



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

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### ABSTRACT

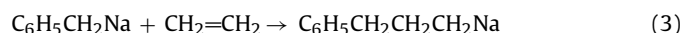
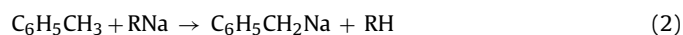
The toluene methyl group alkylation by propene over a basic catalyst, approximated by the Na<sub>2</sub> molecule, was modeled by the B3LYP/6-311++G\*\* method. The process starts by formation of the PhCH<sub>2</sub>Na molecule in complex with the NaH molecule. Then, the two reaction paths are considered: Path A at which PhCH<sub>2</sub>Na...NaH complex is dissociated, and Path B at which the whole PhCH<sub>2</sub>Na...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 PhCH<sub>2</sub>Na 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 Na<sub>2</sub> molecule is a catalyst: it is re-constructed in the last stage and can return to the beginning step of formation of the PhCH<sub>2</sub>Na 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

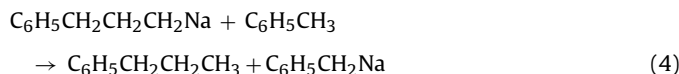
Alkylation is the introduction of an alkyl group into a molecule by substitution or addition. There are several types of alkylation such as substitution for hydrogen bound to carbon, nitrogen, or oxygen, or addition to a metal to form a metal–carbon bond, or to a tertiary amine to form quaternary ammonium 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].

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:



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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-Al<sub>2</sub>O<sub>3</sub> 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/K<sub>2</sub>CO<sub>3</sub> 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 Na<sub>2</sub> 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, Na<sub>2</sub>, the PhCH<sub>2</sub>Na sodium toluenate 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 PhCH<sub>2</sub>Na molecule, a matter of 15 kcal/mol, yet in fact this required additional 30 kcal/mol to dissociate the PhCH<sub>2</sub>Na...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 PhCH<sub>2</sub>Na...HNa rather than the free PhCH<sub>2</sub>Na molecule and has gone through a 30 kcal/mol barrier. We found that the reaction ends with the Na/H exchange between PhC<sub>3</sub>H<sub>7</sub>Na 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 Na<sub>2</sub> 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 Na<sub>2</sub>, Na<sub>8</sub>, Na<sub>18</sub>, and Na<sub>20</sub> 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 Na<sub>2</sub> 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 Na<sub>2</sub> 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 Na<sub>2</sub> 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 PhCH<sub>2</sub>Na...HNa complex formed in the sodium toluenate 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.

