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Fixation of Nitrogen in Solution in the Presence of Transition Metal Complexes

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The review presents the results of studies in the last decade on the reduction of molecular nitrogen in aprotic and protic media. The products, intermediate complexes, and mechanisms of these reactions are considered. The relation between the mechanisms of the N_2 reduction reactions discovered recently and the mechanism of biological nitrogen fixation is discussed. The bibliography includes 161 references.

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I. INTRODUCTION

Ten years have elapsed since the discovery by Vol'pin and Shur of the first system fixing molecular nitrogen in solutions of transition metal complexes[1]. During this period, the concepts of the chemistry of N_2 have undergone radical changes. In the first place it was found that nitrogen readily reacts with many low-valent transition metal derivatives to form complex nitrides and also derivatives of hydrazine and organonitrogen compounds. In a study of the reaction of hydrazine with $RuCl_3$ in 1965, Allen and Senoff obtained for the first time a complex of molecular nitrogen[2]. After several months, a similar complex was obtained directly from molecular nitrogen[3]. These studies gave rise to a new field of coordination compounds in which N_2 enters as a ligand into the coordination sphere of the metal. It was discovered that in the formation of complexes nitrogen can be very reactive, competing successfully for a coordination site with ammonia and water, for example, and complexes containing N_2 in the coordination sphere are sometimes very stable and withstand heating to 200°C.

Contrary to the expectations of the chemists who synthesised them, the N_2 complexes discovered in the first years proved to be incapable of activating nitrogen with respect to further reactions, for example with respect to reduction to ammonia. It was not until 1969 that intermediate nitrogen complexes capable of undergoing further reactions were detected[4] and in some cases subsequently isolated and investigated.

Finally, systems in which nitrogen is reduced to hydrazine and ammonia in aqueous and aqueous alcoholic solutions in the presence of molybdenum and vanadium complexes, sometimes even at room temperature and atmospheric pressure[5,6], were discovered in 1970.

Thus nitrogen ceased to be an inert gas, which had been thought capable of reacting under the usual conditions only with metallic lithium. On the other hand, the biological fixation of nitrogen achieved by many bacteria and algae in the presence of water and oxygen at the normal temtemperatures and pressures, which had previously been completely puzzling, has now lost its unique features.

The studies on the biological fixation of nitrogen in recent years permit conclusions concerning the mechanism of this reaction. The involvement of transition metal (iron and molybdenum) compounds in the reduction of N_2 can now be regarded as proved and the relation between the enzymatic process and its chemical models is becoming increasingly clear. Whereas previously biological fixation of nitrogen, which indicated the possibility in principle of N_2 reactions under mild conditions, led chemists to seek non-enzymatic model systems, nowadays further progress towards the understanding of the mechanism of the enzymatic process is undoubtedly associated with the investigation of non-biological models, where the investigation of the mechanism is always simpler than in biological systems.

Further simulation of the biological fixation of nitrogen and the study of the mechanism of enzymatic fixation can probably be carried out simultaneously, with a comparison of the results of experiments under enzymatic and non-enzymatic conditions. Such a comparison will be made in the concluding section of the present review.

The review does not deal with the results of studies on stable nitrogen complexes with transition metal compounds (see for example the reviews in the literature[7-9] concerning these substances).

II. GENERAL CONSIDERATIONS

Nitrogen fixation is understood as a process involving complete or partial dissociation of the N≡N bond. This process can be oxidation or reduction of nitrogen depending on whether the electronegativity of the atoms forming a bond with nitrogen is greater or smaller than that of nitrogen. Since reactions in which nitrogen is oxidised by molecular oxygen with formation of oxidation products such as N_2O, NO, NO_2, and N_2O_5 are endothermic, at low temperatures the equilibria are displaced towards the formation of free N_2 and O_2. Oxidants more powerful than oxygen are capable, in principle, of oxidising nitrogen; for example, it has been stated that molecular oxygen in its excited singlet state reacts with N_2 to form nitrogen oxides[10]. Oxygen atoms and carbenes can react with nitrogen to form N_2O and diazo-compounds[11-14]. However, the majority of known reactions involving nitrogen, which occur under mild conditions, may be regarded as reductive. Reagents which are thermodynamically capable of interacting with N_2, including metals and hydrogen, behave

as electron donors in relation to N_2. This review is therefore concerned with the reduction of molecular nitrogen in solutions.

The nitrogen molecule has certain characteristic features which distinguish it from other related unsaturated compounds, for example acetylene (see, for example, Borod'ko and Shilov [7]).

In the first place, in the dissociation of a triple bond most of the energy (about 130 out of 225 kcal) is consumed in the dissociation of the first linkage [15,16]. This determines the stability of the nitrogen molecule in relation to one- or two-electron reactions, i.e. reactions in which the dissociation of one π-linkage in nitrogen results in the formation of one or two new linkages with the latter. For example, the H_2 molecule and even the H atom are incapable of adding to nitrogen, since the formation of a single N–H bond (on addition of the H atom) or of two N–H bonds (on addition of the H_2 molecule) do not compensate the energy expended on the dissociation of the π-linkage in the nitrogen molecule (and of the H–H bond when H_2 is added) and these reactions are strongly endothermic:

$$\cdot H + N_2 \rightarrow \cdot N_2H - 21 \text{ kcal, (Ref.16)}$$

$$H_2 + N_2 \rightarrow N_2H_2 - 49 \text{ kcal.}$$

On the other hand, similar reactions involving carbon–carbon π-linkages are strongly exothermic. For example, we have for acetylene

$$\cdot H + C_2H_2 \rightarrow \cdot C_2H_3 + 40 \text{ kcal,}$$

$$H_2 + C_2H_2 \rightarrow C_2H_4 + 42 \text{ kcal.}$$

After the dissociation of the first π-linkage in nitrogen and the formation of an azo-compound, further successive dissociations of each of the remaining two linkages requires much less energy, so that, following the addition of three H_2 molecules to the N_2 molecule, the overall energy of the N–H bonds compensates the energy expended on the dissociation of the triple bond and the overall ammonia formation reaction is exothermic. These thermodynamic characteristics of the reactions of molecular nitrogen to a large extent determine its behaviour on reduction.

Only very powerful reducing agents (such as metallic lithium) are capable of undergoing the one-electron reactions

$$\cdot X + N_2 \rightarrow X{-}N{=}N\cdot$$

The intermediate formation of the $\cdot N_2H$ radical in aqueous solution, suggested by Bauer [17], appears very unlikely at present.

The two-electron processes $X_2 + N_2 \rightarrow XN_2X$ are much more favourable from the thermodynamic standpoint and are probably more common. However, if one begins with molecular hydrogen, then not only the reaction where the final product is di-imide(N_2H_2) but also the hydrogenation of nitrogen to ammonia with the intermediate formation of di-imide cannot occur at normal temperatures, since the activation energy for this reaction must be not less than 49 kcal, which corresponds to a negligible rate. This explains the finding that the usual hydrogenation catalysts, which catalyse the addition of hydrogen to olefins and acetylenes, are incapable of catalysing the hydrogenation of nitrogen.

In order to explain the reduction of nitrogen via the N_2H_2 stage under mild conditions (for example under the conditions of the biological fixation of nitrogen), it has been suggested [18] that the formation of N_2H_2 may be accompanied by the coupled exothermic oxidation reaction, the energy of which exceeds the deficit of energy for the formation of N_2H_2. Later, it was shown that the biological fixation of nitrogen does not require coupled oxidation, so that this mechanism is not obligatory (although of course in certain yet unknown cases it may operate).

New possibilities of obviating the thermodynamic difficulties in the reduction of molecular nitrogen are discovered when account is taken of the formation of intermediate mononuclear and dinuclear complexes of nitrogen with transition metal compounds:

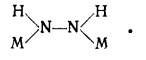
$$M + N_2 \rightleftarrows MN_2;\ MN_2 + M' \rightleftarrows MN_2M'.$$

Here and henceforth M is a transition metal compound.

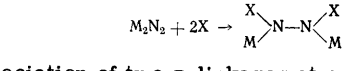
The reduction potential of M (as usually understood, i.e. corresponding to a one-electron transfer)† can be much lower in the formation of the complex than is required for the dissociation of a single π-linkage in the nitrogen molecule (the complexes formed are stabilised by the interaction of the filled *d* orbitals of M and the π orbitals of nitrogen). The subsequent two-electron reduction of nitrogen in the complex, even with the intermediate formation of di-imide, can be facilitated when di-imide forms a complex with M or M', [19] the heat of formation of the di-imide complex being greater than the heat of formation of the complex with molecular nitrogen.

Indeed, comparatively stable complexes of metal compounds with di-imide and its derivatives are known, although hitherto they have been obtained largely from sources other than molecular nitrogen. For example, when hydrazine reacts with $CuCl_2$, a copper(I) complex of di-imide is formed [20]. It has been shown by X-ray diffraction analysis [21] that zero-valent nickel forms a mononuclear complex with azobenzene, which has a structure of the type of π-complexes with olefins, where the interatomic distance r(N–N) = 1.385 Å, which is close to the length of a single N–N bond in hydrazine and evidently corresponds to an appreciable electron transfer to N_2Ph_2. The authors [21] regard this complex as a model of the intermediate complex with N_2H_2 in nitrogen fixation.

If a complex of this kind has a dinuclear structure, it can evidently be regarded as a hydrazine derivative:



In this connection it is easy to imagine a mechanism [7,16] in which the initial dinuclear complex with N_2 is converted into a hydrazine derivative in a single stage under the influence of an additional two-electron reducing agent 2X:



The dissociation of two π-linkages at once in the four-electron reduction under the influence of four atoms of a one-electron reducing agent is much more favourable on energy grounds than the dissociation of a single π-linkage in a two-electron process. Thus the reaction

$$N_2 + 2H_2 \rightarrow N_2H_4 - 22 \text{ kcal}$$

involves the expenditure of 27 kcal less than in the formation of di-imide from N_2 and H_2.

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†The reduction potential E_0 is reckoned from the hydrogen potential and corresponds to the free energy of the reaction $M + H^+ \rightarrow M^+ + \frac{1}{2}H_2$ at pH 0. In the present review we are dealing with reducing agents more powerful than hydrogen and having negative values of E_0. The potential will be regarded as higher or lower if its absolute value is correspondingly greater or smaller.

Thus the M_2N_2 complex can play the role of a seed where the subsequent four-electron process removes or diminishes the thermodynamic difficulties which exist in successive one- or two-electron reduction.

The reducing agent X can exist in solution independently of the complex or can be linked to M (for example, the hydrogen atom in the hydride M–H linkage). A fairly common special case of this "four-electron" mechanism may involve the employment of additional electrons from one or both atoms of M forming the complex with N_2. For example, one can formulate the reactions

1. $M_2N_2 + X \rightarrow M{=}N{-}\overset{\displaystyle X}{\overset{|}{N}}{-}M$
2. $2M + N_2 \rightarrow M{=}N{-}N{=}M$ or 

(in the second case the dinuclear complex is evidently no longer a hydrazine derivative). The latter reaction is possible when M is a fairly powerful two-electron reducing agent.

It is significant that the formation of complexes with transition metals makes it possible to distribute the dissociation energy of the π-linkages of N_2 in uniform steps, while the "usual" one- or two-electron reduction requires the main energy expenditure in the first stage, i.e. requires a particularly powerful reducing agent.

The consideration of the reduction of nitrogen in protic media, in particular in an aqueous medium, is of considerable interest. In this instance, which occurs, for example, in the biological fixation of nitrogen, solven protons are employed for forming the hydrogen atoms of ammonia:

$$N_2 + 6\bar{e} + 6H^+ \rightarrow NH_3 \ .$$

The thermodynamics of the successive reduction of nitrogen becomes more favourable in aqueous solution compared with non-polar media, since ammonia, hydrazine, and probably di-imide are hydrated in water with a considerable energy gain, while the initial molecular nitrogen is hardly hydrated at all. The table below lists the enthalpies of formation of ammonia and the intermediates from the elements in the gas phase, in water, and acid solution.

	$N_2 \xrightarrow{H_2} N_2H_2$	$N_2H_2 \xrightarrow{H_2} N_2H_4$	$N_2H_4 \xrightarrow{H_2} 2NH_3$
$\Delta H_{298(gas)}$, kcal mole^{-1}	49	22.7	−22
(Soln. H_2O)	(33.5) *	8.2	−38.4
(Soln. in acid)		−1.8	−64

*On the assumption that the heat of hydration of N_2H_2 is close to the heat of hydration of the N_2H_4 molecule and two NH_3 molecules.

However, in the aqueous phase the reaction with the intermediate formation of di-imide requires reducing agents which are more powerful than molecular hydrogen. An approximate estimate yields −1.1 V for the reduction potential of di-imide in water. Under these conditions, a new difficulty arises in the aqueous solution because reducing agents having reduction potentials much higher than that of molecular hydrogen cannot exist in water, since they must react with the latter to form molecular hydrogen:

$$M + H_2O \rightarrow M^+ + OH^- + {}^1/_2H_2 \ .$$

Therefore one- or two-electron reduction of nitrogen in aqueous solution with the intermediate formation of N_2H_2 is virtually impossible.

The reduction potential of M can be much lower than −1.1 V if a four-electron reduction mechanism is adopted. Reducing agents having a reduction potential sufficient to convert nitrogen into hydrazine (−0.23 V) are known and can exist in aqueous solution (for example Cr^{2+} or V^{2+} salts).

Protonation of N_2 in the M_2N_2 complex by an acid or the formation of a hydrogen bond with a water molecule facilitates the four-electron reduction with formation of a hydrazine derivative:

$$M_2N_2 \overset{H^+}{\rightleftarrows} M{=}N{-}\overset{\displaystyle +}{\overset{|}{N}}{=}M \leftrightarrow M{=}N{-}\underset{\displaystyle H}{\overset{|}{N}}{-}M^+ \xrightarrow{H^+} N_2H_4 \ .$$

Thus the four-electron mechanism of the reduction of nitrogen with formation of a dinuclear complex ensures, in principle, the possibility of reducing N_2 to hydrazine (as the intermediate or final product) in an aqueous medium.

However, when the reaction proceeds via hydrazine or its derivative, the free energy of the process (bearing in mind the impossibility of the existence of an unduly powerful reducing agent in aqueous solution) must be close to zero. This imposes significant limitations on the thermodynamic properties of the catalyst M which ensures the reduction of nitrogen. Its reduction potential must not be higher than that of the reducing agent and, on the other hand, it cannot be too small, since M must itself be a reducing agent strong enough to reduce nitrogen.

Under these conditions, it is necessary that the heat of formation of the complex M_2N_2 should also be optimal. With increase and decrease of the stability of the complex, the rate of reaction should rapidly decrease, in the first case owing to a decreased rate of reduction of bound nitrogen and in the second owing to a lower concentration of the intermediate complex.

Apparently the stability of dinuclear complexes with N_2 can vary within wide limits and is not related directly to the reduction potential of M, since many stable N_2 complexes are known both with powerful and weak reducing agents. Thus, in order to select a catalyst M for an aqueous medium, capable of catalysing the reducing of nitrogen with formation of hydrazine as an intermediate or final product, one must begin with the fact that both the reduction potential of M and the M–N bond energy must be restricted to comparatively narrow limits. It becomes clear from the foregoing discussion why rapid reduction of nitrogen in an aqueous medium must be a rare exception among the large number of reduction systems. We may note that a combination of suitable thermodynamic properties of the catalyst M is by itself insufficient for the reaction with nitrogen, since the reaction requires that M must have also a suitable ligand environment (a free site for nitrogen, accessibility to the action of the reducing agent) and the two atoms M in the initial complex must be separated by an appropriate distance.

Table 1 shows that on passing to acid media it is possible to employ even weaker reducing agents, since protonation stabilises the resulting hydrazine (or ammonia). However, one must bear in mind that at low pH values the reaction between the reducing agent and water to liberate hydrogen, which is usually catalysed by acids, is accelerated.

