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Comparison between Alkylation and Transalkylation Reactions using ab Initio Approach

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Abstract

This study concerns thermodynamic and kinetic regularities of benzene alkylation with propylene and diisopropylbenzene transalkylation by investigating reaction mechanism. For each step, thermodynamic parameters, such as pre-exponential factor and activation energy were determined. Ab initio approach was used for this purpose. Also effects of solvation and ions formation were taken into account. Finally, comparative analysis of two processes was made.

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Keywords: cumene, alkylation, transalkylation, electrophilic substitution, quantum chemistry, transition state, Wheland intermediate;

1. Introduction

1.1 Background

Cumene is an important raw material in petrochemistry to obtain phenol and its co-product – acetone[1]. Usually cumene is produced at the same facility that manufactures phenol. Its synthesis is based on the alkylation of benzene with propylene using acid catalysts.

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The main technology now used for cumene producing is a process catalyzed by phosphoric acid loaded on ceyssatite patented by the Universal Oil Products Company (UOP Co.)[2]. $AlCl_3$ is also chosen as the catalyst.

However, such materials usually introduce various problems such as corrosion, harmful effects on the environment[3]. Some processers used BF_3, but it had controlling difficulties in comparison with $AlCl_3$, and the BF_3 process requires higher temperature and pressure to operate[4]. Since 1965, acid zeolite is of great interest for cumene manufacture[5], but only recently it has been commercialized by Dow, Mobil, CD Tech, UOP and

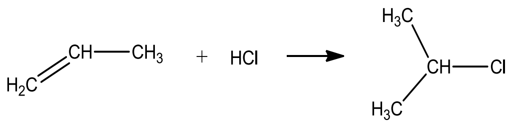
Enichem[5-7]. Despite that, zeolite catalysts were widely used because of their safety[7], easy deactivation by coking, short regeneration cycle, and hard reaction condition became problems. A new type of catalyst for this process – ionic liquids – was developed[8], but is not commercialized. In spite of new catalysts emergence, process with aluminum chloride stays actual for many cumene producers. It is necessary to increase cumene production, because nowadays demand for cumene rose up to 12 million tons in 2011 and keeps growing[9].

1.2 Reaction

The alkylation reaction of benzene with propylene is carried out in the presence of Lewis acids. It is known that alkylation occurs through activation of the olefin by catalyst, and then activated complex reacts with benzene and alkylbenzenes[10].

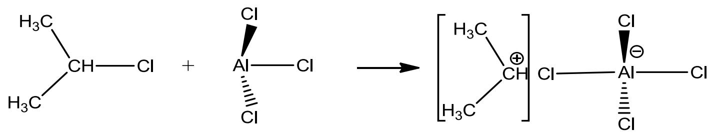
Mechanism includes four steps:

1. Interaction of propylene with hydrogen chloride, resulting in the formation of propylchloride that easily breaks down into ions:



(1)

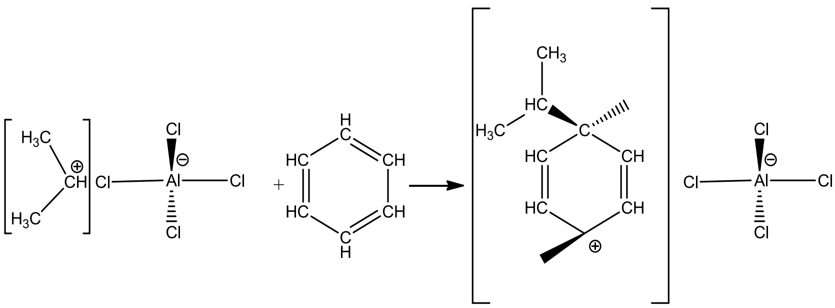
2. The second step is the formation of carbocation:



(2)

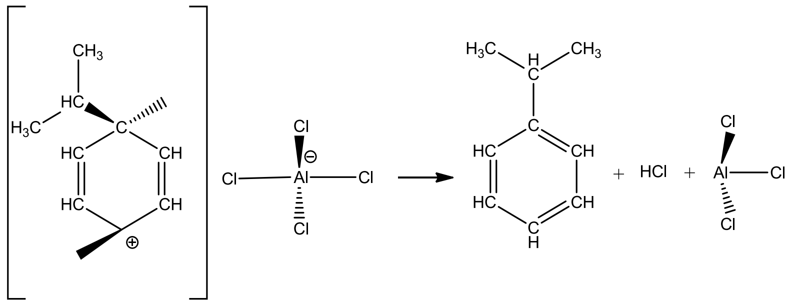
The formation of polarized complexes between aluminum halide and alkyl halide is proved by the isotopic exchange between aluminum halides and alkyl halide[11].

