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CATALYTIC REDUCTION OF HYDRAZINE TO AMMONIA BY THE REDUCED SPECIES OF $[Mo_2Fe_6S_8L_9]^{3-}$ AND $[Fe_4S_4L_4]^{2-}$ ($L = SPh$, SCH_2CH_2OH)

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Hydrazine can be reduced to NH_3 catalytically in the presence of $[Mo_2Fe_6S_8L_9]^{3-}$ or $[Fe_4S_4L_4]^{2-}$ ($L = SPh$, SCH_2CH_2OH) in H_2O or MeOH/THF by the controlled potential electrolysis. The maximum current efficiency in the electrochemical reduction of N_2H_4 attains 97% and the turnover number of NH_3 produced per 1 h is 23 in MeOH/THF.

The reduction of N_2 to NH_3 by nitrogenase has been suggested to proceed *via* enzyme-bound N_2H_2 and N_2H_4 as intermediates.[1)] In fact, the formation of N_2H_4 was confirmed in the reduction of N_2 by *Klebsiella pneumonia*,[2)] and some dinitrogen-molybdenum and -tungsten complexes reacted with mineral acids to afford N_2H_4 as well as NH_3.[3)] The reduction of N_2H_4 to NH_3 also was successfully conducted by the catalyst composed of sodium molybdate, L-cystein, and $NaBH_4$ with the turnover number of 4.2 NH_3 mol/(Mo-cystein complex mol)h.[4)] The amount of H_2 which would evolve concomitantly, however, has not been determined, though the determination of H_2 is essentially important for examining the selectivity of such a catalytic system. Recently, we have found that N_2 can be reduced to NH_3 by the electrochemically reduced species of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ and $[Fe_4S_4(SPh)_4]^{2-}$.[5)] This result has driven us to study the reduction of N_2H_4 by the same catalysts. This letter reports the catalytic reduction of N_2H_4 to NH_3.

The reduction of N_2H_4 was conducted on an Hg working electrode in an H_2O or MeOH/THF solution containing $[R_4N]_3[Mo_2Fe_6S_8L_9]$ ($R = n$-Bu for $L = SPh$,[6a)] $R = Et$ for $L = SCH_2CH_2OH$[6b)]) or $[R_4N]_2[Fe_4S_4L_4]$ ($R = n$-Bu for $L = SPh$,[7a)] $R = Me$ for $L = SCH_2CH_2$-

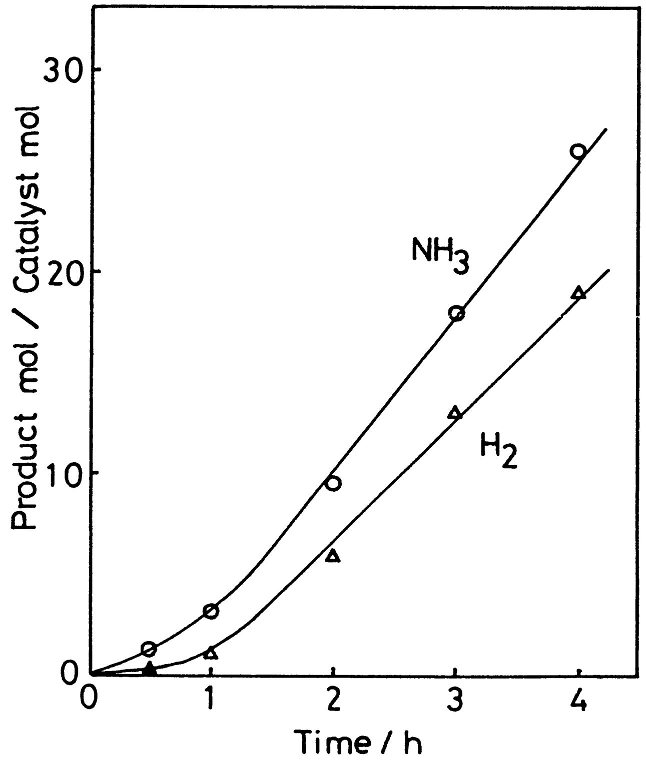

Fig. 1. The reduction of N_2H_4 by the reduced species of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ (-1.30 V *vs.* SCE) suspended in H_2O at pH 12.0.

