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Article

Mathematical Modeling of Induction Period of The Olefins Hydroalumination Reaction By Diisobutylaluminiumchloride Catalyzed with Cp_2ZrCl_2

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Abstract. Method of mathematical modeling of induction period for reaction of olefins hydroalumination by alkylalanes in presence of Cp_2ZrCl_2 was developed. The kinetic model of reaction of olefins hydroalumination by alkylalanes with presence the catalyst Cp_2ZrCl_2 was built. The values of kinetic parameters of reaction of olefins hydroalumination by alkylalanes in presence of Cp_2ZrCl_2 which describes well an experimental data were determined. Obtained values are allowed to describe an induction period in all experimentally investigated area. The stages of mechanism of reaction of olefins hydroalumination by alkylalanes in presence of Cp_2ZrCl_2 which determine an existence of induction period were found. The software of mathematical modeling of induction period which allows defining stages determined an existence of induction period was developed. It can be used for wide class of investigated reactions.

Keywords: Olefin hydroalumination, organoaluminium compounds, detailed elaboration, information-analytical system, mathematical description, dimer, catalytic cycle.

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1. Introduction

Investigation of mechanism of homogeneous metalcomplex catalysis is important problem of modern chemistry [1 – 4]. The reactions which run with complex of transitional metals are complicated processes [5]. Modern physical and chemical methods cannot define the structure of all intermediates which take part in complex catalytic processes [6]. Therefore we have mathematical ambiguity of solution in solving the inverse problems of searching for kinetic parameters. In science school of Dzhemilev U.M. the fundamental catalytic reactions of hydro-, carbo- and cycloalumination of unsaturated compounds was worked out [7].

In the last year investigations of mechanism of given processes were started [8, 9]. The aim of these investigations is building the kinetic model of given reactions. For the reaction of olefins hydroalumination by alkylalanes in presence of catalyst Cp_2ZrCl_2 the existence of induction period was shown experimentally [9]. Induction period is some time interval $[0;T_{ind}]$, such that we have a slow accumulation of reaction product during this time interval. Out of this interval the fast accumulation of reaction product observed. Induction period exist in various chemical systems, however, for the processes of homogeneousmetalcomplex catalysis, particularly, for the reaction of olefins hydroalumination the question about induction period is not investigated.

Thus, the mathematical modeling of induction period in reactions with metalcomplex catalysts is important and relevant.To find kinetic parameters of such chemical reactions that will ensure that the induction period is not a trivial problem.

The main aim of this work is investigation of the mechanism of olefins hydroalumination reaction by alkylalanes in presence of catalyst Cp_2ZrCl_2, mathematical modeling of induction period, building a kinetic model of process, detachment the stages which define the characteristics of induction period.

2. Mathematical modeling of induction period of the olefins hydroalumination reaction by alkylalanes catalyzed with Cp_2ZrCl_2

Let's consider the system of differential equations which describe the kinetics of some chemical reaction

$$\frac{dx_i}{dt} = \sum_{j=1}^{r} \gamma_{ji} w_j , \tag{1}$$

where i=1..n, j=1..r, n – a number of process members, r – a number of elementary stages, xi – concentration of substance Xi,γ_{ji}- stoichiometriccoefficients of substances, wj – velocity of jth stage.

The system (1) was solved with use of the "time division" method. Firstly we made a numerical integration of system (1) by explicit method of Runge-Kutta with variable step (but with implicit scheme of Eiler for the "fast" variables). Then by knowing a computational solution we divide the time interval $(0;\infty)$ on a chain of subintervals. On each of these subintervals the initial system simplified to the subsystem differential-algebraic equations by the following rules:

1) If on some time interval the absolute value of rate of normalized concentration change of i^{th} substance is less then absolute value of rate of normalized concentration change of other substance then i^{th} equation of initial system can be written as
$$\dot{a}_i(t) = 0,$$
where$a_i(t)$ – concentration of i^{th} substance at time t.
2) If on some time interval the absolute value of rate of normalized concentration change of i^{th} substance is less then absolute value of some items on the right hand side of the equation (1), then ith differential equation of initial system can be replaced by algebraic equation
$$0 = \sum_{j=1}^{r} \gamma_{i,j} w_j(a(t)),$$
wherewj – the velocity of jth stage, γ_{ji}- stoichiometric coefficients.
3) If on some time interval on the right hand side of the Eq. (1) there are some items which are less by its absolute value in comparison with the rest items, we can ignore these items.

We know some works [10] dedicated to investigation of induction period. But we don't know any works about modeling of induction period in catalytic processes, in particular, in reaction of olefinshydroalumination by alkylalanes in presence of catalyst Cp_2ZrCl_2.

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Experimental data was obtained in laboratory of structure chemistry in the Institute of Petrochemistry and Catalysis of Russian Academy of Sciences.

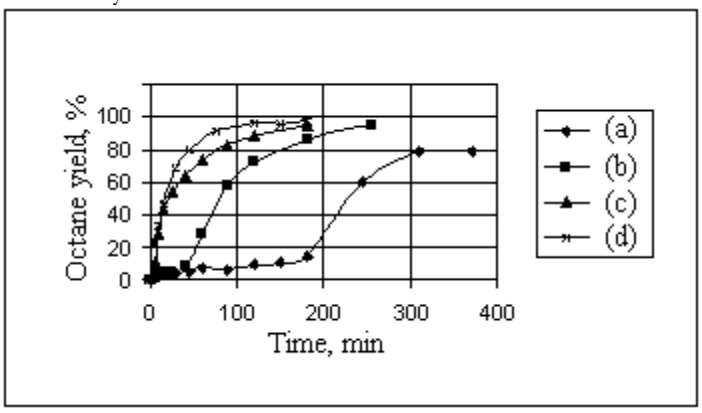

Fig.1. Example of induction period in reaction of octene-1 hydroalumination with $ClAlBu^i_2$ in presenceof Cp_2ZrCl_2 (solvent (vehicle) – C_6H_6, mole ratio:(a) Cp_2ZrCl_2: $ClAlBu^i_2$:olefine = 0.18:12:10, (b) Cp_2ZrCl_2:$C_lA_lBu^i_2$:olefine = 0.3:12:10,(c) Cp_2ZrCl_2: $C_lA_lBu^i_2$:olefine = 0.5:12:10, (d) Cp_2ZrCl_2:$ClAlBu^i_2$:olefine = 1:12:10)

The problem of induction period modeling for reaction of olefins hydroalumination with catalyst Cp_2ZrCl_2 is appeared. For different schemes of given reaction we need:

1) to create methods and algorithms for the induction period modeling, to make the calculating experiment which model an induction period;
2) to define kinetic parameters of reaction which describe given experimental data (for different initial concentrations of catalyst and different temperatures of reaction) as good as it possible.
3) to clear up which of the reaction stages define an existence of induction period.

