Catalytic reduction of acetylene and dinitrogen with the participation of the iron-molybdenum cofactor of nitrogenase and synthetic polynuclear molybdenum(III) complexes

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Catalytic reduction of acetylene and dinitrogen was carried out by sodium, zinc, and europium amalgams in the presence of polymolybdenum clusters and the iron-molybdenum cofactor of nitrogenase isolated from the enzyme. The activity of both catalysts toward acetylene changes in the sequence Zn(Hg) < Eu(Hg) < Na(Hg), increasing as the redox potential of the reducing agent is shifted to the negative region. The catalytic reduction of N_2 occurs only by the action of sodium and europium amalgams and only in the presence of synthetic polymolybdenum complexes; in the case of Na(Hg), the main product is hydrazine; in the case of Eu(Hg), it is ammonia.

Key words: nitrogen fixation, metal clusters; acetylene, dinitrogen, multi-electron reduction, FeMo-cofactor of nitrogenase.

In 1964, M. E. Volpin and V. B. Shur published pioneering work[1] demonstrating the possibility of reducing molecular nitrogen in solutions of metal complexes. This work laid the foundation for a new area in chemistry: the low-temperature chemistry of molecular nitrogen. The first systems reducing N_2 under mild conditions contained transition metal (titanium, iron, molybdenum, and others) compounds in combination with strong reducing agents, such as organomagnesium and organolithium compounds, metal hydrides, and free metals. The further study of these systems showed that the reaction of the reducing agent and a transition metal compound results in the reduction of the latter, and the derivative of the transition metal in the low oxidation state that formed reacts with dinitrogen to give complex nitrides. The subsequent hydrolysis of the reaction mixture gives ammonia.[2]

Of course, the reaction with dinitrogen can occur only in an aprotic medium, because the strong reducing agents used are unstable in protic solvents (water, alcohols) and react with the solvent. The amount of ammonia (after hydrolysis of the products) does not exceed the stoichiometric amount calculated with respect to the transition metal taken; however, catalytic systems were also observed.[2] For example, in the reaction of N_2 with the $TiCl_4$—Al—$AlBr_3$ mixture (with an excess of the reducing agent Al—$AlBr_3$), the amount of ammonia formed after the hydrolysis of the products is hundreds of times greater than that of titanium taken.

However, no catalytic reduction of N_2 involving protons was observed in the first works.

Nevertheless, in the well-known process of biological nitrogen fixation, which also involves the transition metals iron and molybdenum, the N_2 reduction involves protons of water. The stoichiometric equation of this complicated reaction catalyzed by the nitrogenase enzyme includes the biological reducing agent ferredoxin or flavodoxin (*in vivo*) or dithionite in experiments *in vitro* and takes into account the conjugated hydrolysis of adenosine triphosphate (ATP).

$$N_2 + 8\,H^+ + 8\,e^-(S_2O_4^{2-}) + 16\,MgATP \longrightarrow$$
$$\longrightarrow 2\,NH_3 + H_2 + 16\,MgADP + 16\,PO_4^{2-}$$

The enzymatic process occurs under the action of considerably weaker reducing agents than those in the first nitrogen-reducing Volpin—Shur systems. Protons of the medium most likely participate in the early stages of the reaction without preliminary formation of nitrides.

Nitrogenase also catalyzes the reduction of several other substrates: acetylene, isonitriles, azides, *etc.* Acetylene is selectively transformed into ethylene during the enzymatic process, and this reaction is a standard test for biochemical determination of catalytic activity of nitrogenase.

To bring together chemical nitrogen-fixation systems and enzymatic nitrogen reduction with comparatively weak reducing agents under mild conditions in protic media, the main principle of enzymatic catalysis should be applied: improvement of the organization of the catalytic system.

In the case of molecular nitrogen, this requirement implies the possibility of multi-electron reduction cata-

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lyzed by a polynuclear transition metal complex, which is capable of reacting with N_2 to form an intermediate complex. This method for N_2 activation follows from the analysis of the thermodynamics of successive cleavage of three bonds of the nitrogen molecule. This analysis shows that in the case of comparatively weak one- and two-electron reducing agents (sufficiently strong, however, to reduce N_2 to ammonia), the catalyst should open up the possibility of four- or six-electron reduction, because one- and two-electron reduction is thermodynamically very difficult. Multi-electron reduction can be performed by polynuclear transition metal complexes (see, *e.g.*, reviews[3–5]).