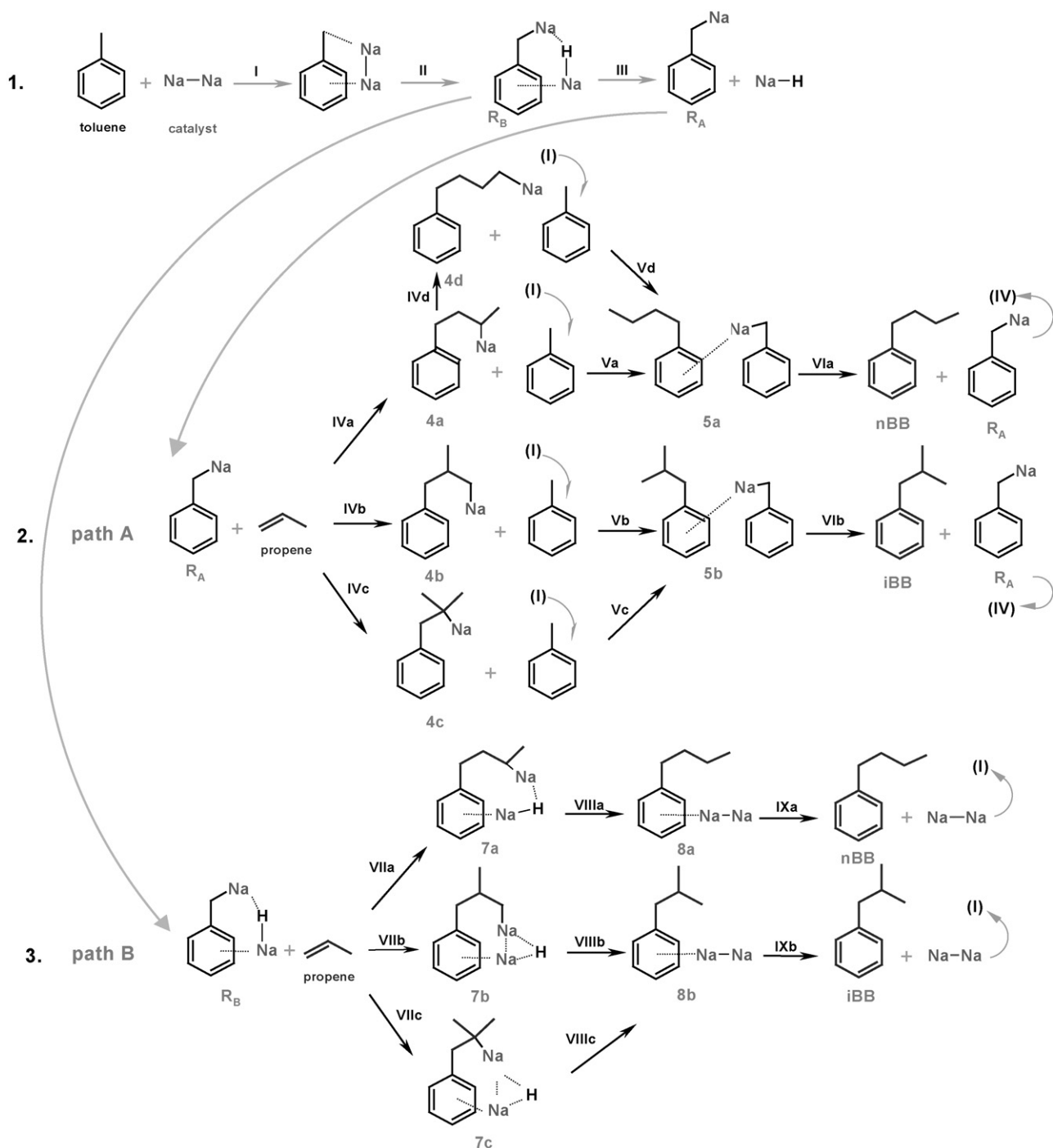
## 2. Calculations

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

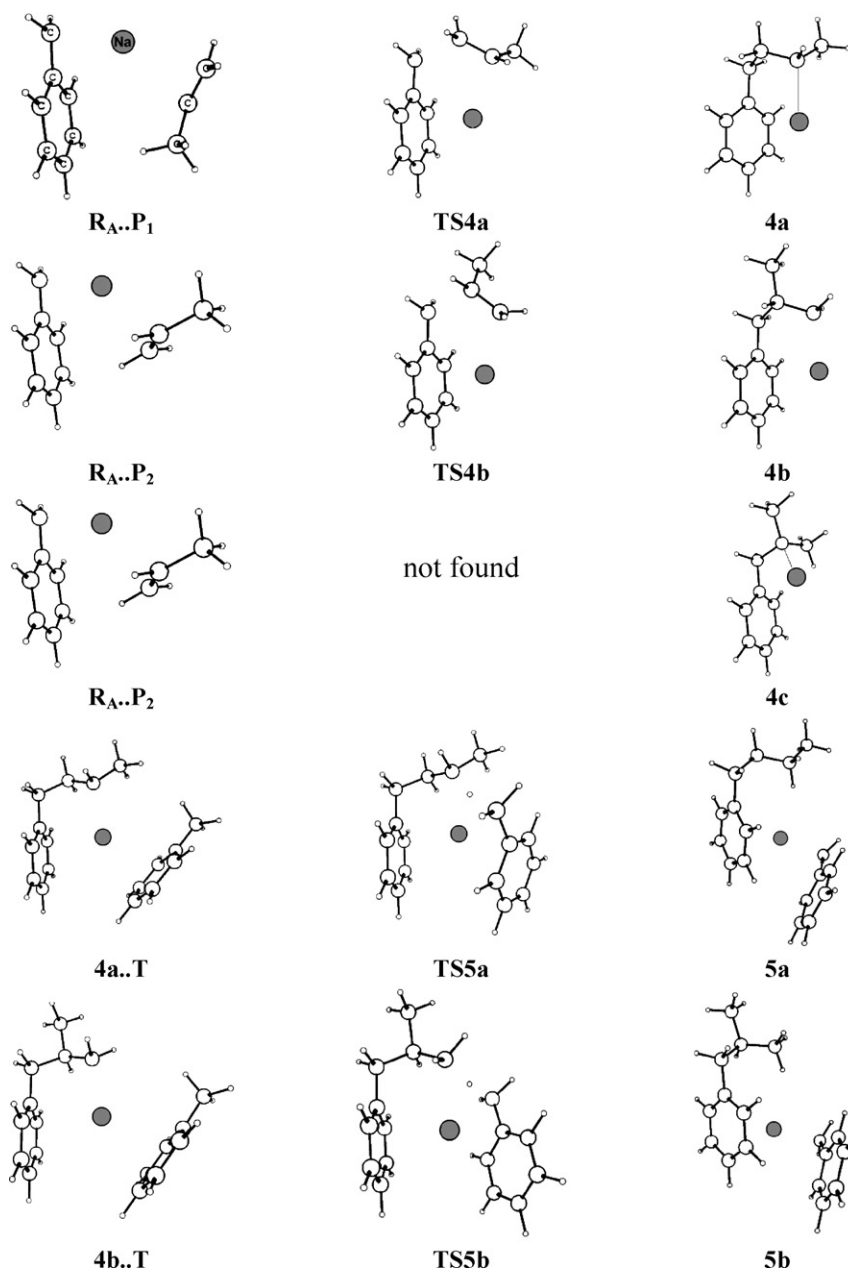
The propene molecule, as an alkylating agent, can be attached either through the C1 or methyl substituted C2 alkene atom. Thus two isomers can be formed: one elongated by the *n*-propyl and the second elongated by the iso-propyl group. Because we consider the catalytic reaction over a basic catalyst, 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 Na<sub>2</sub> molecule, the adsorption step is equivalent to the formation of a complex between toluene and the Na<sub>2</sub> molecule (point 1, Scheme 1). This is a barrierless process after which the complex is stabilized by 3 kcal/mol (in terms of  $\Delta G_{298}$ ) [32]. Next, the Na/H exchange occurs and the PhCH<sub>2</sub>Na molecule is



**Scheme 1.** The considered stages of toluene alkylation by propene over Na<sub>2</sub> the model basic catalyst. T-toluene; P-propene; TS-transition state.

