Electrocatalytic Reduction of Dioxygen by New Water Soluble Cobalt(II) Tetrakis-(1,2,5,6-tetrafluoro-4-*NN'N"*-trimethylanilinium)-*β*-octabromoporphyrin in Aqueous Solutions

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Received April 3, 1999

New water soluble and highly electron deficient cobalt(II) tetrakis-(1,2,5,6-tertrafluoro-4-*NN'N"*-trimethylanilinium)-*β*-octabromoporphyrin [$Co^{II}(Br_8TTFP)(Y)_2$] was synthesized and used for the electrocatalytic reduction of dioxygen. The first reduction of synthesized [$Co^{II}(Br_8TTFP)(Y)_2$] involves one electron process to give metal centered [$Co^{I}(Br_8TTFP)(Y)_2$]. The reduction of potential [$E_{1/2} = -0.32$ V] of [$Co^{II}(Br_8TTFP)(Y)_2$] shifts positively 370 mV compared with that of [$Co^{II}(TTFP)(Y)_2$] due to the substituted bromide to *β*-pyrrole positions. The electrochemically reduced [$Co^{I}(Br_8TTFP)(Y)_2$] binds dioxygen and catalytically reduces it to HOOH by $2e^-$ transfer. Cyclic and hydrodynamic voltammetry at a glassy carbon electrode in dioxygen-saturated aqueous solutions are used to study the electrocatalytic pathway.

Introduction

The evolution of new catalysts for multielectron reduction of dioxygen has receive a great deal of attention for practical applications such as biological reactions, as well as for fuel cells and air batteries over the past two decades.[1-13] Porphyrins or phthalocyanines of cobalt and iron are known as effective catalysts for dioxygen reduction. Dioxygen is reduced to hydrogen peroxide or water via $2e^-$ or $4e^-$ transfer by effective catalyst. Among the various metalloporphyrins, the cobaltporphyrins have been well studied. It has been reported that water-soluble bisporphyrin structures[18-24] or monomeric cobaltporphyrins coordinated with ruthenium complexes[14-17] act as effective catalysts for the $4e^-$ reduction of dioxygen to water in acidic solutions at a pyrolytic graphite electrode. The electrocatalytic reduction of dioxygen involves the binding of dioxygen to the Co(II) species followed by the reduction of the adduct. The metalloporphyrins possessing halogen substituents on the ring periphery are known to be distorted structures, positively shifted potentials, and robust catalysts for organic oxidation. Recently it was reported that cobalt tetrakis-(*N*-trimethyl-pyridyl)-*β*-octabromoporphyrin [$Co(Br_8TMpyP)$] catalyzed the reduction of dioxygen.[25] The catalytic mechanism by Co (Br_8TMpyP) as a catalyst involves the binding of dioxygen to Co(I) species to give Co(I)-O_2. However, the catalytic mechanism by $Co(Br_8TPPS)$ possessing negative charges involves the binding of dioxygen to Co(II) species to give Co(II)-O_2 due to the dependence upon the reduction potential of Co(II)/Co(I) couple.[26] It was also suggested that these cobaltporphyrins do not adsorb on the glassy carbon electrode surface. Previously, we reported[27] that dioxygen is reduced electrocatalytically to HOOH by $Co^{II}(TTFP)(Y)_2$ as a catalyst, and then the generated HOOH is reduced to water by $Co^{I}(TTFP)(Y)_2$. In the present work, electrocatalytic reduction of dioxygen in dioxygen saturated aqueous solutions has been studied by cyclic voltammetry and hydrodynamic voltammetry at a glassy carbon electrode using new water soluble cobalt tetrakis-(1,2,5,6-tetrafluoro-4-*NN'N"*-trimethylanilinium)-*β*-octabromoporphyrin [$Co^{II}(Br_8TTFP)$] (Figure 1). The electron withdrawing effects of -octabromo and o, m-fluoro substituents of $Co^{II}(Br_8TTFP)$ have been expected to show a positive shift in the potential of dioxygen reduction. Co(I) species generated from the reduction of $Co^{II}(Br_8TTFP)$ before the dioxygen reduction is useful for the electrocatalytic reduction of dioxygen in various pH solutions. The electrochemical results will be discussed to determine the mechanism of the catalytic reduction of dioxygen.