In result of experimental investigation of process mechanism the following scheme suggested.

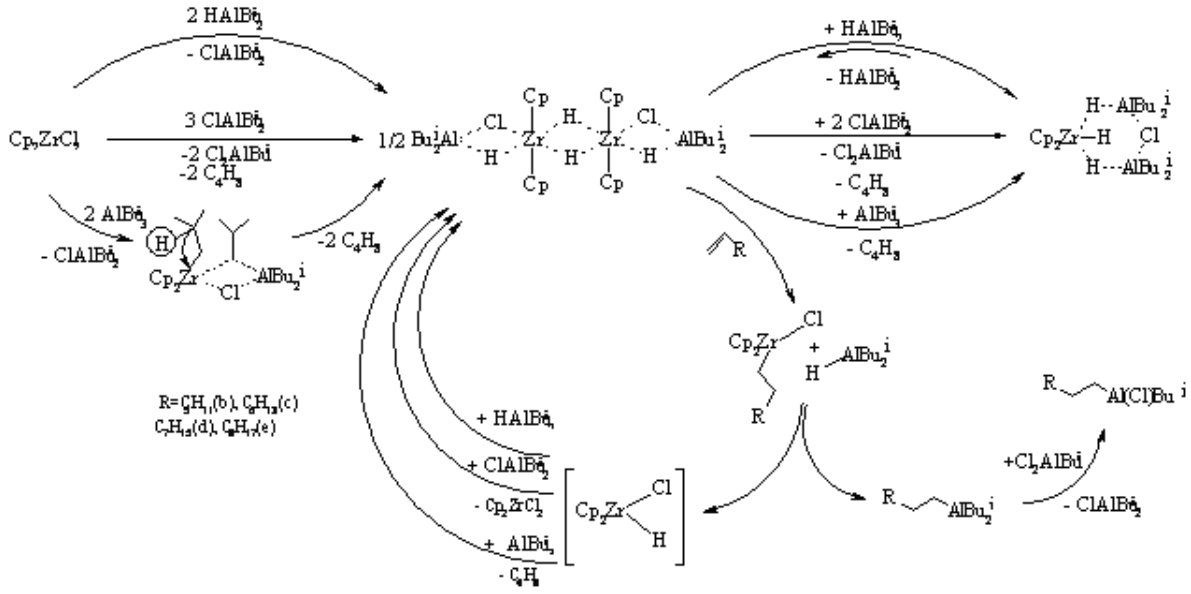

Fig. 2. Mechanism of olefins hydroalumination reaction by alkylalanes in presence of catalyst Cp_2ZrCl_2.

We suggested the conditions for the occurrence and the evolution of induction period [9]. For the existence of induction period with length T the fulfillment of two following condition is needed:

The change of concentration of substance X_i on time segment [T-ΔT;T] must be a little, that is

$$\left|x_i(\mathrm{T}) - x_i(\mathrm{T}\text{-}\Delta\mathrm{T})\right| \le \varepsilon,$$

where ε and T-ΔT are small values.

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Out of time segment [T-ΔT;T] the abrupt change of concentration of substance X_i observed, that is $\frac{|x_i(T) - x_i(T-\Delta T)|}{\Delta T} << \frac{|x_i(T+\Delta L) - x_i(T)|}{\Delta L}$ or $\frac{|x_i(T) - x_i(T-\Delta T)|}{\Delta T} >> \frac{|x_i(T+\Delta L) - x_i(T)|}{\Delta L}$, where $\Delta T>0$, $\Delta L>0$– the different increments of temperature T.

3. Schemes of the Olefins Hydroalumination Reaction by Alkylalanes Catalyzed with Cp_2ZrCl_2

In this work three possible schemes of olefins hydroalumination reaction by alkylalanes in presence of the catalyst Cp_2ZrCl_2 are considered:

1.

(1) $$Cp_2ZrCl_2 + 3ClAlBu^i_2 \rightarrow \frac{1}{2}\left[Cp_2ZrHCl \times HAlBu^i_2\right]_2 + 2Cl_2AlBu^i + 2C_4H_8$$

(2) $$\frac{1}{2}\left[Cp_2ZrHCl \times HAlBu^i_2\right]_2 + 2ClAlBu^i_2 \rightarrow Cp_2ZrH_2 \times HAlBu^i_2 \times ClAlBu^i_2 + Cl_2AlBu^i + C_4H_8$$

(3) $$\frac{1}{2}\left[Cp_2ZrHCl \times HAlBu^i_2\right]_2 + 2CH_2CHR \rightarrow Cp_2Zr\left(CH_2CH_2R\right)Cl + Bu^i_2\left(CH_2CH_2\right)R$$

(4) $$Cp_2Zr\left(CH_2CH_2R\right)Cl + 3ClAlBu^i_2 \rightarrow Bu^iClAl(CH_2CH_2)R + \frac{1}{2}\left[Cp_2ZrHCl \times HAlBu^i_2\right]_2 + Cl_2AlBu^i + 2C_4H_8$$

(5) $$Cp_2Zr\left(CH_2CH_2R\right)Cl + ClAlBu^i_2 \rightarrow Cp_2ZrCl_2 + Bu^i_2Al\left(CH_2CH_2\right)R$$

(6) $$Bu^i_2Al\left(CH_2CH_2\right)R + Cl_2AlBu^i \rightarrow Bu^iClAl\left(CH_2CH_2\right)R + ClAlBu^i_2$$

2.

