Synthesis of polyacetylene with titanocene—aluminum hydride catalysts

E. A. Rozova, A. B. Erofeev, A. I. Sizov, and B. M. Bulychev★

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 8946

Heterometallic hydride titanocene—aluminum complexes $Cp_2Ti(\mu\text{-}H)_2AlH(X)$ and $(Cp_2Ti)_2AlH_4X$ are highly efficient homogeneous catalysts for acetylene polymerization. The binuclear complex of the composition $Cp_2Ti(\mu\text{-}H)_2AlH_2$ at 2.2—3.2 *M* concentrations in ether—toluene solutions exhibits the maximum activity in this reaction. It is believed that the mechanisms of the isomerization of olefins and the polymerization of acetylene are similar and, correspondingly, the compositions and structures of the active sites in both processes are close to each other. The polyacetylene formed with hydride catalysts (mostly the *cis*-isomer) after doping with iodine has an electrical conductivity of $1.5—2.0 \cdot 10^4$ Ohm^{-1} cm^{-1}.

Key words: titanocene; hydrides; aluminum; catalysis; polyacetylene.

Several types of catalysts for polymerization of acetylene have been described,[1—5] among which the classical Ziegler—Natta system, *i.e.*, $Ti(OBu)_4—AlR_3$, is the best known catalyst.[3—5] The morphology of the polymer obtained with this system, as well as its molecular weight and electrophysical and structural properties depend on a great number of factors, including such an uncertain factor as the time of aging or "ripening" of the catalyst. In this respect, the use of single-component catalysts or, at least, single-component precursors of strictly defined compositions seems to be more attractive, since it offers more possibilities for standardizing the conditions of the catalytic reaction. However, as the literature data indicate, when alkylaluminum compounds are used as co-catalysts, titanium—aluminum complexes, stable under normal conditions and possessing catalytic activity, cannot be obtained due a variety of fast redox processes.[6] In a series of works devoted to the study of interactions in the $Cp_2TiCl(Cp_2TiCl_2)—LiAlH_4(AlH_3)$ systems, where Cp is $\eta^5\text{-}C_5H_5$, we showed that the bi- and trinuclear hydride complexes formed are relatively stable, can be isolated in the individual state, and moreover exhibit very high catalytic activity in the isomerization and hydrogenation of olefins.[7—10] At the same time, these compounds do not catalyze polymerization of lower olefins under ambient conditions, though they react with them to give alkylmetal hydride derivatives.[9,10]

In the present work we report the results of a study of the polymerization of acetylene on titanocene—aluminum hydride catalysts.

Experimental

All of the synthetic operations were carried out under dry argon or *in vacuo*. The solvents were dried and purified just prior to use by boiling and distillation over $LiAlH_4$. Bi- and trinuclear complexes were synthesized according to the known procedures.[8—15]

$$Cp_2TiCl + LiAlH_4 \xrightarrow{L} Cp_2TiH_2AlH_2 + LiCl \quad (1)$$

$$Cp_2TiCl + 2LiAlH_4 \xrightarrow{L} \{Cp_2TiH_2AlH_2 + LiAlH_4\} + LiCl \quad (2)$$

$$Cp_2TiCl_2 + 2LiAlH_4 \xrightarrow{L} \{Cp_2TiH_2AlH_2 \cdot AlH_3\} + \frac{1}{2}H_2 + 2LiCl \quad (3)$$

$$Cp_2TiCl + AlH_3 \xrightarrow{L} Cp_2TiH_2AlH(Cl) \quad (4)$$

$$2Cp_2TiCl + LiAlH_4 \xrightarrow{L} (Cp_2Ti)_2AlH_4Cl + LiCl \quad (5)$$

$$Cp_2TiH_2AlH_2 + HNR_2 \xrightarrow{L} Cp_2TiH_2AlH(NR_2) + H_2 \quad (6)$$

$$Cp_2TiH_2AlH_2 + HOR \xrightarrow{L} Cp_2TiH_2AlH(OR) + H_2 \quad (7)$$

$$(Cp_2Ti)_2AlH_4Cl + NaOR \xrightarrow{L} (Cp_2Ti)_2AlH_4OR + NaCl \quad (8)$$

$$(Cp_2Ti)_2AlH_4Cl + LiMe \xrightarrow{L} (Cp_2Ti)_2AlH_4Me + LiCl, \quad (9)$$

(L is a solvent)

The solutions were separated from the precipitates by filtration and used as catalysts after determining their concentration.

