Reactions of methylaluminoxane and trimethylaluminum with zirconium and titanium tetracyclopentadienyl derivatives

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Gas volumometry, gas chromatography, mass spectrometry, and ESR were used to study reactions of methylaluminoxane (MAO) and Me_3Al with Cp_4Zr, Cp_4Ti, and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). It was shown that the reaction is accompanied by evolution of methane, whose amount exceeds the initial concentration of the starting metallocene or free radical by a few hundred times, but in all the cases is no more than 15% of the starting amount of the Me—Al fragments in the organoaluminum compound. Metal-centered radicals were detected by ESR in the systems with Zr and Ti metallocene derivatives. Mechanism of the observed reactions is discussed.

Key words: polycondensation, organoaluminum compounds, metallocenes.

Earlier, we have found[1,2] that soluble and heterogenized catalytic systems based on Cp_4Zr and methylaluminoxane (MAO) display high catalytic activity in the processes of polymerization and copolymerization of ethylene. The catalytic systems under consideration are also of interest as the model objects in the study of the mechanism of metallocene-catalyzed polymerization of olefins.

According to the X-ray crystallographic data,[3] a Cp_4Zr molecule includes three π-bound and one σ-bound cyclopentadienyl groups. The analogous titanium compound, Cp_4Ti, contains two π-bound and two σ-bound cyclopentadienyl groups. Apparently, these differences are responsible for the fact that the tris(π-cyclopentadienyl) fragment in the Cp_4Zr molecule remains preserved during its reactions with organoaluminum compounds (OAC) (for example, with triethylaluminum), in contrast to the titanium analog, but rather forms a complex of the composition $Cp_3ZrH...AlEt_3$.[4] This example gives the basis to suggest that the $[Cp_3Zr^-]$ structural unit can be preserved in both the reactions of Cp_4Zr with MAO and polymerization of ethylene involving this system.

The present study is a continuation of the works,[5—10] in which it has been shown that the reaction of transition metal derivatives with trimethylaluminum (TMA) and MAO is accompanied by evolution of methane, whose amount, normalized to the concentration of the transition metal compound, allows to suggest a catalytic process of the OAC decomposition.

The purpose of the present studies is to investigate reactions of MAO and TMA with zirconium and titanium tetracyclopentadienyl derivatives, as well as with the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) model compound using gas volumometry and to obtain information on the mechanism of the process under consideration. Such information, together with other studies on the reactions of metallocenes with different OAC under the model conditions (*i.e.* in the absence of a monomer) and during polymerization process, will be helpful in establishing the structure and clarifying mechanism of the action of active centers in metallocene catalytic systems during polymerization processes of olefins and possible approaches to their deactivation.

Experimental

The Cp_4Zr and Cp_4Ti samples were synthesized according to the known procedures,[1,11] MAO and TMA (Aldrich) were used as toluene solutions with the concentrations of 1.54 and 2 mol L^{-1}, respectively, without additional purification. Tetralin (Fluka) and toluene (pure for analysis grade) were dried over molecular sieves 5 Å, distilled, and stored over sodium wire. Experiments on the study of the rate of the gas evolution were carried out on a glass vacuum installation with capacities calibrated in volume, which was equipped with a mercury manometer, thermostat, magnetic stirrer, and a device for the sequential addition of reactants. All the experiments were performed at 60 °C. In the typical experiment, a solution of metallocene or TEMPO in tetralin (10 mL) was placed into a glass reactor and incubated, then a solution of OAC in toluene (5 mL), which was preliminary degassed *in vacuo,* was added to the mixture with stirring. Evolution of gaseous products was observed for 6 h (in all the experiments, the reaction reached a plateau on the expiry of this time). The gaseous products were analyzed by gas chromatography on a LKhM-80 instrument equipped with

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a catharometer and a column of 3 m in length and 2 mm in diameter filled with Polysorb-1 with the particle sizes of 200—250 μm; the temperature mode: the isotherm at 100 °C for 5 min, then heating to 250 °C at the rate of 8 °C min^{-1}. Composition of the liquid phase was determined by a combination of gas chromatography and mass spectrometry (GC-MS) on a Perkin—Elmer Clarus 500 instrument (USA). ESR spectra were recorded on a EPR-2 spectrometer.

