16th International Scientific Conference "Chemistry and Chemical Engineering in XXI century" dedicated to Professor L.P. Kulyov, CCE 2015

Thermodynamic Analysis of Benzene Alkylation with Ethylene

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Abstract

Thermodynamic and kinetic regularities of benzene alkylation with ethylene in the presence of aluminium chloride with the methods of quantum chemistry were defined. The method used in this study is Semi-empirical method based on Neglecting of Diatomic Overlap approximation at PM3 level. All obtained data will be used for the mathematical model development of the considered process possessing high predictive potential.

Keywords: Alkylation; ethylbenzene; thermodynamics; transitional state; energy of activation; model.

1. Introduction

The alkylation of benzene with ethylene is widely used in petrochemical industry. Ethylbenzene is used as an intermediate in production of styrene, also as a paint solvent, and in pharmaceuticals industry. The world capacity of ethylbenzene production by benzene alkylation with ethylene is around $22 \cdot 10^6$ t per year[1].

In many industrial processes, alkylation reactions are still performed using Friedel-Crafts acid catalysts, which are highly corrosive. They are dangerous to handle and to transport as they corrode storage and disposal containers. Often, the products need to be separated from the acids using generally difficult and energy intensive processes. The use of acid catalyst in alkylation continued to be the leading technology until the 1980s, when zeolite catalysts[2, 3] became widespread in use. Since the 1980s, alkylation using Friedel-Crafts acid catalysts has been discarded in favour of alumina-silica zeolite catalysts, the first is that they are not corrosive to the equipment since they are stable

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bulk solids and do not travel through the process, the second is that they additionally limit higher transalkylated products through reduced diffusion of the heavier products, which results in a high selectivity for ethylbenzene[4]. Despite this, in Russian industry technology of ethylbenzene production the use of acid catalyst is still widespread. Increase of this production efficiency remains an acute problem for which decision mathematical modelling is a convenient tool.

Recently, more and more attention is paid to modelling of multicomponent catalytic processes of chemical and petrochemical industry. However, mathematical model development requires carrying out a large number of experimental studies in laboratory or in industrial conditions. To reduce them by comparing various chemical synthesis schemes it is necessary to use the laws of chemical thermodynamics. Thermodynamic modelling provides information about process energy and reaction products structure, allows evaluating qualitatively and quantitatively the possibility of reactions, and determines the optimal parameters of the process, ensuring the maximum yield of target product at the lowest production cost. Besides, such analysis allows reducing mathematical description of the process in the model preparation.[5-9]

The objective of this work is to identify and study the thermodynamic and kinetic regularities of the benzene alkylation with ethylene in the presence of aluminum chloride with the use of quantum chemical methods for mathematical model of petrochemical process construction possessing high predictive potential.

2. Object of study

In the presence of acid catalyst the process of benzene with ethylene alkylation occurs at temperature 110 – 135 °C and at pressure 0.5 - 3.0 atm.[10, 11]

It is known that alkylation proceeds through activation of the olefin catalyst, and then the activated complex reacts with benzene and alkylbenzene.[12, 13]

The mechanism offered in literature includes four stages:

1. Interaction of ethylene with hydrogen chloride resulting in the formation of ethyl chloride, which is easily decayed into ions:
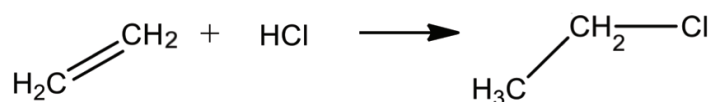

2. Formation of a carbcation:
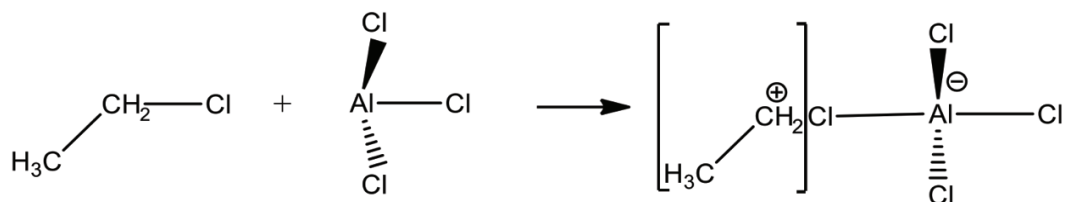
The formation of polarized complexes between aluminum halide and alkyl halide is proved by the presence of isotopic exchange between aluminum halides containing labeled halogen and alkyl halide.

