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Electrochemical Carboxylation Coupled with Nitrite Reduction Catalyzed by $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$

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Abstract: The controlled-potential electrolysis of CO_2-saturated CH_3CN containing $[Fe_4S_4(SPh)_4]^{2-}$, NO_2^-, $PhCOCH_3$, and a dehydration agent at −1.25 V vs SCE catalytically produced not only N_2 accompanied by a small amount of N_2O but also $PhCOCH_2COO^-$ with the mole ratio 1:7. $N_2O_2^{2-}$ as a precursor of N_2O was confirmed in the reaction mixture. The reduction of NO_2^- catalyzed by the reduced species of $[Fe_4S_4(SPh)_4]^{2-}$, therefore, proceeds via NO^-, $N_2O_2^{2-}$, and N_2O, where $PhCOCH_3$ plays the role of proton source in each reaction step and the resulting $PhCOCH_2^-$ reacts with CO_2 to afford $PhCOCH_2COO^-$. The stoichiometry of the CO_2 fixation coupled with NO_2^- reduction may be expressed as follows: $2NO_2^- + 8PhCOCH_3 + 8CO_2 + 6e^- \rightarrow N_2 + 8PhCOCH_2COO^- + 4H_2O$. On the basis of this stoichiometry, the current efficiencies for the formation of N_2 and $PhCOCH_2COO^-$ are 70 and 78%, respectively. Similar CO_2 fixation coupled with NO_2^- reduction was also conducted in the presence of phenylacetylene, cyclohexanone, and acetone as proton sources.

The reduction of CO_2 has been of much interest to cope with not only the predicted energy shortage in the near future but also the increase in the concentration of CO_2 in air. Among electrochemical,[1] photoelectrochemical,[2] and photochemical CO_2 reductions,[3] electrochemical CO_2 reduction using homogeneous catalysts seems to have a bright prospect from the viewpoint of reducing energy consumption since the direct reduction of CO_2 on metallic cathodes requires potentials more negative than −2.0 V vs SCE.[1a] Although the production of highly reduced products such as CH_4[4] and CH_3OH[5] has been reported in some CO_2 reductions, the products in most of the electrochemical CO_2 reductions have been limited to CO[1a-l] and HCOOH.[1a,b,p-t] On the other hand, CO_2 as an electrophile smoothly reacts with carbanions and organometallic compounds such as Grignard reagents[6] and RM (M = Li,[7] Na[8]) to afford the corresponding carboxylic acids (carboxylation). In connection with this, electroreductive carboxylation of aryl halide has been conducted in the presence of Pd[9] and Ni[10] complexes at −2.4 to −2.9 V vs Ag/Ag^+. The electrochemical carboxylation of organic molecules without carbon–halogen bonds is also another important method for the utilization of CO_2.

Recently, we reported that NO_2^- forms an adduct with the reduced species of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ with liberation of a terminal PhS^- ligand and is reduced to NH_3 via NH_2OH (eq 1) under

$$NO_2^- + 7H^+ + 6e^- \rightarrow NH_3 + 2H_2O \tag{1}$$

controlled-potential electrolysis at −1.25 V vs SCE in H_2O.[11] Such an assimilatory reduction of NO_2^- to NH_3 is caused by the increase in electron density of NO_2^- upon coordination to the reduced form of the cluster. If the same cluster has the ability to catalyze a similar multielectron reduction of NO_2^- in the presence of organic molecules with an active hydrogen as a proton source under a CO_2 atmosphere, a catalytic carboxylation of the resulting carbanions would be expected. Such a CO_2 fixation coupled with NO_2^- reduction seems to be of much interest from the viewpoint not only of biological CO_2 fixation but also the nitrogen cycle, which regulates the amounts of inorganic nitrogen compounds such as N_2, NH_3, NO_2^-, and NO_3^-. Most of the higher plants and microorganisms that are not provided with the ability of N_2 fixation reduce NO_3^- and NO_2^- to NH_3 (assimilatory reduction),[12] which is the only inorganic nitrogen compound metabolized by microorganisms. Some photosynthetic bacteria have been estimated to use electrons in a 4:1 ratio for CO_2 fixation and NO_3^- reduction.[13] On the other hand, anaerobic bacteria use NO_2^- and NO_3^- as oxidants in place of O_2 and evolve N_2 via N_2O (dissim-

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ilatory reduction).[14] Iron–sulfur proteins participate as an electron-transfer catalyst not only in assimilatory and dissimilatory reductions of NO_n^- ($n = 2, 3$) but also in CO_2 fixation in biological systems.[15] This study undertakes electrochemical carboxylation coupled with NO_2^- reduction, catalyzed by $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ under controlled electrolysis at −1.25 V vs SCE in CO_2-saturated CH_3CN. Part of this paper has appeared recently.[16]

Experimental Section

Materials. The preparations of $(Bu_4N)_2[Fe_4S_4(SPh)_4]$,[17] $(Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$,[18] $(Et_4N)NO_2$,[19] and $PhCOCH_2COOH$[20] were described elsewhere. Solvents were purified by distillation over dehydrating agents (P_2O_5 for CH_3CN, CaO for dimethylformamide (DMF), and $CaSO_4$ for CH_3COCH_3) and stored under N_2. Molecular sieves 3A were dehydrated at 473 K under reduced pressure. Acetophenone, phenylacetylene, and cyclohexanone were dried with molecular sieves 3A in CH_3CN. Commercially available guaranteed reagent grade acetoacetic acid lithium salt and phenylpropiolic acid were used as authentic samples.

