



Side-chain alkylation of toluene with propene over a basic catalyst A DFT study

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ABSTRACT

The toluene methyl group alkylation by propene over a basic catalyst, approximated by the Na₂ molecule, was modeled by the B3LYP/6-311++G** method. The process starts by formation of the PhCH₂Na molecule in complex with the NaH molecule. Then, the two reaction paths are considered: Path A at which PhCH₂Na...NaH complex is dissociated, and Path B at which the whole PhCH₂Na...NaH complex enters in the next reaction step. Next, at the two paths both insertion of the propene double bond into the C–Na bond and the Na/H exchange, leading to one of the isomers of butylbenzene, are examined. At Path A, the PhCH₂Na molecule plays role of catalyst: it is re-formed in the last stage and can return to the propene insertion step. At Path B, the Na₂ molecule is a catalyst: it is re-constructed in the last stage and can return to the beginning step of formation of the PhCH₂Na molecule. The energy levels at Path A are always above those of Path B, whereas the barriers at the essential steps of Path A are always significantly lower than the appropriate ones at Path B. Path A seems to be preferred kinetically while Path B thermodynamically. At the two paths isobutylbenzene is favored over *n*-butylbenzene by both thermodynamic and kinetic factor. This is in good agreement with experimental findings. We interpret Path A as describing the reaction in the bulk gas phase whereas Path B as describing the reaction at the metal surface. Because, the number of molecules is usually greater in the bulk than in the surface Path A, which is practically the same as that described by Pines et al. more than fifty years ago, is the main mechanism describing the toluene side chain alkylation by propene over a basic catalyst.

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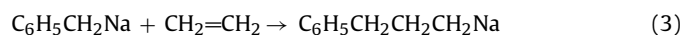
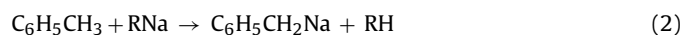
1. Introduction

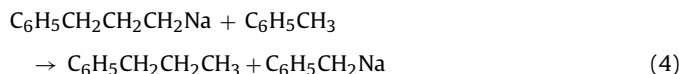
Alkylation is the introduction of an alkyl group into a molecule by substitution or addition. There are several types of alkylation such as substitution for hydrogen bound to carbon, nitrogen, or oxygen, or addition to a metal to form a metal–carbon bond, or to a tertiary amine to form quaternary ammonium compound, and miscellaneous additions to sulfur, silicon etc. 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. The largest use of alkylation is in refineries for the production of alkylates that are used in gasoline [1–3]. Other major alkylation products include ethylbenzene [4,5], cumene [6,7], linear alkylbenzene [8,9], and till not long ago tetramethyl lead and tetraethyl lead [10].

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Alkylation is carried out in the presence of both acidic and basic catalysts [1]. In 1877 Friedel and Crafts discovered what is now known as the Friedel–Crafts reaction: the alkylation or acylation of an aromatic compound catalyzed by aluminum chloride as a Lewis acid [11]. In presence of an acidic catalyst the alkylation of an (alkyl) aromatic compound occurs at the ring. Alkylation of alkylaromatic compounds in presence of a basic sodium catalyst was studied by Pines, Vesely and Ipatieff in 1955 [12]. On the contrary to the alkylation over an acid catalyst, in presence of a basic catalyst the side alkyl chain of an aromatic compound is alkylated. Thus by changing the acid–base properties of a catalyst one can direct the reaction either to substitute the aromatic ring or to extend or branch the side-chain. Pines et al. proposed [12] the following scheme for alkylation of toluene over a basic Na catalyst:





Because of technological importance [13–18], let us mention that in mid 1960s Sidorenko et al. [13] studied the alkylation of toluene with methanol using alkali metal exchanged X- and Y-type zeolites and proposed a mechanism in which methanol is converted to formaldehyde which then reacts with toluene to produce styrene and ethylbenzene. Notice, that the alkylation of toluene with methanol over an acid catalyst produces a mixture of xylenes [19–23].

Different alkylations over superbasic catalysts have been utilized in industrial technologies. For instance, the basic alkylation of the cumene side chain yielding *t*-amylobenzene proceeds at 408 °C over superbasic K/KOH/g-Al₂O₃ catalyst, with cumene conversion equal to 99.9% and selectivity towards *t*-amylobenzene equal to 99.6% [24,25]. Over superbasic catalysts such as K/CaO or Na/K₂CO₃ at 410 °C, the methyl group of *o*-xylene is attacked by butadiene to form 5-(*o*-tolyl)-2-pentene [26]. Also, over basic catalysts *o*-xylene alkylated with butadiene dimethyl-2,6-naphthalenedicarboxylate, a reactant to form polyethylene naphthalate (PEN) which is supposed to supplant polyethylene terephthalate (PET), is produced [27]. Also *p*-xylene is alkylated by butene with 81% selectivity [28].

