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Fig. 1. Effect of H_2 on nitrogen fixation by the system $Ti(OC_2H_5)_4$ + (iso-$C_4H_9)_3Al$ in toluene (N_2 pressure everywhere 30 atm; N_2 and H_2 were everywhere diluted with Ar to a total pressure of 120 atm)

Figure 1: Fig. 1. Effect of H_2 on nitrogen fixation by the system $Ti(OC_2H_5)_4$ + (iso-$C_4H_9)_3Al$ in toluene (N_2 pressure everywhere 30 atm; N_2 and H_2 were everywhere diluted with Ar to a total pressure of 120 atm)

Abstract

Full Text

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NITROGEN FIXATION ON TRANSITION-METAL COMPLEXES THAT ACTIVATE HYDROGEN

(Presented by Academician M. I. Kabachnik, February 15, 1965)

Recently it was shown that molecular nitrogen is fixed under mild conditions by systems formed upon the interaction of salts or complexes of transition metals with carbanion or hydride-ion donors ([1-3]). One of the important tasks in solving the problem of nitrogen fixation is to carry out the direct reaction of nitrogen with hydrogen under the conditions of coordination catalysis. In this connection, systems capable of activating both molecular nitrogen and molecular hydrogen may be of considerable interest.

In the present work the possibility of nitrogen fixation by complex catalysts for homogeneous hydrogenation of olefins and the influence of hydrogen on this process were investigated. The ability of systems of this kind to activate hydrogen was recently studied by Breslow et al. ([4]). We investigated the interaction of nitrogen with systems formed in the reaction of acetylacetonates of a number of transition metals (as well as tetraethoxytitanium) with Li-, Mg-, and Al-organic compounds.

Fig. 1. Effect of H_2 on nitrogen fixation by the system $Ti(OC_2H_5)_4$ + (iso-$C_4H_9)_3Al$ in toluene (N_2 pressure everywhere 30 atm; N_2 and H_2 were everywhere diluted with Ar to a total pressure of 120 atm).

From the experimental data presented in Table 1 it is seen that the systems studied are capable of fixing nitrogen at room temperature with formation of ammonia (after hydrolysis of the reaction products). The most active proved to be systems based on tetraethoxytitanium and vanadium(IV) acetylacetonate (NH_3 yield up to 0.30-0.35 M per 1 M of transition-metal compound),* as well as the acetylacetonates of Cr(III), Mo(VI), and Mn(III) (yield up to 0.10-0.14 M

NH_3). Systems based on the acetylacetonates of Fe(III) and Ni(III) possess significantly lower activity (yield up to 0.05 M NH_3). Cobalt(III) acetylacetonate is practically inactive in nitrogen fixation.

Molecular hydrogen has different effects on the complex systems that fix nitrogen. In most cases, either inhibition of nitrogen fixation by hydrogen is observed, or H_2 does not affect the course of the process (for example, vanadium acetylacetonate in a mixture with n-C_4H_9Li in heptane). However, for the system $Ti(OC_2H_5)_4$ + Al(iso-$C_4H_9)_3$ in toluene, a substantial increase in the yield of ammonia upon introduction of molecular—

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* Here and below, the yield of ammonia is given in moles per 1 mole of transition-metal compound.

molecular hydrogen. As can be seen from Fig. 1, an increase in the yield of NH_3 is observed over a wide range of N_2:H_2 ratios in the gas mixture. At the same time, the maximum yield of ammonia is reached at an N_2:H_2 ratio of approximately 3:1.

Thus, in the present work the fundamental possibility has been shown of activating nitrogen on complex catalysts of homogeneous hydrogenation.

Table 1*

Transition-metal compound	Organometallic compound**	Solvent	N_2 pressure, atm	H_2 pressure, atm	NH_3 yield, mol per 1 mol of transition-metal compound
$Ti(OC_2H_5)_4$	C_2H_5MgBr	Ether	100	–	0.08
Same	C_2H_5MgBr	Ether	50	50	0.04
Same	n-C_4H_9Li	Heptane	100	–	0.1
Same	n-C_4H_9Li	Heptane	50	50	0.07
Same	(iso-$C_4H_9)_3Al$	Heptane	100	–	0.06
Same	Same	Toluene	100	–	0.33
Same	Same	Toluene	50	50	0.50
$VO(C_5H_7O_2)_2$	C_2H_5MgBr	Ether	100	–	0.12
Same	C_2H_5MgBr	Ether	50	50	0.03
Same	n-C_4H_9Li	Heptane	75	–	0.32
Same	Same	Heptane	38	35	0.29
Same	Same	Heptane	38	–	0.27