(1) $$Cp_2ZrCl_2 + ClAlBu^i_2 \leftrightarrow Cp_2ZrClBu^i + Cl_2AlBu^i$$

(2) $$Cp_2ZrClBu^i + ClAlBu^i_2 \rightarrow Cp_2ZrHClClAlBu^i_2 + C_4H_8$$

(3) $$Cp_2ZrHClClAlBu^i_2 + ClAlBu^i_2 \rightarrow Cp_2ZrH_2ClAlBu^i_2 + C_4H_8 + Cl_2AlBu^i$$

(4) $$2\,Cp_2ZrH_2ClAlBu^i_2 \leftrightarrow \left[Cp_2ZrH_2ClAlBu^i_2\right]_2$$

(5) $$\left[Cp_2ZrH_2ClAlBu^i_2\right]_2 \rightarrow Cp_2ZrH_2HAlBu^i_2ClAlBu^i_2 + Cp_2ZrHCl$$

(6) $$Cp_2ZrH_2HAlBu^i_2ClAlBu^i_2 + CH_2CHR \rightarrow Cp_2Zr\left(CH_2CH_2R\right)Cl + 2\,HAlBu^i_2$$

(7) $$Cp_2ZrH_2ClAlBu^i_2 + CH_2CHR \rightarrow Cp_2Zr\left(CH_2CH_2R\right)Cl + HAlBu^i_2$$

(8) $$Cp_2ZrH_2ClAlBu^i_2 + CH_2CHR \rightarrow Bu^i_2Al\left(CH_2CH_2R\right) + Cp_2ZrHCl$$

(9) $$Cp_2ZrHCl + HAlBu^i_2 \rightarrow Cp_2ZrH_2ClAlBu^i_2$$

(10) $$Bu^i_2Al\left(CH_2CH_2R\right) + Cl_2AlBu^i \leftrightarrow ClBu^iAl\left(CH_2CH_2R\right) + ClAlBu^i_2$$

(11) $$Cp_2ZrHCl + ClAlBu^i_2 \rightarrow Cp_2ZrHClClAlBu^i_2$$

3.

(1) $$Cp_2ZrCl_2 + ClAlBu^i_2 \leftrightarrow Cp_2ZrClBu^i + Cl_2AlBu^i$$

(2) $$Cp_2ZrClBu^i + ClAlBu^i_2 \rightarrow Cp_2ZrHClClAlBu^i_2 + C_4H_8$$

(3) $$Cp_2ZrHClClAlBu^i_2 + ClAlBu^i_2 \rightarrow Cp_2ZrH_2ClAlBu^i_2 + C_4H_8 + Cl_2AlBu^i$$

(4) $$2\,Cp_2ZrH_2ClAlBu^i_2 \leftrightarrow \left[Cp_2ZrH_2ClAlBu^i_2\right]_2$$

(5) $$Cp_2ZrH_2ClAlBu^i_2 + CH_2CHR \rightarrow Cp_2Zr(CH_2CH_2R)Cl + HAlBu^i_2$$

(6) $$\left[Cp_2ZrH_2ClAlBu^i_2\right]_2 + HAlBu^i_2 \rightarrow Cp_2ZrH_2HAlBu^i_2ClAlBu^i_2 + Cp_2ZrH_2ClAlBu^i_2$$

(7) $$Cp_2ZrH_2ClAlBu^i_2 + HAlBu^i_2 \rightarrow Cp_2ZrH_2HAlBu^i_2ClAlBu^i_2$$

(8) $$Cp_2ZrH_2HAlBu^i_2ClAlBu^i_2 + CH_2CHR \rightarrow Cp_2Zr\left(CH_2CH_2R\right)Cl + 2\,HAlBu^i_2$$

(9) $Cp_2Zr(CH_2CH_2R)Cl + HAlBu^i_2 \rightarrow Cp_2ZrHCl + Bu^i_2Al(CH_2CH_2R)$

(10) $\left[Cp_2ZrH_2ClAlBu^i_2\right]_2 + ClAlBu^i_2 \rightarrow Cp_2ZrH_2HAlBu^i_2ClAlBu^i_2 + Cp_2ZrHClClAlBu^i_2$

(11) $Cp_2ZrHCl + HAlBu^i_2 \rightarrow Cp_2ZrH_2ClAlBu^i_2$

(12) $Cp_2ZrHCl + ClAlBu^i_2 \rightarrow Cp_2ZrHClClAlBu^i_2$

(13) $Bu^i_2Al(CH_2CH_2R) + Cl_2AlBu^i \leftrightarrow ClBu^iAl(CH_2CH_2R) + ClAlBu^i_2$

(14) $Cp_2ZrCl_2 + HAlBu^i_2 \leftrightarrow Cp_2ZrHClClAlBu^i_2$

(15) $Cp_2ZrHClClAlBu^i_2 + HAlBu^i_2 \leftrightarrow Cp_2ZrH_2ClAlBu^i_2 + ClAlBu^i_2$

Let's use the following contraction for substances of reaction: $X_1=Cp_2ZrCl_2$, $X_2=ClAlBu^i_2$, $X_3=\left[Cp_2ZrHCl\times HAlBu^i_2\right]_2$, $X_4=Cl_2AlBu^i$, $X_5=C_4H_8$, $X_6=Cp_2ZrH_2\bullet HAlBu^i_2\bullet ClAlBu^i_2$, $X_7=CH_2CHR$, $X_8=Cp_2Zr(CH_2CH_2R)Cl$, $X_9=Bu^i_2Al(CH_2CH_2)R$, $X_{10}=Bu^iClAl(CH_2CH_2)R$, $X_{11}=Cp_2ZrClBu^i$, $X_{12}=Cp_2ZrHClClAlBu^i_2$, $X_{13}=Cp_2ZrH_2ClAlBu^i_2$, $X_{14}=HAlBu^i_2$, $X_{15}=Cp_2ZrHCl$, $R=C_5H_{11}$, C_6H_{13} , C_7H_{15} , C_8H_{17} , $Cp=C_5H_5$, $Bu^i=C_4H_9$.

4. Kinetic measurements of the olefins hydroalumination reaction with $ClAlBu^i_2$ catalyzed with Cp_2ZrCl_2

Let's consider the first scheme of olefins hydroalumination reaction by diisobutylaluminiumchloride in presence of Cp_2ZrCl_2. This scheme was suggested on the base of experimental investigations represented in work [11]:

	Velocities of stages:
$X_1+3X_2 \xrightarrow{k_1} \frac{1}{2}X_3+2X_4+2X_5$	$w_1 = k_1x_1x_2^3$
$\frac{1}{2}X_3+2X_2 \xrightarrow{k_2} X_6+X_4+X_5$	$w_2 = k_2x_2^2\sqrt{x_3}$
$\frac{1}{2}X_3+2X_7 \xrightarrow{k_3} X_8+X_9$	$w_3 = k_3\sqrt{x_3}x_7^2$
$X_8+3X_2 \xrightarrow{k_4} X_{10}+\frac{1}{2}X_3+X_4+2X_5$	$w_4 = k_4x_2^3x_8$
$X_8+X_2 \xrightarrow{k_5} X_1+X_9$	$w_5 = k_5x_2x_8$
$X_9+X_4 \xrightarrow{k_6} X_{10}+X_2$	$w_6 = k_6x_9x_4$

$[w_i]$= mole/(l·min) , (i=1..6); $[x_j]$=mole/l, (j=1..10).

