

Modern information technologies in construction of kinetic models for reactions of metal complex catalysis

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Abstract For detailed study of complex chemical reactions mechanisms experiment is conducted for selected private reactions. This causes a problem of kinetic parameters getting—the same set of rate constants must describe both public and private reaction stages, and also a general mechanism. In this paper, solution of this problem for a reaction of olefins hydroalumination is proposed. To optimize the computational process a methodology of parallelization is elaborated. On the base of parallel computations, a kinetic model for the reaction assigned is constructed, and on its base, the physical and chemical conclusions about reaction mechanism are done. © 2012 The Chinese Society of Theoretical and Applied Mechanics. [doi:10.1063/2.1204303]

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Complex reaction of olefins hydroalumination (OHR) is a part of the system of metal complex catalysis reactions and represents a complex multistage process consisting of successive and parallel stages. Therefore, when studying OHR partial reaction with organoaluminium compounds (OACs) (HAlBu₂ⁱ-DIBAG; ClAlBu₂ⁱ-DIBAH; AlBu₃ⁱ-TIBA) and olefins (heptene-1, octene-1, nonene-1, decene-1) have been identified and detailed to elementary stages. On this basis the general reaction mechanism has been worked out in detail. In this paper the general mechanism of OHR with DIBAH is considered.

Investigation of this reaction is also being carried out abroad. One of the first record of reaction conduction in soft conditions (10 °C–20 °C) was made in Ref. 1. In Ref. 2 authors studied in details reaction of OHR with TIBA.

Experimenters at RAS Institute of Petrochemistry and Catalysis (IPC RAS) suggested several mechanisms for the reaction. At initial stage a general scheme with OACs DIBAG (HAlBu₂ⁱ), DIBAH (ClAlBu₂ⁱ), TIBA (AlBu₃ⁱ) was considered on the base of overall equations. Then isolation of a key complex was carried out and experiments on its interaction with various OACs and olefins were conducted. At the third stage separations of schemes for isolated particular reactions of key complex with OACs and olefins on the base of elementary reactions were realized. And finally general schemes for OHR with DIBAH were considered on the base of the separated reactions.³

Kinetics of considered reaction can be described by

a system of ordinary nonlinear differential equations

$$\begin{aligned} \frac{dx_i}{d\tau} &= \frac{F_i - x_i F_N}{N}, \quad i = 1, 2, \dots, I, \\ F_i &= \sum_{j=1}^J \nu_{ij} W_j, \quad \frac{dN}{d\tau} = F_N = \sum_{j=1}^J \delta_j W_j, \\ \delta_j &= \sum_{i=1}^I \nu_{ij}, \\ w_j &= k_j^0 \exp\left(-\frac{E_j^-}{RT}\right) \prod_{i=1}^M (x_i N)^{|\alpha_{ij}|} - \\ & k_{-j}^0 \exp\left(-\frac{E_j^+}{RT}\right) \prod_{i=1}^M (x_i N)^{\beta_{ij}}. \end{aligned} \quad (1)$$

with initial conditions

$$\tau = 0, \quad x_i(0) = x_i^0, \quad N = 1, \quad (2)$$

where x_i are mole fractions of reacting agents; W_j is the j th reaction rate, kmol/(m³·s⁻¹); N is the number of mixture moles, mol/s; I is the number of agents; J is the number of stages; ν_{ij} are stoichiometric coefficients; E_j^- , E_j^+ are activation energies, kcal (4 186 J)/mol; R is absolute gas constant, 8.31 J/(mol·K); T is temperature, K; α_{ij} and β_{ij} are negative and positive elements of the matrix (ν_{ij}) ; k_j^0 , k_{-j}^0 are pre-exponential factors. Kinetic equations for OHR are given in Table 1.

Mechanisms of compound reactions of metal complex catalysis contain a significant amount of rate constants and activation energies for direct and inverse reactions. Computational experiments on studying of some physical and chemical processes, such as occurrence of the induction periods and their dependence on quantity of the catalyst, are carried out on the base of developed kinetic models. Also on their basis optimization of experiments on reaction time reduction or maximal product yield finding are conducted.