Results and Discussion

Studies of the reaction of MAO with Cp_4Zr and Cp_4Ti. It was found that the reactions of MAO with Cp_4Zr and Cp_4Ti lead to the formation of solid gelatinous products and evolution of methane. Amount of the evolved gas in the Cp_4Zr—MAO system varied within the range of 3.5 to 319 mol of CH_4 (mol of zirconocene)$^{-1}$ depending on the concentration of metallocene (Table 1). This fact indicates that evolution of methane is a chain process with respect to zirconocene, and zirconocene is its initiator. Kinetics of the evolution of methane is given in Figure 1. The total amount of evolved methane is directly proportional to the molar ratio Al/Zr in the system (Fig. 2, see Table 1). To sum up, when the concentration of MAO is constant and equal to 0.77 mol L^{-1}, the amount of methane formed during equal periods of time is inversely proportional to the concentration of zirconocene, *i.e.* $[CH_4] \sim [Zr]^{-1}$. Gas chromatography showed the presence of ethane and hydrogen in trace amounts among the reaction products. The ESR recorded a signal with the *g*-factor 1.998 corresponding to the reduction product of the starting zirconocene.[12]

Studies of the Cp_4Ti—MAO system (Table 2) showed that an increase in the molar ratio Al/Ti leads to the decrease in the amount of the methane formed. Traces of ethane and hydrogen were also found in the reaction products. The ESR spectrum of the product consists of three components (the *g*-factors 1.978, 1.985, and 1.989) due to the reduction products of the starting titanium compound. In both cases, no hyperfine structure of the ESR lines was observed at low temperatures and high dilution of the solution, that indicates the fact that OAC is not a part of the Zr^{III} and Ti^{III} complex compositions.

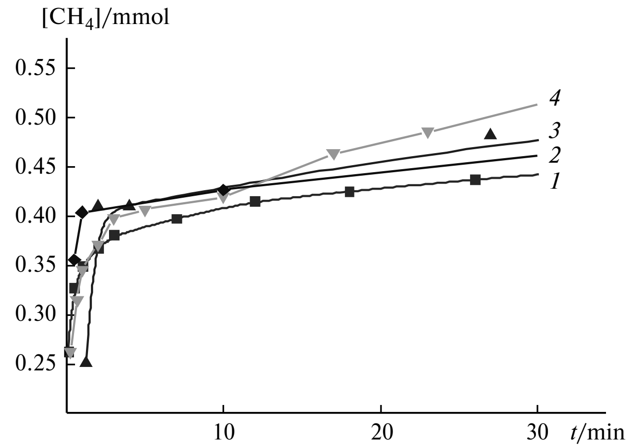


Fig. 1. Kinetics of methane evolution in the Cp_4Zr—MAO system at 60 °C in the tetralin—toluene (2 : 1) solvent mixture; [MAO] = 0.77 mol L^{-1}, $[Cp_4Zr] = 5.6 \cdot 10^{-3}$ (*1*), $4.3 \cdot 10^{-3}$ (*2*), $7.8 \cdot 10^{-4}$ (*3*), $3.1 \cdot 10^{-4}$ mol L^{-1} (*4*).

