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Prospects for new nitrogen fixation processes

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Chemists have long tried to emulate the apparently easy fixation of nitrogen which takes place in biological systems, and during the past 15 years they have uncovered a number of new and unexpected reactions. Some of these might form the basis of new processes for nitrogen fixation, but at this stage of development none appears likely to compete with existing processes. Nevertheless, the new reactions indicate some exciting possibilities and some may demonstrate the chemistry which lies at the basis of nitrogen fixation by bacteria.

Introduction

Recent developments in the chemistry of molecular nitrogen (dinitrogen), which might have application in new nitrogen fixation processes, concern the reactions of the gas at room temperatures and pressures. These are of three types. The first, usually known as the 'nitriding reaction', is old and well established but has received a new extension into the organometallic field. In this first type of reaction dinitrogen is treated with very strong reducing agents to produce metallic nitrides or nitrido-complexes which may be hydrolysed to ammonia or by reaction with certain organic substances converted into organo-nitrogen compounds. The second is a completely new reaction. It involves the formation of coordination compounds which contain dinitrogen as a ligand bonded to a transition metal. In some of these compounds the ligating dinitrogen is sufficiently reactive to be protonated by acids to yield hydrazine or ammonia; they also yield organic nitrogen compounds by reaction with alkyl halides (Chatt 1975). The third type involves the reaction of molecular nitrogen with transition metal salts in aqueous solutions to produce hydrazine or ammonia directly. A few reactions of this type are reasonably well established, but many have been reported to give ammonia in such low yields that there is some doubt about their authenticity.

Nitriding reactions

Molecular nitrogen or, as it is now named, 'dinitrogen', owes its chemical inertness to the large energy separation between its filled molecular orbital of highest energy, the $3\sigma_g$-orbital at -15.6 e.v. and its vacant orbitals of lowest energy the $1\pi_g$ at about -7 e.v. The strongest oxidizing agent, molecular fluorine, is not sufficiently reactive to remove electrons from the $3\sigma_g$-orbitals, nor are the strongest reducing agents, the alkali metals, capable of putting them into its $1\pi_g$-orbital. In fact only the very electropositive metals which form very stable nitrides, such as lithium, the alkaline earths, and some early transition metals react with dinitrogen at, or moderately above, room temperature. Magnesium reacts similarly at a red heat. In all such cases metal nitrides are produced and these are readily hydrolysed to ammonia. But such reactions can never form the basis of a new process for ammonia. The metals concerned are highly reactive energy intensive substances and much too expensive raw materials for ammonia production.

Ten to 15 years ago some titanium compounds, particularly bis(cyclopentadienyl)titanium chlorides, were shown to take up dinitrogen to form nitrido-complexes when they were reduced in ether or other solvent with Grignard reagents or alkali or other very electropositive metal at room temperature (Vol'pin & Shur 1966; van Tamelen, Boche & Greeley 1968). These reactions produce soluble nitride complexes which by hydrolysis produce ammonia, or by reaction with some organic compounds; e.g. ketones, followed by hydrolysis, produce amines (see, for example, van Tamelen & Rudler 1970). Provided the hydrolysis was carried out using a quantitative amount of the protic reagent, for example an alcohol, the hydrolysis product could be reduced again by sodium or Grignard reagents under dinitrogen to produce more nitride so rendering the process cyclic in a batchwise fashion. The processes needed to make materials such as alkali metals, magnesium or aluminium, are so energy intensive that methods of ammonia production depending on them would not be viable; they do not appear to have any relevance to the chemistry of the nitrogenase reaction, and will not be discussed further.