Physical Measurements. Electronic absorption spectra were measured with a Union SM-401 spectrophotometer. Spectrophotoelectrochemical experiments were carried out with an optically transparent thin-layer electrode,[21] consisting of a Pt-gauze electrode in a 0.5-mm quartz cuvette, a Pt-wire auxiliary electrode, and a saturated calomel electrode (SCE). Electrochemical measurements of $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ were performed in a Pyrex cell equipped with a glassy carbon (GC) working electrode, a Pt auxiliary electrode, an SCE, and a nozzle for bubbling N_2 or CO_2. Cyclic voltammetry was performed with a Hokuto Denko HB-401 potentiostat, a Hokuto Denko HB-107 function generator, and a Watanabe Electric Inc. 3077 X–Y recorder. The cathodic polarization was conducted in DMF with a GC electrode. Various CO_2 concentrations in DMF containing $(Bu_4N)_2[Fe_4S_4(SPh)_4]$, $NaNO_2$, $PhCOCH_3$ or CH_3COCH_3, and Bu_4NBr were prepared by bubbling CO_2 into the solution for a few seconds. The solution was stirred magnetically for a short period and then allowed to stand for 15 min. The CO_2 concentrations in the solution were determined with a gas chromatograph filled with Gaschropack 54 (2-m column) by sampling the liquid phase through a septum cap attached to the top of the cell with syringe techniques.

Carboxylation Coupled with NO_2^- Reduction. Carboxylation coupled with NO_2^- reduction catalyzed by $[Fe_4S_4(SPh)_4]^{2-}$ or $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ was carried out under controlled-potential electrolysis conditions at −1.25 V vs SCE in CO_2-saturated CH_3CN. The cell consisted of a GC working electrode, a Pt auxiliary electrode, and an SCE reference electrode;[22] the GC and Pt electrodes were separated with a Nafion membrane. The volumes of these compartments were 45, 30, and 10 cm^3. The working electrode cell was connected to a volumetric flask with a stainless tube. After a stream of CO_2 was passed through the electrolysis cell and the volumetric flask for 30 min to displace air, molecular sieves 3A and a CH_3CN solution containing $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ or $(Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$, Et_4NNO_2,[23] RH (R = $PhCOCH_2$, c-$C_6H_9(O)$, CH_3COCH_2, and $PhC{\equiv}C$), and Bu_4NBr were introduced into the electrode compartments. Then the electrolysis cell was placed in a thermostat at 298 K and the solution was stirred magnetically for 30 min. Electrochemical carboxylation coupled with NO_2^- reduction was started by applying the electrolysis potential to the GC working electrode with a potentiostat (−1.25 V vs SCE). The charge consumed in the electrolysis was measured by a Hokuto Denko HF-201 coulometer.

Product Analysis. At a fixed time interval, 0.1-cm^3 portions of gas not only in the working electrode cell but also in the volumetric flask were sampled with a pressure-lock syringe (Precision Sampling) through septum caps attached to the tops of those compartments. Gas analysis was performed on a Shimazu gas chromatograph GC-3BT with a 2.0-m column filled with molecular sieves 13X at 343 K using He (40 cm^3/min) as a carrier gas. The volume of gaseous phase in the volumetric flask connected to the working electrode cell was determined from the height of the meniscus of water. The analysis of the products in the solution was performed at a fixed time interval by sampling 0.3-cm^3 portions of the solution in the working electrode cell with syringe techniques through a septum cap. After the solution was mixed with the same volume of H_2O, the mixture was centrifuged, followed by filtration with a membrane filter. The filtrate was analyzed not only by HPLC with columns packed with ODS and Shodex Ionpack KC-811 but also by a Shimazu isotachophoretic analyzer IP-2A.[24] The amount of $N_2O_2^{2-}$ in the reaction mixture was also determined with an isotachophoretic analyzer by using $Cd(NO_3)_2$ (6.0 mmol/dm^3) and $CH_3(CH_2)_4COOH$ (10.0 mmol/dm^3) as leading and terminal electrolytes, respectively.[24] The analysis of NO_2^- in the solution was conducted by a colorimetric method.[25]

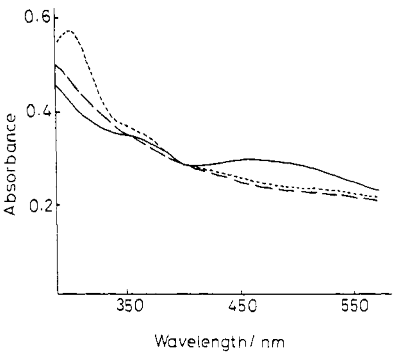

Figure 1. Electric absorption spectra of $[Fe_4S_4(SPh)_4]^{2-}$ (0.5 mmol/dm^3) (—) and $[Fe_4S_4(SPh)_4]^{3-}$ produced at −1.25 V vs SCE in the absence (– – –) and the presence (- - -) of $NaNO_2$ (50 mmol/dm^3) in DMF.

