CHEMISTRY LETTERS, pp. 1203-1206, 1982.

DINITROGEN FIXATION CATALYZED BY THE REDUCED SPECIES OF $[Fe_4S_4(SPh)_4]^{2-}$ AND $[Mo_2Fe_6S_8(SPh)_9]^{3-}$

Koji TANAKA, Yoshiyuki HOZUMI, and Toshio TANAKA*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

Dinitrogen can be reduced to NH_3 under the condition of controlled potential electrolyses in the presence of $[Fe_4S_4(SPh)_4]^{2-}$ or $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ in MeOH/THF or in H_2O. The maximum current efficiency in the electrochemical reduction is 1.6 % for the reduction of N_2 in MeOH/THF and the total yield of NH_3 based on the cluster is 195 % for 4 d.

Recently, much attention has been paid to non-enzymatic model systems composed of molybdenum complexes and iron-sulfur clusters involving Fe_4S_4 core directing toward facile N_2 reduction under mild conditions as nitrogenase. The iron-sulfur cluster in such studies has been considered as only an electron transfer catalyst from reducing agents such as BH_4^- and $S_2O_4^{2-}$ to molybdenum complexes.[1-3] We found, however, that C_2H_2 is reduced by the electrochemically reduced species of $[Fe_4S_4(SPh)_4]^{2-}$ ($[4\text{-Fe}]^{2-}$)[4] as well as $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ ($[Mo\text{-Fe}]^{3-}$)[5] catalytically in MeOH/THF to give C_2H_4 selectively without evolving H_2 gas, and C_2D_2 is reduced by the same catalyst in H_2O at pH 6.0 to afford *cis*-$C_2D_2H_2$ stereoselectively.[6] The similarity of these reactions to nitrogenase has driven us to study the reduction of N_2 by the same catalysts. This letter reports the reduction of N_2 by the electrochemically reduced species of $[4\text{-Fe}]^{2-}$ and/or $[Mo\text{-Fe}]^{3-}$ in protic solvents (Eq. 1).

$$N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3 \qquad (1)$$

The reduced species of the anionic clusters, $[4\text{-Fe}]^{n-}$ ($n = 3, 4$) and $[Mo\text{-Fe}]^{5-}$, were prepared by controlled potential electrolyses using a Hg working electrode, at the reduction potentials of $[4\text{-Fe}]^{2-}$ (2-/3-: -1.25 V, 3-/4-: -1.65 V *vs.* SCE)[7] or

$[Mo\text{-}Fe]^{3-}$ (4-/5-: -1.25 V *vs.* SCE)[7] in a MeOH/THF solution or in an aqueous suspension containing the $[n\text{-}Bu_4N]^+$ salts of $[4\text{-}Fe]^{2-}$ or $[Mo\text{-}Fe]^{3-}$. Lithium chloride (0.5 mol dm^{-3}) and NaOH-H_3PO_4 buffer were used as supporting electrolytes in MeOH/THF and in H_2O, respectively. The reduction of N_2 was carried out by bubbling N_2 gas purified through 10N H_2SO_4 with a flow rate of ca. 3 cm^3min^{-1} into the working electrode cell. The effluent gas from the working electrode cell was trapped into 0.1N H_2SO_4. After the reaction was stopped, 1N H_2SO_4 (10 cm^3) was added into the working electrode cell and the solution was evaporated to dryness under reduced pressure. The residue was alkalized by 2N NaOH (10 cm^3), followed by vaccum distillation into a trap cooled by liquid nitrogen, and the amount of NH_3 was determined by the indophenol method.[8] Ammonia absorbed in the 0.1N H_2SO_4 trap was analyzed similarly. Thus, $[4\text{-}Fe]^{4-}$ (16 μmole) prepared by the controlled potential electrolysis at -1.70 V *vs.* SCE in MeOH/THF (1:1 v/v) produced 2.5 μmole NH_3 for 24 h at 25°C. Almost the same amount of NH_3 was produced when the $[P(CH_2\text{-}Ph)Ph_3]^+$ salt of $[4\text{-}Fe]^{2-}$ was used in place of the $[n\text{-}Bu_4N]^+$ salt, while in the absence of $[4\text{-}Fe]^{2-}$ no NH_3 has been detected either in the working electrode cell or in the acid trap. These results indicate that the nitrogen source to give NH_3 in MeOH/THF is not the $[n\text{-}Bu_4N]^+$ cation but dinitrogen. The current efficiency for the formation of NH_3 calculated from the Eq. 2, however, is quite low (< 0.1 %),

