

Electron Transfer Reduction of Acetylene by Catalysis of Partially *p*-Mercaptomethyl Substituted Polystyrene–Molybdenum(IV) Complexes in Protic Solvent

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(Received December 15, 1980)

ABSTRACT: Molybdenum(IV) complexes supported on partially *p*-mercaptomethyl substituted cross-linked polystyrene were prepared. A binary system of the above molybdenum complexes and ferredoxin model compound, $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$, has excellent catalytic activity for the reduction of acetylene, compared to the corresponding unsupported molybdenum complexes. The reduction and reductive cleavage of dinitrogen were also investigated as a nitrogenase model reaction.

KEY WORDS Molybdenum(IV) Complex / Reduction of Acetylene /
Reduction of Dinitrogen / Catalysis of Polymer–Metal Complex /

The MoFe protein components of *Clostridium pasteurianum*¹ and *Azotobacter vinelandii* (Az. V)² nitrogenase and the FeMo cofactor (FeMo-co)² from Az. V were isolated; their K-edge X-ray absorption fine structure (EXAFS) analyses indicated that the molybdenum is coordinated by three or four organic and inorganic sulfides. The FeMo-co has ca. 8% activity of native nitrogenase for the selective reduction of acetylene to ethylene with NaBH_4 .³ In an attempt to find a functional enzyme model, the μ -dioxodi(oxomolybdenum)(V) complex coordinated by L-cysteine ligand, $[\text{Mo}_2\text{O}_4(\text{cys})_2]^{2-}$, was examined as a component of catalyst in nitrogenase model reaction for the reduction of acetylene and dinitrogen.^{4–6} Recently, an oxomolybdenum complex supported on insulin was found to have catalytic activity for the reductive cleavage of dinitrogen.⁷ The activity of this polypeptide–Mo complex was reported to be definitely higher than that observed for the Mo complexes of cysteine or other simple organic thiols. In our previous studies,⁸ we have found that L-cysteine-containing copolypeptide–Mo(V) complexes had a higher catalytic activity than the corresponding non-supported Mo(V) complexes for the reduction of phenylacetylene and azobenzene. This high activity of

polypeptide–Mo complexes was tentatively concluded as a result of preventing deactivation by the aggregation of a reduced catalytically active molybdenum species. Similar effect is significant for catalysis by Mo complexes supported on cross-linked polystyrene. This report deals with the catalytic reduction of acetylene with NaBH_4 by a binary system of Mo(IV) complexes of partially *p*-mercaptomethyl substituted polystyrene and ferredoxin model compound, $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$. Reduction of dinitrogen was also examined using a catalyst system best suited for the acetylene reduction.

EXPERIMENTAL

Instrumentation

Visible and UV spectra were taken with a JASCO-UVIDEK 5A spectrometer at room temperature. The identification and quantitative determination of the products in the reduction of acetylene were made by a Yanaco gas chromatograph model G80 equipped with Porapak N as column packing material at 40–160°. NMR spectra were taken with a Varian XL-100.

Reagents

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under an argon atmosphere. *n*-Hexane, diethylether, petroleum ether, methanol, and ethanol were purified by conventional methods.

Tetrakis(dimethylamino)molybdenum(IV)

This compound was prepared by the method reported by Bradley *et al.*⁹ Mo(NMe₂)₄ (0.02 mol) was obtained by the reaction of MoCl₅ (0.22 mol) with LiNMe₂ (1.1 mol). The product, an air-sensitive purple solid, was purified by sublimation at 70° under 1×10^{-3} mmHg.

Hexakis(dimethylamido)dimolybdenum(III)

The method reported by Chisholm *et al.*¹⁰ was used. The residue, from which Mo(NMe₂)₄ was completely distilled, was heated to 100–120° under 0.5×10^{-4} mmHg for 6 h to afford pale yellow crystals of Mo₂(NMe₂)₆ sublimed at the cooled part. The crude air-sensitive product was purified by resublimation. *Anal.* Calcd. for C₁₂H₃₆N₆Mo₂: C, 31.58%; H, 7.95%; N, 18.42%. Found C, 30.27%; H, 7.69%; N, 18.64%.