In context of this study it is important to stress that isobutylbenzene (IBB) may be synthesized by toluene alkylation with propene over a basic catalyst [29,30]. IBB is a reactant in synthesis of an anti-inflammatory drug *ibuprofen* [31].

This study is a continuation of our recent DFT (B3LYP/6-311++G**) investigations on alkylation of toluene with ethylene over a basic catalyst modeled by the Na₂ molecule [32]. We assumed that the singlet state configuration was preserved throughout all reaction steps. In that study we demonstrated that in presence of the basic catalyst, Na₂, the PhCH₂Na sodium toluenolate formation has been preferred more than the formation of the isomeric *o*-, *m*-, and *p*-sodium toluenates (a matter of at least 7 kcal/mol). The process required ca. 35 kcal/mol to be supplied to the reaction system. Moreover, we showed that the ethene insertion into the C–Na bond occurred seemingly more easily for the free PhCH₂Na molecule, a matter of 15 kcal/mol, yet in fact this required additional 30 kcal/mol to dissociate the PhCH₂Na...HNa complex that has been formed in the previous step. We concluded that the ethylene insertion into the C–Na bond to elongate the alkyl chain occurred for the PhCH₂Na...HNa rather than the free PhCH₂Na molecule and has gone through a 30 kcal/mol barrier. We found that the reaction ends with the Na/H exchange between PhC₃H₇Na and toluene, which requires the 18 kcal/mol barrier to be overcome. Finally, we confirmed the general reaction scheme proposed by Pines, Vesely and Ipatieff more than fifty years ago [12].

A very crucial point of our previous and the present modeling has been selection of the Na₂ molecule as a model catalyst. Therefore, here, we repeat [32] the arguments for such a choice. In most cases, known reactions of side alkyl chain elongation proceed over basic catalysts which are an alkali metal supported on oxide surfaces [12,24–27,33]. Modeling of structure of heterogeneous catalysts surface by quantum chemical methods is itself quite a task [34,35]. 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 [36–38]. Sodium at a surface [39,40] and in the gas phase [41] exists in a form of small clusters. In a number of small sodium clusters only Na₂, Na₈, Na₁₈, and Na₂₀ possess the closed shell structure [42,43].

In our recent study [32] and 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 Na₂ molecule. This very molecule is definitely basic, can accept the H atom, exhibits the Na...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 treat the catalyst model simplified to the Na₂ molecule just as the first approximation of a more sophisticated surface structures.

In this paper we are analyzing computationally the toluene alkylation by propene over the model Na₂ catalyst. Two products can be formed in such an alkylation: *n*-butylbenzene and isobutylbenzene. As for toluene alkylated with ethylene two reaction paths are possible for the alkylation: Path A started by dissociation of the PhCH₂Na...HNa complex formed in the sodium toluenolate formation, and Path B, for which the dissociation is not assumed as a preliminary condition. We are answering the question of which product is thermodynamically and/or kinetically preferred? and we propose mechanisms of the studied alkylation. In particular we suggest interpretation of Path A and Path B.

2. Calculations

The calculation were performed by using the B3LYP method [44–48] combined with the 6-311++G** bases set [49] as implemented in the Gaussian 03 suite of programs [50]. For each minimum on PES it was tested that all harmonic frequencies were positive, whereas for each transition state (TS) 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. [51] For all transition states, the intrinsic reaction coordinate (IRC) routine [52] 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 [53]. The partial charges localized at atoms were calculated to match the electrostatic potential at the van der Waals surface [54].

3. Results and discussion

The propene molecule, as an alkylating agent, can be attached either through the C1 or methyl substituted C2 alkene atom. Thus two isomers can be formed: one elongated by the *n*-propyl and the second elongated by the iso-propyl group. Because we consider the catalytic reaction over a basic catalyst, alkylation of the toluene by propene leads only to substitution at the methyl group, and as we showed before [32], the six products substituted at the benzene ring can be excluded. Still, to analyze the toluene methyl group alkylation one should consider three reactions for each of two reaction paths (Scheme 1). For these reactions we discuss energetics and activation barriers in terms of Gibbs free energies, G_{298} .

In a preliminary step of the alkylation reaction (described before [32]) the toluene molecule is adsorbed at the catalyst surface. For catalyst approximated by the Na₂ molecule, the adsorption step is equivalent to the formation of a complex between toluene and the Na₂ molecule (point 1, Scheme 1). This is a barrierless process after which the complex is stabilized by 3 kcal/mol (in terms of ΔG_{298}) [32]. Next, the Na/H exchange occurs and the PhCH₂Na molecule is

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