3. In the third stage, the electrophilic attack of benzene with the carbocation occurs, intermediate - σ-complex is formed, which possesses high energy value:
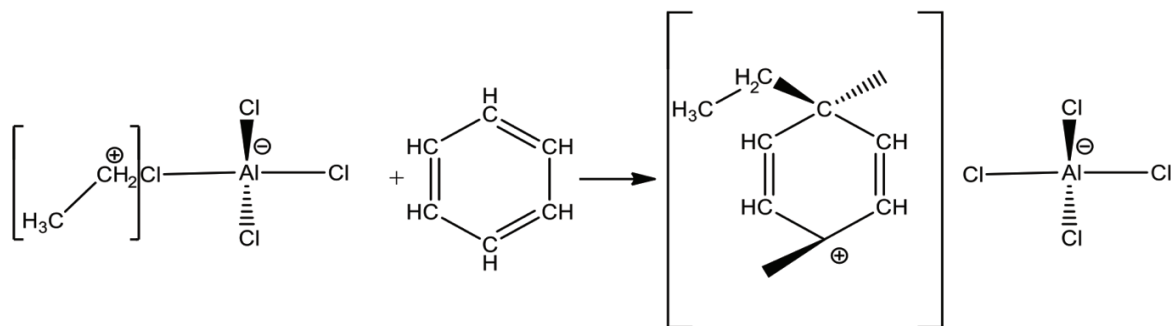
This stage is limiting.

4. The final stage includes hydrogen abstraction from the intermediate, restoration of the catalyst, and formation of the product:
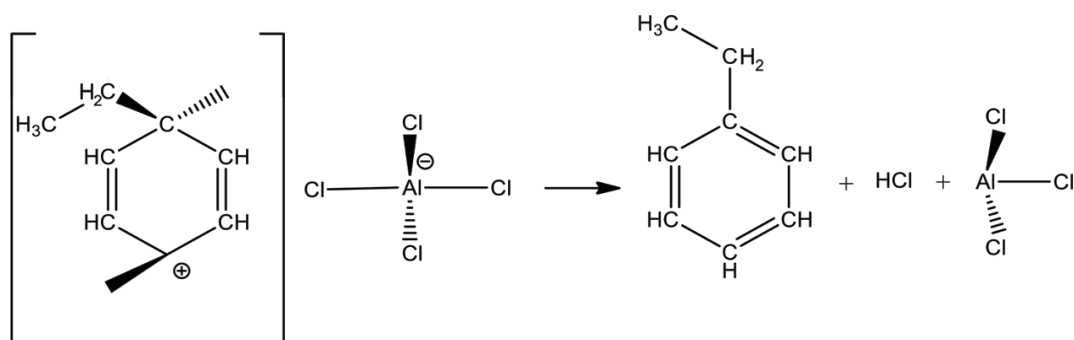
3. Research methods

Numerical studies have been conducted using the Semi-empirical method based on NDDO (Neglecting of Diatomic Overlap) approximation at PM3 level in the computational chemistry software Gaussian[14]. Modern semi-empirical methods often provide satisfactory accuracy in the description of valence interactions without requiring large computational resources.

The considered reactions proceed in the liquid phase, so it was necessary to take into account the solvation effect. The model of limit polarization by Thomas (polarized continuum model (C-PCM)) was used. It defines a cavity (or space) as a series combination of blocked nuclear spheres. Benzene was adopted as a solvent because the ratio of benzene to ethylene in the industry is maintained at the level of (8-14) : 1.

During the search for the transition state the method of square synchronous transit was used based on the fact that it is possible to carry out a family of parabolas connecting the point of reagent and the point of product on the SPE (surface of potential energy). The vertices of these parabolas approach to the transition state point. If the parameters of the parabolas are varied minimizing the norm of the gradient (this requires the calculation of energy and the gradient in the points lying on the parabolas), the search process can meet the transition state point.[15 - 18]

When calculating the following conditions were set: temperature – 393 K, pressure – 1 atm., catalyst – $AlCl_3$.

Activation energy and pre-exponential multiplier in Arrhenius' equation were determined with the theory of absolute rates of chemical reactions (the theory of transition state):

1. For calculation of the pre-exponential multiplier in the Arrhenius' equation the following expression is used:

$$k_0 = \chi \frac{k \cdot T}{h} e^{\frac{\Delta S_0^{\neq}}{R}} \qquad (1)$$

wherein χ – transmittance (transmission factor); k– Boltzmann's constant ($1.38 \cdot 10^{-23}$ J/K); T – temperature, K; h – Planck's constant ($6.62 \cdot 10^{-34}$ *J/sec*), $S_0^{\neq}$ – enthalpy of activation, *kJ/mole*, R – gas constant. For bimolecular reaction:

$$k_0 = \chi \frac{k_b \cdot T}{h} e^{\frac{RT}{RT}} = \chi \frac{k_b \cdot T}{h} e \tag{2}$$

2. For calculation of activation energy:

$$E_a = \Delta H^{\neq} + nRT \tag{3}$$

wherein $\Delta H^{\neq}$ – enthalpy of activation.