Preparation of Partially *p*-Chloromethyl-Substituted Cross-Linked Polystyrene

p-Chloromethylated polystyrene (17 g) of the product of Peptide Institute (divinylbenzene 2%, 100–200 mesh, Cl: 1.34 mmol g⁻¹) was suspended in THF (120 ml) under an argon atmosphere. To this suspension was added the required amount of *n*-butyllithium in hexane with stirring for 3 h at room temperature. Water was added to the suspension and the polymer was filtered and washed with water and then ethanol. By this method, two samples of different *p*-chloromethyl group content were prepared. *Anal.* Found for polystyrene No. 1 (a starting polystyrene): C, 88.90%; H, 7.55%; Cl, 3.59%. Found for polystyrene No. 2: C, 89.62%; H, 7.69%; Cl, 2.72%. Found for polystyrene No. 3: C, 89.47%; H, 7.67%; Cl, 2.36%.

p-Mercaptomethyl-Substituted Polystyrene

A mixture of partially *p*-chloromethylated polystyrene in ethanol and the required amount of thiourea (1.5 eq. of *p*-chloromethyl groups in polystyrene) in water were refluxed for 12 h. After cooling to room temperature, the product was hydrolyzed

by the addition of aq. NaOH (2 eq. of thiourea), and the suspension was refluxed for 3 h. The reaction mixture was cooled below 5°C and acidified to a pH of 2 with 6*N* sulfuric acid. The polymer was separated by filtration, washed with water and then with ethanol. *Anal.* Found for polystyrene No. 1: C, 88.61%; H, 7.71%; S, 2.78%. Found for polystyrene No. 2: C, 88.61%; H, 7.82%; S, 1.97%. Found for polystyrene No. 3: C, 88.81%; H, 7.83%; S, 1.49% (conversion, 85%).

Ligand Substitution Reaction of Mo(NMe₂)₄ with 2-Propanethiol

To Mo(NMe₂)₄ (3.9×10^{-2} mmol) in THF (20 ml) was added 2-propanethiol (1.6×10^{-1} mmol) with stirring under argon atmosphere. The solution was shaken at room temperature for 3 h; the THF was then removed by distillation under reduced pressure. The residual reddish brown solid was insoluble in THF and other organic solvents.

Preparation of Partially *p*-Mercaptomethylated Polystyrene-Mo(IV) Complexes

Mo(NMe₂)₄ (2 eq. of thiol groups in polymer) was added to a suspension of partially *p*-mercaptomethylated polystyrene in THF under an argon atmosphere. The mixture was stirred at room temperature for 24 h, and then the polymer-Mo(IV) complex was separated by filtration and washed with THF so as to remove any unreacted Mo complexes. *Anal.* Mo, Found for the complex with polystyrene No. 1: 4.46%; for polystyrene No. 2: 3.18%; for polystyrene No. 3: 2.58%. Quantitative determination of Mo was conducted according to the method reported by Pribil *et al.*¹¹

Reduction of Acetylene by Catalysis of Partially *p*-Mercaptomethylated Polystyrene-Mo(IV) Complex with NaBH₄

The polystyrene-Mo(IV) complex (1.0×10^{-4} mmol to Mo) and ferredoxin model complex, [Fe₄S₄(SPh)₄][N-*n*Bu₄]₂ (1.0×10^{-4} mmol) were mixed in THF (4.6 ml) under an argon atmosphere. NaBH₄ (7.9 mmol) as a reducing agent was then added to the above solution. After replacing argon with acetylene in a reaction vessel ethanol (7.6 ml) and methanol (3.0 ml) were added to the above mixture, and the solution was stirred vigorously in a water bath kept at 30°C. Reaction products in vapor and in solution taken out with a syringe were

quantitatively analyzed by GLC at a certain time interval of the reaction.