Transition-metal compound	Organometallic compound**	Solvent	N_2 pressure, atm	H_2 pressure, atm	NH_3 yield, mol per 1 mol of transition-metal compound
Same	Same	Toluene	83	–	0.35
Same	Same	Toluene	43	40	0.02
Same	(iso-$C_4H_9)_3Al$	Toluene	100	–	0.07
Same	(iso-$C_4H_9)_3Al$	Toluene	50	50	0.05
$Cr(C_5H_7O_2)_3$	C_2H_5MgBr	Ether	100	–	0.03
Same	*n*-C_4H_9Li	Heptane	100	–	<0.01
Same	(iso-$C_4H_9)_3Al$	Heptane	100	–	0.02
Same	Same	Heptane	50	50	0.03
Same	Same	Toluene	100	–	0.14
Same	Same	Toluene	50	50	0.06
Same	Same	Toluene	50	–	0.14
$Mn(C_5H_7O_2)_3$	C_2H_5MgBr	Ether	100	–	<0.01
Same	*n*-C_4H_9Li	Heptane	100	–	<0.01
Same	*n*-C_4H_9Li	Heptane	50	50	0.06
Same	(iso-$C_4H_9)_3Al$	Toluene	100	–	0.09
Same	Same	Toluene	50	50	0.02
Same	Same	Heptane	100	–	<0.10
$MoO_2(C_5H_7O_2)_2$	C_2H_5MgBr	Ether	100	–	0.14
Same	C_2H_5MgBr	Ether	40	32	0.05
Same	*n*-C_4H_9Li	Heptane	75	–	0.07
Same	Same	Heptane	38	35	0.07
Same	Same	Toluene	83	–	0.07
Same	Same	Toluene	43	40	<0.01
Same	(iso-$C_4H_9)_3Al$	Toluene	100	–	0.09
Same	(iso-$C_4H_9)_3Al$	Toluene	50	50	<0.01
$Fe(C_5H_7O_2)_3$	C_2H_5MgBr	Ether	100	–	0.02
Same	*n*-C_4H_9Li	Heptane	100	–	0.05

Transition-metal compound	Organometallic compound**	Solvent	N_2 pressure, atm	H_2 pressure, atm	NH_3 yield, mol per 1 mol of transition-metal compound
Same	*n*-C_4H_9Li	Heptane	50	50	<0.01
Same	(iso-$C_4H_9)_3Al$	Heptane	100	–	<0.01
Same	Same	Heptane	50	50	0.02
$Ni(C_5H_7O_2)_2$	Same	Toluene	100	–	0.04
$Ni(C_5H_7O_2)_2$	Same	Toluene	50	50	<0.01

* All experiments were carried out at room temperature for 9-10 h.
** The molar ratio of C_2H_5MgBr and *n*-C_4H_9Li to the transition-metal compound was 9:1 throughout; for (iso-$C_4H_9)_3Al$ it was 6:1.

genation. The absence of an inhibiting effect of hydrogen on some complex systems that fix nitrogen has been found, and systems have been discovered for the first time for which additions of molecular hydrogen increase nitrogen fixation.

Experimental Part

The experiments were carried out according to the standard procedure ([1]). Into a stainless-steel autoclave of 50 ml capacity were charged 30 ml of a solution of the organometallic compound in the corresponding solvent and a sealed thin-

a walled glass ampoule containing $3 \cdot 10^{-3}$ mole of the acetylacetonate of the transition metal or tetraethoxytitanium. The reagents are loaded in a stream of argon. The autoclave is filled under pressure with pure nitrogen or a mixture of nitrogen and hydrogen. The glass ampoule thereby breaks. The autoclave is shaken on a rocker (120 complete oscillations per minute) for 9-10 hr and is then left overnight without shaking. The gas is carefully released through a Tishchenko bottle with sulfuric acid; the reaction mixture is decomposed with 7 ml of methanol and 10 ml of 20% H_2SO_4, passing the gases evolved through the same Tishchenko bottle with sulfuric acid. The contents of the autoclave and the Tishchenko bottle are washed with 150 ml of distilled water, transferred to a flask, and evaporated to a volume of 60 ml. The residue is made alkaline with 25 ml of 40% KOH, and the ammonia is distilled off with a Kjeldahl attachment, together with water, into a receiver containing 0.1 N HCl. The excess acid is back-titrated with 0.1 N NaOH. The ammonia formed in the experiments was identified by reaction with Nessler' s reagent and by conversion into nitrogen under the action of a sodium hypobromite solution.

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