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Table 1. Kinetic equations for OHR.

	DIBAG	TIBA
Specification I (Scheme 1)	$w_1 = k_1x_1 - k_{-1}x_2^2; w_2 = k_2x_2x_5 - k_{-2}x_8;$	$w_1 = k_1x_1 - k_{-1}x_2^2; w_2 = k_3x_2x_{14};$ $w_3 = k_4x_{12}; w_4 = k_2x_2x_5 - k_{-2}x_8;$
Specification II (Scheme 2)	$w_1 = k_1x_1 - k_{-1}x_2^2; w_2 = k_2x_1x_5;$ $w_3 = k_3x_2x_5;$	$w_1 = k_1x_1 - k_{-1}x_2^2; w_2 = k_5x_2x_{14};$ $w_3 = k_4x_1x_{14};$
	DIBAH	OLEFINS
Specification I (Scheme 1)	$w_1 = k_1x_1 - k_{-1}x_2^2; w_2 = k_5x_2x_9;$ $w_3 = k_6x_9x_{10}; w_4 = k_4x_{12};$ $w_5 = k_2x_2x_5 - k_{-2}x_8;$	$w_1 = k_1x_1 - k_{-1}x_2^2;$ $w_2 = k_7x_2x_3; w_3 = k_8x_2x_3;$ $w_4 = k_9x_5x_7; w_5 = k_2x_2x_5 - k_{-2}x_8;$
Specification II (Scheme 2)	$w_1 = k_1x_1 - k_{-1}x_2^2; w_2 = k_7x_2x_9 - k_{-7}x_5x_{10};$ $w_3 = k_6x_1x_9; w_4 = k_8x_{10}x_9;$ $w_5 = k_3x_2x_5; w_6 = k_2x_1x_5;$	$w_1 = k_1x_1 - k_{-1}x_2^2; w_2 = k_9x_2x_3;$ $w_3 = k_{10}x_4x_5; w_4 = k_{11}x_7x_5;$ $w_5 = k_2x_1x_5; w_6 = k_3x_2x_5;$ $w_7 = k_{12}x_8x_3;$
General reaction (Scheme 3)	$w_1 = k_{13}x_{15}x_9 - k_{-13}x_{18}x_{11}; w_2 = k_{14}x_{18}x_9; w_3 = k_8x_{10}x_9; w_4 = k_{-1}x_2^2 - k_1x_1;$ $w_5 = k_9x_2x_3; w_6 = k_2x_1x_5; w_7 = k_3x_2x_5; w_8 = k_{12}x_8x_3; w_9 = k_{10}x_4x_5;$ $w_{10} = k_6x_1x_9; w_{11} = k_{11}x_7x_5; w_{12} = k_{15}x_7x_9;$ $w_{13} = k_{16}x_6x_{11} - k_{-16}x_{19}x_9; w_{14} = k_{17}x_{15}x_5 - k_{-17}x_{10};$ $w_{15} = k_{-7}x_{10}x_5 - k_7x_2x_9.$	

For solution of chemical kinetic inverse problems it is necessary to create a uniform system which would include a database of kinetic information, calculation of variation for components of reaction concentrations, minimization criterion (deviation of calculated values from experimental data), and definition of stages activation energy. Set of these subsystems and structure of communications between them for construction of kinetic models generates information-analytical system of inverse chemical kinetic problems (IAS ICKP).⁴ IAS ICKP consists of 4 main blocks: (1) input information flows of kinetic measurements; (2) output information flows of kinetic parameters; (3) methods for processing of kinetic information; (4) technical means of data processing (personal computers or supercomputers).

Solution of chemical kinetics problems sometimes requires essential time spending (from several months to a year). So, a question of calculation time reduction appears, and authors decided to make calculations in series-parallel way.⁴ Use of three-level model of parallelizing during solution of inverse kinetic problem allowed authors to reduce running time up to 160 times.

After experimental data processing for the first specification of partial reactions there have been found kinetic parameters for stages (Table 2) with deviation < 10%.