Acetylene was purified from admixtures and water by passing it through a number of wash bottles with solutions of chemical absorbents,[16] and the final removal of oxygen, hydrogen, methane, and other gas admixtures was carried out by double low-temperature vacuum sublimation.[17]

Polymerization of acetylene was carried out in a 300 mL cylindrical glass reactor. Prior to the process, the reactor was thoroughly evacuated, filled with argon and then 2/3 filled with toluene, and cooled to the required temperature. After that, about 3 L of purified acetylene was admitted into the reactor through a siphon, and the calculated amount of a solution of the catalyst was added with vigorous stirring. The

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 405—409, March, 1994.

polymerization was normally complete after 25—30 min, the reaction mass was kept for an additional 30—40 min and heated to the ambient temperature. The reactor was transferred into a glove box and depressurized in an atmosphere of anhydrous N_2. To free the polymer from the catalyst, the powdered polyacetylene (PA) gel was kept in a 6 % methanolic solution of anhydrous HCl for 24 hours, subjected to extraction with a $MeOH—C_6H_6$ (2 : 3 v/v) mixture in a Soxhlet apparatus, and dried *in vacuo* at ~20 °C until the solvent was entirely removed.

Results and Discussion

The reaction of acetylenic hydrocarbons with alkali metal hydridoaluminates in donor-type organic solvents (L) is described by the stoichiometric scheme of metallation.[18—20]

$$MAlH_4 + 4HC{\equiv}CR \xrightarrow{L} MAl(C{\equiv}CR)_4 + 2H_2\,, \qquad (10)$$

The conversion of acetylene in the presence of molecular binuclear titanocene hydridoaluminates of the composition $Cp_2Ti(\mu\text{-}H)_2AlH(X)\cdot OEt_2$, where Cp = $\eta^5\text{-}C_5H_5$, X = H, Cl, R, OR, NR_2, occurs under catalytic conditions and ends after 20—30 min with a dark-brown PA gel. After washing and drying *in vacuo*, the gel turns into a black mass with a metallic luster. Rather thin films of this substance can be prepared on the surface of a glass plate or a KBr plate, after they have been wet by a solution of the catalyst and polymerization of acetylene has been carried out from the gaseous phase. IR spectra of these films exhibit an intense absorption band at 745 cm^{-1} characteristic of the *cis*-isomer and a weak band at 1020 cm^{-1} typical[5] of the *trans*-isomer of PA, *i.e.*, polymerization of acetylene with these catalysts results in the predominant formation of the *cis*-product. The bulk electrical conductivity of 0.2—0.3 mm thick PA samples obtained by drying the gel between two porous metallic plates measured by the four-contact method with direct current amounts to $1—2\cdot10^{-4}$ $Ohm^{-1}\cdot cm^{-1}$. During aging of the samples in air their electric conductivity gradually decreases to $10^{-8}—10^{-9}$ $Ohm^{-1}\cdot cm^{-1}$ and reaches a constant value within 1.5—2 months (the degree of oxidation is 22—25 % w/w). Doping the freshly prepared and unoxidized PA films with iodine from the gaseous phase leads to an increase in the electrical conductivity to values of $1.5—2.0\cdot10^4$ $Ohm^{-1}\cdot cm^{-1}$ close to those reported for this material.[21]

The results of the study of polymerization and its conditions are summarized in Table 1. It should be noted that in order for the experiments to be reproducible, thorough purification of the monomer is required, due to the high sensitivity of hydride catalysts to oxygen, moisture, and a variety of organic compounds containing readily reducible functional groups.

