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REDUCTION OF ACETYLENE TO ETHYLENE CATALYZED BY THE REDUCED SPECIES OF $[Fe_4S_4(SPh)_4]^{2-}$ AND $[Mo_2Fe_6S_9(SPh)_8]^{3-}$: A MODEL REACTION TO NITROGENASE

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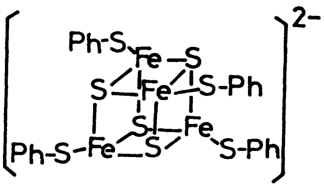
Reduction of acetylene to ethylene is catalyzed by $[Fe_4S_4(SPh)_4]^{n-}$ ($[4\text{-}Fe]^{n-}$, n = 3, 4) or $[Mo_2Fe_6S_9(SPh)_8]^{m-}$ ($[Mo\text{-}Fe]^{m-}$, m = 4, 5) produced by controlled potential electrolysis of $[4\text{-}Fe]^{2-}$ or $[Mo\text{-}Fe]^{3-}$ in MeOH/THF and in H_2O. The catalytic activity increases in the order $[Mo\text{-}Fe]^{4-} \ll [4\text{-}Fe]^{3-} \simeq [Mo\text{-}Fe]^{5-} < [4\text{-}Fe]^{4-}$.

Nitrogenase is well known to catalyze the reduction not only of dinitrogen but also of a variety of small unsaturated molecules, such as C_2H_2, N_3^-, HCN, *etc.* In the absence of any substrates nitrogenase reduces protons to H_2 and the amount of H_2 evolved is diminished in the presence of substrates.1,2) In particular, C_2H_2 saturated in solutions consumes almost all electrons transferred from nitrogenase and practically inhibits H_2 evolution.3) Thus, the examination of H_2 evolution accompanied by the reduction of substrate seems to be very important in nitrogenase model reactions. It has recently been reported that $[4\text{-}Fe]^{3-}$ can reduce C_2H_2 in the presence of CH_3COOH as a proton source to give C_2H_4 in a 60% yield,4) but there is no description on H_2 evolution. This letter reports the reduction of C_2H_2 to C_2H_4 catalyzed by the electrochemically reduced species of $[4\text{-}Fe]^{2-}$ (**1**)5) or $[Mo\text{-}Fe]^{3-}$ (**2**)6) and the concomitant evolution of H_2.



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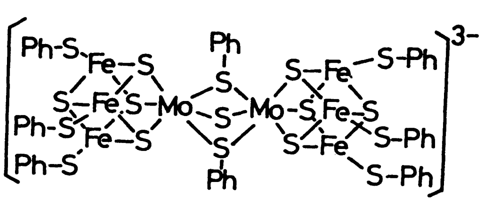

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Table 1. Reaction Conditions and the Activity of Catalysts in MeOH/THF

Catalyst	$[4\text{-Fe}]^{3-}$	$[4\text{-Fe}]^{3-}$	$[4\text{-Fe}]^{4-}$	$[4\text{-Fe}]^{4-}$	$[\text{Mo-Fe}]^{5-}$	$[\text{Mo-Fe}]^{5-}$
Potential[a]	-1.25	-1.25	-1.60	-1.60	-1.25	-1.25
Substrate	none	C_2H_2	none	C_2H_2	none	C_2H_2
Activity for C_2H_4[b]		0.012		0.069		0.011
Activity for H_2[b]	0.015	~0	0.086	0.003	0.004	~0

[a] V *vs*. SCE. [b] C_2H_4 or H_2 mole/(min. catalyst mole).

Controlled potential electrolysis at the reduction potentials of $[4\text{-Fe}]^{2-}$ or $[\text{Mo-Fe}]^{3-}$ (Table 1) was carried out in a MeOH/THF (1:1 v/v, 40 cm^3) solution containing the tetrabutylammonium salt of $[4\text{-Fe}]^{2-}$ (48 μmol) or $[\text{Mo-Fe}]^{3-}$ (24 μmol) and LiCl (9.6 mmol) as a supporting electrolyte. The reaction cell consisted of three compartments; a working electrode of Hg, an auxiliary electrode separated from the working electrode by a glass frit, and a SCE reference electrode. Although no reaction occurred between $[4\text{-Fe}]^{2-}$ or $[\text{Mo-Fe}]^{3-}$ and MeOH as a proton source, the reduced species of $[4\text{-Fe}]^{2-}$ or $[\text{Mo-Fe}]^{3-}$ was capable of reducing protons arising from MeOH to evolve H_2. The rate of H_2 evolution increased in the order $[\text{Mo-Fe}]^{5-} < [4\text{-Fe}]^{3-} < [4\text{-Fe}]^{4-}$ (Table 1). The H_2 evolution, however, was drastically depressed in the controlled potential electrolysis of $[4\text{-Fe}]^{2-}$ or $[\text{Mo-Fe}]^{3-}$ in MeOH/THF saturated with C_2H_2. Alternatively, the reduction of C_2H_2 took place to evolve C_2H_4. It should be noted that no H_2 evolution practically occurred in the reaction of C_2H_2 with $[4\text{-Fe}]^{3-}$ or $[\text{Mo-Fe}]^{5-}$ in MeOH/THF as in the reaction with nitrogenase.[7)] In addition, the rate of C_2H_2 reduction with $[\text{Mo-Fe}]^{5-}$ was found to be fairly faster than that of H_2 evolution in the absence of C_2H_2. This result indicates that C_2H_2 is reduced more easily than protons with $[\text{Mo-Fe}]^{5-}$.

