Cobalt Tetraphenylporphine Electrocatalyzed N_2O Reduction in DMF Solution

Meguru Tezuka* and Masakazu Iwasaki
Department of Environmental Engineering, Saitama Institute of Technology, Okabe, Saitama 369-0293

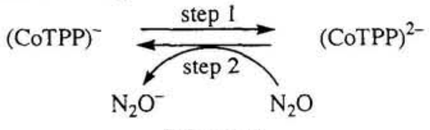
(Received June 25, 1998; CL-980476)

The electrocatalytic reduction of N_2O in the presence of cobalt tetraphenylporphine (CoTPP) was investigated by means of cyclic voltammetry (CV). Based on the kinetical treatment of the data, the rate constant for the electron transfer to N_2O from CoTPP dianion could be determined and the activation energy of the step was estimated as 39.5 kJ mol^{-1}.

Lately, special attention has been paid to the chemistry of nitrous oxide, since it is one of the main compounds responsible for the greenhouse effect causing the global warming. An increasing number of attempts have been made to develop the electrochemical methods for transformation of nitrous oxide to environmentally benign substances. Several groups have studied the electroreduction of N_2O on metal[1-3] or oxide semiconductor[4] electrodes. Recently, the reduction of N_2O at gas diffusion electrodes with various metal catalysts was reported.[5] Taniguchi et al. found that Ni(II) complexes of macrocyclic polyamines catalyzed the reduction of N_2O on a mercury electrode in an aqueous solution.[6] However, to our knowledge, there have been few studies where the electron transfer to N_2O in aprotic solutions was quantitatively discussed by using electroanalytical methods. 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 N_2O catalyzed by CoTPP in DMF solution, focusing on the kinetical consideration of the electron transfer step from the reduced catalyst to N_2O.

In Figure 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 electrode at 298 K. Under an Ar atmosphere (Figure 1b), 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 N_2O into the electrolyte (Figures 1c-e.), the voltammogram of CoTPP was deformed. That is, the peak current of the second reduction wave increased with higher N_2O content in bubbling gas and the corresponding re-oxidation peak disappeared. On the other hand, the first redox wave was substantially unaffected by the presence of N_2O. In addition, it should be noted that N_2O would not be reduced up to -2.2 V vs. SCE without the catalyst (Figure 1a). 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 N_2O molecule to regenerate CoTPP monoanion (step 2). As a consequence, the catalytic current is to be observed.



Scheme 1.

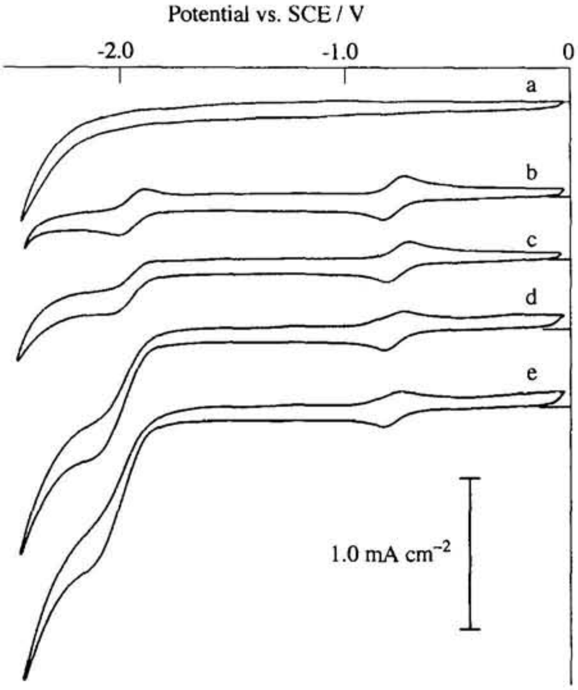


Figure 1. Cyclic voltammograms of CoTPP in the presence of N_2O. CoTPP: 1 mM in 0.1 M $TBABF_4$ - DMF, v: 50 mVs^{-1} on glassy carbon, a: 0.02 atm N_2O without CoTPP, b: 0 atm N_2O, c: 0.02 atm N_2O, d: 0.2 atm N_2O, e: 0.5 atm N_2O

According to the theory concerning the electrochemical catalytic current,[7] 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/v, where C is the concentration of N_2O dissolved in the solution[8] and v is the potential sweep rate, and simply formulated as Eq.1 unless the value of the parameter is extremely low,[9] 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.

$$\frac{i}{i_d} = \frac{1}{0.466}\left(\frac{RT}{nF}\right)^{1/2} k^{1/2}\left[\frac{C}{v}\right]^{1/2} \qquad (1)$$

Figure 2 is a plot of i/i_d against $[C/v]^{1/2}$ on the basis of the CV data obtained by varying either N_2O 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 ca. 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 3.35×10^2 mol^{-1} dm^3 s^{-1}.