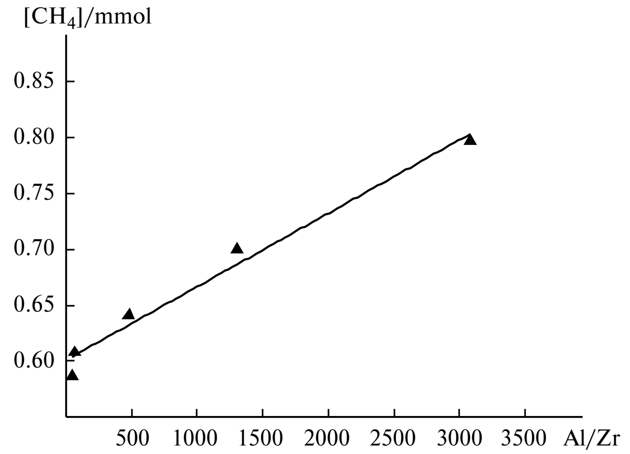


Fig. 2. Amount of methane formed in the Cp_4Zr—MAO system versus the Al/Zr molar ratio. Experiments were carried out at 60 °C in the tetralin—toluene (2 : 1) solvent mixture, [MAO] = 0.77 mol L^{-1}, the reaction time was 6 h.

Table 1. Evolution of methane in the Cp_4Zr—MAO system at 60 °C in the tetralin—toluene (2 : 1) solvent mixture, [MAO] = 0.77 mol L^{-1}, the reaction time was 6 h

$[Cp_4Zr]$ /mol L^{-1}	$[CH_4]$ /mmol	$[CH_4]/[Zr]$	$[CH_4]/[MAO]$
$1.69 \cdot 10^{-2}$	0.59±0.01	3.5	0.077
$1.14 \cdot 10^{-2}$	0.66±0.01	5.7	0.085
$1.6 \cdot 10^{-3}$	0.64±0.01	40.3	0.083
$5.9 \cdot 10^{-4}$	0.70±0.01	119.0	0.091
$2.5 \cdot 10^{-4}$	0.80±0.01	319.0	0.104

Table 2. Evolution of methane in the Cp_4Ti—MAO system at 60 °C in the tetralin—toluene (2 : 1) solvent mixture, [MAO] = = 0.77 mol L^{-1}, the reaction time was 6 h

$[Cp_4Ti]$ /mol L^{-1}	$[CH_4]$ /mmol	$[CH_4]/[Ti]$	$[CH_4]/[MAO]$
$6.2 \cdot 10^{-3}$	0.86±0.01	13.9	0.112
$3.1 \cdot 10^{-3}$	0.67±0.01	21.7	0.087
$1.54 \cdot 10^{-3}$	0.70±0.01	45.5	0.091
$7.7 \cdot 10^{-4}$	0.60±0.01	77.4	0.077
$1.5 \cdot 10^{-4}$	0.57±0.01	373.0	0.075

Replacement of MAO with TMA does not affect the character of dependence of the $[CH_4]/[Zr]$ molar ratio from the concentration of metallocene (Table 3). This

Table 3. Evolution of methane in the Cp_4Zr—TMA system at 60 °C in the tetralin—toluene (2 : 1) solvent mixture, [TMA] = 0.77 mol L^{-1}, the reaction time was 6 h

$[Cp_4Zr]$ /mol L^{-1}	$[CH_4]$ /mmol	$[CH_4]/[Zr]$	$[CH_4]/[TMA]$
$5.6 \cdot 10^{-3}$	0.43±0.01	7.6	0.055
$4.3 \cdot 10^{-3}$	0.50±0.01	12.5	0.069
$1.7 \cdot 10^{-3}$	0.64±0.01	37.9	0.083
$7.8 \cdot 10^{-4}$	0.50±0.01	63.5	0.064
$3.1 \cdot 10^{-4}$	0.44±0.01	140.0	0.057

effect is different for zirconium and titanium compounds. In the case of zirconium compound, replacement of MAO in the Cp_4Zr—OAC system with TMA leads to a decrease in the yield of the gases formed (*cf.* Tables 1 and 3), while in the case of titanium compound, the amount of the evolved gases remains unchanged.

Note that in all the cases under consideration, the total molar amount of methane calculated per one mole of the Me—Al fragments in OAC does not exceed 14% (after the reaction progress was monitored for 6 h and the process of gas evolution reached a plateau).