The increase of pH on passing to alkaline media can increase the reduction potential of M, since in the reaction

$$M + OH^- \rightarrow MOH + e$$

the reduction potential increases linearly with pH ($E_0 = E_0^0 + 0.059pH$). However, one must also take into account the fact that in the reactions

$$N_2 + 4e + 4H_2O \rightarrow N_2H_4 + 4OH^-,$$
$$N_2 + 6e + 6H_2O \rightarrow 2NH_3 + 6OH^-,$$

and also in

$$2e + H_2O \rightarrow {}^1/_2H_2 + OH^-,$$

the reduction potentials of NH_3, N_2H_4, and H_2 likewise increase linearly with pH, the slope being the same as for M and therefore the difference between the reduction potentials ΔE will be independent of pH. An alkaline medium will in fact favour the thermodynamics of the reduction of nitrogen in those cases where the dependence of the redox potential on Ph is more marked than for hydrazine, which should imply the formation in an alkaline medium of certain new compounds which are more powerful reducing agents than the compound existing in an acid medium [as, for example, in the case of titanium(II) salts, which are moderately strong reducing agents in an acid medium, while in an alkaline medium they liberate hydrogen from water]. Evidently, this corresponds to the formation of ionised species with a high effective negative charge at the metal atom of the reducing agent.

This discussion is based on the assumption that the most economical pathway to the reduction of nitrogen from the standpoint of energy expenditure is the formation of hydrazine derivatives from the complex with N_2.

If account is taken of the possibility of six-electron reduction of nitrogen directly to ammonia, then the process should, in principle, be achieved by weaker reducing agents. However, the probability of such a mechanism is itself apparently very low, since it requires simultaneous and considerable shifts of a large number of nuclei in a single step[22].

Thus preliminary consideration of the possible involvement of transition metal compounds in the reactions involving the reduction of molecular nitrogen shows how the formation of intermediate complexes can give rise to a mechanism in which the thermodynamic difficulties involved in the reduction of N_2 are overcome.

III. REDUCTION OF NITROGEN IN APROTIC MEDIA

1. Nitrogen-fixing Systems

Vol'pin and Shur discovered in 1964 the reduction of nitrogen at room temperature in ethereal and hydrocarbon media in the presence of transition metal compounds ($CrCl_3$, $MoCl_5$, WCl_6, $FeCl_3$, $TiCl_4$) when they react with powerful reducing agents ($LiAlH_4$, EtMgBr, i-Bu_3Al).[1] Ammonia was isolated after the hydrolysis of the reaction product in the presence of nitrogen. The results were then confirmed[23] in experiments with labelled $^{15}N_2$ nitrogen.

Some of these and similar systems were known previously and were used in catalysis, particularly as catalysts of the polymerisation and hydrogenation of olefins and acetylenes. Thus their capacity to activate unsaturated compounds was known.

Moreover, many investigators flushed their systems with nitrogen, which they regarded as inert and there is evidence (see, for example, Refs. 24 and 25) that in the presence of nitrogen certain differences in the behaviour of such systems compared with that *in vacuo* or in an atmosphere of argon were observed even before 1964. Nitrogen sometimes retarded the catalytic polyermisation reaction. Ammonia was actually isolated from the products of the reaction carried out in an atmosphere of nitrogen. Nevertheless, the widely held view that nitrogen is inert evidently prevented many investigators from reaching definite conclusions concerning this reaction before 1964 and this is why Vol'pin and Shur's work initiated a new stage in the study of the reduction of nitrogen in solution.

In the first experiments of Vol'pin and Shur appreciable yields of the reduction product [up to 25% of ammonia (after the hydrolysis of the product) relative to the amount of transition metal employed] was observed at comparatively high nitrogen pressures (150 atm). Soon Vol'pin and his coworkers succeeded in obtaining more active systems. Thus in the reaction of N_2 with the products of the reaction of Cp_2TiCl_2($Cp = \pi$-C_5H_5) with EtMgBr in ether the yield of ammonia (after hydrolysis) was 67% per mole of the titanium compound employed, even at atmospheric pressure[26]. On increasing the pressure, the yield of ammonia became nearly quantitative.

Later it was shown[27] that free metals, for example, magnesium activated by iodine, can be used as reducing agents and that simple purely inorganic systems such as $TiCl_4 + Mg(MgI_2) + N_2$ can be used to reduce nitrogen.

Evidently, the role of the non-transition metal or the organometallic compound consists primarily in the reduction of the transition metal compound, such reduction being known to proceed frequently via alkyl or aryl derivatives of transition metals. Indeed, it has been found[28] that the reduction of nitrogen can be carried out also without a specially added reducing agent on heating solutions of dialkyl and diaryl derivatives Cp_2TiR_2 in an atmosphere of N_2. In this case nitrogen is reduced under the influence of low-valent titanium derivatives formed as intermediates or as final products of the thermal decomposition of the organotitanium compounds.

The reduction of nitrogen (albeit with a low yield of the product) has been observed also on heating with nitrogen a previously prepared solution of dicyclopentadienyltitanium(II).[28] Thus molecular nitrogen was found to be capable of reacting in solution with many transition metal compounds.

Subsequent studies in many laboratories in different countries led to the discovery of various systems interacting with nitrogen (see the appropriate reviews[24,25,29-33]).

The range of transition elements and reducing agents is now very large: Henrici-Olive and Olive[34] and also van Tamelen et al.[35] used successfully as reducing agents naphthalene derivatives of alkali metals (lithium, sodium, and potassium). Bayer and Schurig[36] showed that alkali metals (Li, Na, K, Rb, and Cs), alkaline earth metals (Mg and K), and the lanthanides (La and Ce) can serve as reducing agents.

Bell and Brintzinger obtained about 1 mole of ammonia (after hydrolysis) per mole of $FeCl_3$ using as a reducing agent the doubly charged anion formed by treating 2,6-dimethylnaphthalene with lithium[37].

Apart from the transition metal compounds already mentioned, vanadium[34,38], manganese[39], and cobalt[27,39] chlorides, tetraalkoxy-derivatives of titanium[40-43], vanadium, chromium, molybdenum, manganese, and nickel acetylacetonates[40], cyclopentadienyl derivatives of zirconium[36] and niobium[44], and triphenylphosphine complexes of titanium[45] and iron[39] proved to be active.

Negative results have also been published. For example, dicyclopentadienyltitanium dichloride, which forms an exceptionally active system with organomagnesium compounds, does not reduce nitrogen in the presence of tri-

isobutylaluminium[30]. The explanation is probably that in the latter case the reduction terminates with the formation of stable titanium(III) complexes[46,47]. Cobalt and manganese compounds proved to be inactive in many cases[30].

Nickel, palladium, copper, and platinum compounds apparently could not be used at all in systems reducing N_2 in solutions[1,30,39].

The yields of ammonia (after the hydrolysis of the products) are extremely varied and in different systems can amount to between a fraction per cent and one mole of ammonia per mole of the transition metal compound employed. In several cases between one and two moles of ammonia are formed per mole of the transition metal.

It was reasonable to attempt the catalytic reduction of nitrogen, for example by a catalytic hydrogenation process. It was found that hydrogen usually inhibits the reaction, lowering the yield of the product[36,40,48] even in those systems where catalytic hydrogenation of olefins is possible. In some cases hydrogen does not have much influence on the yields of products (for example, in the reactions involving vanadyl and molybdenyl acetylacetonates with LiBu). In certain systems, for example, $Ti(OEt)_4$ + $(i\text{-}Bu)_3Al + N_2$, an appreciable increase of the yield of ammonia (after hydrolysis) was observed following the introduction of molecular hydrogen[40]. However, with increase of hydrogen pressure, the yield of ammonia passes through a maximum (increasing approximately by a factor of 1.5) and then falls.

In none of the instances was catalytic hydrogenation observed. However, Vol'pin and his coworkers[39,49,50] achieved the catalytic reduction of nitrogen under the influence of a more powerful reducing agent. Thus metallic aluminium reduces nitrogen at 130°C and a pressure of 100 atm in the presence of titanium tetrachloride and aluminium bromide. Metallic aluminium without additives is known to react with nitrogen only at much higher temperatures. The yield of ammonia after hydrolysis can reach hundreds of ammonia molecules per molecule of the added titanium compound. The reaction takes place in benzene or aluminium bromide melt, which (like titanium tetrachloride) is necessary for catalytic reduction.

Lithium aluminium hydride can be used as a reducing agent instead of aluminium. In this case up to 100 moles of ammonia (after hydrolysis) per mole of the initial titanium tetrachloride can be formed even at 60–70°C when the reactions are performed in a molten mixture of aluminium bromide and chloride. A catalytic system can also be obtained (up to 10 moles of ammonia per mole of titanium) when the nitrogen–hydrogen mixture is heated to 130°C with a mixture of $(BuO)_4Ti + (i\text{-}Bu)_3Al + AlBr_3$ in the presence of benzene. Hydrogen activates the system in this case, since in its absence only two moles of ammonia per mole of titanium are obtained.

Here we may note that, although catalytic hydrogenation of nitrogen has not so far been observed in solutions, Japanese workers showed recently that the introduction of alkali metals strongly activates heterogeneous catalysts of the gas-phase synthesis of ammonia. Thus Tamaru and coworkers[51,52] observed that the reaction of iron, cobalt, titanium, and molybdenum complexes of phthalocyanines with metallic sodium resulted in the formation of a donor–acceptor complex which can catalyse the synthesis of ammonia from nitrogen and hydrogen starting from a temperature as low as 110°C. Ozaki, Aika, and Hori[53,54] showed that alkali metals sharply increase the catalytic activity of ruthenium, osmium, iron, molybdenum, and other metals in the synthesis of ammonia, ruthenium activated by potassium being capable of catalysing the reaction at a temperature as low as 146°C and atmospheric pressure. There is no doubt that alkali metals enhance the electron-donating properties of the metal atoms in the catalyst (this is shown particularly by the activity series Cs > K > Na), which apparently occurs in many instances also in the fixation of nitrogen in solutions.

Van Tamelen and coworkers[42] achieved the cyclic hydrolysis-reduction in the $(i\text{-}C_3H_7O)_4Ti + NaNp + N_2$ system in tetrahydrofuran (THF). By adding successively small amounts of isopropyl alcohol, it was possible to hydrolyse the product to ammonia and then regenerate it with metallic sodium, after which it was again capable of reacting with nitrogen. Thus it was possible to accumulate up to 3.4 moles of ammonia per mole of titanium alkoxide in the course of 5 such cycles. Following the addition of aluminium tri-isopropoxide, the system was capable of forming 2.75 moles of ammonia per mole of titanium in only one cycle.

Van Tamelen and coworkers also reported the electrochemical reduction of nitrogen[41,43] in dimethoxyethane at a nichrome cathode using an aluminium anode. After eleven days at 40 V, the formation of 10.2 millimoles of ammonia (6.1 moles of ammonia per mole of titanium) was observed. It was noted that an appreciable amount of aluminium (15.1 millimoles) was lost under these conditions from the anode during electrolysis and that aluminium could apparently also behave as a reducing agent.

The reduction of nitrogen in solutions is usually inhibited by compounds such as carbon monoxide and acetylenes[24,29]. Moisture and oxygen naturally also reduce the yield since they interact with nitrogen-reducing systems.

2. Reaction Products

Nitrides. Ammonia is usually formed in the hydrolysis of the nitrogen reduction products in aprotic media. Among the products which hydrolyse with formation of ammonia, amides, imides (M–NH_2, M–NH–M), or nitrides might have been expected, since ammonia itself should not be stable in nitrogen-reducing systems containing metals or organometallic compounds.

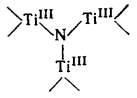
Soon after the first reports by Vol'pin, it was observed[55] that in the products of the reaction carried out in $(C_2D_5)_2O$ and using C_2D_5MgBr as the reducing agent the ammonium salt formed after decomposition of acid does not contain deuterium atoms. This evidently indicates that before hydrolysis the product did not contain deuterium atoms linked to nitrogen, i.e. that it was probably a nitride.

This conclusion was confirmed further by the observation (of ammonia) in a number of studies of systems in which the reactants did not contain nitrogen at all (for example $TiCl_4 + Mg + MgI_2 + N_2$).

If the involvement of the solvent in the reaction is not postulated, there is virtually no doubt about the formation of nitrides as the products in such a system. Aluminium nitride is evidently the product of the reduction of nitrogen in the catalytic system $Al + TiCl_4 + AlBr_3 + N_2$ (where the reduction can be carried out in the aluminium bromide melt). The detailed structures of the nitride products are unknown for the majority of the systems.

Vol'pin and coworkers[39,50] found that the complex $C_6H_6TiCl_2 2AlCl_3$, obtained in the reduction of titanium tetrachloride by aluminium in the presence of aluminium chloride and benzene by the method of Natta et al.[56],

reacts with nitrogen at 130°C with formation of the compound having the elemental composition $(C_6H_6)[TiCl_2 2AlCl_3]_3N$ and hydrolysed with formation of ammonia. This product is probably a complex nitride incorporating three titanium atoms per nitrogen atom:



A thorough investigation of the products of the reaction of nitrogen in the system $TiCl_3(THF)_3 + Mg + N_2$ and $VCl_3(THF)_3 + Mg + N_2$ was carried out by Yamamoto and coworkers [57,58]. In both systems the reaction proceeds at room temperature and atmospheric pressure, the amount of ammonia formed not exceeding one mole per mole of the transition metal. After the absorption of 0.5 mole of nitrogen per mole of titanium in the first system (2.5 gramme-atoms of magnesium are employed at the same time), a black diamagnetic powder with the composition $TiNMg_2Cl_2(THF)$ can be isolated from solution and the stoichiometry of the process can be represented by the equation

$$TiCl_3(THF)_3 + 2.5Mg + 0.5N_2 \rightarrow TiNMg_2Cl_4THF + 0.5MgCl_2(THF)_2 .$$

When the product is decomposed by HCl, ammonia and hydrogen are formed. The structure of the molecule formed in the reaction with nitrogen is not clear, but it is probably not monomeric and cannot be represented as a derivative of titanium(III) and magnesium(II), this being indicated by the evolution of hydrogen in the reaction with HCl. A complex of bipyridyl with zero-valent magnesium can be isolated when the reaction product is treated with bipyridyl. In terms of its chemical properties, the product behaves as a nitride: it evolves ammonia on hydrolysis, does not evolve nitrogen on heating to 200°C and, on treatment with pyridine, bipyridyl, and benzoyl chloride, magnesium can be removed from the product either partly or completely, but the nitrogen formed in these processes remains bound to titanium and can be evolved in the form of ammonia only by hydrolysis.

The reaction with nitrogen in the system $VCl_3(THF)_3 + Mg + N_2$ proceeds similarly (although somewhat more slowly), the product being the complex $VNMg_2Cl_2(THF)$. It is also diamagnetic, does not evolve nitrogen on heating, and hydrolyses with evolution of ammonia, i.e. it is evidently a complex nitride. However, nitrides are not the only possible products of the reduction of nitrogen in such systems.

As already stated, in certain cases hydrogen increases the yield of ammonia after the hydrolysis of the reaction products [40]. Presumably in certain instances it enters into the composition of the product. Indeed, it has been found [59] that hydrogen atoms are linked to the nitrogen atoms, i.e. a complex imide M–NH–M may be formed in this case.

In an early study by Van Tamelen [60] metallic potassium was added to a solution containing a suspension of dialkoxytitanium dichloride and nitrogen was passed into the system. The formation of free ammonia, which was driven out of the system with the nitrogen, was then observed. The evolution of ammonia continued for several weeks and after its cessation the addition of metallic potassium gave rise to the formation of fresh ammonia. The overall yield of ammonia reached only 10–15% relative to titanium. If, as claimed by the authors, ammonia is not formed owing to the traces of moisture in nitrogen, presumably the solvent serves as a source of hydrogen atoms by reacting with the nitride, which is the primary product.

Organonitrogen compounds. The studies by Vol'pin and coworkers [30,61-64] first established the possibility of forming organonitrogen compounds in the reduction of molecular nitrogen with isolation of aromatic amines after hydrolysis. In the systems $Cp_2TiCl_2 + LiPh + N_2$ and $Cp_2TiPh_2 + LiPh + N_2$ in ether the hydrolysis of the products of the reaction with nitrogen (20°C, N_2 pressure 100 atm) led to the detection of aniline (0.15 mole of aniline together with 0.65 mole of ammonia per mole of the titanium compound).

When *p*-tolyl-lithium or *m*-tolyl-lithium are employed as the reducing agents, mainly *p*- and *m*-toluidines respectively are found in the reaction products, i.e. nitrogen largely replaces the lithium.