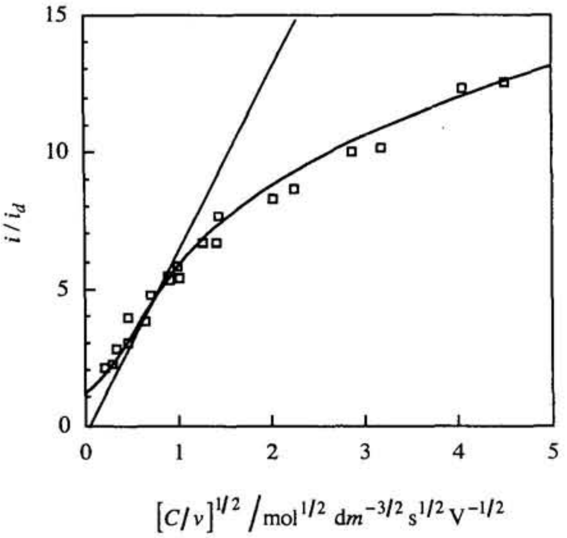


Figure 2. The dependence of i / i_d on $[C/v]^{1/2}$ in 0.1 M $TBABF_4$ – DMF containing 1 mM CoTPP on glassy carbon at 298 K. C: 4 - 100 mM, v: 5-100 mVs^{-1}

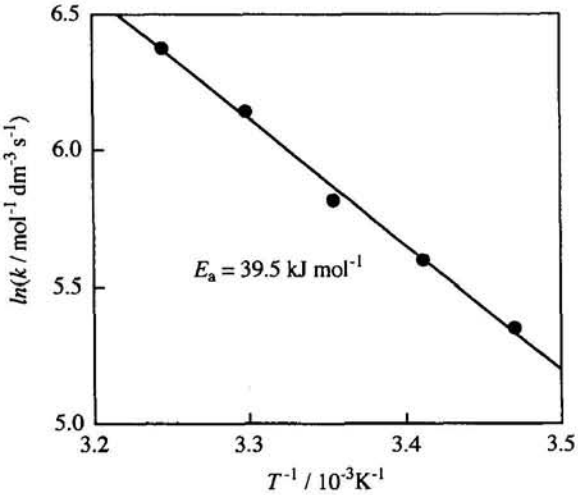


Figure 3. Arrhenius plot of k in step 2.

Similarly, the rate constants were determined under the different temperature conditions: $k = 2.11 \times 10^2$ mol^{-1} dm^3 s^{-1} at 288 K, 2.70×10^2 mol^{-1} dm^3 s^{-1} at 293 K, 4.65×10^2 mol^{-1} dm^3 s^{-1} at 303 K and 5.87×10^2 mol^{-1} dm^3 s^{-1} at 308 K. The temperature dependence of k is exhibited as an Arrhenius plot in Figure 3. From the slope of the line, the activation energy was estimated to be 39.5 kJ mol^{-1}.

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

References and Notes

1 K. E. Johnson and D. T. Sawyer, *J. Electroanal. Chem.*, **49**, 95 (1974).
2 G. Ritzoulis, *J. Electroanal. Chem.*, **327**, 209 (1992).
3 G. Attard and A. Ahmadi, *J. Electroanal. Chem.*, **389**, 175 (1995).
4 A. Kudo and A. Mine, *J. Electroanal. Chem.*, **426**, 1 (1997).
5 M. Shibata, K. Murase, and N. Furuya, *Denki Kagaku*, **65**, 1039 (1997).
6 I. Taniguchi, T. Shimpuku, K. Yamashita, and H. Ohtaki, *J. Chem. Soc., Chem. Commun.*, **1990**, 915.
7 Z. Galuz, "Fundamentals of Electrochemical Analysis," John Wiley & Sons., New York (1976), p311.
8 The solubility of N_2O in DMF under various N_2O contents in the bubbling gas was determined by means of gas chromatography in the range of temperature from 288 K to 308 K. For example, it was 0.208 M under pure N_2O atmosphere at 298 K. It was also revealed that the solubility was proportional to N_2O partial pressure and not influenced by the presence of tetraalkylammonium salts.
9 Equation 1 can be derived according to Ref. 7, assuming that the substance to be reduced, namely N_2O, 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 independent of the potential sweep rate, although it was somewhat larger than 60mV.