Results and Discussion

Interaction of $[Fe_4S_4(SPh)_4]^{2-}$ with NO_2^-. It has been reported that $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ has no interaction with NO_2^-, whereas the reduced species of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ reversibly reacts with NO_2^- to afford the adduct with dissociation of a terminal PhS^- ligand.[11] A similar interaction between $[Fe_4S_4(SPh)_4]^{2-}$ and NO_2^- was observed in the electronic absorption spectra: a DMF solution of $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ shows two absorption bands centered at 360 and 470 nm, as shown by the solid line in Figure 1. The spectrum was not affected by the addition of a large excess of $NaNO_2$. The controlled-potential electrolysis of $[Fe_4S_4(SPh)_4]^{2-}$ at −1.25 V vs SCE in the presence of $NaNO_2$ in DMF results in the disappearance of the 470-nm band accompanied by the appearance of a new band at 306 nm, as shown by the dotted line in Figure 1, which is remarkably different from the spectrum of $[Fe_4S_4(SPh)_4]^{3-}$ (the broken line in Figure 1) prepared under controlled-potential electrolysis of $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ at the same potential in the absence of $NaNO_2$ in DMF. The 306-nm band observed only in the reduced species of $[Fe_4S_4(SPh)_4]^{2-}$ in the presence of $NaNO_2$ results from the PhS^- anion liberated from the cluster, since the band position and the feature coincide with those in the spectrum of PhS^- prepared by the electrochemical reduction of PhSH with a Pt electrode at −1.50 V vs SCE in DMF.[11] In addition, the absorptivity at 306 nm in the spectrum of $[Fe_4S_4(SPh)_4]^{3-}$ in the presence of $NaNO_2$ indicates that 1 mol of PhS^- (ϵ_M = 19 800 $mol^{-1}\ dm^3\ cm^{-1}$) dissociates from 1 mol of the cluster, suggesting the formation of an adduct of the cluster and NO_2^- upon liberation of a PhS^- ligand. The electrochemical reoxidation of the resulting cluster–NO_2^- adduct at −0.50 V vs SCE brought about the decrease and the increase in the absorbance at 306 and 470 nm, respectively. The spectrum obtained after 1 h was almost consistent with that of $[Fe_4S_4(SPh)_4]^{2-}$. Thus the electrochemical redox cycle of $[Fe_4S_4(SPh)_4]^{2-}$ in the presence of NO_2^- reveals that NO_2^- coordinates to the reduced species of $[Fe_4S_4(SPh)_4]^{2-}$ upon dissociation of a terminal PhS^- ligand.

Cyclic Voltammograms of $[Fe_4S_4(SPh)_4]^{2-}$ in the Presence of NO_2^-, $PhCOCH_3$, and CO_2 in DMF. The cyclic voltammogram

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[23] Et_4NNO_2 prepared by the reaction of $AgNO_2$ with Et_4NBr was usually contaminated by a small amount of Ag^+, which decomposes $[Fe_4S_4(SPh)_4]^{2-}$. Therefore, Ag^+ was removed from the crude product by the controlled-potential electrolysis at −0.50 V vs SCE in CH_3CN.

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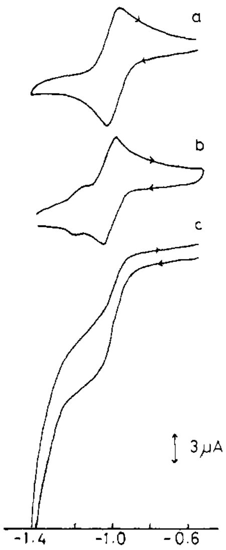

Figure 2. Cyclic voltammograms of $[Fe_4S_4(SPh)_4]^{2-}$ (1.1 mmol/dm^3) in the absence (a) and in the presence of $NaNO_2$ (72 mmol/dm^3) (b), and of $[Fe_4S_4(SPh)_4]^{2-}$ in the presence of $NaNO_2$, $PhCOCH_3$ (1.8 mol/dm^3), and CO_2 (230 mmol/dm^3) (c) in DMF containing Bu_4NBr (0.1 mol/dm^3); dE/dt = 100 mV/s.

of $[Fe_4S_4(SPh)_4]^{2-}$ in DMF shows cathodic and anodic waves at −0.98 and −1.04 V vs SCE, respectively, due to the (2−/3−) redox couple (Figure 2a). The addition of $NaNO_2$ to the solution resulted in the appearance of weak cathodic and anodic waves at −1.14 and −1.20 V as shoulders of the $[Fe_4S_4(SPh)_4]^{2-/3-}$ redox waves. When a potential of −1.40 V is applied to the working electrode for 3 min, so that all the cluster existing on the electrode surface may be reduced to $[Fe_4S_4(SPh)_4]^{3-}$, followed by a potential sweep between −1.40 and −0.50 V, the redox couple at $E_{1/2} = -1.17$ V $((E_{pc} + E_{pa})/2)$ is observed more clearly (Figure 2b). The newly appearing $E_{1/2} = -1.17$ V redox couple may be associated with the previously mentioned cluster–NO_2^- adduct. The cyclic voltammogram of $[Fe_4S_4(SPh)_4]^{2-}$ in the presence of $NaNO_2$ was essentially unchanged upon addition of $PhCOCH_3$, suggesting that the NO_2^- ligated on the cluster is not reduced in the presence of $PhCOCH_3$ as a proton source. On the other hand, a strong cathodic current due to the reduction of NO_2^- (vide infra) flows at potentials more negative than −1.17 V vs SCE when CO_2 is bubbled into the DMF solution containing $[Fe_4S_4(SPh)_4]^{2-}$, NO_2^-, and $PhCOCH_3$ (Figure 2c). Furthermore, the strong irreversible cathodic current almost disappeared when N_2 was bubbled into the solution for 30 min. It should be noted that the threshold potential of the strong cathodic current observed only in the CO_2-saturated solution (Figure 2c) is consistent with the cathode peak potential of the redox couple of the cluster–NO_2^- adduct in the CO_2-free solution (Figure 2b). This observation indicates that CO_2 effectively enhances the reduction of NO_2^- in the presence of $PhCOCH_3$ since such a strong cathodic current never flows in the absence of NO_2^-, $PhCOCH_3$, or CO_2. The cyclic voltammogram of CO_2-saturated DMF containing $[Fe_4S_4(SPh)_4]^{2-}$, NO_2^-, and cyclohexanone or CH_3COCH_3 as a proton source also showed the strong cathodic current due to the reduction of NO_2^- at potentials more negative than −1.17 V vs SCE.