GC-MS method showed the presence of tetralin monomethylated products. Their amount somewhat increases with the increase in the concentration of metallocene (Table 4). In the case of Cp_4Zr, the amount of the methylated product considerably exceeds the concentration of metallocene (by 8—59 times depending on the concentration of metallocene).

All these observations give a basis to suggest that, like in the decomposition of MMe_n (see Ref. 13), where MMe_n are Ti, Cr, W, Re, and other metal polymethyl derivatives, the reactions of Cp_4M (M = Zr, Ti) with MAO and with TMA proceed by radical mechanism. To confirm this assumption, we studied the reaction of MAO with the stable free radical, TEMPO.

The amount of methane formed in the MAO—TEMPO system reduced to the amount of TEMPO is linearly dependent on the concentration of TEMPO (Table 5). The amount of the evolved methane varies within the range of 1.5 to 89 mol of CH_4 (mol of TEMPO)$^{-1}$. When Cp_4Zr was added to the system, the amount of the liberated methane increased.

Table 4. Alkylation of tetralin upon the action of the Cp_4Zr—MAO system

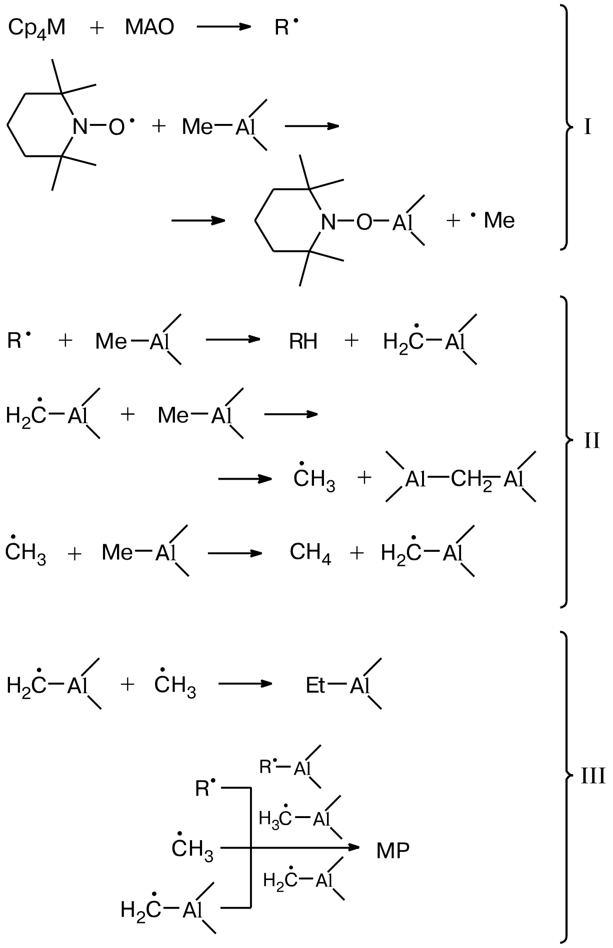
[Zr]	Σ Me—$C_{10}H_9$	ΣMe—$C_{10}H_9$/[Zr]
mol L^{-1}		
$5.9 \cdot 10^{-4}$	$3.5 \cdot 10^{-2}$	58.6
$4.9 \cdot 10^{-3}$	$3.9 \cdot 10^{-2}$	7.9

Table 5. Evolution of methane in the TEMPO—MAO system at 60 °C in the tetralin—toluene (2 : 1) solvent mixture, [MAO] = 0.77 mol L^{-1}, the reaction time was 6 h

[TEMPO] /mol L^{-1}	$[CH_4]$ /mmol	$[CH_4]$/[TEMPO]	$[CH_4]$/[MAO]
$3.9 \cdot 10^{-2}$	0.62±0.01	1.6	0.081
$2.9 \cdot 10^{-2}$	1.07±0.01	3.6	0.140
$1.8 \cdot 10^{-2}$	0.93±0.01	4.8	0.103
$5.3 \cdot 10^{-3}$	0.83±0.01	15.7	0.107
$8.0 \cdot 10^{-4}$	0.71±0.01	88.5	0.092

The results of our experiments and the found effects indicate a free-radical mechanism of the methane formation in the reactions of MAO with metallocene compounds and TEMPO. The mechanism of this process can be shown by a simplified Scheme 1 suggested earlier[14] based on the data on the gas evolution in the Cp_2ZrCl_2—Me_3Al and Cp_2TiCl_2—Me_3Al systems.

