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MULTIELECTRON REDUCTION OF ALKYLAZIDE BY A $(n\text{-}Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$ - MODIFIED GLASSY CARBON ELECTRODE

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A multielectron reduction of RN_3 ($R = CH_3$, HOC_2H_4) giving NH_3, N_2H_4, and RNH_2 has been succeeded for the first time by the electrochemically reduced species of $(n\text{-}Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$ not only dissolved in MeOH/THF (1:1 v/v) containing CH_3N_3 but also modified on a glassy carbon electrode in water containing $HOC_2H_4N_3$. The turnover number for the formation of NH_3 in the latter system reached more than 1×10^4 in 2 h, based on the Mo-Fe cluster.

Biological studies have established that the function of nitrogenase involves $MgATP^{2-}$-activated electron transfer from Fe-proteins to Mo-Fe-proteins which reduces molecular nitrogen with eight electrons[1,2] (Eq. 1). It may, therefore, be very

$$N_2 \quad + \quad 8H^+ \quad + \quad 8e^- \longrightarrow 2NH_3 \quad + \quad H_2 \qquad (1)$$

important to construct electron transfer systems which can provide electrons rapidly to catalysts capable of the multielectron reduction of nitrogenase substrates. Recently, we have shown that $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ ($[Mo\text{-}Fe]^{3-}$)[3] catalyzes the reductions of C_2H_2 to C_2H_4,[4] CH_3NC to hydrocarbons and CH_3NH_2, and CH_3CN to C_2H_6 and NH_3[5] under the controlled potential electrolysis conditions in water or in MeOH/THF (1:1 v/v), as model reactions to nitrogenases. This letter reports the multielectron reduction of RN_3 ($R = CH_3$, HOC_2H_4) by the electrochemically reduced species of $[Mo\text{-}Fe]^{3-}$ dissolved in MeOH/THF and modified on a glassy carbon electrode.[6]

The interaction of the molybdenum-iron cluster with CH_3N_3 was examined in DMF containing $(n\text{-}Bu_4N)_3[Mo\text{-}Fe]$ (5.0×10^{-4} mol dm^{-3}), CH_3N_3 (5.0×10^{-3} mol dm^{-3}), and $n\text{-}Bu_4NClO_4$ as a supporting electrolyte. Although the electronic absorption spectrum of $[Mo\text{-}Fe]^{3-}$ has not been changed at all in the presence of CH_3N_3, the spectral feature of $[Mo\text{-}Fe]^{4-}$ produced in an OTTLE (Optically Transparent Thin Later Electrode) cell[7)] under the electrolysis at -1.10 V vs. SCE in the presence of CH_3N_3 changes remarkably from that of $[Mo\text{-}Fe]^{4-}$ prepared similarly in the absence of CH_3N_3, as shown in Fig. 1; the 306 nm band[8)] assignable to the dissociated PhS^- ligand appears only in the presence of CH_3N_3 owing to the lability of terminal PhS^- for substitution reactions, while the bridging PhS^- ligand is inert to the reactions.[9)] The oxidation of $[Mo\text{-}Fe]^{4-}$ in the presence of CH_3N_3 under the electrolysis at -0.6 V vs. SCE resulted in a decrease of the absorbance at the 306 nm band and the final spectrum obtained after 1 h was almost consistent with that of $[Mo\text{-}Fe]^{3-}$. Thus, CH_3N_3 can interact only with the reduced form of the molybdenum-iron clusters.

Under the electrolysis conditions at -1.25 V vs. SCE with an Hg working electrode in MeOH/THF (1:1 v/v, 20 cm^3) containing $(n\text{-}Bu_4N)_3[Mo\text{-}Fe]$ (8.0×10^{-4} mol dm^{-3}), CH_3N_3 (6.6×10^{-2} mol dm^{-3}), and LiCl (0.24 mol dm^{-3}) as a supporting electrolyte under He atmosphere, the reduction of CH_3N_3 produced equal amounts of CH_3NH_2 and N_2 with a current efficiency nearly 100%, suggesting that almost all electrons transfered from the electrode to the clusters are consumed in the two-electron reduction of CH_3N_3 (Eq. 2). On the other hand, when the initial concentration of CH_3N_3 is decreased to 8.7×10^{-3} mol

