

# About the Role of $Fe_n$ Type Clusters in the Reduction of Dinitrogen

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**Abstract:** The biological and abiological reduction of dinitrogen supposes the existence of some  $MoFe_3S_4$  type clusters linked by cysteinic S in the protein inside,  $[Fe_3O_4(H_2O)_{12}]^{2+ / 3+}$  respectively, in an iron hydroxide (model) or of some complex dinitrogen combination beside a powerful reducer. The dinitrogen reduction takes place in stages.

**Keywords:** nitrogen fixation

## 1. Introduction

Although for a long time various objections had been raised against dinitrogen coordination during the last decades a new class of coordinative compounds of transitional metals with dinitrogen has been developed and diversified, many of them being particularly stable.

This new class coordinative compounds has a particular importance both from a theoretical and practical point of view as it could contribute to elucidating the mechanism of biological conversion of dinitrogen into ammonia and at the same time it could open new elaboration ways of some unconventional ways of ammonia synthesis under mild conditions of temperature and pressure.

The interest manifested by the specialists towards this reduction ways of dinitrogen fixation has stimulated various researches and the publication of a large volume of specialized papers and monographies [1-6].

The area of the preoccupation connected to the formation of dinitrogen compounds and dinitrogen reactions, under mild conditions supposes the existence of two methods, and namely :

The biological method of genetic modification which should enable the genes passing from the nitrogen fixation bacteria to other organisms [7-10,14,15];

Catalytic system which should enable the dinitrogen fixation, as far as possible, under usual condition of temperature and pressure [11-13].

### Biological fixation of dinitrogen

On the basis of some recent researches of biological fixation of atmospheric nitrogen and its conversion into ammonia, one has established that at the basis of the process there is a complex enzymatic system, known under the denomination of nitrogenase [16-18].

It is in the presence of this catalytic system that the breaking of the triple link  $N \equiv N$  and  $NH_3$  forming by hydrogen atoms linking, become possible. Structurally, the nitrogenase is a complex enzyme with molybdenum and iron content, consisting actually of two proteins:

- **Molybdoferredoxine**, a bigger protein, molecular weight 180,000 – 300,000, in the structure of which there are 1-3 molybdenum atoms, 17-36 iron atoms and 14-28 free sulphur atoms, out of which 50% are engaged in the forming of some  $MoFe_3S_4$  clusters. Of all the elements it is only the vanadium which can replace the molybdenum so that the protein activity be not lost whereas the presence of some elements such as Cd, Cu, Zn, Ni inhibits the process;

- **Azoferrredoxine**, a smaller protein, molecular weight 40,000 – 60,000, in the structure of which there are 2-4 iron atoms and 1-4 sulphur atoms which make up one  $Fe_4S_4$  cluster.

The mechanism of biological fixation of dinitrogen has been elaborated by Schrauzer, Shilov and others. At present, one has accredited the idea that the dinitrogen reduction takes place on molybdoferredoxine, the process being conditioned by the existence in the system of the monomagnesian salt of ATP, on the basis of a mechanism which includes diazene and hydrazine as intermediaries.

Actually, the dinitrogen reduction takes place in stages, through some species of the type  $N_2H_x$  ( $x = 1-4$ ). In this process, the azoferrredoxine has the role of electron conveyor between the reducing agent and the molybdoferredoxine which stocks them in the clusters of the type  $Fe_4S_4$ . Here from they pass through the active centre to the formed ammonia is replaced by the dinitrogen and the process starts again.

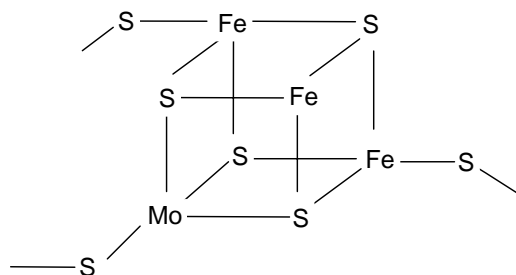


Figure 1. Structure of molibdoferredoxine

### Chemical models for the reductive fixation of dinitrogen

The first studies concerning the reduction fixation of dinitrogen have been carried out in aprotic media by means of the coordinative compounds of the transitional metals and they were due to Volpin, who developed a rich activity in the field. Mention should also be made of the papers of Shilov, Tamelen, Yamamoto and others [18-28].

