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ABSORPTION OF DIHYDROGEN BY $[Fe_4S_4(SPh)_4]^{2-}$ AND $[Mo_2Fe_6S_8(SPh)_9]^{3-}$, AND THE H-D EXCHANGE REACTION BETWEEN H_2 AND D_2 CATALYZED BY THE REDUCED SPECIES OF THESE CLUSTERS

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Two and four molar amounts of H_2 can be absorbed quantitatively by $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$, respectively, in dimethylformamide, and the H_2-absorbed clusters exhibit the metal-hydride stretching bands in the matrix of polyvinylchloride films. Moreover, the reduced species of the clusters prepared chemically or electrochemically catalyze the H-D exchange reaction between H_2 and D_2. The active species for the catalytic reaction are shown to be $[Fe_4S_4(SPh)_4]^{4-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{5-}$.

Nitrogenase is composed of iron-sulfur and molybdenum-iron-sulfur containing proteins, which catalyzes the reduction not only of dinitrogen but also of a variety of small unsaturated molecules such as C_2H_2, RCN, RNC, and HCN.[1)] Nitrogenase catalyzes also the H-D exchange reaction between D_2 and H_2O (Eq. 1) in the course of

$$D_2 + H_2O \rightleftharpoons HD + HDO \qquad (1)$$

the N_2-fixation.[1-5)] The same H-D exchange reaction is catalyzed by hydrogenase containing iron-sulfur proteins.[6,7)] Typical functions of hydrogenase involving the Fe_4S_4 core in biological systems are widely accepted as uptake and evolution of H_2 in the course of activation of substrates.[7,8)] The H_2 evolution in the reaction of the reduced species of $[Fe_4S_4(SPh)_4]^{2-}$ ($[4\text{-}Fe]^{2-}$) and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ ($[Mo\text{-}Fe]^{3-}$) with PhSH,[9)] MeOH,[10)] and H_2O[10)] has previously been reported by Holm *et al.* and the present authors. This letter reports the absorption of H_2 and D_2 by $[4\text{-}Fe]^{2-}$ and $[Mo\text{-}Fe]^{3-}$ in dimethylformamide (DMF), and the H-D exchange reaction between H_2 and D_2 catalyzed by the reduced species of these clusters.

The $Bu^n{}_4N$ salts of $[4\text{-}Fe]^{2-}$ and $[Mo\text{-}Fe]^{3-}$ were prepared by the literature methods.[11,12)] The amount of H_2 absorbed by the cluster was determined by the use of a glass apparatus shown in Fig. 1, which consists of two *ca.* 2 cm^3 round flasks A and B connected by two bridges; one is equipped with a stopcock C and the other with a manometer D in which liquid paraffin is placed. After a fixed amount of the cluster (10-30 mg) is placed in the flask A, A and B were completely replaced with He and H_2 at ordinary pressure, respectively; then liquid paraffin prevented the gases from mixing. One cm^3 of DMF was injected through a rubber septum into the flask A to dissolve the cluster, the whole apparatus was thermostated at 30±0.1°C, and the DMF solution was stirred magnetically. After the apparatus attained thermal equilibrium, the DMF solution was exposed to H_2 gas by opening the stopcock C. The amount of H_2

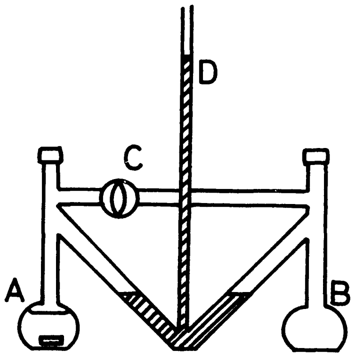

Fig. 1. An apparatus for the determination of amounts of H_2 absorbed by $[4\text{-Fe}]^{2-}$ and $[\text{Mo-Fe}]^{3-}$.

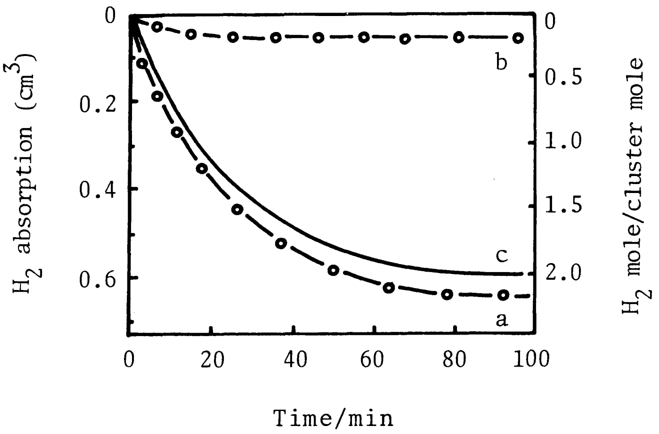

Fig. 2. The amounts of H_2 absorbed by $[4\text{-Fe}]^{2-}$ (15.0 mg) in DMF (1.0 cm^3) (a) and only the solvent DMF (1.0 cm^3) (b); c = a − b.

absorbed by the solution was determined from the change of the meniscus of liquid paraffin in the manometer D.