Reduction and Reductive Cleavage of Dinitrogen by Catalysis of the Polystyrene-Mo(IV) Complex with NaBH₄

Polystyrene-Mo(IV) complex (1.97×10^{-2} mmol to Mo) and $[\text{Fe}_4\text{S}_4(\text{SPh})_4][\text{N}-n\text{Bu}_4]_2$ (1.97×10^{-2} mmol) were mixed in THF (4.6 ml) under an argon atmosphere. Then, NaBH_4 (2.0 mmol) was added to the above solution. After replacing argon with oxygen-free nitrogen in a reaction vessel, a mixture of ethanol (7.4 ml) and methanol (3.0 ml) was added to the mixture, and under a circulation system dinitrogen was introduced into the vigorously stirred catalyst solution in a water bath kept at 30°C. At hourly intervals, NaBH_4 (2.0 mmol) was added to the solution over a period of 4 h. The reaction mixture was completely distilled under reduced pressure into aq. 3N H_2SO_4 stored in a reservoir. The distillates from this mixture in aq. H_2SO_4 were removed under reduced pressure, and the residue was alkalinized by aq. 3N NaOH , followed by complete distillation into a trap cooled by liquid nitrogen. The distillates were divided into equal amounts of two portions, each whose quantity of hydrazine and ammonia was determined by colorimetry with *p*-dimethylaminobenzaldehyde and indophenol methods,¹² respectively. The reaction product with hydrazine had an absorption maximum at 475 nm, and that with ammonia had one at 620 nm. Reduction of dinitrogen by a binary system of random copolypeptide⁸-Mo(NMe_2)₄ and $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ was carried out by a method similar to that for the polystyrene-Mo(NMe_2)₄ systems.

RESULTS AND DISCUSSION

Preparation of Catalyst

In view of the importance of low-valent Mo species without oxo ligands in the FeMo-co, we looked for suitable catalyst precursors containing low-valent Mo species with readily replaceable ligands. Tetrakis(dimethylamido)-molybdenum(IV)⁹ was found to be a useful catalyst precursor, capable of reacting with alcohols and thiols without any change in the formal oxidation state. The following model reaction with simple organic thiol compounds was examined first. Thus, 1-

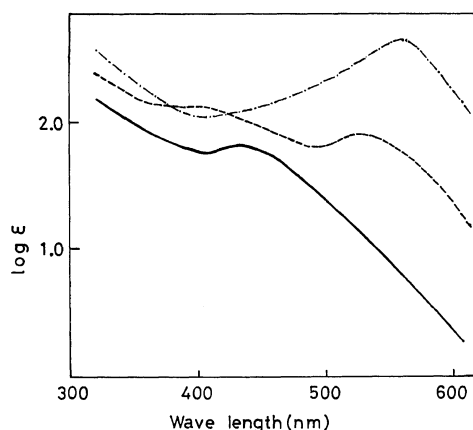
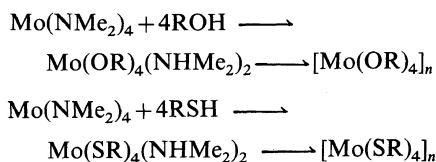
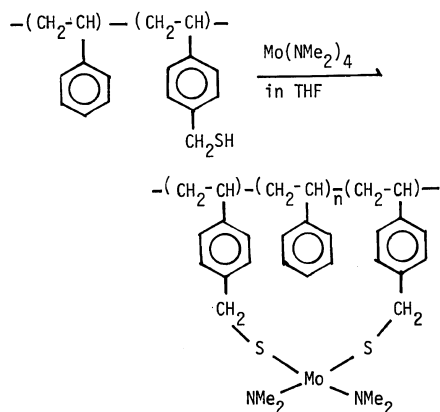


Figure 1. Electronic absorption spectra of $\text{Mo}(\text{NMe}_2)_4$ (—) and the reaction products of $\text{Mo}(\text{NMe}_2)_4$ with 1-propanethiol (---) and phenylmethanethiol (-·-·-) in THF.