- (IVa) PhCH2Na + C3H6 -> PhCH2CH2CHNaCH3; ( $R_A + P_1 \rightarrow TS4a \rightarrow 4a$ )  
 (IVb) PhCH2Na + C3H6 -> PhCH2CH(CH3)CH2Na; ( $R_A + P_2 \rightarrow TS4b \rightarrow 4b$ )  
 (IVc) PhCH2Na + C3H6 -> PhCH2CNa(CH3)2; ( $R_A + P_2 \rightarrow 4c$ )  
 (IVd) PhCH2CH2CH2NaCH3 -> PhCH2CH2CH2CH2Na ( $4a \rightarrow 4d$ )  
 (Va) PhCH2CH2CH2NaCH3 + PhCH3 -> PhCH2CH2CH2CH3...PhCH2Na; ( $4a + T \rightarrow TS5a \rightarrow 5a$ )  
 (Vb) PhCH2CH(CH3)CH2Na + PhCH3 -> PhCH2CH2(CH3)2...PhCH2Na; ( $4b + T \rightarrow TS5b \rightarrow 5b$ )  
 (Vd) PhCH2CH2CH2CH2Na + PhCH3 -> PhCH2CH2CH2CH3...PhCH2Na; ( $4d + T \rightarrow TS5d \rightarrow 5a$ )  
 (VIa) PhCH2CH2CH2CH3...PhCH2Na -> PhCH2CH2CH2CH3 + PhCH2Na; ( $5a \rightarrow nBB + R_A$ )  
 (VIb) PhCH2CH2(CH3)2...PhCH2Na -> PhCH2CH2(CH3)2 + PhCH2Na; ( $5b \rightarrow iBB + R_A$ )  
 (VIIa) PhCH2Na...NaH + C3H6 -> PhCH2CH2CHNaCH3...NaH; ( $R_B + P_1 \rightarrow TS7a \rightarrow 7a$ )  
 (VIIb) PhCH2Na...NaH + C3H6 -> PhCH2CH(CH3)CH2Na...NaH; ( $R_B + P_2 \rightarrow TS7b \rightarrow 7b$ )  
 (VIIc) PhCH2Na...NaH + C3H6 -> PhCH2CNa(CH3)2...NaH; ( $R_B + P_2 \rightarrow 7c$ )  
 (VIIIa) PhCH2CH2CHNaCH3...NaH -> PhCH2CH2CH2CH3...Na2; ( $7a \rightarrow TS8a \rightarrow 8a$ )  
 (VIIIb) PhCH2CH(CH3)CH2Na...NaH -> PhCH2CH(CH3)2...Na2; ( $7b \rightarrow TS8b \rightarrow 8b$ )  
 (IXa) PhCH2CH2CH2CH3...Na2 -> PhCH2CH2CH2CH3 + Na2; ( $8a \rightarrow nBB + Na2$ )  
 (IXb) PhCH2CH(CH3)2...Na2 -> PhCH2CH(CH3)2 + Na2; ( $8b \rightarrow iBB + Na2$ )



**Fig. 1.** The B3LYP/6-311++G<sup>\*\*</sup> optimized geometries of reactants, TSs, and products in the following reactions:  
 (IVa)  $\text{PhCH}_2\text{Na} + \text{C}_3\text{H}_6 \rightarrow \text{PhCH}_2\text{CH}_2\text{CHNaCH}_3$ ; ( $\text{R}_A + \text{P}_1 \rightarrow \text{TS-4a} \rightarrow 4\text{a}$ )  
 (IVb)  $\text{PhCH}_2\text{Na} + \text{C}_3\text{H}_6 \rightarrow \text{PhCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Na}$ ; ( $\text{R}_A + \text{P}_2 \rightarrow \text{TS-4b} \rightarrow 4\text{b}$ )  
 (IVc)  $\text{PhCH}_2\text{Na} + \text{C}_3\text{H}_6 \rightarrow \text{PhCH}_2\text{CNa}(\text{CH}_3)_2$ ; ( $\text{R}_A + \text{P}_2 \rightarrow 4\text{c}$ )  
 (Va)  $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{NaCH}_3 + \text{PhCH}_3 \rightarrow \text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \dots \text{PhCH}_2\text{Na}$ ; ( $4\text{a} + \text{T} \rightarrow \text{TS5a} \rightarrow 5\text{a}$ )  
 (Vb)  $\text{PhCH}_2\text{CH}(\text{CH}_3)(\text{CH}_2\text{Na}) + \text{PhCH}_3 \rightarrow \text{PhCH}_2\text{CH}_2(\text{CH}_3)_2 \dots \text{PhCH}_2\text{Na}$ ; ( $4\text{b} + \text{T} \rightarrow \text{TS5b} \rightarrow 5\text{b}$ )  
 (Vd)  $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Na} + \text{PhCH}_3 \rightarrow \text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \dots \text{PhCH}_2\text{Na}$ ; ( $4\text{d} + \text{T} \rightarrow \text{TS5d} \rightarrow 5\text{a}$ )

formed much easier than the isomeric *o*-, *m*-, and *p*-sodium toluenates ( $\text{NaC}_6\text{H}_4\text{CH}_3$ ). The reaction towards  $\text{PhCH}_2\text{Na}$  is favored both thermodynamically (a matter of 7 kcal/mol) and kinetically (barrier lower by ca. 20 kcal/mol) [32].

Then, two situations are possible: either after the Na/H exchange the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex formed dissociates and the single  $\text{PhCH}_2\text{Na}$  molecule in complex with  $\text{NaH}$  molecule is reacting with propene (Path A: point 2, Scheme 1) or the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex does not dissociates and the  $\text{PhCH}_2\text{Na}$  moiety of the stable complex is reacting with propene (Path B: point 3, Scheme 1). Here, the energetics and reaction profiles for these two Paths are considered in details.

3.1. Path A: the reaction between  $\text{PhCH}_2\text{Na}$  and  $\text{CH}_2=\text{CHCH}_3$  towards  $\text{PhC}_4\text{H}_9$

3.1.1. Insertion of  $\text{CH}_2=\text{CHCH}_3$  into the C–Na bond

As we have shown before [32], the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex dissociation into the separate  $\text{PhCH}_2\text{Na}$  and  $\text{NaH}$  molecules requires ca. 33 kcal/mol to be supplied to the system. The  $\text{PhCH}_2\text{Na}$  molecule released is then attacked by the alkylating agent, i.e., the propene molecule.



