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Abstract

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Nitrogen Fixation on Complex Catalysts

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The problem of fixing molecular nitrogen under mild conditions has still not been solved. Most of the reactions known for nitrogen, including catalytic ones, proceed under severe conditions associated with the use either of high temperatures and pressures or of electrical discharges. Only the enzyme systems of certain species of bacteria and algae are capable of efficiently fixing atmospheric nitrogen at ordinary temperature and pressure.

The nature of the active centers of these enzymes and the mechanism of their action are still unknown; however, the participation in this process of enzymes containing transition metals (Mo, Fe) makes it possible to suppose that the first act of biological nitrogen fixation is its activation through the formation of a π-complex with a metal. The next stage may consist in the transfer of activated hydrogen from an organic substrate to the nitrogen molecule, with its reduction to ammonia.

$$\Phi - \mathrm{Me} + \mathrm{N_2} \longrightarrow \Phi - \mathrm{Me} \leftarrow \overset{\mathrm{N}}{\underset{\mathrm{N}}{\|}} \xrightarrow{[\mathrm{H}]} \mathrm{NH_3}.$$

Proceeding from these ideas, we assumed that activation of molecular nitrogen could also be achieved without the participation of biological systems, through its formation of π-complexes with coordinatively unsaturated compounds of transition metals. In search of compounds of this kind that activate nitrogen, we turned to complex catalysts formed by the interaction of transition-metal salts with Mg-, Li-, or Al-organic compounds and lithium aluminum hydride. These systems very readily form complexes with olefins, acetylenes, carbon monoxide, and other ligands. For this reason, in a number of cases they are capable of catalyzing cyclization reactions of olefins and acetylenes, their polymerization, hydrogenation, etc. We undertook a systematic study of the possibility of nitrogen fixation on such complex catalysts at room temperature (see Table 1).

It did in fact turn out that a number of complex catalysts are capable of activating molecular nitrogen with formation of ammonia. Thus, when nitrogen at atmospheric pressure is passed through a mixture of anhydrous $CrCl_3$ and an excess of $LiAlH_4$ in diethyl ether, ammonia is formed in an amount of 2 mole % based on the initial $CrCl_3$.* With an increase of the nitrogen pressure to 150

atm, the yield of ammonia increases to 7 mole %. The chlorides of a number of other transition metals (Cu_2Cl_2, $TiCl_4$, $FeCl_3$, $CoCl_2$, $PdCl_2$) under the same conditions (at 1 atm N_2) did not catalyze the formation of ammonia.

Noticeable activity is exhibited by systems obtained by the interaction of transition-metal halides with a Grignard reagent. When N_2 was passed through a mixture of anhydrous $CrCl_3$ and an excess of an ethereal solution of C_2H_5MgBr at room temperature, ammonia was formed in an amount of 0.7 mole %. When the nitrogen pressure was increased to 150 atm, the yield of NH_3 rose to 17%. It was established that the activity of these catalysts depends to a noticeable extent on the nature of the solvent and decreases upon replacement

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* Here and everywhere below, the yield of ammonia is given in mole percent relative to the initial salt of the transition metal.

ether to the more solvating tetrahydrofuran (THF) and dimethoxyethane (DME). In addition, replacement of C_2H_5MgBr by C_6H_5MgBr also leads to a decrease in the yield of ammonia.

In studying the catalytic action of salts of other transition metals in mixtures with C_2H_5MgBr under N_2 pressure, it was found that, like $CrCl_3$, other metal halides of the same subgroup also possess similar activity (WCl_6, 14.7% NH_3; $MoCl_5$, 7.5% NH_3). Systems involving $TiCl_4$ (10.4%) and $FeCl_3$ (8.8%) also show appreciable activity. Salts of the other metals studied ($NiCl_2$, $PdCl_2$, Cu_2Cl_2, $CoCl_2$) are almost inactive under these conditions.

