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Electrochemical Reduction of Oxygen at Co(II)-3,4-bis (salicylidene diimine)toluene Complex supported Glassy Carbon Electrode

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Electrochemical reduction of oxygen has been carried out at glassy carbon electrode and carbon ultramicroelectrode, the surface of which is modified with a new Co(II)-Schiff base complex, Co(II)-3,4-bis(salicylidene diimine)toluene in 1 M KOH solution. The results obtained from cyclic voltammetric and chronoamperometric experiments are consistent with the formation of the reasonably stable superoxide ions as a primary electron transfer reaction product. The exchange rate constant obtained for oxygen reduction is about 0.02 cm/s.

Introduction

Reduction of dioxygen species in both aqueous and nonaqueous solutions has been receiving a great deal of attention due to its implications in practical applications such as fuel cells and batteries, as well as biological reactions.[1,2] It is well established that the first species generated upon reducing oxygen is superoxide ion.[2] The generation of superoxide ions in nonaqueous solutions has been demonstrated electrochemically[2-4] as well as spectroscopically.[5] While evidence has been presented for the presence of superoxide ion in aqueous solution by monitoring ESR signals during the electrochemical reduction of oxygen at low temperature,[6] it is generally very difficult to observe its generation due to its high reactivity with water. This is true even in strong alkaline solutions.

We have been studying the oxygen reduction because the reaction is used as a cathode reaction in fuel cells and metal air batteries.[7-8] Because the oxygen reduction occurs *via* several intermediates including generation of superoxide ions during the first step, which reduces overall coulombic efficiencies of the reaction, many transition metal chelate based catalysts have been studied with hopes to reduce the intermediate steps.[9-16] Phthalocyanines or porphyrins of cobalt and iron are known as effective catalysts for oxygen reduc-

tion. Carbon based oxygen electrodes are modified by the adsorption of these macromolecular compounds, which mediate the electron transfer. Oxygen is reduced to hydrogen peroxide and/or water at these modified electrodes *via* a two- or four- electron transfer reaction. Collman *et al.*[16-18] and Anson *et al.*[15,19-21] have synthesized and characterized cobalt cofacial porphyrin derivatives as oxygen reduction catalysts in an effort to reduce the intermediate step during the oxygen reduction since the rate of the overall reaction is often limited by one or more steps of the reduction. As a result, some of these compounds were found to reduce dioxygen species directly to water *via* a four- electron transfer reaction.[16-26]

In our present report, we describe Co(II)-Schiff base complex, Co(II)-3,4-bis(salicylidenediimine)toluene, Co(II)(o-BSDT)(H_2O)$_2$, which is shown to catalyze the oxygen reduction *via* predominantly a single electron, rather than multielectron, transfer reaction. The catalytic effect is large and the reaction occurs *via* one- electron transfer to produce superoxide ions. The superoxide ion produced at the Co(II) (o-BSDT)(H_2O)$_2$ modified electrode shows a reasonable stability in aqueous KOH solution.

Experimental

Pyridine (Fischer Scientific), potassium ferricyanide (Mal-

linckrodt Chemical), potassium hydroxide (Alfa ultra pure), ethanol (Merck), 3,4-diaminotoluene (Aldrich) and salicylaldehyde (Merck) were used as received. KOH solution for electrochemical experiments was prepared using doubly distilled deionized water.

The elemental analysis (C, H, N) was performed with a Yanaco-CHN Coder MT-3 analyzer and the cobalt content was determined with a Perkin-Elmer model 603 atomic absorption spectrophotometer, respectively. Infrared and UV-visible spectra were recorded with Shimadzu IR-430 infrared and Hitachi-557 UV-visible spectrophotometers. Thermogravimetric analysis was carried out with a Perkin-Elmer model 2 thermogravimetric analyzer. An EG & G Princeton Applied Research model 273 potentiostat/galvanostat was used for electrochemical measurements.