Ratio (2) for specification I is satisfied in some temperature interval. Having constructed dependence of $\ln k$ on $1/T$ for k_1 and k_{-1} on the base of Arrhenius equation, authors noticed that lines $\ln k_1$ and $\ln k_{-1}$ intersect at $k_1^0 = 5462$, $k_{-1}^0 = 4250$ (Fig. 1).

Thus, ratio (2) is violated for temperatures above 127 °C.

For the second specification there also have been found reduced values of kinetic parameters (Table 3) with deviation < 8.5%. Lines $\ln k_1$ and $\ln k_{-1}$ intersect

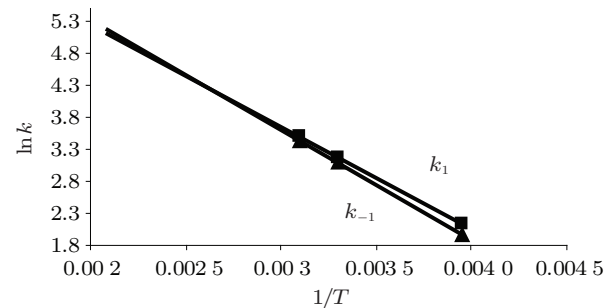


Fig. 1. Change of rate constants depending on temperature (specification I).

Table 2. Kinetic parameters for specification I.

$T/^\circ\text{C}$	k_1	k_{-1}	k_2	k_{-2}	k_3	k_4	k_5
-60	2	2.6	4	0.2	0.01	0.1	0.1
-40	4	5	15	1.7	0.03	0.6	0.1
7	13	15	177	69	0.2	13	2.2
30	23	24	434	280	0.4	44	6.3
50	31	33	873	802	0.6	110	13
E_i	3.4	3	6.7	10	5	8.7	7.7
$T/^\circ\text{C}$	k_6	$k_7(k_8)$				k_9	
-60	0.0	heptene	octene	nonene	decene	0.15	
-40	0.1					0.8	
7	0.2	0.04	0.04	0.03	0.04	14	
30	0.6	0.07	0.08	0.07	0.09	45	
50	1.5	0.11	0.14	0.14	0.15	102	
E_i	7.9	4	5.8	6	5.6	8	

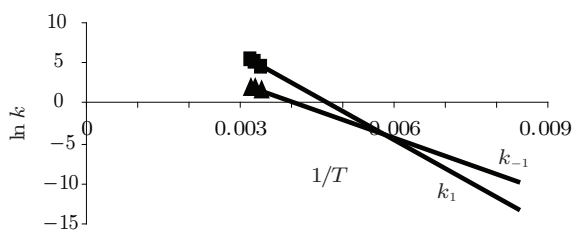


Fig. 2. Change of rate constants depending on temperature (specification II).

Table 3. Kinetic parameters in specification II.

$T/^\circ\text{C}$	k_1	k_{-1}	k_2	k_3	k_4
-20	1.4	14	2	69	0.2
-10	2	24	3	117	0.25
7	3.4	55	6	266	0.4
E_i	4.5	7	6	7	4
$T/^\circ\text{C}$	k_5	k_6	k_7	k_{-7}	k_8
-20	0.01	0.1	0.4	37	23
-10	0.01	0.2	0.8	86	51
7	0.03	1	2	312	177
E_i	8	12	8	11	10
Olefin	$T/^\circ\text{C}$	k_9	k_{10}	k_{11}	k_{12}
heptene	5	0.2	660	0.62	0.001
	7	0.3	678	0.65	0.001
E_i		14	1	3.5	22
octene	10	0.3	720	0.7	0.002
	12	0.4	786	0.7	0.003
E_i		14	7	6	27
nonene	5	0.2	745	0.6	0.001
	12	0.3	802	0.7	0.002
E_i		11	1.7	3.5	13
decene	5	0.28	223	0.62	0.002
	7	0.29	400	0.65	0.003
E_i		8	25	3.5	11

at a point $k_1^0 = 1 \times 10^4$, $k_{-1}^0 = 1.43 \times 10^7$; in this case $T = 173 \text{ K} = -100^\circ\text{C}$ (Fig. 2).

Such temperatures are found extremely rare in experiments, so second specification of private reactions characterize well experimental and theoretical data.