The characteristic feature of these reactions is that they are produced in systems formed of a transitional metal complex unsaturated from a coordinative point of view, capable of complexing and activating the dinitrogen and a reducing agent which is strong enough to function as an electron source as compared to the activated dinitrogen. The reactions take place in organic solvents under normal conditions of temperature and pressure (Table 1).

No matter used system and the nature of the reducing agent, all the dinitrogen fixation reactions have at their basis a common mechanism with that presented in figure 3, and which is developed in more stages.

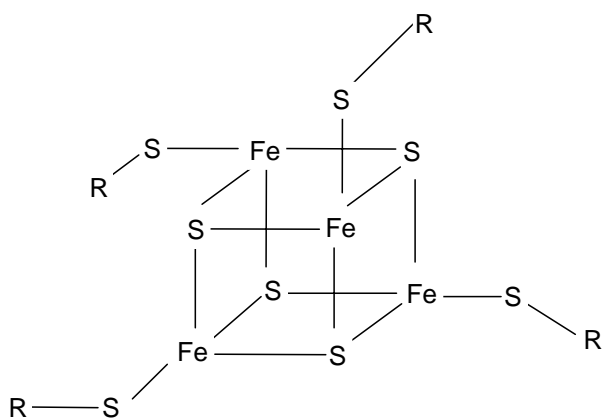


Figure 2. Structure of azoferredoxine

TABLE 1. Systems capable of the reductive fixation of dinitrogen in aprotic media and the yields in ammonia

Crt.no.	System	Reactivities ratio	Solvent	Yield in NH <sub>3</sub> (moles NH <sub>3</sub> /g metal)
1.	$[(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2] + \text{EtMgBr}$	1 : 9	Ether	0.67
2.	$[(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2] + \text{Li}$	Li excess	THF	0.75
3.	$[(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2] + \text{Li/Hg}$	1 : 10	THF	0.77
4.	$[(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2] + \text{C}_{10}\text{H}_8\text{Li}$	1 : 6	THF	0.96
5.	$[(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2] + \text{C}_{10}\text{H}_8\text{Na}$	1 : 4.3	THF	0.90

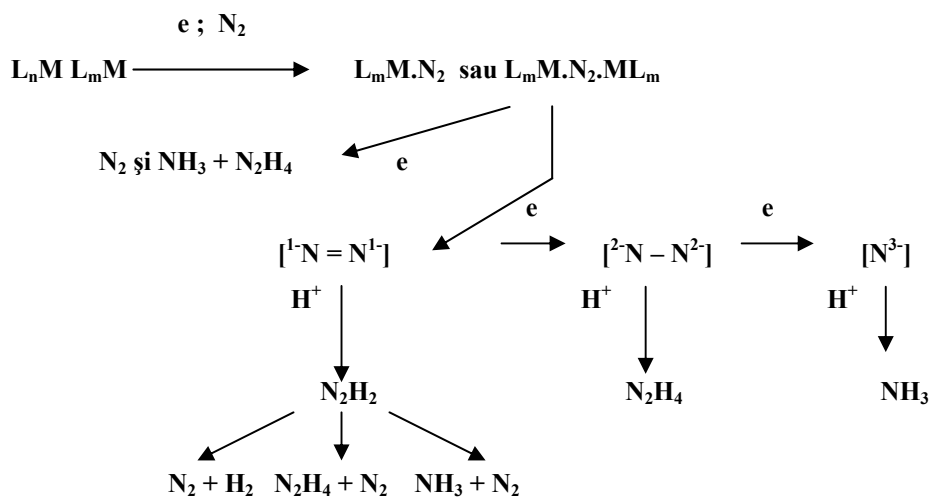


Figure 3. Mechanism of reductive fixation reactions of dinitrogen in aprotic media

Comparing the chemical systems capable of the dinitrogen fixation in aprotic media with the enzymatic ones, Volpin and Shur [25, 26] have ascertained that they have the following common features :

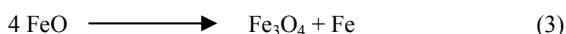
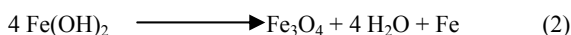
➤ The transitional metal represented by **molybdenum**

**or vanadium** in the enzymatic reactions and by **titanium, vanadium, molybdenum** or others in the chemical ones, is compared in the active centre;

➤ In both of cases the **dinitrogen is reduced to ammonia**.

