Macromol. Symp. **2003**, *204,* 151—158

Electrochemical Reduction of Carbon Dioxide Catalyzed by Cofacial Dinuclear Metalloporphyrin

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Summary: Cofacial dinuclear metalloporphyrins exhibited a catalytic activity for the electrochemical reduction of carbon dioxide. The cofacial dinuclear porphyrin was automatically generated by mixing a cationic cobalt porphyrin (CoTMPyP) and an anionic metalloporphyrin (MTPPS) in solution. The redox system of this complex was examined by electrochemical methods. According to the cyclic voltammogram, the catalytic active species was generated at -1.8V vs. Ag/Ag^+, which was considered to be a monovalent cobalt porphyrin, Co(I)TMPyP. The catalytic activity of the dinuclear complex was two times greater than that of the mononuclear one because the anionic porphyrin acted as an electron mediator.

Keywords: carbon dioxide; catalysts; electrochemistry; metalloporphyrin; reduction

Introduction

The reduction of carbon dioxide is a significant research field due to the abundance of carbon source in order to reduce global warming. Electrochemical reduction is a useful method to directly convert carbon dioxide into other chemicals, however it requires much energy, i.e., the electrode potential has to be significantly negative. Since carbon dioxide is a very stable compound, it requires a high overpotential to reduce. Furthermore, the reduction products are usually of little value; the two main electron reduction compounds are formic acid and carbon monoxide.[1] To overcome these drawbacks, it is necessary to produce a multielectron transfer process. If the theoretical thermodynamic potential to reduce carbon dioxide is less negative through high electron reduction process, the reduction product will be a more valuable compound like methanol or methane.[2]

A multinuclear metal complex may cause a multielectron transfer because it has many redox sites in its structure. As a result, the complex works as a multielectron transfer catalyst.

We have investigated the cofacial dinuclear porphyrin complex are a multielectron catalyst.[3] In this article, we report that its complex mechanism as a catalyst for electrochemical reduction of carbon dioxide.

DOI: 10.1002/masy.200351413

Experimental

Free-base porphyrins were purchased from Tokyo Kasei, Inc., and the other chemicals were from Kantoh Chemical Company, Inc., and used as received. (5,10,15,20-tetrakis(N-methyl-4-pyridinio)porphyrinato)cobalt(II) (CoTMPyP) and (5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrinato) cobaltate(II) (CoTPPS) were prepared as already described.[4] The other metalloporphyrins (MTPPS, M=metal) were synthesized using a method similar to CoTPPS. H_2TPPS·4Na and a metal(II) salt (chloride or acetate) were refluxed in a polar solvent (H_2O or DMF) under an Ar atmosphere. The product was purified by column chromatography (Merck basic alumina / MeOH-H_2O) or reprecipitation after cation exchange (Amberlite GC120, Na^+ form). Every reaction and the fraction from the chromatography were monitored by UV-vis spectroscopy and the maximum wavelength and absorption coefficient were compared to the reference values.[5] The product was obtained as the M(III)TPPS(OH)· 4Na form estimated from the UV-vis data for the cases of Cr, Mn and Fe porphyrin. The cofacial dinuclear metalloporphyrins (CoTMPyP-MTPPS) were prepared by mixing equal equivalents of each ionic porphyrin in solution.

The UV-vis spectra were obtained using a Shimadzu UV-2400PC spectrometer with a quartz cell with an optical path length of 1cm. The MALDI TOF-MS was obtained using a Shimadzu/Krato KOMPACT MALDI mass spectrometer. Dithranol was used as the matrix.

