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Some Results in the Catalytic Reduction of Dinitrogen

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Abstract: The proposed mechanism of dinitrogen reduction in a binuclear M-N=N-M complex bound to a polynuclear reducing agent makes it natural to use the catalytic complex for the electrochemical reduction of dinitrogen at the surface of the cathode

Keywords: electrochemical reduction, dinitrogen, Mo(III) compounds.

1. Introduction

The electroconductivity of protic media which can be increased in the presence of ionic species favours the use of electrolysis for dinitrogen reduction. The availability of electrons at the cathode makes it possible to ensure the multielectron reduction which is thermodynamically favourable for dinitrogen.

Again, the parallel dihidrogen production usually competes with N_2 reduction. Therefore a material must be chosen for the cathode wich is a poor catalyst for H_2 formation and gives rise to a high overvoltage. Mercury abd lead are obvious candidates. At a sufficiently negative potential of mercury cathode, alkai metal ions (Na^+), are discharged at the cathode to form an amalgam which may be a real reducing agent for dinitrogen in chemical reduction. Another possibility is purely electrochemical reduction by electron transfer directly to the coordinated dinitrogen molecule. Dinitrogen reduction under electrolysis conditions was observed for the first time in 1977 [1] for the system containing a mercury cathode with $Ti(OH)_3$-Mo(III) [2] and for the similar system also containing guanidine, with which the system becomes a homogeneous solution [3].

A strong dependence of the product yields on current density was observed [4]. Maximum NH_3 yield was observed at a current density of 0.5 $A.cm^{-1}$. The authors [4] explain this phenomenon in terms of the influence of current density on the charge on the cathode surface. At 0.5 $a.cm^{-1}$ the surface has a close to zero charge, which corresponds to the optimum conditions for the adsorption of negatively charged hydroxide on the surface and its further participation in N_2 reduction. At lower current density, a sufficiently negative redox potential is not ensured and the reaction rate drops. At higher densities, a negative charge is created at the cathode surface which hinders the adsorption of negatively charged hydroxide. In optimum conditions the current yield reaches 43% with respect to hydrazine and 4% with respect to ammonia.

2. Experimental

This system is very simple as the function of its main components :sodium amalgam and Mo(III) complexes are the reductant and the catalyst, respectively.

The catalytic complex can be obtained by reduction of a methanol solution of $MoCl_5$ by sodium amalgam. If a new portion of sodium amalgam is now shaken with the methanol solution of Mo(III) compound in an autoclave under N_2 pressure, wery small amounts of hydrazine are detected ~ 1×10^{-5} M with similar catalyst concentration). Attempts to markedly increase the N_2H_4 yield by increasing the catalyst concentration have failed because of parallel H_2 formation, which is accelerated to a much greater extenr than the N_2 reduction.

The N_2H_4 yield is very sensitive to small amounts of impurities in the solution and the results are poorly reproducible.

The yield can be increased and becomes more reproducible if Mg^{2+} salts are added to a methanol solution of $MoCl_5$ prior to its reduction. Though the N_2H_4 yields remain rather low (up to $2 – 5 \times 10^{-5}$ M), the reaction can be followed kinetically[5].

This investigation has led to the conclusion that the reaction proceeds at the amalgam surface, and that the rate-controlling step is the electron transfer from amalgam to the catalytic complex which coordinates dinitrogen reversibly in the N_2 atmosphere.

It follows that in order to further increase the efficiency of the catalytic system, one must strengthen the adsorption ability of the catalytic complex and facilitate the electron transfer from the amalgam.

However, attempts to improve the catalytic system by adding various substances, including surface active materials, did not produce any noticeable positive results for quite a long time.

3. Results and discussion

Real progress was achieved only when a certain phospholipid, for example – phosphatidycholine (PC) and its synthetic analogs were used as co-catalysts. The idea was prompted by the knowledge of phospholipid participation in the activities of many so-called phospholipid-dependent enyzmes. The presence of phosphatidycholine produced marked effects on both the reaction rate and the product yield [6,7] (table 1). Ammonia was found to be a co-product of the reaction, together with hydrazine, whereas without PC no ammonia is formed.

The specificity of phosphatidylcholine is a remarkable feature of the co-catalysis. No other phospholipid tested produces effect, though the reaction is easily inhibited or stopped completely. Moreover, even small chenges in the molecule of PC, such as replacement of an ester group by a similar ether group, produce a strong inhibiting instead of enhancing effect.