4. Results and discussions

At the first stage all products and reagents at each stage for each of the considered reactions were optimized, and frequencies of fluctuations as well as enthalpies, Gibbs's energy and entropy of the main reactions of alkylation process of benzene with ethylene under the conditions of the industry were calculated. The calculations results are given in Table 1.

Table 1. The calculated thermodynamic characteristics of the main reactions of alkylation process of benzene with ethylene (T=393 K and P=1 atm.)

Reaction	ΔH, kJ/mole	ΔS, J/mole·K	ΔG, kJ/mole
$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5$	-114.13	-128.48	-70.06
$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2$	-112.56	-139.24	-64.80
$C_6H_4(C_2H_5)_2 + C_2H_4 \rightarrow C_6H_3(C_2H_5)_3$	-116.22	-169.55	-58.06
$C_6H_6 + C_6H_4(C_2H_5)_2 \rightarrow 2C_6H_5C_2H_5$	-1.57	10.76	-5.26
$C_6H_6 + C_6H_3(C_2H_5)_3 \rightarrow C_6H_4(C_2H_5)_2 + C_6H_5(C_2H_5)$	2.10	41.08	-11.99
$C_2H_4 + C_2H_4 \rightarrow C_2H_4C_2H_4$	-138.07	-126.81	-94.58
$C_6H_6 + C_2H_4C_2H_4 \rightarrow C_6H_5(C_2H_4C_2H_5)$	-72.13	-164.31	-15.77
$C_6H_6 + C_3H_6 \rightarrow C_6H_5C_3H_7$	-91.60	-165.18	-34.95
$2 C_6H_6 + C_2H_4 \rightarrow 2C_6H_4CH_3$	-132.97	-118.71	-92.26
$C_6H_4CH_3 + C_2H_4 \rightarrow C_6H_3CH_3(C_2H_5)$	-114.10	-129.49	-69.69

Thermodynamic properties for most of the hydrocarbons considered in this process are not given in literature. This caused the necessity to determine the thermodynamic characteristics of the main reactions of alkylation process using the methods of quantum chemistry.

The list of reactions was based on the published data, as well as the data on the component structure of the input and output streams of the alkylator received from the monitoring results of ethylbenzene production in the presence of aluminium chloride at the reactor plant of JSC "Angarsk polymer plant". Table 2 shows the component structure of the input and output streams of the alkylator 11.17.2014.

Table 2. Input and output component composition of alkylator

Component	Concentration, % wt.
Raw	
benzene	86
ethylene	6
polyalkylbenzene*	8
Products	
benzene	52
toluene	2.6
ethylbenzene	34.3
isopropylbenzene	0.3
ethyltoluene	3.3
sec-butylbenzene	1.1
diethylbenzene	6.4

*Polyalkybenzene: mixture of isopropylbenzene, ethyltoluene, sec-butylbenzene and diethylbenzene

The next step of the studies was to find transition states of reactions of benzene alkylation with ethylene in the presence of Lewis acids by QST2 method at PM3 level. Compliance of the found transition states was proved by the presence of one negative value of Hessian matrix corresponding to the imaginary fluctuation. Usually, the transition state is characterized by one imaginary fluctuation related to a saddle point of the first order.

For each of these reactions (Table 1) the thermodynamic parameters of the transition state were determined. The results of the calculations of these parameters for the benzene alkylation reaction with ethylene are shown in Tables 3-4.

Table 3. The thermodynamic parameters for each main step of benzene alkylation reaction with ethylene at temperature of 393 K and pressure 1 atm.

Stage of benzene alkylation with ethylene	ΔH, kJ/mole	ΔS, J/mole·K	ΔG, kJ/mole
Stage 1	57.87	-115.80	-18.15
Stage 2	22.84	-72.55	2.04
Stage 3	70.90	-115.17	-31.40
Stage 4	7.49	175.05	-22.55
Sum	114.13	-128.48	-70.06

Table 4. Activation enthalpy, Gibbs free energy of activation, activation entropy, kinetic parameters for each step of benzene alkylation reaction with ethylene at temperature 393 K and pressure 1 atm.