Carboxylation Coupled with NO_2^- Reduction. The controlled-potential electrolysis at −1.25 V vs SCE in CO_2-saturated CH_3CN containing $(Bu_4N)_2[Fe_4S_4(SPh)_4]$, $PhCOCH_3$, Et_4NNO_2, and Bu_4NBr produced N_2 accompanied by a small amount of N_2O, and the amounts of those products increased with time, suggesting that $PhCOCH_3$ plays the role of proton source in the dissimilatory reduction of NO_2^- (eq 2 and 3). On the other hand,

$$2NO_2^- + 6H^+ + 4e^- \rightarrow N_2O + 3H_2O \quad (2)$$

$$2NO_2^- + 8H^+ + 6e^- \rightarrow N_2 + 4H_2O \quad (3)$$

$PhCOCH_2COO^-$ as the carboxylation product of $PhCOCH_3$ was generated only in the initial stage of the electrolysis. This result indicates that H_2O formed in eq 2 and 3 functions as a proton source rather than $PhCOCH_3$ in the dissimilatory reduction of NO_2^-.[26] In order to avoid the participation of H_2O as a proton source in the reduction of NO_2^-, the same electrochemical NO_2^- reduction was conducted in the presence of molecular sieves 3A as a dehydration agent under otherwise the same conditions, in which not only N_2 accompanied by a small amount of N_2O but also $PhCOCH_2COO^-$ were formed with the mole ratio 1:7 (Figure 3). The turnover number for the formation of $PhCOCH_2COO^-$ based on the amount of $[Fe_4S_4(SPh)_4]^{2-}$ was 70 at 100 C passed in the electrolysis. In addition, 25 μmol of $N_2O_2^{2-}$[27] as a precursor of N_2O was confirmed in the solution at this stage. If all the protons required in eq 3 are supplied by $PhCOCH_3$ and the resulting $PhCOCH_2^-$ is trapped by CO_2, the mole ratio of N_2 and $PhCOCH_2COO^-$ would be 1:8 (eq 4), which is very close to the

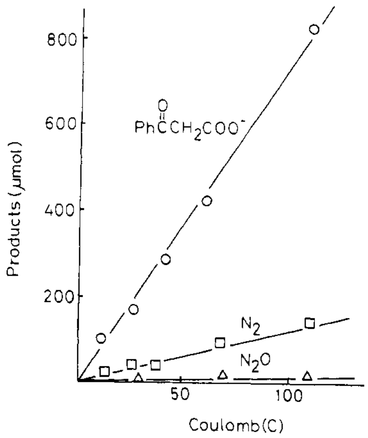

Figure 3. Electrochemical carboxylation coupled with NO_2^- reduction under controlled-potential electrolysis at −1.25 V vs SCE in CO_2-saturated CH_3CN containing $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ (11.8 μmol), Et_4NNO_2 (0.88 mmol), $PhCOCH_3$ (34.8 mmol), Bu_4NBr (1.6 mmol), and molecular sieves 3A (1.2 g).

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

observed value. Thus $PhCOCH_3$ effectively plays the role not only of a proton source but also of a trapping agent of CO_2 under anhydrous conditions. It should be noted that the present CO_2 fixation (eq 4) proceeds with one-electron reduction since eight molecules of $PhCOCH_2COO^-$ are generated with six electrons and two negative charge of NO_2^-. This is in marked contrast to most of the electrochemical CO_2 fixation, in which CO_2 is reduced to CO and/or HCOOH with two electrons and two protons (eq 5 and 6). On the basis of the stoichiometries of eq 2–4, the current

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (5)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \quad (6)$$

efficiencies for the formation of N_2, N_2O, and $PhCOCH_2COO^-$ were 70, 6.6,[28] and 78%, respectively (entry 1 in Table I). In addition, the electrochemical reoxidation of the final solution[29] at −0.60 V vs SCE in the presence of 5 M excess of PhSH recovered the electronic absorption bands at 470 nm due to $[Fe_4S_4(SPh)_4]^{2-}$ with about 90% absorptivity of the original electronic absorption spectrum of the cluster, suggesting that most

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[26] The accumulation of OH^- due to consumption of H^+ (from H_2O) in the dissimilatory reduction of NO_2^- may also assist the decomposition of $PhCOCH_2COO^-$.

[27] As the analysis of $N_2O_2^{2-}$ was conducted in an aqueous solution (see Experimental Section), this value may be less than the actual one since the decomposition of $N_2O_2^{2-}$ is accelerated by the presence of ketone and CO_2 in an aqueous solution.[43]

[28] The amounts of N_2O and N_2 dissolved in CH_3CN have not been determined.

[29] Before the electrochemical oxidation was started, 100 C had been passed in the electrochemical carboxylation coupled with NO_2^- reduction.

