—Communication—

Electrochemical Reduction of CO₂ Mediated by Co^{II}TPP/Co^ITPP Redox Couple on GC and Pt in DMF

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Received December 10, 1990 ; Accepted March 20, 1991

Cobalt porphyrins¹⁾ and cobalt phthalocyanines^{2,3)} are known to be active catalysts for electrochemical reduction of CO₂ in aqueous solution but, so far, these complexes have not been studied in aprotic media. Aprotic media⁴⁻⁶⁾ have advantages of (1) less tendency to interact with radicals electrochemically produced and (2) preclusion of hydrogen evolution at cathodic potentials. In DMF, which has cathodic potential limit of -3.5 V(vs. Hg),⁷⁾ the Co^{II}/Co^I redox peak of cobalt(II) tetraphenylporphyrin (Co^{II}TPP) was observed at -0.77 V(SCE),⁸⁾ while Co^I porphyrins were reported to be active species for the reduction of CO₂.¹⁾ Therefore, Co^{II}TPP is expected to mediate the electrochemical reduction of CO₂ at less negative potentials by means of its redox reaction.

Co^{II}TPP and tetra-*n*-butylammonium tetrafluoroborate (TBAF) were used as received. DMF was dried with molecular sieve 3A for at least 3 days before use. Cyclic voltammetry and controlled-potential electrolysis were carried out in three compartment cell at room temperature, in which 0.7 cm² glassy carbon (GC) or 1 cm² 80 mesh Pt net was used as the working electrode, SCE as reference electrode and a

Pt wire as counter electrode. The volume of 0.3 mM Co^{II}TPP/0.1 M TBAF/DMF solution was 5 ml in the working electrode compartment. The electrolyses were carried out with CO₂ bubbling which avoids retardation by CO₂ diffusion.

Figure 1 shows typical cyclic voltammograms (CV) of Co^{II}TPP at the sweep rate of 50 mV/sec on GC in DMF under Ar (curve a) or CO₂ (curve b) atmosphere.

Figure 1. CV of 0.3mM Co^{II}TPP in 0.1M TBAF/DMF on GC. Sweep rate = 50mV/sec.

From Fig.1, the formal potential ($E_{1/2}$) of Co^{II}TPP/Co^ITPP redox was found to be -0.8 V, which is close to the value reported by Walker *et al.*⁸⁾ In the presence of CO₂, the reduction current was observed at more negative potentials than $E_{1/2}$. In a separate experiment, no reduction current was observed in the absence of Co^{II}TPP. These facts indicate that Co^ITPP plays a role of a mediator of the CO₂ reduction.

Figure 2 shows CVs of Co^{II}TPP at the

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Key Words: CO₂ reduction, Co^{II}TPP, DMF

sweep rate of 50 mV/sec on Pt under Ar (curve a) or CO₂ (curve b) atmosphere. In the presence of CO₂, the cathodic current was enhanced at more negative potentials than -0.5 V. This indicates that Co^{II}TPP on Pt is more active for the reduction of CO₂ than that on GC. The difference between CVs on Pt and GC is mostly due to transient reaction of CO₂ on Pt, since this reaction damped gradually during initial 10 min, and then the CV was almost identical to that on GC. During the controlled-potential electrolysis at -1.5 V on Pt, the current density was maintained at 0.1 mA/cm² for several hours. This value was about 6 times larger than that of the electrolysis at -1.5 V without Co^{II}TPP.

Figure 2. CV of 0.3mM Co^{II} TPP in 0.1M TBAF/DMF on Pt. Sweep rate = 50mV/sec.

These findings further substantiate that the CO₂ reduction is mediated by Co^{II}TPP/Co^ITPP redox couple. Formate ions were found to be the main reduction product both on GC and Pt after electrolysis at -1.5 V, which were identified by the characteristic absorption peak of C=O stretching at 1720 cm⁻¹ and COO⁻ at 1610 and 1321 cm⁻¹, respectively, on FT-IR ATR spectra of the catholyte. These peaks imply that formate ions were in the form of ammonium salt in DMF. From IR peak

intensity, current efficiency of formate ion production was found to be about 10% on both Pt and GC. Hydrogen evolution was also observed by differential electrochemical mass spectroscopy (DEMS) at more negative potentials than -1.0 V. No carbon containing gaseous products such as CO and CH₄ were detected by gas chromatography, in either case where the electrolysis was carried out with or without CO₂ bubbling.

To summarize, Co^{II}TPP was found to play a role of a mediator in the electrochemical reduction of CO₂ even in dried DMF; the reduction current was enhanced at more negative potentials than E_{1/2} of Co^{II}TPP/Co^ITPP. In comparison with the case without mediator, the reduction took place at less negative overvoltage.⁴⁻⁶⁾ Formate was the main reduction product of controlled-potential electrolysis at -1.5 V.

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