Copolymerization of acetylene with ethylene in the presence of dibenzenetitanium(0)

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The interaction between acetylene and dibenzenetitanium(0) at a room temperature results in the acetylene polymerization and its reduction to ethylene, ethane, and methane at the expense of H atoms of the acetylene molecule. The catalytically active species capable of copolymerizing acetylene with ethylene that are formed during the reaction or are added into the system originate from the interaction of dibenzenetitanium(0) with acetylene.

Key words: dibenzenetitanium(0), acetylene, ethylene, reduction, copolymerization, oxidative addition.

We have shown earlier[1] that Ti^0 bis-arene complexes do not react with alkenes but acetylene readily polymerizes in the presence of these complexes. Polyacetylene formed can be used for the production of lithium accumulators.[2] The interaction of acetylene and ethylene with dibenzenetitanium(0) at a room temperature was studied in this work.

Experimental

The Ti^0 bis-arene complex, dibenzenetitanium, was prepared by co-condensation of the Ti atoms vaporized in a high vacuum with a solid benzene matrix cooled with liquid nitrogen.[1,3] After defrosting, the benzene solution of dibenzenetitanium was introduced into a cell combined with a vacuum circular setup, and acetylene was passed through the cell at ~20 °C. The gas phase was periodically sampled for GLC analysis on a Biokhrom-3 chromatograph (flame-ionization detector, 0.4×300 cm column packed with Al_2O_3). The ESR spectra were recorded on an SE/X 2544 radiospectrometer (Radiopan, Poznan). The IR spectra of the samples were obtained on a Specord IR-75 spectrophotometer in the KBr pellets. The DSC thermograms of the polymer melting and crystallization were obtained on a DSM-2M instrument at the 16 °C min^{-1} rate of heating/cooling. The polymer weighed samples were 5—7 mg.

Results and Discussion

The Ti^0 bis-arene complexes are diamagnetic compounds,[3] which are very sensitive to oxygen and highly soluble in benzene and toluene. Their solutions are red-coloured (λ_{max} = 505 nm). During the interaction of the Ti^0 complex with acetylene, gaseous reaction products (methane, ethane, and ethylene) are evolved, the starting solution is decolorized, and a polymer is precipitated. The products of the reaction between dibenzenetitanium and acetylene are presented in Table 1. When an excess of acetylene interacts with the titanium complex (C_2H_2 : Ti = 85 : 1), a violet polyacetylene film is formed on the walls of the reaction vessel. When the C_2H_2 : Ti ratio was decreased to 8 : 1, only traces of the polyacetylene film were found. The major reaction product is distinctly different in appearance. This is a black round lump of ~1 mm diameter. In this case (see Table 1, run *2*), the ethylene content in the gas phase decreases. This loss of ethylene can be due to its polymerization. Experiment with a mixture of ethylene and acetylene confirmed this suggestion (see Table 1, run *3*). Even traces of the polyacetylene film were not found after run *3*, and the main reaction product represented black spherical particles 3—4 mm in diameter. These particles are formed during stirring the liquid phase because of adhesion of small particles initially precipitated from the solution. The yield of the solid product increased by 100 times compared to the previous run. This fact confirms the participation of ethylene in polymerization.

Earlier[1] we showed that the Ti^0 complex does not react with ethylene. Hence, the active species responsible for the catalysis of ethylene polymerization arise from the interaction of the Ti^0 complex with acetylene. It is known that the C≡C and C—H bonds in the acetylene molecule can be broken in the presence of transition metal complexes. The insertion of a transition metal atom at the C≡C bond produces carbyne compounds, which can further transform into methane.[4,5] The cleavage of the C—H bond in the acetylene molecule by transition metal complexes is usually accompanied by

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 754—756, May, 2002.

Table 1. Products of interaction between dibenzenetitanium(0) and acetylene

Run	$C_0{}^a$ /mol mL^{-1}	V/mL	p^b/Torr (Ti : C_2H_2)^c	t/min	Yield of the reaction products/mol			Polymer	
					CH_4	C_2H_4	C_2H_6	Type	Yield /g per 1 g Ti
1	$2 \cdot 10^{-5}$	6	450 (1 : 85)	55	$0.26 \cdot 10^{-7}$	$1 \cdot 10^{-6}$	$0.33 \cdot 10^{-7}$	Violet film	16
2	$2 \cdot 10^{-5}$	8	50 (1 : 8)	21	$0.25 \cdot 10^{-7}$	$2.5 \cdot 10^{-6}$	$1.9 \cdot 10^{-7}$	Traces of violet film and black sperical lump in 24 h	0.1
				80	$0.49 \cdot 10^{-7}$	$0.5 \cdot 10^{-6}$	$0.44 \cdot 10^{-6}$		
3	$2.6 \cdot 10^{-5}$	3	200 (1 : 150)	1440 (24 h)^d	—	—	—	Black spherical particle	40

[a] Concentration of the initial solution.

[b] Acetylene initial pressure.

[c] Molar ratio.