Table 1. Results of the experiments on polymerization of acetylene in the presence of bimetallic aluminum—titanocene hydride catalysts

Composition (method for the preparation) of the catalyst	Conditions of the process	C^*/M	Yield of PA**
$Cp_2TiH_2AlH_2$ (equation (1))	Et_2O/ArR, −60 °C	1.5	1.4
		2.2	7.4
		2.3	9.7
		3.1	7.6
		3.2	5.0
		3.3	6.4
		3.7	7.7
		4.2	3.9
	THF, NEt_3, −60 °C	2.5	Traces
	Et_2O/ArR, 20 °C	3.3	2.2
$\{Cp_2TiH_2AlH_2 + LiAlH_4\}$ (equation (2))	Et_2O/ArR, −60 °C	2.2	3.4
$Cp_2TiH_2AlH_2\cdot AlH_3$ (equation (3))	The same	2.5	Traces
		3.6	Traces
$Cp_2TiH_2AlH(Cl)$ (equation (4))	« «	1.0	2.0
		1.1	3.9
		2.9	5.5
		3.4	6.0
$Cp_2TiH_2AlH(NEt_2)$ (equation (6))	« «	2.2	5.3
$Cp_2TiH_2AlH(OEt)$ (equation (7))	« «	2.5	4.2
$(Cp_2Ti)_2AlH_4Cl$ (equation (5))	« «	2.5	—
		3.0	—
		3.4	—
$(Cp_2Ti)_2AlH_4OBu$ (equation (8))	« «	1.1	Traces
		2.1	5.6
$(Cp_2Ti)_2AlH_4Me$ (equation (9))	« «	2.3	7.0
		3.0	4.9
		3.8	4.5

* Concentration of the catalyst. ** The yield of PA is given in g $mmol^{-1}$ of the catalyst.

The data of Table 1 indicate that the maximum yield of PA is observed when the simplest representative of the series of bimetallic complexes, $Cp_2Ti(\mu\text{-}H)_2AlH_2\cdot OEt_2$, is used as the catalyst and when the reaction is carried out at a temperature below −60 °C. As the temperature of the synthesis increases, not only is there a decrease in the yield of PA, but also an increase in the proportion of the *trans*-isomer in it. The "PA yield" *vs* "concentration of the catalyst" curve (Fig. 1) displays a clearly defined extremum dependence, which is probably associated with diffusion restrictions caused by polymerization processes occurring very rapidly in concentrated solutions of the catalyst and capsulation of most of it in the structure of the insoluble gel. Therefore, we carried out all of the subsequent studies at catalyst concentrations of 2.2—3.2 *M*.

The binuclear complex $Cp_2Ti(\mu\text{-}H)_2AlH_2\cdot OEt_2$ is also known to be the most efficient catalyst of isomerization of olefins among compounds of this type.[9] Moreover, in the character of both processes a number of similar regularities can be followed which may attest to similar

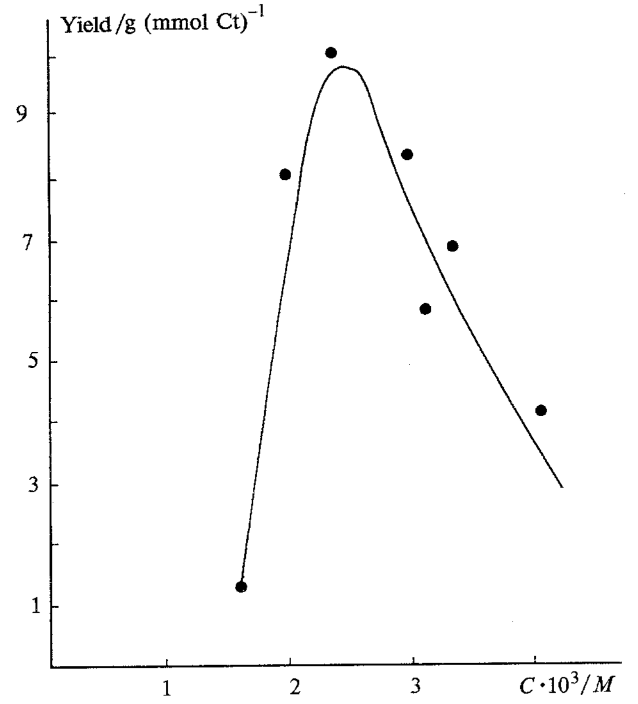


Fig. 1. The dependence of the yield of polyacetylene on the concentration of a solution of complex $Cp_2Ti(\mu\text{-}H)_2AlH_2$ (T_{exp} = −60 °C).