In the presence of *o*-tolyl-lithium a mixture of all three isomers is found in the product. The authors suggest that the isomers are produced via the intermediate formation of dihydrobenzene in a complex with titanium. In analogous systems involving aliphatic organolithium compounds only insignificant yields of aliphatic amines were observed.

Van Tamelen and Rudler demonstrated the possibility of obtaining organonitrogen compounds by treating the nitrides formed as primary products with compounds containing the carbonyl group [65]. Thus when ketones or acid chlorides are added to the reaction product subsequent to the absorption of nitrogen in the $Cp_2TiCl_2 + Mg + N_2$ system, amines or nitriles are formed in the reaction mixture after several days.

$$R_2CO \rightarrow R_2CHNH_2 + (R_2CH)_2NH ,$$
$$RCOCl \rightarrow RCN .$$

These data indicate a comparatively high reactivity of the nitride derivatives, which distinguishes them from the usual nitrides, formed, for example, on combustion of metals in nitrogen. Subsequently such reactions were investigated by Dormond et al. [66]

Hydrazine. In 1969 studies by two groups of investigators demonstrated simultaneously that, in addition to ammonia, hydrazine may be formed in nitrogen-fixing systems in aprotic media [4,67], i.e. a product of incomplete reduction of nitrogen may be observed after the hydrolysis of the primary products.

In the system $(i\text{-}C_3H_7O)Ti + NaNp + N_2$ in THF [67] the yield of hydrazine following the hydrolysis of the products increased with decrease of the molar ratio $[Ti^{IV}]/[NaNp]$ to give maximum yields of 15–19% (relative to titanium), ammonia being formed together with hydrazine (the ratio $2NH_3/N_2H_4$ varied in the range 3.3–5). The compound forming hydrazine can be reduced further to nitrides by an excess of NaNp.

When $(i\text{-}C_3H_7O)_4Ti$ is replaced by $CoCl_2$, $MoCl_5$, WCl_6, $CrCl_3$, $NiBr_2$, or $FeCl_3$, hydrazine is not formed.

A complex of molecular nitrogen, dissociating reversibly with evolution of nitrogen (see below), is formed in the system $Cp_2TiCl_2 + i\text{-}C_3H_7MgCl + N_2$ at low temperatures (between −80° and −100°C) [4,68]. At −60°C in the presence of excess isopropylmagnesium chloride nitrogen is reduced, evidently via the intermediate formation of the above complex, to a hydrazine derivative, which hydrolyses to form N_2H_4. At such low temperatures nitrides are hardly formed and subsequent reduction to ammonia derivatives proceeds only above 0°C.

Appreciable yields of hydrazine were obtained later in reactions with nitrogen in the systems $TiCl_4 + Al + AlBr_3$, [39] $FeCl_3(Ph_3P)_2 + i\text{-}C_3H_7MgCl$, [69] $MoCl_5 + i\text{-}C_3H_7MgCl$, [69] $FeCl_3 + LiPh$, [70] and $FeCl_3 + Mg$. [71] The results of some of these studies will be discussed in greater detail in the next section.

3. The Mechanism of the Reduction of Nitrogen in Aprotic Media

Many systems capable of reducing nitrogen in aprotic media in the presence of many transition metal compounds, various reducing agents, in different solutions, and under different reduction conditions refute the idea that the reaction mechanism is always the same. In most cases even the nature of the nitride reduction products is still obscure and the reaction mechanism can be discussed only in the broadest outline. The reduction of nitrogen was sometimes investigated in order to elucidate the reaction mechanism, but the results obtained in these studies are also frequently contradictory, are being revised, and cannot be regarded as unambiguous.

The involvement of powerful reducing agents together with transition metal compounds made it necessary to assume from the very beginning that N_2 is activated by compounds of transition metals in a low state of oxidation which are formed under the influence of reducing agents.

Such activation must involve the formation of a complex of nitrogen and the metal atom and, as early as 1966, it was possible to suggest on the basis of general considerations and certain analogies, including the analogy with the reaction of methylene and nitrogen discovered at that time [13,14],

$$CH_2 + N_2 \rightleftarrows CH_2N_2 ,$$

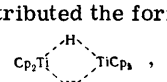
that nitrogen is activated by "carbene-like" compounds such as $Ti^{II}d^2$ and $Fe^{II}d^6$. However, the specific mechanism of the reduction remained unknown and various workers put forward different hypotheses to account for the results.

The involvement of hydrides in the reduction of nitrogen. It has been shown that hydrides which evolve hydrogen on hydrolysis (HD under the influence of D_2O) are formed in many nitrogen-fixing systems. The involvement of hydride linkages in catalytic reactions, particularly in the hydrogenation of olefins, suggested that the M–H bond can be involved also in the reduction of nitrogen, for example by the insertion of the N_2 molecule with formation of M–N=N–H.

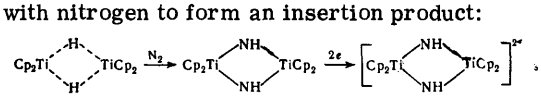
Systems incorporating Cp_2TiCl_2, which are homogeneous and in certain cases (for example, with EtMgBr) effectively reduce nitrogen even at atmospheric pressure, have been investigated in greatest detail from the standpoint of the mechanism. It has been established [55] that hydrides are formed in this system together with nitrides simultaneously with the reduction of nitrogen.

The inhibiting effect of hydrogen, which was observed for many nitrogen-fixing systems (see above), can be explained by the fact that the hydrides formed in the reaction of low-valent transition metal derivatives with hydrogen are mostly inactive in relation to nitrogen.

Nevertheless, on the basis of ESR data for the Cp_2TiCl_2 + EtMgBr + N_2 system, Brintzinger [72] concluded that the hydride, to which he attributed the formula



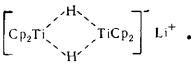
reacts with nitrogen to form an insertion product:



This hypothesis, which is attractive in view of its simplicity, was subsequently extended to biological nitrogen fixation [73]. However, it was not confirmed in subsequent investigations.

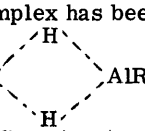
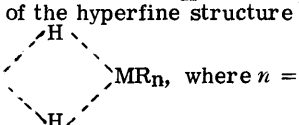
In the first place, this mechanism contradicts data [55] showing the absence of NH groups in the product. Moreover, as shown subsequently by Brintzinger himself [74], the ESR signal which has been attributed to the product of the reaction with nitrogen is not in practice associated with the nitrogen. The triplet signal of the dihydride was found to belong to a monomeric species to which Brintzinger attributed the formula of the anion $[Cp_2TiH_2]^-$. [74] This dihydride does not change in the presence of nitrogen [36] and is probably a side product.

Henrici-Olive and Olive showed by the ESR method that a species containing two hydrogen atoms per tervalent titanium atom is formed in the system Cp_2TiCl_2 + LiNp. [75] In this case the hyperfine structure of the spectrum indicates the involvement of the lithium atom in the complex and the formula of a dimer with titanium in different valent states (bivalent, tervalent) was attributed to this complex: [31]



It is suggested that nitrogen forms a complex with bivalent titanium, this being followed by reduction under the influence of lithium naphthalide.

A similar dinuclear structure of the hydride has been suggested for the system Cp_2TiCl_2 + EtMgBr, [31] it being postulated that the reaction of nitrogen with bivalent titanium in the complex does not alter the ESR signal of the titanium(III) hydride, which remains unchanged.

Presumably the hydride products are in reality related to the hydride complex observed previously—the product of the reaction of Cp_2TiCl_2 with $(i\text{-}Bu)_3Al$ and of Cp_2TiCl_2 with $(i\text{-}Bu)_2AlH$). This complex has been investigated by ESR and the formula  was attributed to it on the basis of the hyperfine structure [76]. The general formula  where n = 2, 1, or 0 for aluminium, magnesium, lithium (or sodium) respectively, can probably be attributed to the dihydride complexes. Like their aluminium precursor, titanium(III) dihydride complexes involving magnesium, lithium, and sodium are evidently inactive with respect to nitrogen and are side products.

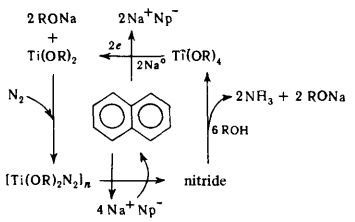
The formation of hydrides inactive in relation to nitrogen apparently constitutes a general phenomenon in the reduction of nitrogen in aprotic media. However, as already mentioned, in certain cases nitrogen can also increase the yield of the reduction product. In these systems, which usually contain alkoxy-derivatives of titanium, one cannot rule out the involvement of hydrides in the fixation of nitrogen, but the available data are still insufficient for more specific conclusions concerning the mechanism.

The degree of oxidation of the transition metal. The degree of oxidation of the transition metal in compounds active with respect to nitrogen has been discussed in a number of studies. Most of these refer to systems including titanocene derivatives. On the basis of ESR data, Vol'pin and coworkers [27] concluded that in these systems the reaction with nitrogen begins after the disappearance of titanium(III), i.e. the degree of oxidation of titanium is less than three. It has been concluded [77] that the Cp_2Ti^- ion [which may be regarded as a derivative of

titanium(I)] reacts with nitrogen. As already stated, Olive suggested that titanium(II) in a complex with a hydride derivative of titanium(III) is active in relation to nitrogen.

Maskill and Pratt [78] and Bayer and Schurig [36] postulated that zero-valent titanium complexes are active.

Bivalent titanium compounds were assumed to be active by van Tamelen and coworkers [32]. Thus in systems incorporating $Ti(OR)_4$, which have been investigated in greatest detail in these studies and which permit cyclic hydrolysis-reduction, the following mechanism in which the $Ti(OR)_2$ species reacts with nitrogen has been adopted [79]:



Titanium(II) and vanadium(II) complexes are assumed to be active in relation to nitrogen by Yamamoto et al. [37] in the systems $TiCl_3(THF)_3$ + Mg and $VCl_3(THF)_3$ + Mg. The study of the reduction of nitrogen in the systems VCl_3 + LiNp and $CrCl_3$ + LiNp [31,80] by ESR showed that the metals in these systems must be very highly reduced.

We may note that precisely in these instances, evidently involving very powerful reducing agents, the yield of ammonia per atom M under the conditions of high Red/M ratios reaches 2. It is interesting to note that the yield of reduction products in the VCl_3 + LiNp + N_2 system depends on the order in which the reducing agent and the vanadium compound are mixed in an atmosphere of nitrogen [38]. If a solution of lithium naphthalide is added to a solution of VCl_3, the amount of nitrogen absorbed reaches 0.39 mole per mole of VCl_3. If, on the other hand, a VCl_3 solution is added to a solution of lithium naphthalide, up to 0.7 mole of N_2 is reduced.

Kinetic data and preliminary conclusions concerning the structure of the intermediate complexes. Maskill and Pratt [78,81] employed a kinetic approach for the homogeneous system Cp_2TiCl_2 + EtMgBr + N_2. They established that, when the system is flushed with nitrogen, the species formed on reduction of dicyclopentadienyltitanium dichloride which is active with respect to nitrogen can exist for a long time in the absence of nitrogen, since the yield of products and the rate of their accumulation depend little on whether nitrogen is passed in immediately after mixing the reactant or after a long time‡. It was discovered that, above 0.5 atm, the rate of reaction is independent of the nitrogen pressure and, in the presence of a sufficient excess of the reducing agent, is independent of the concentration of ethylmagnesium bromide. Under these conditions, the rate was found to be proportional to the square of the initial concentration of the titanium compound.

‡We may note that in the study of Nechiporenko et al. [55] the yield fell sharply when nitrogen was introduced to the reaction mixture only when some time elapsed after the mixing of the reactants. Evidently, this difference from the result of Maskill and Pratt [81] is due to the fact that the system of Nechiporenko et al. [55] was static and the gases evolved could react with the active species. Indeed, it was subsequently shown that ethylene in the system investigated forms the π-crotyl complex $Cp_2Ti(\pi\text{-}C_4H_7)$. [82]

The results indicate the formation of a dinuclear complex when two reduced titanium derivatives interact. Evidently the interaction determines the rate of the entire process when the nitrogen pressure is in excess of 0.5 atm and the subsequent reaction with nitrogen proceeds rapidly. It is interesting to note that qualitatively similar kinetics (proportionality to the square of the concentration of the transition metal compound, the attainment of a limiting rate with respect to the nitrogen and reducing agent concentrations) were observed subsequently in a study of another homogeneous system—$FeCl_3$ + LiPh + N_2 (see below) [70]. In this case one can also conclude that a dinuclear complex is formed.

In the systems investigated by Yamamoto [37], $TiCl_3(THF)_3$ + Mg + N_2 and $VCl_3(THF)_3$ + Mg + N_2, the rate of reaction in THF is consistent with first order with respect to the concentration of the initial chlorides, the amount of unconsumed magnesium, and the N_2 pressure. The amount of reduced nitrogen does not, however, exceed one molecule for two titanium atoms. Hence, it follows that the most probable mechanism involves the formation of a complex by nitrogen with a dinulcear species containing reduced titanium and subsequent reduction of the activated nitrogen by magnesium.

In general, in those cases where the yields of products approach one NH_3 molecule (after hydrolysis) per transition metal atom the formation of a dinuclear complex, in which two transition metal atoms are linked to two nitrogen atoms, is probable. As stated above, the yield of ammonia often approaches two molecules per transition metal atom. As already mentioned, this has been observed for highly reducing systems. These results probably correspond to mononuclear complexes with subsequent reduction by non-transition metal atoms, for example:

$$MN_2 + LiNp \rightarrow M{-}N{=}N{-}Li + Np \xrightarrow{LiNp} N^{3-}.$$

On this hypothesis, it is possible to account for the different results obtained for different orders of mixing of the reactants [38]. If the vanadium compound is added to the reducing agent, i.e. the reaction proceeds in the presence of lithium naphthalide, there is a possibility of the formation of the complex V–N=N–Li and up to one mole of N_2 per mole of the transition element can be reduced. For the reverse order of mixing, the dinuclear complex includes two transition element atoms and the maximum yield corresponds to the reduction of 0.5 mole of N_2 per mole of vanadium.

The study of intermediate complexes with molecular nitrogen. Bearing in mind the very high ionisation potential of the nitrogen molecule (367 kcal mole^{-1}), the negative sign and high absolute magnitude of its electron affinity (−84 kcal mole^{-1}), [7] and the high dissociation energy of the first π-linkage which is ruptured, it might have been possible to conclude long ago that complex formation is essential as the first stage in the activation of nitrogen.

After the discovery by Allen and Senoff of the first complex with bivalent ruthenium [2] and the first proof that such complexes can be obtained directly from molecular nitrogen [3,83], it appeared that the activation of nitrogen by complex formation received direct confirmation. The first studies on the properties of the complexes appeared to support this hypothesis. It has been concluded that [2,84] nitrogen in the complex can be reduced to ammonia on treatment with sodium tetrahydroborate. However, subsequent careful tests using $^{15}N_2$ showed [7,85–87] that the reports concerning the reduction of nitrogen in the complex were incorrect and that in reality nitrogen in the complexes is

not reduced either by sodium tetrahydroborate or by other reducing agents. With increase of the number of known stable mononuclear and dinuclear complexes (see the reviews [7-9]), an increasing number of such complexes were tested to check the possibility of further reactions of the nitrogen bound in them and each time the results proved to be negative. Initially the studies on the complexes with nitrogen and the reduction reactions in the Vol'pin–Shur systems developed in parallel and there were no points of contact between them.

It was not until 1969 that the first reports of complexes with nitrogen in which the nitrogen ligand is capable of further reactions were published. The number of such complexes then began to increase and some of them could be isolated and investigated in detail. These studies in fact yield the most definite conclusions concerning the mechanism of the reduction of nitrogen.

Van Tamelen et al. [79] were the first to report a complex with nitrogen capable of further reduction. According to their data [79], this complex is formed when a benzene solution of dimeric titanocene is stirred for three weeks in an atmosphere of nitrogen. During this period, more than 0.9 mole of nitrogen is absorbed per mole of monomeric titanocene.