Even the changes in the aliphatic tail length in PC molecule have some effect on the catalytic action, and in particular change the N_2H_4/NH_3 ratio.

In the presence of PC, a measurable reaction rate is observed even at room temperature and atmospheric N_2 pressure. This allowed simplication of the kinetic experiments and thus accelerated further investigation.

Subsequent improvement in the catalyst has been achieved by the consecutive acidification , by HCl in methanol; alkalination , by $NaOCH_3$ in methanol; of the catalyst solution. Part of the molybdenum precipitates during this procedure, while the remaining solution displays greater activity per molybdenum atom. The relative yield of ammonia simultaneously drops (from 50 to 10% hydrazine), after this procedure.

Finally, a further considerable acceleration of the reaction rate and an increase in product yield are observed when organic phosphines are introduced into the reaction solution[7] (table 2 and figure 1).

The effect differs depending on the nature of the phosphine added, the most significant increase being observed for such phosphines as Me_3P aand Bu_3P (where Me – methyl and Bu – butyl).

TABLE 1. Development of the catalytic system based on Na(Hg) + Mo(III) (methanol, 20 ^oC).

System	Specific rate $[N_2]_{red}/[Mo]$ x t (sec^{-1})	Yield($N_2H_4+NH_3$)	
		Per Mo turnover number	Per reducing agent,%
Mo(III) + Na(Hg) 70 atm N_2	< 0.0001	0.5	0.004
+ Mg^{2+} 70 atm N_2	0.0003	2.5	0.02
+ PC 70 atm N_2	-	25.0	0.25
+ PC 1 atm N_2	0.05	3.5	0.03
Catalyst improved			
+ R_3P 1 atm N_2	0.4	200 – 1000	5 – 10
+ R_3P 70 atm N_2	-	~ 10000	30
Nitrogenase 1 atm N_2	~ 0.6	-	-

TABLE 2. Influence of phosphines on hydrazine yield(1 atm N_2 ; 20^{o}C; [Mo] = 1-3 x 10^{-5}M) $^{a)}$.

PR_3	[PC] x 10^5 (M)	[PR_3] x 10^5 (M)	[N_2H_4] x 10^5 (M)
-	62	0	3
$Ph_2PCH_2CH_2PPh_2$	75	1740	8
$P(NMe_2)_3$	52	920	11
Ph_3P	75	1000	13
$EtPPh_2$	42	760	23
$MePPh_2$	36	680	82
Me_2PPh	42	24	84
Bu_3P	52	550	110
Me_3P	40	560	150

a)results are given for approximately optimum concentrations.

It is of interest that phosphine action is observed only in the presence of phosphatidylcholine. The general effect on the reaction rate of all the catalytic improvements mentioned reaches several orders of magnitude, as compared with the initial catalyst

At 1 atm N_2, the yield of N_2H_4 per reductant – sodium amalgam – reaches several percent. At 50 atm N_2, the yield rises to 30 % and the turnover number approaches 104.

What is the mechanism of co-catalytic action, first of the phospholipid ?

We now know that phosphatidylcholine forms a film on the amalgam surface, incorporating the catalytic complexes and bringing them closer to the electron donor.

The specificity of PC is at least partly due to the positive charge on the quaternary nitrogen, which helps to keep the film closer to the negatively charged surface, and also to the chemical nature of the negative portion of the PC molecule which binds the catalytic complexes. Apparently this portion is suitable for complex formation with the catalyst, since, as already mentioned, even comparatively minor changes in the composition of the phospholipid destroy the catalytic activity.

The role of phosphines is somewhat less clear. According to their usual functions, they probably form complexes with molybdenum, thus stabilizing its low-valency state. However, it is unlikely that a molybdenum atom bound to a phosphine is active toward reduction of N_2. The phosphines exhibit only quantitative effects; even the N_2H_4:NH_3 ratio in the presence of phosphines remains the same as in their absence.

Thus , the nature of the catalytic complex activity in N_2 reduction very likely does not chenge under the action of phosphines. Therefore, it may be suggested that the reduction of N_2 proceeds via a polynuclear complex, which involves molibdenum ions playing the role of electron transfer agents helping to bring the electrons from the amalgam surface to the coordinated N_2 molecule. It is these molybdenum ions that coordinate the phosphine molecule, facilitating the reduction of Mo, which is in fact the step of the electron transfer from the amalgam (figure 2). There is further evidence for the polynuclear structure of the catalytic complex. The effect of Mg^{2+} ions may be explained by assuming that they form some kind of bridge to stabilize molxbdenum ions in the cluster.