The molybdenum-iron protein, which is the main part of nitrogenase, contains the so-called P-cluster and iron-molybdenum cofactor (FeMoco), and the latter is believed to activate and reduce N_2 and other substrates. Both clusters have a considerable electron capacity; they can act in combination, which most likely allows the collective transfer of electrons to the coordinated N_2 molecule.

Presently, the composition and structure of the FeMo-cofactor are reliably established. The cofactor has the $MoFe_7(S^{2-})_9$ (homocitrate) formula. Nine sulfide groups are bridges that unify molybdenum and iron into a prismatic cluster including six coordinationally unsaturated Fe atoms and two more metal atoms at both sides: at one side, the Mo atom in the octahedral environment, and at the other side, the Fe atom in the tetrahedral environment. These two atoms allow the binding of the cofactor with the protein (the Fe atoms performs this binding *via* the SH group of cysteine, and the Mo atom, *via* the imidazole residue of histidine).

It can be assumed that the central coordinationally unsaturated Fe atoms (all six or, at least, four) react with the N_2 molecule to form a complex with four and even six Fe—N contacts. The polynuclear and "multi-contact" character of the complex results in a comparatively high negative charge on the N atoms of the coordinated N_2 molecule and a considerable decrease in the multiplicity of the bond between the N atoms, which facilitates its subsequent cleavage during protonation.

We demonstrated in several works (see Refs. 3—5) that polynuclear complexes containing metal atoms with sufficiently strong reducing properties can in fact reduce N_2 under mild conditions in protic media to form hydrazine or ammonia.

Catalytic reduction cannot be easily performed in protic media, because additional conditions along with polynuclearity should be fulfilled: first of all, a sufficiently narrow interval of redox potentials. We succeeded in developing catalytic systems capable of efficiently reducing N_2 to hydrazine and ammonia that involved polynuclear molybdenum complexes in methanol. Sodium amalgam ($E_0 = -1.8$ V) or a mercury cathode with a similar potential (for the electrochemical reduction) were used as reducing agents. The reaction occurs on the surface; therefore, surface active cocatalysts are used: a phospholipid (phosphatidylcholine) or polyvinyl alcohol. The catalyst is incorporated into the surfactant film on the amalgam surface, electrons are transferred from the amalgam to the complex, and protons are transferred from solvent (MeOH) molecules to the catalyst.[3–5]

The multi-electron character of the catalytic process is due to the possibility of using an unrestricted number of electrons of the donor. If a similar mechanism takes place in the enzymatic process as well, the nitrogenase cofactor isolated from the enzyme and adsorbed on the amalgam surface or another multi-electronic reducing agent can act in a similar manner.

The iron-molybdenum cofactor was isolated from the MoFe-protein of nitrogenase as early as in 1977,[6] but researchers believed until recently that it acts as a catalyst only in the enzyme,[7] although an opinion that it can be used as a catalyst without the protein has been published earlier.[8] Perhaps, the opinion that the protein must be necessarily involved appeared due to the previous attempts to use the cofactor as a catalyst in purely chemical systems or in media that destroy the structure of FeMoco (aqueous buffer solutions), or because unsuitable reagents (for example, one- or two-electron donors) were used as reducing agents.

It is known from X-ray diffraction study[16] of the MoFe-protein that FeMoco is immersed in the protein globule by approximately 10 Å, which explains its stability to the action of water in the protein-bound state. When FeMoco is separated from the protein, the protective environment is destroyed, and FeMoco is easily hydrolyzed under the action of water and alcohols.[7] Therefore, to develop catalytic systems involving FeMoco, one should use aprotic media with various polarities. To obtain reduction products from substrate molecules coordinated on the reduced cofactor, one should use specially added substances that do not destroy the catalyst structure and whose pK_a values are sufficient for protonation.