A single compartment cell, which housed a proper working (see below), Hg/Hg$_2$SO$_4$ (sat'd K$_2$SO$_4$) reference and platinum wire counter electrodes, was used for electrochemical measurements. A glassy carbon electrode (geometric area, 0.071 cm^2) or Bioanalytical System's carbon ultramicroelectrode (diameter, 10 μm) was used as a working electrode. Both electrodes were polished to a mirror finish with 1 μm alumina powder, subsequently cleaned in an ultrasonic cleaning bath to remove solid particles, and finally rinsed with a copious amount of doubly distilled deionized water before use. To prepare a catalyst modified electrode, the electrode was then dried in an oven and coated with the catalyst molecule, Co(II)(o-BSDT)(H$_2$O)$_2$, by dipping in a 10 mM Co(II)(o-BSDT) (H$_2$O)$_2$ solution in pyridine.

A quadridentate Schiff base ligand, 3,4-bis(salicylidene diimine)toluene, (o-BSDTH$_2$), was prepared by a following method. 0.1 mole 3,4-diamino toluene solution in ethanol was slowly added to the same volume of 0.1 mole salicylaldehyde in ethanol under the nitrogen atmosphere. When the mixed solution was slowly stirred, a yellow o-BSDTH$_2$ precipitate was obtained. Yield : 97.1%; Elemental analysis (%) : C = 76.38, H = 5.52, N = 8.50 (Cal. C = 76.34, H = 5.49, N = 8.48); UV-vis (DMSO, λ$_{max}$, ε×10^{-4} cm^{-1}M^{-1}): 336 (2.19), 272 (2.37); IR (KBr, cm^{-1}): 2650, 1612, 1560, 1268, 1178; TGA (weight loss, %): 111-360 ℃ = 30.41, 360-470 ℃ = 69.59.

The complex, Co(II)(o-BSDT)(H$_2$O)$_2$ was prepared by slowly adding 0.1 mole o-BSDTH$_2$ in ethanol to the same volume of 0.1 mole Co(NO$_3$)$_2$·6H$_2$O in ethanol while stirring under the nitrogen atmosphere. A dark brown precipitate thus obtained was then recrystallized from ethanol and dried at 80 ℃ under reduced pressure. Yield : 79.2%; Elemental analysis (%); Co = 13.84, C = 59.57, H = 4.63, N = 6.71, H$_2$O = 8.50 (Cal. Co = 13.92, C = 59.58, H = 4.76, N = 6.62); UV-vis (DMSO, λ$_{max}$, ε×10^{-4} cm^{-1}M^{-1}): 465 (0.56), 373 (1.02); IR (KBr, cm^{-1}): 3400, 1608, 1528, 1245, 1140, 805, 555; TGA (weight loss, %): 100-270 ℃ = 8.63, 270-640 ℃ = 73.35, 640 ℃ = 18.02.

Results and Discussion

The results of elemental analysis of the Schiff base ligand, o-BSDTH$_2$, and the Co(II)(o-BSDT)(H$_2$O)$_2$ complex agree well with predicted compositions of the proposed complex on Scheme 1.

Also, the content of cobalt is in excellent agreement with the proposed complex of one base molecule with one cobalt

o-BSDTH$_2$

Co(II)(o-BSDT)(H$_2$O)$_2$
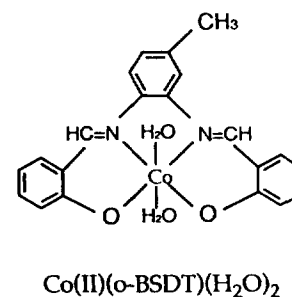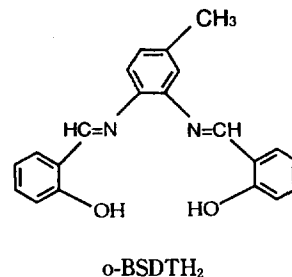
Scheme 1.

(II) ion. The complex is not soluble in water but soluble in relatively nonpolar solvents such as pyridine.

The thermogravimetric analysis result shows that two hydrate water molecules are driven away between 100-270 ℃ and one mole of CoO is formed above 640 ℃ for the postulated mole of Co(II)(o-BSDT)(H$_2$O)$_2$.