	$\Delta H \neq$, kJ/mole	$\Delta G \neq$, kJ/mole	$\Delta S \neq$, J/mole·K	The pre-exponential term, A_0 in the Arrhenius equation	Energy of activation, E_a, kJ/mole	The equilibrium constant, k
$\dfrac{C_2H_4 + HCl}{TS_1}$	111.03	151.68	-118.57	$4.96 \cdot 10^7$	113.88	$9.57 \cdot 10^{-1}$
$\dfrac{CH_3Cl + AlCl_3}{TS_2}$	-19.33	8.50	-81.21	$2.09 \cdot 10^9$	-16.48	$9.98 \cdot 10^{-1}$

$CH_3AlCl_4 + C_6H_6$ $\overline{\hspace{2em}}$ TS_3	149.64	187.33	-109.97	$1.17 \cdot 10^8$	152.50	$9.47 \cdot 10^{-1}$
$C_8H_9AlCl_4$ $\overline{\hspace{2em}}$ TS_4	-3.09	9.84	-37.73	$1.63 \cdot 10^{11}$	-0.24	$9.97 \cdot 10^{-1}$

Similarly, the thermodynamic parameters of transition state for ethylbenzene alkylation reaction, diethylbenzene alkylation, transalkylation of benzene with diethylbenzene, triethylbenzene transalkylation of benzene, reaction of propylene formation, reaction of isopropylbenzene formation, reaction of benzene alkylation with propylene, the formation of toluene, and ethylbenzene formation occur.

As a result of numerical studies the thermodynamic and kinetic regularities of the benzene alkylation with ethylene in the presence of aluminium chloride were defined. The kinetic parameters of the main process reactions are shown in Table 5.

Table 5. Kinetic parameters of reactions of benzene alkylation with ethylene at temperature of 393 K and pressure of 1 atm.

Reaction	A_0, sec^{-1}	E_a, kJ/mole	k, sec^{-1}
$C_6H_6 + C_2H_4 \rightarrow C_6H_5C_2H_5$	$1.17 \cdot 10^8$	152.49	$6.3 \cdot 10^{-13}$
$C_6H_5C_2H_5 + C_2H_4 \rightarrow C_6H_4(C_2H_5)_2$	$1.57 \cdot 10^7$	141.61	$2.36 \cdot 10^{-12}$
$C_6H_4(C_2H_5)_2 + C_2H_4 \rightarrow C_6H_3(C_2H_5)_3$	$3.51 \cdot 10^6$	142.82	$3.64 \cdot 10^{-13}$
$C_6H_6 + C_6H_4(C_2H_5)_2 \rightarrow 2C_6H_5C_2H_5$	$1.23 \cdot 10^6$	171.86	$1.76 \cdot 10^{-17}$
$C_6H_6 + C_6H_3(C_2H_5)_3 \rightarrow$ $C_6H_4(C_2H_5)_2 + C_6H_5(C_2H_5)$	$4.97 \cdot 10^4$	179.91	$6.06 \cdot 10^{-20}$
$C_2H_4 + C_2H_4 \rightarrow C_2H_4C_2H_4$	$4.96 \cdot 10^7$	113.88	$3.62 \cdot 10^{-8}$
$C_6H_6 + C_2H_4C_2H_4 \rightarrow C_6H_5(C_2H_4C_2H_5)$	$4.24 \cdot 10^9$	106.42	$3.04 \cdot 10^{-5}$
$C_6H_6 + C_3H_6 \rightarrow C_6H_5C_3H_7$	$3.14 \cdot 10^7$	248.58	$2.86 \cdot 10^{-26}$
$2 C_6H_6 + C_2H_4 \rightarrow 2C_6H_4CH_3$	$1.32 \cdot 10^7$	221.05	$5.51 \cdot 10^{-23}$
$C_6H_4CH_3 + C_2H_4 \rightarrow C_6H_3CH_3(C_2H_5)$	$5.09 \cdot 10^7$	140.01	$1.25 \cdot 10^{-11}$

As a result of comparison of kinetic parameters determined using quantum chemical methods for two competing alkylation and transalkylation reactions, it was defined that the former has the lowest activation energy (152.49 kJ/mole at the value of pre-exponential multiplier in the Arrhenius's equation $1.17 \cdot 10^8$) for the transalkylation reaction of diethylbenzene activation energy and pre-exponential multiplier in Arrhenius equation are equal to 171.86 kJ/mole and $1.23 \cdot 10^6$, respectively. Therefore, the greatest contribution to the total yield of the target product - ethylbenzene - makes secondary transalkylation reaction formed in the previous stages of di- and triethylbenzene.