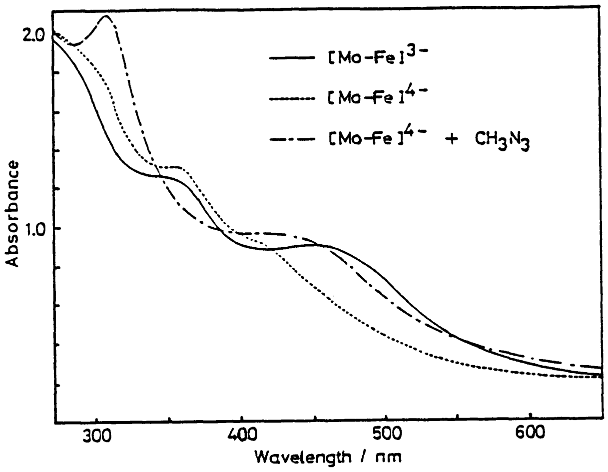

Fig. 1. Electronic absorption spectra of $[Mo\text{-}Fe]^{n-}$ (n=3 and 4, 5.0×10^{-4} mol dm^{-3}) in the absence and presence of CH_3N_3 (5.0×10^{-3} mol dm^{-3}) in DMF.

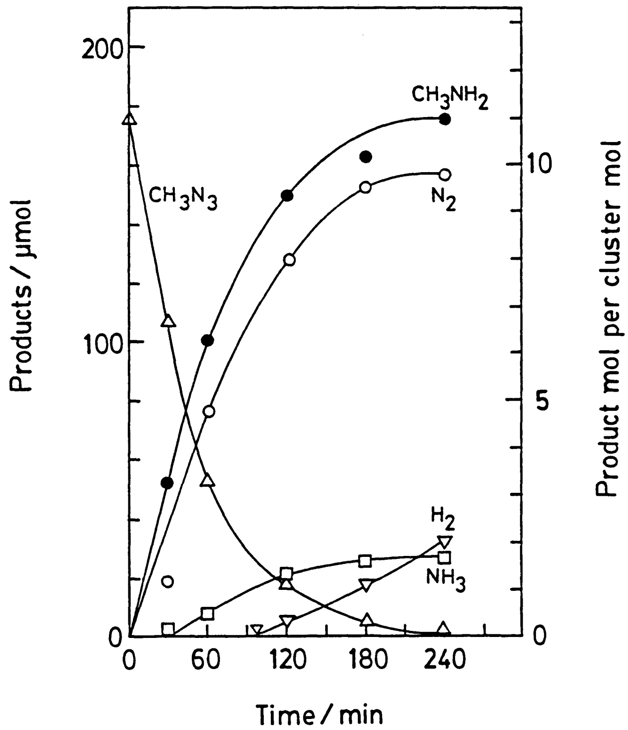

Fig. 2. The reduction of CH_3N_3 catalyzed by $[Mo\text{-}Fe]^{3-}$ (8.0×10^{-4} mol dm^{-3}) under the electrolysis at -1.25 V vs. SCE in MeOH/THF (20 cm^3). The amount of N_2H_4 formed is omitted owing to too small to plot in Fig.

$$CH_3N_3 + 2H^+ + 2e^- \longrightarrow CH_3NH_2 + N_2 \qquad (2)$$

$$CH_3N_3 + 6H^+ + 6e^- \longrightarrow CH_3NH_2 + N_2H_4 \qquad (3)$$

$$CH_3N_3 + 8H^+ + 8e^- \longrightarrow CH_3NH_2 + 2NH_3 \qquad (4)$$

dm^{-3}, the six and eight electron reductions of CH_3N_3 take place to afford small amounts of N_2H_4 (Eq. 3) and NH_3 (Eq. 4), respectively, after the lapse of 30 min as well as CH_3NH_2 and N_2 as shown in Fig. 2, which also reveals the existence of an induction period for the H_2 evolution. It should be noted that even in the higher concentration of CH_3N_3 than 1 x 10^{-2} mol dm^{-3}, the reactions of Eqs. 3 and 4 occurred after the concentration of CH_3N_3 was lowered down to ca. 8 x 10^{-3} mol dm^{-3} with the progress of Eq. 2. Thus, in a homogeneous system the electron transfer from the electrode to the cluster may not be so effective for the multielectron reduction of CH_3N_3, since only the clusters on the electrode surface can accept additional electrons from the electrode to promote the multielectron reductions.