## 2. Experimental

The  $\text{Fe}(\text{OH})_2$  activity in the reductive fixation of dinitrogen is controversial. The system is, probably, the simplest of all the chemical systems capable of dinitrogen reduction. Schrauzer [19] has published an article on the systems which release hydrogen of the  $\text{Fe}(\text{OH})_2$  aqueous suspension type and which react with many elementary Fe forming  $\text{Fe}_3\text{O}_4$  respectively, by  $\text{Fe}(\text{OH})_2$  disproportioning :



For  $\text{N}_2\text{H}_4$  and  $\text{NH}_3$  forming, various mechanisms have been proposed. The elementary iron generated by  $\text{Fe}(\text{OH})_2$  disproportioning, is dispersed in such a way, as to be able to react with more reducing substrates. The dihydrogen releasing is inhibited by  $\text{C}_2\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ . The inhibition observed for the dihydrogen releasing from  $\text{Fe}(\text{OH})_2$  by unsaturated hydrocarbons is attributed to the interaction with elementary iron, generated in the reaction conditions.

The  $\text{C}_2\text{H}_2$  reduction mechanism, by  $\text{Fe}_n$  type clusters generated from  $\text{Fe}(\text{OH})_2$  is presented in figure 4.

The fact that dinitrogen inhibits, in a similar way, the dihydrogen releasing in iron suspension, suggests that this substrate is also reduced. This fact has been confirmed by experiences with  $\text{N}_2$  enriched in  $^{30}\text{N}_2$  as substrate and by direct colorimetric determination of  $\text{N}_2\text{H}_4$  and  $\text{NH}_3$ . The reduction mechanism, of dinitrogen by the  $\text{Fe}_n$  type clusters generated from  $\text{Fe}(\text{OH})_2$  are presented in figure 5.

## 3. Results and discussion

A number of experimental data concerning dinitrogen reduction in systems with  $\text{Fe}(\text{OH})_2$  are given in table 2 and figure 6.

By similitude with a system in the specialized literature we could draw, for the possible structure of the precipitates and co-precipitates the following conclusions. It is very likely that a  $\text{Fe}^{2+}$  and  $\text{OH}^-$  ions organization respectively, exists in the form of cuboidal clusters in order that the stereochemical and energetical conditions for the dinitrogen reduction be created. Identically as in the effects have been ascertained, the same supposition may be made for the Fe/O clusters (figure 7).

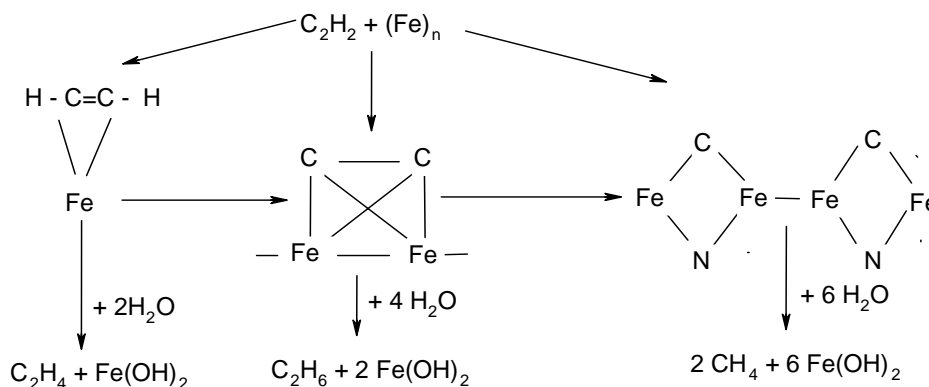


Figure 4. Mechanism of  $\text{C}_2\text{H}_2$  reduction by  $\text{Fe}_n$  clusters