Table 1*

Catalytic system**	N_2 pressure, atm	Solvent	Amount of NH_3 (mol. % based on initial salt)
$CrCl_3$—$LiAlH_4$	1	ether	2.0
$CrCl_3$—$LiAlH_4$	150	ether	7.0
$CrCl_3$—$LiAlH_4$	1	THF	0.4
$CrCl_3$—$LiAlH_4$	1	DME	0.2
$CrCl_3$—$LiAlH_4$	150	THF	3.7
$CrCl_3$—$LiAlH_4$	150	DME	3.2
$CrCl_3$—C_2H_5MgBr	1	ether	0.7
$CrCl_3$—C_2H_5MgBr	150	ether	16.8
$CrCl_3$—C_2H_5MgBr	150	THF	3.2
$CrCl_3$—C_6H_5MgBr	150	ether	3.5
$CrCl_3$—C_6H_5MgBr	150	THF	1.1
$CrCl_3$	150	ether	0
C_2H_5MgBr	150	ether	0
$LiAlH_4$	150	ether	0

Catalytic system**	N_2 pressure, atm	Solvent	Amount of NH_3 (mol. % based on initial salt)
$MoCl_5$—C_2H_5MgBr	150	ether	7.5
WCl_6—C_2H_5MgBr	150	ether	14.7
$FeCl_3$—C_2H_5MgBr	150	ether	8.8
$TiCl_4$—C_2H_5MgBr	150	ether	10.4
$TiCl_4$—(iso-$C_4H_9)_3Al$	150	heptane	25.0

* All experiments were carried out at room temperature. Experiments at atmospheric pressure were conducted for 6–7 h; under pressure, for 10–11 h.
** The salt of the transition metal in experiments with $LiAlH_4$ was taken in an amount of $2.3 \cdot 10^{-3}$ mol; in the remaining experiments, $7 \cdot 10^{-3}$ mol. The molar ratio of $LiAlH_4$ or RMgBr to the transition-metal salt was 9:1 throughout; the ratio of (iso-$C_4H_9)_3Al$ to $TiCl_4$ was 3:1.

Ziegler-type catalysts for olefin polymerization also possess an analogous ability to activate nitrogen. Thus, for example, the system

$$TiCl_4 + Al(\text{iso-}C_4H_9)_3$$

in heptane leads to the formation of ammonia with a yield of 25%. The results of some experiments are given in Table 1.

On the basis of the experimental data obtained up to the present time, it is difficult to judge with sufficient reliability the mechanism of activation of the nitrogen molecule in these systems. Nevertheless, it seems probable that this mechanism includes the formation of a π-complex of the nitrogen molecule with an alkyl derivative of a transition metal or with its hydride (formed by the action of RMgBr, R_3Al, or $LiAlH_4$ on the metal salt).

In the case of reaction with RMgBr, addition of hydrogen to the activated nitrogen molecule can apparently occur both as a result of intramolecular transfer of hydrogen from alkyl groups bound to the transition metal and as a result of dehydrogenation of C_2H_5MgBr or of the solvent.

$$CrCl_3 + 3RMgBr \xrightarrow{\text{ether}} [R_3Cr \cdot 3Et_2O] \xrightarrow{N_2} > Cr \leftarrow \begin{matrix} N \\ \| \\ N \end{matrix} \xrightarrow{[H]} NH_3.$$

This scheme for the mechanism of nitrogen activation is close to the mechanism proposed by Zeiss for explaining the cyclization reaction of acetylenes in the presence of $CrCl_3 + RMgBr$ systems in THF, and also for explaining the mechanism of obtaining $Cr(CO)_6$ from the same mixtures in ether ([1]).

Thus, in the present work the fundamental possibility of nitrogen activation on complex catalysts has been demonstrated. Investigations in this area are continuing.