PROTONATION OF LIGATING DINITROGEN

The more exciting and novel chemistry comes from the study of dinitrogen complexes of transition metals. Since Bortels's (1930) discovery that traces of molybdenum are essential for nitrogen fixation by bacteria, chemists have attempted to obtain complex compounds of dinitrogen by its reaction with molybdenum or other transition metal compounds. They had singularly little success until the past decade. The first well defined dinitrogen complex was obtained indirectly by Allen & Senoff (1965) by the reaction of hydrazine with ruthenium trichloride in aqueous solution (reaction 1)

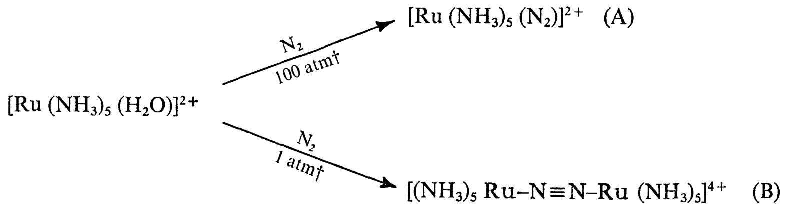
$$RuCl_3 + N_2H_4 \longrightarrow [Ru(NH_3)_5(N_2)]Cl_2 + N_2. \tag{1}$$

Since this discovery a great number of well defined dinitrogen complexes have been obtained from transition metals of all but the vanadium group from the titanium to the nickel groups in the periodic table (see Sellmann 1974). Usually they are produced in aprotic media, such as ether or tetrahydrofuran (thf), by strong reduction of suitable complexes, usually halido (tertiary phosphine) complexes, of the appropriate transition metal and dinitrogen at ordinary temperatures and pressures. Commonly used reducing agents are aluminium trialkyls, magnesium metal, sodium amalgam, or sodium tetrahydroborate. On occasion dinitrogen complexes have been produced in protic media (ethanol) by sodium tetrahydroborate reduction of transition metal complexes in the presence of dinitrogen, e.g. reaction (2) (Sacco & Rossi 1967)

$$[CoCl_2(PPh_3)_2] + PPh_3 + N_2 \xrightarrow[NaBH_4]{EtOH} [CoH(N_2)(PPh_3)_3]. \tag{2}$$

This reaction involves the intermediate formation of the hydride complex $[CoH_3(PPh_3)_3]$ from which dihydrogen is displaced by dinitrogen.

There is only one example of a well defined dinitrogen complex being obtained from dinitrogen in aqueous solution at room temperature (reaction 3) (Harrison, Weissberger & Taube 1968)



(3)

† 1 atm = 101 325 Pa.

This reaction is of particular interest because it shows that when dinitrogen is presented to a suitable transition metal site it is sufficiently reactive to replace water from the coordination shell of the metal, even in aqueous solution. Similar reactions are known in which dinitrogen replaces dihydrogen or ammonia from a metal site. Reaction 3 is also interesting in that it gives illustrative examples of the two ways in which dinitrogen can attach itself to transition metals, either as a terminal ligand as in (A) or as a bridging ligand as in (B).

In the terminal dinitrogen complexes the dinitrogen molecule is bonded by one end to the metal atom, analogous to the bonding of ligating carbon monoxide in carbonyl complexes. In general the dinitrogen is not activated sufficiently for reduction to ammonia by such combination with the metal. This is also true of bridging dinitrogen in its complexes. However, a very few exceptions have been discovered, and from the view of nitrogen fixation they are particularly interesting.

The exceptional terminal dinitrogen complexes are those of molybdenum and tungsten. They have the general formula $[M(N_2)_2(PR_3)_4]$, where $M = Mo$ or W and $PR_3 = PMe_2Ph$ or $PMePh_2$, and contain the metal in the zero oxidation state. The metal has six electrons more than in the commonly occurring hexavalent state. On treatment with oxo-acid at room temperature, these exceptional complex compounds lose a molecule of dinitrogen and the remaining one is converted into ammonia in yields of up to 90 % (reaction 4) (Chatt, Pearman & Richards 1975)

$$[M(N_2)_2(PMe_2Ph)_4] \xrightarrow[\text{MeOH}]{H_2SO_4} N_2 + 2NH_3 + M^{VI} \text{ products.} \tag{4}$$

