

Adsorption of Macrocyclic Cobalt Complex on a Glassy Carbon Electrode for the Electrocatalytic Reduction of O₂

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It was found that the adsorption of a cobalt(III) complex with a macrocyclic ligand, *C-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane* (hmc), was induced on a glassy carbon electrode by heavily oxidizing the electrode surface. Adsorption properties are discussed. The glassy carbon electrode with the adsorbed complex was employed to see the catalytic activities for the electro-reduction of O₂. In the presence of oxygen, reduction of (hmc)Co³⁺ showed two cathodic waves in cyclic voltammetry. Compared to the edge plane graphite electrode at which two cathodic waves were also observed in a previous study, catalytic reduction of O₂ occurred in the potential region of the first wave while it happened in the second wave region with the other electrode. A rotating disk electrode after the same treatment was employed to study the mechanism of the O₂ reduction and two-electron reduction of O₂ was observed. The difference from the previous results was explained by the different reactivity of the (hmc)CoOOH²⁺ intermediate, which is produced after the two-electron reduction of (hmc)Co³⁺ in the presence of O₂.

Introduction

A cobalt complex with a macrocyclic ligand, *C-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane* [(hmc)Co³⁺], has been reported as a catalyst for the electrochemical reduction of O₂.^{1,2} Different electrodes including a glassy carbon and a roughly polished edge plane graphite (EPG) were employed. At the glassy carbon electrode the electrochemistry of the complex molecules followed a diffusion controlled process but its adsorption was observed on the other electrode. The overall reaction scheme appeared the same at both electrodes but some differences in the reactivities of the catalyst and intermediates were reported. It was first reduced to (hmc)CoOOH²⁺ intermediate by two-electron transfer in the presence of O₂ and further reduced to (hmc)Co²⁺ and H₂O₂ at more negative potentials.^{1,2} Such two step reductions appeared as two separated cathodic waves in cyclic voltammetry. Since O₂ could be catalytically reduced only after the second reduction, the reduction of (hmc)CoOOH²⁺ intermediate acted as a barrier in the overall catalytic reduction of O₂. Recently, it was reported that the (hmc)CoOOH²⁺ reactivity was highly affected by the kind and the surface states of the carbon electrodes.³ The oxidation of the carbon electrodes produced surface functional groups and some of them such as carboxylic or phenolic groups supplying protons made the surface more acidic. As the reaction of (hmc)CoOOH²⁺ was pH-dependent, it was also affected by the density of those groups. Eventually, controlling the surface state or solution pH is a way to affect the overall reduction of O₂.

In the present study, it was found that the adsorption of the (hmc)Co²⁺ complex could be induced by simply electrochemically oxidizing the glassy carbon electrode surface. Adsorption of metal complexes or organic compounds on the glassy carbon electrode surface is relatively weak compared to the EPG electrode probably because of its hydrophobic surface and fewer surface functional groups.^{4,5} There are several reports about the induced adsorption of

some compounds by similar treatments.⁶⁻⁸ Bowers *et al.* showed incorporation of metal cations and aromatic organic redox species by oxidizing the electrode in sulphate, carbonate, and phosphate electrolytes,⁹ but such incorporation appeared to be electrolyte dependent because it did not happen in other electrolyte, for example, CF₃COOH solution as will be discussed in this study. Possible interactions between the (hmc)Co²⁺ and the surface will be discussed to explain the adsorption.

The electrode on which the cobalt catalyst was adsorbed was employed to study the electrocatalytic reduction of O₂. Different reactivities of the cobalt intermediate, the (hmc)CoOOH²⁺ complex, on the pretreated electrode will be compared with the previous results.^{1,2}

Experimental

Materials. Commercial reagent grade chemicals were used as received. Macrocyclic ligand (hmc) and [(hmc)Co](CF₃SO₃)₂ were synthesized according to procedures and stored under argon in the refrigerator.¹⁰⁻¹² The distilled water was further purified by passage through a purification train (Milli-Q, Millipore Co.) and used for the solution preparation. Glassy carbon rod (Tokai Carbon Co., GC-20S) was mounted to stainless steel shaft with a heat shrinkable polyolefin tubing.

Apparatus and procedures. Electrochemical experiments were carried out in a home made two-compartment cell closed with a Teflon cap through which the electrodes and gas bubbling system were fitted. A Pine Instrument Co. potentiostat (Model RDE 3) and an X-Y recorder (Yokogawa Co. Model 3025) were used for both cyclic voltammetry and rotating disk voltammetry measurements. The working electrode was the glassy carbon electrode (area, 0.28 cm²). For the purpose of rotating the electrode, it was fitted to a commercial rotator (Pine Instrument Co., Model AFMSRX). To obtain a clean surface, it was grinded with 600 grit SiC paper, next with 1200, and finally polished

with 0.3 μm alumina. This polished electrode was sonicated for about 30 seconds in a purified water before use. After the electrochemical oxidation treatment, this procedure was followed to get a flat and low current background voltammogram free of surface redox waves.