Experimental Part

Reaction of nitrogen with a mixture of $LiAlH_4$ and $CrCl_3$ at atmospheric pressure. Into a 4-necked flask of 150 ml capacity, equipped with a stirrer ensuring gas circulation, a reflux condenser-

connected to a Tishchenko bottle containing 20 ml of 20% H_2SO_4, and with a dropping funnel, 40 ml of absolute ether is charged under an N_2 atmosphere, cooled to -75°, and 0.79 g of $LiAlH_4$, 0.37 g of anhydrous $CrCl_3$, and 40 ml of ether are added. A stream of nitrogen is passed through the mixture with vigorous stirring and the cooling is removed, allowing the contents of the flask to warm spontaneously to room temperature. At this temperature nitrogen is continued to be passed through for 7 hr, maintaining a volume in the flask of ~ 80 ml by periodically adding absolute ether from the dropping funnel.

The passage of N_2 is stopped and, with cooling, the excess $LiAlH_4$ is carefully decomposed with 5 ml of methanol and then 5 ml of 20% H_2SO_4. The contents of the flask and of the Tishchenko bottle are washed with 150 ml of distilled water and evaporated to a volume of 60 ml. The residue is alkalized with 20 ml of 40% KOH and the ammonia is distilled, together with water, from a Kjeldahl apparatus into a receiver containing 15 ml of 0.01 N HCl. The excess acid is back-titrated with 0.01 N NaOH. In parallel, the same experiment is carried out, but with argon passed through. The difference between the titrations in the two experiments (4.85 ml of 0.01 N NaOH) corresponds to 2 mol.% NH_3, calculated on the initial $CrCl_3$. The nitrogen for the experiment was purified from oxygen by passage over copper at 760° and was then dried over $CaCl_2$, KOH, and conc. H_2SO_4. Other experiments at atmospheric pressure were carried out analogously.

Reaction of nitrogen with a mixture of C_2H_5MgBr and $CrCl_3$ in ether under pressure. Into a 50-ml stainless-steel autoclave are charged 30 ml of an ethereal solution of C_2H_5MgBr (containing 0.06 mole of C_2H_5MgBr) and a sealed thin-walled glass ampoule containing 1.11 g of anhydrous $CrCl_3$. The autoclave is filled with nitrogen to a pressure of 150 atm. In doing so, the glass ampoule bursts. The autoclave is rocked on a shaker (120 full swings per min) for 10–11 hr and is then left overnight without shaking. The autoclave is cooled and the nitrogen is carefully released through a Tishchenko bottle (20 ml of 20% H_2SO_4). The mixture is carefully decomposed (with cooling to -50°) with 7 ml of methanol and then 7 ml of 10% H_2SO_4, passing the evolved gases through the same Tishchenko bottle with H_2SO_4. The contents of the autoclave and of the Tishchenko bottle are transferred to a flask and then evaporated; NH_3 is determined analogously to that described above, distilling it into a receiver with 20 ml of 0.1 N HCl solution and back-titrating the excess acid with 0.1 N NaOH solution. Other experiments under pressure were carried out analogously.

Reaction of nitrogen with a mixture of $(iso\text{-}C_4H_9)_3Al$ and $TiCl_4$ in heptane. Into a 50-ml stainless-steel autoclave are charged 30 ml of dry heptane, a thin-walled ampoule with $TiCl_4$, and, in a stream of Ar, 6 ml of distilled tri-

isobutylaluminum. The autoclave is filled with nitrogen to 150 atm and rocked on a shaker for 10-11 hr. After workup of the experiment analogous to the preceding one, NH_3 is distilled off; yield 25 mol.% (based on $TiCl_4$).

The ammonia formed in the experiments was identified by reaction with Nessler' s reagent, potentiometric titration, conversion into nitrogen under the action of sodium hypobromite solution, and conversion into urotropine by reaction with formaldehyde; the melting point of urotropine picrate was 179°.

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CITED LITERATURE

1. W. Herwig, W. Metlesics, H. Zeiss, *J. Am. Chem. Soc.*, **81**, 6203 (1959).

Note: Figure translations are in progress. See original paper for figures.