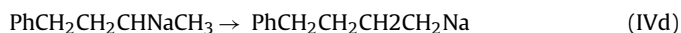
**Table 1**  
The B3LYP/6-311++G\*\* Gibbs free energies  $G_{298}$  (hartree) and the Gibbs free energies referred to the reactants in the single process ( $\Delta G'_{298}$ ) and in whole process ( $\Delta G_{298}$ ) (kcal/mol) at Path A for the reactions presented in Scheme 1

System	$G_{298}$	$\Delta G_{298}$	System	$G_{298}$	$\Delta G_{298}$
<b>I</b>					
Reactants			[T + Na <sub>2</sub> + P + T]	-985.599680	0.0
R <sub>0</sub>	-596.157991	0.0	R <sub>0</sub> + [P + T]	-985.592354	4.6
TS1	-596.100311	36.2	TS1 + [P + T]	-985.534674	40.8
1	-596.155203	1.7	1 + [P + T]	-985.589566	6.3
<b>IVa</b>					
[R <sub>A</sub> .P <sub>1</sub> ]	-551.117915	0.0	[R <sub>A</sub> .P <sub>1</sub> ] + [T + NaH]	-985.537062	39.3
TS4a	-551.082884	22.0	TS4a + [T + NaH]	-985.502031	61.3
4a	-551.107544	6.5	4a + [T + NaH]	-985.526691	45.8
<b>IVb</b>					
[R <sub>A</sub> .P <sub>2</sub> ]	-551.117191	0.0	[R <sub>A</sub> .P <sub>2</sub> ] + [T + NaH]	-985.536338	39.7
TS4b	-551.086798	19.1	TS4b + [T + NaH]	-985.505945	58.8
4b	-551.112753	2.8	4b + [T + NaH]	-985.531900	42.5
<b>Va</b>					
[4a.T]	-822.643162	0.0	[4a.T] + NaH	-985.519317	50.4
TS5a	-822.611973	19.6	TS5a + NaH	-985.488128	70.0
5a	-822.661815	-11.7	5a + NaH	-985.537970	38.7
<b>Vb</b>					
[4b.T]	-822.648454	0.0	[4b.T] + NaH	-985.524609	47.1
TS5b	-822.619045	18.5	TS5b + NaH	-985.495200	65.6
5b	-822.662991	-9.1	P <sub>A</sub> Vb + NaH	-985.539146	38.0
<b>Vd</b>					
[4d.T]	-822.640441	0.0	[4d.T] + NaH	-985.516596	52.1
TS5d	-822.616589	15.0	TS5d + NaH	-985.492744	67.1
5a	-822.661815	-13.4	5a + NaH	-985.537970	38.7
<b>VI</b>					
nBB	-389.43435		nBB + [TNa + NaH]	-985.541236	36.7
iBB	-389.43537		iBB + [TNa + NaH]	-985.542253	36.0
<b>X</b>					
nBB	-389.43435		nBB + [T + Na <sub>2</sub> ]	-985.599665	0.0
iBB	-389.43537		iBB + [T + Na <sub>2</sub> ]	-985.600682	-0.6
P (propene)	-117.891371				
T (toluene)	-271.542992				
PhCH <sub>2</sub> Na	-433.230733				
Na <sub>2</sub>	-324.622325				
NaH	-162.876155				



Reaction between PhCH<sub>2</sub>Na and propene can possibly lead to three isomers: (3-sodium-butyl)-benzene (4a), (3-sodium-2-methyl-propyl) benzene (4b) and (2-sodium-2-methyl-propyl) benzene (4c). In each of these structures the sodium atom attached to the alkyl chain is in the same time coordinated to the π-electron system of the benzene ring (Fig. 1). By analogy to some of the intramolecular hydrogen bond structures such conformations can be named “scorpio structures” [55]. Two of the isomers, (4a) and (4b), are formed in a straightforward insertion of the propene double bond into the C–Na bond. The calculated barrier heights for these reactions are 22 and 19 kcal/mol, respectively ( $\Delta G_{298}$ , Table 1). Thus, the kinetic constant  $k$  for these reactions can be estimated to 0.000463 and 0.062 s<sup>-1</sup> for (4a) and (4b), respectively (Table 2). Formation of (4c) is more complicated and requires more energy. When the propene central C2 atom approaches the CH<sub>2</sub>Na group, the H-atom attached to it jumps to the C1 atom and the CH<sub>3</sub> group is formed. Simultaneously, the C2–C(Na) bond is formed in a concerted way. Inspection into the partial charges in the course of the reaction indicates that, in such a process, the propene moiety must go through a dimethylcarbocation. The barrier height for the reaction towards (4c) is ca. 50 kcal/mol (Table 1). Thus, in practice, the formation of (4c) is kinetically disfavored.

We also considered the formation of (4-sodium-butyl) benzene (4d) by Na rearrangement in (4a) from position C3 to C4 with simultaneous H shift in opposite direction:



Note that although (4d) is not a probable product of toluene alkylation with propene it can be a main product of alkylation of ethylbenzene with ethylene over a superbasic catalysts [32]. However, rearrangement of (4a) to (4d) requires as much energy as 62 kcal/mol to be supplied to the system to overcome the barrier (Fig. 2, Table 1). Nevertheless, we describe this process in more

**Table 2**  
The reaction rates estimated from the Arrhenius equation:  $k = A \exp(-\Delta G/RT)$  for the reactions presented in Scheme 1

Reactions	$k_{298}$ [s <sup>-1</sup> ]
<b>Path A</b>	
IVa	0.00046
IVb	0.06186
Va	0.02660
Vb	0.17032
<b>Path B</b>	
VIIa	7.293E-16
VIIb	8.74661E-13
VIIIa	3.37523E-12
VIIIb	9.74619E-14

