Electrochemical Reduction of Carbon Dioxide Catalyzed by Cofacial Dinuclear Metalloporphyrin

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Electroreduction of carbon dioxide was homogeneously carried out using cofacial dinuclear metalloporphyrin CoTMPyP-MTPPS. The reduction was catalyzed by Co(II)TMPyP which generated at -1.8 V vs. Ag/Ag⁺. More excellent catalytic activity was observed in the presence of H₂O in comparison with that for mononuclear one. The catalytic activity depended on the central metal of TPPS because they worked as an electron mediator.

Key Words : Cofacial Porphyrin, Electrochemical Reduction, Carbon Dioxide, Homogeneous Catalyst

1 Introduction

The reduction of carbon dioxide has interested many researchers because it simultaneously provides both an abundant carbon source and effective solution of global warming. Electrochemical methods are useful for this purpose, but carbon dioxide requires a very negative potential to be reduced due to its high overpotential, and the main products were two-electron reduction compounds, *e.g.*, formic acid.¹⁾ To overcome these problems, various metal complexes were investigated as homo/heterogeneous catalysts.²⁾ Here we use a cofacial dinuclear metalloporphyrin (Fig.1) as the catalyst, which are conveniently prepared and found that it is a very effective multi-electron transfer catalyst for the reduction of carbon dioxide, even though the mononuclear metalloporphyrin was extensively investigated as a catalyst for the reduction of carbon dioxide and its reduction mechanism is known.³⁾

2 Experimental

2.1 Chemicals

The free base porphyrins were purchased from Tokyo Kasei Inc. and other chemicals were from Kantoh Chemical Company Inc. All materials were reagent grade 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 described before.⁴⁾

Other metalloporphyrins (MTPPS, M = metal) were synthesized in the similar method of CoTPPS. H₂TPPS · 4Na and one equivalent metal(II) salt(chloride or acetate) were refluxed in polar solvent(H₂O or DMF) under a N₂ atmosphere. The products were purified by chroma-

tography(Merck basic alumina/MeOH-H₂O) or reprecipitation after cation exchange(Amberlite GC 120, Na⁺ form). Every reaction and the fraction of chromatography was monitored by UV-vis spectra compared its maximum wavelength and absorption coefficient with the reference value.⁵⁾ The products were obtained as M(III)TPPS(OH) · 4 Na form estimated from UV-vis data in the cases of Cr, Mn and Fe porphyrin.

Cofacial dinuclear metalloporphyrins (CoTMPyP-MTPPS) to measure their catalytic activities were prepared by mixing equal equivalent of each ionic porphyrin solution. The formation of dinuclear complex was identified by MALDI TOF-MS and Job's method based on UV-vis spectra as described⁴⁾ and the dimerization equilibrium constants were estimated to be *ca.* 10⁶ (mol dm⁻³)⁻¹ in DMSO.

2.2 Spectroscopic measurements

The UV-vis spectra were obtained using a Shimadzu UV-2400PC spectrometer with a quartz cell (optical path length: 1 cm). MALDI TOF-MS were obtained on a Shimadzu/Kratos KOMPACT MALDI mass spectrometer. Dithranol was used as a matrix.

2.3 Electrochemical measurements

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. Solution for the measurement was prepared by dissolving a porphyrin complex and a tetraethylammonium perchlorate(TEAP) in pure DMSO or aqueous DMSO(H₂O:DMSO = 1:9(v/v)) then bubbled by Ar or CO₂ gas for 30 min. The atmosphere was kept during the measurement to flow each gas. A 3 mm diameter glassy carbon disk electrode was used as the working electrode and polished with 0.05 mm alumina paste before the experiments. The auxiliary electrode was a coiled platinum wire separated from the working electrode by a fine-porosity frit. The reference electrode was Ag/Ag⁺. The formal potential was normalized to the

Fig. 1 Cofacial dinuclear metalloporphyrin.

ferrocene-ferrocenium couple in acetonitrile.