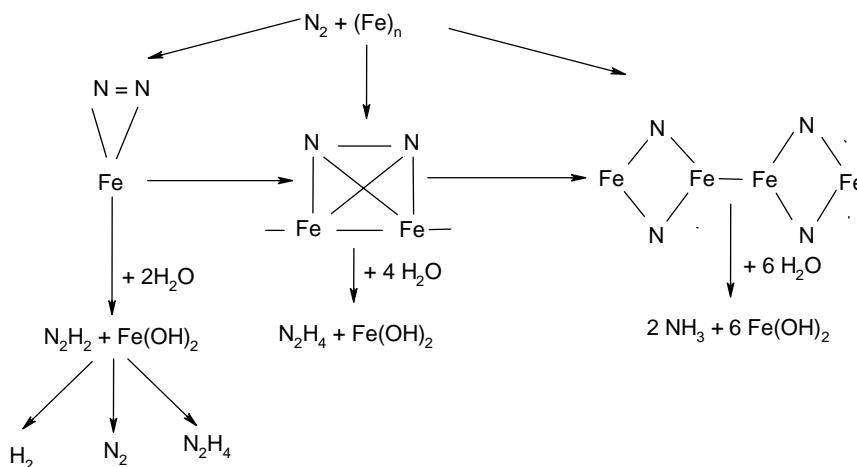
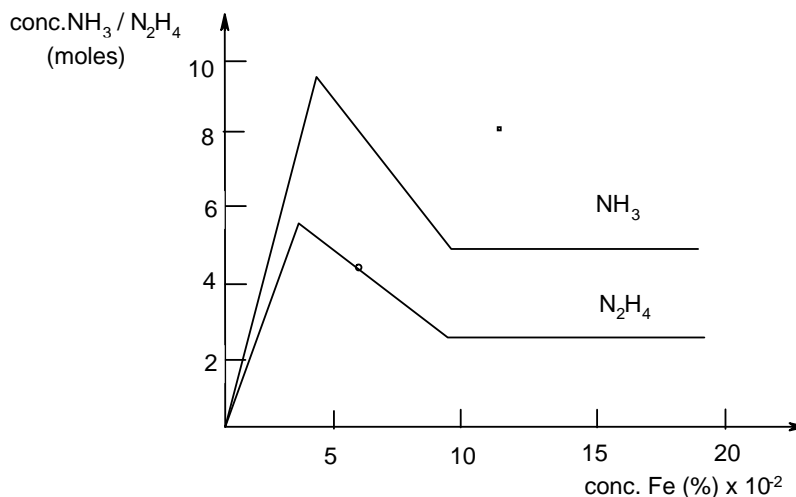
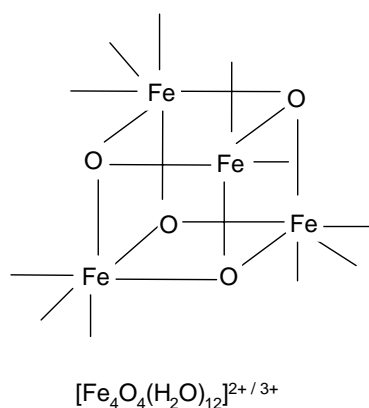


Figure 5. Reduction mechanism of dinitrogen by  $\text{Fe}_n$  type clusters

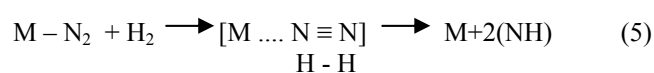
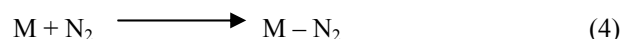
TABLE 2. Results concerning dinitrogen reduction in systems with  $Fe(OH)_2$  (room temperature and atmospheric pressure)

Crt. no.	pH value	Reaction duration (min.)	Concentration Fe x 10 <sup>-2</sup> (%)	Solution colour	NH <sub>3</sub> moles/L x 10 <sup>-5</sup>	N <sub>2</sub> H <sub>4</sub> moles/L x 10 <sup>-5</sup>
1.	12.5	20	1	grey	3.97	3.2
2.	13.0	20	2	grey	7.10	4.4
3.	13.0	20	2.2	grey	7.90	4.8
4.	13.2	20	4	grey	9.53	5.8
5.	13.2	20	10	grey	5.55	2.7
6.	12.8	20	20	grey	5.56	2.8