Table I. Electrochemical Carboxylation Coupled with NO_2^- Reduction Catalyzed by $[Fe_4S_4(SPh)_4]^{2-}$ (4Fe) and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ (MoFe) under Controlled-Potential Electrolysis at −1.25 V vs SCE[a]

entry	cluster	proton donor	products[b] (μmol)	current eff, % RCOO⁻	current eff, % N_2[c]	current eff, % N_2O[c]
1	4Fe	$PhCOCH_3$	$PhCOCH_2COO^-$ (800)	78	70	6.6
2	MoFe	$PhCOCH_3$	$PhCOCH_2COO^-$ (520)	50	98	
3	4Fe	$PhC{\equiv}CH$	$PhC{\equiv}CCOO^-$ (310)	30	67	9.2
4	4Fe	$C_6H_{10}(O)$	$2\text{-}C_6H_9(O)COO^-$ (415)	40	90	0.5
5	4Fe	CH_3COCH_3[d]	$CH_3COCH_2COO^-$ (34)	3.3	73	19
6[e]	4Fe	$PhCOCH_3$	none		0	0
7[f]	4Fe	$PhCOCH_3$	none	0		

[a] In CO_2-saturated CH_3CN containing the Bu_4N salt of 4Fe or MoFe (11.8 μmol), Et_4NNO_2 (0.88 mmol), proton donors (34.8 mmol), Bu_4NBr (1.6 mmol), and molecular sieves 3A (1.2 g). [b] 100 C was passed in the electrolysis. [c] Gaseous phase. [d] $MgSO_4$ was used in place of molecular sieves 3A. [e] In the absence of CO_2. [f] In the absence of Et_4NNO_2; only the reduction of $[Fe_4S_4(SPh)_4]^{2-}$ takes place in the absence of either CO_2 or NO_2^- and thereafter no cathodic current flows.

of the clusters retain the Fe_4S_4 core during the electrolysis.

The molybdenum–iron–sulfur cluster $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ has also an ability of catalyzing the CO_2 fixation coupled with NO_2^- reduction; the controlled-potential electrolysis at −1.25 V in CO_2-saturated CH_3CN containing $(Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$, Et_4NNO_2, $PhCOCH_3$, and Bu_4NBr in the presence of molecular sieves 3A produced N_2 and $PhCOCH_2COO^-$ with current efficiencies 98 and 60%, respectively (entry 2 in Table I). As expected from the quite high current efficiency for the formation of N_2, no assimilatory reduction of NO_2^- affording NH_3 (eq 1) took place under the conditions. This is in marked contrast to the selective formation of NH_3 via NH_2OH in the reduction of NO_2^- by the same cluster under the electrolysis at −1.25 V vs SCE in H_2O (pH 10.0).[11] Such an alternation of the reaction products from N_2 via N_2O in CO_2-saturated CH_3CN to NH_3 via NH_2OH in H_2O implies the presence of a common intermediate NO^- ($pK_a = 4.7$ for free HNO)[30] in both NO_2^- reductions. In aqueous conditions, NO^- formed by the two-electron reduction of NO_2^- on the molybdenum–iron–sulfur cluster, therefore, undergoes further two electron reduction, affording NH_2OH under the electrolysis conditions. On the other hand, the dissociation of NO^- from the cluster may take place in dry CH_3CN prior to the subsequent two-electron reduction of NO^- on the cluster because the rate of the reduction in CH_3CN should be very slow compared with that in H_2O due to the low acidity of $PhCOCH_3$ as the proton source. Hyponitrite dianion ($N_2O_2^{2-}$) as a precursor of N_2O may, therefore, be formed by a dimerization of NO^-[31] dissociated from the cluster, whereas a rapid protonation of NO^- ligated on the cluster in H_2O may lead to the formation of NH_2OH. Thus, those dissimilatory and assimilatory reductions of NO_2^- in CO_2-saturated CH_3CN and in H_2O, respectively, seem to be controlled by the acidity of the proton sources. Although we have not succeeded in the isolation of the cluster–NO_n^- (n = 1, 2) adduct, the view that the cluster–NO^- adduct is formed by the dehydration (two-electron reduction) of NO_2^- on the cluster suggests that NO_2^- is bonded to the cluster with the nitrogen atom (nitro form) rather than with the oxygen atom (nitrito form).

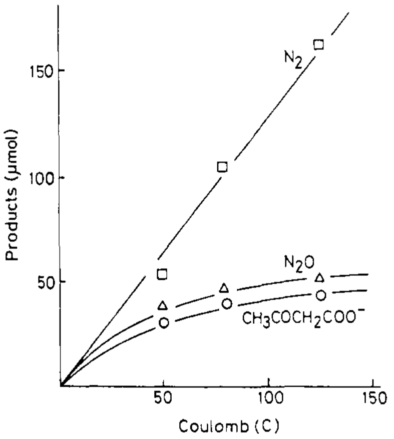

Figure 4. Electrochemical carboxylation coupled with NO_2^- reduction under controlled-potential electrolysis at −1.25 V vs SCE in CO_2-saturated CH_3CN containing $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ (11.8 μmol), Et_4NNO_2 (0.88 mmol), CH_3COCH_3 (50 mmol), Bu_4NBr (1.6 mmol), and $MgSO_4$ (1.2 g).