We have shown in the recent works that when zinc or sodium amalgams are used as electron donors (in aprotic solvents with thiophenol as the proton source), the FeMo-cofactor becomes an efficient catalyst for reduction of such nitrogenase substrates as acetylene, azide, and nitriles, although no reproducible reduction has as yet been observed for N_2 itself.[9–11]

Thus, it is possible to study the reduction of nitrogenase substrates with the same electron donor using both the isolated FeMo-cofactor and synthetic polynuclear complexes as catalysts.

It can be assumed that comparison of the results of these studies will elucidate the unsolved problems of the enzymatic reduction of N_2 (in particular, the role of the P-cluster and hydrolysis of ATP) and will solve the problems of the chemical catalysis (in particular, determination of the value of the redox potential of the amalgam and the nature of the amalgam-forming metal). This should stimulate the further development of catalytic systems reducing N_2.

In this work, we studied the reduction of acetylene and N_2 under the action of sodium, zinc, and europium amalgams.

Experimental

Acetylene was reduced in a glass vessel, which was pre-evacuated and filled with argon. A metal amalgam and a solution of the catalytic complex with the corresponding additives were placed in the vessel in an argon flow. The reaction vessel was evacuated to remove argon and filled with acetylene to the necessary pressure. During experiments, the amalgam and solution were stirred on a magnetic stirrer selecting the regime of maximum pulverization of the amalgam. This method allowed good reproducibility to be obtained in kinetic experiments for comparison of results. In experiments with induced potential, acetylene was reduced in an electrochemical cell (in which zinc amalgam served as the cathode) without stirring the amalgam and solution. Samples of the gas phase were taken to analyze the reaction products by GLC.

The reduction of N_2 was carried out in a similar vessel with the distinction that a capillary was inserted into the vessel, and samples from the liquid phase could be taken through the capillary to determine hydrazine and ammonia contents.[12]

Hydrazine was determined by spectrophotometry after an acidic solution of *p*-dimethylaminobenzaldehyde was added to the sample.

Ammonia was determined according to the procedure developed by us. A saturated solution (2 mL) of NaOH in MeOH was added to the solution (6 mL) under study. The mixture was refrozen *in vacuo* into a flask containing 2 drops of 12 *M* HCl. The dry residue was heated for 30 min to ~100 °C to ensure complete liberation of ammonia. Then all the solvent was again refrozen *in vacuo* from the flask to a separate flask, and tridistilled water (2.2 mL), a 6% solution of phenol in water (0.22 mL), and a saturated solution of NaOCl (0.06 mL) were added to the dry residue. The amount of ammonia was determined spectrophotometrically by the absorption at $\lambda = 630$ nm. Special experiments with addition of the known amount of NH_3 showed that this procedure allows one to determine ammonia with sufficient accuracy.

Cluster $[Mg_2Mo_8O_{22}(OMe)_6(MeOH)_4]^{2-}[Mg(MeOH)_6]^{2+}\times$ $\times 6MeOH$ (Mo_8-complex) was synthesized from $MoCl_5$ and $MgCl_2$ in MeOH as described previously.[13] A solution of the cluster with a greater number of Mo atoms was obtained by polymerization of the Mo_8-complex in a weakly acidic medium. Hereinafter this compound is arbitrarily designated as the 16-nuclear Mo_{16}-complex, although this cluster is known only to have a larger volume and to contain a greater number of molybdenum atoms than Mo_8. To obtain the active form of the catalyst, the molybdenum-magnesium complexes were reduced by sodium amalgam to the trivalent state of molybdenum (Mo^{III}). The number of the Mo atoms in the complex remained unchanged.[13] A solution of the catalyst thus obtained retains its activity unchanged for several years.

The iron-molybdenum cofactor of nitrogenase (FeMoco) was isolated from the MoFe-protein of *Azotobacter vinelandii* bacteria using the column method described by Orme-Johnson and co-workers.[14,15] The Fe : Mo ratio in the samples varied from 7 to 12 (according to the exact formula FeMoco, it should be equal to 7). The increased values of the Fe : Mo ratio are most likely related to an admixture of Fe-containing compounds formed during the decomposition of the P-clusters. The results obtained showed that the admixture iron had no noticeable effect on the catalytic activity of FeMoco.