Experimental Section

Synthesis of $Co^{II}(Br_8TTFP)$. The $CF_3SO_3^-$ salt of tetrakis-(1,2,5,6-tetrafluoro-4-*NN'N"*-trimethylanilinium) porphyrinato cobalt [Co(TTFP)], which is soluble in aqueous

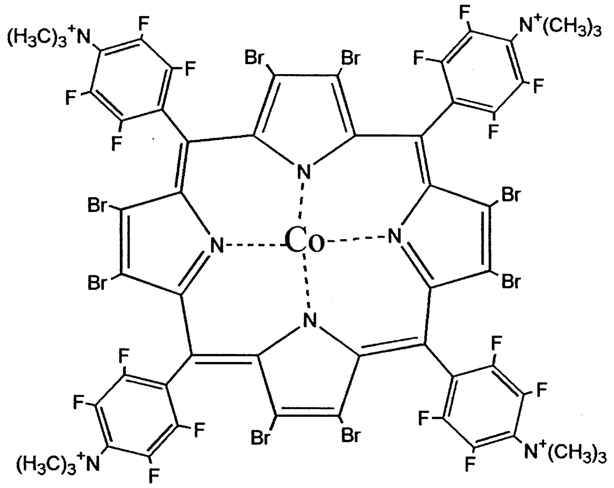

Figure 1. Structure of new water soluble cobaltporphyrin employed in the present study.

solutions in the entire pH range, was procured from Mid-Century Chemicals Co., USA. Co(TTFP) (50 mg) was dissolved in methanol (50 mL) and chloroform (50 mL), and liquid bromine (0.5 mL) was added to the Co(TTFP) solution while stirring the solution vigorously. The reaction mixture was stirred over a period of 72 hours to give the brominated product [Co(Br_8TTFP)] at room temperature. During the progress of the reaction, Co(Br_8TTFP) was precipitated in the solution. The precipitate was separated from the solution by filtering and washed with chloroform continuously until traces of adsorbed free bromine were removed from the precipitate. The resulting products were subjected to silica gel column eluting with a mixture of chloroform/methanol. The ^{1}H NMR spectrum of Co(Br_8TTFP) revealed no peak corresponding to the pyrrole protons, suggesting that Co(TTFP) (β-pyrrole protons: 9.69) was completely brominated to Co(Br_8TTFP). The UV-visible spectrum of Co(Br_8TTFP) in H_2O showed λ_{max} of 450 nm, 570 nm and 658 nm, and that of Co(TTFP) in H_2O λ_{max} 424 nm and 538 nm.

Instrumental. The voltammetric measurements were accomplished with a three electrode potentiostat [Bioanalytical Systems (BAS) 100B/W]. A platinum-wire electrode separated from the analyte compartment by a medium porosity glass frit was used as an auxiliary electrode. A Ag/AgCl electrode supplied by BAS was used as a reference electrode, with a potential is approximately –45 mV relative to a saturated calomel electrode (SCE). A 3.0 mm diameter glassy carbon was employed as a working electrode for the redox reactions of cobaltporphyrin. Working electrode surfaces were highly polished with alumina paste before each experiment. Absorption spectra were recorded on a Jasco V-530 spectrophotometer equipped with an HMC-358 constant temperature cell holder, and an optical path length is 0.2 mm. Rotating disk experiments were conducted using a BAS RDE-1 instrument. Rotating ring-disk experiments were conducted using a AFRDE-5 rotator (Pine Instrument Company). A glassy carbon disk and glassy carbon disk/platinum ring electrodes were used. The ring collection efficiency (N = 0.17) was determined using a solution of ferrocene. The dioxygen concentration in O_2-saturated solutions was 1.2 mM at room temperature. All reported potentials were with respect to a Ag/AgCl electrode. Sulfuric acid (Fischer scientific), potassium hydroxide (Alfa ultra pure), potassium nitrate (Wako pure), and buffer solutions (Fischer scientific) were used as received. All solutions for electrochemical and spectroscopic experiments were prepared using doubly-distilled deionized water.