The electrochemical analysis was performed using an electrochemical work station (BAS Co., Ltd., Model 660) under the following conditions. Cyclic voltammetry was carried out in a conventional two-compartment cell. A sample solution for the measurement was prepared by dissolving a porphyrin complex and tetraethylammonium perchlorate (TEAP) in pure DMSO or aqueous DMSO (H_2O:DMSO = 1:9(v/v)). Through the sample solution was bubbled an Ar or a CO_2 gas for 30 min before measurement and the atmosphere and the gas flow were maintained during the measurements. A 3mm diameter glassy carbon disk electrode was used as the working electrode, which was well polished with 0.05 mm alumina paste before each experiment. The auxiliary electrode was a coiled platinum wire and was separated from the working electrode by a fine-porosity frit. The reference electrode was Ag/Ag^+. Its potential was normalized to the ferrocene–ferrocenium couple in acetonitrile. Rotating disk voltammetry was carried out using the same instruments and conditions but a 6mm diameter glassy carbon electrode was used as the working electrode. The disk rotation rate was 1000 rpm. The reduction products were qualitatively detected by gas chromatography (Shimadzu GC-14B) for carbon monoxide and hydrogen, and by a colorimetric test for formaldehyde.[6]

Results and Discussion

Formation of Cofacial Dinuclear Metalloporphyrin

The synthesis of a cofacial dinuclear metalloporphyrin linked with covalent bonds was generally quite complicated.[7] With ionic bonds, however, the synthesis is very easy. Mixing a (tetrakis(N-methylpyridil) porphyrin (cationic, abbreviated as TMPyP) and a (tetra(4-sulfonatophenyl)porphyrin (anionic, TPPS) in solution, the cofacial dinuclear porphyrin (Figure 1) was quickly formed by formation of ionic bonds between the cationic and anionic substituents. Each porphyrin should be metallated before being mixed. The formation of the dinuclear porphyrin was confirmed by Job's method based on the UV-vis spectra in solution; the observed drastic decrease of Solet band attributed to π-stacking which indicated the cofacial fashion, and was confirmed by MALDI-TOF MS of the solid. The equilibrium constant for the dimerization was estimated to be ca. 10^6 M^{-1} in DMSO.[4]

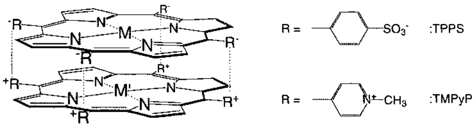

Fig. 1. Cofacial dinuclear porphyrin complex (M, M' = Co, Cu, Fe, etc.).

Electrochemical Properties and Catalysis for Reduction of Carbon Dioxide

Cyclic voltammograms (CVs) of the each mononuclear cobalt porphyrin (CoTMPyP and CoTPPS) and the cofacial dinuclear cobalt-cobalt porphyrin (CoTMPyP-CoTPPS, abbreviated Co-Co) were measured in DMSO under an Ar atmosphere (Figure 2). The CoTPPS showed three redox couples at -0.3V, -1.2V, and -2.4V vs. Ag/Ag^+. As was a typical pattern for the cobalt porphyrin complex,[8] these redox couples were attributed to the redox of the cobalt; Co(III)/(II), Co(II)/(I), and Co(I)/Co(0), respectively. In contrast, the CV of the CoTMPyP was complicated because it involved the redox of the pyridinium substituents as well as that of the cobalt.[9] The redox couple at -0.2V was attributed to Co(III)/(II). The waves around -1.2V resulted from the redox of the pyridinium substituents and subsequent electron transfer between the cobalt center and the porphyrin ring, that involved six electrons. The redox couple at -1.8V had not yet been reported to the best of our knowledge, however, it was estimated to be due to the redox of Co(II)/(I) because the cobalt remained in the divalent state at this potential.[9] The CV of the dinuclear porphyrin Co-Co appeared to be the sum of the voltammogram of each mononuclear porphyrin. The redox potentials for the Co-Co were almost identical with those for the mononuclear porphyrins; meanwhile, the shape of the redox couple at -1.8V for Co-Co was more clearly observed than that for CoTMPyP. The difference suggested that the environment of the CoTMPyP was changed by the dinuclearization; the CoTMPyP was prevented by the CoTPPS from coordinating with a solvent as an axial ligand that often made the redox couple irreversible.[4] Therefore, the difference also indicated that the dinuclear complex remained at -1.8V without dissociation.