Initial concentrations (mole/l): $x_1(0)$=0.03 mole/l; $x_2(0)$=2.03 mole/l; $x_7(0)$=1.69 mole/l; $x_i(0)$=0, $i\neq$1,2,7.

The mole concentrations of substances CH_2CHR and $Bu^iClAl(CH_2CH_2)R$ are experimentally measurable characteristics for schemes I-III.

Experimental data was obtained in reactor with the magnetic mixer (Fig. 3).

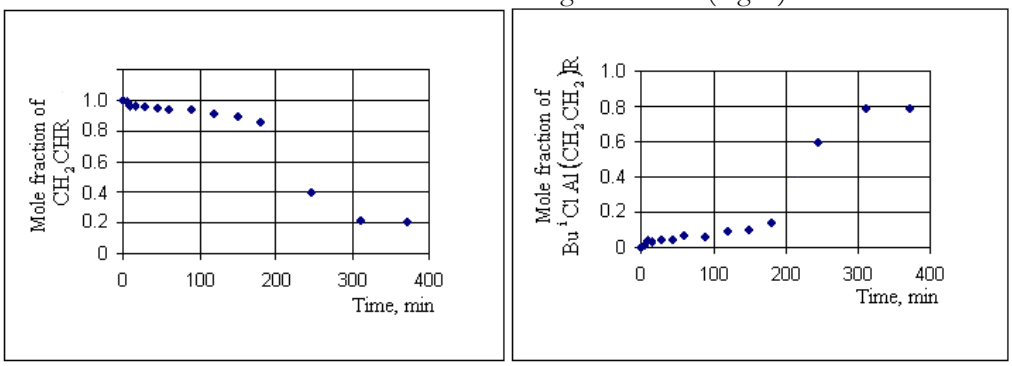

Fig. 3. Experimental concentrations of reagent CH_2CHR and reaction product $Bu^iClAl(CH_2CH_2)R$.

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For the first scheme of reaction with the informational-analytic system of chemical kinetics inverse problems the kinetic parameters which describe the experimental data for different initial concentration of catalyst Cp_2ZrCl_2 were found (Table 1). The graphs of correspondence between experimental data and calculation values of reaction product $BuiClAl(CH_2CH_2)R$ for different initial concentrations of catalyst Cp_2ZrCl_2 are given below at Fig. 4.

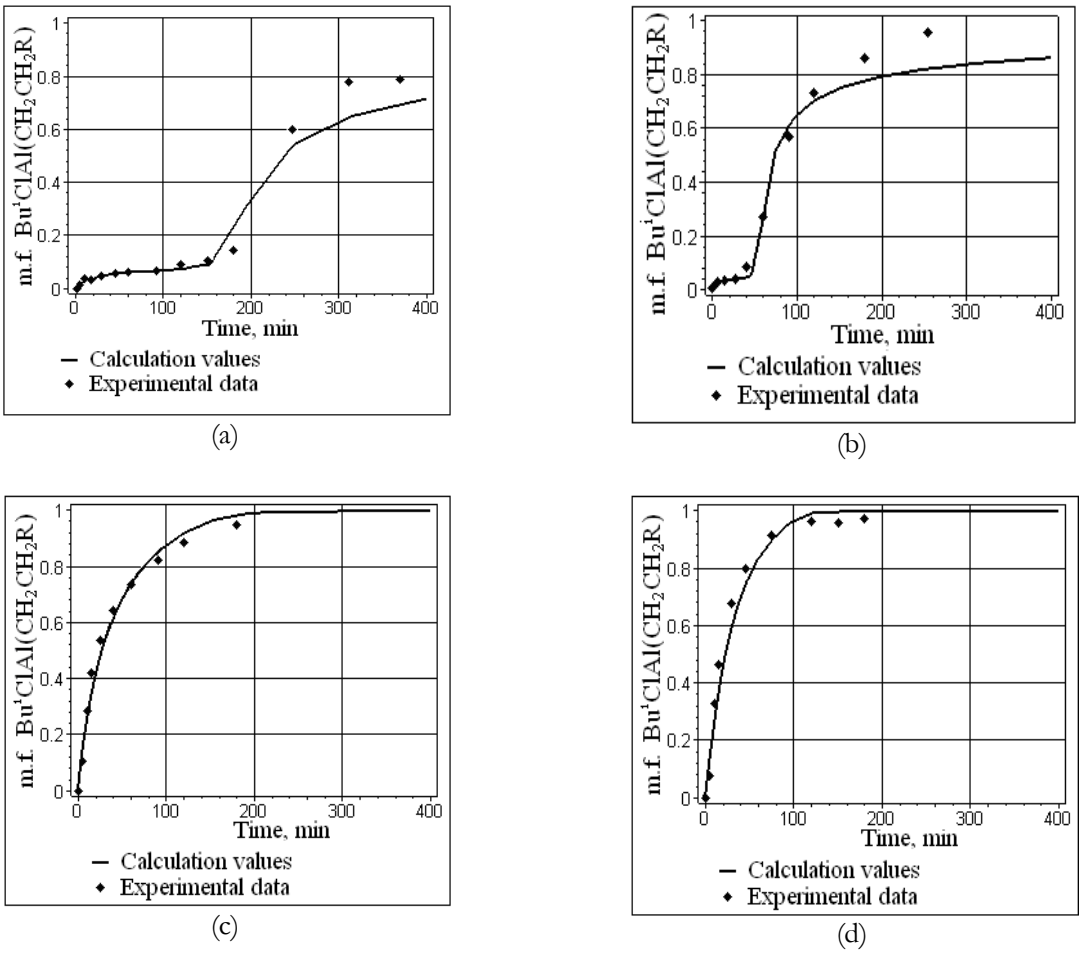

Fig. 4. Correspondence between experimental data and calculation values of reaction product $BuiClAl(CH_2CH_2)R$ for the temperature t=20° and initial concentrations of catalyst a) $[Cp_2ZrCl_2]$=0.03 mole/l, b) $[Cp_2ZrCl_2]$=0.05 mole/l, c)$[Cp_2ZrCl_2]$=0.08 mole/l, d) $[Cp_2ZrCl_2]$=0.16 mole/l), olefine – octene-1.

