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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

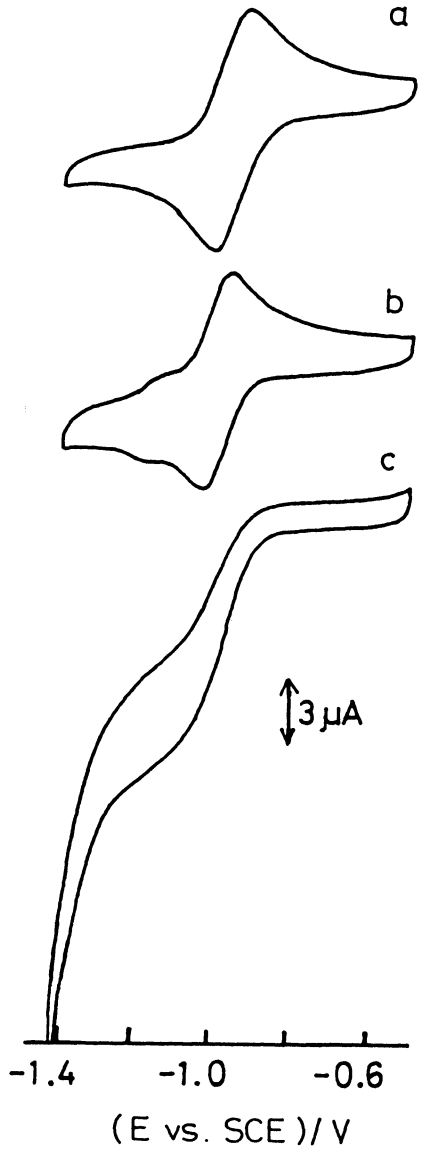

Fig. 1. Cyclic voltammograms of $[Fe_4S_4(SPh)_4]^{2-}$ (**1**; 1.1 mmol/dm^3) in the absence (a) and presence of $(Et_4N)_2NO_2$ (72 mmol/dm^3) (b), and **1** in the presence of (Et_4N)-NO_2 (72 mmol/dm^3), $PhCOCH_3$ (1.8 mol/dm^3), and saturated CO_2 (c) in dry-CH_3CN containing Bu_4NBr (0.1 mol/dm^3);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

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

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.

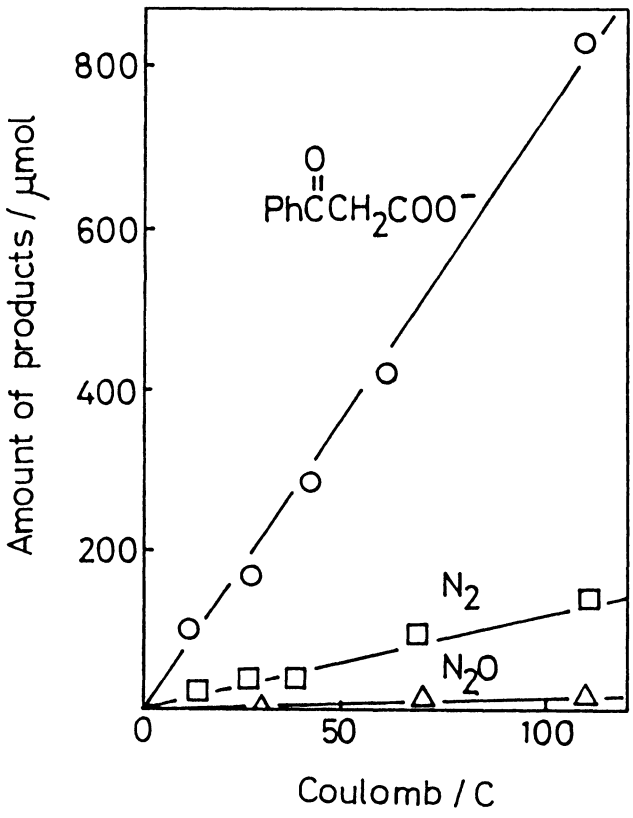

Fig. 2. The amounts of N_2, N_2O, and $PhCOCH_2COO^-$ formed in the CO_2 fixation coupled with $(Et_4N)NO_2$ (0.88 mmol) reduction, catalyzed by **1** (11.8 μmol) under the controlled potential electrolysis at -1.25 V vs. SCE in CO_2-saturated CH_3CN (17 cm^3) containing $PhCOCH_3$ (34.8 mmol) and Bu_4NBr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

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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]

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