The infrared spectrum of a solution of the titanocene complex with nitrogen shows a band at 1960 cm^{-1}, which has been tentatively assigned to the NN vibration in the complex, although experiments with $^{15}N_2$, which would confirm this hypothesis, were evidently not carried out. Nowadays this assignment of the frequency appears doubtful, in particular because the NN frequency in the intermediate complexes is usually much lower. The complex with nitrogen is formed reversibly and decomposes with the evolution of nitrogen when the nitrogen over the solution is replaced by argon. Measurements of the molecular weights showed that the complex is dimeric and the formula $(Cp_2TiN_2)_2$ was attributed to it. On treatment with sodium naphthalide the nitrogen in the complex is reduced quantitatively to ammonia: $(Cp_2TiN_2)_2 \xrightarrow{e} \xrightarrow{H^+} 4NH_3$. We may note that this result is unusual for metallocene systems, which in other cases give rise to at most one mole of ammonia per mole of titanium. More detailed data on this complex were not subsequently published.

Complexes with quite different properties were discovered in the same year in the nitrogen-fixing systems $Cp_2TiCl_2 + RMgX + N_2$ (R = i-Pr or Et).[4] The most definite results were obtained for isopropylmagnesium chloride. On the hypothesis that the intermediate complexes must be unstable, the authors [4] attempted to detect the formation of the complexes on sharp cooling of the solution.

When the reaction of isopropylmagnesium chloride with dicyclopentadienyltitanium dichloride was carried out at −60°C and the solution was cooled further under nitrogen to between −80° and −100°C, an intensely blue complex with nitrogen was formed rapidly and reversibly (λ_{max} = 610 nm). Spectroscopic study of the reversible complex formation reaction with nitrogen subsequently showed that the complex incorporates two titanium atoms per nitrogen molecule and that its heat of formation is only 5 kcal $mole^{-1}$.[88] Evidently this complex can be isolated from solution in the system $Cp_2TiCl + i\text{-}C_3H_7MgCl + N_2$.[89] It is somewhat more stable in the solid state than in solution, but decomposes slowly at a temperature as low as −70°C with liberation of nitrogen. The composition of the complex corresponds to the formula $(Cp_2TiR)_2N_2$. A more stable intermediate complex, formed in the system $Cp_2TiCl_2 + (i\text{-}C_3H_7)MgCl + N_2$ in the presence of triphenylphosphine, has also been reported[4]. The complex with nitrogen is likewise intensely coloured (λ_{max} = 420 and 520 nm). On treatment with alcohol, the complexes evolve nitrogen and on standing in the presence of an excess of a reducing agent the nitrogen bound in the complex is converted into a nitride, which hydrolyses to form ammonia.

A more stable complex, analogous to the blue complex $(Cp_2TiR)_2N_2$ in composition, was isolated by Teuben and de Liefde Meijer in the reaction between Cp_2TiPh and N_2 in toluene at −78°C.[90] In this case the complex slowly evolves nitrogen above 0°C and rapidly at 70°C. Subsequently a number of $(Cp_2TiR)_2N_2$ complexes, where R = *o*-, *m*-, or *p*-tolyl, benzyl, or pentafluorophenyl, were obtained similarly [91,92].

In all cases the complexes are formed reversibly in toluene solution and give rise to the appearance of an intense blue colour (λ_{max} = 600–630 nm). The complexes are diamagnetic. Their infrared spectra do not show appreciable absorption corresponding to the vibration of the NN bond. The complexes with nitrogen exhibit extremely varied thermal stabilities. Thus the *m*-tolyl complex decomposes only at 75°C, the *o*-tolyl complex evolves nitrogen at −20°C, and the 2,6-dimethylphenyl derivative is not formed at all.

The structure of the complexes is still obscure but, according to infrared spectroscopic data, the nitrogen molecule is probably located symmetrically between two titanium atoms or a structure of the π-complex type is formed.

The extremely large extinction coefficient in the region of the visible absorption maximum suggests that the blue adducts with nitrogen are charge-transfer complexes. In accordance with the formula, it is reasonable to assume that the degree of oxidation of the species reacting with nitrogen is three [91,92] and that the structural formula of the complex is, for example,

$$Cp_2Ti\diagdown N \diagup\!\diagdown N \diagup TiCp_2.$$

However, the nitrogen complexes with metal compounds having the d^1 electronic configuration are at any rate very unusual and the origin of the intense blue absorption band is not clear for this type of structure. In order to retain the earlier hypothesis that bivalent titanium must be active in the relation to nitrogen, one can postulate the structure

$$[Cp_2Ti^{II}] \rightarrow N{\equiv}N \rightarrow [R_2Ti^{IV}Cp_2]$$

or

$$[Cp_2TiR]^- \rightarrow N{\equiv}N \rightarrow [Cp_2TiR]^+$$

and regard these complexes as analogous to the intensely coloured dinuclear complexes with nitrogen containing univalent rhenium, which were first obtained and investigated by Chatt et al.[93] Here nitrogen behaves as a bridge between the donor (Re^I) and the acceptor, which can be a compound incorporating metals with the d^0 electronic configuration, for example:

$$Re^I \rightarrow N{\equiv}N \rightarrow AlR_3.$$

The dinuclear complexes $(Cp_2TiR)_2N_2$ evidently constitute the first stage in the activation of nitrogen in the system under consideration. Their hydrolysis results in the liberation of molecular nitrogen without appreciable reduction. When $(Cp_2Ti\ i\text{-}C_3H_7)_2N_2$ is treated with an excess of $i\text{-}C_3H_7MgCl$, new complexes are formed which evolve hydrazine on hydrolysis after reduction at low temperatures or ammonia at temperatures above 0°C.

The nitrogen in the complex $(Cp_2TiPh)_2N_2$ can be reduced at −20°C with sodium naphthalide in THF.[91,92] This results in the formation of products, which hydrolyse with liberation of hydrazine and ammonia and also the formation of traces of aniline, the overall yield being quantitative with respect to the nitrogen in the complex. About half the nitrogen is converted into hydrazine. There is evidence that the cyclopentadienyl structure is destroyed on reduction.

In the search for intermediate complexes corresponding to more highly reduced states of nitrogen, the system $Cp_2TiCl + CH_3MgI$ was investigated[94,95] in ether. In this case Cp_2TiCH_3 is evidently formed in solution in the first stage and on cooling to −100°C reacts with nitrogen, forming an intensely blue complex. On standing for about 1 h at −70°C, the blue complex gradually disappears and a dark complex with the composition $(Cp_2Ti)_2N_2$, which is stable at room temperature, is deposited from the solution.

The infrared spectrum of this complex shows a band at 1285 cm^{-1}, shifting to 1235 cm^{-1} when $^{14}N_2$ is replaced by $^{15}N_2$, which shows that it belongs to the NN vibration.

Measurement of the magnetic susceptibility showed that the magnetic moment of the complex decreases reversibly with decrease of temperature, which suggests an equilibrium between the singlet and triplet states of the complex. It can be represented schematically as follows:

$$\underset{\text{triplet}}{Cp_2Ti^{III}-N=N-Ti^{III}Cp_2} \rightleftarrows \underset{\text{singlet}}{CpTi^{IV}=N-N=Ti^{IV}Cp_2} .$$

The difference between the energies of these two states amounts to only 85 cal $mole^{-1}$ according to the measurements of Ivleva et al.[96]

When the complex is treated with a methanol solution of hydrogen chloride at −60°C, the formation of equal amounts of nitrogen and hydrazine is observed, the sum nitrogen + hydrazine being equivalent to half the amount of titanium, in agreement with the above formula. When the complex is treated with hydrogen chloride in ether, the main products are nitrogen and ammonia (the yield of ammonia is about 30% with respect to titanium) and hydrazine is hardly formed at all. These results can be explained by the fact that in the hydrolysis of the complex the primary product is di-imide, which, depending on the conditions, subsequently disproportionates to nitrogen and hydrazine or to nitrogen and ammonia:

$$(Cp_2Ti)_2N_2 + 2HCl \rightarrow 2Cp_2TiCl + N_2H_2 ,$$
$$2N_2H_2 \rightarrow N_2 + N_2H_4 ,$$
$$3N_2H_2 \rightarrow 2N_2 + 2NH_3 .$$

Thus the complex can be regarded as a derivative of di-imide, although, according to the infrared spectroscopic data, the multiplicity of the NN linkage in the complex is probably less than two.

The complex, which evidently corresponds to the next stage in the reduction of nitrogen in the coordination sphere of titanium, was isolated in the reduction of titanocene by isopropylmagnesium chloride in the presence of nitrogen at −60°C for 3 h in ethereal solution[97]. According to analysis, its composition is $(Cp_2Ti)_2N_2MgCl$. The complex is paramagnetic, its magnetic susceptibility corresponding to one electron for two titanium atoms. According to infrared spectroscopic data, the NN vibration lies at 1260 cm^{-1}, as shown by the isotopic shift of the band to 1220 cm^{-1} when $^{15}N_2$ is used in the synthesis instead of $^{14}N_2$. In accordance with these data, the structure of the complex can be represented in the following form:

$$Cp_2Ti^{III}-N=N \rightarrow Ti^{II}Cp_2 \leftrightarrow Cp_2Ti^{IV}=N-N-Ti^{III}Cp_2 ,$$
$$\qquad\qquad\quad | \qquad\qquad\qquad\qquad\quad \diagdown$$
$$\qquad\qquad MgCl \qquad\qquad\qquad\quad MgCl$$

the second formula being preferable. When the complex $(Cp_2Ti)_2B_2MgCl$ is treated with an alcoholic solution of hydrogen chloride at −60°C, more than 80% of nitrogen is converted into hydrazine, evidently via the reaction

$$(Cp_2Ti)_2N_2MgCl + 4HCl \rightarrow Cp_2TiCl_2 + Cp_2TiCl + MgCl_2 + N_2H_4 .$$

The remainder of the bound nitrogen is converted into molecular nitrogen with simultaneous evolution of hydrogen.

When the complex $(Cp_2Ti)_2N_2MgCl$ is allowed to stand with a solution of $i\text{-}C_3H_7MgCl$ in ether at room temperature, the product is $Cp_2TiN(MgCl)_2$, which hydrolyses with formation of ammonia. Thus the sequence of stages in the reduction of nitrogen in the Cp_2TiCl_2 (or Cp_2TiCl) + RMgX systems can be represented as follows:

$$Cp_2TiCl \xrightarrow{RMgX} Cp_2TiR \underset{}{\overset{N_2}{\rightleftharpoons}} 0.5[(Cp_2TiR)_2N_2] \rightarrow 0.5[(Cp_2Ti)_2N_2] \xrightarrow{RMgX} \rightarrow$$
$$\downarrow H^+ \qquad\qquad \downarrow H^+$$
$$N_2 \qquad\qquad N_2H_2$$
$$\rightarrow 0.5[(Cp_2Ti)_2N_2MgX] \rightarrow Cp_2TiN(MgX)_2 .$$
$$H^+ \swarrow \quad \searrow RhLi,H^+ \qquad \downarrow H^+$$
$$N_2H_4 \qquad NH_3, PhNH_2 \qquad NH_3$$

It is interesting that, when the complex $(Cp_2Ti)_2N_2MgCl$ is treated with phenyl-lithium, the hydrolysis of the product results in the formation, together with ammonia, of an appreciable amount of aniline (up to 1% relative to titanium). These data and those of other investigations[91,98] concerning the formation of traces of aniline in the reduction of the complex of $(Cp_2TiR)_2N_2$ by sodium naphthalide indicate the possible mechanism of the formation of aniline in the Vol'pin–Shur systems when phenyl-lithium is employed as the reducing agent. Vol'pin and coworkers[61-64] suggest that the hydrolysis product (aniline) is formed via the insertion of nitrogen in the Ti–Ph bond:

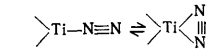
$$Ti-Ph + N_2 \rightarrow Ti-N=N-Ph \rightarrow \text{products.}$$

We now see that the Ph–N linkage can be formed also when phenyl-lithium acts on the intermediate dinuclear complexes formed in the multistage reduction of nitrogen.

Several elegant results concerning the nature and properties of the complexes in the systems containing titanocene were obtained in Brintzinger's studies[98-100]. Titanium compounds interacting with molecular nitrogen were discovered in these investigations: bis(pentamethylcyclopentadienyl)titanium(II), dicyclopentadienyltitanium(II), and its complex with triphenylphosphine. A solution of $[C_5(CH_3)_5]_2Ti$ reacts with carbon monoxide to form the dicarbonyl and with nitrogen at very low temperatures to form a complex which may be an analogue of the dicarbonyl and at a higher temperature to form an intensely coloured blue dinuclear complex containing one nitrogen molecule for two titanium atoms. The complex is in equilibrium with nitrogen and has λ_{max} = 568 nm. Dicyclopentadienyltitanium was obtained in the reactions, discovered by the authors, involving the decomposition of the hydride Cp_2TiH at room temperature. The hydride is formed in the reaction of $Cp_2Ti(CH_3)_2$ with hydrogen. When solutions of titanocene obtained in this way are cooled in the presence of nitrogen, intensely blue solutions of the complex (λ_{max} = 597 nm, $\epsilon \simeq 10^4$) are formed. The complex can be isolated from solution and has the composition $(Cp_2Ti_2)N_2$ according to the data of Bercaw et al.[101] When it is treated with solutions of lithium naphthalide the coordinated nitrogen is reduced and ammonia is evolved on hydrolysis. The complex of titanocene with triphenylphosphine $Cp_2Ti(PPh_3)$ (λ_{max} = 521 nm) interacts with nitrogen. In toluene solution at room temperature 0.33 mole of N_2 is absorbed per mole of titanium. When the resulting adduct is heated to 110°C, approximately

half the nitrogen is converted into an ammonia derivative and the remainder is evolved in the form of free nitrogen.

Bercaw et al. reported recently [101] that at low temperatures in the presence of nitrogen the dinuclear complex $\{[C_5(CH_3)_5]_2Ti\}_2N_2$ is converted into the mononuclear complex $[C_5(CH_3)_5]_2TiN_2$. ^1H, ^{13}C, and ^{15}N NMR data led them to the conclusion that in the last complex there is a reversible rearrangement of the nitrogen in the complex:



It is readily seen that all the properties of the dinuclear nitrogen complexes with titanocene obtained in a number of investigations [98-100] agree with those of the complexes $[Cp_2TiR]_2N_2$ described above, while their compositions are analogous to those of the di-imide complex, which has completely different properties.

Further investigations should show whether the above discrepancies are related to experimental inaccuracies in any of the above investigations or whether these complex nitrogen-fixing systems can indeed contain complexes with nitrogen having the same compositions and different properties and complexes of different compositions and extremely close properties.

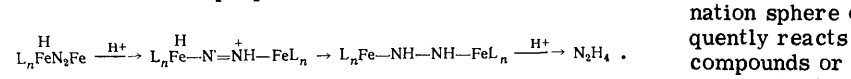
Interesting complexes with nitrogen, capable of undergoing further reduction reactions, were detected in nitrogen-fixing systems containing iron:

$$FeCl_3(PPh_3)_2 + i\text{-}C_3H_7MgCl + N_2\ ^{69,102},$$
$$FeCl_3 + LiPh + N_2\ ^{70}.$$

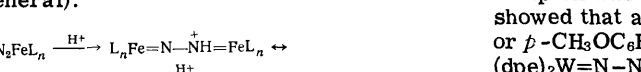
In the first of these systems in ether at −50°C a relatively unstable complex is formed with molecular nitrogen, which slowly decomposes in solution with evolution of nitrogen at a temperature as low as 0°C.

The band at 1760 cm^{-1} (there is an isotopic shift to 1710 cm^{-1} on replacement of $^{14}N_2$ by $^{15}N_2$) in the infrared spectrum corresponds to the NN vibration.