For the electrochemical oxidation of the glassy carbon electrode, the potential was initially scanned to 2.0 V (vs Ag/AgCl), held for 1 or 2 minutes, and reversed to -0.5 V in 0.1 M CF_3COOH supporting electrolyte. Several repeated scans between 0.5 V and -0.5 V after the oxidation treatment gave a stable background current. To adsorb $(\text{hmc})\text{Co}^{2+}$ on the pretreated electrode, it was dipped into a 0.5 mM $(\text{hmc})\text{Co}^{2+}$ solution containing no oxygen in 0.1 M CF_3COOH for about 30 seconds. Even though $(\text{hmc})\text{Co}^{2+}$ was adsorbed on the electrode, its form was presumed to be in its oxidized state if the potential of the several hundred mV positive of its formal potential was applied. All the experiments followed this procedure unless otherwise mentioned. A freshly prepared electrode was used for each measurement.

Potentials were measured and quoted with respect to a Ag/AgCl (3 M NaCl) reference electrode with a potential of 0.22 V vs NHE. Supporting electrolyte used through the whole experiments was 0.1 M CF_3COOH . All the experiments were conducted at the ambient temperature (22 ± 2 °C). Parameters employed in the calculation of Levich currents for the reduction of O_2 were: kinematic viscosity of water, 0.01 cm^2/s ; $[\text{O}_2]$ in air saturated solutions, 0.28 mM; diffusion coefficient of O_2 , 1.7×10^{-5} cm^2/s .²

Results and Discussion

Induction of adsorption of $(\text{hmc})\text{Co}^{2+}$ on an electrochemically oxidized glassy carbon electrode.

The redox reactions of $(\text{hmc})\text{Co}^{2+/3+}$ couple followed diffusion controlled process at a polished glassy carbon electrode as indicated in our previous report.¹ Figure 1A is a cyclic voltammogram obtained in 0.1 M CF_3COOH using a glassy carbon electrode with a mirror-like surface polished with 0.3 μm alumina. Figure 1B is a set of voltammograms from a solution containing 0.4 mM $(\text{hmc})\text{Co}^{2+}$ with the electrode used for Figure 1A. Levich¹³ and Landles-Sevcik¹⁴ plots from rotating disk voltammetry and cyclic voltammetry, respectively, showed linearity for the reduction of $(\text{hmc})\text{Co}^{3+}$ and the oxidation of $(\text{hmc})\text{Co}^{2+}$.¹ However, at high rotation rates or scan rates, deviations from the linearity, especially, for the electro-oxidation of the $(\text{hmc})\text{Co}^{2+}$ complex were observed and this was explained by the need of axial coordination of a suitable ligand to the metal center for its oxidation in a previous report.¹⁵ No evidence of the adsorption of the complexes was found in the experiment of Figure 1B and the currents were mainly from the dissolved species.

When the polished electrode was heavily electro-oxidized, huge background current was measured as in Figure 1C. The pretreatment of the electrode was carried out by initially scanning the potential to 2.0 V, holding it for 2 min, and reversing its direction to -0.5 V in pure supporting electrolyte. The voltammogram showed a large reduction current at first and a stable shape resulted after several repeated scans within the potential range shown in the Figure.

