CHEMISTRY LETTERS, pp. 1951-1954, 1987.

Carbon Dioxide Fixation Coupled with Nitrite Reduction, Catalyzed by 4Fe4S Cluster

Koji TANAKA,* Ryuhei WAKITA, and Toshio TANAKA*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamada-oka, Suita, Osaka 565

The reduction of $(Et_4N)NO_2$ catalyzed by $(Bu_4N)_2$-$[Fe_4S_4(SPh)_4]$ in the presence of $PhCOCH_3$ and Molecular Sieves 3A as a proton source and a dehydration agent, respectively, under the controlled potential electrolysis at -1.25 V *vs*. SCE in CO_2-saturated CH_3CN catalytically produced not only N_2 with a small amount of N_2O as a precursor of N_2 but also $PhCOCH_2COO^-$.

The amounts of inorganic nitrogen compounds such as N_2, NH_3, and NO_3^- are regulated by the nitrogen cycle. Ammonia is a single inorganic nitrogen compound which can be converted into organic nitrogen compounds directly. Most of green plants and bacteria which are incapable of N_2 fixation reduce nitrate and/or nitrite involved in soil to produce ammonia (assimilation). On the other hand, dissimilatory reductases reduce those substrates to evolve N_2 *via* N_2O. It has been estimated that photosynthetic bacteria consume electrons for CO_2 fixation and assimilatory NO_3^- reduction with the ratio 4:1 in biosyntheses.1) Iron-sulfur proteins participate as electron transfer catalysts in those reactions.2) This letter describes carbon dioxide fixation coupled with NO_2^- reduction, catalyzed by $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ 3) (1).

Recently, we have reported that $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ catalyzes assimilatory and dissimilatory reductions of NO_3^- under the controlled potential electrolysis at -1.25 and -1.00 V *vs*. SCE, respectively, in water (Eqs. 1 and 2).4) We have

$$NO_3^- + 9H^+ + 8e^- \longrightarrow NH_3 + 3H_2O \quad (1)$$

$$2NO_3^- + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O \quad (2)$$

found that the reduction of NO_2^- is also catalyzed by **1** under the controlled potential electrolysis at -1.25 V vs. SCE even in dry CH_3CN containing $PhCOCH_3$ as a proton source in place of water. The cyclic voltammogram (CV) of **1** shows the (2-/3-) redox couple at $E_{1/2}$ = -0.97 V vs. SCE in dry CH_3CN (Fig. 1a). The addition of $(Et_4N)NO_2$ to the solution results in the appearance of a weak redox couple at $E_{1/2}$ = -1.17 V[5] as a shoulder of the original redox couple of **1** (Fig. 1b), and the pattern of the CV was essentially unchanged upon addition of $PhCOCH_3$. A strong cathodic current, however, flows at more negative potentials than -1.17 V when the solvent was saturated with CO_2 in order to trap the deprotonated species of $PhCOCH_3$ (Fig. 1c). The threshold potential of the cathodic current agrees with the reduction potential of the **1**-NO_2^- system, suggesting that CO_2 effectively enhances the reduction of NO_2^- by **1** in the presence of $PhCOCH_3$ since such a strong cathodic current was not observed in the absence of either NO_2^-, $PhCOCH_3$, or CO_2. The controlled potential electrolysis by using a glassy carbon electrode at -1.25 V in a CO_2-saturated CH_3CN (17 cm^3) containing **1** (11.8 μmol), $(Et_4N)NO_2$ (0.88 mmol), $PhCOCH_3$ (34.8 mmol), and Bu_4NBr (1.6 mmol) selectively produced only N_2; the reduction of CO_2 has