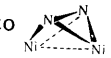
The Raman spectrum contains an exceptionally intense band at 1760 cm^{-1}. [103] This corresponds to the dinuclear fragment FeN_2Fe with high polarisability of the NN bond. Molecular nitrogen is completely evolved from the complex both on heating and on decomposition by carbon monoxide and ethyl alcohol. However, on treatment with hydrogen chloride, hydrazine is formed together with molecular nitrogen. It has been concluded [69,102] that the role of HCl consists in the protonation of the coordinated N_2 molecule, which promotes its partial reduction in accordance with the proposed mechanism:



At the present time the following mechanism appears more likely (and more general):



In the $FeCl_3$–$LiPh$–N_2 system at room temperature and atmospheric nitrogen pressure the reaction also leads to the formation of a complex with nitrogen [70]. Kinetic data (proportionality of the rate of reaction to the square of the concentration of iron, independence of nitrogen pressure above 200 torr and of the concentration of phenyl-lithium) shows that in this case the rate is limited by the formation of a dinuclear complex of the reduced iron compound (without nitrogen), which is followed by rapid coordination of nitrogen. Presumably the intermediate complex with nitrogen is also dinuclear. In this case neither the intermediate complex with nitrogen nor the final product were isolated from solution and the compositions were not determined, but the reduced iron compound is presumably stabilised by phenyl-lithium, since the independence of the rate of reaction of the concentration of phenyl-lithium is observed only in the presence of a large excess of the reducing agent.

When a solution of the product is treated with hydrogen chloride, hydrazine, nitrogen, and ammonia are formed (28, 9, and 15% of the iron content respectively). Possibly the intermediate complex is in this case to some extent analogous to the dinuclear nitrogen complex with zerovalent nickel stabilised by phenyl-lithium [104] and having the composition $\{[(PhLi)_3Ni]_2N_2.2Ft_2O\}_2$. It follows from the X-ray diffraction analysis of this stable complex [105] that the fragment Ni_2N_2 has a structure close to , the length of the NN bond (1.35 Å) being intermediate between those of single and double bonds. The lithium atoms in the phenyl-lithium molecules in the complex adjoin nitrogen atoms and exhibit electron-accepting properties, enhancing electron transfer from the nickel atom. There have as yet been no reports stating whether or not the nitrogen bound in the complex can be converted into hydrazine or another reduced compound.

In the $FeCl_3$–Mg–N_2 system in tetrahydrofuran a dinuclear complex stable at room temperature is also formed. Its composition corresponds to the formula $[(THF)_{1.5}MgCl_3Fe]_2N_2$. The complex reacts with HCl to form hydrazine [71].

Some of the examples quoted show that the instability of the complex is not a necessary condition for the involvement of nitrogen in the coordination sphere of the metal in further reactions, at least in those cases where powerful reducing agents take part in the formation of the complexes. New attempts to introduce into the reaction the nitrogen in the coordination spheres of known stable complexes are of interest in this connection.

Vol'pin et al. [106] showed that, when the complex $(Ph_3P)_3CoHN_2$ reacts with lithium napthalide in the presence of titanium tetrachloride and other transition metal compounds, the nitrogen bound in a complex with cobalt is reduced to ammonia after hydrolysis. In the absence of added transition metal salts the nitrogen is not reduced.

However, it has been established [107] that under these conditions nitrogen is initially displaced from the coordination sphere of cobalt in the form of free N_2 and subsequently reacts in the usual way with reduced titanium compounds or other additives.

The first successful attempt to introduce into the reaction with organic compounds the nitrogen in a mononuclear complex was made by Chatt et al. [108] These workers showed that acid chlorides RCOCl (R = CH_3, C_2H_5, C_3H_7, or p-$CH_3OC_6H_4$) react with *trans*-$W(N_2)_2(dpe)_2$ to form $(dpe)_2W{=}N{-}NHCOR$, where dpe = $PhPCH_2CH_2PPh_2$. The nitrogen in the reaction product is protonated, presumably owing to traces of moisture, which gives rise to hydrogen chloride. The complex can be deprotonated on reaction with triethylamine to form a new series of complexes $WCl(dpe)_2N_2COR$ having a band at 1338 cm^{-1} in the infrared corresponding to a vibration of the complex (there is a shift to 1298 cm^{-1} when the nitrogen is replaced by $^{15}N_2$). An analogous reaction with RCOCl has been discovered for the molybdenum complex of *trans*-$Mo(N_2)_2(dpe)_2$.

Another interesting reaction, discovered by Chatt et al.[109], consists in the protonation of nitrogen in *trans*-$M(N_2)(dpe)_2$ with formation of an N_2H_2 complex:

$$trans\text{-}M(N_2)_2(dpe)_2 \xrightarrow[(THF)]{HX} M(dpe)_2X_2N_2H_2 + N_2$$

(M = W or Mo; HX = HBr or HCl for W and HBr for Mo). It is suggested that the N_2H_2 group is bound to M, giving the structure

$$M\langle^{NH}_{NH}\| \quad \text{or} \quad M{=}N{-}NH_2 .$$

Thus the reduction of nitrogen to a di-imide derivative or hydrazine is caused by protonation (as suggested above for the iron complex). However, in mononuclear complexes protonation has so far precluded the isolation of the reduced products (N_2H_2, N_2H_4, or NH_3) from the coordination sphere of the metal and these results are naturally also consistent with the view that the reduction of nitrogen in a dinuclear complex should in general proceed more readily than in a mononuclear complex.

Sellman and coworkers[110-113] recently obtained new data for mononuclear and dinuclear complexes of manganese, tungsten, and chromium, with di-imide as a possible intermediate in the reduction of nitrogen. In this case the complexes were formed by the oxidation of hydrazine and not directly from molecular nitrogen and their structures and properties should naturally be examined with a certain degree of caution in relation to the mechanism of the reduction of nitrogen in the coordination sphere of the metal.

IV. REDUCTION OF NITROGEN IN PROTIC MEDIA

For a long time the biological fixation of nitrogen achieved by certain micro-organisms and algae constituted the only known nitrogen reduction reaction involving protons derived from water:

$$N_2 + 6e + 6H^+ \rightarrow 2NH_3 .$$

The attempt to carry out this reaction under non-biological conditions was begun a very long time ago. As early as 1916 Zenghelis[114] claimed that, when nitrogen is passed into hydrochloric acid in which metallic zinc dissolves a certain amount of ammonia is formed evidently by the action of hydrogen *in statu nascendi* on nitrogen.

Subsequently analogous attempts were frequently repeated. It was reported in a patent[115] that nitrogen is hydrogenated to ammonia in aqueous solutions of molybdenum hydride derivatives.

Haight and Scott[116] reported in 1964 the formation of small amounts of ammonia in the electrochemical reduction of nitrogen or in its reduction by chemical reducing agents in the presence of molybdate or tungstate. Subsequently similar results were obtained[117] using compounds of a whole series of transition metals.

It is noteworthy that, in view of the low yield of ammonia and the comparatively large amounts of the starting materials, there was always some doubt whether or not molecular nitrogen was the source of the detected ammonia. Small amounts of ammonia can be formed from impurities in the initial reagents, for example, metal nitrides or nitrogen oxides (which are reduced to ammonia under the reaction conditions). The studies by the present author and his coworkers frequently led to the detection of small amounts of ammonia in attempts to reduce nitrogen in protic media, but subsequent careful tests showed that molecular nitrogen was not the source of ammonia.

In testing for the fixation of small amounts of nitrogen one usually employs a technique involving labelled $^{15}N_2$ nitrogen, which was developed previously and was used successfully to investigate the reduction of nitrogen in biological systems. The formation of $^{15}N_2$ and $^{15}N^{14}N$ nitrogen, in amounts appreciably exceeding its natural content, in the hypobromite oxidation of the ammonia formed constitutes qualitative evidence of the fixation of nitrogen and can be used in quantitative measurements of the yield of ammonia. This method has been employed[118] in an attempt to reproduce the data for the fixation of nitrogen described by Haight and Scott[116] and Yatsimirskii and Pavlova[117], but the result was negative. There is also other evidence (see, for example, Hardy and Knight[119]) that the reduction of nitrogen under the conditions employed by the above authors[116,117] does not in fact occur.

Positive results with $^{15}N_2$ constitute an essential criterion of the validity of the results obtained when the amounts of ammonia formed are small (this must be recalled if only because analogous studies without a special test of the results continue to be reported). However, one should note that the excess of mass 29 over its natural abundance in the mass spectrum of nitrogen obtained by the oxidation of the evolved ammonia does not by itself constitute unambiguous evidence for the reduction of nitrogen and has to be tested, since it may be the result of a random contamination of the ionisation chamber of the mass spectrometer by organic substances (for example ether), which yield on ionisation fragments having a mass of 29. Evidently reproducible agreement between the results of chemical analysis (with $^{14}N_2$) and mass spectrometric analysis (with $^{15}N_2$) must be obtained.

Considerable advances have been made recently in the study of nitrogenase—the enzyme which catalyses the biological fixation of nitrogen (see, for example, the reviews of Hardy et al.[19] and Ohmes and Grundemann[20]). It is useful to examine simultaneously biological and non-biological nitrogen fixation, since progress in this field is undoubtedly largely due to the joint efforts of chemists and biologists.

1. Nitrogenase as a Catalyst of the Reduction of Nitrogen

Detailed data on nitrogenase are of course the scope of the present review. Here we shall briefly describe the features of the reduction of nitrogen in the presence of nitrogenase from the chemists' point of view.

The enzyme isolated from micro-organisms is a combination of two proteins, one of which (MoFe-protein) contains molybdenum, iron, sulphide groups, and mercapto-groups, with 1 or 2 molybdenum atoms and 20–30 iron atoms per molecule. The other (Fe-protein) contains 2 iron atoms and also sulphide and mercapto-groups. In the presence of the isolated enzyme nitrogen can be reduced by a specially added reductant—sodium dithionite. The reaction requires the presence of ATP, the reduction of nitrogen to ammonia being accompanied by the coupled hydrolysis of ATP.

In the absence of nitrogen hydrogen is evolved owing to transfer of electrons to water protons. All three nitrogenase reactions (hydrolysis of ATP, evolution of hydrogen, and the reduction of nitrogen) are possible only in the presence of both nitrogenase components—MoFe-protein and Fe-protein.

Apart from nitrogen, in the presence of the nitrogenase component other compounds containing a triple-bond can

be reduced: acetylene, nitrous oxide, isonitriles, and nitriles. Ethylene (*cis*-dideuterioethylene when the reaction is carried out in heavy water) is the product of the reduction of acetylene. Ethylene is not a substrate of nitrogenase and does not undergo further reduction.

When the system is saturated by the substrate, the rates of all the nitrogenase reactions are determined by the transfer of electrons and are thus independent of the nature of the substrate. The activation energy for the reaction amounts to 14 kcal mole^{-1} above 20°C. The presence of magnesium ions is essential for the nitrogenase reaction, possibly in order to carry out the ATPase process.

An important result concerning the structure of the enzyme was obtained by Likhtenshtein (see, for example, Ref. 120). It was found that the iron atoms entering into the composition of the MoFe-protein are combined with one another, forming a cluster of linked atoms.

It is interesting that molybdenum, which is absolutely essential for the catalysis of the reduction of nitrogen by nitrogenase, can nevertheless be replaced by vanadium. The remaining elements proved to be inactive. It proved possible recently to isolate nitrogenase containing vanadium instead of molybdenum [121,122] and showing activity for N_2.

2. Reduction of Nitrogen by Mixed Hydroxides in the Presence of Molybdenum and Vanadium Compounds

Positive and reproducible results in attempts to reduce nitrogen in protic media were obtained for the first time in 1970 and were published in a number of reports [5,6,123,124]. In their search for systems of this kind, the authors began with predictions [7] based on a theoretical treatment [16], taking into account results obtained in the study of the biological fixation of nitrogen. In the first place reagents with a reduction potential close to that of active nitrogenase and sufficient for the formation of hydrazine from nitrogen ($E_0 = -0.23$ V at pH 0) were chosen. These reducing agents must simulate the section of nitrogenase which activates electrons. It follows from theoretical considerations that the activators of molecular nitrogen must have a fully defined set of properties. It was therefore natural to select, by analogy with the biological fixation of nitrogen, compounds of molybdenum (and also vanadium, which can replace molybdenum in nitrogenase), on the hypothesis that at a sufficient reduction potential these compounds form species suitable for the activation of nitrogen.

It was suggested that the intermediates formed (for example, Mo=N–NH–Mo) must be hydrolysed with formation of hydrazine, which appears as the final or intermediate product. This hypothesis was largely responsible for success in the search for nitrogen-fixing systems, since, in contrast to ammonia, the appearance of small amounts of hydrazine from impurities is unlikely, the available analytical tests for hydrazine are very sensitive, and, having detected hydrazine, it was possible to select optimal conditions empirically.

The first system in which the formation of hydrazine from nitrogen in a protic medium was observed was Ti^{3+}–$Mo^{V\text{-}VI}$–N_2 (in aqueous or anhydrous alcohol in an alkaline medium). Subsequently the Cr^{2+}–Mo^{V}–N_2 and V^{2+}–Mo^{V} systems were discovered and it was found that, as in biological systems, vanadium compounds can replace molybdenum with retention of activity in relation to N_2. In this connection vanadium(II) compounds proved to be capable of reducing nitrogen in an aqueous medium without the addition of other transition metal compounds.

The Ti^{3+} – $Mo^{V\text{-}VI}$ – N_2 system [5,6,123–125]. In this case the reduction of nitrogen is observed only in a highly alkaline medium (at pH ≥ 10.5). With increase of the concentration of alkali, the yield of hydrazine passes through a maximum. Without the addition of molybdenum compounds ($MoOCl_3$, MoO_4^{2-}), the reaction hardly occurs.

Small amounts of hydrazine were detected even at room temperature and atmospheric pressure. The yield of hydrazine increases with nitrogen pressure and temperature.

At 90–110°C and a nitrogen pressure of 100–150 atm the system is catalytic with respect to molybdenum: several tens of nitrogen molecules can be reduced to hydrazine and ammonia per molybdenum atom. The reduction of $^{15}N_2$ proved to be consistent with the results obtained using light nitrogen.

The increase of the yield following the addition of other metal (Mg, Ca, or Ba) salts proved to be extremely interesting. Magnesium salts (chloride or sulphate) have a particularly marked effect.

The addition of these salts retards the reaction of titanium(III) hydroxide with water (which results in the evolution of hydrogen) and there is a simultaneous increase of the yield of hydrazine. It proved to be a maximum for the ratio Mg : Ti = 1 : 2.

At low temperatures hydrazine is virtually the only nitrogen reduction product. Above 85°C ammonia appears, its relative yield increasing with temperature. A kinetic study showed [125] that ammonia is a secondary product and is formed on reduction of hydrazine. Carbon monoxide and acetylene inhibit the reaction. In the presence of carbon monoxide a yellow carbonyl compound of molybdenum, in which the oxidation state of molybdenum is three, passes into the solution. Under these conditions, acetylene is reduced to ethylene, the reaction occurring also without molybdenum compounds.

In the absence of nitrogen the system evolves hydrogen from water irreversibly. Under these conditions, hydrogen cannot, of course, reduce nitrogen to hydrazine in an alkaline medium. However, it has been shown [126] that in an acid medium hydrogen can be used as a reducing agent for titanium(IV) (in the presence of platinum) and, after increasing the alkalinity of the solution, the resulting titanium(III) can (in the presence of molybdenum) reduce nitrogen to hydrazine. Thus, under the conditions of alternate increase of the acidity and alkalinity of the solution, hydrogen can reduce nitrogen to hydrazine; the energy deficiency is then in fact made good by the energy of neutralisation of the acid by alkali.

The temperature variation of the rate yields an activation energy for the reduction of nitrogen to hydrazine of 13 kcal mole^{-1}. [125] The attempts to employ instead of molybdenum other transition elements combined with titanium(III) were unsuccessful. Only vanadium compounds (for example $VOCl_2$) proved to be capable of replacing molybdenum with partial retention of activity in relation to nitrogen.

The Cr^{2+} – Mo^{V} – N_2 system [6,126]. Nitrogen is reduced to hydrazine when an aqueous alcoholic suspension of chromium(II) hydroxide is mixed with an $MoOCl_3$ solution in an atmosphere of nitrogen. In this case the reaction proceeds at an appreciable rate even in room temperature and the minimal concentration of alkali at which nitrogen is reduced to hydrazine is appreciably less than in the presence of titanium(III). The catalytic yields in relation to molybdenum were not determined in this system.