Plots of the amounts of H_2 absorbed by $[4\text{-Fe}]^{2-}$ in DMF (curve a) and by only the solvent DMF (curve b) against time are shown in Fig. 2, which indicates that the H_2 absorption is completed within 1 h, when $[4\text{-Fe}]^{2-}$ takes up two molar amounts of H_2 (curve c). Similarly, a DMF solution of $[\text{Mo-Fe}]^{3-}$ absorbed four molar amounts of H_2. These results correspond to the absorption of one hydrogen atom per one metal atom. It should, however, be noted that the H_2 absorption was largely dependent on the antecedents of the cluster used; the cluster seems to decompose gradually on exposure to air, resulting in decreasing the amount of H_2 absorbed. The H_2 absorption was, therefore, measured for the cluster immediately after preparation.

Although enzyme-bound hydrides have been suggested to exist as an intermediate in the H-D exchange reaction (Eq. 1) catalyzed by hydrogenase,6) no direct evidence has been reported for the existence of such an intermediate. Several attempts to detect ν(metal-H) bands of the present H_2-absorbed clusters by solution IR spectroscopy have failed, because there have not been found any good solvents to satisfy transparency in the IR region between 2250 and 1700 cm^{-1}, where ν(metal-H) bands are expected to appear.13) The IR spectra of H_2-absorbed clusters have, however, been successfully recorded in a matrix of polyvinylchloride (PVC) films as follows; a tetrahydrofuran solution of powdered PVC ($n \simeq 1000$) was added to an acetonitrile solution of H_2- or D_2-absorbed $[4\text{-Fe}]^{2-}$ or $[\text{Mo-Fe}]^{3-}$. After stirring for 5 min, the solution was dropped on a KRS-5 plate and then dried under H_2 or D_2 atmosphere. The H_2-absorbed $[4\text{-Fe}]^{2-}$ and $[\text{Mo-Fe}]^{3-}$ in the PVC matrices thus prepared exhibit a weak band at 1675 cm^{-1}, and two weak bands at 1860 and 1785 cm^{-1}, respectively, as shown in Fig. 3. A PVC film itself prepared similarly under N_2 atmosphere displayed no band in the 2200-1600 cm^{-1} range except for a weak absorption due to PVC at 1950 cm^{-1}. Thus, the bands observed in the H_2-absorbed clusters should be assigned to ν(metal-H), though it is not obvious which band is due to ν(Mo-H) or ν(Fe-H) in H_2-absorbed $[\text{Mo-Fe}]^{3-}$. The assignments for ν(metal-H) are supported from the IR spectra of D_2-absorbed $[4\text{-Fe}]^{2-}$ and $[\text{Mo-Fe}]^{3-}$ in the same matrix prepared under D_2 atmosphere, which have shown no band in the 1900-

1600 cm^{-1} region. Instead, D_2-absorbed $[4\text{-}Fe]^{2-}$ exhibited a weak band at 1203 cm^{-1} assignable to ν(Fe-D), while the ν(metal-D) bands have not been observed in D_2-absorbed $[Mo\text{-}Fe]^{3-}$, probably because of being concealed behind a very strong band due to PVC centered at 1300 cm^{-1}. The result that ν(metal-H) frequencies, in particular that of ν(Fe-H) of $[4\text{-}Fe]^{2-}$, are relatively low suggests the possible existence of bridging Fe---H---Fe linkages. However, another possiblity of the terminal hydride may not be excluded, because some dihydridometal complexes such as MH_2L_2 (M = Fe, Os; L = diphosphine) are known to exhibit ν(metal-H) bands around 1720 cm^{-1}.[14)]

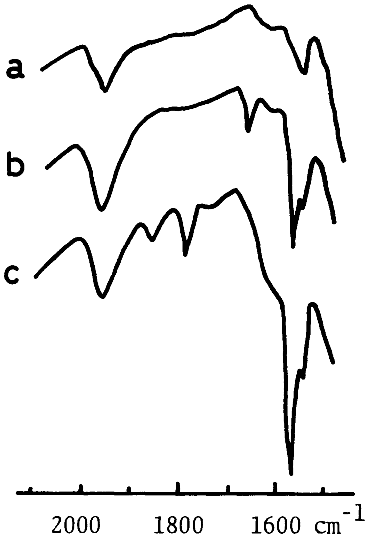

Fig. 3. IR spectra of PVC (a), and H_2-absorbed $[4\text{-}Fe]^{2-}$ (b) and H_2- absorbed $[Mo\text{-}Fe]^{3-}$ in the PVC matrices.