Rotating disk voltammetry was carried out using the same instruments and conditions but a 6 mm 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-14 B) for carbon monoxide and hydrogen, and by colourimetric test for formaldehyde.⁶⁾

3 Results and Discussion

Cofacial dinuclear metalloporphyrins were synthesized from the anionic (tetra(4-sulfonatophenyl)porphyrin, TPPS) and the cationic (tetrakis(N-methylpyridil) porphyrin, TMPyP) porphyrin that had been previously metalated.⁴⁾ Cyclic voltammograms (CV) of the dinuclear cobalt complex under Ar showed many reversible redox waves at -1.0 to -1.5 V and at -1.8 V vs. Ag/Ag^+ (Fig. 2). This latter wave became irreversible and the reductive current was increased in a CO_2 atmosphere, which indicates that the reduction of CO_2 takes place.³⁾ This reductive current change was clearer with the addition of water to the solvent, because the reduction process needs a proton donor,⁷⁾ therefore water played the role as a proton source. Long time bulk electrolysis results in the formation of carbon monoxide, hydrogen, and formaldehyde as the reduction products.

To quantitatively compare the catalytic activity of the dinuclear complex with that of the mononuclear complex, rotating disk voltammetry (RDV) was measured for each porphyrin. In some cases, the voltammograms showed two steps of the limiting current. For example, the voltammogram of the mononuclear CoTMPyP solution obviously showed the first plateau current at -2.0 V. Then the current was increased again at -2.1 V and showed the second limiting current at -2.4 V. The current increase at -2.1 V was also observed for the blank solution, *i.e.* a solution containing only the supporting electrolyte, so that was originated from the heterogeneous direct reduction of carbon dioxide at the electrode surface.

The RDV results (Table 1) show that the limiting current of the dinuclear complex was about twice greater

Fig. 2 Cyclic Voltammograms of 0.5 mM CoTMPyP-CoTPPS in DMSO-water(9:1) under Ar (dotted) and CO_2 (bold). Supporting electrolyte; 0.2 M TEAP, Scan rate; 20 mVs^{-1} . ($\text{M} = \text{mol dm}^{-3}$).

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

porphyrin	Non aqueous		10% H_2O Addition	
	-2.0 V	-2.3 V	-2.0 V	-2.3 V
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

than the simple sum of the mononuclear one. Therefore, it is obvious that the catalytic activity for the reduction is enlarged by dinuclearization.

From the RDV results, CoTMPyP has catalytic activity but CoTPPS does not. The CV of each charged porphyrin measured in the same conditions showed three simple kinds of redox waves for CoTPPS at 0.3, -1.2 , and -2.4 V vs. Ag/Ag^+ which were attributed to Co(III/II) , Co(II/I) , and Co(I/0) , respectively,⁸⁾ but the Co(III/II) and Co(II/I) waves did not change under Ar and CO_2 . Generally CO_2 reduction is homogeneously catalyzed by Co(0) porphyrin, but in our case Co(0) was unable to generate at -1.8 V vs. Ag/Ag^+ , where the current increased. Taking into account the potential, Co(0)TPPS was not utilized in this catalysis. CoTMPyP had many redox waves at -1.0 to -1.5 V, which identified as the six-electron reduction of the methylpyridinium groups and the porphyrin ring of TMPyP, and at -1.8 V vs. Ag/Ag^+ . The redox properties of CoTMPyP have already been reported in detail⁹⁾ and described that TMPyP maintains the Co(II) valance state at that potential. The redox wave at -1.8 V vs. Ag/Ag^+ was estimated to be due to the Co(II)/(I) couple. The catalytic active species is Co(I)TMPyP . CoTPPS acts as an electron mediator to CoTMPyP during the reduction.¹⁰⁾

The main catalytic center was CoTMPyP based on the mechanism suggesting that the catalyst maybe becomes more active allowing the use of other metal elements than cobalt. The catalyses of CoTMPyP-MTPPS were measured by RDV, where M were various transition metals. The limiting current of the RDV revealed that the catalysis was facilitated when the central metal of the MTPPS was either cobalt or copper (Fig. 3). However for the other metals, the catalysts were nearly equal or even

Fig. 3 The changes of maximum limiting currents of RDV; where CoTMPyP-MTPPS complex is abbreviated to Co-M (Co-H₂ means CoTMPyP-H₂TPPS) and "Co" means mononuclear CoTMPyP.

less active by dinuclearization. This difference was due to the ability of the central metal to be an electron mediator. The redox potentials of the catalyst and the electron mediator were so close that multi-electron transfer readily occurred.

4 Conclusion

Cofacial dinuclear metalloporphyrins were synthesized and their catalytic activity for the reduction of carbon dioxide was electrochemically demonstrated. Co(I)TMPyP possesses an excellent catalytic activity, which was emphasized by the dinuclearization with CoTPPS or CuTPPS which acts as an electron mediator.

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