3. At the third stage, the electrophilic attack of benzene by carbocation forms intermediate called Wheland intermediate or σ-complex, which has a high energy value. It is a rate limiting step.



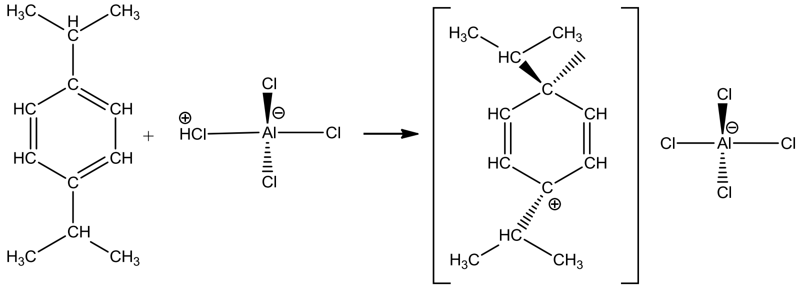
(3)

4. The last step includes elimination of hydrogen from intermediate, reduction of catalyst and product formation:



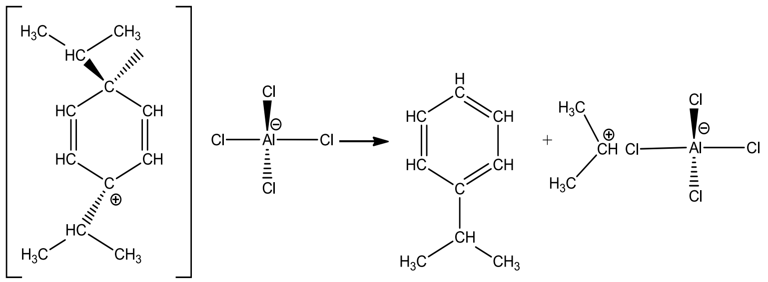
(4)

Transalkylation reaction proceeds by nucleophilic substitution Sn1 and nucleophilic substitution Sn2 mechanism[12]. Sn1 mechanism was assumed to proceed for this case because of stable carbocation formation and steric hindrance. Sn1 eliminates alkyl through Wheland intermediate formation[13]:



(5)

In the second step, Wheland intermediate discomposes into cumene and ionic pair:



(6)

Then, ionic pair attacks benzene as in alkylation process.

2. Computational methods

2.1 Method and basis

The calculations were performed using density functional theory (DFT) at the B3LYP level of theory[14]. This method has high accuracy in relation to experimental results. The basis selected for these calculations is the 6-31++G(d,p) basis. The polarization functions were necessary because of the polar molecules formation.

Calculations were performed for reactions with benzene in the liquid phase, so it was necessary to include effects of nearby molecules interaction. For this purpose, a well tested polarized continuum model was used (C-PCM). In this model, the surrounding medium is modeled as a continuous conductor, and the electrostatic forces felt on the solute cavity are calculated[15]. These reactions use a benzene: propylene ratio ranging from 3:1 to 10:1, so benzene exists in high excess to the catalyst and other reactants, which justifies its use as a solvent.

Calculations were performed considering process conditions: temperature – 395 K, pressure – 1.6 atm., catalyst – $AlCl_3$.

2.2 Optimization

The first stage of the calculations was to optimize all the products and reactants for each step in each reaction, and perform calculations of molecule vibration frequency; also the enthalpies, Gibbs energies and entropies were determined. Obtained data is presented in table 1.

2.3 Transition State Search

Transition states were defined by QST2 B3LYP/6-31++G(d,p) method. Match of found transition state structure was proved by the presence of one negative eigenvalue of the Hessian matrix, which corresponds to an imaginary vibration.