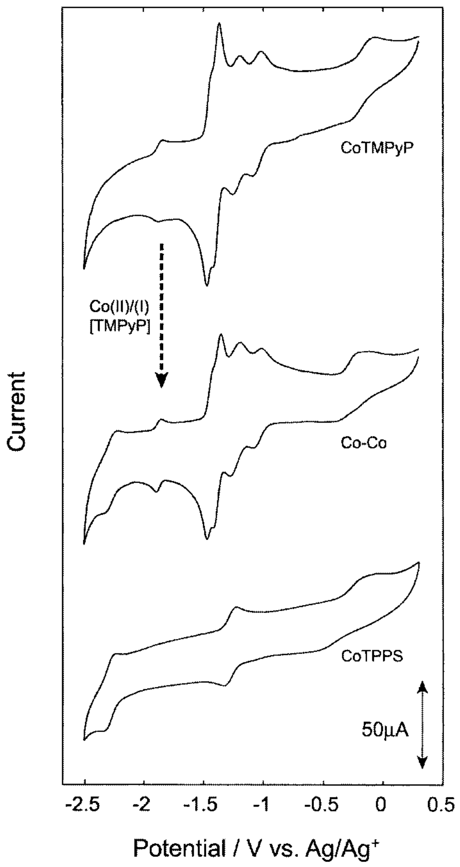

Fig. 2. Cyclic voltammograms for each mononuclear and dinuclear porphyrin complexes in aqueous DMSO under an Ar atmosphere. Scan rate: 20mV/s.

The CV of the Co-Co exhibited a significant change under the carbon dioxide atmosphere (Figure 3). The redox couple at -1.8V became irreversible with a significant increase in the reduction current, which suggested that the reduction of the carbon dioxide occurred.[10] The reduction current grew more intense upon the addition a little water to the solution, because the reduction process required a proton source.[11] Since the increase in the reduction current was not observed at this potential without the complex, it was certain that the reduction was catalyzed by the complex. The catalytic active species was presumed to be the Co(I)TMPyP by taking into account the potential where the reduction occurred. The progress of the reduction for the carbon dioxide was confirmed by a long bulk electrolysis experiment. Carbon monoxide and formaldehyde were detected as the reduction products and hydrogen was a byproduct.

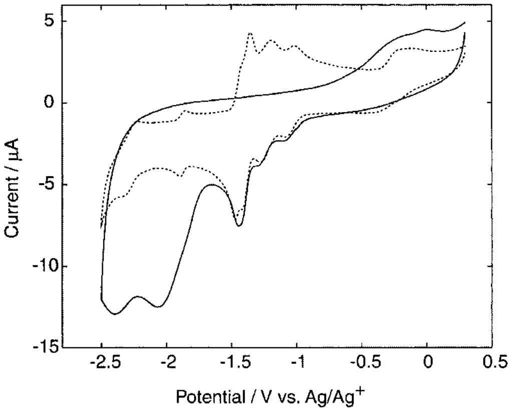

Fig. 3. Cyclic voltammograms for the Co-Co in aqueous DMSO under an Ar (dotted) and a CO_2 (bold) atmosphere. Scan rate: 20mV/s.

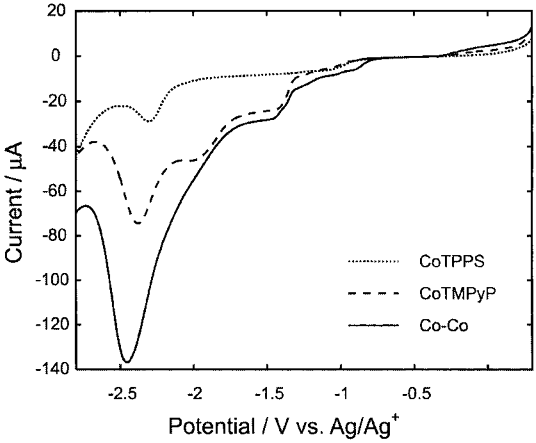

Fig. 4. Rotating disk voltammograms for each mononuclear and dinuclear complexes in aqueous DMSO under a CO_2 atmosphere. Scan rate: 5mV/s.