Results and Discussion

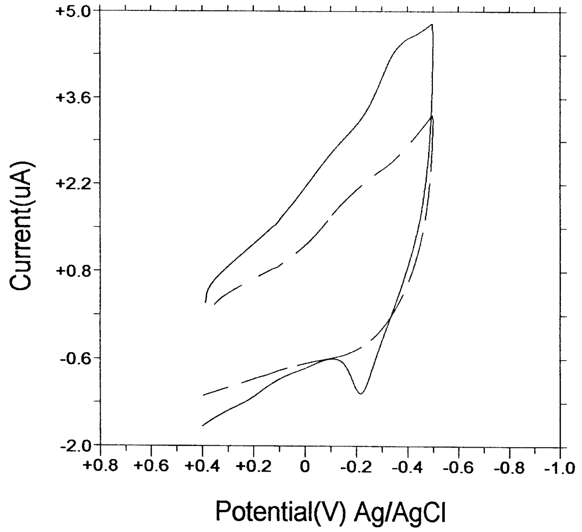

Figure 2. Cyclic voltammograms for the reduction of Co^{II}(Br_8TTFP)$(Y)_2$ in 0.05 M H_2SO_4 aqueous solution on the glassy carbon (100 mV/s scan rate), for dissolved Co^{II}(Br_8TTFP)$(Y)_2$, B: for dissolved 0.5 mM Co^{II}(Br_8TTFP)$(Y)_2$ (solid line) and for adsorbed Co^{II}(Br_8TTFP)$(Y)_2$ (dashed line).

Electroreduction of Co^{II}(Br_8TTFP)$(Y)_2$ at various pHs. Co^{II}(Br_8TTFP)$(Y)_2$ bears sixteen fluorides on the ortho and meta positions of phenyl groups bonded to *meso* positions of the porphyrin ring and four positive charges on the trimethylanilinium entities and eight bromides to β-pyrrole positions (see Figure 1). Figure 2 shows cyclic voltammetric curves (CVs) recorded at a glassy carbon electrode in a 0.5 mM Co^{II}(Br_8TTFP)$(Y)_2$ $\{Y = H_2O$ or $HO^-\}$ acidic solution. There are two cathodic responses, at –0.11 V and –0.37 V, for Co^{II}(Br_8TTFP)$(Y)_2$ dissolved in the 0.05 M H_2SO_4 aqueous solution (the solid line of Figure 2), but the CV of adsorbed Co^{II}(Br_8TTFP)$(Y)_2$ on the glassy carbon reveals one cathodic peak at –0.14 V in a pure 0.05 M H_2SO_4 solution (the dashed line of Figure 2). When it is compared with CVs of dissolved and adsorbed Co^{II}(Br_8TTFP)$(Y)_2$, the peak near –0.11 V measured from dissolved Co^{II}(Br_8TTFP)$(Y)_2$ evidently arises from adsorbed Co^{II}(Br_8TTFP)$(Y)_2$. The peak at –0.11 V shown in the solid line of Figure 2 matches the peak obtained in the dashed line of Figure 2. The peak at –0.37 V shown in the solid line of Figure 2 can be attributed to the reduction of Co^{II}(Br_8TTFP)$(Y)_2$ dissolved in the 0.05 M H_2SO_4 solution due to the absence of its peak in the adsorbed Co^{II}(Br_8TTFP)$(Y)_2$. The difference in the reduction potential between adsorbed and dissolved Co^{II}(Br_8TTFP)$(Y)_2$ suggests unusually favorable interactions between the electrode surface and the reduced cobalt center. The half-wave potential $E_{1/2}$ (–0.32 V) of the first reduction for adsorbed Co^{II}(Br_8TTFP)$(Y)_2$ is comparable to the $E_{1/2}$ (–0.31 V) of the first reduction for Co^{II}/Co^{I} couple of cobalt tetrakis-(*N*-methylpyridyl)-β-octabromoporphyrin Co^{II}(Br_8TMpyP) in 0.05 M H_2SO_4 solution.[25] The spectrum of reduced form generated from the reduction of Co^{II}(Br_8TTFP)$(Y)_2$ is obtained by holding the potential of the working electrode at –0.5 V under argon atmosphere in the 0.05 M H_2SO_4 solution. The optical spectra of the reduced form exhibits a Soret band maximum at 432 nm and Q bands at 558 nm and 579 nm. The change of Soret band from 450 nm to 432 nm indicates that the absorbance at 432 nm is a result of Co^{I}(Br_8TTFP)$(Y)_2$ obtained from metal-centered $1e^-$ reduction of Co^{II}(Br_8TTFP)$(Y)_2$.[10] Therefore the first