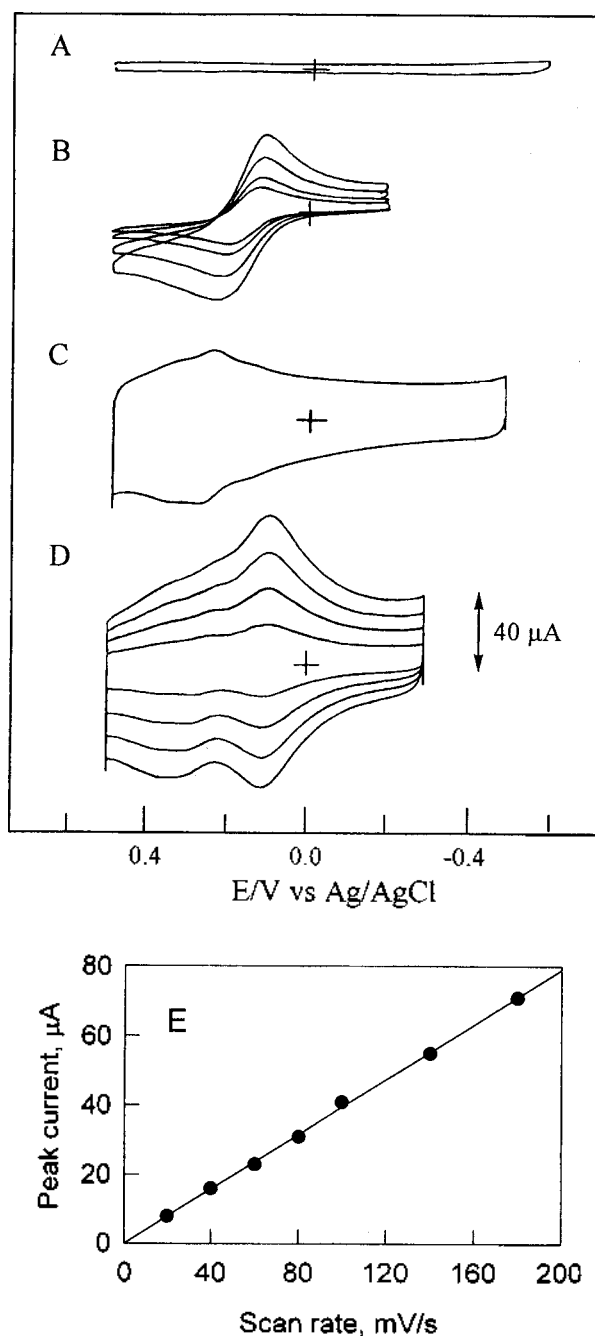


Figure 1. (A) Cyclic voltammogram in pure supporting electrolyte with a glassy carbon electrode polished with 0.3 μm alumina. Scan rate, 50 mV/s. (B) Same as (A) except the solution contains 0.4 mM $(\text{hmc})\text{Co}^{2+}$. Scan rates used were 10, 20, 50, 100 mV/s from the voltammogram of the lowest current. (C) Same as (A) except the electrode was electrochemically oxidized as explained in the text. Scan rate, 50 mV/s. (D) Cyclic voltammograms in pure supporting electrolyte after the $(\text{hmc})\text{Co}^{2+}$ was adsorbed on the electrode used in (C). Scan rates used were 20, 40, 60, 80 mV/s from the voltammogram of the lowest current. (E) Cathodic peak currents in (D) after the subtraction of the background currents against scan rates. Supporting electrolyte, 0.1 M CF_3COOH .

This kind of observation was already reported and explained in early reports.^{4,6} The background current was much

higher than a typical charging current which is due to a double layer capacitance and small redox peaks were shown at around 0.25 V. Many new surface functional groups containing oxygen atoms such as carboxylic acids, acid anhydrides, alcohols, phenols, and quinones are known to be formed during the oxidation process⁴ and the increased currents were explained by the faradaic reactions of some of such groups, especially, quinones.^{4,6,16} The oxidized surface of the electrode could be converted to the original state used for Figure 1A by polishing it with grit SiC papers and alumina powder as explained in the experimental section.

Induction of the adsorption of (hmc)Co²⁺ molecules was realized by simply dipping the pretreated electrode into the solution containing the complex. After transferring it to the pure supporting electrolyte, voltammograms of Figure 1D were the results. The adsorption of the species was quick and quite stable redox waves with a formal potential at 0.10 V persisted during several initial potential scans (more repeated scans resulted in the slow decrease of the peak currents because of the loss of the complex molecules into the solution). The cathodic peak currents after the subtraction of the background currents were linearly proportional to the scan rates as shown in Figure 1E.¹⁷ This result indicates that the (hmc)Co²⁺ complex was adsorbed on the electro-oxidized glassy carbon electrode. On a roughly polished edge plane graphite (EPG) electrode in a previous study, adsorption of the same species also occurred² and the nature of interaction of the complex with the electrode surface may be similar to the glassy carbon electrode because the EPG electrode has affluent surface functional groups as indicated by large background currents. For the adsorbed species on the electro-oxidized glassy carbon surface, the peak width at the half-height of the cathodic peak was measured as 140 mV at scan rate of 50 mV/s. That value is more than the Nernstian value of 90.6 mV¹⁷ and this can be interpreted as repulsive interactions among molecules adsorbed.¹⁸ However, on the EPG surface, the peak shape was narrower and attractive interactions exist.² The formal potential of the (hmc)Co^{3+/2+} couple is 0.10 V in their adsorbed state and more negative than that in the dissolved state which was measured as 0.16 V.

