =$

$$E^\circ(\text{O}_2/\text{O}_2^{\cdot-}) + (2.3RT/F)(\log [\text{H}^+] - \log K_a) \quad (12)$$

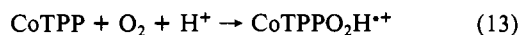
rate constant for the acid-catalyzed electron transfer from $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ to dioxygen can be calculated as $1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ in the same way as for electron transfer from ferrocene derivatives to metal porphyrins by using eq 9–11. In this calculation, the value of the self-exchange rate constant of $\text{O}_2/\text{O}_2^{\cdot-}$ ($k_{22} = 1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) has been derived from the kinetic analysis for outer-sphere electron transfer reactions from ruthenium(II) amine complexes to dioxygen.^{38,39} The calculated value agrees well with the experimental value, as also shown in Figure 6. Such an agreement demonstrates that the electron transfer from $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ to dioxygen in the absence of MTPP^+ also proceeds by an outer-sphere mechanism.

Inner-Sphere Electron-Transfer Pathways. The rate constants of electron transfer from CoTPP to dioxygen in the presence of

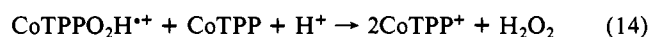
(29) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
 (30) The work terms are neglected, since in the present case one of the reactants and products is uncharged.
 (31) Yang, E. S.; Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1980**, *84*, 3094.
 (32) Rohrbach, D. F.; Deusch, E.; Heineman, W. R.; Pasternack, R. F. *Inorg. Chem.* **1977**, *16*, 2650.
 (33) Pasternack, R. F.; Spiro, E. G. *J. Am. Chem. Soc.* **1978**, *100*, 968.
 (34) Langley, R.; Hambricht, P. *Inorg. Chem.* **1985**, *24*, 1267.

(35) The observed smaller value for electron transfer from $\text{Fe}(\text{C}_5\text{Me}_5)_2$ to CoTPP^+ may be suggestive of nonadiabatic behavior of this system due to the steric effect; see: Nielson, R. M.; Golovin, M. N.; McManis, G. E.; Weaver, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 1745.
 (36) Sawyer, D. T.; Calderwood, T. S.; Yamaguchi, K.; Angelis, C. T. *Inorg. Chem.* **1983**, *22*, 2577.
 (37) The one-electron reduction potential of dioxygen in H_2O at $\text{pH} = 1$ is -0.18 V vs SCE,^{21a} which is about the same as that in MeCN at 0.10 M HClO_4 . Although the one-electron reduction potential of dioxygen in the absence of an acid in MeCN (-0.86 V vs SCE) is more negative than that in H_2O (-0.40 V vs SCE), this difference is canceled out due to the difference in the $\text{p}K_a$ values of HO_2^* (4.6 and 12 in H_2O and MeCN, respectively).
 (38) McDowell, M. S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1984**, *23*, 2232.
 (39) Stanbury, D. M.; Haas, O.; Taube, H. *Inorg. Chem.* **1980**, *19*, 518.

HClO₄ in MeCN at 298 K can also be calculated by using eq 9-11. In contrast with electron-transfer reactions involving ferrocene derivatives, the observed values in Table III are 10⁹-fold larger than the calculated values, as shown in Figure 6. The huge enhancement of the observed rates relative to the calculated ones may be attributed to a strong inner-sphere character in the acid-catalyzed electron transfer from CoTPP to dioxygen. Such a strong inner-sphere nature suggests that the electron transfer gives a complex, CoTPPO₂H⁺, in which a strong interaction between CoTPP⁺ and HO₂[•] causes a significant reduction of Gibbs energy change of electron transfer from CoTPP to dioxygen in the presence of HClO₄ (eq 13). The further reduction of HO₂[•]



to H₂O₂ by CoTPP in the presence of HClO₄ may proceed via CoTPPO₂H⁺ (eq 14), since the oxidizing ability of HO₂[•] is



increased by the ligand to metal charge-transfer (LMCT) interaction with CoTPP⁺. Thus, the combination of an outer-sphere electron transfer from Fc to CoTPP⁺ with an inner-sphere electron transfer from CoTPP to O₂ in the presence of HClO₄ constitutes an efficient catalytic cycle, as shown in Scheme I.

The same type of interaction in Co(TIM)O₂H³⁺ as in CoTPPO₂H⁺ may reduce the energy barrier for electron transfer from ferrocene derivatives to Co(TIM)³⁺ in the presence of HClO₄ and dioxygen in MeCN. The rate constants of electron transfer from ferrocene derivatives to Co(TIM)³⁺ cannot be obtained directly, since the electron transfer is not only reversible but also endothermic. However, the rate constants can be estimated by the calculation based on eq 9-11 from the values of the one-electron oxidation potential of Co(TIM)³⁺ (-0.12 V vs SCE) and the reported value of the self-exchange rate constant (6.0 × 10⁻² M⁻¹ s⁻¹),⁴⁰ together with the corresponding values for ferrocene derivatives noted above. In Figure 7, the observed rate constants log *k*_{obs} of electron transfer from various ferrocene derivatives to Co(TIM)³⁺ in the presence of O₂ (1.3 × 10⁻² M) and HClO₄ (1.0 × 10⁻² M) are plotted against the oxidation potentials of ferrocene derivatives (*E*_{ox}^o). On the other hand, the calculated dependence of log *k*₁₂ on *E*_{ox}^o is shown by the dotted line. The observed rate constants of various ferrocene derivatives are larger than the calculated ones by about the same magnitude irrespective of ferrocene derivatives, indicating the inner-sphere nature of the electron transfer. At present, however, the exact mechanism of the inner-sphere electron transfer is not known.