mechanisms of these reactions. For example, when complexes of the composition $Cp_2Ti(\mu\text{-}H)_2AlH(X)\cdot OEt_2$ monosubstituted at the Al atom, *i.e.*, having one terminal Al—H bond, were used as the catalysts, the catalytic activity in both processes was approximately half that of the unsubstituted hydridoaluminate with two Al—H terminal bonds, all other conditions being the same, and the binuclear chloride $Cp_2Ti(\mu\text{-}H)_2AlCl_2\cdot OEt_2$ did not exhibit catalytic properties in these reactions at all. In both cases catalysis is only observed in ethereal solutions of the catalyst and substrate. When a base L stronger than ether, for example THF or NR_3, is introduced to the system, the catalytic activity of all of the types of binuclear compounds entirely disappears. We believe that this is due to the fact that ether molecules are displaced from the coordination sphere of aluminum, which forms complexes with stronger $R_3N{\to}Al$ and $C_4H_8O{\to}Al$ donor-acceptor bonds. These complexes are not destroyed by the action of the substrate and thus the first step of the catalytic process, the coordination step, becomes impossible.[9]

Introducing lithium hydridoaluminate into the solution of the catalyst results in a lowering of the rates of both isomerization[22] and polymerization. In the presence of AlH_3, hydrometallation,[22] rather than isomerization of the olefin, is observed, while polymerization is entirely blocked. It is of interest that the inhibiting effect of aluminum alkylhydrides on the metallation of acetylenes with alkali metal hydridoaluminates was observed previously[19] and explained by the fact that the admixture species of binary alkali metal hydride, which probably[19] catalyze this process described by Eqs. (12) and (13), are bound according to reaction (11).

$$MH + AlH_{3-n}R_n \xrightarrow{L} MAlH_{4-n}R_n \quad (n = 0\div2) \qquad (11)$$

$$MH + HC{\equiv}CR \xrightarrow{L} MC{\equiv}CR + H_2 \qquad (12)$$

$$MC{\equiv}CR + MAlH_4 \xrightarrow{L} MAlH_3(C{\equiv}CR) + MH \textit{ etc.} \qquad (13)$$

Actually, when a powder of an alkali metal hydride is introduced into this "blocked" system, the metallation reaction begins once again and occurs thereafter without complications.[19] However, with the aid of the results obtained in the present work, another interpretation of the inhibiting of both processes can be suggested, based on the assumption that the previously described[11,23,24] complex compounds of the composition $MAlH_4\cdot AlH_3$ and $Cp_2TiH_2AlH_2\cdot AlH_3$ form in the solution. In this case the unblocking action of an alkali metal hydride may be explained by the destruction of $Al_2H_7^-$ binuclear anions according to reaction (14) which is formally similar to reaction (11) but is opposite in the type of action.

$$MAlH_4\cdot AlH_3 + MH \to 2MAlH_4 \qquad (14)$$

When secondary amines, reacting with $MAlH_4$ to give the corresponding amides, which in turn readily react with acetylenes (Eqs. (15), (16)), are introduced to the $MAlH_4$—HC≡CR—L system, metallation is noticeably accelerated.[19,20]

$$MAlH_4 + HNR_2 \xrightarrow{L} MAlH_3NR_2 + H_2 \qquad (15)$$

$$MAlH_3NR_2 + HC{\equiv}CR \xrightarrow{L} MAlH_3(C{\equiv}CR) + HNR_2 \textit{ etc.} \qquad (16)$$

However, the presence of NR_2 or OR groups incorporated in the bimetallic catalyst does not result in any unusual change in the catalytic properties, in contrast, for example, to those found for complex $Cp_2Ti(\mu\text{-}H)_2AlH(Cl)$ (see Table 1). It has also been observed that these compounds behave similarly in the isomerization of hexene-1 (Table 2), whereas in the case of its hydrogenation the reaction rate dramatically increases and becomes even higher than that found for trinuclear complexes $(Cp_2Ti)_2AlH_4X$. The latter may be explained[10] by equilibrium (17) established in the solution, which shifts to the left upon the action of olefin or acetylene and shifts to the right upon the simultaneous action of hydrogen and olefin.