The concentration dependence of the quantity of adsorbed (hmc)Co²⁺ was estimated by using single step chronocoulometry.¹⁹ The potential was stepped from -0.2 V to +0.5 V and intercepts from the charge vs (time)^{1/2} plots were measured at different concentrations of (hmc)Co²⁺ in the solution. Because of the large background current as in Figure 1C, the intercept obtained in pure supporting electrolyte was subtracted from each measurement. Figure 2A is the result of the dependence of the surface coverage of adsorbed (hmc)Co²⁺ on the concentration of the complex in the solution. It reaches a limiting value of 2.3×10^{-9} mol/cm² (over geometric area) at the concentration of about 50 μ M of (hmc)Co²⁺. The amount of surface coverage is more than a typical value of 5.0×10^{-10} mol/cm² estimated in the case of monolayer adsorption.⁴ Multilayer might be formed over the surface but its formation seems less likely considering the positive charges of the complexes. Another possibility is that micropores were formed during the pretreatment⁶ and microscopic area available for the adsorption is much larger than the geometric area.

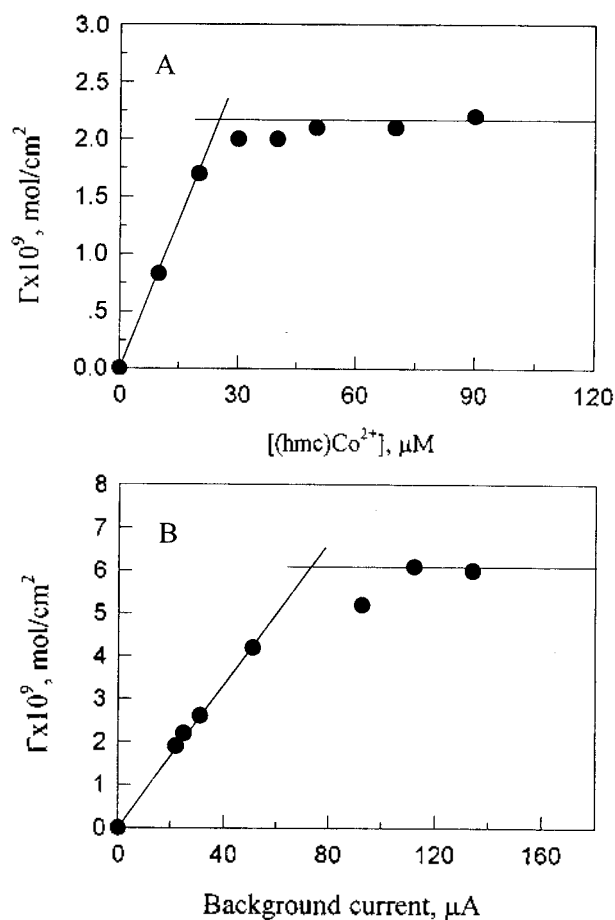


Figure 2. Concentration dependence of the quantity of (hmc)Co²⁺ adsorbed on the electro-oxidized glassy carbon electrode. (B) Dependence of the quantity of adsorbed (hmc)Co²⁺ on the background current height.

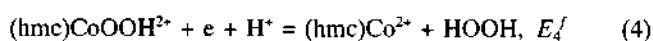
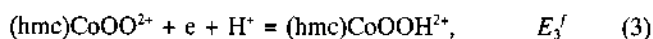
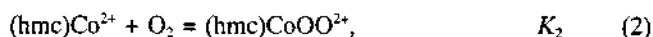
In Figure 2B, the surface coverage shows increase with background current which grew as the oxidative treatment time became longer. In this experiment the quantity of adsorbed (hmc)Co²⁺ was measured from the cyclic voltammograms in the pure supporting electrolyte after the pretreated electrode was immersed into the solution containing 0.5 mM (hmc)Co²⁺. The height of the background current is a good indication of the degree of electro-oxidation of the electrode surface since the faradaic reactions of some of the surface functional groups produced during the pretreatment contribute to the total current.^{4,5,20} If micropores were newly formed as more electro-oxidation was carried out, the microscopic area would increase and more sites would be available for the adsorption of the complex. However, even though the height of the background current continuously increased, the surface coverage was saturated in about 6.0×10^{-9} mol/cm², which means that no more sites were available for the adsorption. The number of micropores might be saturated or the diffusion of the cobalt complex into the pores might be limited at a certain depth and the adsorption stopped.

At present, the origin of interaction of the (hmc)Co²⁺ with the pretreated electrode surface is not clear. One possible explanation is an axial coordination of the surface functional groups to the cobalt center. However, even after the axial

position of the cobalt center was substituted by NCS⁻ anion, adsorption of the cobalt complex with the NCS⁻ anion attached occurred as confirmed by the fact that the adsorbed species showed more negative formal potential which was the value anticipated with NCS⁻ anion as the axial ligand.¹⁵ This result means that the adsorption is not from the coordination to the axial position of the cobalt complex by surface functional groups. Ionic exchange of the protons of the surface carboxylic groups by (hmc)Co²⁺ cations is another possibility. Some alkali metal ions and organic compounds were adsorbed at electrochemically pretreated electrodes.^{6-8,21} Their adsorption depended on the solution pH prepared for a pretreatment or adsorption processes. Interaction between the surface and hydrophobic organic ligand can also be considered.²² The electro-oxidation of the glassy carbon electrode makes the surface more hydrophilic,⁵ but hydrophobic organic surface functional groups also may be produced. To understand the origin of the adsorption of the (hmc)Co²⁺ on the oxidized carbon surface, more studies need to be carried out.