Table 1. Normalized constants of stages rates of reaction for different initial concentrations of Cp_2ZrCl_2(t=20°C, olefine – octene-1).

Concentration Cp_2ZrCl_2, mole/l	k_1	k_2	k_3	k_4	k_5	k_6
0.03	0.27	0.12	14.67	0.027	0.019	0.024
0.05	0.81	0.12	14.67	0.027	0.019	0.024
0.08	0.35	0.16	14.67	0.148	0.081	0.099
0.16	0.35	0.16	14.67	0.071	0.081	0.099

$[k_i]$ = min-1, i=1...6.

Though within the framework of scheme I the satisfactory description of experimental data was obtained, the found constants of the stages rates depend on the change of concentration of catalyst Cp_2ZrCl_2.

The scheme I is the simplest scheme of olefins hydroalumination by alkylalanes reaction in presence of catalyst Cp_2ZrCl_2. In this scheme the order of stages 1-4 is equal to 2.5, 3.5 and 4. Reactions in this scheme are not elementary. These reactions are some total transformations because their orders are more than 2.

On the base of experimental data (detachment the intermediate complexes and investigation of their reactivity) [12] and theoretical calculations (the quantum chemical studies performed with DFT method) [13] the detailed elaboration of stages 1-4 in scheme I was made. It allowed avoiding fractional values of stage coefficients. It was shown that complex $Cp_2ZrH_2 \cdot HAlBu^i_2 \cdot ClAlBu^i_2 (X_6)$ (we think before that it inert) must react with olefins CH_2CHR (X_7). Later it was confirmed experimentally. So, in scheme II the following stage was added:

$$Cp_2ZrH_2 \cdot HAlBu^i_2 \cdot ClAlBu^i_2 + CH_2CHR \rightarrow Cp_2Zr\left(CH_2CH_2R\right)Cl + 2\,HAlBu^i_2$$

Detailed scheme II of reaction of olefins hydroalumination by alkylalanes catalyzed with Cp_2ZrCl_2 has the following view:

	Stages rates:
$X_1 + X_2 \underset{k_{12}}{\overset{k_1}{\rightleftarrows}} X_{11} + X_4$	$w_1 = k_1 x_1 x_2 - k_{12} x_{11} x_4$
$X_{11} + X_2 \xrightarrow{k_2} X_{12} + X_5$	$w_2 = k_2 x_2 x_{11}$
$X_{12} + X_2 \xrightarrow{k_3} X_{13} + X_5 + X_4$	$w_3 = k_3 x_2 x_{12}$
$2X_{13} \underset{k_{13}}{\overset{k_4}{\rightleftarrows}} X_3$	$w_4 = k_4 x_{13}^2 - k_{13} x_3$
$X_3 \xrightarrow{k_5} X_6 + X_{15}$	$w_5 = k_5 x_3$
$X_6 + X_7 \xrightarrow{k_6} X_8 + 2X_{14}$	$w_6 = k_6 x_6 x_7$
$X_{13} + X_7 \xrightarrow{k_7} X_8 + X_{14}$	$w_7 = k_7 x_7 x_{13}$
$X_{13} + X_7 \xrightarrow{k_8} X_9 + X_{15}$	$w_8 = k_8 x_7 x_{13}$
$X_{15} + X_{14} \xrightarrow{k_9} X_{13}$	$w_9 = k_9 x_{14} x_{15}$
$X_9 + X_4 \underset{k_{14}}{\overset{k_{10}}{\rightleftarrows}} X_{10} + X_2$	$w_{10} = k_{10} x_4 x_9 - k_{14} x_2 x_{10}$
$X_{15} + X_2 \xrightarrow{k_{11}} X_{12}$	$w_{11} = k_{11} x_2 x_{15}$

$$[w_i] = \frac{\text{mole}}{\text{l} \times \text{min}}, \; i = 1..11.$$

Initial concentrations: $x_1(0) = 0.03$ mole/l, $x_2(0) = 2.03$ mole/l, $x_7(0) = 1.69$ mole/l, $x_i(0) = 0$, $i \neq 1,2,7$.

For the concerned scheme of reaction of olefins hydroalumination by alkylalanes catalyzed with Cp2ZrCl2 the constants of stages rates which provide the closeness between experimental data and calculation values for the different initial concentrations of catalyst were found (Table 2). The graphs of correspondence between experimental data and calculation values of reaction product $Bu^iClAl(CH_2CH_2)R$ for the different initial concentrations of catalyst Cp_2ZrCl_2 are given below at Fig. 5:

