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THE CATALYTIC REDUCTION OF N_3^- TO NH_3 BY THE REDUCED SPECIES OF $[Fe_4S_4L_4]^{2-}$, $[Mo_2Fe_6S_8L_9]^{3-}$ ($L = SCH_2CH_2OH$), AND A RELATED ANION IN H_2O OR IN MeOH/THF: EVIDENCE FOR THE FORMATION OF N_2H_2 AND N_2H_4 AS INTERMEDIATES

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The N_3^- ion can be reduced by $[Fe_4S_4L_4]^{2-}$, $[Mo_2Fe_6S_8L_9]^{3-}$ ($L = SCH_2CH_2OH$), and $[Fe_4S_4(SPh)_4]^{2-}$ catalytically under the controlled potential electrolysis conditions in H_2O or in MeOH/THF (1:1 v/v) to give NH_3 and N_2 together with H_2. The formation of N_2H_2 and N_2H_4 was confirmed as intermediates in these reactions.

Recently, we have reported that $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ catalyze the reduction of C_2H_2 to C_2H_4,[1] CH_3NC to hydrocarbons and CH_3NH_2, and CH_3CN to C_2H_6 and NH_3[2] under the controlled potential electrolysis conditions in H_2O or in MeOH/THF (1:1 v/v). The reduction of ionic substrates such as N_3^- by the same catalysts seems to be of interest in the viewpoint of the versatility of those catalysts as nitrogenase model reactions. The reduction of N_3^- by nitrogenase gives an equal amount of NH_3 and N_2.[3] We now describe the reduction of N_3^- by the electrochemically reduced species of $[Fe_4S_4L_4]^{2-}$,[4] $[Mo_2Fe_6S_8L_9]^{3-}$,[5] ($L = SCH_2CH_2OH$), and $[Fe_4S_4(SPh)_4]^{2-}$;[6] the reaction proceeds catalytically *via* N_2H_2 and N_2H_4 as intermediates to give NH_3 and N_2 with mole ratio 1:2.

The reduction of N_3^- was carried out in H_2O or in MeOH/THF containing the cluster anions by the controlled potential electrolysis on an Hg electrode under He atmosphere. The electrolysis cell was the same type as that described in the previous papers.[1,2] Reaction products, H_2 and N_2 in the gaseous phase, and N_2H_4 in the solution were determined by the gas chromatography and the spectrophotometric titration,[7] respectively. Ammonia in the solution was determined by the both methods.[8]

The N_3^- ion can be reduced to NH_3 and N_2 with concomitant H_2 evolution by the controlled potential electrolysis at -1.25 V *vs.* SCE of an aqueous solution (12 cm^3) containing NaN_3 (0.37 M) ($M = mol\ dm^{-3}$) and $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ [9] (0.37 mM) at pH 7.0 buffered with H_3PO_4-NaOH (0.37 M). However, plots of the amounts of the products *vs.* the reaction time showed gradual downward curvature. After the electrolysis for 80 min, the absorption band centered at 400 nm due to $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ in the solution was weakened to about one half, suggesting that the cluster gradually decomposed during the electrolysis, probably because of the instability of $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ in water.[4] When $HSCH_2CH_2OH$ was present in excess (2.9 mM), however, the amounts of H_2, N_2, and NH_3 increased linearly with the electrolysis time (Fig. 1), and $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ remained unchanged, as evidenced by its absorption spectrum, even after 80 min. The ratio of the amount of NH_3 produced in the reduction of N_3^- to the amount of the cluster exceeded unity in 30 min, suggesting that the reaction proceeded catalytically.[11] Similar results have been obtained in the reduction of N_3^- by $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ [12] under the controlled potential electrolysis at -1.25 V *vs.* SCE. The mole ratios of the reaction products to NH_3 formed in each reaction are summarized in Table 1; the amounts of N_2 and H_2 produced are about 2 times and more than 10 times that of NH_3, respectively.

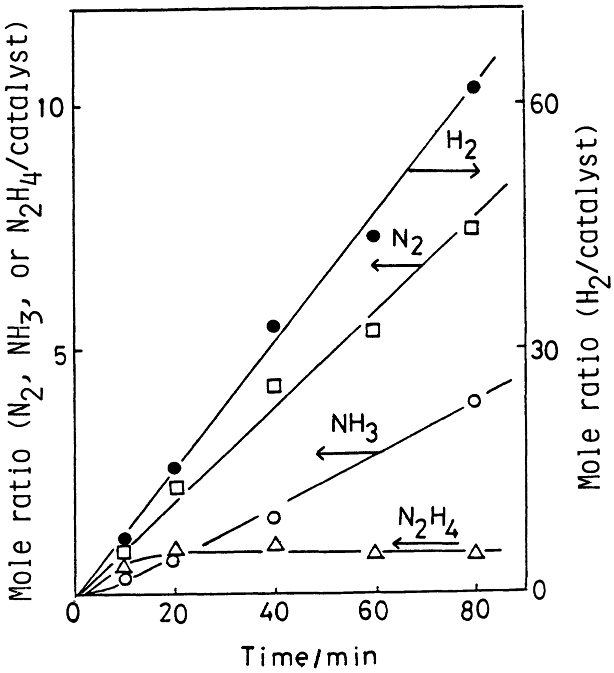


Fig. 1. The reduction of N_3^- (0.37 M) catalyzed by $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ in H_2O at pH 7.0 under the electrolysis conditions at -1.25 V *vs.* SCE in the presence of excess $HSCH_2CH_2OH$.