O₂-electrocatalysis by (hmc)Co²⁺ adsorbed on a glassy carbon electrode. It was reported that the (hmc)Co²⁺ complex played a catalytic role in the electro-reduction of O₂ when it was dissolved in solution or adsorbed on the EPG surface.^{1,2} A reaction scheme was described in the previous two reports.^{1,2} With the catalyst adsorbed on the glassy carbon electrode in the present work, it will be interesting to see how the catalytic reduction of O₂ proceeds and compare it with the results in different environments. Figure 3A is a voltammogram in an air saturated solution with an oxidatively pretreated glassy carbon electrode as in Figure 1C. Reduction of O₂ occurred at about -0.2 V, which was a little more positive potential than that with the untreated glassy carbon electrode in the same solution. The oxidatively treated electrode is prone to take impurity ions from the solution²¹ and they may catalyze the reduction of O₂ giving a potential shift in the positive direction. Actually, the potential was influenced by the ways of cleaning the cell and it is necessary to be careful in preparing the cell system. There is another explanation for the shift of the potential that surface groups produced during the electro-oxidation work as catalysts.⁶

Figure 3B is a voltammogram in the same condition as in Figure 3A with the electrode on which the (hmc)Co²⁺ complex was adsorbed, and two cathodic waves were measured at 0.20 V and 0.05 V. In both previous cases when the complexes were in solution and adsorbed on EPG surface, the same reaction scheme was employed to explain the electrochemical responses.^{1,2}



where E^f and K denote a formal potential and an equilibrium constant, respectively. In both systems, two cathodic waves were shown and the first wave was a two-electron reduction of (hmc)Co³⁺ in the presence of O₂ into (hmc)CoOOH²⁺ via reactions 1 through 3. The second one was a

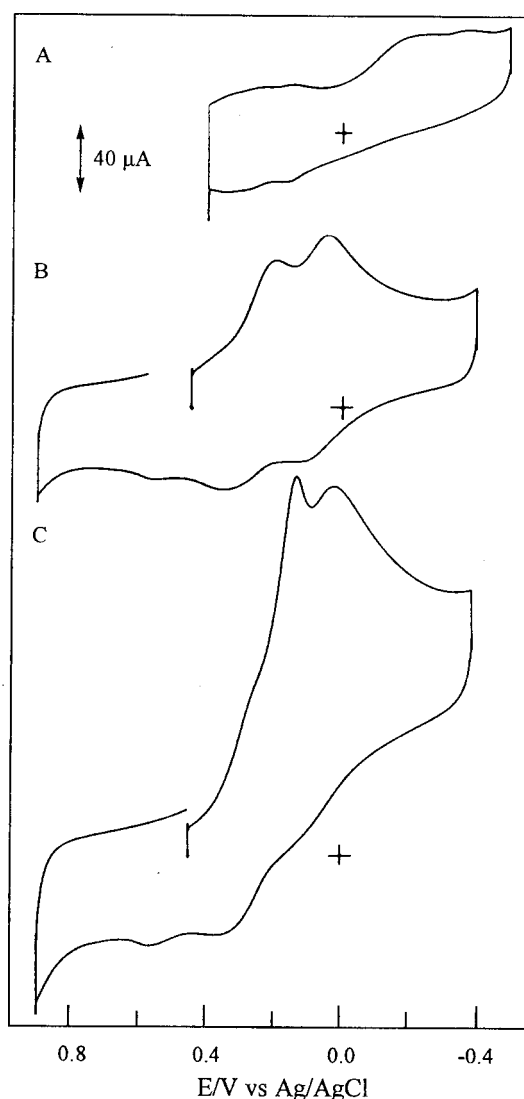


Figure 3. (A) Cyclic voltammogram in an air saturated solution with the electro-oxidized glassy carbon electrode used in Figure 1C. (B) Same as (A) except that (hmc)Co²⁺ was adsorbed on the electrode. (C) Repeat of (B), but the solution saturated with pure O₂ was used. Supporting electrolyte, 0.1 M CF₃COOH. Scan rate, 50 mV/s.