The spectra show weak OH$^-$ bands for o-BSDTH$_2$ ligand at 2650 cm^{-1} while strong hydroxide bands are shown at 3400 cm^{-1} for the complex. Perhaps the hydroxides in the base may be in a fairly strongly hydrogen bonded state, which may weaken the hydroxide stretching motion. It can be seen also that CH=N bands in the complex are shifted to a higher energy regions to 1528 cm^{-1}. Similar trends are shown for C-O and C-N bands as well. Also, two bands at 805 cm^{-1} and 555 cm^{-1}, assigned to Co(II)-N and Co(II)-O, are clearly seen. According to Ueno and Martel,[27] a characteristic absorption band for M(II)-N and M(II)-O bonds, should appear in spectral regions of 650-850 cm^{-1} and 400-600 cm^{-1}. We expect that the metal-oxygen bond would be of ionic nature while the metal-nitrogen bonds covalent. The UV-visible spectrum obtained in DMSO solution shows a π-π* band absorption maximum at 373 nm and a d-π* charge transfer band at 465 nm. These observations are consistent with the proposed structure.

Reduction of Oxygen at Co(II)(o-BSDT)(H$_2$O)$_2$ Modified Electrodes. The oxygen reduction in aqueous solutions can be inefficient because the reaction has many intermediate steps, and the intermediate species produced in each step requires a different amount of energy for further reduction. To make the matter worse, slow chemical reactions may be coupled between these electron transfer reactions. These reactions, following the electron transfer and coupled to give an overall oxygen reduction, make the overpotential for the reaction unreasonably large. There could therefore be two fundamentally different approaches to find a good reduction catalyst. A better way would be to reduce many intermediate steps into one, making the reaction a
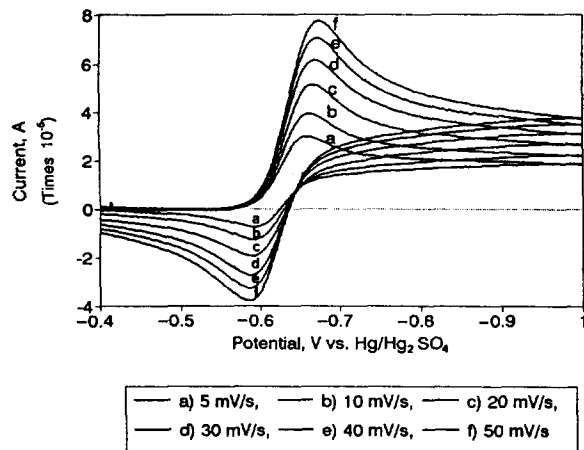
Electrochemical Reduction of Oxygen

Bull. Korean Chem. Soc. **1995**, *Vol. 16, No. 1* 23

Figure 1. Cyclic voltammograms recorded for the oxygen reduction in an oxygen saturated 1.0 M KOH solution at various scan rates: (a) 5, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 mV/s.

single step four electron transfer. It is a battle to make all reactions occur somehow in a single step. The second approach is to find a catalyst, which is capable of making the first electron transfer reaction electrochemically reversible. If the first electron transfer is reversible, the overpotential would be small. The compounds synthesized by Collman et al.[17] belong to the first category, while the compound we report here appears to give a property desired for the second type of the catalyst.

Figure 1 shows a series of cyclic voltammograms recorded at various scan rates in a 1 M KOH solution. The number of electrons transferred in the electrode reaction for a reversible couple can be determined from the seperation between the peak potentials,

$$\Delta E_p = E_{pa} - E_{pc} \cong \frac{0.059}{n}$$

where E_{pa}, E_{pc} and n are anodic peak potential, cathodic peak potential, and number of electrons trnsferred, respectively.

Thus a one-electron process exhibits a ΔE_p of approximately 0.059 V.[28] At slower scan rates, the peak separation, ΔE_p, for cathodic and anodic cyclic voltammetric peak potentials is about 60-70 mV depending on the scan rate, indication that the number of electrons transferred should be 1.0. The ratio of the anodic to cathodic peak current approaches to 1 (about 0.85-0.92), suggesting that the primary electron transfer product generated upon oxygen reduction must be reasonably stable. These observations indicate that the first product of the electron transfer reaction is reasonably stable on the cyclic voltammetric time scale and, thus, reoxidized during the reverse potential scan.