It should be emphasized that the formation of N_2H_4 was confirmed in the present study. The formation of N_2H_4 has been proposed in the reduction of N_3^- on an Hg electrode in strong acidic media (> 4 M H_2SO_4);[13] but N_2H_4 has not been identified in the reduction of N_3^- not only by nitrogenase but also by any of the non-enzymatic catalysts examined so far.[14] The amount of N_2H_4 produced in the present reaction increased with time for initial 15 - 20 min and thereafter remained almost constant, whereas the amount of NH_3 still continued to increase (Fig. 1). This fact indicates that the reduction of N_3^- to NH_3 proceeds *via* N_2H_4 as an intermediate. In fact, N_2H_4 has been reduced to NH_3 without evolving N_2 in an aqueous solution (74 mM N_2H_4) containing $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ (0.80 mM) or $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ (0.80 mM) at pH 7.0 under the controlled potential electrolysis at -1.25 V *vs.* SCE with the current efficiency 5.4 or 17%.[15]

It has been proposed that N_2H_2 might be the first intermediate in the reduc-

Table 1. The reduction of N_3^- (0.37 M) catalyzed by the clusters (0.37 mM) in H_2O at pH 7.0 under the electrolysis conditions at -1.25 V *vs.* SCE

Cluster	Mole ratio of the products			TON(NH_3)[a]
	N_2H_4/NH_3	N_2/NH_3	H_2/NH_3	
$[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$	0.21	2.0	17	2.8
$[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$	0.077	1.9	15	5.0

[a] Turnover number; (amount of NH_3/amount of the cluster)/h.

tion of N_2 by nitrogenase.[3] However, the existence of either free or enzyme-bound N_2H_2 has not been demonstrated so far, because of the instability of N_2H_2 at room temperature. Stilbene, though hardly soluble in water, easily reacts with N_2H_2 to give dibenzyl[16] and does not react with the clusters under the present electrolysis conditions in MeOH/THF. The reduction of N_3^- was conducted in an MeOH/THF (1:1 v/v) solution containing *n*-Bu_4NN_3 (13 mM), $[Fe_4S_4(SPh)_4]^{2-}$ [17] (0.79 mM), *trans*-stilbene (0.20 M), and LiCl (0.19 M) as a supporting electrolyte. As seen in Fig. 2, the amounts of N_2 and dibenzyl produced increased with time; the mole ratio of N_2 to dibenzyl was 3.0/1.1. The formation of dibenzyl is evidently attributable to the reaction of *trans*-stilbene with N_2H_2 which is formed by the reduction of N_3^-. This result indicates that N_2H_2 is an intermediate in the reduction of N_3^- to N_2H_4 and NH_3 in the absence of *trans*-stilbene. Moreover, the mole ratios of N_2 and H_2 to NH_3 produced in the absence of *trans*-stilbene are 3.1/1.0 and 11/1.0, respectively,[18] which are similar to those obtained by using $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ and $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ as catalysts in water, suggesting that the reduction of N_3^- by $[Fe_4S_4(SPh)_4]^{2-}$ in MeOH/THF proceeds *via* the same reaction pathways as that by other two clusters in water.