Figure 6. NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> yield dependence on Fe concentration in the reaction mixture (t = 20 °C, p = 1 atm.)Figure 7. Proposed model for the clusters of the type  $[Fe_4O_4(H_2O)_{12}]^{2+/3+}$ 

#### 4. Conclusions

1. The effected studies for elucidating the mechanism which is to be found at the basis of the biological and abiological conversion of dinitrogen have led to the conclusion that two stages seem to be important in this process, and namely: absorption and activation of dinitrogen and reduction of activated dinitrogen. For the systems of complex combination type, the two stages may be represented by the N<sub>2</sub> molecule coordination and subsequent splitting of the N ≡ N molecule through the molecular hydrogen :



2. The possible mechanisms of dinitrogen reduction by the Fe<sub>n</sub> type clusters generated from Fe(OH)<sub>2</sub> are in figure 5 and they, as the experimental data existent at present, indicate an insufficient activity of N<sub>2</sub> molecule which still remains in ert enough to Fe.

## REFERENCES

1. Allen, A.D.; *Chem. Comm.*, **1965**, 621.
2. Cramer, S.P.; *J. Am. Chem. Soc.*; **1978**, 100, 3398.
3. Hardy, R.W.F.; Knight, E.; *Bacterial Proc.*; **1967**, 112.
4. Hardy, R.W.F.(Ed.); *Dinitrogen Fixation*, II, Wiley Interscience, New York, **1978**.
5. Hardy, R.W.F.; Burns, R.C.; *Advances in Chemistry Series (Bioinorganic Chemistry)*, **1971**, 100, 219.
6. Henderson, R.A.; *Adv. Inorg. Chem. Radiochem.*; **1983**, 27, 197.
7. Hera, C.R.; Probleme de agrofitehnie teoretică și practică, **1980**, 1, 21.
8. Hughes, M.N.; *The Inorganic Chemistry of Biological Processes*, John Wiley and Sons, London, **1974**.
9. Janet, S.I.; *The Biology of Nitrogen Fixing Organisms*, McGraw-Hill, London, **1979**.
10. Mishutin, E.N.; *Biological Fixation of Atmospheric Nitrogen*, McMillan, London, **1971**.
11. Newton, W.E.(Ed.); *Recent developments in Nitrogen Fixation*, Academic Press, London, **1977**.
12. Newton, W.E.(Ed.); *Proceedings of 1<sup>st</sup> International Symposium on Nitrogen Fixation*, Washington State University Press, **1976**.
13. Parshall, G.W.; *J. Am. Chem. Soc.*; **1967**, 90, 1822.
14. Popescu, A.; Probleme de genetică teoretică și aplicată, XII, **1980**, 1, 81.
15. Popescu, A.; Probleme de agrofitehnie teoretică și aplicată, II; **1980**, 1, 1.
16. Postage, J.R.(Ed.); *The Chemistry and Biochemistry of Nitrogen Fixation*, Plenum Press, London, **1971**.
17. Rao, Subba N.S.; *Recent Advances in Biological Nitrogen Fixation*, Edward Arnold Ltd.; London, **1980**.
18. Schrauzer, G.N.; *Advances in Chemistry Series (bioinorganic Chemistry)*, **1971**, 100, 1.
19. Schrauzer, G.N.; *Angew. Chem.*, **1975**, 87, 579.
20. Shilov, A.E.; *Kinet. Katal.*, **1969**, 10, 1402.
21. Shilov, A.E.; *Uspekhi. Khim.*; **1974**, 43, 863.
22. Străjescu, M.; Gabruș, R.; *Rev. Chim.*; **1983**, 34(4), 264.
23. Thorneley, R.N.F.; *Nature (London)*, **1978**, 272, 557.
24. Van Tamelen, E.E.; *Acc. Chem. Res.*; **1970**, 3, 361.
25. Gabruș Iuliu Radu, „Elemente de Chimie Bioanorganica”, Ed. Dacia, Cluj Napoca, **2003**.
26. Volpin, M.E.; Shur, V.B.; *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **1964**, 1728.
27. Walker, C.C.; Yates, M.G.; *Biochemie*, **1978**, 60, 225.
28. Yamamoto, A.; Ikeda, S.; *Chem. comm.*, **1969**, 841.
29. Henderson, R.A.; *Adv. Inorg. Chem. Radiochem.*; **1983**, 27, 197.