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Voltammetric Study on CO_2 Reduction Electrocatalyzed by Cobalt Tetraphenylporphine in DMF Solution

Meguru TEZUKA* and Masakazu IWASAKI
Department of Environmental Engineering, Saitama Institute of Technology, Okabe, Saitama 369-02

The homogeneous catalysis of cobalt tetraphenylporphine (CoTPP) in the electroreduction of CO_2 was investigated by means of cyclic voltammetry (CV). Based on the kinetical treatment of the data, the rate constant for the electron transfer to CO_2 from CoTPP dianion could be determined and the activation energy of the step was estimated as 34.5 kJ/mol.

It is well known that the direct reduction of carbon dioxide requires quite negative potential. Therefore, a great deal of effort has been devoted to searching for catalysts to reduce the overpotential. The transition metal complexes of tetraazamacrocycles including phthalocyanines(Pc)1) or tetraphenylporphines(TPP)2) have been found to act as electrocataysts for CO_2 reduction in aqueous systems. Previously, one of us reported that the tetranuclear iron-sulfur clusters also catalyzed the electroreduction of CO_2 in nonaqueous solution.3) It seems that an aprotic medium might be favorable for the purpose of elucidating the action of catalysts, because there could be minimized the influence of following steps, e.g., protonation.

In this paper, we would like to describe the voltammetric study on the electroreduction of CO_2 catalyzed by CoTPP, focusing on the kinetical consideration of the electron transfer step from the reduced catalyst to CO_2. Recently, the mediation of CoTPP in CO_2 reduction was briefly reported by another group.4) However, to our knowledge, there have been few studies where the electron transfer to CO_2 in aprotic solutions was quantitatively discussed by using electroanalytical methods.

In Fig. 1 are shown the cyclic voltammograms of Co(II)TPP (1 mM) in DMF containing 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) on a glassy carbon electrode5) at 298 K. Under an Ar atmosphere (Fig. 1a), CoTPP gave two reversible one-electron redox waves; at -0.8 V vs. SCE, CoTPP was reduced to the monoanion and around -1.9 V to the dianion. Bubbling the mixture gas of Ar and CO_2 into the electrolyte (Fig. 1b-e), the voltammogram of CoTPP was deformed. That is, the peak current of the second reduction wave increased with higher CO_2 content in bubbling gas and the corresponding re-oxidation peak disappeared. On the other hand, the first redox wave was not substantially affected by the presence of CO_2 in disagreement with Ref. 4, where it was described that the reduction current increased at more negative potentials than -0.8 V in the presence of CO_2. In addition, it should be noted that CO_2 would not be reduced up to -2.5 V vs. SCE without the catalyst. These results might be consistently interpreted by Scheme 1; The monoanion of CoTPP is electroreduced to the dianion (step 1), which consecutively releases the electron to CO_2 molecule to regenerate CoTPP monoanion (step 2). As a consequence, the catalytic current is to be observed.

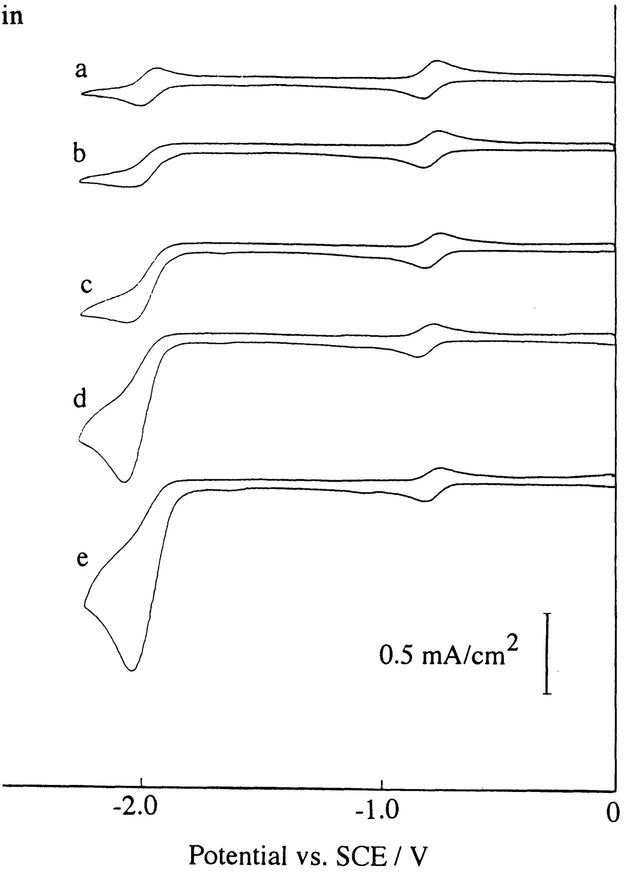
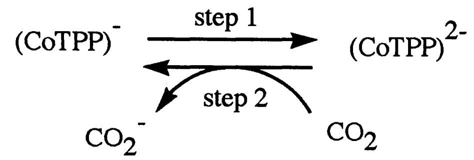