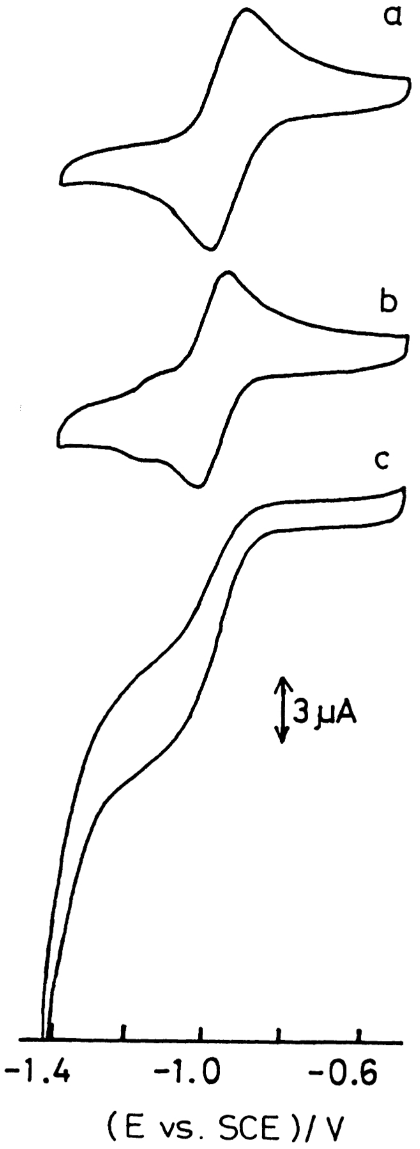

Fig. 1. Cyclic voltammograms of $[Fe_4S_4(SPh)_4]^{2-}$ (**1**; 1.1 mmol/dm^3) in the absence (a) and presence of $(Et_4N)_2NO_2$ (72 mmol/dm^3) (b), and **1** in the presence of $(Et_4N)NO_2$ (72 mmol/dm^3), $PhCOCH_3$ (1.8 mol/dm^3), and saturated CO_2 (c) in dry-CH_3CN containing Bu_4NBr (0.1 mol/dm^3); dE/dt = 100 mV/s.

hardly occurred. On the other hand, the same electrolysis conducted in the presence of Molecular Sieves 3A as a dehydration agent produces not only N_2 (current efficiency 70%) with a small amount of N_2O as a precursor of N_2 but also $PhCOCH_2COO^-$,[6] whose amount was about 7 times larger than that of N_2 (Fig. 2). The stoichiometry of the present CO_2 fixation coupled with NO_2^- reduction may, therefore, be expressed by Eq. 3.

$$8PhCOCH_3 + 2NO_2^- + 8CO_2 + 6e^- \longrightarrow 8PhCOCH_2COO^- + N_2 + 4H_2O \qquad (3)$$

Electrochemical NO_n^- (n = 2, 3)[4,7] and CO_2[8] reductions catalyzed by transition metal complexes including Fe_4S_4 clusters[9] have been studied, independently so far. The products in most of the latter reaction have, however, been limited to CO and/or $HCOO^-$. The direct conversion of CO_2 to organic compounds other than $HCOO^-$ is highly desired in the view point of the utilization of CO_2.[10] Thus, the present reaction is the first example which has succeeded in CO_2 fixation coupled with NO_2^- reduction affording keto acid.