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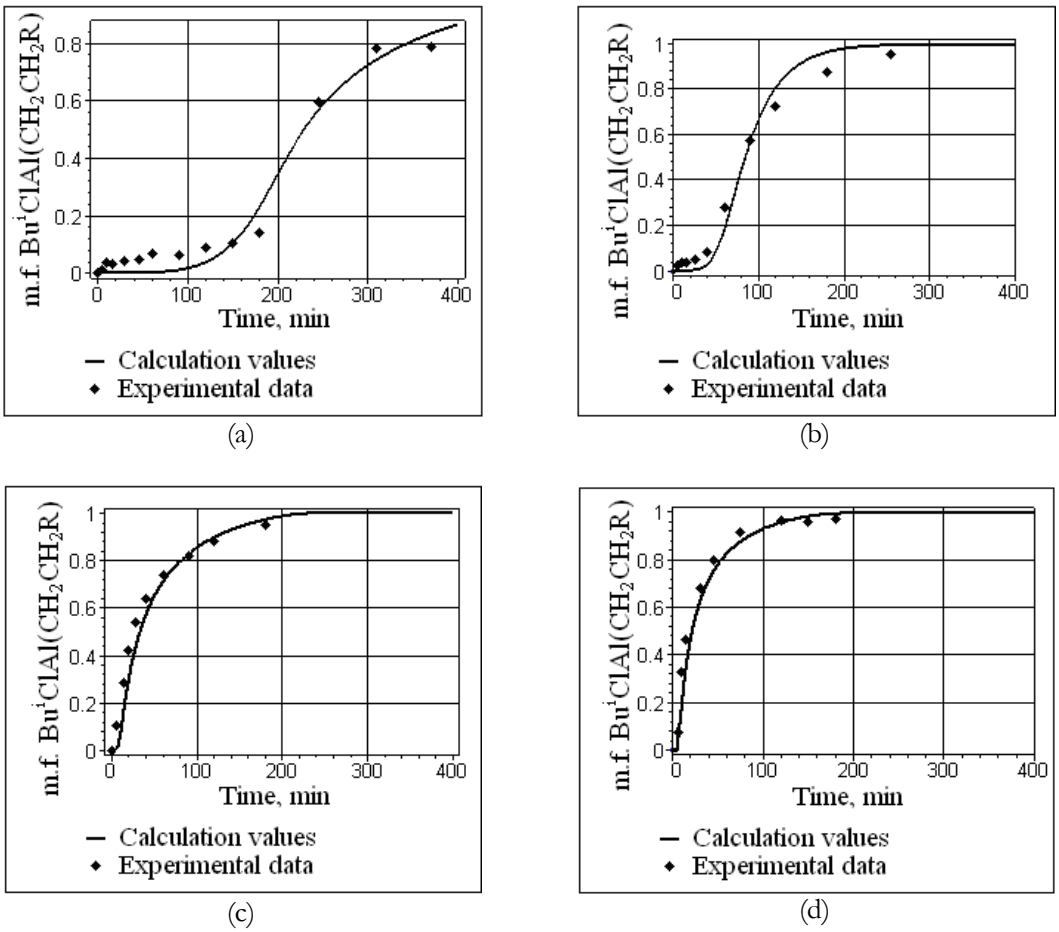

Fig. 5. Correspondence between experimental data and calculation values of reaction product Bu^{i}ClAl(CH$_2$CH$_2$)R for the temperature t=20°C and initial concentrations of catalyst (a) [Cp$_2$ZrCl$_2$]=0.03 mole/l, (b) [Cp$_2$ZrCl$_2$]=0.05 mole/l, (c)[Cp$_2$ZrCl$_2$]=0.08 mole/l, (d) [Cp$_2$ZrCl$_2$]=0.16 mole/l), olefine – octene-1.

Table 2. Normalized constants of the stage rates of reaction (for different initial concentrations of Cp$_2$ZrCl$_2$).

Concentration Cp$_2$ZrCl$_2$, mole/l	k_1	k_2	k_3	k_4	k_5	k_6	k_7
0.03	2.16	0.004	918.68	0.00065	0.0065	0.00033	0.00005
0.05	2.16	0.009	918.68	0.00065	0.0065	0.00033	0.00005
0.08	2.16	0.097	918.68	0.00065	0.0065	0.00033	0.00005
0.16	2.16	0.097	918.68	0.00065	0.0065	0.00033	0.00005

Concentration Cp$_2$ZrCl$_2$, mole/l	k_8	k_9	k_{10}	k_{11}	k_{12}	k_{13}	k_{14}
0.03	4.24	0.00028	0.098	506.21	0.00015	0.00013	0.49
0.05	10.28	0.00028	0.098	506.21	0.00015	0.00013	0.49
0.08	30.12	0.00028	0.098	506.21	0.00015	0.00013	0.49
0.16	30.12	0.00028	0.158	506.21	0.00015	0.00013	0.49

$[k_i]=\min^{-1}$, $i=1..14$.

Thought within the framework of scheme II a satisfactory description of experimental data was found, the constants k_2, k_8 and k_{10} of stage rates depends on change of initial concentration of catalyst Cp$_2$ZrCl$_2$.

As a result, further experimental investigations had a complication of scheme II. Since in scheme II according to stages 6 and 7 the formation of diisobutylaluminiumchloride (X_{14}) is possible, we added stages with participation of this reagent, namely, stages 6, 9, 14 and 15.

(6) $X_3+X_{14} \rightarrow X_6+X_{13}$

(9) $X_8+X_{14} \rightarrow X_{15}+X_9$

(14) $X_1+X_{14} \leftrightarrow X_{12}$

(15) $X_{12}+X_{14} \leftrightarrow X_{13}+X_2$

Moreover, the possible stage 10 of the dimer complex $[Cp_2ZrH_2ClAlBui_2]_2$interaction with diisobutylaluminiumchloride was added:

$$[Cp_2ZrH_2ClAlBu^i_2]_2 + ClAlBu^i_2 \rightarrow Cp_2ZrH_2HAlBu^i_2ClAlBu^i_2 + Cp_2ZrHClClAlBu^i_2 .$$

Experimentally the ratios of constants of stage rates for some stages were found:

$$k_5 >> k_8 , k_7 > k_4 > k_{17} .$$

Detailed scheme III of reaction of olefins hydroalumination by alkylalanes in presence of Cp_2ZrCl_2 has the following view:

	Stages rates: $[w_i]=\frac{\text{mole}}{\text{l}\times\text{min}}$,
$X_1+X_2 \underset{k_{16}}{\overset{k_1}{\rightleftarrows}} X_{11}+X_4$	$w_1 = k_1x_1x_2 - k_{16}x_4x_{11}$
$X_{11}+X_2 \xrightarrow{k_2} X_{12}+X_5$	$w_2 = k_2x_2x_{11}$
$X_{12}+X_2 \xrightarrow{k_3} X_{13}+X_5+X_4$	$w_3 = k_3x_2x_{12}$
$2X_{13} \underset{k_{17}}{\overset{k_4}{\rightleftarrows}} X_3$	$w_4 = k_4x_{13}^2 - k_{17}x_3$
$X_{13}+X_7 \xrightarrow{k_5} X_8+X_{14}$	$w_5 = k_5x_7x_{13}$
$X_3+X_{14} \xrightarrow{k_6} X_6+X_{13}$	$w_6 = k_6x_3x_{14}$
$X_{13}+X_{14} \xrightarrow{k_7} X_6$	$w_7 = k_7x_{13}x_{14}$
$X_6+X_7 \xrightarrow{k_8} X_8+2X_{14}$	$w_8 = k_8x_6x_7$
$X_8+X_{14} \xrightarrow{k_9} X_{15}+X_9$	$w_9 = k_9x_8x_{14}$
$X_3+X_2 \xrightarrow{k_{10}} X_6+X_{12}$	$w_{10} = k_{10}x_2x_3$
$X_{15}+X_{14} \xrightarrow{k_{11}} X_{13}$	$w_{11} = k_{11}x_{14}x_{15}$
$X_{15}+X_2 \xrightarrow{k_{12}} X_{12}$	$w_{12} = k_{12}x_2x_{15}$
$X_9+X_4 \underset{k_{18}}{\overset{k_{13}}{\rightleftarrows}} X_{10}+X_2$	$w_{13} = k_{13}x_4x_9 - k_{18}x_2x_{10}$
$X_1+X_{14} \underset{k_{19}}{\overset{k_{14}}{\rightleftarrows}} X_{12}$	$w_{14} = k_{14}x_1x_{14} - k_{19}x_{12}$
$X_{12}+X_{14} \underset{k_{20}}{\overset{k_{15}}{\rightleftarrows}} X_{13}+X_2$	$w_{15} = k_{15}x_{12}x_{14} - k_{20}x_2x_{13}$