Fig. 1. Cyclic Voltammograms of CoTPP in DMF Solution in the Presence of CO_2. CoTPP 1 mM in 0.1 M $TBABF_4$-DMF, v: 50 mV/s on glassy carbon. a: 0% CO_2, b: 1% CO_2, c: 5% CO_2, d: 30% CO_2, e: 100% CO_2



Scheme 1.

According to the theory concerning the electrochemical catalytic current,[6] the ratio of CV peak currents of the catalytic wave to non- catalytic one, i/i_d can be expressed as a function with the parameter, $C(CO_2)/v$, where $C(CO_2)$ is the concentration of CO_2 dissolved in the solution[7] and v is the potential sweep rate, and simply formulated as Eq.1 unless the value of the parameter is extremely low,[8] where k is the rate constant in step 2, R, gas constant, T, temperature, n, the number of the electron involved in the step, and F, Faraday constant.

$$\frac{i}{i_d} = \frac{1}{0.466}(RT/nF)^{1/2}\, k^{1/2}\, [C(CO_2)/v]^{1/2} \quad (1)$$

Figure 2 is a plot of i/i_d against $[C(CO_2)/v]^{1/2}$ on the basis of the CV data obtained by varying either CO_2 content in the bubbling gas or v. The linear relationship, as expected from the theory, can be seen when i/i_d is less than 5. In the region giving i/i_d larger than 5, the curve appears to tend to the saturation. For the present, this reason is not evident. It might be one of the most probable explanation that the reverse reaction of step 2 could be no longer negligible under such conditions. Anyhow, from the slope of linear portion of the curve, we could calculate the value of k at 298 K as 8.22 mol^{-1} dm^3 s^{-1}.

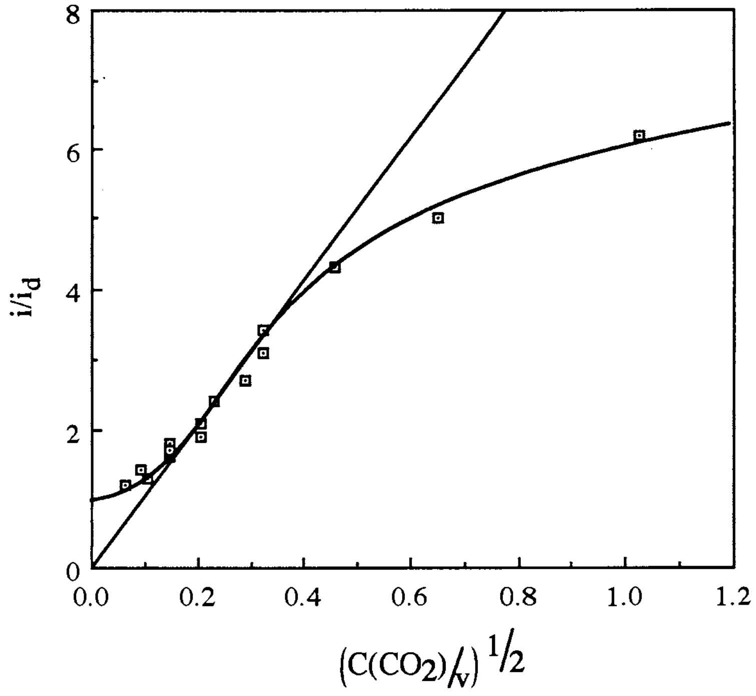


Fig. 2. The Dependence of i/i$_d$ on $[C(CO2)/v]^{1/2}$ in DMF.
C(CO2): 2.1 - 21.1 mM,
v: 20-500 mV s^{-1} on a glassy carbon electrode at 298 K.