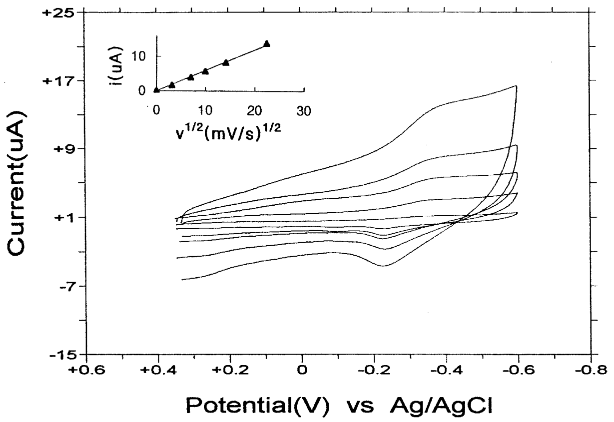

Figure 3. Cyclic voltammograms for the reduction of $Co^{II}(Br_8TTFP)(Y)_2$ in 0.05 M H_2SO_4 aqueous solution on the glassy carbon as a function of scan rate (10, 50, 100, 200, 500 mV/s). The inside plot represents the analysis of peak current vs (scan rate)$^{1/2}$ for the couple of Co(II)/Co(I).

reduction of $Co^{II}(Br_8TTFP)(Y)_2$ to $Co^{I}(Br_8TTFP)(Y)_2$ may be metal centered and involves one electron process.

Likewise there are two cathodic responses at –0.15 V and –0.37 V for $Co^{II}(Br_8TTFP)(Y)_2$ dissolved in a pH = 7 buffer solution containing 0.2 M KNO_3, but one reduction peak at near –0.15 V for $Co^{II}(Br_8TTFP)(Y)_2$ adsorbed on a glassy carbon electrode. And there are two cathodic responses at –0.17 V and –0.38 V for $Co^{II}(Br_8TTFP)(Y)_2$ dissolved in a pH = 10 buffer solution but one reduction peak at near –0.17 V for $Co^{II}(Br_8TTFP)(Y)_2$ adsorbed on a glassy carbon electrode. The peak currents of the first reduction of dissolved $Co^{II}(Br_8TTFP)(Y)_2$ increase linearly with the square root of the scan rate at pH = 1, 7, and 10, indicating a diffusion controlled process (see Figure 3).

Electrocatalytic reduction of dioxygen by $Co^{II}(Br_8TTFP)(Y)_2$. The presence of $Co^{II}(Br_8TTFP)(Y)_2$ in the 0.05 M H_2SO_4 solution results in a positive shift of the reduction potential for dioxygen reduction, and this process occurs at E_{pc} = –0.13 V. The reduction potential of dioxygen in the presence of $Co^{II}(Br_8TTFP)(Y)_2$ is shifted by 0.7 V in a positive direction compared with the shift in the absence of $Co^{II}(Br_8TTFP)(Y)_2$ at 100 mV/s. The effect of scan rate on the peak current for the reduction of dioxygen in the presence of $Co^{II}(Br_8TTFP)(Y)_2$ in the 0.05 M H_2SO_4 solution is shown in Figure 4. CVs for reduction of dioxygen with $Co^{II}(Br_8TTFP)(Y)_2$ adsorbed on the glassy carbon electrode in pure 0.05 M H_2SO_4 solution are identical to CVs measured in dissolved $Co^{II}(Br_8TTFP)(Y)_2$ in 0.05 M H_2SO_4 solution. The linearity shown in the plot of the peak current vs the square root of the scan rate indicates that electrocatalytic reduction of dioxygen is a diffusion controlled process when the dioxygen concentration is held constant. The first reduction process corresponding with the Co^{II}/Co^{I} couple upon adsorption of $Co^{II}(Br_8TTFP)(Y)_2$ on the glassy carbon electrode surface is located at E_{pc} = –0.11 V at 100 mV/s, and the electrocatalytic reduction peak potential of dioxygen is –0.13 V at the same scan rate.