In order to further show that the number of electrons transferred is close to 1.0, chronoamperometric experiments at the $Co(II)(o\text{-}BSDT)(H_2O)_2$ modified glassy carbon electrode and similarly modified carbon ultramicroelectrode were carried out. To calibrate the area of the $Co(II)(o\text{-}BSDT)(H_2O)_2$ modified electrode, was performed a control experiment with a solution containing potassium ferricyanide. Figure 2 and 3 show chronoamperometric results obtained at a $Co(II)(o\text{-}BSDT)(H_2O)_2$ modified electrode for the reduction of 10.0
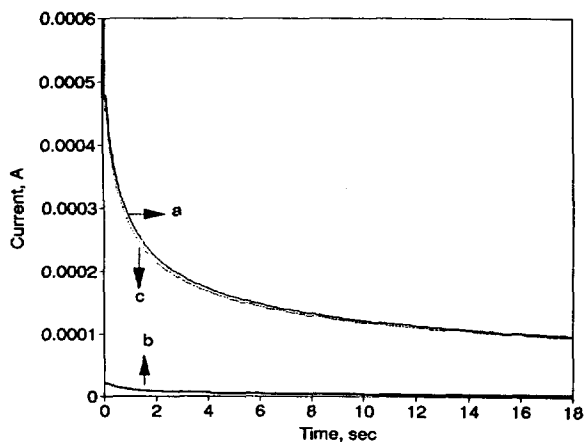

Figure 2. Chronoamperometric curves at the $Co(II)(o\text{-}BSDT)$ $(H_2O)_2$ modified glassy carbon eletrode for the reduction of 10 mM ferricyanide in 1.0 M KNO_3 (a), 1.0 M KNO_3 (b), and after background subtraction (c). The potential stepped was -0.3 V vs. Hg/Hg_2SO_4.
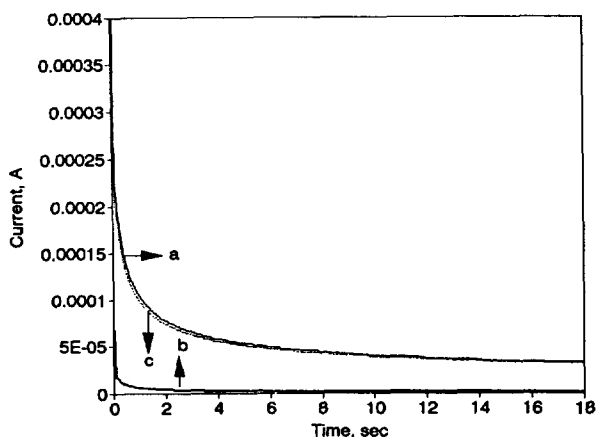

Figure 3. Chronoamperometric curves at the $Co(II)(o\text{-}BSDT)$ $(H_2O)_2$ modified glassy carbon eletrode for the reduction of oxygen in 1 M KOH solution; (a) O_2-saturation, (b) N_2-saturation, and (c) after background subtraction. The potential was -0.8 V vs. Hg/Hg_2SO_4.

mM ferricyanide in 1.0 M KNO_3 solution (Figure 2) and that for the oxygen reduction in 1.0 M KOH solution (Figure 3). Figure 4 and 5 show result plotted according to the modified Cottrell equation, i.e.,

$$i(t) \times t = \frac{nFAD_0^{1/2}C_0^* t^{1/2}}{\pi^{1/2}}$$

which was simply obtained by multiplying t on both sides of the Cottrell equation.[29] Here $i(t)$, t, n, A, D_0, and C_0^* are the current at time t, time, number of electrons transferred, electrode area, diffusion coefficient of the oxidant, and the bulk concentration of the oxidant, respectively. Since concentrations and diffusion coefficients of oxidants used in two experiments and also the number of electrons transferred for the reduction of the ferricyanide ion to ferrocyanide are known, the number of electron transferred in oxygen reduction can be calculated from the two slopes. Using the concen-
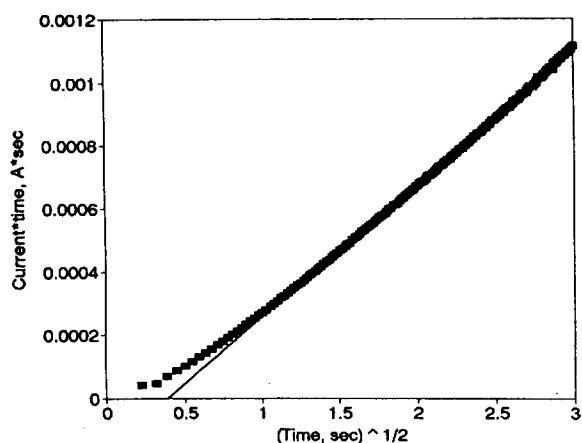
Figure 4. Modified Cottrell plots for chronoamperometric results shown in Figure 2.
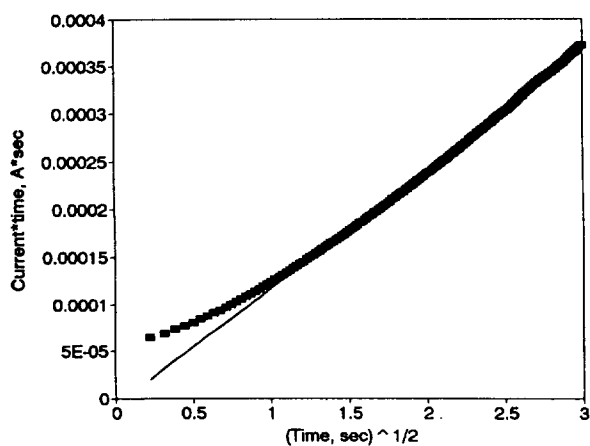