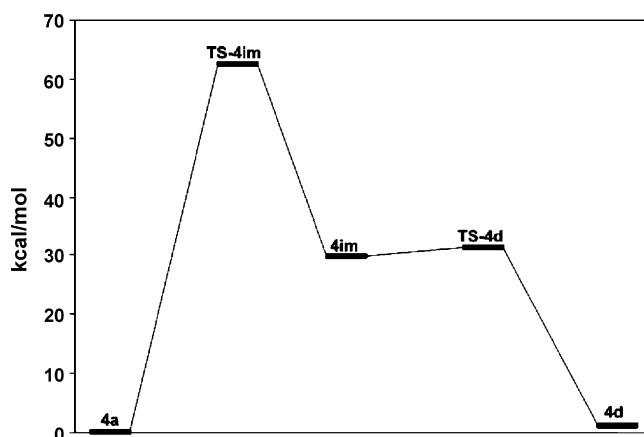


Fig. 2. Energetic profile for the intramolecular side chain rearrangement of the Na and H atoms in the *n*-Ph-C<sub>4</sub>H<sub>9</sub>Na molecule.

details. The (4a) molecule is stabilized in the scorio conformation (Fig. 1). In the TS structure the alkyl C3-Na distance increases and the Na atom shifts more into the center of the benzene ring. In the TS structure the transferring proton is in between of the C4 and C3 atoms. Next, ca. 30 kcal/mol below the barrier, an intermediate (4im) (with all positive frequencies) is formed. In (4im) the transferring H atom is bound to both the alkyl C3 atom and the Na atom. The C3-H distance is high: ca. 1.2 Å. Next, the chain conformational changes, which require ca. 1.5 kcal/mol barrier to be overcome, lead to formation of (4d).

In conclusion, in the set of reactions IV at Path A practically only (4a) and (4b) can be formed with slight kinetic preference for (4b). Comparison of the Gibbs free energies of (4a) and (4b) shows that (4b) is also thermodynamically favored by ca. 3.3 kcal/mol (Table 1). This is important since, in the next step, the (4b) molecule is transformed into iso-butylbenzene which is shown to be in excess in the alkylation products [29]. Because (4c) and (4d) are disfavored kinetically below we consider only the reactions of (4a) and (4b).

Table 3

The B3LYP/6-311++G\*\* estimated  $\Delta G_{298}$  values (kcal/mol) for the 4a and 4im reactants, the TS-4im TS-4d transition states, and the 4d product

Structure	$G_{298}$	$\Delta G_{298}$ kcal/mol
4a	-551.107544	0.0
TS-4im	-551.008278	62.3
4im	-551.060104	29.8
TS-4d	-551.057541	31.4
4d	-551.105684	1.2

### 3.1.2. Na/H exchange

In the next alkylation step (V), the product of the process IV, i.e., either (4a) or (4b), reacts with the toluene molecule and the Na atom of the reactant is exchanged with the H-atom of the toluene methyl group. Toluene is present in the system as a reactant and, in effect of the Na/H exchange, the active sodium toluenate (PhCH<sub>2</sub>Na) is re-constructed and reenters into the process IV.



The barriers for the Na/H exchange are equal to 19.6 and 18.5 kcal/mol and kinetic constants can be estimated to 0.170325 and 0.02660 s<sup>-1</sup> for (5a) and (5b), respectively (Table 2). The barrier high difference is small, yet again in agreement with experimental findings [29], the reaction towards branched side chain product is favored. The energetic profiles in the neighborhood of TS structures determined by the IRC routine are presented in Fig. 3.

Just after the Na/H exchange, the PhCH<sub>2</sub>Na and alkylbenzene molecules formed are bound in the complexes, namely PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>...PhCH<sub>2</sub>Na (5a) and PhCH<sub>2</sub>CH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>...PhCH<sub>2</sub>Na (5b). The complexes are stabilized mainly by the Na interaction with the  $\pi$ -electrons of the partner molecule (Fig. 1). Comparison of the Gibbs free energies of (5a) and (5b) shows that again the former is thermodynamically

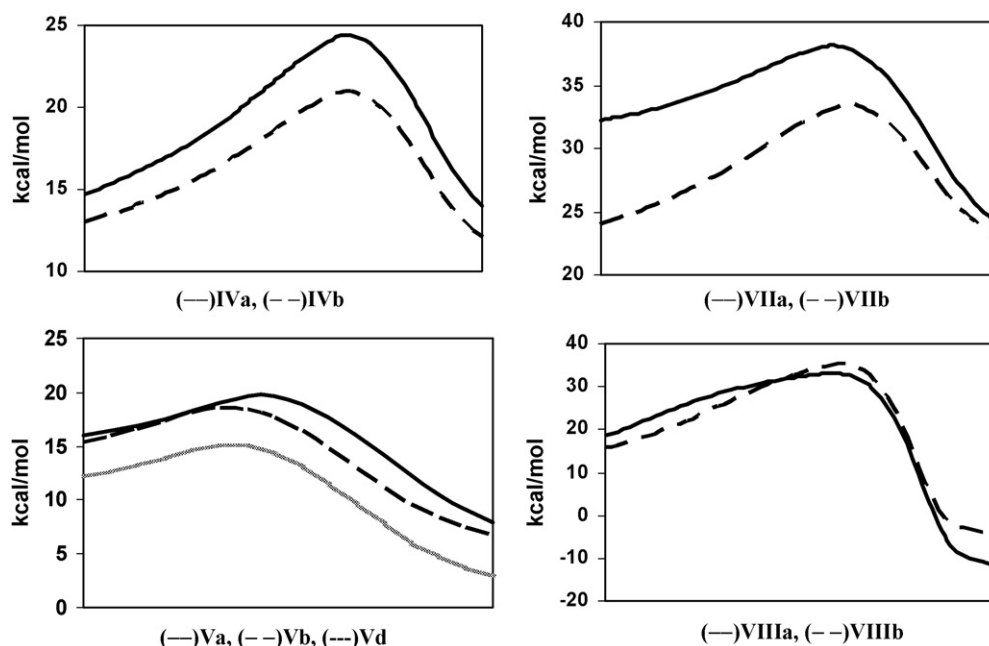


Fig. 3. The reaction profiles (top fragment of the profile) calculated by the IRC method at the B3LYP/6-311++G\*\* level for reactions (Scheme 1).