Initial concentrations: $x_1(0) = 0.03$ mole/l; $x_2(0) = 2.03$ mole/l; $x_7(0) = 1.69$ mole/l; $x_i(0) = 0,\ i \neq 1,2,7$.

For concerned scheme of reaction of olefins hydroalumination by alkylalanes the constants of stages velocities which provide closeness between experimental data and calculation values for different initial concentrations of catalyst were found (see Tables 3-4).

The graphs of correspondence between experimental data and calculation values of reaction product $Bu^iClAl(CH_2CH_2)R$ are given below:

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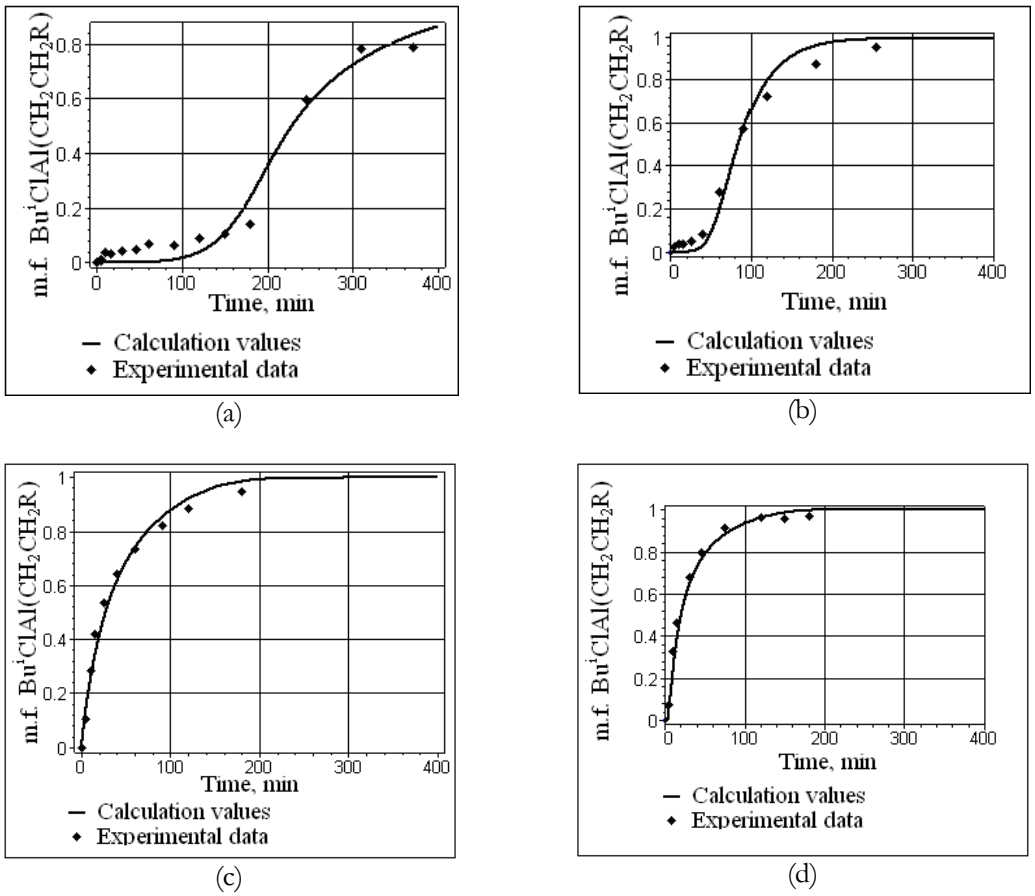


Fig. 6. Correspondence between experimental data and calculation values of reaction product $Bu^iClAl(CH_2CH_2)R$ for the temperature t=20°C and initial concentrations of catalyst (a) $[Cp_2ZrCl_2]$=0.03 mole/l, (b) $[Cp_2ZrCl_2]$=0.05 mole/l, (c)$[Cp_2ZrCl_2]$=0.08 mole/l, (d) $[Cp_2ZrCl_2]$=0.16 mole/l), olefine – octene-1).

Table 3. Normalized constants of stages velocities of reaction (for different initial concentrations of Cp_2ZrCl_2).

Concentration Cp_2ZrCl_2, mole/l	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	k_9	k_{10}
0.03	2.15	0.04	31.59	0.049	15.50	0.00013	0.40	0.0052	18.27	0.00001
0.05	2.15	0.04	31.59	0.049	15.50	0.00013	0.40	0.0052	18.27	0.00001
0.08	2.15	0.90	31.59	0.049	15.50	0.00013	0.40	0.0052	18.27	0.00001
0.16	2.15	0.90	31.59	0.049	15.50	0.00013	0.40	0.0052	18.27	0.00001

Concentration Cp_2ZrCl_2, mole/l	k_{11}	k_{12}	k_{13}	k_{14}	k_{15}	k_{16}	k_{17}	k_{18}	k_{19}	k_{20}
0.03	13.02	0.00010	0.69	0.00012	0.072	0.039	0.0010	0.012	0.00036	26.05
0.05	13.02	0.00010	0.69	0.00012	0.072	0.039	0.0010	0.012	0.00036	26.05
0.08	13.02	0.00010	0.69	0.00012	0.072	0.039	0.0010	0.012	0.00036	26.05
0.16	13.02	0.00010	0.69	0.00012	0.072	0.039	0.0010	0.012	0.00036	26.05

$[k_i]=\min^{-1}$, $i=1..20$.