3. Results and discussion

3.1 Thermochemistry calculations

Table 1. Thermodynamic parameters for all components

	$\varepsilon_0 + H_{corr}$, Hartree	$\varepsilon_0 + G_{corr}$, Hartree	S, cal/(mol·K)
$AlCl_3$	-1623.226165	-1623.276056	79.259
$AlCl_4^-$	-2083.648831	-2083.707992	93.986
C_6H_6	-232.160353	-232.207239	74.485
$CH(CH_3)_2Cl$	-578.655672	-578.704698	77.884
$C_6H_5CH(CH_3)_2$	-350.023727	-350.087693	101.618
C_3H_6	-117..836330	-117.878542	67.060
HCl	-460.793870	-460.822585	45.618
$CH(CH_3)_2^+$	-118.179142	-118.222527	68.923
$CH(CH_3)_2\,AlCl_4$	-2201.901343	-2201.977219	120.540
$[C_6H_6CH(CH_3)_2]^+[AlCl_4]^-$	-2433.964736	-2434.047528	131.525
$[C_6H_5\,(CH(CH_3)_2)_2]^+[AlCl_4]^-$	-2552.814562	-2552.908556	150.911
$C_6H_4(CH(CH_3)_2)_2$	-467.886866	-467.968045	128.964

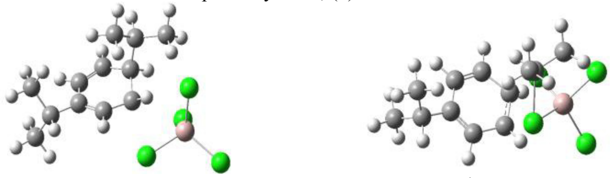
Finally, the next structures were found.

a b

Fig 1. (a) transition states for the first step of alkylation; (b) transition states for the second step of alkylation

a b

Fig 2. (a) transition states for the third step of alkylation; (b) transition states for the fourth step of alkylation



a b

Fig 3. (a) transition states for the first step of transalkylation; (b) transition states for the second step of transalkylation

Table 2. Thermodynamic parameters for transition states

	$\varepsilon_0 + H_{corr}$, Hartee	$\varepsilon_0 + G_{corr}$, Hartree	S, cal/(mol·K)
		Alkylation	
TS_1	-578.59	-578.64	81.93
TS_2	-2201.89	-2201.97	119.76
TS_3	-2434.01	-2434.10	152.67
TS_4	-2433.96	-2434.03	102.94
		Transalkylation	
TS_1	-2551.86	-2552.04	185.35
TS_2	-2551.89	-2551.89	119.57
TS_3	-2434.01	-2434.10	152.67
TS_4	-2433.96	-2434.03	102.94

Thermodynamic parameters for each step and activation enthalpy, activation Gibbs energy and activation entropy were determined (table 3 and table 4).

Table 3. Thermodynamic parameters of each step

	ΔH, kJ/mol	ΔS, J/mol*K	ΔG, kJ/mol
		Alkylation	
Step 1	-66.88	-145.68	-9.33
Step 2	-51.21	-153.25	9.32
Step 3	175.80	-265.86	280.82
Step 4	-128.72	397.62	-285.78
Sum	-71.00	-167.17	-4.97
		Transalkylation	
Step 1	10.87	-430.95	181.09
Step 2	-58.57	298.30	-176.40
Step 3	175.80	-265.86	280.82
Step 4	-128.72	397.62	-285.78
Sum	-0.62	-0.89	-0.26

Table 4. Activation enthalpy, activation Gibbs energy, activation entropy, kinetic parameters of each step