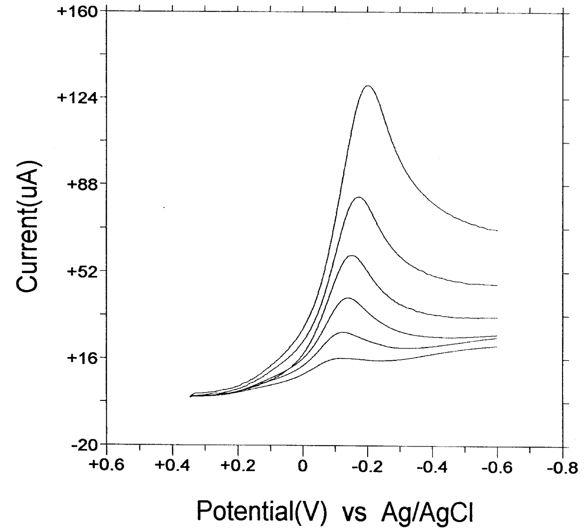

Figure 4. Cyclic voltammograms for the reduction of dioxygen in the presence of $Co^{II}(Br_8TTFP)(Y)_2$ in 0.05 M H_2SO_4 solution at different scan rates (10, 20, 50, 100, 200, 500 mV/s) on a glassy carbon electrode.

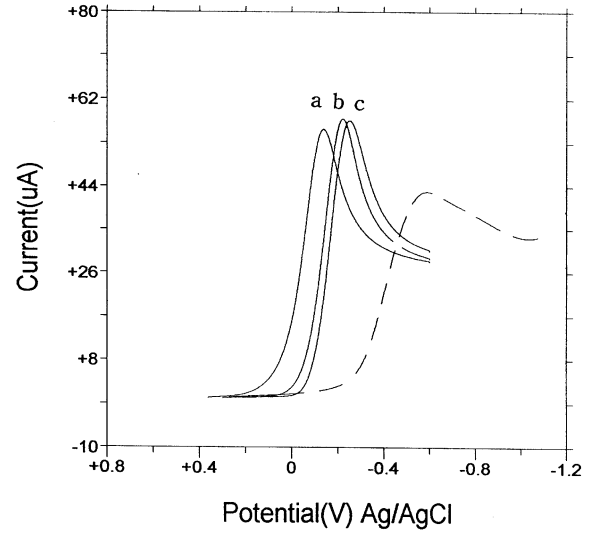

Figure 5. The effect of pH for the reduction potential of dioxygen in the presence of $Co^{II}(Br_8TTFP)(Y)_2$. **a**: pH=1, **b**: pH=7, **c**: pH=10, dashed line: bare electrode at pH=1 in the absence of $Co^{II}(Br_8TTFP)(Y)_2$.

Meanwhile, Figure 5 illustrates the effect of pH on the reduction potential of dioxygen in the presence of $Co^{II}(Br_8TTFP)(Y)_2$. The reduction potential of dioxygen in the presence of $Co^{II}(Br_8TTFP)(Y)_2$ coincides with the reduction potential of $Co^{II}(Br_8TTFP)(Y)_2$ adsorbed on a glassy carbon electrode in various pH solutions. This agreement indicates that the potential governing dioxygen reduction is the reduction potential of $Co^{II}(Br_8TTFP)(Y)_2$ to $Co^{I}(Br_8TTFP)(Y)_2$, and this is consistent with an EC mechanism that has been proposed for other water-soluble metalloporphyrins.[25] The reduction potential of dioxygen at bare electrode in the absence of $Co^{II}(Br_8TTFP)(Y)_2$ is almost the same in various pH solutions (pH = 1, 7, 10). Based on these observations, it is suggested that $Co^{I}(Br_8TTFP)(Y)_2$ generated from adsorbed $Co^{II}(Br_8TTFP)(Y)_2$ is an active catalyst in the electrocata-

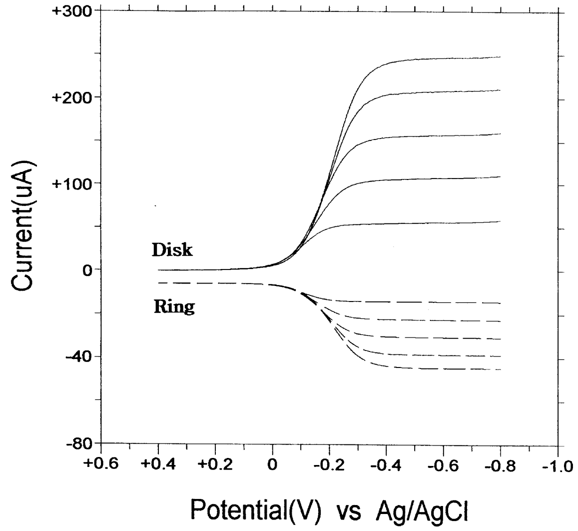

Figure 6. RRDE voltammograms (E_r = +1.0 V) of dioxygen reduction for an dioxygen-saturated solution of $\mathrm{Co^{II}(Br_8TTFP)(Y)_2}$ in 0.05 M $\mathrm{H_2SO_4}$ solution at 10 mV/s scan rate, the rotation rates are 100, 400, 900, 1600, and 2500 rpm.

lytic reduction of dioxygen to HOOH.