one-electron reduction of (hmc)CoOOH²⁺ as in Eq. (4). The final product, (hmc)Co²⁺, could bind another remaining O₂ to give (hmc)CoOO²⁺ and further consequent reductions covering Eqs. (3)-(4) continued. Electrocatalytic reduction of O₂ occurred in the potential region of the second wave and this cathodic peak grew with the increase in O₂ concentration. However, with the complex on the electro-oxidized glassy carbon electrode in the present study, a careful observation of the voltammogram of Figure 3B led to different interpretation. If voltammograms were measured repeatedly under the condition used in Figure 3B, the second peak decreased while the first one kept its constant shape. This implies that the second wave was due to the catalyst unreacting with O₂ and decreased with time as it was lost into the solution. Actually, the voltammogram of Figure 3B was the first measurement after the electrode coated with the catalyst was freshly prepared. After several measurements, re-

moving oxygen from the solution should give a voltammogram like Figure 1D but the redox waves of the adsorbed catalyst almost disappeared because of its dissolution. Even with the electrode on which only a small amount of the catalyst molecules remained at this stage, addition of O_2 into the solution gave the same wave as the first cathodic wave of the Figure 3B while the current of the second one was almost negligible. In the potential region of the first wave, the O_2 was catalytically reduced and only a fraction of the adsorbed catalyst molecules was used for the reaction. The reactions 1 through 4 rather than the reactions including only Eqs. (1), (2), and (3) in the previous results occurred at close potentials and gave one voltammetric wave. The remaining complex not participating in the reaction with O_2 was reduced at a more negative potential, 0.05 V, which is close to that in the case of no O_2 presence as in Figure 1D.

Figure 3C is another result to show that the catalytic O_2 reduction appears in the potential region of the first cathodic wave. If the O_2 concentration was increased by bubbling the solution with pure O_2 gas instead of air, a large increase in current of the first cathodic wave was observed but no change with the second one at about 0.05 V. Additional supply of O_2 led to more catalytic cycles for the reduction of substrates and resulted in the enhancement of the current. This is a different result from that of the previous study with the complex on EPG surface where the reduction of $(hmc)CoOOH^{2+}$ proceeded at a more negative potential and appeared as a separate cathodic wave.² On the electrochemically oxidized glassy carbon electrode, the reduction of the cobalt hydroperoxide intermediate needed less overpotential and overlapped with the preceding reactions. Recently, it was reported that the reduction of $(hmc)CoOOH^{2+}$ intermediate was pH-dependent and affected by the surface states of carbon electrodes.³ Pretreatment such as electrochemical oxidation produced more surface functional groups and some of them made the surface more acidic, which enhanced the activities of the reactions involving proton-transfer.²³ The electro-oxidized glassy carbon electrode surface became quite acidic (even more than 0.1 M CF_3COOH supporting electrolyte) and the $(hmc)CoOOH^{2+}$ was reduced at a more positive potential than on EPG surface which had probably less density of surface functional groups.

Rotating disk voltammetry. Rotating disk voltammetry has been a useful tool giving information about the mechanisms of the catalyzed reductions of dioxygen. Especially, the number of electrons involved and the rate constant between the catalyst confined on electrode surface and the substrate can be determined.^{24,25} Figure 4A shows current-potential curves recorded in an air saturated solution with a rotating glassy carbon electrode on which the $(hmc)Co^{2+}$ complex was adsorbed. Because of the gradual desorption of the complex during the measurement a freshly prepared electrode was used for each voltammogram. In Figure 5, limiting currents were plotted against the square roots of the rotation speeds according to the Levich equation.²⁶ They are denoted as filled squares and above the solid line which was calculated based on the diffusion limiting reduction of O_2 to H_2O_2 . A similar positive deviation was also observed with the catalysts on the EPG surface and it was assigned to the additional contribution from the reduction of H_2O_2