Metal amalgams were prepared by dissolution of the corresponding metals in mercury.

Results and Discussion

Acetylene reduction

Both the polymolybdenum clusters and FeMo-cofactor of nitrogenase are efficient catalysts for the reduction of acetylene by zinc, europium, and sodium amalgams. The results of some experiments are presented in Table 1.

In the case of Zn(Hg), addition of the cocatalyst (thiophenol) plays an important role in the action of the both catalysts.[10] In the absence of thiophenol, yields of the reaction products in the catalysis by the polymolybdenum complexes are close to stoichiometric values with respect to the molybdenum complex.

The reaction in DMF containing the FeMo-cofactor but without thiophenol does not occur at all, because the medium contains no protons capable of participating in the reduction. Addition of other proton donors, for example, citric acid, allows the catalytic reduction, but the catalyst activity decreases rapidly. Thus, thiophenol stabilizes the system, and the reaction proceeds for several hours with an unchanged rate.

When Na(Hg) is used as the reducing agent in the presence of the polymolybdenum complexes, a phospholipid (phosphatidylcholine) and phosphines (tributylphosphine) exert the cocatalytic effect. In this case, the polymolybdenum clusters and FeMoco differ dramatically in stability. The first compound is sufficiently stable for a long time, while the second compound is completely decomposed within less than 1 h. The stability of the cofactor in the presence of Eu(Hg) is low as well: it loses completely its activity within ~0.5 h.

In the case of Eu(Hg), the reaction involving the polymolybdenum complexes occurs without cocatalyst additives as well, and unlike phospholipid, thiophenol does not have a noticeable effect. In DMF, the FeMo-cofactor requires, of course, a proton donor, which is the thiophenol added.

The data in Table 1 demonstrate that the rate of acetylene reduction under the action of the both catalysts increases in the sequence Zn(Hg) < Eu(Hg) < Na(Hg) in parallel with an increase in the reductive capability of the amalgams (E_0 = −0.8, −1.4, and −1.8 V, respectively). This is confirmed when the reaction of acetylene reduction is carried out in the presence of the Mo_8-complex in the electrochemical cell with Zn(Hg) as the cathode: the rate of acetylene reduction increases as the induced potential is shifted to the negative region to −1.7 V (Fig. 1). This dependence indicates the adsorption character of the process: the reaction rate is determined by the stage of electron transfer to the reaction center. It is interesting that

Table 1. Reduction of acetylene in the presence of FeMoco and polynuclear Mo^{III} complex (Mo_{16}) by Na, Eu, and Zn amalgams[a]

Amalgam	Catalyst	Yield of $(C_2H_4 + C_2H_6)$ [b]	C_2H_6/C_2H_4	Additives of cocatalyst
Na(Hg)	Mo_{16}	170	0.56	—
Na(Hg)	Mo_{16}	2144	0.78	Phosphatidylcholine
Na(Hg)	Mo_{16}	214	0.73	Bu^n_3P
Na(Hg)	Mo_{16}	2252	1.04	Phosphatidylcholine and Bu^n_3P
Na(Hg)	Mo_{16}	4200	1.04	Phosphatidylcholine, Bu^n_3P, and NaOMe [c]
Na(Hg)	FeMoco	190	0.09	PhSH
Eu(Hg)	Mo_{16}	39	0.57	—
Eu(Hg)	Mo_{16}	367[d]	0.49[d]	PhSH
Eu(Hg)	Mo_{16}	1053	0.60	Phosphatidylcholine and Bu^n_3P
Eu(Hg)	FeMoco	150[e]	0.27	PhSH
Zn(Hg)	Mo_{16}	60	0.20	Phosphatidylcholine and Bu^n_3P
Zn(Hg)	FeMoco	30	0.015	PhSH

[a] Solvent: for Mo_{16}-complexes, aqueous MeOH; for FeMoco, DMF; volume of the solution 6 mL, temperature 25 °C, duration of the reaction 15 min, volume of Na(Hg) (0.6 wt.%) 1 mL, Eu(Hg) (0.9 wt.%) 0.5 mL, Zn(Hg) (2 wt.%) 0.5 mL.
[b] In moles per one mole of catalyst.
[c] Experiments with N_2 show that the addition of NaOMe eliminates the induction period, which evidently decreases the yield in the previous experiment.
[d] Duration of reaction 30 min.
[e] Duration of reaction 5 min.