Figure 5. Modified Cottrell plots for chronoamperometric results shown in Figure 3.
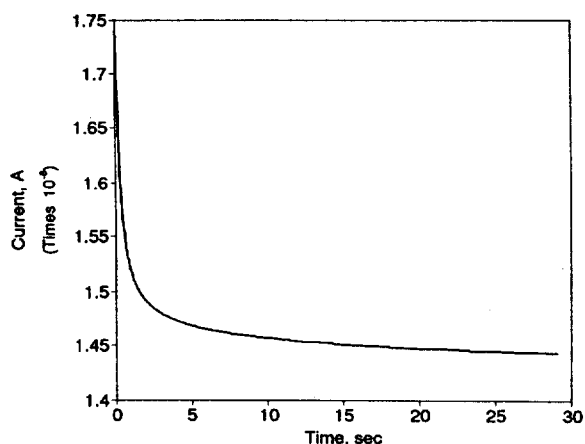

Figure 6. Chronoamperometric curve after background subtraction at the $Co(II)(o\text{-}BSDT)(H_2O)_2$ modified carbon ultramicroelectrode for the reduction of 10 mM ferricyanide in 1.0 M KNO_3 solution. The potential was -0.4 V *vs.* Hg/Hg_2SO_4.

trations of 10.0 and 1.0 mM for potassium ferricyanide and oxygen and diffusion coefficients[30,31] of 6.5×10^{-6} and 2.5×10^{-5}
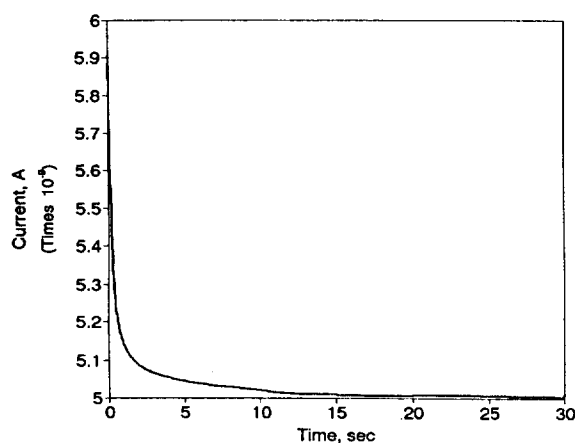

Figure 7. Chronoamperometric curve after background subtraction at the $Co(II)(o\text{-}BSDT)(H_2O)_2$ modified carbon ultramicroelectrode for the reduction of oxygen in 1 M KOH solution. The potential was -1.1 V *vs.* Hg/Hg_2SO_4.
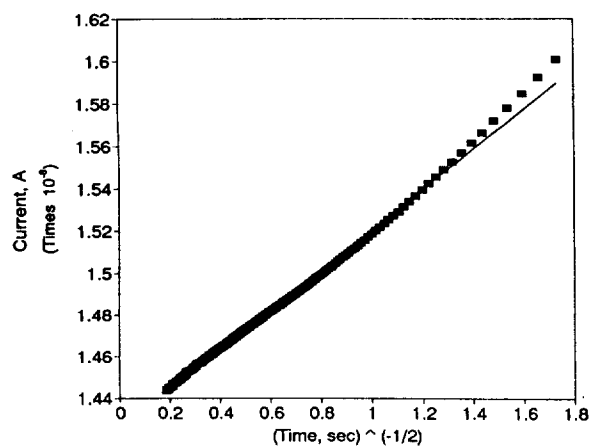

Figure 8. A classical Cottrell plot for chronoamperometric result shown in Figure 6.

cm^2/s, the number of electrons transferred is 1.2.