propanethiol and phenylmethanethiol were added to $\text{Mo}(\text{NMe}_2)_4$ in THF in a molar ratio of 4 : 1 and the absorption spectra of $\text{Mo}(\text{NMe}_2)_4$ and of the reaction mixtures of $\text{Mo}(\text{NMe}_2)_4$ with the above thiols were compared in order to detect the reaction. $\text{Mo}(\text{NMe}_2)_4$ had a peak at 435 nm ($\epsilon=65.4$). The reaction mixture with 1-propanethiol had two peaks at 404 nm ($\epsilon=122$) and 532 nm ($\epsilon=73.8$) and the one with phenylmethanethiol had a peak at 560 nm ($\epsilon=457$) (Figure 1). By analogy with the formation of the hexacoordinate molybdenum(IV) complex, $\text{Mo}(\text{OR})_4\text{L}_2$ ($\text{L}=\text{NHMe}_2$), by the reaction of $\text{Mo}(\text{NMe}_2)_4$ with trimethylsilylanol,¹⁰ such compounds as $\text{Mo}(\text{SR})_4(\text{NHMe}_2)_2$, may be postulated as a solution reaction products. However, attempts to isolate these compounds failed, giving only polymeric associates of $[\text{Mo}(\text{SR})_4]_n$ insoluble in THF. Molybdenum alkoxide, $\text{Mo}(\text{OR})_4$, oligomerizes by means of alkoxide groups serving as μ -alkoxo ligands.¹⁰ Since a hexa-coordinated prismatic tetrathiolato Mo(IV) complex, $\text{Mo}(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{-CH}_2\text{S})_2$, was reported,¹³ the tetrathiolato complex obtained from $\text{Mo}(\text{NMe}_2)_4$ probably has a hexacoordinate structure similar to bridging thiolato ligands. On the basis of the above



ligand exchange reaction, we prepared the molybdenum(IV) complexes of partially *p*-mercaptomethyl substituted cross-linked polystyrene (abridged as PS-SH). The ratio of molybdenum to thiolato groups in the PS-SH molybdenum complexes was calculated from the values of the quantitative analysis of molybdenum metal and sulfur atom. These ratios were 0.536 for polystyrene No. 1, 0.540 for polystyrene No. 2, and 0.579 for polystyrene No. 3. These results indicated that one molybdenum metal coordinated with two thiolato groups on the average, in spite of variable *p*-mercaptomethyl substitutions. The observed ligand-to-metal ratio (=2) is supported in the reaction of $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]_2$ with cross-linked polystyrene bearing a variety of diphenylphosphine substitutions, where two moles of cyclooctadiene are displaced to give a product in which rhodium is coordinated by two phosphine ligands of the polymer.¹⁹ A recent EXAFS study of cross-linked polystyrene-supported Rh(I) catalyst revealed a bidentate structure similar to that mentioned above.²⁰



Reduction of Acetylene with NaBH_4 by Catalysis of a Mixed System of $\text{Mo}(\text{NMe}_2)_4$, Phenylmethanethiol and Ferredoxin Model Compound, $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$

Catalytic activity and selectivity in the reduction of acetylene was examined for the catalyst system, $\text{Mo}(\text{NMe}_2)_4/\text{PhCH}_2\text{SH}$. The relative amount of phenylmethanethiol varied from 1:1 to 1:4. The results of the reduction of acetylene are summarized in Table I. The main product from reduction was ethylene and small amounts of butadiene and ethane were also produced. The addition of phenylmethanethiol to the system decreased the formation

of ethylene and increased the formation of butadiene. Therefore, the incremental addition of thiols caused the butadiene/ethylene ratio to increase steadily. The turnover number decreased by the addition of phenylmethanethiol. Stiefel *et al.* reported that on reducing acetylene in protic media by catalysis of $[\text{Mo}_2\text{O}_4(\text{cys})_2]^{2-}$, the ratio of butadiene to ethylene varied, depending on the buffer solution used, while role of the buffer was obscure.¹⁴