Compared to the zeolite catalyzed reaction, alkylation reaction with $AlCl_3$ catalyst has a much higher energy of activation. Since it would appear that these processes still occur on similar time scales, it is speculated that the zeolite reaction would be limited by diffusion, well the $AlCl_3$ reaction is limited by its activation energy [3].

The received kinetic parameters provide the basis for creating mathematical model of the process that will predict the quality of received alkylate depending on the structure of raw materials, temperature conditions of the

process and contact time of the reagents in the reactor.

5. Conclusion

1. Received from quantum chemical modelling using semi-empirical method based on NDDO approach (Neglecting of Diatomic Overlap) at PM3 level, values of enthalpy, entropy and Gibbs energy of activation allow determining the kinetic parameters of each reaction step, benzene alkylation with ethylene, the values of which have confirmed that the limiting stage is the stage of the total transalkylation mechanism.

2. The determined thermodynamic and kinetic regularities of benzene alkylation with ethylene will be used to create a mathematical model suitable for predicting the quality indicators of received alkylate depending on technological mode of alkylation process.

Acknowledgements

References

1. Niels Hansen. Theoretical Investigation of Benzene Alkylation with Ethene over H-ZSM-5. *J. Phys. Chem. C* 2008; **112**:15402–1541.
2. Mohammed C., Hamid A., Eyad A., Peter P. Edwards, Ahmad. S., Saud A. Selective zeolite catalyst for alkylation of benzene with ethylene to produce ethylbenzene. *Appl Petrochem Res* 2012; **2**:73–83.
3. Chris Paolucci. Ab Initio Catalyst Comparison for Ethylbenzene Synthesis from Alkylation. *University of Notre Dame Department of Chemical and Biomolecular Engineering:* CBE 40447; 2012.
4. I. M. Gerzeliev, S. N. Khadzhiev, I. E. Sakharova. Ethylbenzene synthesis and benzene transalkylation with diethylbenzenes on zeolite catalysts. *Petroleum chemistry 51* 2011; **1**:39–48.
5. E. S. Khlebnikova, A. V. Bekker, E. N. Ivashkina. Hydrodynamics of reactant mixing in benzene with ethylene alkylation. *Procedia Chemistry* 2014; **10**:297-304.
6. E. D. Ivanchina, E. S. Chernyakova, I. V. Yakupova. Mathematical modelling method application for optimisation of catalytic reforming process. *Procedia Chemistry* 2014; **10**:197-202.
7. S.F. Kim, N.V. Usheva, O.E. Moyzes, E.A. Kuzmenko, M.A. Samborskaya, E.A. Novoseltseva. Modelling of dewatering and desalting processes for large-capacity oil treatment technology. *Procedia Chemistry* 2014; **10**:448 – 453.
8. Hamid Ganji, Jafar S. Ahari, Amir Farshi, Majid Kakavand Modelling and Simulation Of Benzene Alkylation Process Reactors For Production Of Ethylbenzene. *Petroleum & Coal 46* 2004; **1**:55-63.
9. Ali N. Ebrahimi, Ashkan Z. Sharak, Seyyed A. Mousavi, Faeze Aghazadeh, and Ahmad Soltani, Modification and optimization of benzene alkylation process for production of ethylbenzene. *Chemical Engineering and Processing 50* 2011; **1**:31–36.
10. H. Fiege. *Ulmann's Encyclopedia of Industrial Chemistry*; 1987.
11. Meyers R.A. *Handbook of Petrochemicals Production Process*. McGraw-Hill professional; 2005.
12. M. Gomez Gallego, M. A. Sierra. *Organic Reaction Mechanisms*. First Edition; 2004.
13. K. Weissermel and H.J. Harp. *Industrial organic chemistry*. VCH Publishers, New York; 1997.
14. J.W. Ochterski. *Thermochemistry in Gaussian* 2000; p. 1–17.
15. Attila Szabo and Neil S. Ostlund. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Dover Publications: New Ededition; 1996,
16. Warren J. Hehre. *A Guide to Molecular Mechanics and Quantum Chemical Calculations*. Wavefunction; 2002.
17. Demaison J., Boggs J.E., Császár A.G. (Eds.). *Equilibrium Molecular Structures: From Spectroscopy to Quantum Chemistry*. CRC Press; 2011.
18. T.A. Klimova, V.V. Bochkarev, L.S. Soroka. Modeling of the aniline with nitrobenzene reaction by PM6 method. *Procedia Chemistry* 2014; **10**:448 – 453.