$$\text{current efficiency} = \frac{\text{Moles of } NH_3 \text{ produced}}{\text{Coulombs consumed}/(69480 \times 3)} \times 100 \qquad (2)$$

suggesting that most of electrons transferred from the Hg electrode to $[4\text{-}Fe]^{2-}$ were consumed for H_2 evolution. In biological N_2-fixation, about 75 % electrons transferred to nitrogenase are utilized for the N_2 reduction, the remainder being used for the reduction of protons to evolve H_2.[9] As described in the previous paper,[6] H_2 evolution from MeOH by $[4\text{-}Fe]^{3-}$ and $[Mo\text{-}Fe]^{5-}$ produced under the controlled potential electrolysis in MeOH/THF (1:1 v/v) is about one-sixth and one-twentieth the amounts of that by $[4\text{-}Fe]^{4-}$, respectively. Thus, under the expectation to depress H_2 evolution, the reduction of N_2 by $[4\text{-}Fe]^{3-}$ as well as $[Mo\text{-}Fe]^{5-}$ (produced at -1.30 V *vs.* SCE) was examined. The results for the reduction of N_2 by these reduced species in MeOH/THF with various volume ratios are summarized in Table 1, which indicates that the current efficiency for the NH_3 formation by $[4\text{-}Fe]^{3-}$ is apparently improved, although the amount of NH_3 produced in the reduc-

Table 1. Reduction of N_2 in MeOH/THF at 25°C for 24 h; LiCl (0.5 mol dm^{-3})

Catalyst[a)]	MeOH/THF v / v	NH_3 μmole	Current efficiency %	NH_3/Catalyst mole/mole
$[4\text{-Fe}]^{3-}$ [b)]	7 : 3	1.34	0.22	0.084
	5 : 5	2.67	0.67	0.17
	3 : 7	3.39	1.6	0.21
	1 : 9	1.36	1.3	0.085
$[\text{Mo-Fe}]^{5-}$ [b)]	9 : 1	1.21	0.09	0.076
	7 : 3	2.56	0.18	0.16
	5 : 5	1.68	0.10	0.11
	3 : 7	0.99	0.51	0.06
None	5 : 5	≈0		

a) 16 μmole. b) Produced at -1.30 V *vs*. SCE.

tion by either species is not so different from that by $[4\text{-Fe}]^{4-}$. Both the maximum current efficiency and the largest amount of NH_3 are obtained in the reduction by $[4\text{-Fe}]^{3-}$ in MeOH/THF with volume ratio 3:7, while the volume ratio of MeOH/THF to give maximum current efficiency is inconsistent with that to produce the largest amount of NH_3 in the reduction by $[\text{Mo-Fe}]^{5-}$ (Table 1).

Iron-proteins and molybdenum-iron-proteins may be both essential factors in biological N_2-fixation. The reduction of N_2, therefore, was examined under the controlled potential electrolysis of an equimolar solution of $[4\text{-Fe}]^{2-}$ and $[\text{Mo-Fe}]^{3-}$ at -1.30 V (*vs*. SCE) in MeOH/THF with mole ratio 3:7, but there has been no appreciable increase in the amount of NH_3 produced compared with that by $[\text{Mo-Fe}]^{5-}$ alone.

