Brief Communications

Product of ditoluenetitanium(0) oxidation with oxygen as a new catalyst for ethylene polymerization

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The reaction of ditoluenetitanium(0) with oxygen affords an intermediate oxidation product: a titanium(II) complex that catalyzes ethylene polymerization.

Key words: ditoluenetitanium(0), ethylene, oxygen polymerization.

We have previously[1,2] shown that ditoluenetitanium(0) catalyzes acetylene polymerization and ethylene—acetylene copolymerization but does not react with pure ethylene. In this work, we studied the role of oxygen in the reaction of ditoluenetitanium(0) with ethylene at room temperature.

Experimental

Ditoluenetitanium, *viz.*, bisarene titanium(0) complex, was synthesized by the cocondensation of titanium atoms vaporized in a high vacuum (10^{-5} Torr) with the solid toluene matrix cooled with liquid nitrogen.[1,3] After defrosting, a red toluene solution of ditoluenetitanium(0) was transferred in an inert atmosphere to a reaction flask, and an excess of unreacted titanium was filtered off with a glass filter.

Ditoluenetitanium(0) was oxidized with oxygen at room temperature purging oxygen into a homogeneous solution of ditoluenetitanium(0) in toluene ($2 \cdot 10^{-5}$ (mole of Ti) mL^{-1}, volume 50 mL, initial oxygen pressure 50 Torr). The oxygen absorption was monitored by a pressure drop in the reaction flask attached to a manometric vacuum setup ($V = 150$ mL) through a narrow flexible hose. The oxygen pressure comparable with the partial toluene pressure under the reaction conditions provided the slow supply of oxygen to the reaction flask. This procedure resulted in the formation of a black precipitate of compound **1**, whose amount increased during the reaction course. The layer of unreacted ditoluenetitanium(0) above the precipitate prevented the further oxidation of product **1**. The procedure was repeated until the initial solution of ditoluenetitanium(0) was completely decolorized. The reaction time was 15—20 min.

For measuring the IR spectrum, product **1** was evacuated at room temperature in a vacuum of 10^{-2} Torr to remove toluene. The synthesized product was triturated in Nujol in an inert atmosphere.

The reaction of compound **1** with DCl was carried out in a closed volume (200 mL) under a gas pressure of 600 Torr (20 mL of toluene, $7.6 \cdot 10^{-3}$ mole of DCl, $1.5 \cdot 10^{-4}$ mole of Ti, 30 h). During the reaction black product **1** transformed into solid yellow product **2**. The latter was distilled in a vacuum of 10^{-2} Torr together with toluene at room temperature. Product **2**, which is insoluble in toluene, precipitated as a yellow substance, and then toluene was decanted *in vacuo*.

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Sample **2** was prepared for measuring the IR spectrum by its triturating in Nujol in an inert atmosphere, and during this procedure a minor amount of toluene that remained after decanting was evaporated.

IR spectra were recorded on a Specord IR-75 spectrophotometer.

Magnetic susceptibility was measured by the Faraday method[4] at 80—293 K in an interval of field intensity of 1—10 kOe in an inert atmosphere. The sample was also prepared in an inert atmosphere.

Ethylene polymerization was carried out at 18.5 °C under a constant ethylene pressure of 540 Torr (total volume of the setup 480 mL, volume of the reaction flask 80 mL). To prepare the polymerization catalyst, a solution of ditoluenetitanium(0) (7 mL, $2 \cdot 10^{-5}$ (mole of Ti) mL^{-1}) was placed in the reaction flask and oxidized similarly to the synthesis of compound **1**. Ethylene was fed into the reaction flask with magnetic stirring. The amount of absorbed ethylene was measured manometrically.

Results and Discussion

Bisarene titanium(0) complexes are diamagnetic compounds, which are highly sensitive to oxygen and well soluble in toluene.[5] The solutions are red-colored (λ_{max} = 512 nm).

Upon the slow oxygen supply, we obtained an intermediate product of ditoluenetitanium(0) oxidation with oxygen (**1**). Compound **1** is a black substance insoluble in toluene, and it becomes lighter in oxygen excess to form the titanium(IV) compound. To determine the oxidation state of titanium in compound **1**, we measured its magnetic susceptibility. The results of the measurement indicate that compound **1** is diamagnetic. It was also found that compound **1** is readily hydrolyzed with water to evolve 1.0 mole of H_2 per 1 mole of Ti. These facts suggest that product **1** is a titanium(II) compound.

The IR spectrum of compound **1** was measured in an inert atmosphere, ν/cm^{-1}: 1600 (δ(OH)) m, 3450 (ν(OH)) m. The spectrum also contains a series of weak absorption bands (AB) that cannot be analyzed reliably. The observed AB attributed to vibrations of the OH group suggest the presence of this group in the composition of compound **1**.