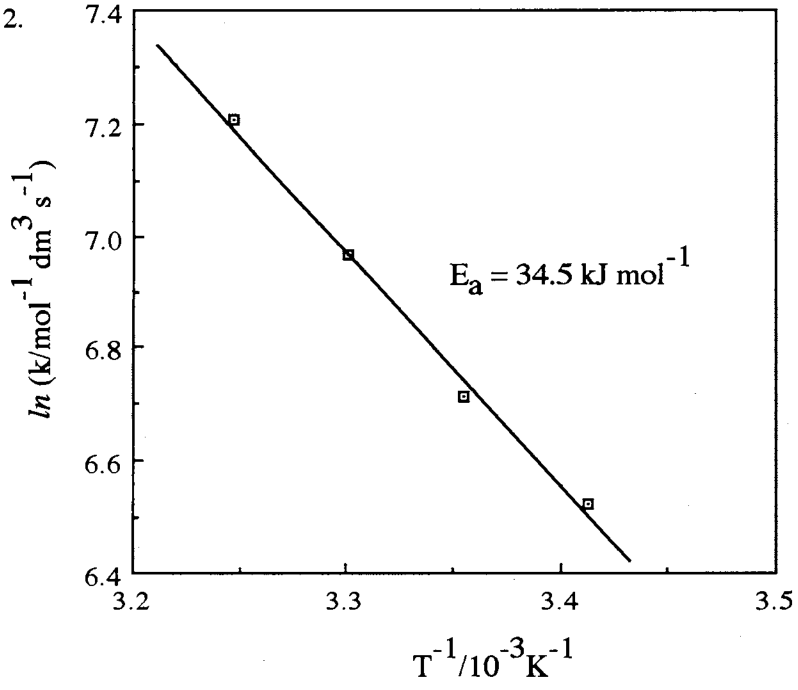


Fig. 3. Arrhenius Plot of k in step 2.

Similarly, the rate constants were determined under the different temperature conditions: k = 6.82×10^2 mol^{-1} dm^3 s^{-1} at 293 K, 10.6×10^2 mol^{-1} dm^3 s^{-1} at 303 K, and 13.5×10^2 mol^{-1} dm^3 s^{-1} at 308 K. The temperature dependence of k is exhibited as an Arrhenius plot in Fig. 3. From the slope of the line, the activation energy was estimated to be 34.5 kJ/mol.

Further work to get more detailed information about the catalytic function of CoTPP is under way.

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4) T. Atoguchi, A. Aratama, and M. Enyo, *Denki Kagaku*, **59**, 526(1991).
5) A glassy carbon electrode (3 mmϕ) was polished with alumina powder after each several potential cycles in the CV measurement and subject to the subsequent use. Otherwise, the reproducible results were not assured, especially in DMF solutions.
6) Z. Galuz, "Fundamentals of Electrochemical Analysis," John Wiley & Sons., New York (1976), p. 311.
7) The solubility of CO_2 in DMF under various CO_2 contents in the bubbling gas was determined experimentally in the range of temperature from 293 K to 308 K. For example, it was 0.211 M under pure CO_2 atmosphere at 298 K. It was also revealed that the solubility was proportional to CO_2 partial pressure and not influenced by the presence of tetraalkylammonium salts.
8) Equation 1 can be derived according to Ref. 6, assuming that the substance to be reduced, namely CO_2, exists in large excess and the electrode process(step 1) is reversible and sufficiently fast, and furthermore, the reverse reaction of step 2 is negligible. The present CV conditions appear to fulfill these requirements thoroughly. Actually, in regard to each redox wave of CoTPP, the ratio of cathodic and anodic peak currents was virtually unity and the interval of the peak potentials was approximately 60 mV.

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