The $[4\text{-}Fe]^{2-}$ and $[Mo\text{-}Fe]^{3-}$ clusters were found also to catalyze the H-D exchange reaction between H_2 and D_2 (Eq. 2) in the presence

$$D_2 \;+\; H_2 \rightleftharpoons 2HD \qquad (2)$$

of reducing agents or under the condition of controlled potential electrolyses. Although a mixture of H_2 and D_2 (mole ratio 3:1) at ordinary pressure has undergone no H-D exchange reaction on a stirred hexamethylphosphorictriamide (HMPA, 4 cm^3) solution of $[4\text{-}Fe]^{2-}$ (0.1 mmol) or $[Mo\text{-}Fe]^{3-}$ (0.05 mmol), the reaction smoothly proceeded by adding sodium acenaphthylenide (0.38 mmol) as a reducing agent to the HMPA solution, giving an equilibrium mixture of H_2, HD, and D_2 in 2 days (Table), as confirmed with a gaschromatograph according to the literature.[14)] On the other hand, no H-D exchange has occurred in the presence of sodium acenaphthylenide alone in HMPA, though the sodium salts of some aromatic radical anions such as disodium phthalocyanide are known to catalyze the reaction (Eq. 2).[16)] Thus, the reduced species of $[4\text{-}Fe]^{2-}$ and $[Mo\text{-}Fe]^{3-}$ function as catalysts for the H-D exchange between H_2 and D_2.

Recently, Holm *et al.* have reported the isolation of the analytically pure Et_4N salts of $[4\text{-}Fe]^{3-}$ and $[Mo\text{-}Fe]^{5-}$ by the reduction of the same salts of $[4\text{-}Fe]^{2-}$ and $[Mo\text{-}Fe]^{3-}$, respectively, by sodium acenaphthylenide in HMPA.[9,17)] In view of the redox potentials of $[4\text{-}Fe]^{2-}$ (2-/3-: -1.02 V, 3-/4-: -1.75 V *vs.* SCE) and the acenaphthylenide anion (-1.70 V *vs.* SCE) in DMF, the reduction of the former by the latter is expected to give only $[4\text{-}Fe]^{4-}$ or a mixture of $[4\text{-}Fe]^{3-}$ and $[4\text{-}Fe]^{4-}$ in solution. It is, therefore, not evident which is the active species for the H-D exchange reaction, $[4\text{-}Fe]^{3-}$ or $[4\text{-}Fe]^{4-}$. In order to clarify this ambiguity, the controlled potential electrolysis at the reduction potentials of $[4\text{-}Fe]^{2-}$ as well as $[Mo\text{-}Fe]^{3-}$ was carried out in a DMF (15 cm^3) solution containing the $Bu^n{}_4N$ salt of $[4\text{-}Fe]^{2-}$ (47 μmol) or $[Mo\text{-}Fe]^{3-}$ (30 μmol) and $Bu^n{}_4NClO_4$ (4.0 mmol) as a supporting electrolyte under H_2/D_2 (3:1) at ordinary pressure. The reaction cell consisted of three compartments; a working and an auxiliary carbon electrodes which were separated

Table The H-D Exchange Reaction Catalyzed by the Reduced Species of $[4\text{-Fe}]^{2-}$ and $[\text{Mo-Fe}]^{3-}$ at 30°C

	Initial mole ratio			Final mole ratio[a]			$\frac{[HD]^2}{[H_2][D_2]}$
	H_2	HD	D_2	H_2	HD	D_2	
Reductant[b]	68	3	29	68	4	28	
$[4\text{-Fe}]^{2-}$	70	5	25	70	4	26	
$[\text{Mo-Fe}]^{3-}$	73	4	23	73	3	24	
$[4\text{-Fe}]^{2-}$ + Reductant	70	3	27	50	41	9	3.7
$[\text{Mo-Fe}]^{3-}$ + Reductant	72	8	20	46	43	11	3.7

[a] After 48 h. [b] $Na^+C_{12}H_{10}^-$.

by a glass frit, and a SCE reference electrode. The result has indicated that neither $[4\text{-Fe}]^{3-}$ produced at -1.25 V nor $[\text{Mo-Fe}]^{4-}$ at -1.08 V showed catalytic activity for the H-D exchange reaction within a week. On the other hand, the reaction was observed to occur in the gaseous phase only in the working electrode cell containing $[4\text{-Fe}]^{4-}$ and $[\text{Mo-Fe}]^{5-}$ produced at -1.90 and -1.70 V, respectively; the original ratio of H_2 to D_2 (3:1) in the gaseous phase in the counter electrode cell remained unchanged. The equilibrium constants obtained for Eq. 2 catalyzed by $[4\text{-Fe}]^{4-}$ and $[\text{Mo-Fe}]^{5-}$ were both 3.7 at 30°C, which is in agreement with the reported value ($K = 3.25$ at 25°C).[18] Thus, it is concluded that the active species in the present H-D exchange reaction (Eq. 2) are $[4\text{-Fe}]^{4-}$ and $[\text{Mo-Fe}]^{5-}$.

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