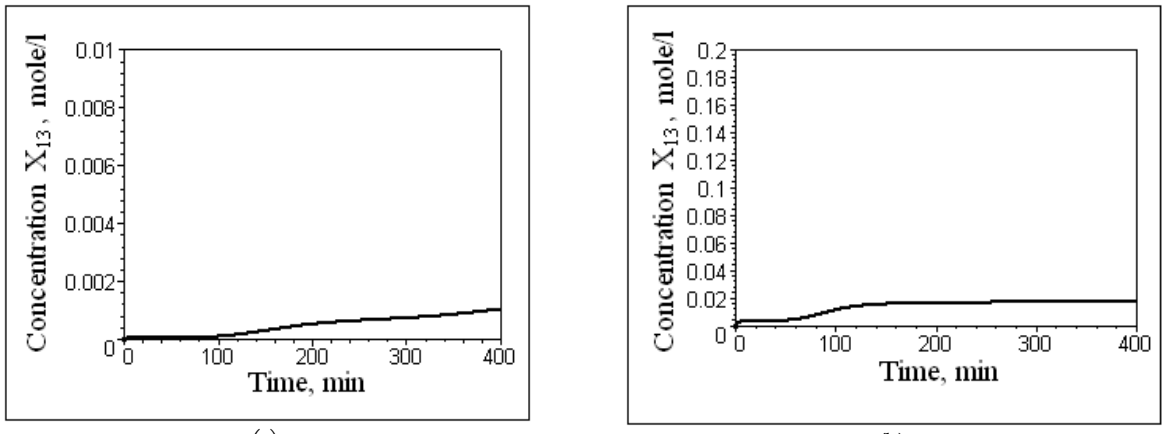
Table 4. Normalized constants of stage velocities of reaction (for different initial concentrations of Cp_2ZrCl_2).

Temperature, °C	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	k_9	k_{10}
20	2.15	0.04	31.59	0.049	15.50	0.0001	0.40	0.0052	18.27	0.000013
30	2.55	0.05	37.58	0.06	16.50	0.0002	0.61	0.0076	35.29	0.000021
40	3.42	0.39	45.46	0.11	25.50	0.0003	0.92	0.0094	80.26	0.000029

Temperature,°C	k_{11}	k_{12}	k_{13}	k_{14}	k_{15}	k_{16}	k_{17}	k_{18}	k_{19}	k_{20}
20	13.02	0.00010	0.69	0.00012	0.072	0.039	0.0010	0.012	0.0003	26.05
30	130.12	0.00012	0.89	0.00016	0.101	0.067	0.0013	0.023	0.0004	27.03
40	145.03	0.00017	1.25	0.00027	0.143	0.085	0.0017	0.031	0.0007	42.01

$[k_i]=\min^{-1}$, $i=1..20$.

Note that obtained set of constants of stages rates which corresponds to initial concentrations of catalyst $[Cp_2ZrCl_2]$=0.03 mole/l and $[Cp_2ZrCl_2]$=0.015 mole/l (for these initial concentrations experimental graphs of concentration for reagent Cp_2ZrCl_2 and reaction product$Bu^iClAl(CH_2CH_2)R$ have the induction period) are not differ from each other. So we found one set of kinetic parameters such that it described two experimental data with induction period.



(a) (b)

Fig. 7. Change of the concentration of intermediate $[Cp_2ZrH_2ClAlBu^i_2]$ (X_{13}) in time (t=20 °C, olefine – octene-1, (a) $[Cp_2ZrCl_2]$=0.03 mole/l, (b) $[Cp_2ZrCl_2]$=0.05 mole/l).

In the scheme III the key complex which charges with process of olefins hydroalumination is intermediate $[Cp_2ZrH_2ClAlBu^i_2]$ (X_{13}).

As can be seen in Fig.7, the length of induction period closely related with the start of formation of this complex. At initial time the low speed of ligand exchange between initial substances Cp_2ZrCl_2 (X_1) and $ClAlBu^i_2$ (X_2) (stages 1 and 2, constants k_1, k_2, energy activation of stage 2 is E_A=20.5 kilocalorie/mole) is observed. Therefore a long time for formation of $[Cp_2ZrH_2ClAlBu^i_2]$ (X_{13}) which quickly spend by inverse reaction with $ClAlBu^i_2$ in stage 15(k_{20}) and by direct reactions in stages 4 and 7 (stages of formation of nonactive in reactions with olefins complexes $[Cp_2ZrH_2ClAlBu^i_2]_2$ (X_3) and $[Cp_2ZrH_2HAlBu^i_2ClAlBu^i_2]$ (X_6)) is needed.

Additional increase of concentration $[Cp_2ZrH_2ClAlBu^i_2]$ (X_{13}) is possible only after reaction of this complex with olefine, that is, after start a catalytic cycle in which a formation of reaction product $ClBu^iAl(CH_2CH_2R)$ (X_{10}) take place. In this cycle a recovery of $[Cp_2ZrH_2ClAlBu^i_2]$ (X_{13}) runs through the complex Cp_2ZrHCl (X_{15}) in stage 11.

Increase of initial substance Cp_2ZrCl_2 (X_1) concentration leads to increase a speed of ligand exchange on first stages of process and, hence, to increase a speed of formation of complex $[Cp_2ZrH_2ClAlBu^i_2]$ (X_{13}) which start a catalytic cycle with participation the olefine. Therefore a decrease of induction period length is taken place.

5. Conclusion

The main results of this investigation:

1. Method of mathematical modeling of induction period for reaction of olefins hydroalumination by alkylalanes in presence of Cp_2ZrCl_2 was developed.
2. The kinetic model of reaction of olefins hydroalumination by alkylalanesin presence of the catalyst Cp_2ZrCl_2 was built.
3. The values of kinetic parameters of reaction of olefins hydroalumination by alkylalanes in presence of Cp_2ZrCl_2 which describes well an experimental data were determined. Obtained values are allowed to describe an induction period in all experimentally investigated area.
4. The stages of mechanism of reaction of olefins hydroalumination by alkylalanes in presence of Cp_2ZrCl_2 which determine an existence of induction period were found.
5. The software of mathematical modeling of induction period which allows defining stages determined an existence of induction period was developed. It can be used for wide class of investigated reactions.

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