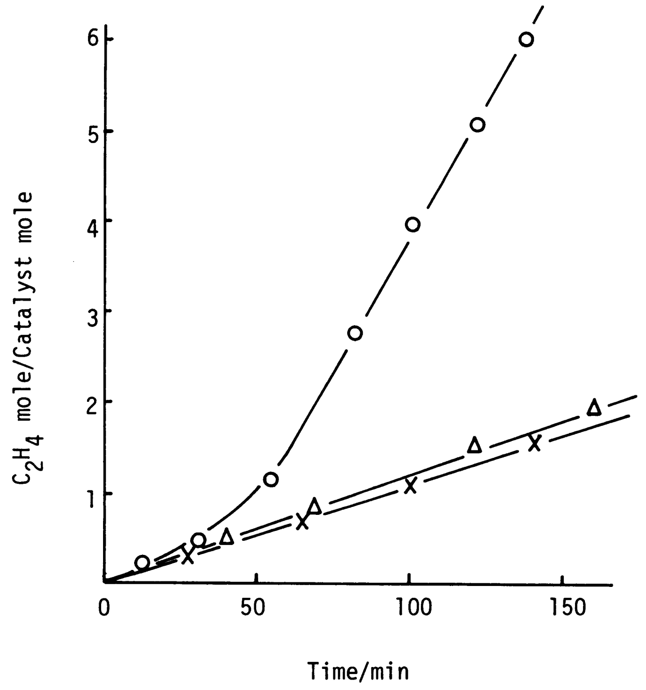
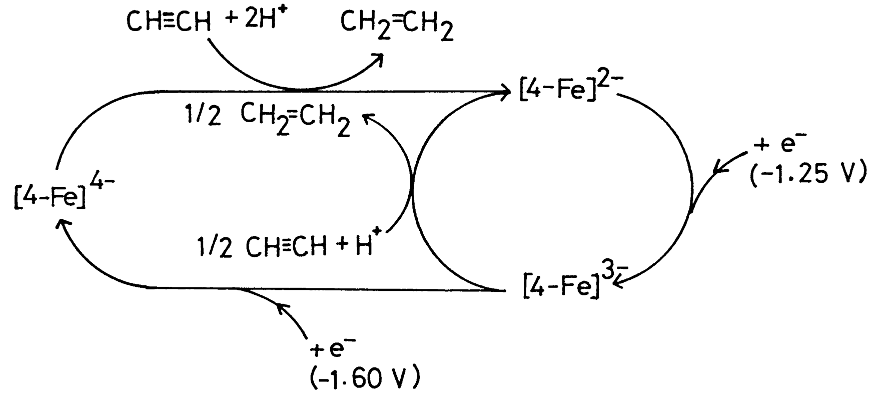


Figure 1. Plots of (C_2H_4 mole)/(catalyst mole) *vs*. time in the presence of $[4\text{-Fe}]^{4-}$ (o), $[4\text{-Fe}]^{3-}$ (Δ), or $[\text{Mo-Fe}]^{5-}$ (X).

As shown in Fig. 1, there was found a

Scheme



linear relation between the amount of C_2H_4 produced and the reaction time in the reaction of C_2H_2 with $[4\text{-Fe}]^{n-}$ (n = 3, 4) or $[\text{Mo-Fe}]^{5-}$, suggesting that the reaction proceeds catalytically. A gentle grade indicated by the circle for the initial period of 50 min is probably due to the catalytic reduction with a mixture of $[4\text{-Fe}]^{4-}$ and $[4\text{-Fe}]^{3-}$, the latter of which may be formed in the rapid electron transfer reaction between $[4\text{-Fe}]^{4-}$ and $[4\text{-Fe}]^{2-}$ in solution (Eq. 1, 2). After

$$[4\text{-Fe}]^{2-} \xrightarrow{+2e^- \ (-1.60\ \text{V})} [4\text{-Fe}]^{4-} \qquad (1)$$

$$[4\text{-Fe}]^{4-} + [4\text{-Fe}]^{2-} \xrightarrow{\text{fast}} 2[4\text{-Fe}]^{3-} \qquad (2)$$