[d] Ethylene initial pressure was 400 Torr.

the oxidative addition of both fragments formed to the metal atom.[6] One can suggest that Ti^0 in our system is oxidized through a similar reaction to form ethynylhydrido complex, which interacts with acetylene to form ethylene, whereas the reaction with ethylene leads to ethane. These transformations can occur in the same transition complex due to the cleavage of the Ti—H bonds in the ethynylhydrido complex and the H atom transfer to the acetylene molecule to form the C—H bond of alkene.[7] Acetylene itself rather than a solvent (benzene) is a source of hydrogen when methane, ethylene, and ethane are formed from acetylene. Experiment with deuterated acetylene of the isotope composition $C_2D_2 : C_2H_2 = 70 : 30$ at a 10-fold excess of acetylene to titanium and the initial pressure of 200 Torr confirms this suggestion. The absorption bands at 2145 and 2200 cm^{-1} of the stretching vibrations of the CD_2 group of deuteriumpolyethylene[8] are seen in the IR spectrum of the black polymer product. Hence, the reduction of deuteroacetylene to deuteroethylene in this system occurs at the expence of the H atoms of acetylene.

Acetylene dehydrogenation seems to be accompanied by the formation of carbyne-like low-valent titanium compounds (possibly linear polymers).[7] This is confirmed indirectly by a black color of the polymer product obtained.

According to the ESR spectroscopic data, the initial diamagnetic Ti^0 complex transforms into a paramagnetic compound upon the interaction of dibenzenetitanium with acetylene. The ESR spectrum of the paramagnetic compound is a singlet with the g-factor of 1.993. One can suggest that the active sites of polymerization arising in the system are the molecules of a Ti^I compound. A similar assumption on the Ti^I participation in the reaction center of ethylene polymerization has been reported earlier.[9]

The black polymeric product (see Table 1, run *3*) is not dissolved in boiling decalin and represents an elastic material unlike the known powdery polyethylene and acetylene—ethylene block-copolymer, which are formed in the presence of the Zigler catalysts.[10] To recognize the ethylene—acetylene copolymer, the polymeric product was extracted with xylene on a Soxhlet apparatus. If a mixture of two polymers, polyacetylene and polyethylene, was produced by the reaction, the latter could be dissolved in boiling xylene. However, pure polyethylene was not found in this experiment. Therefore, one can suggest that the polymer obtained is a copolymer of ethylene and acetylene. Nevertheless, a comparison of the DSC thermograms for two polymers synthesized with the use of dibenzenetitanium and in the $VOCl_3—Al(Bu^i)_3$ catalytic system gives evidence of an essential difference between these polymeric products. It has been reliably proved for the latter catalyst[11] that the polymeric products are ethylene—acetylene block-copolymers and polyacetylene blocks in a copolymer chain have different lengths. Depending on the content of the polyacetylene blocks, the color of the copolymers formed changes from light-blue to dark-blue and even black similarly to that of polymers synthesized by us. A typical thermogram of the ethylene—acetylene block-copolymer is shown in Fig. 1 (curve *2*), where two peaks are clearly seen: the endothermic peak of melting of the polyethylene blocks (m.p. 120—130 °C depending on the content of the polyacetylene blocks) and the exotermic peak (at $T > 200$ °C) caused by oxidation of the conjugated double bonds in the polyacetylene blocks with the air oxygen that is present in a calorimetric cell. The DSC pattern for the polymer synthesized by us differs substantially. First, a broad peak is seen in the 80—100 °C range. Second, a peak for polyethylene melting is shifted to a higher temperature region, and this corresponds to the ethylene homopolymer. Third, the exothermic peak typical of the known ethylene—acetylene block-copolymers is absent. These data confirm the fact of ethylene polymerization in the system, but the polymer obtained cannot be unambigu-

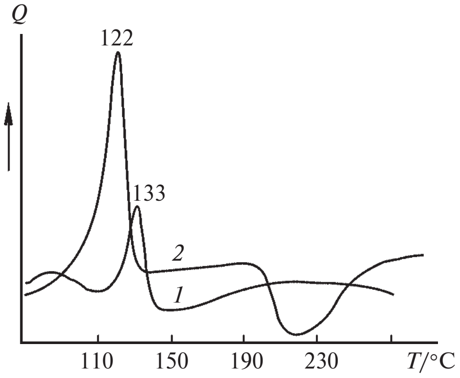

Fig. 1. DSC thermograms of the polymers synthesized with the use of dibenzenetitanium (*1*) and catalytic system $VOCl_3$—$AlBu^i{}_3$ (*2*); *Q* is the heat effect.

ously categorized as the known ethylene—acetylene block-copolymers.

The IR spectrum of the product obtained (ν/cm^{-1}: 3040 v.w, 3010 m, 2910 v.s, 2840 v.s, 1785 w, 1470 s, 1460 s, 1375 m, 1010 s, 905 v.w, 890 v.w, 738 m, 728 m, 718 m, 440 m.br) can be easily divided to two spectra: that of polyacetylene (PA) and that of polyethylene (PE). Some conclusions on the structure of the product components can be drawn from the examination of the spectroscopic data. The polyacetylene component is a mixture of *cis*- and *trans*-conformers (72 and 28%, respectively). The PA isomer composition was determined from the ratio of intensities of the absorption bands (a.b.) at 1328 cm^{-1} (δ(CH), *cis*-PA) and 1010 cm^{-1} (δ(CH), *trans*-PA) according to a procedure described earlier.[12] The PA chains are not long, since the intensity of the band of the combination vibration at 1785 cm^{-1} is small.