The complex compounds are themselves made from gaseous nitrogen by reactions of the general type given in reaction (5) (thf = tetrahydrofuran)

$$[WCl_4(PMePh_2)_2] + 2PMePh_2 + 2N_2 \xrightarrow[\text{thf}]{\text{Mg}} [W(N_2)_2(PMePh_2)_4]. \tag{5}$$

The formation of the dinitrogen complexes of molybdenum or tungsten involves the use of expensive reducing agents. The molybdenum or tungsten complex is destroyed by the acid and cyclic or catalytic processes for converting dinitrogen into ammonia cannot be evolved directly from reaction (4). The significance of reaction (4) is the demonstration that in a protic medium, in this case methanol/sulphuric acid, the dinitrogen molecule is more easily reduced than H^+. Electrons pass from the metal into the dinitrogen molecule which, by picking up hydrogen ions from the solution, undergoes a splitting of the strong $N \equiv N$ triple bond and produces two molecules of ammonia. It seems very probable that reaction (3) is a model for the uptake of dinitrogen by the enzyme nitrogenase, and reaction (4) for the final chemical stage in its reduction to ammonia on the enzyme. The six electrons for the nitrogenase reaction will not be stored in one molybdenum atom, as in the above tertiary phosphine complexes, but supplied as needed via the molybdenum atom from the electron storage system of iron-sulphur clusters (Fe_4S_4) which are present in nitrogenase.

Reaction (4) shows that it is possible for dinitrogen, modified by attachment to an element such as molybdenum or tungsten as in the above tertiary phosphine complexes, to be reduced to ammonia in high yield in a protic medium. It opens up the possibility of preparing an electrode with complex metal sites tailored to pick up dinitrogen and feed electrons into it in a protic electrolyte (e.g. water) to produce ammonia. If ammonia were produced in this manner it would require, at 100 % efficiency, slightly less energy than is needed to produce dihydrogen from water. A manufacturing process based on that reaction could never be viable in competition with the present day Haber process as a method of centralized fertilizer manufacture. Nevertheless, if a highly efficient electrode for the reduction of dinitrogen at atmospheric pressure could be devised, it would require a much cheaper plant and open up the possibility of reducing atmospheric nitrogen in irrigation channels using some form of low grade or intermittent energy, such as wind, tide or sun, to provide the current to the electrode. This did not appear possible only 5 years ago. Now the chemistry of dinitrogen shows that it is possible but it is still far from being realized.

The only bridging dinitrogen complexes known to react with acids to give almost quantitative yields of nitrogen hydrides are bridged titanium and zirconium complexes. The titanium complexes have been known for some years but their structures and reactions are not well defined because the compounds themselves are formed only at low temperatures and decompose below room temperature. They are produced by the reduction of $[\mathrm{Ti(cp)_2Cl}_n]$ ($n = 1$ or 2; cp = π-cyclopentadienyl) by Grignard reagents, RMgX, at −80 °C in ether, and have been assigned the formula $[\mathrm{(cp)_2Ti(R){-}N{\equiv}N{-}Ti(R)(cp)_2}]$. On warming their solutions to −60 °C, dinitrogen is released, but by treatment with more Grignard reagent and then with hydrogen chloride, both at that low temperature, hydrazine is produced 'almost quantitatively' (Shilov, Shilova, Kvashina & Vorontsova 1971; Shilov 1974).

Recently a well defined zirconium complex, possibly an analogue of the titanium compound, has been prepared from bis(pentamethylcyclopentadienyl)zirconium dichloride and it is stable at room temperature. X-ray crystallography has shown it to have the structure $[\mathrm{(Me_5cp)_2Zr(N_2){-}N{\equiv}N{-}Zr(N_2)(Me_5cp)_2}]$ ($\mathrm{Me_5cp}$ = π-pentamethylcyclopentadienyl). On treatment with acid at −60 °C in solvents such as tetrahydrofuran or toluene it produces hydrazine in about 80 % yield according to reaction (6) (Manriquez, Sanner, Marsh & Bercaw 1976)

$$[\mathrm{(Me_5cp)_2Zr(N_2){-}N{\equiv}N{-}Zr(N_2)(Me_5cp)_2}] + 5\mathrm{HCl} \longrightarrow 2[\mathrm{ZrCl_2(Me_5cp)_2}] + 2\mathrm{N_2} + \mathrm{N_2H_5Cl}. \tag{6}$$