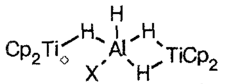
$$\{Cp_2TiH_2AlH(X)\}_2 \rightleftharpoons (Cp_2Ti)_2AlH_4X + AlH_2X \qquad (17)$$

As the data of Tables 1 and 2 indicate, the activity of trinuclear compounds in the isomerization of olefins and

Table 2. Rates of isomerization (W_1) and hydrogenation (W_2) of 1-hexene (20 °C, 1 atm, ether) at bimetallic aluminum—titanocene hydride catalysts

Composition of the catalyst	W_1/mol C_6H_{12} · · (g-at. Ti)$^{-1}$ min^{-1}	W_2/mol H_2 · · (g-at. Ti)$^{-1}$ min^{-1}
$Cp_2TiH_2AlH_2$*	20	0
$Cp_2TiH_2AlH(Cl)$*	6	80
$Cp_2TiH_2AlH(OMe)$	6	150
$Cp_2TiH_2AlH(OEt)$	0.6	280
$Cp_2TiH_2AlH(OBu)$	13	>400
$Cp_2TiH_2AlH(NEt_2)$	11	>400
$(Cp_2Ti)_2AlH_4Cl$**	4	125
$(Cp_2Ti)_2AlH_4OBu$	7	325
$(Cp_2Ti)_2AlH_4NEt_2$	8	265

* See Ref. 9. ** See Ref. 10.

polymerization of acetylene is noticeably lower than that of binuclear compounds, and $(Cp_2Ti)_2AlH_4Cl$, exhibiting weak isomerizing properties,[10] does not catalyze the polymerization at all. When the chlorine atom in this compound is replaced by a donor group (R, OR, NR_2), the catalytic activity of the trinuclear complexes in all types of reactions under consideration increases, which may be explained[7,10] by an increase in the electron density at the metal atoms resulting in partial dissociation of the Ti—H—Al bonds and formation of complexes with a coordination-unsaturated titanium atom, for example,  $Cp_2Ti\overset{H}{\underset{X}{\lessgtr}}\overset{H}{Al}\overset{H}{\underset{H}{\lessgtr}}TiCp_2$, or even in the complete decomposition of the starting compound.

$$(Cp_2Ti)_2AlH_4X \rightleftharpoons Cp_2TiH_2AlH_2 + Cp_2TiX \qquad (18)$$

It is assumed that the extent and the path of the dissociation of trinuclear compounds is determined not only by the nature of X but also by the nature of the substrate.

Thus, the experimental data considered in the present work provide further evidence for the previously stated[7—10] concept of the nature and mechanism of the catalytic action of binuclear titanocene—aluminum hydride complexes. The central point of this scheme is the assumption that at least two types of active sites can occur in solutions. One of them is formed from trinuclear compounds and is responsible for the catalysis of hydrogenation reactions and the other is formed from binuclear complexes and is responsible for the catalysis of isomerization and, as the results of the present study imply, polymerization of acetylene.

The work was carried out with the financial support of the Russian Foundation for Basic Research, project No. 93-03-5757.