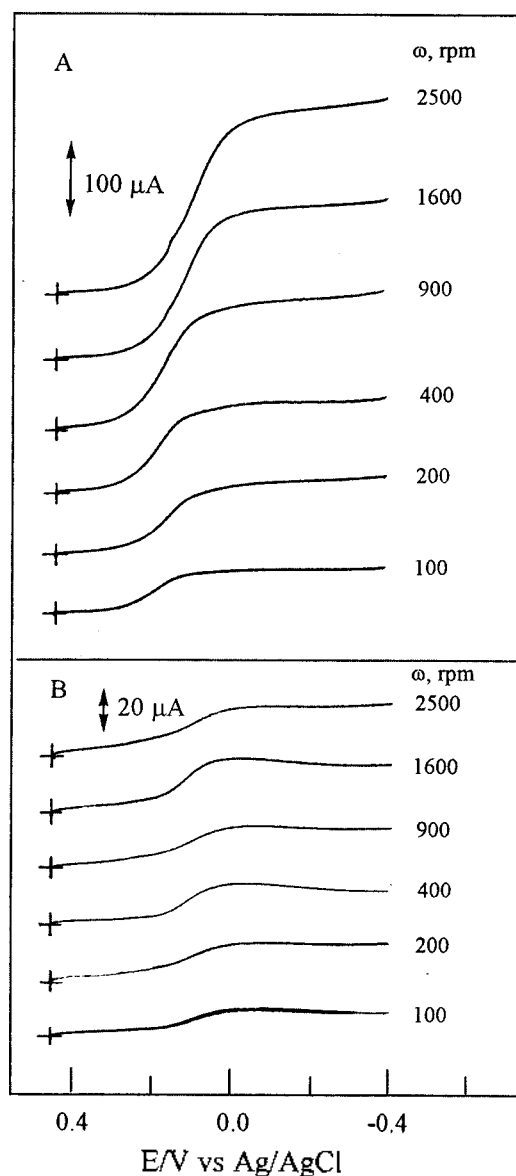


Figure 4. (A) Current-potential curves for the reduction of O_2 in an air saturated solution with a rotating glassy carbon electrode on which $(hmc)Co^{2+}$ was adsorbed. (B) As in (A) except the solution contained 0.28 mM H_2O_2 and no O_2 . The electrode rotation rates were indicated. Supporting electrolyte, 0.1 M CF_3COOH . Scan rate, 5 mV/s. The cross marks are the starting points of the curves which indicate zero currents.

since it slowly reacts with $(hmc)Co^{2+}$.^{2,27} In fact, in another H_2O_2 solution containing no O_2 , plateau currents were measured with the same electrode as used for Figure 4A and are illustrated in Figure 4B. The concentration of 0.28 mM of H_2O_2 for the solution was employed for the experiment with the assumption that the reduction of the O_2 in the air saturated solution would produce H_2O_2 of an equivalent level of concentration. The plateau currents were almost rotation speed independent, which would be resulted when the reaction rate between the catalyst and the substrate is slow. The plateau currents in Figure 4B were subtracted from those in Figure 4A and the corrected values were plotted as filled circles in Figure 5. They were quite close to the

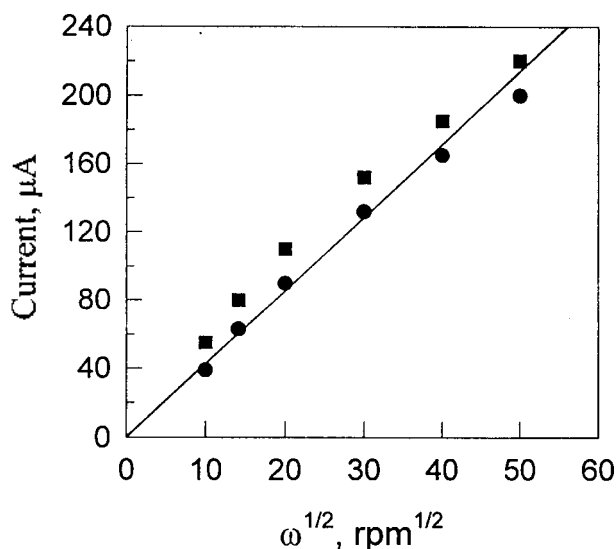


Figure 5. Levich plots of the plateau currents (■) measured in Figure 4A and another plots after the subtraction of the currents for the reduction of H₂O₂ (●). The solid line follows the calculated currents for the diffusive convection controlled reduction of O₂ to H₂O₂.

solid line and it might be concluded that the O₂ was catalytically reduced to H₂O₂ which was further reduced slowly.

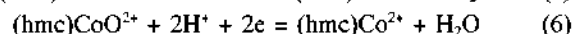
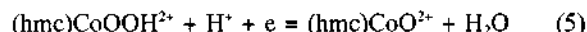
The negative deviation from the Levich plot at high rotation rates makes the evaluation of the second-order rate constant of the complex with O₂ possible by converting the data for Koutecky-Levich plot.²⁵ However, in this experiment, that evaluation was not tried because of the ambiguities in the values of the plateau currents of Figure 4A and 4B. They were not constant at repeated measurements because the complex was gradually lost into the solution. Furthermore the unknown fraction of the catalyst reacting with O₂ was another reason for the difficulty in the calculation of the rate constant.

The catalytic reduction waves in the rotating disk voltammetry were measured at more negative potentials than the wave in the cyclic voltammetry. The half-wave potentials shifted in a negative direction as the rotation speed of the electrode increased as shown in Figure 4A. On the electrochemically oxidized glassy carbon electrode the reduction of (hmc)CoOOH²⁺ which is a rate determining step was activated by the enhanced acidity due to the surface functional groups and its potential appeared quite positive in the cyclic voltammogram. Active protonation from the surface is presumed to precede in the reduction of (hmc)CoOOH²⁺.³ In rotating disk voltammetry, however, the (hmc)CoOOH²⁺ might be rapidly swept out of the surface before the protonation and its reduction requires larger overpotential.