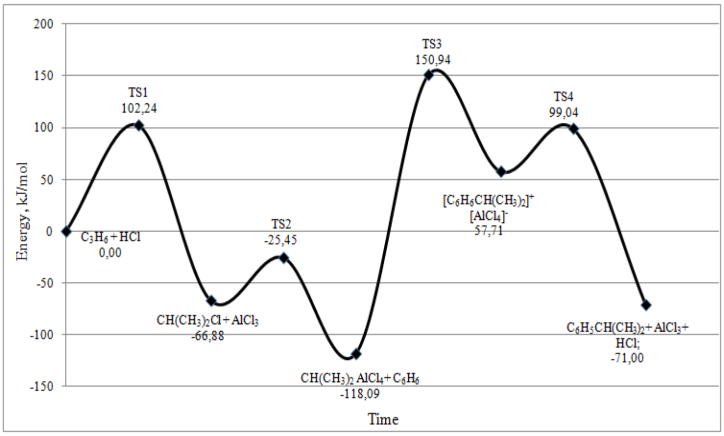
	$\Delta H_{\neq}$, kJ/mol	$\Delta G_{\neq}$, kJ/mol	$\Delta S_{\neq}$, J/mol*K	A_0	E_a, kJ/mol	$K_{eq.}$
C_3H_6 + HCl **TS_1**	98.96	149.78	-128.74	$2.06 \cdot 10^7$	102.24	$9.63 \cdot 10^{-1}$
$CH(CH_3)_2Cl + AlCl_3$ **TS_2**	-28.74	33.04	-156.50	$1.28 \cdot 10^6$	-25.45	$9.92 \cdot 10^{-1}$
CH(CH3)2$AlCl_4$ + C_6H_6 **TS_3**	147.66	223.80	-177.35	$1.58 \cdot 10^5$	150.94	$9.45 \cdot 10^{-1}$
$[C_6H_6CH(CH_3)_2]^+[AlCl_4]^-$ **TS_4**	95.76	119.99	-119.67	$5.11 \cdot 10^7$	99.04	$9.70 \cdot 10^{-1}$

Table 5. Activation enthalpy, activation Gibbs energy, activation entropy, kinetic parameters of each step

	$\Delta H_{\neq}$, kJ/mol	$\Delta G_{\neq}$, kJ/mol	$\Delta S_{\neq}$, J/mol*K	A_0	E_a, kJ/mol	$K_{eq.}$
$C_6H_4(CH(CH_3)_2)_2$ + H^+AlCl4$^-$ **TS_1**	152.85	36.60	-188.18410	$5.34 \cdot 10^4$	156.13	$9.91 \cdot 10^{-1}$
$[C_6H_5(CH(CH_3)_2)_2]^+[AlCl_4]^-$ **TS_2**	43.10	36.019	-131.22687	$1.61 \cdot 10^7$	46.39	$9.91 \cdot 10^{-1}$
$CH(CH_3)_2 AlCl_4$+ C_6H_6 **TS_3**	147.66	223.80	-177.349	$1.58 \cdot 10^5$	150.94	$9.45 \cdot 10^{-1}$
$[C_6H_6CH(CH_3)_2]^+[AlCl_4]^-$ **TS_4**	95.76	119.99	-119.667	$5.11 \cdot 10^7$	99.04	$9.70 \cdot 10^{-1}$

3.3 Reaction pathway

Figure 4 shows energy profile of process and confirms that Wheland intermediate formation step is rate limiting.



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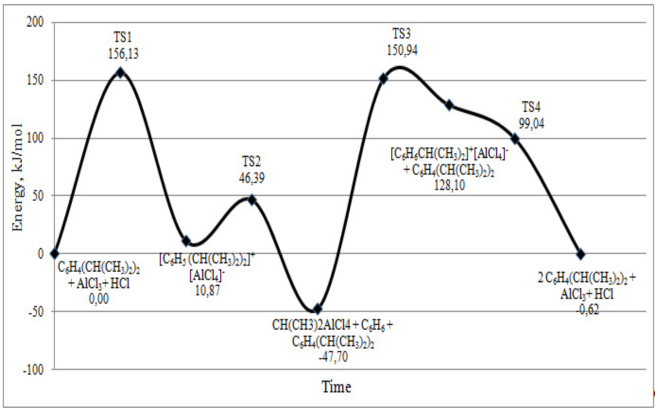

b

Fig 4. (a) energy profile of benzene alkylation with propylene; (b) energy profile of benzene transalkylation with diisopropylbenzene

4. Conclusions

It was calculated that activation energy of benzene alkylation with propylene is 150.94 kJ/mol and activation energy of diisopropylbenzene dealkylation is 156.13 kJ/mol. When calculations are performed without considering solvent effects, enthalpy of process was -94.61 kJ/mol for alkylation and 0.62 kJ/mol for transalkylation. It is caused by the fact, that dealkylation process as a part of transalkylation requires higher energy for the process.

5. Acknowledgement

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