During this reaction each zirconium atom delivers up two electrons to the dinitrogen molecule which appears as hydrazine. It would thus appear that the bridging dinitrogen molecule is the one which is reduced. However, labelling experiments using $^{15}\mathrm{N_2}$ for the two terminal dinitrogen ligands indicate quite definitely that only half of the hydrazine comes from the bridging dinitrogen molecule and the other half from the terminal dinitrogen molecules. It is evident, therefore, that the reaction is more complex than it first appears. However, again this reaction shows that electrons can be passed from a metal atom into a dinitrogen molecule in the presence of hydrogen ions to give a nitrogen hydride in very good yield.

It seems unlikely that in the nitrogenase system the molybdenum atom changes oxidation state from six to zero and back to six again as dinitrogen is picked up and reduced. Much more probably it picks up and reduces the dinitrogen to ammonia in some intermediate oxidation state. If a useful electrolytic process for the production of ammonia on-site in irrigation channels is to be evolved, we must make use of the reduction of dinitrogen under similar chemical conditions to those which one supposes to exist in nitrogenase. The production of ammonia and of hydrazine from ligating dinitrogen shows nothing more than the feasibility of such processes and the prospect that they could be highly efficient. The known reactions are not likely by any evolution to become such processes.

REDUCTION OF DINITROGEN IN AQUEOUS SOLUTION

There have been many attempts to obtain ammonia by reactions of simple molybdenum and other transition metal compounds with dinitrogen in aqueous solutions in the presence of reducing agents, but the only claim to near quantitative yields are from Shilov and co-workers (see Shilov 1974). High yields of hydrazine have been obtained by the contact of nitrogen gas at 10 atm pressure with the mixture of precipitated hydroxides at pH 10 obtained by the addition of caustic potash to vanadium(II) chloride and magnesium chloride in water. Even at atmospheric pressure yields of 75 % based on the oxidation of vanadium(II) to vanadium(III) have been claimed. By the addition of pyrocatechol and such substances, Shilov and co-workers have been able to obtain homogeneous solutions which similarly react with dinitrogen to give hydrazine and/or ammonia in quite good yield (Shilov 1974). However, there appears to be no way to reduce the vanadium(III) back to vanadium(II) at the high pH necessary for the reduction to ammonia. Thus the reaction cannot be rendered cyclic except by alternate addition of acid and alkali at the stages of the reduction of vanadium(III) and reduction of dinitrogen respectively.

Many other claims of the reduction of dinitrogen to ammonia in aqueous solutions have been made, but the yields in relation to the quantity of reducing agent consumed are so small as to be of no interest to us here.

The Shilov vanadium system is interesting because it indicates that dinitrogen can be activated by an aquated metal ion, vanadium(II), in an open shell electronic state. All of the complex compounds discussed in the last section have the metals in a closed shell state, but it is almost certain that the molybdenum in nitrogenase must be in an open shell state.

Generally, I conclude that low pressure chemical processes for the production of ammonia as a fertilizer are still far from being realized. Work over the last decade has shown that they are possible and might even become viable when hydrogen must be produced from water. Nevertheless, until oil or natural gas become exorbitantly expensive, it seems unlikely that anything will be discovered which will compete with the Haber process. However, the Haber process can only be considered as an interim solution to the fertilizer problem and can produce fertilizer for cheap food only so long as cheap energy is available. In my opinion, it is still necessary to explore thoroughly the chemistry of dinitrogen, searching for a source of nitrogenous fertilizer which will not consume vast amounts of high grade fuel for its manufacture. Ultimately nitrogenous fertilizer must be obtained from atmospheric nitrogen, water and energy, and a process which uses low grade or intermittent energy, whether the process be biological or chemical, will become necessary.

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