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Abstract

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On the Mechanism of Nitrogen Fixation in the Reacting System

$(C_5H_5)_2TiCl_2$–C_2H_5MgBr

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Recently M. E. Vol' pin and V. B. Shur (^{1}, ^{2}) showed that in a number of systems formed by the interaction of organometallic compounds with salts of transition elements under mild conditions, nitrogen is fixed. Especially active is the system formed by the interaction of ethylmagnesium bromide with biscyclopentadienyltitanium dichloride in ether (^{3}). In this case, even at atmospheric nitrogen pressure, up to one nitrogen atom from N_2 is absorbed per titanium atom. After hydrolysis of the reaction products, ammonia is evolved. It was proposed (^{1}) that in these systems NH_3 is formed as a result of the addition of hydrogen from the molecules of the reagents or solvent to nitrogen, which forms a complex with a compound containing a transition-element atom. On the other hand, it is not excluded that the fixed nitrogen is liberated in the form of ammonia only upon hydrolysis and is contained in the reaction products, for example, as the nitride of one of the metals participating in the reaction*.

The present work was undertaken in order to clarify certain questions concerning the mechanism of the reaction of $(C_5H_5)_2TiCl_2$ with C_2H_5MgBr, and also to determine in what form the nitrogen bound in this system is present.

Examination of changes in the spectra of the solution during the interaction of the reagents shows that the reaction is complex in character. The spectrum of the rapidly formed homogeneous red solution remains almost unchanged for some time (about 1 min), then the color rapidly becomes lighter; subsequently the solution again darkens, and resinous products precipitate from it. After the reaction has proceeded for 2–3 hr at room temperature, ethane and ethylene were found in the gaseous products. When nitrogen is passed through during the same time, its fixation occurs, with no noticeable changes being observed in the composition or quantity of the gaseous reaction products (Table 1).

Table 1

$[(C_5H_5)_2TiCl_2]$ 10^2 M/l	$[C_2H_5MgBr]\cdot$ 10 M/l	Gas passed through	$\frac{NH_3}{Ti}$	$\frac{C_2H_6}{Ti}$	$\frac{C_2H_4}{Ti}$	$\frac{C_2H_4+C_2H_6}{Ti}$
4.2	5.0	He	–	2.73	1.22	3.95
4.2	5.0	N_2	0.41	2.50	1.23	3.73
4.2	5.0	He	–	2.69	1.26	3.95
1.8	1.7	He	–	2.20	1.20	3.40
1.8	1.7	He	–	–	–	4.00
1.8	1.7	N_2	0.27	–	–	4.11
1.8	1.7	N_2	0.30	–	–	4.00
1.8	1.7	N_2	0.40	2.63	1.33	3.96

Approximately one third of all gaseous reaction products (more than 1 mole per mole of Ti) is evolved during the first 5 min, when nitrogen fixation is still practically absent. The amount of bound nitrogen decreases sharply if its passage is begun several hours after mix— of the components. These results indicate reduction of titanocene prior to nitrogen fixation and the intermediate character of the particles interacting with N_2.

When the reaction products are decomposed with water or sulfuric acid, hydrogen formation is observed. Mass-spectrometric analysis of the hydrogen formed upon the action of D_2O showed that its isotopic composition (mainly HD and small amounts of D_2 and H_2) corresponds to hydrolysis of metal hydrides (^{4}).

Table 2

$[(C_5H_5)_2TiCl_2]\cdot 10^2$, mole/l	Purged gas	$\frac{NH_3}{Ti}$	H_2/Ti
1.97	Ar	–	1.95
1.97	Ar	–	2.02
1.80	N_2	0.40	1.30
1.97	Ar	–	2.00
1.80	Ar	–	1.87
1.80	N_2	0.32	1.38

$[C_2H_5MgBr] = 1.7 \cdot 10^{-1}$ mole/l in all experiments.

Table 2 gives the results of several experiments in which the amount of hydrogen formed during hydrolysis of the final products was determined. It may be noted that in the presence of nitrogen, hydrogen is evolved in markedly smaller quantities, i.e., less metal hydride is formed.

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* Recently the authors of work (^{2}) also do not exclude this possibility.

The considerable amount of gases evolved during the reaction and the formation of hydrides indicate deep reduction of titanocene. The infrared spectra of the reaction products also indicate profound changes: the sandwich structure of the titanium derivative is destroyed.

When the reaction was carried out with C_2D_5MgBr as the reducing agent, it was found that the ethane contains mainly C_2D_6. In heavy ether $(C_2D_5)_2O$, the ethane formed during reduction of $(C_5H_5)_2TiCl_2$ by light C_2H_5MgBr contains only about 3% C_2H_5D. Additions of octadeuterotoluene (20%) likewise did not lead to any noticeable increase in the content of C_2H_5D. Thus, it is evident that only an insignificant part of the ethane is formed at the expense of ethyl radicals abstracting H from the solvent. These data confirm a reduction mechanism through intramolecular disproportionation of ethyl groups:

$$\cdots Me < \begin{matrix} C_2H_5 \\ C_3H_5 \end{matrix} \rightarrow \cdots Me + C_2H_4 + C_2H_6,$$

which is characteristic of reactions of this type (^{5}). The diminished yield of ethylene compared with ethane is apparently connected mainly with further transformations of ethylene in the reacting system.