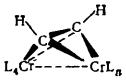
In such systems acetylene is also reduced in the absence of molybdenum, the reaction occurring in acid

solutions of chromium(II) salts as well. In this connection we may note that, in one of the earlier attempts to investigate the reduction of acetylene to ethylene from the standpoint of the simulation of the nitrogenase reaction, a study was made of the process [127]

$$C_2H_2 + 2Cr^{2+} + 2H^+ \rightarrow C_2H_4 + 2Cr^{3+} .$$

This reaction, discovered as early as 1916, [128] is interesting because, as in the case of nitrogenase, acetylene is quantitatively converted into ethylene without further reduction to ethane. The rate of reaction is proportional to the square of the concentration of chromium, which indicates the formation of a dinuclear complex of chromium ions and acetylene. Indeed, on cooling aqueous alcoholic solutions, the reversible formation of a relatively unstable dinuclear complex of acetylene and chromium, the heat of formation of which is only about 2 kcal mole^{-1}, was observed spectroscopically [129].

Further study of the analogous but more stable complex, which is formed in the presence of ammonia and can be isolated from the solution, showed [130] that its structure corresponds most closely to the formula



with a C–C bond close to a single bond and sp^3-hybridised C–H bonds. Thus acetylene in the complex is in fact reduced by a "four-electron" mechanism to an ethane derivative.

The reduction of acetylene in aqueous solution of chromium(II) salts is catalysed by acids and can be represented as follows:

$$2Cr^{2+} + C_2H_2 \rightleftharpoons [CrC_2H_2Cr]^{4+} \xrightarrow{H^+} [CrC_2H_3Cr]^{5+} \xrightarrow{H^+} 2Cr^{3+} + C_2H_4 .$$

Studies [131] on the reduction of other unsaturated compounds in a solution of chromium(II) salts showed that the mechanism involving two chromium ions is general. In acid media nitrogen is not reduced by Cr^{2+} ions, although the reduction potential of chromium(II) $E_0 = -0.40$ V is sufficient to form hydrazine from nitrogen. Admittedly it has been reported [132] that small amounts of ammonia are present in acid solutions in the reduction of nitrogen by zinc in the presence of chromium(VI) compounds, but these results were not confirmed by use of labelled nitrogen and are as usual doubtful.

The formation of small amounts of hydrazine in the electrochemical reduction of nitrogen in acid solutions in the presence of molybdenum complexes has been reported [133]. The yields did not exceed 1% with respect to molybdenum and varied appreciably from experiment to experiment.

The $V^{2+}-N_2$ system [6,124,134,135]. The formation of hydrazine was observed on mixing an aqueous alcoholic suspension, prepared beforehand, of a mixture of vanadium(II) and magnesium hydroxides with an $MoOCl_3$ solution in an atmosphere of nitrogen. In this case appreciable yields of hydrazine were observed at high temperatures and high concentrations of alkali (in excess of 1 M).

Hydrazine is also formed on reduction of nitrogen in aqueous solution by freshly precipitated vanadium(II) hydroxide produced in the presence of added magnesium salts. In this instance the presence of molybdenum compounds is not required.

This, the simplest of the known nitrogen-reducing systems, proved to be the most active. When the optimal conditions are selected, nitrogen is reduced at a high rate in aqueous solutions even at room temperature and under an atmospheric nitrogen pressure. Together with hydrazine, ammonia is formed even at room temperature. The reaction again proceeds only in strongly alkaline media.

In this case magnesium salts proved to be even more important than for other analogous systems: in their absence hydrazine is hardly formed. At room temperature and [atmospheric ?] nitrogen pressure the reaction ceases (the system loses activity) when the yield of reduction products reaches 8–20% relative to the reducing agent, but, on raising the nitrogen pressure to 20–40 atm, the overall yield of hydrazine and ammonia becomes nearly quantitative, i.e. the following reactions take place:

$$4V(OH)_2 + N_2 + 4H_2O \rightarrow 4V(OH)_3 + N_2H_4 ,$$
$$6V(OH)_2 + N_2 + 6H_2O \rightarrow 6V(OH)_3 + 2NH_3 .$$

Vanadium(II) is comparatively readily regenerated by the electrochemical reduction of the vanadium(III) formed. In this connection and bearing in mind that, by selecting appropriate conditions it is possible to drive the reaction solely to the formation of hydrazine, the reaction can be employed as a new method for the synthesis of hydrazine from molecular nitrogen [136].

Kinetic data again show that ammonia is a secondary product formed by the reduction of hydrazine.

The activation energy for the reduction of nitrogen to hydrazine is only 10 kcal mole^{-1}. The vanadium system is also active in the presence of inhibitors of nitrogen fixation [134]. Under these conditions, carbon monoxide hardly retards the reduction of nitrogen. Acetylene competes with nitrogen for active centres (being itself converted into ethylene). Under these conditions, acetylene is only three times more active than nitrogen.

Even the reactivity of oxygen is comparable to that of molecular nitrogen in the reaction in alkaline solutions containing a suspension of vanadium(II) hydroxide in the presence of magnesium hydroxide. Therefore such solutions are capable of fixing nitrogen directly from air. The yield of reduction products is smaller only by a factor of two compared with pure nitrogen [134].

The oxidation-reduction potential of the system was measured and its relation to activity with respect to nitrogen was investigated [137].

3. Reduction of Nitrogen in Homogeneous Solutions of Vanadium Complexes [138,139]

In the search for homogeneous systems capable of fixing N_2 in protic media, Nikonova et al. [138] observed that vanadium(II) complexes with phenols containing two hydroxy-groups in *ortho*-positions relative to one another (catechol, dihydroxynaphthalene, etc.) have this ability. In alcoholic, aqueous alcoholic, and aqueous media the complexes can rapidly reduce nitrogen to ammonia even at room temperature and atmospheric pressure; the yield of ammonia increases with pressure and temperature.

The reaction with nitrogen proceeds in a narrow pH range [139]. The maximum yield in water (about 60% at room temperature, $P_{N_2} \geq 70$ atm) is attained at pH ~ 10. In this case the intermediate formation of hydrazine is not observed, which may be related to its reduction under the experimental conditions. Indeed, it has been shown that hydrazine is rapidly reduced to ammonia by vanadium(II) complexes of catechol.

Simultaneously with the reduction of nitrogen, the complexes decompose water, hydrogen being evolved. Under these conditions acetylene is reduced to ethylene, *cis*-dideuterioethylene being formed from C_2D_2 in H_2O. [140]

4. The Reduction of Nitrogen in Molybdenum–Thiol Systems

Schrauzer and coworkers reported in 1970–1971 the reduction of nitrogen to ammonia by sodium tetrahydroborate in the presence of molybdate and compounds containing mercapto-groups (cysteine, thioglycerol, and glutathione)[141,142]. The authors regard this system as a close model of nitrogenase, although under the optimal conditions the yield of ammonia is extremely small, reaching 0.06–0.1% relative to the initial molybdenum compound after five days at a nitrogen pressure of 140 atm. In later communications[143,144] the authors reported that the results were confirmed with the aid of labelled nitrogen $^{15}N_2$.

Acetylene inhibits the reduction of nitrogen, while carbon monoxide does not affect the yield of ammonia appreciably. In order to account for the absence of the inhibiting capacity of CO (in contrast to the behaviour in the biological fixation of nitrogen), the authors suggest the existence of an additional coordination site at the molybdenum atom (which is occupied by the enzyme in the biological system). However, it is not clear why CO cannot occupy also the second coordination site at the molybdenum atom. It is likewise difficult to imagine that, after its addition to molybdenum, the reactivity of carbon monoxide with respect to N_2 remains unchanged (this is evidently postulated by the authors).

Much higher yields of ammonia (1.5 moles of ammonia per mole of molybdate) have been quoted[145] for the Na_2MoO_4–$FeSO_4$–$NaBH_4$–N_2 system in the presence of 2-aminoethanethiol. However, subsequently the authors[145] were unable to reproduce their results (see Chatt and Leigh[25]). It was found that the system incorporating the pure reactants is virtually inactive with respect to nitrogen and it has been tentatively suggested that the system can begin to reduce nitrogen only after undergoing changes under the influence of certain hitherto unknown factors.

The data reported by Schrauzer and coworkers concerning the activity of molybdenum–thiol systems with respect to nitrogen are also still very contradictory. Thus the role of the added iron salts is obscure. In the first report[141] the authors do not mention iron, while in the next[142] they note that an iron salt is a necessary cocatalyst. Finally, it was stated in a recent communication[144] that an iron salt increases the yield of ammonia only slightly. In the same report[144], it is unexpectedly stated that the primary reaction product is di-imide, which accumulates in the course of 40 min.

It has been reported[146] that nitrogen is not reduced at all by sodium tetrahydroborate in the presence of the molybdenum–glutathione complex. These contradictions are probably related to the low activity of the system with respect to nitrogen.

Much more definite results were obtained for the reduction of other compounds, which can serve as substrates of nitrogenase: acetylene, isonitriles, etc. In particular it has been shown that acetylene[147] yields ethane simultaneously with ethylene, the latter not being an intermediate in the formation of ethane. This distinguishes molybdenum–thiol systems from nitrogenase, in the presence of which the only reduction product is ethylene. The very fact of the formation of ethane in this case constitutes direct confirmation of the possibility of the "four-electron" reduction of acetylene without its emergence from the coordination sphere of the complex.

One of the characteristic features of molybdenum–thiol systems is the activating effect of ATP, which, as stated by Schrauzer et al.[147], simulates the action of ATP on the functioning of nitrogenase. However, it has been established[148,149] that hydrolysis of ATP hardly occurs under the conditions of the operation of molybdenum–thiol system and the accelerating effect of ATP as well as of ADP and other nucleoside phosphates is in fact related to a change in the pH of the medium. Other acids, for example, sulphuric acid, act no less effectively.

Molybdates are not unique catalysts in these systems. For example, in the reduction of isonitriles molybdate can be replaced by compounds of other transition metals (WO_4^{2-}, VO_3^-, Pd^{2+}, Rh^{3+}, Ru^{3+}, Co^{3+}, and Fe^{2+}), some of which are more effective than molybdenum compounds[143].

5. The Cobalt–Porphyrin System

A reduction system containing a soluble porphyrin derivative of cobalt—*meso*-tetra(*p*-phenylsulphonato)-porphinatocobalt(III) (CoTPPS) and sodium tetrahydroborate—was described in a recent study[150]. The authors reported the reduction of nitrogen "on passing pure dry air" through an aqueous solution containing CoTPPS and $NaBH_4$ at pH 10. When the reaction was carried out over a period of one week with a daily addition of sodium tetrahydroborate solution, the authors observed the formation of 0.8–1 mole of ammonia per mole of CoTPPS. However, when these results were tested with the aid of labelled nitrogen[151], it was observed that the entire ammonia detected[150] is not formed from molecular nitrogen but evidently originates from the nitrogen of the porphyrin rings, i.e. the system is not active with respect to N_2. On the other hand, according to these data[150], the system reduces acetylene catalytically to ethylene and partly to ethane. Other unsaturated compounds (azide, cyanide, and acetonitrile) are also reduced catalytically. It is suggested that, under the influence of sodium tetrahydroborate, $Co^{III}TPPS$ is reduced to a cobalt(I) derivative which is involved in the reduction of the substrates. It was established earlier that cobalt(I) derivatives readily reduce nitrous oxide to nitrogen[152,153].

6. Complexes of Iron Compounds

It has been shown[154] that certain nitrogenase substrates can be reduced catalytically in the presence of iron complexes. The reducing agents were sodium tetrahydroborate or sodium dithionite in alcohol, water, or buffer mixtures. In the presence of dichlorotetrapyridineiron(II) as a catalyst sodium azide is reduced by sodium tetrahydroborate to ammonia and nitrogen. Cyanide is reduced to methane and ammonia. On reduction, acetonitrile give rise to ethane and ammonia. Acetylene and methylacetylene are reduced slowly to ethylene and propene and ethylene is reduced fairly rapidly to ethane, the last reaction being strongly inhibited by acetylene, which indicates the formation of stable acetylene complexes. On the basis of their results, the authors conclude that at the present time model experiments do not demonstrate whether molybdenum, iron, or both metals activate nitrogen in the nitrogenase reaction.

It has been noted that low yields of ammonia are formed when molecular nitrogen is reduced by iron complexes. However, without a test using $^{15}N_2$ these results give rise to the usual doubts.

7. The Mechanism of the Reduction of Nitrogen in Protic Media

Since the discovery of systems reducing nitrogen in protic media, only a short time has as yet elapsed and many aspects of the mechanism of the action of these systems still remain obscure.

The isolation of the carbonyl derivative of molybdenum(III) in the Ti^{3+}–$Mo^{V\text{-}VI}$ nitrogen-fixing system in the presence of CO permits the conclusion that nitrogen is also activated by species containing molybdenum(III) (d^3 electronic configuration). Vanadium in the bivalent state, i.e. also in the d^3 electronic configuration, is active in relation to nitrogen.

The high pH values at which hydroxides are active with respect to N_2 provide evidence that the transition metal atoms interacting with N_2 have an effective negative charge. This is evidently required primarily to create a higher reduction potential. In homogeneous vanadium systems phenols, which are powerful electron donors, also probably increase the reduction potential of the system and ensure the reduction of N_2.

However, the results show that a high reduction potential is by itself insufficient for the creation of active systems. Vanadium(II) and molybdenum(III) systems exhibit specific activity in relation to nitrogen and their presence is essential. Presumably the d^3 configuration of molybdenum(III) and vanadium(II) makes them fairly powerful one-electron reducing agents and ensures the stability of the intermediate complex of the type

$$M{=}{=}N{=}{=}N{=}{=}M$$

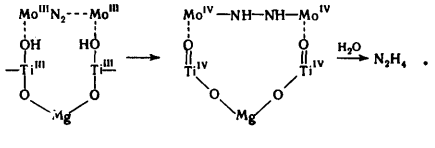
as a result of a dative interaction of the remaining electron pairs at the M atoms with the π-linkage of nitrogen.

The dinuclear structure is indicated particularly by the much higher activity of these systems in relation to acetylene molecules than in relation to ethylene[155]. The role of added metal salts, particularly of magnesium compounds, also confirms the necessity for a polynuclear structure. Data concerning the retardation of the formation of hydrazine in the vanadium system by vanadium(III) ions[156] led to the conclusion that a quartet of four vanadium(II) ions at a short distance from one another is necessary.

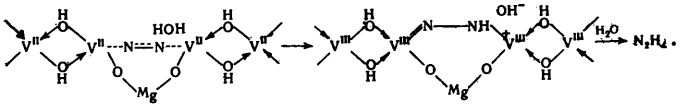
Apparently two vanadium ions form a dinuclear complex with N_2 and two other ions must transfer an additional two electrons to activated nitrogen in order to achieve the four-electron reduction to hydrazine. The magnesium ion (the efficiency of which is related to its small dimensions and the high concentration of charge) evidently forms a suitable structure, moving apart the atoms of the reducing agent to a specific distance with the aid of hydroxo- or oxo-bridging bonds.

These postulates are confirmed by measurements of the magnetic susceptibility of vanadium(II) hydroxide in the presence and absence of magnesium ions[157]. In the presence of magnesium ions the effective magnetic moment per vanadium atom increases, which indicates a decrease of electron exchange between the vanadium atoms.

The following mechanism for the formation of hydrazine in the Ti^{3+}–$Mo^{V\text{-}VI}$–Mg^{2+}–N_2 system has been suggested[124] (bearing in mind that molybdenum takes part in the reaction in the tervalent state):



A similar mechanism can be proposed for systems incorporating vanadium(II) hydroxide, but in this case vanadium ions play the role of all four atoms. One cannot rule out the possibility that a water molecule is involved in the reaction and that the mechanism is heterolytic. For example, the following mechanism can be proposed for the vanadium(II)–magnesium(II) hydroxide:



In homogeneous systems polyoxyaryl ligands also apparently give rise to dinuclear complexes. In all cases it is suggested that a dimolybdenum (or divanadium) structure is created in the intermediate complex and not one with two different metals, for example Mo^{III} and Cr^{II} or Mo^{III} and Ti^{III}.

There is as yet no direct proof of this hypothesis, although in dinuclear complexes in vanadium systems the second atom in the complex cannot of course be other than vanadium. However, bearing in mind that the reducing agent is not specific, it appears more likely that the reducing agents transfer electrons (and hydrogen atoms) to nitrogen activated in the complex containing two molybdenum atoms and in molybdenum systems.