(40) Durham, B.; Endicott, J. F.; Wong, C.-L.; Rillema, D. P. *J. Am. Chem. Soc.* 1979, 101, 847.

Contribution from the Service de Chimie Organique, Université Libre de Bruxelles, B.P. 160, 50 avenue Franklin Roosevelt, 1050 Bruxelles, Belgium, and Department of Chemistry, Katholieke Universiteit Leuven, B-3030 Leuven, Belgium

Resonance Raman Spectra and Spectroelectrochemical Properties of Mono- and Polymetallic Ruthenium Complexes with 1,4,5,8,9,12-Hexaazatriphenylene

A. Kirsch-De Mesmaeker,^{*,†,‡} L. Jacquet,[†] A. Masschelein,^{†,§} F. Vanhecke,^{||} and K. Heremans^{||}

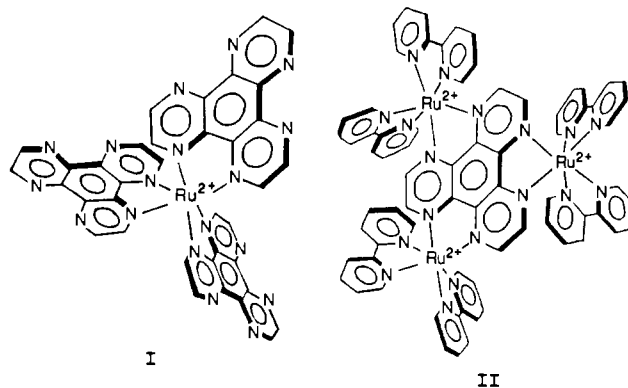
Received December 6, 1988

The resonance Raman spectra of the monometallic heteroleptic complexes of HAT (1,4,5,8,9,12-hexaazatriphenylene) and bpy (2,2'-bipyridine) are discussed as a function of the excitation wavelength, in relation to the MLCT (metal to ligand charge transfer) transitions from the Ru²⁺ to the ligand HAT or bpy and to the spectroelectrochemical correlation obtained from the spectroscopic and electrochemical data. The same analyses are performed with the bi- and trimetallic complexes [Ru(bpy)₂]₂HAT and [Ru(bpy)₂]₃HAT, respectively. In the trimetallic compound, the large and intense MLCT band centered around 580 nm is attributed only to Ru-HAT transitions and the much less intense band, at ~400 nm, to Ru-bpy transitions. SERR (surface enhanced resonance Raman) spectra, recorded when rR measurements were not possible because of some luminescence of the complexes, emphasize specific effects of the silver sol.

Introduction

We have explored previously¹ the possibilities of 1,4,5,8,9,12-hexaazatriphenylene (HAT) as a ligand for transition metals, especially ruthenium. Thus, the trishomoleptic Ru(HAT)₃²⁺ (I) and the heteroleptic complexes with 2,2'-bipyridine (bpy) Ru(HAT)_{*n*}(bpy)_{3-*n*}²⁺ (*n* = 1, 2) were successfully obtained and characterized. The main interest, however, in the HAT ligand stems from its ability to behave as a unique symmetric bridging ligand for polymetallic complexes. Indeed, one can either complex up to three Ru(bpy)₂²⁺ moieties around one central HAT and thus prepare the mono-, bi-, and trimetallic complexes, [Ru(bpy)₂]_{*n*}(HAT) (*n* = 1-3; II, *n* = 3), or one can also start from Ru(HAT)₃²⁺ (I) and chelate two Ru(L)₂²⁺ species (L = ligand) on each HAT to obtain up to seven Ru²⁺ ions in the same molecule.

These HAT complexes present many interesting properties: for instance, Ru(bpy)₂(HAT)²⁺ behaves as a very good DNA in-



tercalator;² it is also, as the bimetallic [Ru(bpy)₂]₂(HAT) species, an attractive synthetic precursor for heterometallic edifices where intramolecular electron and energy transfer could be studied. Moreover, for some derivatives of these polymetallic complexes, their direct electropolymerization or incorporation into a polymer

* To whom correspondence should be addressed.

† Université Libre de Bruxelles.

‡ Senior Research Associate of the National Fund for Scientific Research (Belgium).

§ Research Assistant of the National Fund for Scientific Research (Belgium).

|| Katholieke Universiteit Leuven.

(1) Masschelein, A.; Kirsch-De Mesmaeker, A.; Verhoeven, C.; Naselski-Hinkens, R. *Inorg. Chim. Acta* 1987, 129, L13-16.

(2) Kelly, J.; Tossi, A.; Kirsch-De Mesmaeker, A.; Masschelein, A. To be submitted for publication.