The following points are suggested on the basis of the above results: 1) Since low-valent Mo(III or IV) thiolato complexes have in general insoluble polynuclear structures, $[\text{Mo}(\text{SR})_3$ or $[\text{Mo}(\text{SR})_4]_n$, involving bridging thiolato groups, lower activity on addition of thiols is probably due to the aggregation of molybdenum complexes through thiolato groups. 2) Product selectivity may be due to the covalency of Mo-L (L = ligand) bonds at the active sites, since the covalency at the Mo-thiolate bonding is considered to cause the Mo- $(\eta^2\text{-acetylene})$ bond to become stronger and less ionic and insertion of further molecule of acetylene prior to the protolysis to ethylene may be lessened.

In the preparation of $\text{Mo}(\text{NMe}_2)_4$ by the reaction of MoCl_5 with Me_2NLi , a Mo(III) complex, $(\text{Me}_2\text{N})_3\text{Mo} \equiv \text{Mo}(\text{NMe}_2)_3$, was obtained as crystals.¹⁵ This low-valent molybdenum complex and its alkoxy derivatives have been investigated in detail.¹⁵ In the catalytic reduction of acetylene with $\text{Mo}(\text{NMe}_2)_4$, Mo-Mo multiple bond formation is expected. Thus, we examined how aggregation of a molybdenum complex affects catalytic activity by using a well-defined binuclear molybdenum complex, $\text{Mo}_2(\text{NMe}_2)_6$, as the catalyst. The results of acetylene reduction are shown in Table I and Figure 2. The catalytic activity of $\text{Mo}_2(\text{NMe}_2)_6$ in acetylene reduction was considerably lower than that of the mononuclear complex, $\text{Mo}(\text{NMe}_2)_4$. Thus, it was concluded that Mo-Mo multiple bond formation causes a lowering of catalytic activity.

*Reduction of Acetylene with NaBH_4 by Catalysis of a Mixed System of *p*-Mercaptomethylated Polystyrene-Mo(IV) Complexes and Ferredoxin Model Complexes, $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$*

In order to prevent aggregation of molybdenum complexes, we used the partially *p*-mercaptomethyl substituted cross-linked polystyrene as a ligand. The results of the catalysis of the reduction of acetylene are shown in Table II and Figure 3. The catalytic

Catalysis of Polystyrene-Supported Molybdenum Complex

Table I. Selectivity and activity of catalysis by molybdenum complexes for acetylene reduction with NaBH_4 ^a

Catalyst systems (+ $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$)	Time h	Conversion %	Product			Turnover number mol/mol [Mo], min^{-1}
			Ethylene	Butadiene	Ethane	
			%	%	%	
$\text{Mo}(\text{NMe}_2)_4$	5	28.0	18.5	4.0	1.5	0.19
$\text{Mo}(\text{NMe}_2)_4 + \text{C}_6\text{H}_5\text{CH}_2\text{SH}$	5	7.6	3.3	1.7	2.0	0.05
$\text{Mo}(\text{NMe}_2)_4 + 2\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	5	22.2	5.4	8.7	2.1	0.15
$\text{Mo}(\text{NMe}_2)_4 + 3\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	5	22.0	5.2	5.5	2.8	0.15
$\text{Mo}(\text{NMe}_2)_4 + 4\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	5	14.6	0.1	7.1	0.3	0.10
$\text{Mo}_2(\text{NMe}_2)_6^*$	5	3.6	3.0	0.3	0.3	0.04

^a Conditions: acetylene, 3.93 mmol; NaBH_4 , 7.9 mmol; catalyst, 0.0197 mmol (Mo), ratio of Fe/Mo=4; temperature, 30°C; solvent, EtOH-THF-MeOH (2.5:1.5:1) (total 15.5 ml) (*8:4.5:2, total 14.5 ml).