Similar experiments have been conducted using a carbon ultramicroelectrode and the results are shown in Figure 6 and 7. Notice here that rather large steady state diffusion currents are observed long time after the potential step due to a radial diffusion toward the electrode. Classical Cottrell plots are shown in Figure 8 and 9. Baransky *et al.*[32] have demonstrated that the number of electrons transferred is obtained reliably and unambiguously from results shown in Figures 6-7 and 8-9 using an equation,

$$\frac{n_1}{n_2} = \frac{S_1^{\,2} i_{2\infty}}{S_2^{\,2} i_{1\infty}} \frac{C_2}{C_1}$$

where S and i_∞ are the slopes of the Cottrell plot (Figure 8-9) and the steady state diffusion currents (Figure 6-7) with their respective subscripts for standard (1) and unknown (2) compounds. Other symbols have the same meanings as before. Here again, we used the ferricyanide ion as a standard compound. The number of eletrons transferred in this way is 1.1.
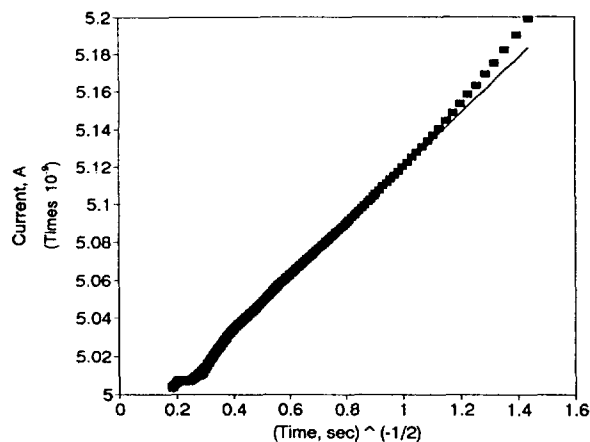
Finally, one can also estimate the exchange rate constant

Figure 9. A classical Cottrell plot for chronoamperometric result shown in Figure 7.

for a quasireversible electrochemical reaction from the variations of a peak seperation, ΔE_p, upon changing scan rates. Nicholson[33] has ψ-values for various ΔE_p-values; the empirical parameter, ψ, obtained from the ΔE_p, is now related to the exchange rate constant k^0 by an equation,

$$\psi = \frac{\gamma k^o}{(\pi a D_o)^{1/2}}$$

where $\gamma = (D_0/D_R)^{1/2}$ and $a = nFv/(RT)$ with $v =$ scan rate and subscripts denoting oxidant (O) or reductant (R). Assuming that γ is approximately 1, an average exchange rate constant is estimated to be about 0.02 cm/s, The exchange rate constant for oxygen reduction reported in aqueous solutions is about 1×10^{-7} cm/s,[34] and our value is about five order of magnitude larger than that reported under ordinary experimental conditions. This is even larger than exchange rate constants obtained for oxygen reduction in dimethylsulfoxide ($\sim 6.3 \times 10^{-4}$) and pyridine ($\sim 3.5 \times 10^{-4}$).[5] While the constant is unexpectedly large for the electrochemical reduction of oxygen, which has been accepted as being irreversible, it certainly explains the shape of cyclic voltammograms shown in Figure 1. It should also be pointed out that cyclic voltammograms of oxygen reduction in nonaqueous media such as dimethylsulfoxide and pyridine, particularly pyridine, have large ΔE_p values, somewhere between 120 and 300 mV.[2-5] Although Sawyer attributes it to the solution ohmic drops due to large solution resistances,[2] the inherent electron transfer kinetics appear to play an important role. Since the ΔE_p values in our case are between 60 and 70 mV, the exchange rate constant must be larger than oxygen reduction reactions in dimethylsulfoxide and pyridine.

Conclusion

The data presented here is consistent with the reduction of dioxygen species to produce superoxide ion as a primary product with a predominantly one electron transfer. The best way to confirm the reaction product would be by spectroelectrochemical experiments.[5] Unfortunately, the reflectance spectroelectrochemical technique cannot be applied to the system due to the low reflectance at carbon electrodes, on which

a large catalytic effect is shown.