The reduction of $HOC_2H_4N_3$ by (n-Bu_4N)$_3$[Mo-Fe] - modified glassy carbon electrode under the controlled potential electrolysis at -1.25 V vs. SCE, therefore, was carried out in an aqueous solution (pH=10) containing $HOC_2H_4N_3$ (5.0 - 15 x 10^{-3} mol dm^{-3}) and H_3PO_4-NaOH buffer (0.2 mol dm^{-3}) as a supporting electrolyte. The reaction produces not only NH_3 but also H_2 without induction periods and the turnover number for the formation of NH_3, based on the amount of modified clusters, attains more than 1 x 10^4 in 2 h, as shown in Fig. 3. The result for the reduction of $HOC_2H_4N_3$ by the

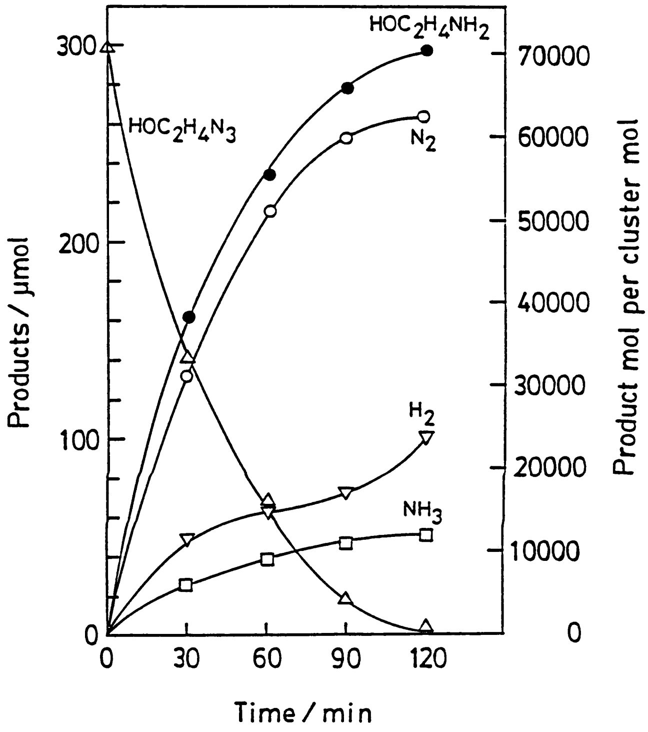

Fig. 3. The reduction of $HOC_2H_4N_3$ catalyzed by a (n-Bu_4N)$_3$[Mo-Fe] (4.2 x 10^{-9} mol) - modified glassy carbon electrode (3.1 cm^2) under the electrolysis at -1.25 V vs. SCE in 0.2 mol dm^{-3} H_3PO_4-NaOH buffer (20 cm^3). The amount of N_2H_4 formed is omitted.

Table 1. Amounts of products for the reduction of $HOC_2H_4N_3$ catalyzed by a $(n\text{-}Bu_4)_3$-[Mo-Fe] (4.2×10^{-9} mol) - modified glassy carbon elctrode at -1.25 V vs. SCE

$HOC_2H_4N_3$ [a]	Time	Product mol per cluster mol				
μmol	min	H_2	N_2	$HOC_2H_4NH_2$	NH_3	N_2H_4
50	120	3.8×10^3	1.0×10^4	1.2×10^4	2.8×10^3	0.9×10^2
100	120	7.3×10^3	2.1×10^4	2.4×10^4	4.4×10^3	1.6×10^2
300	120	2.0×10^4	6.9×10^4	7.1×10^4	1.1×10^4	5.1×10^2
160 [b]	240	1.8	9.8	10.8 [c]	1.8	0.13

a) In a 0.2 mol dm^{-3} H_3PO_4-NaOH buffer (20 cm^3). b) Reduction of CH_3N_3 catalyzed by $[Mo\text{-}Fe]^{3-}$ in MeOH/THF (20 cm^3). c) CH_3NH_2.

modified electrode is summarized in Table 1. The reaction ceased within 2 h irrespective of the initial concentration of $HOC_2H_4N_3$ and the amount of NH_3 formed is proportional to the concentration. Thus, the $(n\text{-}Bu_4N)_3$[Mo-Fe] - modified glassy carbon electrode can effectively be used for multielectron reactions of nitrogenase substrates.

References

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6) The modified electrode was prepared by dropping an MeCN solution (0.1 cm^3) of $(n\text{-}Bu_4N)_3$[Mo-Fe] (4.2×10^{-5} mol dm^{-3}) on a glassy carbon, followed by drying under N_2 atmosphere.
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8) The position and the feature of the band coincide with those of PhS^- formed by the controlled potential electrolysis of PhSH in DMF at -1.50 V vs. SCE.
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