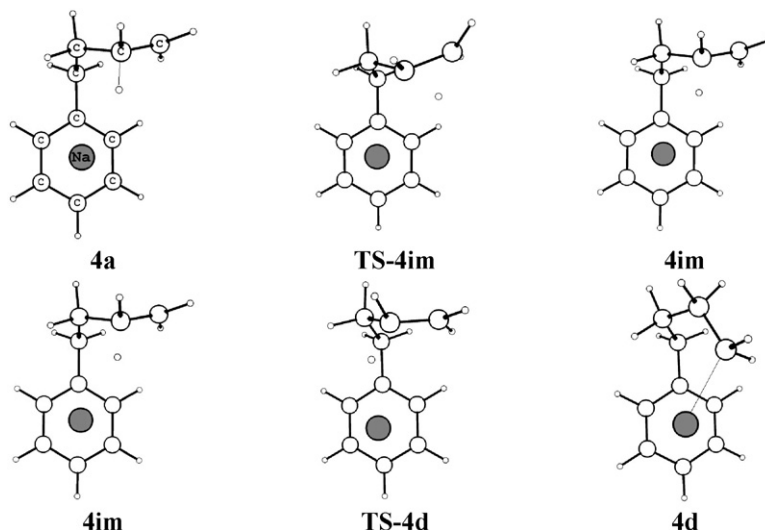


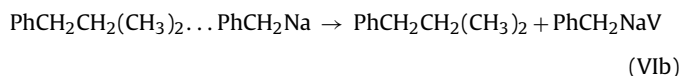
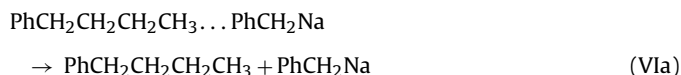
Fig. 4. The B3LYP/6-311++G<sup>\*\*</sup> optimized geometries for the 4a and 4im reactants, the TS-4im and TS-4d transition states, and the 4d product.

less stable than the latter by ca. 0.7 kcal/mol. The two reactions are exoergic: 11.7 and 9.1 kcal/mol is released in the former and the latter, respectively (Table 1).

Let us remark, that if (4d) could be formed its reaction towards (5a) it would be the most favored kinetically in the Na/H exchange (Fig. 4, Table 3).

### 3.1.3. Dissociation of the complex

As a result of the Na/H exchange, the complex between alkylbenzene and sodium toluenate is formed. Isolation of the product, as well as return of the PhCH<sub>2</sub>Na molecule as the reactant to the initial reaction, requires the PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>...PhCH<sub>2</sub>Na (5a) and PhCH<sub>2</sub>CH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>...PhCH<sub>2</sub>Na (5b) complexes to be dissociated.



Surprisingly, in terms of the calculated  $\Delta G$  (at 298.15 K), the signs of the dissociation energies of the (5a) and (5b) complexes are in contradiction to the expectation that the processes are endoergic. Indeed, the separated products are a bit higher in Gibbs free energies than the (5a) and (5b) complexes (a matter of 2 kcal/mol, Table 1). However, if the appropriate total energies are compared the process it is clearly exoergic: the energetic difference between products and reactants of the reactions VIa and VIb is ca. 9 kcal/mol. The similar is true when the ZPE corrected energies (i.e., Gibbs free energies at 0 K) are juxtaposed. Change of the energetic profile with temperature can be interpreted as an increase of the TS entropy term as the temperature is increased.

### 3.1.4. Summary of the energy changes at Path A

At Path A, we assume that sodium toluenate (PhCH<sub>2</sub>Na) is formed already as a result of the reaction between toluene and the Na<sub>2</sub> molecule, and propene and an excess of toluene is present in the system [32]. Then, reaction between sodium toluenate and propene leads to three isomers: (3-sodium-butyl) benzene (4a), (3-sodium-2-methyl-propyl) benzene (4b) and (2-sodium-2-methyl-propyl) benzene (4c). Next, each isomer reacts with a toluene molecule and both *n*-butylbenzene and isobutylbenzene products are formed

and the sodium toluenate is re-formed and can participate in the entrance channel. Remark, that the introductory reaction between toluene and the Na<sub>2</sub> molecule yields the sodium toluenate and NaH molecules. The latter remains in the system and, in our modeling, can symbolize the hydrogen atoms that sit at the metal surface. When the toluene is exhausted and cannot participate in the Na/H exchange, the H atom can be taken “from the surface” which, in this modeling, means that *n*-butylbenzene and isobutylbenzene are formed with simultaneous reformation of the “surface” Na<sub>2</sub> molecule.

Now, let us analyze the energy profile of Path A (Fig. 5). The first barrier of ca. 36 kcal/mol is attributed to the formation of sodium toluenate which is in the complex with the NaH molecule and whose energy is only ca. 6 kcal/mol greater than that of the reactants (Fig. 5). Next, dissociation of the sodium toluenate complex with the NaH molecule requires again ca. 33 kcal/mol to be supplied to the system. In fact, the system, after reaching the TS1 state, has accumulated enough energy for both formation of the sodium toluenate and release of the NaH molecule from the complex. Then,