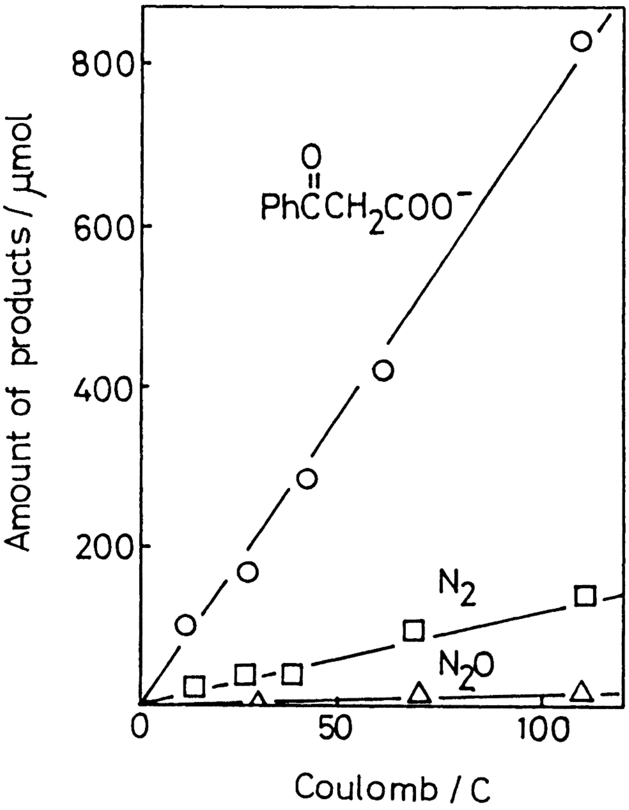

Fig. 2. The amounts of N_2, N_2O, and $PhCOCH_2COO^-$ formed in the CO_2 fixation coupled with $(Et_4N)NO_2$ (0.88 mmol) reduction, catalyzed by **1** (11.8 μmol) under the controlled potential electrolysis at -1.25 V vs. SCE in CO_2-saturated CH_3CN (17 cm^3) containing $PhCOCH_3$ (34.8 mmol) and Bu_4NBr (1.55 mmol).

The authors are grateful to the Ministry of Education for support of this work through Grant-in-Aid for Scientific Research (Grant No. 61125003).

References

1) L. Losda, M. G. Guerreero, and J. M. Vega, "Biology of Inorganic and Sulfur," ed by H. Bothe and A. Trbst, Springer-Verlag, Berlin (1981), pp. 30-63.

2) M. W. W. Adams and L. E. Mortenson, "Molybdenum Enzymes," ed by T. G. Spiro, John Wieley & Sons, New York (1985), pp. 519-593; M. C. W. Evans, "Iron-Sulfur Proteins," ed by T. G. Spiro, John Wieley & Sons, New York (1982), pp. 249-284.

3) L. Que, Jr., M. A. Bobrik, J. A. Ibers, and R. H. Holm, J. Am. Chem. Soc., 96, 4168 (1974).

4) S. Kuwabata, S. Uezumi, K. Tanaka, and T. Tanaka, J. Chem. Soc., Chem. Commun., 1986, 135; S. Kuwabata, S. Uezummi, K. Tanaka, and T. Tanaka, Inorg. Chem., 25, 3018 (1986).

5) NO_2^- undergoes no redox reaction in the present potential region.

6) N_2 and N_2O were determined by GC with a column packed with Molecular Sieves 13X, and $PhCOCH_2COO^-$ by HPLC with columns packed with ODS and a Shodex Ionpak KC-811 as well as by a isotachophoretic analyzer.[8b)]

7) M. H. Barley, K. Takeuchi, W. R. Murphy, Jr., and T. J. Meyer, J. Chem. Soc., Chem. Commun., 1985, 507; W. R. Murphy, Jr., K. Takeuchi, M. H. Barley, and T. J. Meyer, Inorg. Chem., 25, 1041 (1986).

8) a) D. L. DuBois and A. Miedaner, J. Am. Chem. Soc., 109, 113 (1987); b) H. Ishida, K. Tanaka, and T. Tanaka, Organometallics, 6, 181 (1987) and the refs. cited therein.

9) M. Tezuka, Y. Yajima, A. Tsuchiya, Y. Matsumoto, Y. Uchida, and M. Hidai, J. Am. Chem. Soc., 104, 6834 (1982); M. Nakazawa, Y. Mizobe, Y. Matsumoto, Y. Uchida, M. Tezuka, and M. Hidai, Bull. Chem. Soc. Jpn., 59, 809 (1986).

10) H. Ishida, K. Tanaka, and T. Tanaka, Chem. Lett., 1987, 597; H. Torii, H. Tanaka, T. Hamatani, K. Morisaki, A. Jutand, F. Peluger, and J. F. Fauvarque, ibid., 1986, 169.

(Received July 18, 1987)