OH[7b)]) under the controlled potential electrolysis conditions, as described elsewhere.[8)] Hydrazine was reduced to NH_3 with concomitant evolution of H_2 arising from the reduction of hydrogen ions under the controlled potential electrolysis (-1.30 V *vs.* SCE) of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$[9)] (16 μmol) suspended[10)] in an aqueous solution (20 cm^3) of N_2H_4 (1.4 mmol) at pH 12.0 buffered with H_3PO_4-NaOH. The plots of the amount of NH_3 or H_2 produced divided by the amount of the catalyst *vs.* the reaction time were linear after the initial induction period of about 1 h, as shown in Fig. 1. The amounts of NH_3 and H_2 produced attain 26 and 19 times of that of the catalyst in 4 h, respectively, indicating that the reduction of N_2H_4 and hydrogen ions proceeds catalytically. Table 1 summarizes the results of the electrochemical reduction of N_2H_4 by four catalysts[11)] in H_2O at pH 7.0 and 12.0 or in MeOH/THF. The sum of current efficiencies calculated from Eq. 1 for the

$$\text{Current efficiency } (\eta) = \frac{\text{Amount of } NH_3 \text{ or } 2H_2 \text{ produced}}{\text{Quantity of electricity consumed}/96480 \text{ C mol}^{-1}} \times 100 \qquad (1)$$

Table 1. Electrochemical Reduction of N_2H_4 (1.4 mmol) in the Presence of the Cluster Compounds (16 μmol) for 4 h at 25°C

Cluster	Medium	Applied potential	Charge	Amount of product			
				NH_3	H_2	η_{NH_3}	η_{H_2}
		V *vs.* SCE	C	μmol		%	
$[Mo_2Fe_6S_8(SPh)_9]^{3-}$	H_2O, pH 7.0[a]	-1.30	175	283	724	16	80
	H_2O, pH 12.0[a]	-1.30	110	413	311	36	56
	MeOH/THF	-1.25	145	1450	24	97	3.2
$[Fe_4S_4(SPh)_4]^{2-}$	H_2O, pH 7.0[a]	-1.30	268	138	1370	5.0	99
	H_2O, pH 12.0[a]	-1.30	49	97	200	19	79
	MeOH/THF	-1.25	171	790	494	44	56
$[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$	H_2O, pH 7.0[b]	-1.25	316	556	1370	17	83
	H_2O, pH 12.0	-1.25	34	199	62	57	35
$[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$	H_2O, pH 7.0[b]	-1.25[c]	194	109	936	5.4	93
	H_2O, pH 12.0	-1.25	85	110	372	12	84
None	H_2O, pH 7.0	-1.30	0	0	0	—	—

[a] Suspension. [b] $HSCH_2CH_2OH$ (1.0×10^{-2} cm^3) was added in order to stabilize the cluster in H_2O (20 cm^3) at pH 7.0. [c] For 1 h at 25°C.

formation of NH_3 (η_{NH_3}) and H_2 (η_{H_2}) is almost 100% within the experimental errors in most cases; the evolution of N_2 resulting from the decomposition of N_2H_4 has not been observed. Therefore, the reaction involved only the reductions of N_2H_4 (Eq. 2) and hydrogen ions (Eq. 3) taking place competitively.

$$N_2H_4 \quad + \quad 2H^+ \quad + \quad 2e^- \longrightarrow 2NH_3 \tag{2}$$

$$2H^+ \quad + \quad 2e^- \longrightarrow H_2 \tag{3}$$

The catalytic activity of $[Mo_2Fe_6S_8L_9]^{3-}$ was apparently superior to $[Fe_4S_4L_4]^{2-}$ with respect to the formation of NH_3. All the catalysts gave larger η_{NH_3} values at pH 12.0 than at pH 7.0, suggesting that smaller hydrogen ion concentrations favour the formation of NH_3 rather than H_2. In fact, the η_{NH_3} value in an MeOH/THF

(1:1 v/v) solution of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ or $[Fe_4S_4(SPh)_4]^{2-}$ containing LiCl as supporting electrolyte was several times larger than that in H_2O at pH 12.0, as expected from the weak acidity of MeOH; in particular an η_{NH_3} value of 97% was obtained with $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ in MeOH/THF (Table 1).

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9) The cyclic voltammetric anode peak potentials of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ in MeOH/THF were -1.08 and -1.25 V *vs.* SCE for the 3-/4- and 4-/5- processes, respectively.

10) A dimethylsulfoxide solution (0.5 cm^3) of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ (16 μmol) and Triton X-100 (1.5×10^{-2} cm^3) was injected into water (20 cm^3) to disperse the cluster.

11) The anode peak potential of $[Fe_4S_4(SPh)_4]^{2-}$ (2-/3-) in MeOH/THF was -1.25 V *vs.* SCE and those of $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ (3-/4- and 4-/5-) and $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ (2-/3-) in water at pH 7.0 were -0.58, -0.76, and -0.75 V *vs.* SCE, respectivery.

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