Precipitation of a part of the Mo during acidification-alkalination indicates the presence of colloidal particles containing Mo atoms. Among these polynuclear particles, the complexes may be present which are responsible for the formation of ammonia, since after their removal the relative yield of NH_3 goes down.

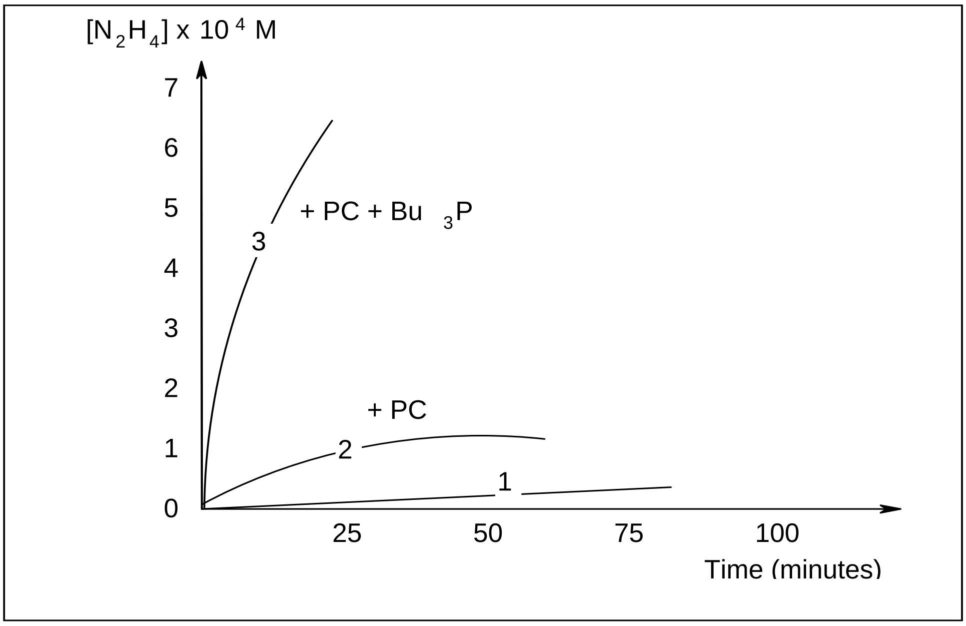

Figure 1. The effect of phosphatidylcholine and phosphines on the rate of N_2 reduction by Na(Hg) in the presence of Mo(III) complexes

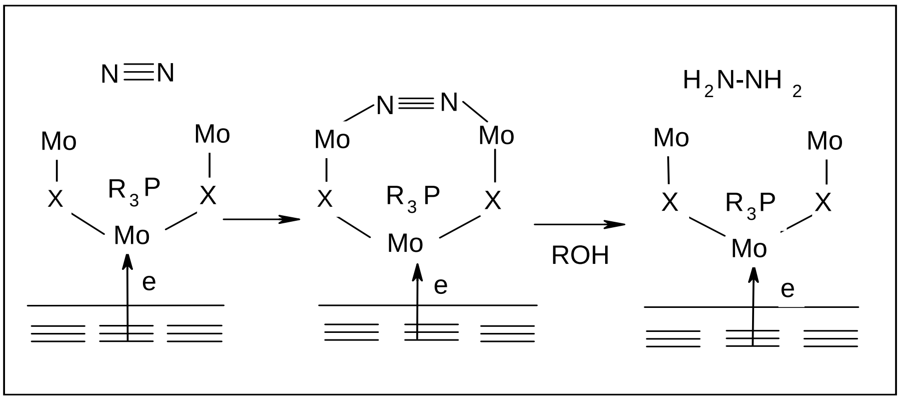

Figure 2. Scheme of the mechanism of dinitrogen reduction by Na(Hg) in the presence of Mo(III)

4. Conclusions

More experimental evidence obtained for enzymatic dinitrogen fixation, as well as for chemical N_2 reductions in solution, support the new concepts developed.

Working along these concepts, new catalytic systems were discovered - like catalytic system with Na(Hg) amalgam - including one with which the specific N_2 reduction rate is not inferior to the enzymatic reduction.

The exact nature of the active catalytic remains unclear, however, and further investigations are needed to draw more detailed conclusions about the system, which is at present the most active chemical system for the catalytic reduction of N_2.

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