the lapse of 50 min, the reaction is catalyzed by $[4\text{-Fe}]^{4-}$ and the rate is about six times faster than that with $[4\text{-Fe}]^{3-}$ or $[\text{Mo-Fe}]^{5-}$, the latter two showing almost the same catalytic activity in the C_2H_2 reduction, though the activity toward H_2 evolution are somewhat different. Most probable catalytic cycles of the C_2H_2 reduction with $[4\text{-Fe}]^{n-}$ are shown in Scheme. On the other hand, $[\text{Mo-Fe}]^{4-}$ exhibited very little catalytic activities toward both C_2H_2 and proton reductions. The product in the reaction of C_2H_2 with $[4\text{-Fe}]^{n-}$ (n = 3, 4) or $[\text{Mo-Fe}]^{5-}$ contained a small amount of C_2H_6. The ratio of C_2H_6 to C_2H_4 in the gaseous phase, however, was very low (< 0.7%), as reported for the nitrogenase reaction (< 0.01%)[3,7,8]

It has been reported that nitrogenase catalyzes the reaction of C_2H_2 with D_2O to produce *cis*-$C_2D_2H_2$ predominantly[7] and $C_6H_5C{\equiv}CC_6H_5$ is reduced by the $[4\text{-Fe}]^{2-}$-$NaBH_4$ system to give stilbene (*cis* : *trans* = 70 : 3).[9] On the contrary, the reaction of C_2H_2 with MeOD (99.5%) catalyzed by $[4\text{-Fe}]^{4-}$ in MeOD/THF afforded various deuterated ethylenes, as shown in Fig. 2a. The distribution of partially deuterated ethylenes produced in the reaction catalyzed by $[4\text{-Fe}]^{3-}$ or $[\text{Mo-Fe}]^{5-}$ in the same solvent was essentially identical. No stereoselectivity for the formation of *cis*- or *trans*-$C_2D_2H_2$ has, however, been observed. This result may be due to the H-D exchange between C_2H_2

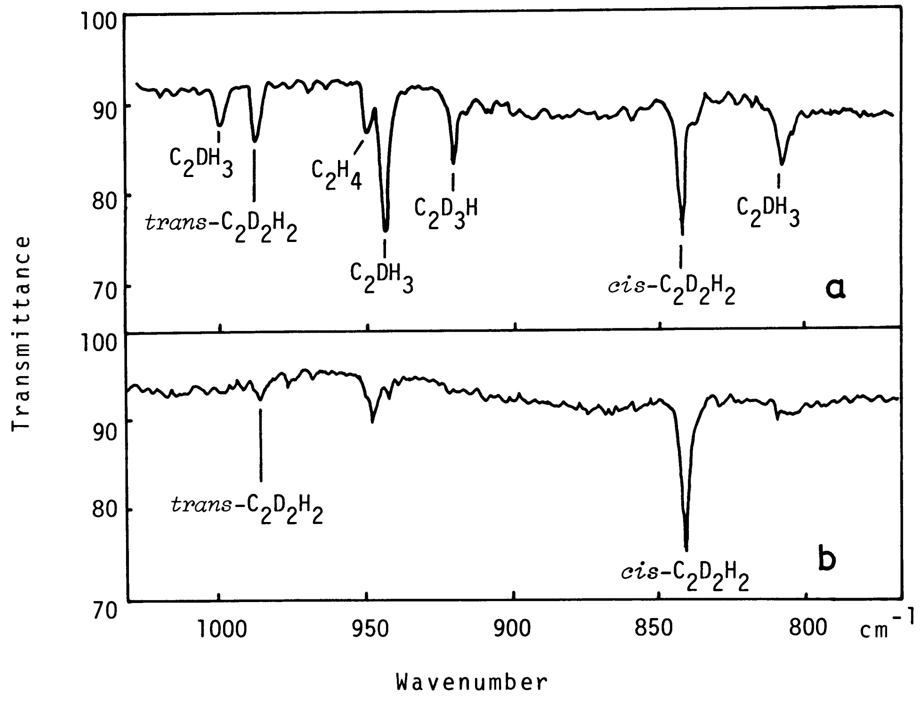


Figure 2. IR spectra of the gaseous products in the reaction of C_2H_2 with MeOD (a) and of C_2D_4 with H_2O at pH = 6.0 (b), catalyzed by $[4\text{-Fe}]^{4-}$.

and MeOD in MeOD/THF, as confirmed by the facts that a large amount of C_2DH (677 cm^{-1}) was found unreacted from the ir spectrum of the gaseous phase and the mass spectrum of the gaseous products showed the existence of C_2D_4 species. In order to depress the H-D exchange, the controlled potential electrolysis at -1.60 V was carried out for a C_2D_2 saturated aqueous suspension of $[4\text{-Fe}]^{2-}$ at pH = 6.0 ± 0.2. Under this condition, stereoselectivity apparently increased to yield *cis*-$C_2D_2H_2$ predominantly, as shown in Fig. 2b.

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