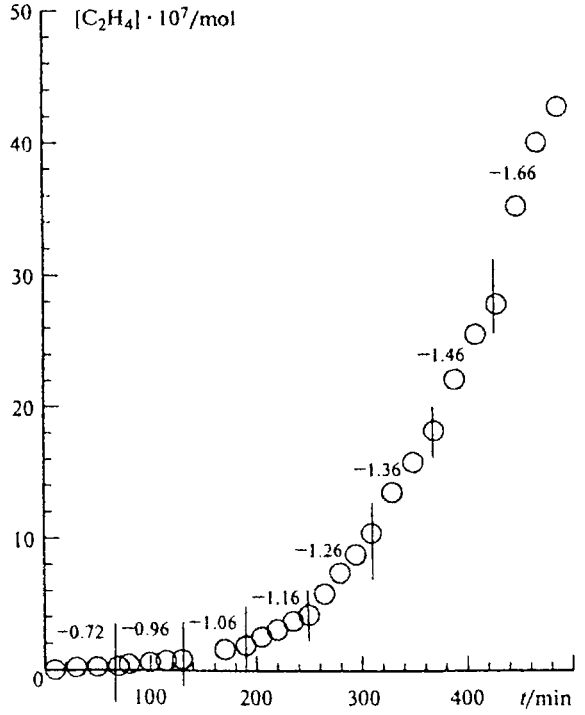

Fig. 1. Kinetics of the formation of ethylene in the reduction of acetylene by zinc amalgam with the participation of the polymolybdenum Mo_8-complex at different induced potentials. Figures on the curves are the values of the induced potential (E/V) relative to the standard hydrogen electrode (SHE).

methane appears in the reaction products at the potential of −1.3 V, and the rate of its formation and yield increase as the potential is further shifted to the negative region (Table 2).

This result suggests that the formation of methane occurs on the surface, otherwise the yield of methane would be independent of the surface potential. In principle, the catalytic reduction of acetylene could be homogeneous if the catalyst (after reduction on the surface) passes into solution and reacts with the substrate. However, it is likely that the catalysts studied remain on the surface during the whole process, at least under the chosen conditions. This is indicated, in particular, by the fact that at the given amount of amalgam

Table 2. Relative yield of products of the reduction of acetylene by Zn amalgam with the participation of the Mo_8-catalyst ($[Mo^{III}_8] = 0.68 \cdot 10^{-2}$ mol L^{-1}) at different induced potentials

E(SHE) /V	$[C_2H_6]/[C_2H_4]$	$[CH_4]/(\Sigma[C_2H_4] + [C_2H_6] + [CH_4])$ (%)
−0.72	0.2	—
−0.96	0.2	—
−1.06	0.2	—
−1.16	0.18	—
−1.26	0.17—0.18	2.9
−1.36	0.17	5.3
−1.46	0.15—0.16	9.6
−1.66	0.17	12.5

and constant rate of stirring, in both cases (polymolybdenum clusters and FeMoco) the rate of formation of the products is almost independent of the volume of the catalytic solution.

It is seen from the data in Table 2 that, unlike methane, the relative yield of ethane (the $[C_2H_6]/[C_2H_4]$ ratio) is almost independent of the induced potential.

Dinitrogen reduction

Presently, the polymolybdenum clusters are the only family of metal clusters in the presence of which N_2 is catalytically reduced in MeOH at room temperature and atmospheric pressure under nonbiological conditions.

As is mentioned, *sodium amalgam* ($E_0 = -1.8$ V) or a mercury cathode with similar potential (for the electrochemical reduction) can be reducing agents. Phosphines along with surfactants can be cocatalysts. The most active of them are strong donors such as Me_3P and Bu_3P. Hydrazine is the main reaction product, and ~10% ammonia are concurrently formed. At room temperature and atmospheric pressure, the yield of the products reaches 1000 cycles per catalyst, which is several percent calculated per the number of electrons in the amalgam (up to 10% at 0 °C). When the N_2 pressure is increased to 100 atm, the yield of the products reaches 30% calculated per amalgam.[3–5]

The reaction in DMF (with addition of alcohol as the proton donor) does not occur: neither hydrazine nor ammonia are formed under similar conditions.