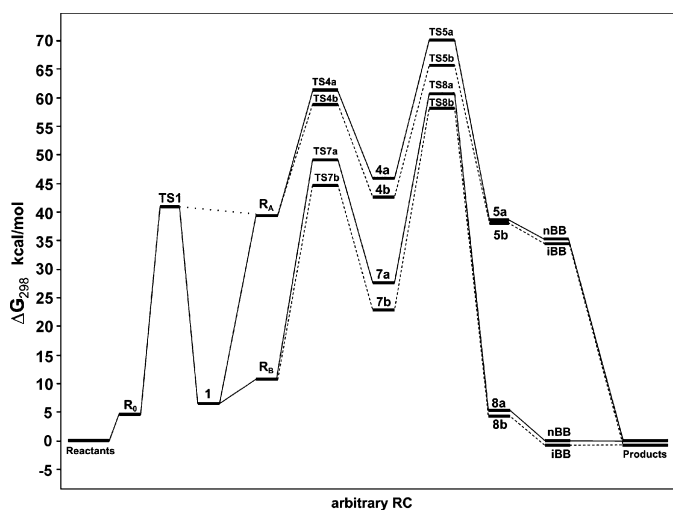


Fig. 5. The energetic profile of the alkylation of toluene by propene in presence of the Na<sub>2</sub> molecule, as a basic catalyst, modeled at the B3LYP/6-311++G<sup>\*\*</sup> level. iBB, nBB—products after dissociation of the Na<sub>2</sub> molecule, the other symbols as in Fig. 1 and Scheme 1.

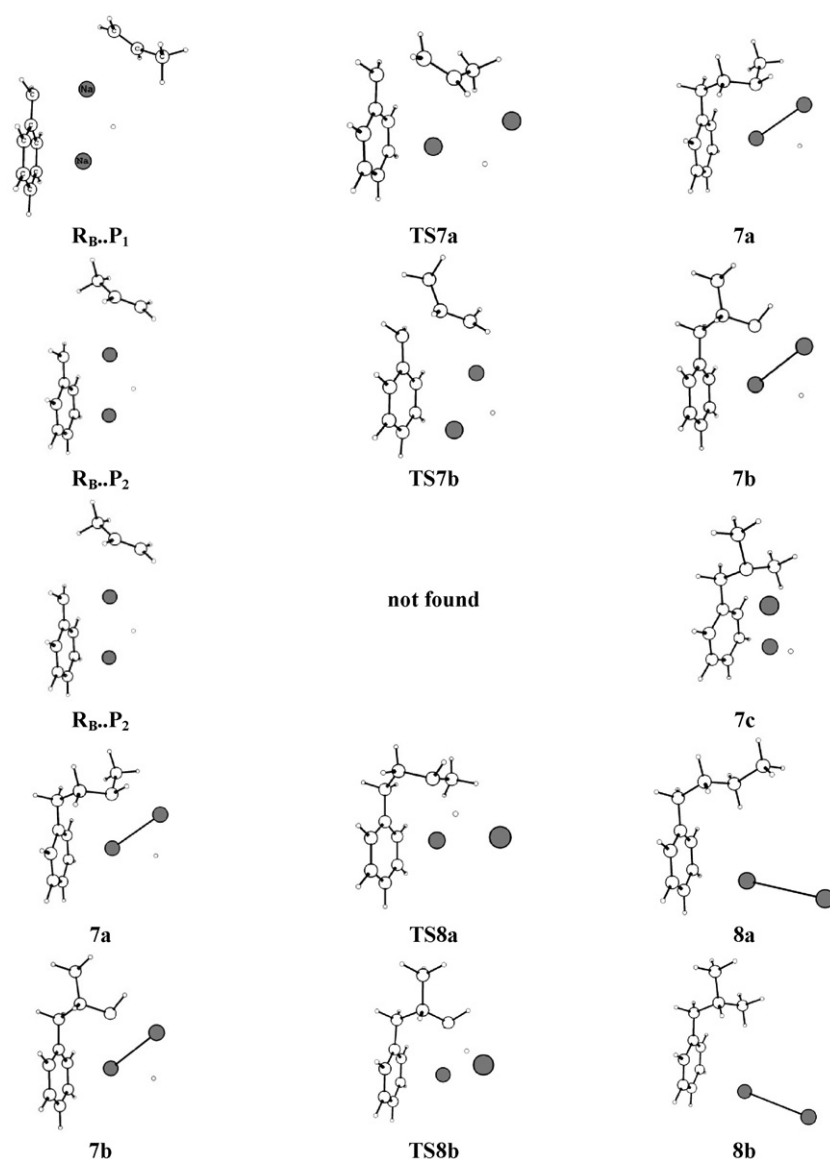
the sodium toluenate reacts with the associated propene molecule and, through the barrier of ca. 22 or 19 kcal/mol, one of the isomers of sodium butylobenzenate is formed. It seems to be a rule that the branched isomer is favored by both thermodynamic and kinetic factor. This is in very good agreement with experimental results: yield of isobutylbenzene is ca. ten-times greater than of *n*-butylbenzene [29]. The next step is sodium butylobenzenate collision with a toluene molecule in which an isomer of butylbenzene is produced and sodium toluenate is re-formed. This process goes through the barrier of ca. 19 kcal/mol. The sodium butylobenzenate molecule can also collide with the NaH molecule and find the track at Path B where the Na/H exchange occurs with reformation of the Na<sub>2</sub> molecule.

Finally, let us notice that once the sodium toluenate is in complex with propene the highest barrier to yield a butylbenzene isomer is only ca. 26 kcal/mol.