Concluding remarks. On the electrochemically oxidized glassy carbon electrode, the reduction of (hmc)Co³⁺ with the O₂ present showed one wave since the reduction potential of the (hmc)CoOOH²⁺ intermediate shifted to the positive direction and all the reactions of Eqs. (1) through 4 occurred at close potentials. One main issue in the studies of O₂ electrocatalysis is to make it occur at more positive potential. With other transition metal complexes as catalysts for O₂ reduction, only one catalytic reduction wave was gen-

erally observed.^{24,28} A generally known barrier is the first one-electron transfer to O₂²⁹ but the reduction of (hmc)CoOOH²⁺ appeared as a barrier in the present system. Its overpotential has much decreased by adsorbing the catalysts on the electro-oxidized glassy carbon electrode. Controlling the carbon electrode surface seems to be one of the ways to shift the reduction potential in the electrocatalysis of O₂ in a positive direction.

Another important issue is the possibility of four-electron reduction without yielding H₂O₂ as an intermediate. During the reduction of (hmc)Co³⁺ in the presence of O₂, (hmc)CoOO²⁺ and (hmc)CoOOH²⁺ have appeared as intermediates.^{1,2} The hydroperoxide complex is an analogous form to hydrogen peroxide but its reactivity is presumed to be different from that of the hydrogen peroxide. Its one-electron reduction simply gave (hmc)Co²⁺ and H₂O₂ as in Eq. (4) but other reaction pathway can also be considered. If O-O bond breakage happens before OOH⁻ anion is dissociated from the cobalt center in the first one-electron transfer process, a reduction without giving H₂O₂ may be achieved. Possible reactions may be suggested as Eqs. (5) and (6).



Espenson *et al.* reported that the cobalt hydroperoxide complex was reduced to produce water molecules when it reacted with a chemical reductant like Fe²⁺ and proposed a Fenton reaction for the mechanism.³⁰ However, the present system followed Eq. (4) to give H₂O₂ as a product. This difference was explained by an inner-sphere electron transfer pathway where the OOH⁻ ligand binds with other suitable metal ion such as Fe²⁺.² For the electrochemical reduction, there may be absence of such bridging groups at electrode surface. Any method to introduce suitable groups on the electrode needs to be pursued in future studies.

Adsorption of catalysts on electrode surfaces have been widely studied.³¹ By simply oxidizing the glassy carbon electrode adsorption of the cobalt complex with organic ligand onto the surface was realized and this method needs to be applied to other transition metal complexes. After systematic studies on this, it may be used more widely as a way to prepare modified electrodes confining catalysts on a glassy carbon electrode.

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The Preparation of Alkenyl Fluorides from Organometallic Reagents

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Fluorination of alkenyllithium reagents can be accomplished in acceptable yield under conditions which give rise to low competitive alkene formation. These reactions are abetted by the use of the low temperature soluble, mild fluorinating agent *N*-fluoro-*N*-*tert*-butylbenzenesulfonamide; "simpler" fluorinating reagents such as F₂, XeF₂ or FClO₃ failed to give acceptable amounts of the fluoroolefin with these alkenyllithiums.

Introduction

Fluoroorganics are of established significance in a variety of therapeutic contexts,¹ and the physical, chemical and physiological effects of replacing hydrogen by fluorine in a variety of classes of compounds has been described from several perspectives.¹⁻⁴ Because of the importance of fluoroorganics, methodologies have been developed for specific introduction of fluorine into a variety of types of organic substrates. Many of these procedures involve highly reactive and often corrosive materials such as F₂,⁵ XeF₂,⁶ FClO₃,⁷ CF₃OF,⁸ CH₃COOF⁹ or fluoroamine derivatives,¹⁰ and most have focused on the preparation of fluoroalkanes or aryl fluorides. In contrast, synthetic methodology for the preparation of fluoroalkenes, especially stereospecifically, is

less well developed.¹¹ General approaches to alkenyl fluorides involve: (1) elimination of the elements of HF from a difluorocompound;¹² (2) "reductive elimination" of fluoride and halide from an α -halo-*gem*-difluoride using a metallic reducing agent;^{11d,13} (3) ring opening of *gem*-chloro-fluorocyclopropanes;^{11e,f,14} (4) condensation of aldehydes or ketones with fluorine-substituted nucleophiles;^{11a,b,c,15} (5) photochemical ring cleavage;¹⁶ (6) elimination of HBr from α -bromofluoro compounds;¹⁷ or (7) fluorination of alkenyl-metallics.¹⁸ This last method for the introduction of fluorine via an organometallic is conceptually general and straightforward: the organometallic would react with a source of "positive" fluorine (robust arylmetallics have already been used in this way to prepare aryl fluorides),¹⁹ and a variety of alkenylmetallics is readily available.