We failed to observe the products of N_2 reduction in the presence of the FeMo-cofactor perhaps due to its instability to the action to the strong reducing agent Na(Hg).

Under conditions in which *zinc amalgam* was used as the reducing agent and the maximum activity with respect to acetylene was observed, both catalysts (polymolybdenum cluster and FeMoco) were inactive toward nitrogen, most likely due to the insufficiently strong reducing properties of Zn(Hg).

Europium amalgam with potential intermediate between those of the other amalgams ($E_0 = -1.4$ V) is a sufficiently strong reducing agent for the catalytic reduction of N_2 in the presence of the Mo_{16}-cluster. The addition of thiophenol results in the formation of both ammonia and hydrazine (Table 3). In the absence of thiophenol, mainly ammonia and only traces of hydrazine are formed.

In the presence of Eu(Hg), the iron-molybdenum cofactor did not give definite results: we did not observe reproducible reduction of N_2 with this catalyst. Perhaps, additional optimization of experimental conditions is needed.

The systems discovered by Vol'pin and Shur, including catalytic systems, allowed the N_2 reduction at low temperatures and pressures to be performed using strong reducing agents. The industrial catalytic synthesis of ammonia involves the weak reducing agent (H_2), but requires drastic conditions. The nitrogenase enzyme makes it possible to carry out the catalytic reduction of N_2 by comparatively weak reducing agents under mild conditions. This is also achieved by the very sophisticated organization of the active center. Of course, the Vol'pin—Shur systems and systems for the high-temperature catalytic synthesis of ammonia require a certain organization. In particular, intermediate complexes with nitrogen, mainly bi- or polynuclear, are formed both in solution and on the surface of the heterogeneous catalyst. This formation requires the corresponding arrangement of the metal atoms in the active center. However, both the spatial and time organization in chemical systems are usually insufficiently perfect. The study of the nitrogenase structure and general theoretical concepts make it possible to approach the enzymatic process in purely chemical catalytic systems.

Table 3. Reduction of N_2 by Na and Eu amalgams in the presence of the polynuclear Mo^{III} complex (Mo_{16})[a]

Amalgam	$[Mo_{16}] \cdot 10^8$	$[PhSH] \cdot 10^6$	$[NH_3] \cdot 10^8$	$[N_2H_4] \cdot 10^8$
	mol			
Na(Hg)[b]	0.37	–	80	840[13]
Eu(Hg)	1.1	0	15	–
Eu(Hg)	1.1	0.2	16	Traces
Eu(Hg)	1.1	5	8.4	3.0
Eu(Hg)	1.1	5	9.2	2.8
Eu(Hg)	1.1	15	Traces	–
Eu(Hg)	6.6	5	13	2.1
Eu(Hg)	6.6	5	11	–

[a] Solvent MeOH, volume of solution 6 mL, temperature 20 °C, duration of reaction 30 min, volume of Eu(Hg) (0.9 wt.%) 0.5 mL, Na(Hg) (0.6 wt.%) 1 mL.
[b] The reaction was carried out in methanol with additives of phosphatidylcholine, Bu^n_3P, and NaOMe.

First of all, a polynuclear complex in which the N_2 molecule is bound to several transition metal atoms already at the activation stage is optimum for sufficient activation of the dinitrogen molecule, which allows its subsequent reduction involving a comparatively weak reducing agent. This occurs in the FeMo-cofactor, most likely due to the corresponding arrangement of the Fe atoms, and in the model polymolybdenum complex, due to the arrangement of the Mo atoms. It can be assumed that the molybdenum(III) complex with the oxygen ligands provides a sufficient decrease in multiplicity of the bond between the N atoms in the polymolybdenum complex, and the iron(II) atoms play a similar role in the iron-molybdenum cofactor: under other equivalent conditions, they are weaker donors than Mo^{III} but supplemented by bridging sulfide ligands. The latter exhibit stronger donor properties than the O atoms. The increase in the catalytic activity in the model polymolybdenum system in the presence of phosphine with strong donor properties is most likely related (at least partially) to the formation of phosphine complexes with

the Mo^{III} atoms (which are not involved in the complex formation with N_2) and enhancement thus of the donor properties of the whole catalytic complex.

