Available online at www.sciencedirect.com

ScienceDirect

Catalysis Communications 8 (2007) 1354–1360

CATALYSIS COMMUNICATIONS

www.elsevier.com/locate/catcom

Alkylation of the toluene methyl group: A DFT study

Sławomir Ostrowski, Jan Cz. Dobrowolski *, Jacek Kijeński

Industrial Chemistry Research Institute, 8 Rydygiera Street, 01-793 Warsaw, Poland

Received 28 July 2006; received in revised form 24 November 2006; accepted 30 November 2006
Available online 5 December 2006

Abstract

Alkylation of the methyl group of toluene was modeled at the B3LYP/6-311++G** level. In the presence of Na_2; the model basic catalyst, the methyl group is more active for the Na/H exchange than the H atoms at the aromatic ring. The $PhCH_2Na$ molecule formed is next alkylated by ethene to produce PhC_3H_6Na. This needs a 30 kcal/mol barrier to be overcome. Finally, the Na/H exchange between PhC_3H_6Na and (unreacted) toluene molecules proceeds through a 18 kcal/mol barrier and ca. 10 kcal/mol is released. The study has confirmed the basic alkylation scheme proposed by Pines, Vesely, and Ipatieff more than 50 years ago.

Keywords: Alkylation; Basic; Catalysis; DFT; Side chain; Toluene

1. Introduction

Alkylation is either the transfer of an alkyl group from one molecule to another or addition of an unsaturated hydrocarbon to a reactant. The alkyl group may be transferred as an alkyl carbocation, a radical, or a carboanion. The alkyl can be generated from alkenes, alcohols, haloalkanes and other more sophisticated alkylation agents. Alkylation is primarily important in petrochemical industry [1,2], for example, in paraffin branching, cumene [3,4], and ethylbenzene [5,6] syntheses as intermediates for antiknok and clean burning gasolines, phenol and acetone, and styrene production, respectively.

Alkylation reactions have been known since the discovery of the Friedel–Crafts alkylation in 1877 [7,8]. Alkylation is carried out in the presence of both acidic and basic catalysts [1]. Alkylation of alkyloaromatic compounds depends strongly on the acid–base properties of a catalyst. Indeed, the acidic catalysts direct the alkylation toward aromatic ring substitution, in agreement with the Friedel–Crafts mechanism [7], whereas basic or superbasic catalysts, such as MgO/K α-Al_2O_3-K, force the reaction towards elongation or branching of the side chain [9,10]. The alkylation over superbasic catalysts has been also utilized in industrial technologies. For example alkylation of the cumene side chain yielding *t*-amylobenzene proceeds at 408 °C over superbasic K/KOH/g-Al_2O_3 catalyst, with cumene conversion equal to 99.9% and selectivity towards *t*-amylobenzene equal to 99.6% [11,12]. Over superbasic catalysts such as K/CaO or Na/K_2CO_3 at 410 °C, the methyl group of *o*-xylene is attacked by butadiene to form 5-(*o*-tolyl)-2-pentene [13]. Also *p*-xylene is alkylated by butene with 81% selectivity [14].

The aim of this study is to understand why alkylation of toluene by ethene over a superbasic catalyst results in the side chain elongation. Such a reaction is assumed to proceed according to the scheme proposed by Pines et al. [9]:

(i) $RX + 2Na \Longleftrightarrow RNa + NaX$
(ii) $PhCH_3 + RNa \Longleftrightarrow PhCH_2Na + RH$
(iii) $PhCH_2Na + C_2H_2 \Longleftrightarrow PhCH_2CH_2CH_2Na.$
(iv) $PhCH_2CH_2CH_2Na + PhCH_3 \Longleftrightarrow PhCH_2CH_2CH_3 + PhCH_2Na$
(v) Successive reactions.

In this paper we consider the following steps of the reaction:

---

* Corresponding author. Tel.: +48 22 5682421.
E-mail address: janek@il.waw.pl (J.Cz. Dobrowolski).

1566-7367/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2006.11.038

(i) Toluene adsorption on a catalyst.

(ii) Formation of $PhCH_2Na$:

$$PhCH_3 + BNa \Longleftrightarrow PhCH_2Na + BH \text{ B stands for a base, Ph stands for phenyl.}$$

(iii) Ethene insertion:

$$PhCH_2Na + H_2C{=}CH_2 \Longleftrightarrow PhCH_2CH_2CH_2Na$$

(iv) Na/H exchange:

$$PhCH_2CH_2CH_2Na + PhCH_3 \Longleftrightarrow PhCH_2CH_2CH_3 + PhCH_2Na.$$

(v) Desorption of propylbenzene.

where the stages (ii), (iii), and (iv) corresponds to Pines stage (i) + (ii), (iii), and (iv) respectively.