The polyethylene component is crystalline. The PE crystals contain fairly long polymethylene chains, since a.b. of the pendular deformation vibration are in the region of 725 cm^{-1}. The PE crystallinity is confirmed by the splitting of the a.b. of the CH_2 scissor and pendular deformation vibrations by 10 cm^{-1} (doublets at 1470, 1460 cm^{-1} and 728, 718 cm^{-1}, respectively).[13] The enhanced intensity of the a.b. at 1375 cm^{-1} ($\delta(CH_3)$ terminal) can be due to the superposition of the a.b. of the deformation vibrations of methylene segments of the *trans-gosh*-conformation in the loops of the PE folded chains.[14] The presence of the a.b. of the stretching and deformation CH vibrations of the =CH—CH_2— fragment at 3010 and 905, 890 cm^{-1}, respectively, can be due to the presence of a junction of the short PA chains with long folded PE chains. The relative contents of the ethylene and acetylene units in the copolymer evaluated from the relative intensities of the a.b. at 1470, 1460 cm^{-1} ($\delta(CH_2)$ PE) and 1328 (δ_{II}(CH) *cis*-conformer of PA), taking into account of *trans*-conformer of PA, are 60 and 40%, respectively.

Hence, we showed for the first time that acetylene is reduced to methane, ethane, and ethylene upon the interaction of dibenzenetitanium(0) with acetylene and acetylene is the source of the H atoms. The copolymerization of acetylene with ethylene was first found, and this reaction is catalyzed by the single-component system containing dibenzenetitanium(0) as the starting complex.

References

1. G. G. Tairova, O. N. Krasochka, V. I. Ponomaryov, E. F. Kvashina, Yu. A. Shvetsov, E. M. Lisetsky, D. M. Kiryukhin, L. O. Atovmyan, and Yu. G. Borod´ko, *Transition*kina, and O. N. Efimova, *Elektrokhimiya*, 1998, **34**, 768 [*Elect Metals Chem.*, 1982, **7**, 189.
2. G. N. Petrova, E. F. Kvashnina, T. N. Danil´chuk, O. S. Roshchup*rochem.*, 1998, **34** (Engl. Transl.)].
3. F. W. S. Benfield, M. L. Green, J. S. Ogden, and D. Young, *J. Chem. Soc.*, *Chem. Commun.*, 1973, 866.
4. Y. Degani and I. Willner, *J. Chem. Soc.*, *Chem. Commun.*, 1985, 648.
5. E. D. Cabrera, J. C. Daran, and Y. Jeannin, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 607.
6. A. E. Shilov and G. B. Shul´pin, *Aktivatsiya i kataliticheskie reaktsii uglevodorodov* [*Activation and Catalytic Reactions of Hydrocarbons*], Nauka, Moscow, 1995, 399 pp. (in Russian).
7. O. N. Temkin and R. M. Flid, *Kataliticheskie prevrashcheniya atsetilenovykh soedinenii v rastvorakh kompleksov metallov* [*Catalytic Transformations of Acetylene Compounds in the Solutions of Metal Complexes*], Nauka, Moscow, 1968, 211 pp. (in Russian).
8. M. Tasumi and T. Shimanouchi, *J. Polimer Sci.*, *A*, 1966, **4**, 1011.
9. N. Furman, L. I. Russiyan, V. N. Noskova, A. P. Lisitskaya, O. V. Bragin, and P. E. Matkovskii, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1526 [*Bull. Russ. Acad. Sci.*, *Div. Chem. Sci.*, 1992, **41**, 1175 (Engl. Transl.)].
10. L. N. Raspopov, P. E. Matkovskii, G. P. Belov, B. N. Noskova, L. N. Russiyan, G. N. Davydova, V. A. Shtarkin, V. M. Rudakov, and A. Kh. Yusupbekov, *Vysokomol. soedin.*, 1991, **33A**, 425 [*Polym. Sci. USSR*, 1991, **33A** (Engl. Transl.)].
11. E. G. Guk, V. A. Marikin, L. P. Myasnikova, and G. P. Belov, *Fiz. Tverd. Tela* [*Solid State Physics*], 1996, **38**, 1940 (in Russian).
12. O. S. Roshchupkina, L. I. Tkachenko, and O. E. Efimov, *Synth. Met.*, **90**, 89.
13. *Ultrarotspektroskopishe Untersuchungen an Polymeren*, Ed. J. Dechant, Akademie Verlag, Berlin, 1972, 369 pp.
14. K. Nakanishi, *Infrared Absorption Spectroscopy*, Holden-Day, Inc., San Francisco; Nancodo Company Limited, Tokyo, 1962, 212 pp.

Received June 27, 2001;
in revised form January 22, 2002