The occurrence of the reduction of NO_2^- by the FeS and MoFeS clusters in the presence of $PhCOCH_3$ ($pK_a = 19$) in CO_2-saturated CH_3CN[32] suggests that organic molecules having active hydrogens with $pK_a \sim 20$ also can be used as reagents in a similar carboxylation coupled with NO_2^- reduction. In fact, the controlled-potential electrolysis at −1.25 V vs SCE in CO_2-saturated CH_3CN containing $(Bu_4N)_2[Fe_4S_4(SPh)_4]$, Et_4NNO_2, $PhC{\equiv}CH$ (pK_a = 21) or cyclohexanone (pK_a = 18), and molecular sieves 3A also produced the corresponding carboxylation products together with N_2 accompanied by a small amount of N_2O, and the current efficiencies for the formation of $PhC{\equiv}CCOO^-$ and oxocyclohexane-2-carboxylate were 30 and 40%, respectively (entries 3 and 4 in Table I). Acetone (pK_a = 20) also played the role of proton source in the reduction of NO_2^-; N_2 was evolved with a current efficiency of 73% in the controlled-potential electrolysis at −1.25 V in CO_2-saturated CH_3CN containing $(Bu_4N)_2$-$[Fe_4S_4(SPh)_4]$, Et_4NNO_2, CH_3COCH_3, and molecular sieves 3A. However, $CH_3COCH_2COO^-$ was not confirmed in the reaction mixture. The proton source in this reaction may be a hydroxyl proton of diacetone alcohol rather than CH_3COCH_3, since the latter undergoes the aldol condensation to afford diacetone alcohol in the presence of molecular sieves 3A.[33] This result suggests that CO_2 fixation does not take place when hydroxyl protons are used as a proton source in the reduction of NO_2^-. As described in a previous section, a dehydration agent is one of the essential components for the carboxylation reaction. Therefore, $MgSO_4$, being inactive toward the condensation of CH_3COCH_3, was used as a dehydration agent in the carboxylation of CH_3COCH_3. The controlled-potential electrolysis conducted in CO_2-saturated CH_3CN containing $[Fe_4S_4(SPh)_4]^{2-}$, NO_2^-, CH_3COCH_3, and $MgSO_4$ produced $CH_3COCH_2COO^-$ together with N_2 and N_2O, but the amount of $CH_3COCH_2COO^-$ is fairly small compared with that of N_2, as shown in Figure 4. The current efficiency for the formation of $CH_3COCH_2COO^-$ was as low as 3.3% at 100 C passed in the electrolysis, and diacetone alcohol was generated as the main product also in this reaction. This may result from a predominant reaction of $CH_3COCH_2^-$ with free CH_3COCH_3 (eq 7) rather than with CO_2. Thus organic molecules with pK_a

$$CH_3COCH_2^- + CH_3COCH_3 \rightarrow CH_3COCH_2C(CH_3)_2O^- \quad (7)$$

~ 20[34] can be used as a proton donor in the reduction of NO_2^-, but those which are subject to the aldol condensation reactions

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(30) Gratzel, M.; Taniguchi, S.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 1003.

(31) Hughes, M. N. *Q. Rev., Chem. Soc.* **1968**, *22*, 1.

(32) The current densities in those electrochemical reductions were 1.0–0.8 mA/cm².

(33) This reaction was confirmed by gas chromatography.

(34) When $CH_3C(O)OC_2H_5$ (pK_a = 25) was used as a proton source in the reduction of NO_2^- by $[Fe_4S_4(SPh)_4]^{2-}$ in the presence of molecular sieves 3A in CO_2-saturated CH_3CN, no appreciable cathodic current due to reduction of NO_2^- flowed under controlled-potential electrolysis at −1.25 V vs SCE.

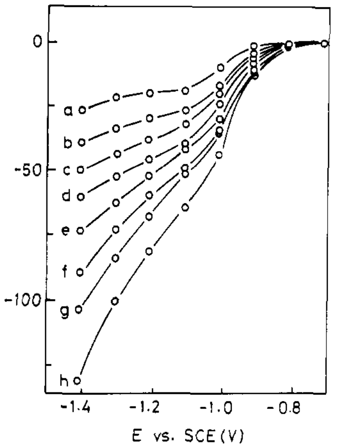

Figure 5. Cathodic polarization of a DMF solution containing $(Bu_4N)_2[Fe_{S4}(SPh)_4]$ (1.9 mmol/dm³), $PhCOCH_3$ (225 mmol/dm³), $NaNO_2$ (48 mmol/dm³), Bu_4NBr (0.1 mol/dm³), and various amounts of CO_2: 0 (a), 6.3 (b), 8.2 (c), 14.3 (d), 19.5 (e), 34.8 (f), 42.2 (g), and 67.3 mmol/dm³ (h).

are not appropriate for the present CO_2 fixation.

Cathodic Polarization for NO_2^- Reduction. In the present study, no appreciable cathodic current due to the reduction of NO_2^- flows in the absence of $PhCOCH_3$, CO_2, or $[Fe_4S_4(SPh)_4]^{2-}$ under the controlled-potential electrolysis at −1.25 V vs SCE, suggesting that all these species are essential components for the electrochemical reduction of NO_2^-. Therefore, if the concentration of one of those species is extremely low compared with those of the others, the rate of the reduction is determined by the species. When a redox reaction on an electrode is controlled by a mass transfer of the electroactive species, the limiting current I_l is expressed by eq 8,[35] where n, F, A, m_0, and $C_0{}^*$ are the number

$$I_l = nFAm_0C_0{}^* \qquad (8)$$

of electrons transferred, the Faraday constant, the area of the electrode, the mass transfer coefficient, and the bulk concentration of the electroactive species, respectively. The current–potential curve for the (2−/3−) redox coupled of $[Fe_4S_4(SPh)_4]^{2-}$ (1.9 mmol/dm³) in DMF shows I_l between −1.0 and −1.30 V vs SCE, which was essentially unchanged even in the presence of $NaNO_2$ (48.0 mmol/dm³) and $PhCOCH_3$ (225 mmol/dm³) (line a in Figure 5). The addition of CO_2 to a DMF solution containing $[Fe_4S_4(SPh)_4]^{2-}$, NO_2^-, and $PhCOCH_3$ causes an increase in I_l due to the reduction of NO_2^- at potentials more negative than −0.80 V, and the value increases with increasing CO_2 concentration (lines b–h in Figure 5). The cathodic polarizations of the DMF solution containing not only $[Fe_4S_4(SPh)_4]^{2-}$ (1.9 mmol/dm³), NO_2^- (48 mmol/dm³), CO_2 (230 mmol/dm³), and various amounts of $PhCOCH_3$ but also $[Fe_4S_4(SPh)_4]^{2-}$ (1.9 mmol/dm³), CO_2 (230 mmol/dm³), $PhCOCH_3$ (225 mmol/dm³), and various amounts of NO_2^- also gave current–potential curves similar to those of Figure 5. Thus the electron transfer from the glassy carbon electrode to $[Fe_4S_4(SPh)_4]^{2-}$ is greatly enhanced by the reduction of NO_2^- in the presence of $PhCOCH_3$ and CO_2.