For general reaction of OHR over DIBAH kinetic models have been constructed with and without taking into account amount of catalyst. Model (1) describes the reaction better. Comparison of calculation and experiment for the general reaction of OHR over ClAlBu_2^i by the model taking into account catalyst (X_{kt} - the cat-

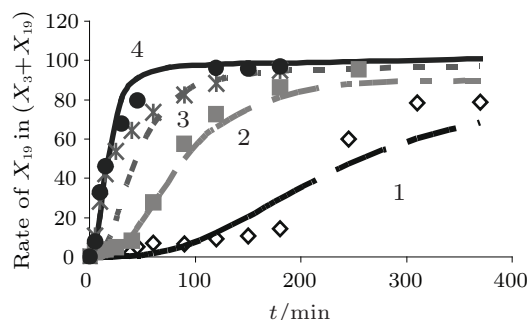


Fig. 3. Graphs of experiment (points) and calculation (lines) for general reaction with octen, $T = 20^\circ\text{C}$: (1) $X_{kt} = 0.18 \text{ mmol}$; (2) $X_{kt} = 0.3 \text{ mmol}$; (3) $X_{kt} = 0.5 \text{ mmol}$; (4) $X_{kt} = 1 \text{ mmol}$.

alyst) is shown in Fig. 3. Average deviation does not exceed 10%.

Values of kinetic parameters for the generalized reaction obtained by mathematical simulation confirm results found by quantum-chemical methods.³ Moreover, an adequate mathematical model of the chemical reaction allows to determine kinetic parameters under conditions which are difficult to establish experimentally.

On the base of constructed kinetic model authors have made some conclusions on the mechanism of reaction. Particularly, Cp_2ZrCl_2 interacts initially with a molecule of ClAlBu_2^i to form Cp_2ZrClBu . This stage has the largest activation barrier. Reaction of key complex dimerization and its interaction with another molecule of the same DIBAG are almost equiprobable. But for OHR over DIBAH, DIBAG is not an initial substance, therefore more probable is dimerization of the key complex resulting in bizirconium complex formation. Knowing activation barriers for reactions, authors have also found a complex considered in specification I inactive with respect to olefins.

Thus, a unified information-analytical system of kinetic researches for complex reactions using the technology of parallel computations for solution of multiparametrical inverse problems of chemical kinetics has been developed. Database of kinetic researches has been designed, and relational data manager in a parallel combination of computational and full scale experiments has been developed. Methods of mathematical modeling for complex reactions of catalytic processes on the base of MSDB of kinetic researches and technique of information processing using both uniprocessor and multiprocessor systems (supercomputers) has been structured. Sequential and parallel algorithms of numerical solution for mathematical description of metal-complex catalysis reactions have been developed and implemented. On the base of worked out information-analytical system kinetic models for the following reactions are constructed.

(1) Isolated particular reaction of OHR by TIBA and DIBAG over Cp_2ZrCl_2 on the base of overall equa-

tions. On the base of computational experiment results dimeric structure of the key complex of reaction has been established.

(2) Intermediate stages of OHR based on the first specification. On the base of computational experiment results temperature of dislocation of the dimeric form into monomer has been determined, and existence of inverse reaction of this complex transition to an active (with respect to olefins) monomer has been established.

(3) General reaction of OHR by DIBAH based on the second specification of original overall stages.

On the base of developed kinetic models mathematical conditions for occurrence and development of induction period adequate to chemical sense of the process have been formulated. Dependence of induction period on catalyst amount has been determined.

Thus, one of the key reactions of metal-complex catalysis and metalloorganic synthesis, which creates new outlook for development of untraditional chemical technologies for obtaining of new materials, catalysts, cocatalysts, light-sensitizing coatings for space and ra-

dio electronics industries, has been examined. Software on calculation of kinetic parameters and induction periods for metal-complex catalysis reactions has been applied in experimental laboratories of IPC RAS for construction of kinetic models for commercially significant chemical reactions, such as benzol alkylation by ethylene over a ceolite catalyst, refinement of pyromellitic dianhydride obtaining from duren.

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