

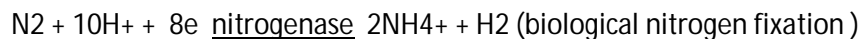
#### 4. NITROGEN FIXATION

The importance of the inorganic-biological nitrogen cycle for life on earth can hardly be overestimated. The importance of nitrogen compounds as fertilizers in agriculture may be taken from the fact that ammonia continues to be one of the leading products of the chemical industry, other large-scale chemicals such as ammonium nitrate, urea, and nitric acid are follow-up products of the industrial "fixation" of nitrogen as obtained from air.

Most of the biological systems which participate in the global nitrogen cycle contain metal-requiring enzymes. Three main processes can be distinguished in the nitrogen cycle: nitrogen fixation, nitrification and denitrification.



Fe catalyst



from biomass

Nitrogenase has been found to contain two components, a Mo-Fe-containing protein and an Fe-containing protein. The Mo-Fe protein contains two Mo and about 30 atoms each of Fe and sulfide (molar mass ~ 220,000). The Fe protein contains two identical subunits, each containing an Fe<sub>4</sub>S<sub>4</sub> cluster (molar mass ~ 60,000).

Presumably, N<sub>2</sub> is complexed by the Mo and the Fe protein, bringing about reduction through electron transfers. Adenosine triphosphate (ATP) is essential for nitrogenase activity.

The discovery of stable complexes of N<sub>2</sub> led to intense study of model compounds and a possible new nitrogen fixation process. Ammonia has been obtained from metal complexes of N<sub>2</sub>.

##### 4.1 Non-biological N<sub>2</sub> fixation

(i) Dinitrogen as a ligand

Consider the molecular orbitals of  $N_2$ .

- N<sub>2</sub> has a triple bond and hence the high dissociation energy of 940 kJ/mol. It also has a symmetrical e-distribution and absence of polarity.
- The lowest vacant molecular orbitals are the two degenerate antibonding p orbitals at -676 kJ, which are too high in energy to be attacked by any but the strongest reducing agents, such as the more electropositive metals. This explains the rapid nitriding of the Li wire (for CO, the two 2p<sup>\*</sup> orbitals are at -772 kJ/mol, and therefore low in energy, hence CO is a better p acceptor than N<sub>2</sub>).
- The highest energy orbital containing electrons (2p<sub>s</sub>) at -1505 kJ is too low in energy to give up electrons to any stable electron acceptor, such as molecular oxygen at room temperature (for CO it is at -1354 kJ/mole, therefore CO is a better s donor). Therefore, N<sub>2</sub> is a weaker s donor and a weaker acceptor of electrons than CO).
- N<sub>2</sub> is stable because of the high energy gap between the LUMO and HOMO, and hence the inertness of molecular dinitrogen (N<sub>2</sub>).

#### (ii) Important parameters in the stability of N<sub>2</sub> complexes

1. Spin-pairing, high covalent character is a prerequisite.
2. the nature of the transition metal (the second and third period transition metals have better covalent bonding capabilities).
3. The significance of the ligands (i.e. they must not be too strongly p-accepting like CO, s donation results in strong M-N bonds). Strong p acceptors will contract the d-electron cloud and decrease p backbonding. Stereochemistry also plays a role (i.e. whether the ligands are bulky or not). Also, the trans-effect and its influence play a significant role.
4. Oxidation state of the metal ion is important, a low ox-state, reducing medium is needed for effective p-backdonation into the N<sub>2</sub> moiety.

#### (iii) Preparation of dinitrogen complexes

Directly from dinitrogen:

Involves the reaction of N<sub>2</sub> with a pre-formed and isolated complex by replacement of labile neutral

or anionic ligands by  $N_2$  (or by a single step reaction of a suitable complex with a reductant under  $N_2$ ).

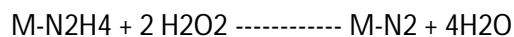
- need a strong reducing agent like Mg to expand the d-cloud of the Mo (in effect it reduces Mo(III) to Mo(0)) and a low oxidation state is obtained which is a prerequisite for dinitrogen fixation.

- Mo is a 4d metal and therefore also has good covalent bonding capabilities.
- thf is a cyclic ether and does not bond strongly to the metal and is readily replaced by dppe which is a good coligand since it is a mild p-acceptor and a chelate, and hence will not compete with N<sub>2</sub>.
- Cl is electronegative (high EN) and will contract the d-cloud of the metal and is a p-acceptor, and hence will compete with dinitrogen and must therefore be replaced.

**Indirect method:**

Dinitrogen can be generated by reaction at a coordinating N moiety (e.g. oxidation of bonded hydrazine)

- M(I) is a thermodynamically and kinetically stable low spin d<sup>6</sup> system (M=Mn)
- Even the strong p-acceptor CO is a coligand since the Cp-pushes a lot of e-density into the d-cloud of the metal (Cp is probably trans to the N<sub>2</sub> so that p-backbonding to N<sub>2</sub> can occur effectively even in the presence of CO).
- H<sub>2</sub>O<sub>2</sub> is a strong oxidising agent, it oxidises bonded hydrazine to dinitrogen.



Tutorial 4

(a) Comment on the inertness of N<sub>2</sub>.

(b) Mention a few metal-containing inorganic systems (both biological and non-biological) that can bind the unreactive dinitrogen. Discuss the coordination chemistry involved in these systems.