The reduction of N_2 was examined also by the cluster dispersed in water; a fixed amount of $[4\text{-Fe}]^{2-}$ dissolved in dimethylsulfoxide (0.5 cm^3) was added to water in the working electrode cell containing Triton X-100 (0.8 mmol dm^{-3}) as a surface active reagent in order to make the cluster disperse well. Such an aqueous suspension bubbled with N_2 at pH 7.0 adjusted with NaOH-H_3PO_4 evolved only H_2 violently under the controlled potential electrolysis at -1.40 V (*vs*. SCE), but no NH_3 has been detected for 24 h. At the initial pH 12.5, however, the electrolysis at the same potential produced about 1 μmole of NH_3 a day; 4.17 μmole of NH_3 was obtained for 4 d, though the current efficiency was very low (about one-twenty sixth of the

Table 2. Reduction of N_2 in H_2O at 25°C; NaOH (6.3×10^{-2} mol dm^{-3}); Triton X-100 (0.8 mmol dm^{-3})

Catalyst[a)] / μmole	Time / h	NH_3 / μmole	Current efficiency / %	NH_3/Catalyst / mole/mole
$[4\text{-Fe}]^{3-}$/16.0	96	4.17	0.06	0.26
$[\text{Mo-Fe}]^{5-}$[b)]/14.0	48	4.60	0.07	0.33
$[\text{Mo-Fe}]^{5-}$/8.0	72	6.99	0.07	0.87
$[\text{Mo-Fe}]^{5-}$/3.5	96	6.81	0.07	1.95
None	48	≈0		

a) Produced at -1.40 V *vs.* SCE. b) The $[P(CH_2Ph)Ph_3]^+$ salts.

maximum value in MeOH/THF), as shown in Table 2. The electrolysis of an aqueous suspension of $[\text{Mo-Fe}]^{3-}$ at the same potential produced more NH_3 than that of $[4\text{-Fe}]^{2-}$ (Table 2), indicating that $[\text{Mo-Fe}]^{5-}$ seems to be more effective than $[4\text{-Fe}]^{3-}$ toward the N_2 reduction in water, in contrast to MeOH/THF solutions. In the controlled potential electrolysis of the clusters dispersed in water, only the cluster anions in contact with Hg electrodes may be reduced and is effective to the N_2 reduction. Thus, a large portion of the cluster anions may not be available for the reduction of N_2. This assumption predicts that the yield of NH_3 increases with decreasing the amount of the clusters used for the reaction. In fact, the yield of NH_3 for 4 d under the condition of controlled potential electrolyses attained to 195 % when 3.5 μmole of $[\text{Mo-Fe}]^{3-}$ was used (Table 2), suggesting that $[\text{Mo-Fe}]^{5-}$ catalytically reduces N_2 to NH_3.

References

1) G. N. Schrauzer, G. W. Kiefer, K. Tano, and P. A. Doemeny, *J. Am. Chem. Soc.*, 96, 641 (1974).

2) G. N. Schrauzer, P. R. Robinson, E. L. Moorehead, and T. M. Vickrey, *J. Am. Chem. Soc.*, 98, 2815 (1976).

3) N. Oguni, S. Shimizu, Y. Iwamoto, and A. Nakamura, *Polym. J.*, 13, 845 (1981).

4) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, 95, 531 (1973).

5) G. Christou, C. D. Garner, F. E. Mabbs, and T. J. King, *J. Chem. Soc., Chem. Commun.*, 1978, 740.

6) K. Tanaka, M. Tanaka, and T. Tanaka, *Chem. Lett.*, 1981, 895.

7) Measured in MeOH/THF (1:1 v/v).

8) Y. Morita and Y. Ogure, *Nippon Kagaku Zasshi*, 84, 816 (1963).

9) J. M. Rivera-Ortiz and R. H. Burris, *J. Bacteriol*, 123, 531 (1975).

(Received May 24, 1982)