In the modeling performed, the Na_2 molecule was used as the model of the superbasic catalyst. To our best knowledge, the alkyloaromatics alkylation over superbasic catalysts has not been modeled by using quantum chemical calculations, so far.

2. Calculations

The calculation were performed by using the B3LYP method [15–19] combined with the 6-311++G** bases set [20] as implemented in the Gaussian 03 suite of programs [21]. For each minimum on the PES it was tested that all harmonic frequencies were positive, whereas for each transition states one imaginary frequency, corresponding to the reaction coordinate, was detected. The transition states were found by applying the QST3 (*Quadratic Synchronous Transit-Guided Quasi-Newton*) developed by Schlegel et al [22]. For all transition stages, the intrinsic reaction coordinate (IRC) routine [23] was also run to verify that the TS found corresponded to the searched reaction path. Estimation of the Gibbs free energies G_{298} for molecules and reactions studied was also executed [24].

3. Results and discussion

In the modeling below, it is assumed that the reacting system preserved the singlet state configuration throughout all reaction steps.

3.1. Reasoning for choice of the Na_2 molecule as a model basic catalyst

In most cases, known reactions of side alkyl chain elongation proceed over basic catalysts which are an alkali metal supported on oxide surfaces [9–14]. Modeling of structure of heterogenous catalysts surface by quantum chemical methods is itself quite a task [25,26]. When additionally a reaction of a medium size molecule must be modeled on the catalyst surface this becomes extremely laborious. Therefore, there is a need for simplification one of the two: a catalyst structure or a molecule structure. Because, we are studying reaction of one or two medium size aromatic molecules, we decided to simplify the model of catalyst structure. It has been shown that sodium in vapor phase acts as a basic catalyst [27–29]. Sodium at a surface [30,31] and in the gas phase [32] exists in a form of small clusters. In a number of small sodium clusters only Na_2, Na_8, Na_{18}, and Na_{20} possess the closed shell structure [33,34]. In this paper, we assume that the studied reaction preserves the closed shell (singlet) configuration of the whole reaction system, because the open shell system would imply a radical mechanism of the reaction which although interesting is beyond this project. Therefore, to model the catalyst we have chosen the simplest, closed shell sodium cluster, i.e., the Na_2 molecule. This very molecule is definitely basic, can accept the H atom, exhibits the $Na \cdots Na$ interactions, can interact with one or two sites of an organic molecule, and is a closed shell system. However, we are aware of difference of such a simple model and for example model of the Na/MgO surface, where at least interaction with oxygen atoms should be considered. Therefore, one can threat the catalyst model simplified to the Na_2 molecule just as the first approximation of a more sophisticated structures.

3.2. Toluene adsorption on a catalyst

The preliminary step of the alkylation reaction is adsorption of the reagent diffunding from bulk into the catalyst surface. In this paper the catalyst is simplified and approximated by the Na_2 molecule. Thus, the adsorption step is here equivalent to the formation of a complex between toluene and the Na_2 molecule (R1, Fig. 1). At the B3LYP/6-311++G** level, such a process is barrierless and the complex formation is endoergic with Gibbs free energy difference between the product and reactants (ΔG_{298}) equal to ca. 3 kcal/mol.

3.3. Formation of the $PhCH_2Na$ molecule

According to Pines et al. [9], the sodium toluenate, $PhCH_2Na$, is formed by the Na atom exchange with a BNa molecule, where B is a base:

$$PhCH_3 + BNa \Longleftrightarrow PhCH_2Na + BH$$

In this study it was assumed that the exchange occurs at the catalyst surface, i.e. a toluene hydrogen atom is replaced by the Na atom and the hydrogen is moved into the surface, and the NaH molecule is formed:

$$PhCH_3 + Na_2 \Longleftrightarrow PhCH_2Na + NaH$$

Because there are four possible sodium toluenates: substituted at *ortho*-, *meta*-, *para*-, and methyl positions, it was first checked the $PhCH_2Na$ molecule to be the most stable thermodynamically (Table 1). The other three isomers are at least 7 kcal/mol less stable than the $PhCH_2Na$ molecule thus this difference seems to be meaningful (Usually, it is assumed that in the energetic prediction the energy