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Alkylation of toluene with cyclohexene over phosphotungstic acid: A combined experimental and computational study

Genkuo Nie, Guozhu Li [*], Decheng Liang, Xiangwen Zhang

Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

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ABSTRACT

C—C bond formation between an aromatic ring and cyclohexene is of great importance for the preparation of bicyclic hydrocarbons. In this work, alkylation of toluene with cyclohexene over phosphotungstic acid (HPW) has been investigated using both experimental reaction kinetics and ab initio density functional theory (DFT) methods. Kinetic models for the formations of *o*-cyclohexyltoluene, *m*-cyclohexyltoluene and *p*-cyclohexyltoluene have been established and used to fit the experimental kinetic data. The reaction rate constants and apparent activation energies for the formation of the three products have been calculated and compared. Based on DFT calculation, the energy profiles with relevant equilibrium and transition states have been determined for the adsorption of reactants, formation & deprotonation of the metastable states and desorption of the products. A metastable state of an adsorbed arenium ion on HPW has been demonstrated. The rate constants (k) for the major elementary steps at different temperatures have been calculated using DFT data. The apparent rate constants are further determined theoretically based on kinetic analysis. Results show that the theoretical calculation fits well with experimental data, both of which have similar tendency changing with temperature. Combined experimental kinetic results and DFT calculations suggest that both the formation and deprotonation of the metastable state play key roles in affecting the product selectivity.

1. Introduction

Friedel-Crafts reaction of toluene with cyclohexene attracts immense interest for the synthesis of cyclohexyltoluene isomers, which are important precursors, intermediates or products in petroleum and chemical industries [1,2]. Initially cyclohexylbenzene derivatives synthesized through Friedel-Crafts reaction was reported by Lagowski et al. in the conversion of cyclohexenes into π-complexed arenes [3]. Then the alkylation of toluene with cyclohexene was investigated using either homogeneous catalysts or heterogeneous solid acids [4,5]. Kandategе et al. employed *p*-toluenesulfonic acid monohydrate as the catalyst and obtained a high yield of cyclohexyltoluene. However, too much catalyst was cost due to the relative weak acidity of *p*-toluenesulfonic acid monohydrate [6]. Solid acids, including H-USY, H-BEA, silica-alumina catalyst, H-Mordenite, Amberlyst-15, SiO_2-$H_3PW_{12}O_{40}$, Al-pillared montmorillonite and Filtrol-24, were also used to catalyze the reaction [5,7]. High ratio of stronger to weaker Brönsted acid sites is necessary if one wants to obtain high alkylate activity and avoid olefin oligomerization [8]. Keggin type phosphotungstic acid ($H_3PW_{12}O_{40}$, abbreviated as HPW) with strong Brönsted acid is a good candidate. Pizzio et al. applied HPW/SiO_2 in the C-alkylation reactions and obtained an amazing monoalkylation product yield [5].

The alkylation of toluene with cyclohexene occurs via a complex reaction network to form several products by monoalkylation, dialkylation, isomerization, and oligomerization. From the elaboration of Jong et al. [9], the rate of alkylation step is faster than hydride transfer which leads to the generation of heavy hydrocarbons. The products with high molecule weight lead to catalyst deactivation. Therefore, alkylation is performed industrially in extreme excess of nucleophilic reagent compared with electrophilic reagent to maximize the relative monoalkylation rate [10,11]. This is in concordance with the analysis of Janik et al. [12]. Detailedly, the desired monoalkylation of toluene with cyclohexene generates three isomers including *ortho*-cyclohexyltoluene (*o*-cyclohexyltoluene), *meta*-cyclohexyltoluene (*m*-cyclohexyltoluene), and *para*-cyclohexyltoluene (*p*-cyclohexyltoluene). However, the selectivity,

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[*] Corresponding author at: Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.

E-mail address: gzli@tju.edu.cn (G. Li).

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the formation mechanisms, and the reaction kinetics of the three monoalkylation products are still not clear.

The proposed mechanism for the alkylation of toluene with cyclohexene over HPW is illustrated in Scheme 1. The reaction is initiated by the adsorption of cyclohexene to form a carbonium cation interacting with a neighboring terminal oxygen atom of HPW. The lowest energy adsorbed state is with a covalent bond formed between an oxygen atom of HPW and a carbon atom of the alkyl species [13]. Then, the adsorbed states react with toluene to form an adsorbed arenium ion of cyclohexyltoluene. Three isomers can form due to the position of the newly formed C—C bond relative to the methyl group of toluene. Finally, cyclohexyltoluene isomers are obtained via deprotonation and desorption from the surface of HPW, and a new adsorption of cyclohexene on HPW can happen.

In the present work, alkylation of toluene with cyclohexene on HPW is explored by a combined experimental and theoretical approach. Data of product selectivity and reaction kinetics have been collected experimentally at various temperatures with toluene/cyclohexene molar ratio of 10:1 in a solvent-free condition. The kinetic models considering the products of monoalkylation (*o*-cyclohexyltoluene, *m*- cyclohexyltoluene, and *p*-cyclohexyltoluene) have been set up. Based on the fitted data, reaction rate constants and activation energies for the formations of all the three products are calculated. Then, first-principle theoretical modeling, in particular, density functional theory (DFT) has been employed to aid the fundamental understanding of HPW-catalyzed alkylation reaction. The interactions of toluene with cyclohexene and relevant elementary reaction steps over the surface of HPW are investigated. The formations of *o*-cyclohexyltoluene, *m*-cyclohexyltoluene, and *p*-cyclohexyltoluene are focused, and relative barriers of different reaction pathways will be compared based on kinetic analysis.