The cathodic polarization of a DMF solution containing $PhCOCH_3$ (225 mmol/dm³), CO_2 (230 mmol/dm³), and NO_2^- (50 mmol/dm³) does not show an appreciable increase in the cathodic current at potentials more positive than −1.30 V vs SCE (line a in Figure 6) since neither of them undergoes a redox reaction on a glassy carbon electrode in this potential region. The addition of small amount of $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ to the solution shows the cathodic current due to the $[Fe_4S_4(SPh)_4]^{2-/3-}$ redox couple at potentials more negative than −0.80 V, and the current density increases with increasing concentration of $[Fe_4S_4(SPh)_4]^{2-}$ (lines b–g in Figure 6) due to the reduction of the cluster accompanied by that of NO_2^-. Plots of I_l obtained at −1.25 V vs SCE against the concentrations of CO_2, NO_2^-, $PhCOCH_3$, and $[Fe_4S_4(SPh)_4]^{2-}$ exhibit four straight lines as shown in Figure 7,[36] which clearly indicates that the I_l values is proportional to the concentrations not only of $[Fe_4S_4(SPh)_4]^{2-}$ but also of CO_2, NO_2^-, and $PhCOCH_3$. The rate-determining step in the cathodic polarization may be the initial dehydration reation of NO_2^- ligated on the cluster with protons of $PhCOCH_3$ since the electron transfer from the electrode to the cluster is not associated with the subsequent dimerization of NO^- affording $N_2O_2^{2-}$ and the decom-

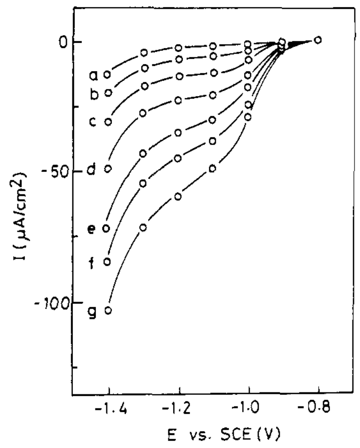

Figure 6. Cathodic polarization of a DMF solution containing $NaNO_2$ (48 mmol/dm³), $PhCOCH_3$ (225 mmol/dm³), CO_2 (230 mmol/dm³), Bu_4NBr (0.1 mol/dm³), and various amounts of $(Bu_4N)_2[Fe_4S_4(SPh)_4]$: 0 (a), 4.5 × 10⁻² (b), 3.3 × 10⁻¹ (c), 6.2 × 10⁻¹ (d), 2 × 10⁻¹ (e), 1.5 (f), and 2.5 mmol/dm³ (g).

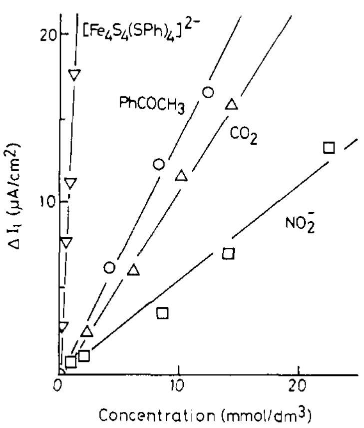

Figure 7. Limiting currents at −1.25 V vs SCE depending on the concentrations of $(Bu_4N)_2[Fe_4S_4(SPh)_4]$, $NaNO_2$, $PhCOCH_3$, and CO_2 in CH_3CN; the concentration of either $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ (1.9 mmol/dm³), $NaNO_2$ (48 mmol/dm³), $PhCOCH_3$ (225 mmol/dm³), or CO_2 (230 mmol/dm³) was varied.

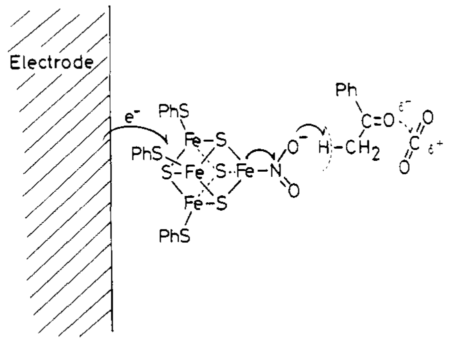

Figure 8. Proposed structure of the rate-determining step in the CO_2 fixation coupled with NO_2^- reduction.

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[35] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 29.

[36] A similar relation was obtained in the cathodic polarization of the $[Fe_4S_4(SPh)_4]^{2-}/NO_2^-/CO_2/CH_3COCH_3$ system in DMF.

position of $N_2O_2^{2-}$ to N_2O (vide infra). The fact that CO_2 as well as $[Fe_4S_4(SPh)_4]^{2-}$, NO_2^-, and $PhCOCH_3$ is involved in the rate-determining step suggests that CO_2 assists the deprotonation of $PhCOCH_3$ in the dehydration of NO_2^- ligated on the cluster maybe due to the interaction between the carbon atom of CO_2 and the carbonyl oxygen of $PhCOCH_3$, as depicted in Figure 8.[37]