V. COMPARISON OF NITROGENASE AND VARIOUS NITROGEN-FIXING SYSTEMS

The problem of which systems simulate the action of nitrogenase and which cannot be regarded as its models is to some extent academic. It appears that an absolute model cannot exist at all and that each reaction investigated from the standpoint of the simulation of nitrogenase simulates only a property or several properties of the enzyme. In the course of development of our knowledge of the mechanism of the action of nitrogenase, and following the discovery of new nitrogen-fixing systems, the models have improved to an increasing degree.

One can agree with the view of Newton et al.[154] that "the crucial test of a nitrogenase model is its ability to catalyse the reduction of molecular nitrogen at ambient temperature and pressure". However, the most general conclusions are apparently obtained not from a comparison of nitrogenase with any one nitrogen reduction reaction, but by examining the sum total of the information concerning both the reaction of nitrogen and systems which do not reduce nitrogen and can be regarded as models only by convention.

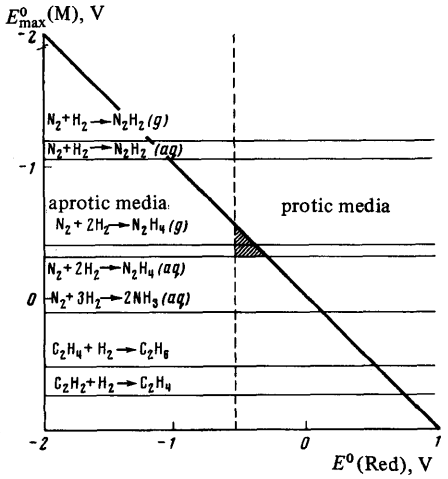
Moreover, the number of nitrogen reduction reactions under the conditions approaching those in which nitrogenase is active is so far small and it is therefore reasonable to consider also the reactions of other nitrogenase substrates. The available results permit the following generalisation. Many transition metals in low valent states can activate and reduce nitrogen to nitrides in aprotic media under the influence of powerful reducing agents. In protic media, including the aqueous medium, moderately strong reducing agents reduce acetylene and other nitrogenase substrates, also in the presence of a large number of various transition metal compounds.

The reduction of nitrogen in protic media (by moderately strong reducing agents) at a fairly high rate has so far been observed only for metals which are effective as part of the active centre of nitrogenase, namely molybdenum and vanadium. This agreement can hardly be fortuitous

and is evidently a consequence of a profound analogy between the mechanism of the action of nitrogenase and of systems reducing nitrogen in protic media.

There is no reason to suppose that in the future systems incorporating other metals in the active centre will not be discovered. However, there is no doubt that molybdenum and vanadium compounds in simple combinations form active nitrogen-fixing systems more readily than other metals.

The explanation of the comparative scarcity of nitrogen-reducing systems is probably related, to a first approximation, to the energetic difficulties which were considered in Section II of the present review.



Schematic representation of the free energy relations of nitrogen-fixing reactions.

The situation is illustrated schematically in the Figure, where the horizontal lines represent the free energies of the corresponding reactions referred to one electron and the inclined line corresponds to the maximum reduction potential of the catalyst M (which must not exceed the potential of the reducing agent Red participating in the reaction). At a given reduction potential, a particular reaction is possible if the corresponding horizontal line is located underneath the inclined straight line. Naturally, the greater the distance between the inclined and horizontal lines the greater the probability of finding a catalyst M for this reaction, other conditions being equal.

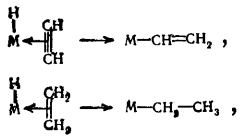
At very high reduction potentials there is a possibility of two-electron reduction of nitrogen. In such instances the rupture of the π-linkage can occur in the mononuclear complex with subsequent formation of the structure M–N=N–M', where M' is a non-transition metal, for example lithium. At even higher potentials there is a possibility of a one-electron mechanism and the transition metal ceases to be necessary for the reduction of nitrogen.

When E^0 is reduced, the formation of a dinuclear complex MN_2M with two transition metals, which is stabilised by the additional interaction of the *d* electrons with the π-linkages of nitrogen, becomes necessary. In this case there is a possibility of further reduction to a hydrazine derivative and then to the nitride with the maximum yield (in catalytic systems) of one nitride molecule per transition metal atom. The majority of the Vol'pin–Shur systems are of this kind. When the difference between E^0 and the value for hydrazine (or its derivative) is large, there is a high probability that the transition metal compound present in the system will be suitable for the activation and reduction of N_2.

On further decrease of E^0 and transition to protic media, the difference between the potentials of the reducing agent and hydrazine falls and the probability of catalytic action by the transition metal is sharply diminished. We have seen that in the presence of reducing agents sufficiently powerful to reduce nitrogen in protic media the transition metal must possess a comparatively rare combination of a specific set of properties. It is not surprising that such systems are encountered rarely and that in the course of evolution nature has chosen the metals which permit the most efficient reduction of nitrogen.

The difference between the potentials of the reducing agent and the acetylene–ethylene pair can remain considerable under these conditions also on further decrease of E^0. Naturally the probability that the transition metal compound will prove suitable is fairly high and many transition metals may be catalytically active.

Here a mononuclear structure of the complex is again possible. The weakness of the π-linkage in acetylene and ethylene permits the reactions



which take place in numerous known catalytic hydrogenation reactions of unsaturated molecules.

From the standpoint of this approach, the structure of the intermediate complex in nitrogenase as well as in nitrogen-fixing systems in protic media must be dinuclear.

Examination of model systems thus confirms the conclusions reached in studies on the mechanism of the activation of nitrogen by nitrogenase, where a dinuclear structure of the intermediate complex is adopted (see, for example, Refs. 19 and 120) and one of the atoms activating the N_2 molecule is definitely molybdenum. It has been by no means clearly shown whether two molybdenum atoms or one molybdenum atom and one iron atom, as suggested in some investigations [19,158], enter into the dinuclear structure of the nitrogenase complex.

As already stated, in model systems the activation of N_2 presumably takes place in dinuclear complexes involving only molybdenum atoms and the reducing agent transfers electrons to the activated nitrogen.

Thus the study of the fixation of nitrogen in model systems currently known suggests that it is more likely that the biological process also involves two molybdenum atoms rather than one molybdenum atom and one iron atom, although this conclusion cannot be regarded as unambiguous.

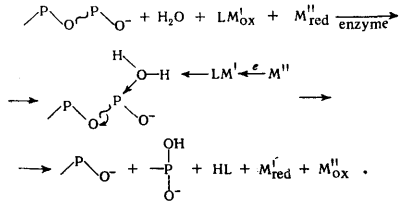
One may note yet another analogy between the nitrogenase and model systems involving hydroxides, which is probably not fortuitous. The metal atoms participating in electron transfer are linked in both cases (in nitrogenase iron ions are linked via bridging sulphide bonds [120] and in the hydroxides Ti^{III}, Cr^{II}, and V^{II} atoms are joined via hydroxo- and oxo-bridges). Presumably this ensures the possibility of many-electron processes involving the nitrogen bound in the complex.

An important characteristic of the biological fixation of nitrogen is the fact that it proceeds as a process coupled with the hydrolysis of ATP. The mechanism of the action of ATP is still obscure.

According to the hypothesis adopted at present[19], the hydrolysis of ATP tends to increase E^0 for the system. Parshall[159] suggests that the phosphorylation of the molybdenum complexes facilitates the formation of molybdenum hydride.

Studies on the changes in the ESR spectra under the influence of ATP have shown[160] that the ATP linked to Fe-protein in nitrogenase does in fact ensure electron transfer from Fe-protein to MoFe-protein. These results are consistent with those of Syrtsova et al.[161] who showed that ATP is not located unduly close to MoFe-protein of nitrogenase, where the nitrogen molecule is evidently activated by combining with the molybdenum atom.

Models of the action of ATP are so far unknown in the reduction of nitrogen in non-biological systems. On the other hand, in many of the examples quoted in the review involving the reduction of both nitrogen and other compounds, an acid which protonates the substrate and facilitates the reduction plays an activating role. In this connection it is possible to suggest[148,149] that an active proton is formed in the hydrolysis of ATP which ensures electron transfer (for example from the iron atom of Fe-protein of nitrogenase to the iron cluster of MoFe-protein). For example, the following chemical mechanism of this coupled process may be suggested:



As a result of the energy of the high-energy bond of ATP the potential of M' (for example of the iron cluster of MoFe-protein) may be sufficiently high to reduce the activated nitrogen molecule.

Naturally the suggested mechanism of the action of ATP requires a definite steric activation by the enzyme molecule, which has not so far been achieved in non-biological studies.

The alkaline medium in model systems creates an effective negative charge on the metal atoms activating molecular nitrogen and increases thereby the reduction potential of the system. In this case there is no need for additional activation by the proton arising in the hydrolysis of ATP and the water proton can prove to be a sufficiently powerful acceptor.

The determination of further details of the relation between the mechanism of the reduction of nitrogen in models systems and its enzymatic reduction would probably require the introduction of a large number of unjustified hypotheses and would not at present be useful for the determination of new and more specific data concerning the mechanism, particularly since the rapid development of this field will evidently make it possible in the near future to employ firmly established experimental facts as a basis.

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During the decade which has elapsed since the discovery of the nitrogen reduction reactions in solutions of transition metal complexes, the chemistry of molecular nitrogen has already required serious revision and considerable expansion. There is no doubt that progress in this field will continue also in the future.

Processes of practical value should presumably be developed in parallel with the discovery of new reactions which are of fundamental interest, particularly reactions which are still closer models of the biological fixation of nitrogen. Although competition with the modern large-scale ammonia synthesis is hardly likely in the immediate future, one may hope that the syntheses of other nitrogen-containing substances will find applications in the laboratory or in industry.

Molecular nitrogen is becoming an increasingly common ligand and reagent in catalytic and non-catalytic reactions.

REFERENCES

1. M. E. Vol'pin and V. B. Shur, Dokl. Akad. Nauk SSSR, **156**, 1102 (1964).
2. A. D. Allen and C. V. Senoff, Chem. Comm., 621 (1965).
3. A. E. Shilov, A. K. Shilova, and Yu. G. Borod'ko, Kinetika i Kataliz, 7, 768 (1966).
4. A. E. Shilov, A. K. Shilova, and E. F. Kvashina, Kinetika i Kataliz, **10**, 1402 (1969).
5. N. T. Denisov, V. F. Shuvalov, N. I. Shuvalova, A. K. Shilova, and A. E. Shilov, Kinetika i Kataliz, **11**, 813 (1970).
6. N. T. Denisov, O. N. Efimov, N. I. Shuvalova, A. K. Shilova, and A. E. Shilov, Zhur. Fiz. Khim., **44**, 2694 (1970) [Russ. J. Phys. Chem., No. 11 (1970)].
7. Yu. G. Borod'ko and A. E. Shilov, Uspekhi Khim., **38**, 761 (1969) [Russ. Chem. Rev., No. 5 (1969)].
8. J. Chatt and R. L. Richards, "The Chemistry and Biochemistry of Nitrogen Fixation", Plenum Press, London, 1971, p. 57.
9. A. D. Allen, R. O. Harris, B. R. Loescher, J. R. Stevens, and R. N. Whiteley, Chem. Rev., **73**, 11 (1973).
10. M. Anbar, J. Amer. Chem. Soc., **88**, 5924 (1966).
11. W. B. De More and N. Davidson, J. Amer. Chem. Soc., **81**, 5869 (1959).
12. D. Katakis and H. Taube, J. Chem. Phys., **36**, 416 (1962).
13. Yu. G. Borod'ko, A. E. Shilov, and A. A. Shteinman, Dokl. Akad. Nauk SSSR, **168**, 581 (1966).
14. A. E. Shilov, A. A. Shteinman, and M. B. Tjabin, Tetrahedron Letters, 4177 (1968).
15. L. Pauling, "The Nature of the Chemical Bond", 3rd Edition, Cornell University Press, New York, 1960, p. 189.
16. G. I. Likhtenshtein and A. E. Shilov, Zhur. Fiz. Khim., **44**, 849 (1970) [Russ. J. Phys. Chem., No. 4 (1970)].
17. N. Bauer, J. Phys. Chem., **64**, 833 (1970).
18. J. Pratt, J. Theoret. Biol., **2**, 251 (1962).
19. R. W. F. Hardy, R. C. Burns, and G. W. Parshall, Adv. Chem. Ser., No. 100, 219 (1971).
20. R. Ohmes and C. Grundemann, Z. Chem., **7**, 268 (1970).
21. R. S. Diecson and J. A. Ibers, J. Amer. Chem. Soc., **91**, 2988 (1972).
22. G. I. Likhtenshtein, Doctoral Thesis, Institute of Chemical Physics of the USSR Academy of Sciences, Moscow, 1971.
23. M. E. Vol'pin, V. B. Shur, and L. P. Bichin, Izv. Akad. Nauk SSSR, Ser. Khim., 720 (1965).
24. M. E. Vol'pin and V. B. Shur, Zhur. Vses. Khim. Obshch. im. Mendeleeva, **12**, 31 (1967).