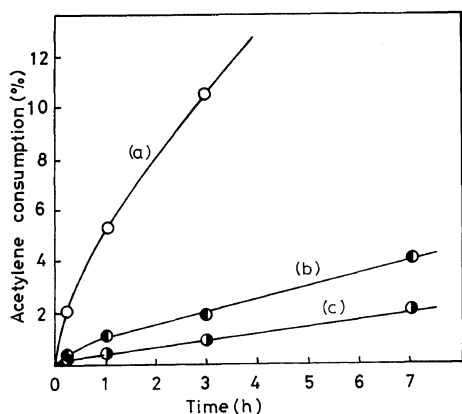


Figure 2. Acetylene reduction by catalysis of (a) $\text{Mo}(\text{NMe}_2)_4$ - $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ (○), (b) $\text{Mo}_2(\text{NMe}_2)_6$ - $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ (●), and (c) $\text{Mo}_2(\text{NMe}_2)_6$ (○). Experimental conditions are the same as in Table I.

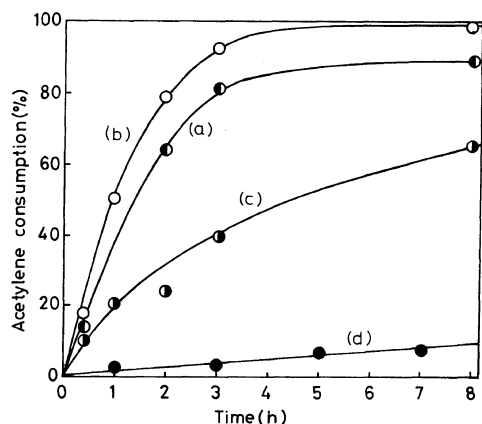


Figure 3. Acetylene reduction by catalysis of a binary system of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ and (a) polystyrene No. 1/ $\text{Mo}(\text{NMe}_2)_4$ (●), (b) polystyrene No. 2/ $\text{Mo}(\text{NMe}_2)_4$ (○), (c) polystyrene No. 3/ $\text{Mo}(\text{NMe}_2)_4$ (●), (d) $\text{Mo}(\text{NMe}_2)_4$ (●). Experimental conditions are the same as in Table II.

Table II. Selectivity and activity of catalysis by the *p*-mercaptomethyl polystyrene-molybdenum complex for acetylene reduction with NaBH_4 ^a

Catalyst systems	Conversion %	Product			Turnover number mol/mol [Mo], min^{-1}
		Ethylene	Butadiene	Ethane	
		%	%	%	
Polystyrene No. 2/ $\text{Mo}(\text{NMe}_2)_4$	9.2	6.7	1.0	0.5	0.20
Polystyrene No. 2/ $\text{Mo}(\text{NMe}_2)_4$ + $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$	94.2	77.5	1.8	13.1	2.40
Polystyrene No. 2/ $\text{Mo}(\text{NMe}_2)_4$ + 2 $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$	99.8	54.6	5.6	34.0	2.62

^a Conditions: acetylene, 3.93 mmol; NaBH_4 , 7.9 mmol; catalyst, 0.01 mmol (Mo); time, 3 h; temperature, 30°C; solvent, EtOH-THF (7.4:4.6 ml).

activity was found to depend on the content of mercaptomethyl groups in polystyrene and generally the polystyrene-supported catalysts were very active compared to the $\text{PhCH}_2\text{SH}/\text{Mo}(\text{NMe}_2)_4$ systems. The highest activity was observed for the molybdenum complex of polystyrene No. 2, which was the one most investigated in this work.

The simple calculation of the amount (%) of mercaptomethyl substitutions on phenyl rings of polystyrene and the average numbers of benzene rings surrounding one molybdenum metal in polystyrene-Mo complexes was carried out based on the results of the elemental analysis of sulfur and molybdenum atoms: 13.3% and 14.3 for polystyrene No. 1, 9.23% and 20.0 for polystyrene No. 2, and 6.98% and 24.8 for polystyrene No. 3.