Further investigations using hydrodynamic voltammetry {rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE)} confirm the formation of hydrogen peroxide as a major product of dioxygen reduction by reduced form $\mathrm{Co^{I}(Br_8TTFP)(Y)_2}$. RRDE voltammograms obtained from the dissolved solution of $\mathrm{Co^{II}(Br_8TTFP)(Y)_2}$ are shown in Figure 6. The disk potential is scanned from +0.6 V to –1.0 V at 10 mV/s in dioxygen-saturated 0.05 M $\mathrm{H_2SO_4}$ solution while the potential of the ring electrode is maintained at +1.0 V. A Levich plot of the disk limiting current against the square root of rotation rate is linear, indicating the occurrence of a diffusion controlled reaction. Ring currents corresponding with the formation of HOOH have been observed under these conditions. The result indicates that the major product of dioxygen reduction by $\mathrm{Co^{I}(Br_8TTFP)(Y)_2}$ is HOOH (almost 100%) by $2e^-$ transfer. The yield of HOOH was calculated by the equation, %HOOH = $(-i_r/Ni_d)/100$ where i_r and i_d are the ring and disk limiting currents, and N is the collection coefficient. Koutecky-Levich plots for dioxygen reduction catalyzed by $\mathrm{Co^{I}(Br_8TTFP)(Y)_2}$ are shown in Figure 7. The dashed line was calculated for the diffusion-convection limited reduction by two electrons.[22] The solid line is obtained from the plateau current of curves. The number of electrons transferred estimated from the slope of Koutecky-Levich plot reveals that the dioxygen reduction by $\mathrm{Co^{I}(Br_8TTFP)(Y)_2}$ occurs in two-electron process. Limiting currents obtained from the plateau result from the electrocatalytic reduction of dioxygen to HOOH by $\mathrm{Co^{I}(Br_8TTFP)(Y)_2}$ acting as a catalyst. On the basis of these results, it can be concluded that $\mathrm{Co^{I}(Br_8TTFP)(Y)_2}$ catalyzes the reduction of dioxygen in a process similar to that observed with $\mathrm{Co^{I}(Br_8TTFP)(Y)_2}$, but the species for the electrocatalytic reduction may be different from that reported for $\mathrm{Co^{I}(Br_8TTFP)(Y)_2}$. Although $\mathrm{Co^{II}(Br_8TTFP)(Y)_2}$ is a highly electron deficient non-planar porphyrin, such as $\mathrm{Co^{II}}$ ($\mathrm{Br_8TMpyP}$), the stable cobaltporphyrin $\mathrm{Co^{II}(Br_8TTFP)(Y)_2}$ adsorbs strongly on the glassy carbon electrode.

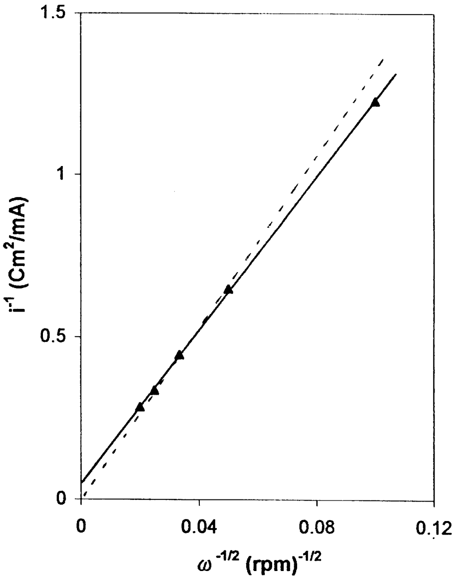

Figure 7. Koutecky-Levich plots for dioxygen reduction catalyzed by $\mathrm{Co^{II}(Br_8TTFP)(Y)_2}$ in 0.05 M $\mathrm{H_2SO_4}$ solution at 10 mV/s scan rate on a glassy carbon disk. The dashed line was calculated for the diffusion-convection limited reduction by two electrons.