Accessibility of additional electrons of the donor (localized near the active center of the catalyst) is an important condition for the catalytic activity. The electron donor most likely favors the reduction of N_2 at the rate-determining stage. During the biological nitrogen fixation, this is provided by the presence of the polynuclear P-cluster in the immediate vicinity of the FeMo-cofactor. In the model systems, in the cases where the catalytic complex is located on the surface of the electron donor (amalgam or cathode), this role is played by this donor. In both cases, *reductive assistance* is manifested, which is optimum in the presence of a multi-electron donor and probably abundant in both biological and purely chemical systems.[5]

The validity of these concepts is confirmed by the possibility of using the FeMo-cofactor of nitrogenase as an efficient catalyst for reduction of acetylene and other nitrogenase substrates (azide, acetonitrile) in purely chemical systems when it is adsorbed on the amalgam surface. It is important that both the polymolybdenum cluster and FeMo-cofactor are capable of multi-electron (four- and six-electron) processes.

We have not observed yet the reproducible reduction of N_2 with the participation of the FeMo-cofactor. Dinitrogen is the most thermodynamically "difficult" substrate, and its reduction requires the fulfillment of several additional conditions for catalysis. As mentioned above, the FeMo-cofactor is unstable in the presence of strong reducing agents. The FeMo-cofactor isolated from nitrogenase contains DMF used for extraction of the cofactor from the MoFe-protein of the enzyme. This fact can also be one of the reasons for inactivity of the cofactor. As shown above, DMF as a solvent is inappropriate for manifestation of the catalytic activity of the polymolybdenum complexes. Perhaps, molecules of DMF, which is a weak bidentate ligand, block the active center. The N_2 molecule, being a very weak nucleophile, may be unable to displace DMF, while acetylene and other substrates most likely replace it easily. We hope that further study will include molecular nitrogen among the substrates of the FeMo-cofactor.

The model polymolybdenum clusters are sufficiently active for the *catalytic* reduction of N_2 by sodium and europium amalgams. Most likely, the zinc amalgam was an insufficiently strong reducing agent. Comparison of the action of the amalgams shows that each of them requires different conditions for adsorption of the catalytic complex (the corresponding additives for Na(Hg), Zn(Hg), and Eu(Hg)). Probably, this is associated with the very different redox potentials of the amalgams chosen, although a certain role of the chemical nature of the metals (Na, Eu, and Zn) cannot be ruled out.

In this work, we managed to somewhat approach nitrogenase in potential using the Eu amalgam. The redox potential of Eu(Hg) (−1.4 V) is 0.4 V less negative than that of Na(Hg). The formation of ammonia as the main reduction product has been observed for the first time in the catalytic system in the solution, which also bridges the gap between this system and the enzymatic system in which (in the case of molybdenum nitrogenase) ammonia is the only product.

The transition from hydrazine to ammonia when a weaker reducing agent is used is a common property of noncatalytic nitrogen fixation systems.[3–5] This can be easily explained by the fact that the electron transfer is retarded as the reducing ability decreases. The formation of hydrazine, which requires a more negative potential than ammonia, is less probable, and the system prefers to "wait" until all six electrons become accessible and two ammonia molecules can be formed.

The catalytic Mo_n—Eu(Hg) system in an aqueous MeOH solution functions at a potential 0.6—0.8 V more negative than that of the enzymatic system. This difference is the quantitative measure of "imperfectness" of the model catalytic system as compared to the enzymatic system and seems to be natural when the considerably more complicated character of the enzyme is taken into account (in particular, ATP is not hydrolyzed in the model system). At the same time, the value of the potential of the reducing agent is 1—1.5 V lower than in the Vol'pin—Shur systems and demonstrates the progress in the area of low-temperature reactions of molecular nitrogen 33 years after its discovery. Undoubtedly, despite difficulties in the work with the inert N_2 molecule, we can hope that this captivating area of chemistry will find further development in the near future.

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