Scheme 1



MP are the molecular products, I is the chain initiation, II is the chain propagation, III is the chain termination.

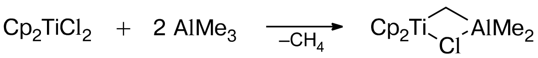
The mechanism shown for the reaction of MAO and TMA with metallocene compounds and TEMPO includes an initiation step (I), chain propagation step (II), and chain termination step (III). Initiation can take place by homolytic cleavage of the metal—carbon bond after transalkylation of the transition metal compounds with OAC, *i.e.*, methyl radicals and products of reduction of transition metals (which will be discussed below) can serve as radicals ($R^{\cdot}$) initiating the polycondensation process.

The chain propagation steps (see Scheme 1) can lead to both isolation of the major gaseous reaction product (CH_4) and formation of new carbon- or aluminum-centered radicals, as well as to polycondensation of OAC.

The chain termination is accompanied by formation of different molecular products (see Scheme 1). The found reaction of methyl radicals with solvents (toluene—tetralin) can also lead to the termination of the chain due to the inclination of benzyl radicals formed from toluene to dimerization.

Formation of methane in the systems including transition metal metallocene derivatives and OAC can be also due to the processes similar to the reaction for the formation of the Tebbe reagent[15] (Scheme 2).

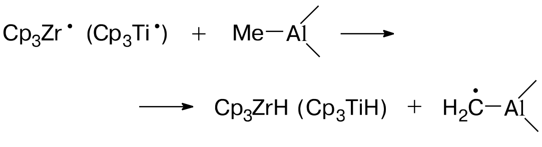
Scheme 2



However, it should be noted that such mechanism does not explain formation of nonstoichiometric amounts of methane, which exceed amount of metallocene taken for the reaction by several hundred times.

In all the systems under consideration, formation of a gelatinous product is accompanied by evolution of gaseous methane, whose amount can reach 370 mol of CH_4 (mol of initiator)$^{-1}$, but in all the cases it does not exceed 10—14% of the amount of the Me—Al fragments in the initial OAC. We assume that this process bears a character of the chain polycondensation with respect to OAC under consideration. In the case of metallocene systems, reduction of a transition metal is observed. The ESR studies indicate that a reduced transition metal contains an unpaired electron and can also react with the Me groups of MAO or TMA (Scheme 3) and, thus, play the role of radical initiating the polycondensation process (marked as $R^{\bullet}$ in Scheme 1).

Scheme 3



Decomposition of Cp_3ZrH or Cp_3TiH can lead to the formation of hydrogen, whose evolution was observed in all the cases.

Compounds Cp_4Zr and Cp_4Ti, in contrast to the free-radical initiator TEMPO, play a dual role in the polycondensation process of OAC. On the one hand, they initiate polycondensation giving metal-centered radicals, which are formed due to the cleavage of the metal—carbon σ-bond. On the other hand, they inhibit polycondensation by recombination of two free radicals in the coordination sphere of a transition metal atom. Apparently, the inhibition effect of radical processes is more pronounced in the case of Cp_4Zr due to the larger radius of the coordination sphere of Zr atom.[16] This assumption also explains the fact that the amount of evolved methane in the case when polycondensation is initiated by the zirconium derivative is antibate to its concentration.

This suggestion finds its confirmation in the works[17—20] devoted to the reactions of catalytic inhibition of radical polymerization processes of methyl methacrylate and styrene with transition metal complexes (Co, Ti, *etc.*).

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