Reduction Pathways of NO_2^-. Hidai et al. have reported that $[Fe_4S_4(SR)_4]^{2-}$ (R = $PhCH_2$, *t*-Bu) and $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ can reduce CO_2 to afford $HCOO^-$ under controlled-potential electrolysis at −2.0 V vs SCE in DMF,[38] where Bu_4N^+ used as an electrolyte plays the role of proton source in the reduction. The acidity of $PhCOCH_3$ as the proton source in the reduction of CO_2 seems to be higher than that of Bu_4N^+ since the controlled-potential electrolysis of −2.0 V vs SCE in CO_2-saturated CH_3CN containing $[Fe_4S_4(SPh)_4]^{2-}$, $PhCOCH_3$, and Bu_4NBr in the presence of molecular sieves 3A afforded not only $HCOO^-$ but also $PhCOCH_2COO^-$ with a current efficiency of 60%. On the other hand, neigher $HCOO^-$ nore $PhCOCH_2COO^-$ was formed in the electrolysis at −1.25 V vs SCE under otherwise the same reaction conditions (entry 7 in Table I). Thus NO_2^- plays a key role in the carboxylation reaction under the electrolysis at −1.25 V.[39] The agreement of the threshold potential of the dissimilatory reduction of NO_2^- with the cathodic peak potential of the cluster–NO_2^- adduct also reveals that $[Fe_4S_4(SPh)_4]^{3-}$ activates NO_2^- rather than CO_2 under controlled-potential electrolysis at −1.25 V.

In biological dissimilatory reduction of NO_2^-, an enzyme-bound nitrosyl has been commonly accepted as an intermediate,[40] though the mechanism with respect to the subsequent pathways for the formation of the N–N bond is still unclear; the dimerization of HNO[41] and nucleophilic attack of a second NO_2^- on an enzyme-bound nitrosyl intermediate[42] have been proposed so far. The N–N bond formation in the present dissimilatory reduction of NO_2^- may be caused by the dimerization of NO^- from the fact of the presence of free $N_2O_2^{2-}$ in the reaction mixture. The most possible reaction pathway of the NO_2^- reduction by the cluster, therefore, is proposed as follows: NO^- formed by the dehydration (two-electron reduction) of NO_2^- on the cluster (eq 9) is dissociated

$$NO_2^- + 2H^+ + 2e^- \rightarrow NO^- + H_2O \tag{9}$$

$$2NO^- \rightleftharpoons N_2O_2^{2-} \tag{10}$$

$$N_2O_2^{2-} + 2H^+ \rightarrow N_2O + H_2O \tag{11}$$

$$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2 \tag{12}$$

from the cluster and dimerizes in the solution to afford $N_2O_2^{2-}$ (eq 10). The hyponitrite dianion $N_2O_2^{2-}$ thus formed is decomposed to N_2O (eq 11), which is further reduced to N_2 (eq 12).[11] It has been elucidated that CO_2 catalyzes the breakdown of $N_2O_2^{2-}$ to N_2O by promoting the isomerization of *trans*-$N_2O_2^{2-}$ to *cis*-$N_2O_2^{2-}$, which has a greater instability than *trans*-$N_2O_2^{2-}$.[43] Therefore, CO_2 may assist the reactions not only of eq 9 but also of eq 11.

Electrochemical NO_n^- (n = 2, 3) reductions catalyzed by transition-metal complexes have been conducted.[11,44] On the other hand, NO_n^- acts as a terminal electron acceptor in electron transport (instead of dioxygen) to oxidize organic molecules in the biological dissimilatory reduction (nitrate respiration). Although NO_3^- was not reduced by the $[Fe_4S_4(SPh)_4]^{2-}$/$PhCOCH_3$/CO_2 system,[45] the present study reveals that NO_2^- used as an electron acceptor from the reduced species of $[Fe_4S_4(SPh)_4]^{2-}$ is endowed with the ability of abstracting protons from organic molecules with $pK_a \sim 20$ in the presence of CO_2 and the resulting carbanions can be trapped by CO_2. In addition, this is the first example that has succeeded in the catalytic carboxylation by the Fe_4S_4 cluster as an analogue of 4Fe4S ferredoxins.

Registry No. $[Fe_4S_4(SPh)_4](Bu_4N)_2$, 52586-83-1; $[MoFe_6S_8(SPh)_9](Bu_4N)_3$, 68197-68-2; Et_4NNO_2, 4294-99-9; CO_2, 124-38-9; $PhCOCH_3$, 98-86-2; $PhC{\equiv}CH$, 536-74-3; $C_6H_{10}(O)$, 108-94-1; CH_3COCH_3, 67-64-1; $PhCOCH_2COO^-$, 29285-17-4; $PhC{\equiv}CCOO^-$, 54293-02-6; 2-$C_6H_9(O)COO^-$, 18705-27-6; $CH_3COCH_2COO^-$, 141-81-1; N_2, 7727-37-9; N_2O, 10024-97-2; NO^-, 14967-78-3; $N_2O_2^{2-}$, 15435-66-2; $[Fe_4S_4(SPh)_4]^{2-}$, 52325-39-0; $[Fe_4S_4(SPh)_4]^{3-}$, 52627-89-1.

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(37) The cluster–NO_2^- adduct is assumed to be the nitro rather than the nitrito form.

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(39) No $HCOO^-$ formation was observed under controlled-potential electrolysis at −1.25 V vs SCE in CO_2-saturated CH_3CN containing $[Fe_4S_4(SPh)_4]^{2-}$, NO_2^-, $PhCOCH_3$, Bu_4NBr, and molecular sieves 3A.

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(45) NO_3^- was not reduced at all under controlled-potential electrolysis at −1.25 V vs SCE in CO_2-saturated CH_3CN containing $(Bu_4N)_2[Fe_4S_4(SPh)_4]$, Et_4NNO_3, $PhCOCH_3$, and Bu_4NBr.