A possible explanation for the highest activity of the polystyrene No. 2-Mo complex is as follows. A mononuclear Mo(III) species, which may be the real active species in the reduction of acetylene, is surrounded by *ca.* 20 phenyl rings of the polymer. The environment of the reactive Mo(III) species is thus in a hydrophobic domain, thus maintaining the catalytic activity and preventing the formation of catalytically inactive polynuclear Mo-Mo bonded species.

The effect of the addition of ferredoxin model complex, $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$, on the catalysis was also examined (Figure 4). A single component system of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ or PS-SH-molybdenum has only

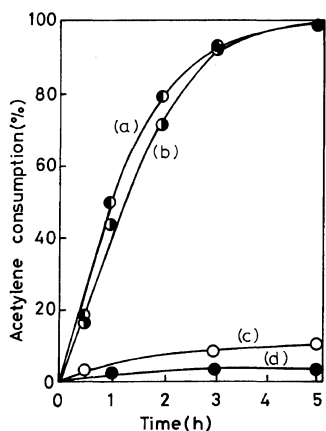


Figure 4. Effect of addition of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ on acetylene reduction by catalysis of polystyrene No. 2/ $\text{Mo}(\text{NMe}_2)_4$ system. Fe/Mo ratios: (a) 8 (●), (b) 4 (●), (c) 0 (○), and (d) $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ only (●). Experimental conditions are the same as in Table II.

very weak activity for the reduction of acetylene. By contrast, in a binary system of both compounds very high catalytic activity was observed, and an increase in the amount of $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ caused an increase in the ethane formation (Table II). This indicates that the reaction products of the molybdenum complex with $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ are the actual catalyst and/or that the cooperative functions between both complexes are very important in the reduction of acetylene. Actually, Otsuka *et al.* prepared an iron-molybdenum mixed cluster compound by the reaction of $\text{Mo}(\text{S}-t\text{Bu})_4$ with a ferredoxin model compound.¹⁶ An investigation of the reaction products between the polystyrene-supported molybdenum(IV) and ferredoxin model compound by the spectroscopic method is now in progress.

In order to obtain information on the mechanism for the formation of ethane and butadiene, the total composition of the gaseous phase of the system was determined at certain time intervals (Figure 5). The results revealed that at the first stage the reduction of acetylene to ethylene takes place predominantly, followed by the reduction of ethylene to ethane, and also that butadiene is formed during the first 3 hours, but not after the complete reaction of acetylene. On the basis of these results, a plausible mechanism was proposed for the reduction of acetylene by the above polystyrene-supported molybdenum catalyst (Figure 6). The active species for the

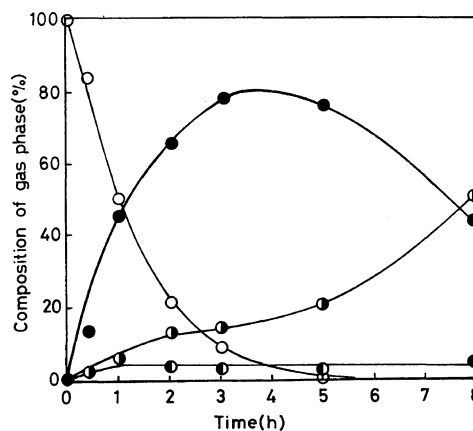


Figure 5. Change in gas phase concentrations of C_2H_2 , C_2H_4 , C_2H_6 , and C_4H_6 in acetylene reduction with a binary system of polystyrene No. 2/ $\text{Mo}(\text{NMe}_2)_4$ and $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ (Fe/Mo=4). C_2H_2 (○); C_2H_4 (●); C_2H_6 (●); C_4H_6 (●). Experimental conditions are the same as in Table II.