The catalytic effect shown at glassy carbon electrode, when modified with $Co(II)(o-BSDT)(H_2O)_2$, may have originated from the enhanced reversibility of the electrochemical reduction of oxygen to its primary product, O_2^-. As a result, the oxygen reduction takes place nearly at the thermodynamic potential because of the stability of super oxide ion.

It is not clear how the superoxide ion is so much stabilized. The best way to maintain the stability for an unstable intermediate species would be to insulate it from the hostile environment, *i.e.* water. The proposed structure of the complex, however, does not appear to allow the electrochemically generated superoxide ion to be completely insulated from the environment, unless it is totally different from that shown above.

Two water molecules coordinated to Co(II) ion in the original compound should have been replaced by hydroxide ions in alkaline solutions. While how the superoxide ion would be stabilized in the hostile aqueous medium is one question, another is how the complex shuttles the electron so effectively from the electrode to oxygen. These questions may be answered when more information about the complex, including its electrochemical, spectroelecrtochemical, and other chemical as well as physical properties. Studies are under way in an effort to elucidate the mechanism involved in this rather unusual observation.

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26   *Bull. Korean Chem. Soc.* **1995**, *Vol. 16, No. 1*

Jung-Sook Kim et al.

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Synthesis and Characterization of Molybdenum(V)-Oxo Complexes with ONO-Donors

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Six-coordinate molybdenum(V)-oxo complexes (PyH)[MoOCl$_2$L] and (R$_4$N)-[MoOCl$_2$L] (R=CH$_3$ and C$_2$H$_5$) with N-salicylidene-2-aminophenol(L^1) and its derivatives(L^2=5-CH$_3$, L^3=3-CH$_3$O, L^4=5,6-C$_4$H$_4$ and L^5=5-NO$_2$) as ONO-donor ligands have been synthesized and the spectral and electrochemical properties of the complexes by elemental analysis, molar conductivity, UV-vis, IR, ^{1}H NMR and CV have been studied.

Introduction

The chemistry of molybdenum-oxo complexes with Schiff base ligands has received the intense attention because of its relevance to the active sites of molybdoenzymes, and many papers have been published in this area.[1]

It is well-known[2] that the biological redox process of the molybdoenzymes involves oxidation states Mo(VI), Mo(V) and Mo(IV). In addition, extended X-ray absorption fine structure (EXAFS) spectroscopic studies have implicated the presence of oxygen and nitrogen atoms at the active sites of oxo-transfer molybdenzymes.[1e,3] In this context we have taken up N-salicylidene-2-aminophenol and its derivatives with ONO-donors as Schiff base ligends:
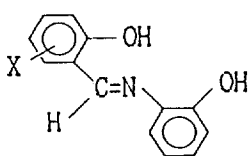
	X	
	H	H$_2$L^1
	5-CH$_3$	H$_2$L^2
	3-CH$_3$O	H$_2$L^3
	5,6-C$_4$H$_4$	H$_2$L^4
	5-NO$_2$	H$_2$L^5

These ligands are of particular interest because chelation may occur either from ON or ONO sites, in principle. It was also reported[4] that functionalities present in the ligands play a vital role in controlling whether the molybdenum-oxo complexes are monomers or polymeric species,as well as the oxo-transfer ability. Thus, with the aim of simulating many characteristic properties for the active sites of molybdoenzymes, We have synthesized a series of dichlorooxomolybdenum(V) complexes (PyH)[MoOCl$_2$L] and (R$_4$N)[MoOCl$_2$L] (R=CH$_3$ and C$_2$H$_5$). In this paper, we report the synthesis, spectral properties and the electrochemical behaviors of the complexes.

Materials. Most chemicals used in synthesis were of reagent grade and used without further purification. Pyidinium pentachloromolybdate(V) (PyH)$_2$[MoOCl$_5$][5] and 5-methylsalicylaldehyde[6] were prepared by literature methods. All the Schiff base (H$_2$L^1-H$_2$L^5) were prepared by the same method as the previous paper and identified by IR and ^{1}H NMR.[7] All solvents were dried by standard procedures and distilled before use.

Physical Measurements. Elemental analyses for C, H,