2. Experimental

2.1. Materials

Phosphotungstic acid (HPW, 99%) and toluene (99.5%) were purchased from Tianjin Guangfu fine chemical research institute. Cyclohexene (98%) was purchased from Jinan Great chemical industry company. Standard chemicals of *m*-cyclohexyltoluene and *p*-cyclohexyltoluene were purchased from Shanghai Eybridge chemical technology company. All the chemicals were used as received.

2.2. Catalytic reactions

Catalytic reactions at 373.15 K (±1 K) and 383.15 K (±1 K) (below the boiling point of the mixture) were performed in a 50 mL three-neck flask equipped with a condensate reflux under mechanical agitation and N_2 atmosphere. Toluene (11.27 g) and cyclohexene (1.00 g) were mixed and heated to a target temperature, and then 0.2 g of HPW was added in the mixture. When the reactions were conducted above the boiling point of the mixture (393.15 K (±1 K) and 403.15 K (±1 K)), a reactor of 100 mL autoclave (EasyChem E100) was used. For each reaction batch at certain temperature, 5–8 samples were taken and analyzed at various time periods. Product mixtures were analyzed quantitatively using a high performance liquid chromatography (HPLC) equipped with an automatic sampler (Agilent Technologies Inc., Agilent 1260, America), a UV detector (254 nm in wavelength) and a ZORBAX Eclipse PAH column (4.6 × 250 mm × 5um) at the column temperature of 298.15 K. The mobile phase began with the mixture of 60% acetonitrile and 40% water (volume fraction) and ended with 100% acetonitrile. Its flow rate was 1.0 mL min^{-1}. The standard working curves of *m*-cyclohexyltoluene and *p*-cyclohexyltoluene were established by external standard method using corresponding standard substances (Fig. S1). The concentrations of *o*-cyclohexyltoluene, *m*-cyclohexyltoluene and *p*-cyclohexyltoluene in the solution were determined according to the standard working curves. An average concentration was used based on the results of three independent measurements [14].

3. Reaction kinetics and activation energy

Typical HPLC spectrum of the product mixture is shown in Fig. 1. All the three products of *o*-cyclohexyltoluene, *m*-cyclohexyltoluene and *p*-cyclohexyltoluene can be detected and finely separated using this HPLC method. The retention time of the reactants and all the products were determined by the comparison of the HPLC patterns of the standard compounds.

Conversion of cyclohexene and selectivities of products are shown in Table S1. Based on our preliminary results, monoalkylation products are the main contents (more than 97.0%). The concentrations of the products of multi-alkylation and cyclohexene oligomerization are negligibly small because of the excess toluene inhibiting the formation of cyclohexene oligomer.

Parallel reactions for the formation of *o*-cyclohexyltoluene, *m*-cyclohexyltoluene and *p*-cyclohexyltoluene happen simultaneously as illustrated in Scheme 2 [15].

Because an excess of toluene is used, the reaction is supposed to be first order with respect to the concentration of cyclohexene [16]. Therefore, the reaction rates of the product formation are proportional to cyclohexene concentration, as shown in Eqs. (1)–(3).

$$\frac{dC_B}{dt} = k_1 C_A \tag{1}$$

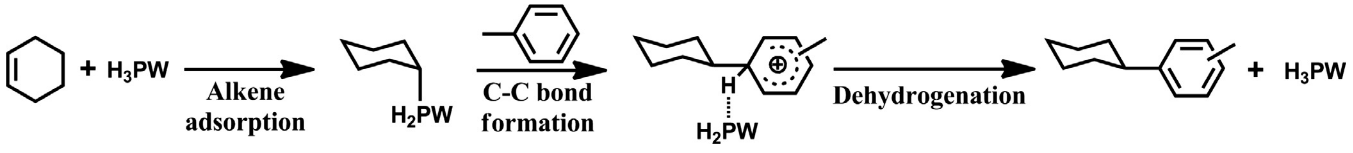
$$\frac{dC_C}{dt} = k_2 C_A \tag{2}$$

$$\frac{dC_D}{dt} = k_3 C_A \tag{3}$$

At the beginning, $C_{B,0} = C_{C,0} = C_{D,0} = 0$. According to stoichiometric relationship,

$$C_B + C_C + C_D + C_A = C_{A,0} \tag{4}$$

where $C_{A,0}$ is the initial concentration of cyclohexene, C_A is the concentration of cyclohexene at time t. C_B, C_C, C_D are the concentrations of *o*-cyclohexyltoluene, *m*-cyclohexyltoluene and *p*-cyclohexyltoluene, respectively. k_1, k_2, k_3 are the reaction rate constants for the formation of *o*-cyclohexyltoluene,



Scheme 1. The mechanism of the alkylation between toluene and cyclohexene over HPW.