In summary, the adsorbed $\mathrm{Co^{II}(Br_8TTFP)(Y)_2}$ but not the dissolved cobaltporphyrin reduces initially to $\mathrm{Co^{I}(Br_8TTFP)(Y)_2}$, and the electrocatalytic reduction of dioxygen by $\mathrm{Co^{I}(Br_8TTFP)(Y)_2}$ generated from the $1e^-$ reduction of $\mathrm{Co^{II}(Br_8TTFP)(Y)_2}$ results in the formation of HOOH by $2e^-$ process.

Acknowledgment. This paper was supported by CNU Research Foundation.

References

1. Forshey, P. A.; Kuwana, T. *Inorg. Chem.* **1981**, *19*, 693.
2. Forshey, P. A.; Kuwana, T.; Kobayashi, N.; Osa, T. *Adv. Chem. Ser.* **1982**, *201*, 601.
3. Ozer, D.; Harth, R.; Mor, U.; Bettelheim, A. *J. Electroanal. Chem.* **1989**, *266*, 109.
4. Ozer, D.; Parash, R.; Broitman, F.; Mor, V.; Bettelheim, A. *J. Chem. Soc., Faraday Trans.* I **1984**, *80*, 1139.
5. Bettelheim, A.; Ozer, D.; Parash, R. *J. Chem. Soc., Faraday Trans. I* **1983**, *79*, 1555.
6. Creager, S. E.; Raybuck, S. A.; Murray, R. W. *J. Am. Chem. Soc*. **1986**, *108*, 4225.
7. Creager, S. E.; Murray, R. W. *Inorg. Chem*. **1987**, *26*, 2612.
8. Perree-Fauvet, M.; Gandemer, A.; Bonvoison, J.; Girerd, J. J.; Boucly-Goester, C.; Boucly, P. *Inorg. Chem*. **1989**, *28*, 3533.
9. Tsang, P. K. S.; Sawyer, D. T. *Inorg. Chem*. **1990**, *29*, 2848.
10. Sazou, D.; Araullo-McAdams, C.; Han, B. C.; Franzen, M. M.; Kadish, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 7879.
11. Bettelheim, A.; Chan, R.; Kuwana, T. *J. Electroanal.*

Chem. **1980**, *110*, 93.

12. Ni, C. L.; Anson, F. C. *Inorg. Chem*. **1985**, *24,* 4754.
13. Durand, R. R.; Anson, F. C. *J. Electroanal. Chem*. **1982**, *134*, 273.
14. Shi, C.; Anson, F. C. *J. Electroanal. Chem*. **1982**, *134*, 273.
15. Shi, C.; Anson, F. C. *Inorg. Chem.* **1995**, *34*, 4554.
16. Steiger, B.; Anson, F. C. *Inorg. Chem.* **1994**, *33*, 5767.
17. Steiger, B.; Anson, F. C. *Inorg. Chem*. **1995**, *34*, 3355.
18. Collman, J. P.; Chang, L. L.; Tyvoll, D. A. *Inorg. Chem*. **1995**, *34*, 1311.
19. Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E. *Angew. Chem*., *Int. Ed. Engl.* **1994**, *33*, 1537.
20. Collman, J. P.; Denisevich, P.; Kanai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc*. **1980**, *102*, 6027.
21. Chang, C. K.; Liu, H. Y.; Abdalmuhdi, I. *J. Am. Chem. Soc*. **1984**, *106*, 2726.
22. Karaman, R.; Jeon, S.; Almarsson, O.; Blasko, A.; Bruice, T. C. *J. Am. Chem. Soc*. **1992**, *114*, 4899.
23. Jeon, S.; Almarsson, O.; Karaman, R.; Blasko, A.; Bruice, T. C. *Inorg. Chem*. **1993**, *32*, 2562.
24. Choi, Y-K.; Jeon, S.; Park, J-K.; Chjo, K-H. *Electrochim. Acta* **1997**, *42*, 1287.
25. D'Souza, F.; Deviprasad, G. R.; Hsieh, Y.-Y. *J. Electroanal. Chem*. **1996**, *411*, 167.
26. D'Souza, F.; Hsieh, Y.-Y.; Deviprasad, R. G. *J. Electroanal. Chem.* **1997**, *426*, 17.
27. Jeon, S.; Lee, H. K.; Kim, S. M. *Bull. Korean Chem. Soc.* **1998**, *19*, 825.