To reveal the composition of compound **1**, we studied the gaseous and solid products of its reaction with gaseous DCl. The reaction turned the solid product yellow from black. Yellow product **2** together with toluene is easily distilled in a vacuum of 10^{-2} Torr at room temperature. Toluene was decanted *in vacuo*, and its residues were removed when triturating sample **2** in an inert atmosphere. In air Ti-containing compound **2** decomposes rapidly. The IR spectrum of solid product **2** was measured in an inert atmosphere, ν/cm^{-1}: 3350 (ν(O—H)) m, 2500 (ν(O—D)) m, 1590 (ν(C=C)) s, 1410 (δ(=CH_2)) m, 1250 (ν(C—C)) w, 1180 (β(CCH)) m, 1110 (ν(C—Cl)) m, 1070 (δ(C—C)) w, 1000 (δ(CH)) m, 860 (δ(Ti—OH)) s, 780 (δ(CH_2)) m, 720 (δ(CC)) s. The presence of the OD group in the composition of molecule **2** is a result, most likely, of the deuterium exchange of the D atoms in the DCl molecule with the H atoms of the OH group. This confirms that the OH group is a component of molecule **1**. The mechanism of the reaction of molecular oxygen with ditoluenetitanium(0) affording the OH group in the composition of compound **1** remains unclear.

The IR spectrum of compound **2** contains no AB at 3100, 1600, and 1500 cm^{-1} characteristic[6] of aromatic compounds. The observed AB belong to the C=C double bonds and the C—C and C—H ordinary bonds.[6] These groups can be formed due to the C—C bond cleavage in the arene ring and its transformation into the linear fragment (L).

The IR spectrum of the gaseous products of the reaction of compound **1** with DCl was measured, ν/cm^{-1}: 2800—3000 (ν(H—Cl) s, 2270 (ν(C—D)) s. The intense AB at 2270 cm^{-1} is assigned to stretching vibrations of the C—D bond of the aromatic ring.[7] Therefore, the interaction of compound **1** with DCl is accompanied by deuteration exchange involving the H atoms of the arene ring. In the absence of compound **1**, no deuterium exchange of the H atoms of the arene ring with a DCl molecule occurs. It can be assumed that the toluene molecule is activated in the system due to complex formation with Ti^{II}. However, after evacuation to remove the solvent, the IR spectrum of solid product **1** contained no AB of toluene. It is most likely that the Ti^{II} complex with toluene has a low complex formation constant and toluene is removed under the conditions of sample preparation. Thus, the composition of synthesized catalyst **1** for ethylene polymerization can be expressed by the formula $OH—Ti^{II}—L \cdot PhCH_3$, where L is the linear fragment containing the C=C multiple bonds and the C—C and C—H ordinary bonds, which are formed due to the C—C bond cleavage of the aromatic ring.

The data on ethylene polymerization in the presence of product **1** are shown in Fig. 1.

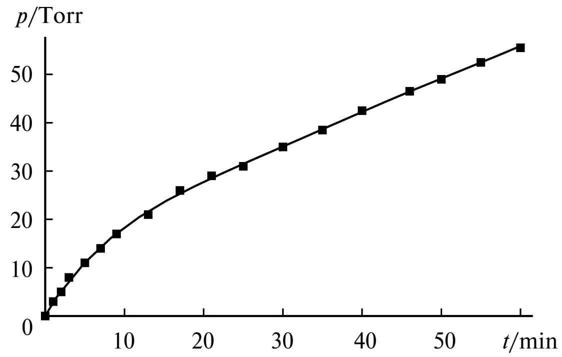

Fig. 1. Ethylene consumption during its polymerization in the presence of catalyst **1** at 18.5 °C (pressure in the system 540 Torr, toluene (7 mL), $2 \cdot 10^{-5}$ (mole of Ti) mL^{-1}).

Under these conditions, the duration of the polymerization process is 95 h. The yield of polyethylene is 6.5 g (g of Ti)$^{-1}$ h^{-1}, and the final yield of polyethylene is 51.5 g (g of Ti)$^{-1}$.

Polyethylene that formed is readily molded without heating to form a transparent film. The IR spectrum of the obtained film was measured, ν/cm^{-1}: 717 ($\delta(CH_2)$) m, 730 ($\delta(CH_2)$) m, 1363 ($\delta(CH_2)$) m, 1470 ($\delta(CH_2)$) s, 2850 ($\nu(CH_2)$) s, 2915 ($\nu(CH_2)$) s. The spectrum observed is identical to the IR spectrum of the polyethylene film.[8] Found (%): C, 83.24; H, 14.05; residue, 1.43. The elemental analysis data (H/C = 2.01) confirm that the reaction of ethylene with product **1** affords polyethylene.

Thus obtained one-component catalyst **1** is more active in ethylene polymerization than the known Natta complex[9] with the composition $Ti^{II}Cl_2 \cdot 2AlCl_3 \cdot C_6H_6$. Unlike product **1**, the Natta complex does not polymerize ethylene under mild conditions and works only under an ethylene pressure of 20—25 atm.[9]

Thus, we prepared for the first time the one-component catalyst for ethylene polymerization by the oxidation of ditoluenetitanium(0) with oxygen to form the Ti^{II} complex. The new method for the synthesis of low-valence titanium complexes gives novel compounds, which cannot be prepared by methods of traditional organometallic chemistry.

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