References

1. V. A. Lopyrev, G. F. Myachina, O. I. Shevaleevskii, and M. L. Khidekel', *Vysokomol. Soedin.*, 1988, **30**, 2019 [*Polym. Sci. USSR*, 1988, **30** (Engl. Transl.)].
2. A. A. Matnishyan, *Usp. Khim.*, 1988, **57**, 656 [*Russ. Chem. Rev.*, 1988, **57** (Engl. Transl.)].
3. G. Natta, G. Mazzani, and P. Corradini, *Atti Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat. Rend.*, 1958, **25**, 2.
4. H. Shirakawa and S. Ikeda, *Polymer J.*, 1971, **2**, 231.
5. H. Shirakawa and S. Ikeda, *Synth. Met.*, 1980, **1**, 175.
6. N. M. Chirkov, P. E. Matkovskii, and F. S. D'yachkovskii, *Polimerizatsiya na kompleksnykh metalloorganicheskikh katalizatorakh* [*Polymerization with Organometallic Complex Catalysts*], Khimiya, Moscow, 1976, 415 (in Russian).
7. B. M. Bulychev, *Polyhedron*, 1990, **9**, 387.
8. E. V. Evdokimova, B. M. Bulychev, and G. L. Soloveichik, *Kinet. Katal.*, 1981, **22**, 170 [*Kinet. Catal.*, 1981, **22** (Engl. Transl.)].
9. B. M. Bulychev, E. V. Evdokimova, A. I. Sizov, and G. L. Soloveichik, *J. Organomet. Chem.*, 1982, **239**, 313.
10. B. M. Bulychev, G. L. Soloveichik, V. K. Bel'skii, and A. I. Sizov, *Metalloorg. Khim.*, 1989, **2**, 82 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
11. B. M. Bulychev, S. E. Tokareva, G. L. Soloveichik, and E. V. Evdokimova, *J. Organomet. Chem.*, 1979, **179**, 263.
12. B. M. Bulychev, N. A. Yakovleva, A. L. Kostenko, and G. L. Soloveichik, *Trans. Chem. Met.*, 1981, **6**, 32.
13. A. I. Sizov, I. V. Moldnitskaj, B. M. Bulychev, A. I. Gusev, E. V. Evdokimova, G. L. Soloveichik, E. B. Chuklanova, and V. I. Andrianov, *J. Organomet. Chem.*, 1987, **335**, 323.
14. A. I. Sizov, I. V. Molodnitskaj, B. M. Bulychev, V. K. Belsky, and G. L. Soloveichik, *J. Organomet. Chem.*, 1988, **344**, 293.
15. T. Yu. Sokolova, A. I. Sizov, B. M. Bulychev, E. A. Rozova, V. K. Belsky, and G. L. Soloveichik, *J. Organomet. Chem.*, 1990, **388**, 16.
16. M. A. Shen, F. E. Kacasz, and J. C. W. Chien, *J. Polym. Sci., Polym. Chem. Ed.*, 1983, **21**, 2787.
17. F. M. Rappoport and A. A. Il'inskaya, in *Laboratornye metody polucheniya chistykh gazov* [*Laboratory Techniques for Preparing Pure Gases*], Goskhimizdat, Moscow, 1963, 362 (in Russian).
18. G. B. Smith, D. H. McDaniel, E. Biehl, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, 1960, **82**, 3560.
19. L. L. Ivanov, V. V. Gavrilenko, and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1964, 1989 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1964, **13**, 1893 (Engl. Transl.)].
20. S. K. Podder, T.-H. Hu, and C. A. Hollingworth, *J. Org. Chem.*, 1963, **28**, 2144.
21. V. M. Skorobogatov and I. V. Krivoshei, *Usp. Khim.*, 1988, **57**, 832 [*Russ. Chem. Rev.*, 1988, **57** (Engl. Transl.)].
22. E. V. Evdokimova, B. M. Bulychev, and G. L. Soloveichik, *Kinet. Katal.*, 1982, **23**, 1109 [*Kinet. Catal.*, 1982, **23** (Engl. Transl.)].
23. H. Nöth and E. Wiberg, *Forschr. Chem. Forsch.*, 1966, **8/3**, 321.
24. V. I. Simagina, V. M. Mastikhin, I. V. Stoyanova, and V. A. Likholobov, *Koord. Khim.*, 1992, **18**, 120 [*Sov. J. Coord. Chem.*, 1992, **18** (Engl. Transl.)].

Received March 18, 1993