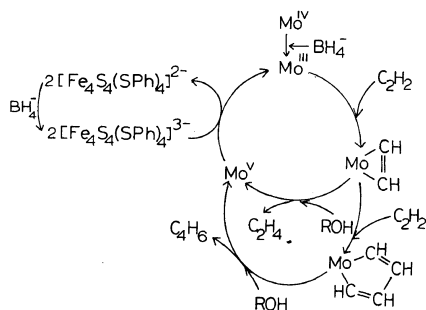


Figure 6. Proposed mechanism for acetylene reduction by catalysis of a binary system of molybdenum complex and $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$.

reduction of both acetylene and ethylene are presumably the same, possibly being the Mo(III) species with coordinative unsaturation although definitive evidence for the presence of the Mo(III) species has not been found. The formal oxidation number of molybdenum in the reduced state of native nitrogenase is unknown. Schrauzer *et al.* proposed a mechanism in which molybdenum(IV) species reacts with acetylene to give ethylene on hydrolysis and ethane is produced through the intermediacy of a $(\mu\text{-}\eta^2\text{-C}_2\text{H}_2\text{-})$ molybdenum(IV) species.⁴ Molybdenum(IV) species are considered to serve as a two electron reducing agents. Schultz *et al.* reported that the electrolytic reduction of a Mo(V)-cysteine complex in the presence of acetylene gives a Mo(III)-acetylene complex.¹⁷ A Mo(III) species with coordinative unsaturation readily interacts probably with acetylene to give a "side-on(η^2)" coordinated complex to afford ethylene on protonation by alcohol. The above η^2 -acetylene intermediate then reacts with another molecule of acetylene to give the molybdenacyclo-

pentadiene species which in turn gives butadiene by protonation with alcohol and then molybdenum is oxidized to Mo(V).

Finally, the efficiency of the polystyrene-supported Mo(IV) catalyst used in the reduction of acetylene was *ca.* 1/100 of the nitrogenase (with NaBH_4 as a reductant) and was one of the most active catalyst among the molybdenum complexes used up until now.

Reduction and Reductive Cleavage of Dinitrogen by Catalysis of a Mixed System of Mo(IV) Complexes and Ferredoxin Model Compound, $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$

Investigation of the reduction of dinitrogen as mimics of nitrogenase action have been primarily carried out the research groups of Shilov¹⁸ and Schrauzer. Very recently Schrauzer *et al.* reported the reduction of dinitrogen by catalysis of the *in situ* system of MoO_4^{2-} and insulin with NaBH_4 at a catalyst concentration as low as 10^{-6} mol l^{-1} .⁷ This system gave ammonia in a good turnover number only for the initial short period, although the actual amount of ammonia determined was quite small. Some typical results on dinitrogen reduction are given in Table III. A binary system of the polystyrene-supported molybdenum(IV) and ferredoxin model compound had a higher activity than the coresponding unsupported Mo(IV) system, thus being similar to the reduction of acetylene. The highest activity was observed in the system of random copolypeptide⁸ containing L-cysteine- $\text{Mo}(\text{NMe}_2)_4$ and $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$. In all cases a small amount of hydrazine accompanied the production of ammonia. The results indicate that the Mo(IV) complexes investigated in this work had

Table III. Reduction and reductive cleavage of dinitrogen by catalysis of molybdenum(IV) complexes and $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ with NaBH_4 ^a

Catalyst systems	Product	
	mol/mol[Mo]	
	Hydrazine	Ammonia
$\text{Mo}(\text{NMe}_2)_4 + [\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$	0.004	0.007
Polystyrene No. 2/ $\text{Mo}(\text{NMe}_2)_4 + [\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$	0.013	0.15
Random copolypeptide $[(\text{Cys-}\gamma\text{-benzylglu}_6)_{4,5}]/\text{Mo}(\text{NMe}_2)_4 + [\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$	0.004	0.37

^a Conditions: dinitrogen, 2000 ml; catalyst, 7.35×10^{-5} mol(Mo); NaBH_4 , 5.88×10^{-3} mol; solvent, THF-EtOH-MeOH (16 : 8 : 8 ml); temperature, 30°C; time, 24 h; Fe/Mo ratio, 4.

weak activity in the reduction of dinitrogen, and shorter reaction time lowered the yield of ammonia. The present catalyst system seems to maintain catalytic activity for a longer period. This is a distinct advantage of the polymer-bound metal complex catalysts.

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