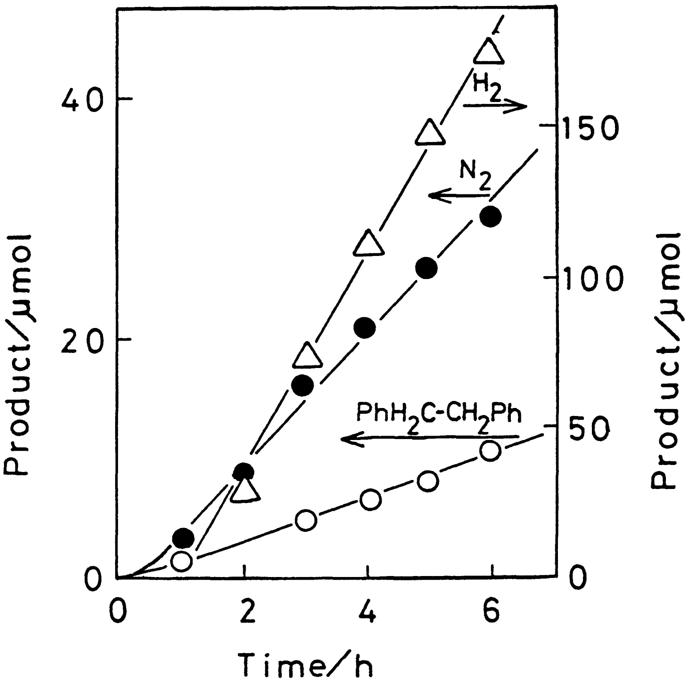
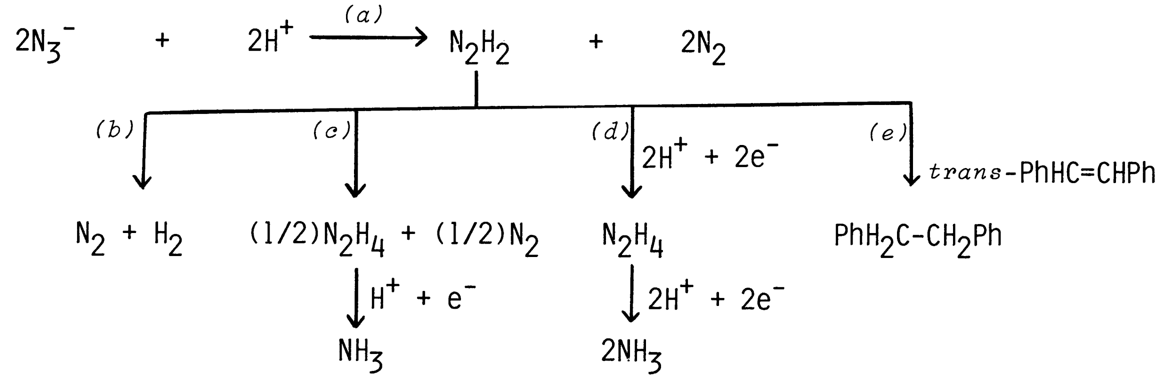


Fig. 2. The reduction of N_3^- (13 mM) by $[Fe_4S_4(SPh)_4]^{2-}$ in the presence of *trans*-stilbene (0.20 M) in MeOH/THF under the electrolysis conditions at -1.25 V *vs*. SCE.

In conclusion, the reduction reaction of N_3^- by the reduced species of the clusters in the absence and the presence of *trans*-stilbene is expressed by Scheme 1; the N_3^- ion first reacts with two protons arising from H_2O or MeOH in the presence of either cluster to give N_2H_2 and N_2 (path *a*). As is well known,[15] N_2H_2 undergoes spontaneous decomposition to N_2 and H_2 (path *b*) or disproportionation to N_2H_4 and N_2 (path *c*) in the absence of *trans*-stilbene. Besides paths *b* and *c*, there may be another path *d* through which N_2H_2 is reduced to N_2H_4 by the reduced species of the clusters. The presence of path *d* is evidenced by the fact that the mole ratio of N_2 to NH_3 (2/1) formed by the reaction in water (Table 1) is less than that (more than 5/2) expected from only paths *a*, *b*, and *c*.[19] It is noteworthy that the mole ratio of N_2 to dibenzyl produced in the presence of *trans*-stilbene is about 3/1, just as expected from only paths *a* and *e*. This

Scheme 1.



result clearly shows that N_2H_2 is almost completely trapped by *trans*-stilbene to give an equal amount of N_2 and dibenzyl.

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9) The Me_4N^+ salt was used. The anode peak potential of the cyclic voltammetry of $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ (2-/3-) in water at pH 7.0 was -0.75 V *vs.* SCE.
10) Neither N_2 nor NH_3 has been produced by the electrolysis of an aqueous solution containing N_3^- (0.37 M), $HSCH_2CH_2OH$ (2.9 mM), and $FeCl_3$ (0.37 mM) in place of $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ at -1.25 V *vs.* SCE.
11) This argument is based on the fact that only one nitrogen atom of N_3^- can be reduced to NH_3, as described in the latter part.
12) The Et_4N^+ salt was used. The anode peak potentials of $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ (3-/4- and 4-/5-) in water at pH 7.0 are -0.58 and -0.76 V *vs.* SCE.
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17) $[Fe_4S_4(SPh)_4]^{2-}$ was used for the reduction of N_3^-, because both $[Fe_4S_4(SCH_2CH_2\text{-}OH)_4]^{2-}$ and $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ are little soluble in MeOH/THF. The anode peak potential of $[Fe_4S_4(SPh)_4]^{2-}$ (2-/3-) in MeOH/THF (1:1 v/v) is -1.25 V *vs.* SCE.
18) A small amount of N_2H_4 was also formed ($N_2H_4/NH_3 \approx 1/100$) in this reaction. This is due to the fact that N_2H_4 is more easily reduced to NH_3 by the clusters in MeOH/THF than in water at pH 7.0.[15)]
19) If the reduction goes through only paths *a* and *c*, the mole ratio of N_2 to NH_3 will be 5/2; the participation of path *b* in addition to paths *a* and *c* brings the mole ratio N_2/NH_3 above 5/2.

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