25. J. Chatt and G. J. Leigh, Chem. Soc. Rev., 121 (1971).
26. M. E. Vol'pin, V. B. Shur, and M. A. Ilatovskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1728 (1964).
27. M. E. Vol'pin, A. A. Belyi, and V. B. Shur, Izv. Akad. Nauk SSSR, Ser. Khim., 2225 (1965).
28. M. E. Vol'pin, V. B. Shur, V. N. Latyaeva, L. I. Vyshinskaya, and L. A. Shul'tsgaizer, Izv. Akad. Nauk SSSR, Ser. Khim., 385 (1966).
29. M. E. Vol'pin and V. B. Shur, Nature, **209**, 1236 (1966).
30. M. E. Vol'pin and V. B. Shur, Organometal. React., **1**, 55 (1970).
31. G. Henrici-Olive and S. Olive, Angew. Chem. Int. Edit., **8**, 650 (1969).
32. E. E. van Tamelen, Acc. Chem. Res., **3**, 361 (1970).
33. G. J. Leigh, see Ref. 8, p. 19,
34. G. Henrici-Olive and S. Olive, Angew. Chem., Int. Edit., **6**, 873 (1967).
35. E. E. van Tamelen, G. Boche, and R. Greeley, J. Amer. Chem. Soc., **90**, 1677 (1968).
36. E. Bayer and V. Schurig, Chem. Ber., **102**, 3378 (1969).
37. L. G. Bell and H. H. Brintzinger, J. Amer. Chem. Soc., **92**, 4464 (1970).
38. T. P. M. Beelen and M. Van Erk, Rec. Trav. chim., **90**, 1197 (1971).
39. M. E. Vol'pin, M. A. Ilatovskaya, and V. B. Shur, Kinetika i Kataliz, **11**, 33 (1970).
40. M. E. Vol'pin, M. A. Ilatovskaya, E. I. Larikov, M. L. Khidekel', Yu. A. Shvetsov, and V. B. Shur, Dokl. Akad. Nauk SSSR, **164**, 331 (1965).
41. E. E. van Tamelen and D. A. Seeley, J. Amer. Chem. Soc., **90**, 4492 (1968).
42. E. E. van Tamelen, G. Boche, and R. Greeley, J. Amer. Chem. Soc., **90**, 1677 (1968).
43. E. E. van Tamelen and B. Akermark, J. Amer. Chem. Soc., 90, 4492 (1968).
44. D. R. Gray and C. H. Brubaker, Chem. Comm., 1239 (1969).
45. M. E. Vol'pin, N. K. Chapovskaya, and V. B. Shur, Izv. Akad. Nauk SSSR, Ser. Khim., 1083 (1966).
46. G. Natta, P. Corradini, and I. Bassi, J. Amer. Chem. Soc., 80, 755 (1958).
47. A. K. Zefirova, N. N. Tikhomirova, and A. E. Shilov, Dokl. Akad. Nauk SSSR, **132**, 1082 (1960).
48. M. L. Khidekel' and Yu. B. Grebenshchikov, Izv. Akad. Nauk SSSR, Ser. Khim., 761 (1965).
49. M. E. Vol'pin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, Chem. Comm., 1074 (1968).
50. M. E. Vol'pin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, Dokl. Akad. Nauk SSSR, **180**, 103 (1958).
51. M. Sudo, M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, J. Amer. Chem. Soc., **73**, 1174 (1969).
52. K. Tamaru, Catalysis Rev., **4**, 161 (1970).
53. A. Ozaki, K. Aika, and H. Hori, Bull. Chem. Soc. Japan, **44**, 3316 (1971).
54. K. Aika, H. Hori, and A. Ozaki, J. Catalysis, 27, 424 (1972).
55. G. N. Nechiporenko, G. M. Tabrina, A. K. Shilova, and A. E. Shilov, Dokl. Akad. Nauk SSSR, **164**, 1062 (1965).
56. G. Natta, G. Mazzanti, and G. Pregaglia, Gazzetta, **89**, 3065 (1959).
57. A. Yamamoto, M. Ookawa, and S. Ikeda, Chem. Comm., 841 (1969).
58. A. Yamamoto, S. Go, M. Ookawa, M. Takahashi, S. Ikeda, and T. Keii, Bull. Chem. Soc. Japan, **45**, 3110 (1972).
59. Yu. A. Shvetsov, L. G. Korableva, G. N. Nechiporenko, M. A. Ilatovskaya, and M. L. Khidekel', Dokl. Akad. Nauk SSSR, **178**, 400 (1968).
60. E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, J. Amer. Chem. Soc., **89**, 5707 (1967).
61. M. E. Vol'pin and V. B. Shur, Izv. Akad. Nauk SSSR, Ser. Khim., 1873 (1966).
62. M. E. Vol'pin, A. A. Belyi, N. A. Katkov, R. G. Kudryavtseva, and V. B. Shur, Izv. Akad. Nauk SSSR, Ser. Khim., 2858 (1969).
63. M. E. Vol'pin, A. A. Belyi, V. B. Shur, N. A. Katkov, I. M. Nekaeva, and R. V. Kudryavtsev, Chem. Comm., 246 (1971).
64. V. B. Shur, E. G. Berkovich, and M. E. Vol'pin, Izv. Akad. Nauk SSSR, Ser. Khim., 2358 (1971).
65. E. E. van Tamelen and H. Rudler, J. Amer. Chem. Soc., **92**, 5253 (1970).
66. A. Dormond, J. C. Le Blane, F. Le Moigne, and J. Tirouflet, Compt. rend., **274**, 1707 (1972).
67. E. E. van Tamelen, R. B. Fechter, and S. W. Schneller, J. Amer. Chem. Soc., **91**, 7196 (1969).
68. A. E. Shilov and A. K. Shilova, Zhur. Fiz. Khim., **44**, 288 (1970) [Russ. J. Phys. Chem., No. 1 (1970)].
69. M. O. Broitman, N. T. Denisov, N. I. Shuvalova, and A. E. Shilov, Kinetica i Kataliz, **12**, 504 (1971).
70. M. O. Broitman, T. A. Vorontsova, and A. E. Shilov, Kinetika i Kataliz, **13**, 61 (1972).
71. B. Jeżowska-Trzebiatowska, P. Sobota, H. Kozłowski, and A. Jezierski, Bull. Acad. polon. Sci., Ser. Sci. Chim., Geol., Geog., **2**, 193 (1972); B. Jeżowska-Trzebiatowska and P. Sobota, J. Organometal. Chem., **46**, 339 (1972).
72. H. H. Brintzinger, J. Amer. Chem. Soc., 88, 4307 (1966).
73. H. H. Brintzinger, Biochem., **5**, 3947 (1966).
74. H. H. Brintzinger, J. Amer. Chem. Soc., 89, 6871 (1967).
75. G. Henrici-Olive and S. Olive, Angew. Chem., Int. Edit., **7**, 386 (1968).
76. A. K. Zefirova, N. N. Tikhomirova, and A. E. Shilov, Dokl. Akad. Nauk SSSR, **132**, 1082 (1960).
77. M. E. Vol'pin, A. A. Belyi, V. B. Shur, Yu. I. Lyakhovetskii, R. V. Kudryavtsev, and N. N. Bubnov, Dokl. Akad. Nauk SSSR, **194**, 577 (1970).
78. R. Maskill and J. M. Pratt, J. Chem. Soc. (A), 1914 (1968).
79. E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, J. Amer. Chem. Soc., **91**, 1551 (1969).
80. G. Henrici-Olive and S. Olive, J. Organomet. Chem., **9**, 325 (1967).
81. R. Maskill and J. M. Pratt, Chem. Comm., 950 (1967).
82. E. F. Kvashina, Yu. G. Borod'ko, E. I. Plakhova, Sh. M. Rukhadze, and A. E. Shilov, Izv. Akad. Nauk SSSR, Ser. Khim., 936 (1970).
83. A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, Chem. Comm., 79 (1967).
84. A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsala, and C. V. Senoff, J. Amer. Chem. Soc., **89**, 5595 (1967).
85. A. D. Allen and F. Bottomley, J. Amer. Chem. Soc., **91**, 1231 (1969).
86. Yu. G. Borod'ko, A. K. Shilova, and A. E. Shilov, Zhur. Fiz. Khim., **44**, 627 (1970) [Russ. J. Phys. Chem., No. 3 (1970)].
87. J. Chatt, R. L. Richards, J. S. Fergusson, and J. L. Love, Chem. Comm., 1522 (1968).
88. Yu. G. Borod'ko, E. F. Kvashina, V. B. Panov, and A. E. Shilov, Kinetika i Kataliz, **14**, 255 (1973).

89. A. E. Shilov, A. K. Shilova, E. F. Kvashina, and T. A. Vorontsova, Chem. Comm., 1590 (1971).
90. J. H. Teuben and H. J. de Liefde Meijer, Rec. Trav. chim., **90**, 360 (1971).
91. J. H. Teuben, Thesis, 1973.
92. J. H. Teuben, J. Organometal. Chem., **57**, 159 (1973).
93. J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, Chem. Comm., 955 (1970).
94. Yu. G. Borod'ko, I. N. Ivleva, S. I. Salienko, A. K. Shilova, and A. E. Shilov, Chem. Comm., 1178 (1972).
95. Yu. G. Borod'ko, I. N. Ivleva, S. I. Salienko, A. K. Shilova, and E. A. Shilov, Zhur. Strukt. Khim., **14**, 1112 (1973).
96. I. N. Ivleva, A. K. Shilova, S. I. Salienko, and Yu. G. Borod'ko, Dokl. Akad. Nauk SSSR, **213**, 116 (1973).
97. Yu. G. Borod'ko, I. N. Ivleva, L. N. Kachapina, S. I. Salienko, A. K. Shilova, and A. E. Shilov, Chem. Comm., 169 (1973).
98. J. E. Bercaw and H. H. Brintzinger, J. Amer. Chem. Soc., **93**, 2045 (1971).
99. R. H. Marvich and H. H. Brintzinger, J. Amer. Chem. Soc., **93**, 2046 (1971).
100. J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, J. Amer. Chem. Soc., **94**, 1219 (1972).
101. J. E. Bercaw, E. Rosenberg, and J. D. Roberts, J. Amer. Chem. Soc., (in the press).
102. Yu. G. Borod'ko, M. O. Broitman, L. M. Kachapina, A. E. Shilov, and L. Yu. Ukhin, Chem. Comm., 1185 (1971).
103. L. N. Kachapina, Yu. G. Borod'ko, A. V. Sazhnikova, I. N. Ivleva, Yu. M. Shul'ga, and M. O. Broitman, Dokl. Akad. Nauk SSSR, **208**, 135 (1973).
104. K. Jonas, Angew. Chem., Int. Edit., **12**, 997 (1973).
105. C. Kruger and Yi-Hung Tsay, Angew. Chem., Int. Edit., **12**, 998 (1973).
106. M. E. Vol'pin, V. S. Lenenko, and V. B. Shur, Izv. Akad. Nauk SSSR, Ser. Khim., 463 (1971).
107. S. Rummel and M. Wahren, Z. Chem., **12**, 389 (1972).
108. J. Chatt, G. A. Heath, and G. G. Leigh, Chem. Comm., 444 (1972).
109. J. Chatt, G. A. Heath, and R. L. Richards, Chem. Comm., 1010 (1972).
110. D. Sellman, Angew. Chem., Int. Edit., **10**, 919 (1971).
111. D. Sellman, J. Organometal. Chem., **44**, c46 (1972).
112. H. Binder and D. Sellman, Angew. Chem., Int. Edit., **12**, 1017 (1973).
113. D. Sellman, A. Brandl, and R. Endell, Angew. Chem., Int. Edit., **12**, 1019 (1973).
114. C. Zenghelis, Compt. rend., **162**, 914 (1916).
115. O. Glemser, BRD P. 956 674 (1957).
116. G. P. Haight and R. Scott, J. Amer. Chem. Soc., **86**, 743 (1964).
117. K. B. Yatsimirskii and V. K. Pavlova, Dokl. Akad. Nauk SSSR, 165, 130 (1965).
118. A. E. Shilov and A. K. Shilova, Kinetika i Kataliz, 10, 1163 (1969).
119. R. W. Hardy and E. Knight, "Progress in Photochemistry", (Edited by L. Rheinhold), New York, 1968, p. 387.
120. A. E. Shilov and G. I. Likhtenshtein, Izv. Akad. Nauk SSSR, Ser. Biol., 518 (1971).
121. C. E. McKenna, J. R. Benemann, and T. G. Taylor, Biochim. Biophys. Res. Comm., **41**, 1501 (1970).
122. R. C. Burns, W. H. Fushman, and R. W. F. Hardy, Biochim. Biophys. Res. Comm., **42**, 353 (1971).
123. N. T. Denisov, V. F. Shuvalov, N. I. Shuvalova, A. K. Shilova, and A. E. Shilov, Dokl. Akad. Nauk SSSR, **195**, 879 (1970).
124. A. E. Shilov, N. T. Denisov, O. N. Efimov, N. F. Shuvalov, N. I. Shuvalova, and A. E. Shilova, Nature, **231**, 460 (1971).
125. N. T. Denisov, G. G. Terekhina, N. I. Shuvalova, and A. E. Shilov, Kinetika i Kataliz, **14**, 939 (1973).
126. V. V. Abalyaeva, N. T. Denisov, M. L. Khidekel', and A. E. Shilov, Izv. Akad. Nauk SSSR, Ser. Khim., 196 (1973).
127. N. T. Denisov, O. N. Efimov, A. G. Ovcharenko, and A. E. Shilov, Teor. Eksper. Khim., **1**, 762 (1965).
128. W. Traube and W. Passarge, Ber., **49**, 1692 (1916).
129. Yu. G. Borod'ko, O. N. Efimov, V. B. Panov, and A. E. Shilov, Zhur. Fiz. Khim., **45**, 248 (1971) [Russ. J. Phys. Chem., No. 2 (1971)].
130. Yu. G. Borod'ko, I. N. Ivleva, V. B. Panov, and Yu. M. Shul'ga, Zhur. Fiz. Khim., **47**, 1374 (1973) [Russ. J. Phys. Chem., No. 6 (1973)].
131. C. E. Castro and R. D. Stephens, J. Amer. Chem. Soc., **86**, 4359 (1964).
132. D. V. Sokol'skii, Ya. A. Dorfman, Yu. M. Shindler, and T. D. Protopopova, Zhur. Obshch. Khim., **41**, 2116 (1971).
133. A. F. Zueva, O. N. Efimov, A. D. Styrkas, and A. E. Shilov, Zhur. Fiz. Khim., **46**, 760 (1972) [Russ. J. Phys. Chem., No. 3 (1972)].
134. N. T. Denisov, E. I. Rudshtein, N. I. Shuvalova, A. E. Shilova, and A. E. Shilov, Dokl. Akad. Nauk SSSR, **292**, 623 (1972).
135. N. T. Denisov, N. I. Shuvalova, and T. V. Butenkova, Kinetika i Kataliz, **15**, No. 6 (1974).
136. N. T. Denisov, V. F. Shuvalova, N. I. Shuvalova, A. K. Shilova, A. E. Shilov, and O. N. Efimov, USSR P. 305 739 (1970); US P. 3 703 354 (1970).
137. D. V. Sokol'skii, Ya. A. Dorfman, Yu. M. Shindler, A. I. Sharopin, and V. S. Emel'yanova, Zhur. Fiz. Khim., **46**, 2929 (1972) [Russ. J. Phys. Chem., No. 11 (1972)]; D. V. Sokol'skii, Ya. A. Dorfman, Yu. M. Shindler, B. Yu. Nogerbekov, and R. G. Sapova, Zhur. Obshch. Khim., 42, 1425 (1972); D. V. Sokol'skii, Ya. A. Dorfman, Yu. M. Shindler, S. S. Stroganov, and A. N. Sharopin, Zhur. Obshch. Khim., **43**, 252 (1973).
138. L. A. Nikonova, A. G. Ovcharenko, O. N. Efimov, V. A. Avilov, and A. E. Shilov, Kinetika i Kataliz, **13**, 1602 (1972).
139. L. A. Nikonova, N. I. Pershikova, M. V. Bodeiko, L. G. Oleinik, D. N. Sokolov, and A. E. Shilov, Dokl. Akad. Nauk SSSR (in the press).
140. L. A. Nikonova, O. N. Efimov, A. G. Ovcharenko, and A. E. Shilov, Kinetika i Kataliz, **13**, 249 (1972).
141. G. N. Schrauzer and G. Schlesinger, J. Amer. Chem. Soc., **92**, 1808 (1970).
142. G. N. Schrauzer, G. Schlesinger, and P. A. Doemeny, J. Amer. Chem. Soc., **93**, 1803 (1971).
143. G. N. Schrauzer, P. A. Doemeny, G. W. Kiefer, and R. H. Fraizer, J. Amer. Chem. Soc., **94**, 7378 (1972).
144. G. N. Schrauzer, G. W. Kiefer, P. A. Doemeny, and H. Kisch, J. Amer. Chem. Soc., **95**, 5582 (1973).
145. R. E. E. Hill and R. L. Richards, Nature, **233**, 114 (1971).
146. D. Werner, S. A. Russel, and H. J. Evans, Proc. Nat. Acad. Sci. USA, **70**, 339 (1973).
147. G. N. Schrauzer, G. Schlesinger, and P. A. Doemeny, J. Amer. Chem. Soc., **93**, 1803 (1971).
148. T. A. Vorontsova and A. E. Shilov, Kinetika i Kataliz, **14**, 1326 (1973).

149. T. A. Vorontsova, A. P. Khrushch, and A. E. Shilov, Kinetika i Kataliz, (in the Press).
150. E. B. Fleischer and M. Krishnamurthy, J. Amer. Chem. Soc., **94**, 1382 (1972).
151. J. Chatt, C. M. Elson, and G. J. Leigh, J. Amer. Chem. Soc., **95**, 2408 (1973).
152. R. G. S. Banks, R. J. Henderson, and J. M. Pratt, Chem. Comm., 387 (1967).
153. L. S. Pu, A. Yamamoto, and S. Ikeda, Chem. Comm., 189 (1969).
154. W. E. Newton, J. L. Corbin, P. W. Schneider, and W. A. Bulen, J. Amer. Chem. Soc., **93**, 268 (1971).
155. A. E. Shilov, Kinetika i Kataliz, **11**, 305 (1970).
156. N. T. Denisov, N. I. Shuvalova, and A. E. Shilov, Kinetika i Kataliz, **14**, 1325 (1973).
157. N. T. Denisov, N. I. Shuvalova, I. N. Ivleva, and A. E. Shilov, Zhur. Fiz. Khim., (in the Press).
158. J. Chatt, J. R. Dilworth, and R. L. Richards, J. R. Sanders, Nature, **224**, 5225 (1969).
159. G. W. Parshall, J. Amer. Chem. Soc., **89**, 1822 (1967).
160. W. H. Orne Johnson, W. D. Hamilton, T. L. Jones, M.-I. W. Tso, R. H. Burris, V. K. Shah, and W. I. Brill, Proc. Acad. Sci. USA, **69**, 3142 (1972).
161. L. A. Syrtsova, G. I. Likhtenshtein, T. N. Pisarskaya, V. L. Berdinskii, V. P. Lezina, and A. U. Stepanyants, Mol. Biol., No. 6 (1974).

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