The hydrogen formed upon decomposition with light water of the reaction products of $(C_5H_5)_2TiCl_2$ with C_2D_5MgBr contained mainly HD, i.e., the metal hydrides are formed with participation of hydrogen from the alkyl group.

Some results obtained using C_2D_5MgBr as the reducing agent and $(C_2D_5)_2O$ as the solvent are relevant to the mechanism of nitrogen fixation.

If, during nitrogen fixation, nitrogen were reduced to ammonia at the expense of hydrogen atoms of ethylmagnesium bromide or of the solvent, then upon hydrolysis of the products with light acid the ammonium salt and the excess acid would have to contain a certain amount of D (taking into account dilution of deuterium by protium as a result of exchange). However, the experimentally determined content of exchangeable deuterium both in the case of C_2D_5MgBr in light ether and in the solution $(C_2D_5)_2O$ proved to be practically at the level of blank experiments carried out without passing nitrogen (Table 3).

In control experiments with addition of ND_3 to the initial reacting mixture in an amount equivalent to the amount of bound nitrogen, an exchangeable D atom is detected in the reaction products. It may be noted that the exchange data indicate that, after the interaction of ammonia in the reacting system (probably with C_2H_5MgBr), one hydrogen atom remains on nitrogen.

Thus, it is evident that ammonia is not formed in the system either as a final or as an intermediate product.

Apparently, this indicates that the bound nitrogen is present in the reaction products in the form of nitrides, which form ammonia upon hydrolysis.

It is possible that the formation of nitrides occurs through the interaction of N_2 with the metal (Mg or Ti) *in statu nascendi*. This is consistent with the deep reduction of the titanium compound observed in the system studied, and with the fact that metals become considerably more active toward nitrogen in a finely divided state.

Table 3

$[(C_5H_5)_2TiCl_2]$· 10^2 mol/l	$[C_2H_5MgBr]$· 10 mol/l	Labeled compound	Gas passed through	$\frac{NH_3}{Ti}$	%D (after hydrolysis of the product with H_2SO_4)
4,0	3,1	C_2D_5MgBr	N_2	0,40	0,18
4,0	3,1	Same	Ar	–	<0,25
4,0	3,1	» »	Ar	–	0,16
1,0	3,1	C_2D_5MgBr, ND_3	Ar	0,40	1,50
3,22	3,0	$(C_2D_5)_2O$	N_2	0,32	0,09
3,22	3,0	Same	N_2	0,40	0,04
3,22	3,0	$(C_2D_5)_2O$, ND_3	Ar	0,40	1,77
1,88	1,65	C_2D_5MgBr	N_2	0,30	<0,3
1,88	1,65	C_2D_5MgBr, ND_3	Ar	0,29	~1,1

Experimental Part

The starting compound for obtaining C_2D_5MgBr and $(C_2D_5)_2O$ was ethyl alcohol labeled with deuterium (90% in the alkyl group). The synthesis was carried out according to the schemes:

$$C_2D_5OH \xrightarrow[KBr]{H_2SO_4} C_2D_5Br \xrightarrow[ether]{Mg} C_2D_5MgBr,$$

$$C_2D_5Br + C_2D_5ONa \rightarrow NaBr + (C_2D_5)_2O;$$

$(C_5H_5)_2TiCl_2$ was synthesized according to the procedure of (6).

The reduction of $(C_5H_5)_2TiCl_2$ and nitrogen fixation were carried out in a vessel connected to a vacuum system, which made it possible, after the reaction, to collect and analyze the gaseous products. The amount of gases was determined from the pressure in a known volume. Hydrogen was transferred into a known volume by means of a Toepler pump.

Gas analysis was carried out chromatographically (ethane, ethylene) and mass-spectrometrically (labeled compounds). Isotopic analysis of hydrogen and ethane was carried out on MX-1302 and MV-2302 mass spectrometers. To determine the N—D bond in the reaction products, the mixture was hydrolyzed with a small amount of sulfuric acid ($H^+/Ti = 14.5$); then, after prolonged standing, a solution of CH_3MgJ or $LiAlH_4$ was added, and isotopic analysis of the evolved methane or hydrogen was performed. Experiments with the special addition of ND_3 were carried out under identical conditions.

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Cited Literature

1. M. E. Vol' pin, V. B. Shur, *DAN*, **156**, 1102 (1964).
2. M. E. Vol' pin, V. B. Shur, *Vestn. AN SSSR*, No. 1, 51 (1965).
3. M. E. Vol' pin, V. B. Shur, M. A. Ilatovskaya, *Izv. AN SSSR, ser. khim.*, 1964, 9.
4. H. Gaylord, *Reduction with Complex Metal Hydrides*, Moscow, 1959, p. 33.
5. A. K. Zeifirova, A. E. Shilov, *DAN*, **136**, 599, 1961.
6. J. Wilkinson, J. M. Birmingham, *J. Am. Chem. Soc.*, **76**, 4281 (1954).

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