Effect of Dinuclearization and Central Metal

The effect of the dinuclearization was quantitatively investigated by the rotating disk voltammetry method. The CoTPPS showed no increase in the current at -1.8V in its rotating disk voltammogram(RDV), which obviously indicated that it was not the catalyst. The CoTMPyP's voltammogram consisted of two steps. The current occurred at the first plateau at -2.0V and again increased from -2.1V until the plateau at -2.4V. The reduction current comparable to the second step was also observed in the blank solution, i.e., in a solution only containing the supporting electrolyte, therefore, it was considered to have originated from the heterogeneous direct reduction of the carbon dioxide at the electrode surface. The Co-Co showed a similar voltammogram to that of the CoTMPyP, although the dinuclear complex showed twice the current as the mononuclear one. Since the CoTPPS showed no reduction current around -1.8V, the disparity in the reduction current between the dinuclear and mononuclear complexes agreed with the disparity in the activity as the catalyst. Because the CoTPPS worked as an electron mediator, [3] the Co-Co exhibited a greater catalytic activity than CoTMPyP.

Table 1. The results of RDV; current (μA) at -2.0V and -2.3V vs. Ag/Ag^+ for each porphyrin complex in aqueous or non-aqueous DMSO under a CO_2 atmosphere.

	Nonaqueous		10% H_2O Addition	
porphyrin	-2.0V	-2.3V	-2.0V	-2.3V
Blank	0.40	3.58	0.80	9.14
CoTPPS	0	4.95	1.08	19.6
CoTMPyP	2.09	4.77	17.3	34.6
Co-Co	2.65	9.54	22.3	67.8

As CoTPPS was the electron mediator, the next question was whether the center metal of the TPPS had to be cobalt, i.e., the efficiency of the electron mediator depended on the kind of the metal. This question was investigated by measuring the RDV in the same way for various hetero-dinuclear complexes CoTMPyP-MTPPS (abbreviated as Co-M, M was a transition metal). The hetero-dinuclear complex was prepared as easily as the Co-Co by complexation of the anionic porphyrin with a transition metal before dinuclearization. The result of the RDV for the Co-M showed that CuTPPS assisted the catalysis of the CoTMPyP the as same as the CoTPPS; whereas the other MTPPS did not assist or even hindered the catalysis, presumably obstructing access of the substrate to the catalyst CoTMPyP. While Co and CuTPPS may have also hindered the catalysis, they worked as an electron mediator that negated their catalysis obstruction.

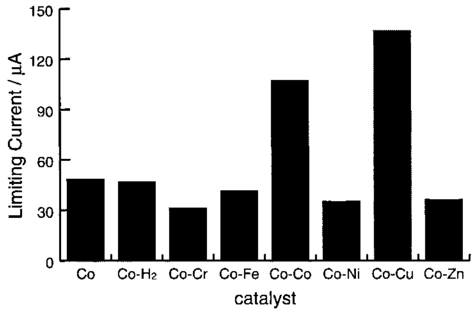

Fig. 5. The change of maximum limiting currents of RDV; where CoTMPyP-MTPPS complex is abbreviated to Co-M (Co-H_2 means CoTMPyP-H_2TPPS) and “Co” means mononuclear CoTMPyP.

Conclusion

The cofacial dinuclear porphyrin was synthesized and found its catalytic activity for the reduction of the carbon dioxide. The Co(I)TMPyP acted as the catalyst and the CoTPPS assisted the catalysis as the electron mediator. For this reason, the catalytic activity of the dinuclear complex Co-Co was two times greater than that of the mononuclear CoTMPyP. The CuTPPS also worked as an excellent electron mediator as CoTPPS, meanwhile the other MTPPS showed the equal or less activity. These cofacial dinuclear porphyrins are expected for a novel catalyst for other reactions.

Ackowledgements

This work was partially supported by Grants-in-Aid for Scientific Research (Nos. 15036262, 15655019、15350073) and the 21st COE Program(Keio-LCC) from the Ministry of Education, Science, Culture and Sports, and a Kanagawa Academy Science and Technology Research Grant(Project No. 23).

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