### 3.2. Path B: the reaction between PhCH<sub>2</sub>Na...NaH and CH<sub>2</sub>=CHCH<sub>3</sub> towards PhC<sub>4</sub>H<sub>9</sub>

#### 3.2.1. Insertion of CH<sub>2</sub>=CHCH<sub>3</sub> into the C–Na bond

The alternative process to that described in Path A is reaction of the propene molecule with the PhCH<sub>2</sub>Na...NaH complex (R<sub>B</sub>), i.e., without assuming that the NaH molecule is dissociated out (Scheme 1). The product of such a reaction is again a complex of a sodium butylobenzenate molecule with the NaH molecule:



**Fig. 6.** The B3LYP/6-311++G\*\* optimized geometries of reactants, TSs, and products in the following reactions:  
 (VIIa) PhCH<sub>2</sub>Na...NaH + C<sub>3</sub>H<sub>6</sub> → PhCH<sub>2</sub>CH<sub>2</sub>CHNaCH<sub>3</sub>...NaH; (R<sub>B</sub> + P<sub>1</sub> → TS7a → 7a)  
 (VIIb) PhCH<sub>2</sub>Na...NaH + C<sub>3</sub>H<sub>6</sub> → PhCH<sub>2</sub>CH(CH<sub>3</sub>)(CH<sub>2</sub>Na)...NaH; (R<sub>B</sub> + P<sub>2</sub> → TS7b → 7b)  
 (VIIc) PhCH<sub>2</sub>Na...NaH + C<sub>3</sub>H<sub>6</sub> → PhCH<sub>2</sub>CNa(CH<sub>3</sub>)<sub>2</sub>...NaH; (R<sub>B</sub> + P<sub>2</sub> → 7c)  
 (VIIIa) PhCH<sub>2</sub>CH<sub>2</sub>CHNaCH<sub>3</sub>...NaH → PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>...Na<sub>2</sub>; (7a → TS8a → 8a)  
 (VIIIb) PhCH<sub>2</sub>CH(CH<sub>3</sub>)(CH<sub>2</sub>Na)...NaH → PhCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>...Na<sub>2</sub>; (7b → TS8b → 8b)



**Table 4**  
The B3LYP/6-311++G\*\* Gibbs free energies  $G_{298}$  (hartree) and the Gibbs free energies referred to the reactants in the single process ( $\Delta G'_{298}$ ) and in whole process ( $\Delta G_{298}$ ) (kcal/mol) at Path B for the reactions presented in Scheme 1

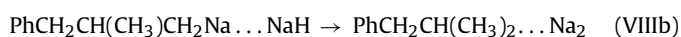
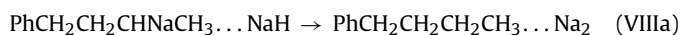
System	$G_{298}$	$\Delta G_{298}$	System	$G_{298}$	$\Delta G_{298}$
<b>I</b>					
Reactants			[T + Na <sub>2</sub> + P + T]	–985.599680	0.0
R <sub>0</sub>	–596.157991	0.0	R <sub>0</sub> + [P + T]	–985.592354	4.6
TS1	–596.100311	36.2	TS1 + [P + T]	–985.534674	40.8
1	–596.155203	1.7	1 + [P + T]	–985.589566	6.3
<b>VIIa</b>					
[R <sub>B</sub> , P <sub>1</sub> ]	–714.039444	0.0	[R <sub>B</sub> , P <sub>1</sub> ] + T	–985.582436	10.8
TS-7a	–713.978654	38.1	TS-7a + T	–985.521646	49.0
7a	–714.012749	16.8	7a + T	–985.555741	27.6
<b>VIIb</b>					
[R <sub>B</sub> , P <sub>2</sub> ]	–714.039750	0.0	[R <sub>B</sub> , P <sub>2</sub> ] + T	–985.582742	10.6
TS7b	–713.985734	33.9	TS7b + T	–985.528726	44.5
7b	–714.020326	12.2	7b + T	–985.563318	22.8
<b>VIIIa</b>					
7a	–714.012749	0.0	7a + T	–985.555741	27.6
TS8a	–713.960015	33.1	TS8a + T	–985.503007	60.7
8a	–714.048330	–22.3	8a + T	–985.591322	5.2
<b>VIIIb</b>					
7b	–714.020326	0.0	7b + T	–985.563318	22.8
TS8b	–713.964207	35.2	TS8b + T	–985.507199	58.0
8b	–714.050067	–18.7	8b + T	–985.593059	4.2
<b>IX</b>					
nBB	–389.43435		nBB + [T + Na <sub>2</sub> ]	–985.599665	0.0
iBB	–389.43537		iBB + [T + Na <sub>2</sub> ]	–985.600682	–0.6
P (propene)	–117.891371				
T (toluene)	–271.542992				
PhCH <sub>2</sub> Na	–433.230733				
Na <sub>2</sub>	–324.622325				
NaH	–162.876155				

In such a reaction the C–Na and C=C are broken and the new C–Na the C–C bonds are formed. As a result either straight or branched side chain is constituted. As before, three products are possible: the NaH complex with (3-sodium-butyl)-benzene (7a), (3-sodium-2-methyl-propyl) benzene (7b), and (2-sodium-2-methyl-propyl) benzene (7c) (Fig. 6). The barriers towards (7a) and (7b) are equal to ca. 38 and 34 kcal/mol, respectively (Table 4). In our modeling, the third barrier towards (7c) was over 50 kcal/mol, however, we did not succeed with optimization of an appropriate TS structure. Formation of the PhCH<sub>2</sub>CNa(CH<sub>3</sub>)<sub>2</sub>...NaH (7c) complex required a dimethyl carbocation to be composed from propene and this was an energy consuming reaction. Therefore, in further study we focused on more competitive reactions of (7a) and (7b). In the two constituted complexes (7a) and (7b) the NaH molecule is stabilized by a  $\pi$ -electron intramolecular interaction between the Na atom of the side chain and  $\pi$ -electrons of the benzene ring. The so arranged structures adopt a “scorpio like” conformations (Fig. 6). However, the barrier at Path B is greater than the appropriate one at Path A in the absolute energy scale the TSs at Path B are below those at Path A by ca. 12–16 kcal/mol (Fig. 5, Table 4). Finally, let us stress that as before the reaction towards branched product (7b) (leading further to isobutylbenzene) is favored by both thermodynamics and kinetics (Table 2).

### 3.2.2. Na/H exchange

At Path B, the Na/H exchange occurs, as an intramolecular process, between an appropriate sodium butylenate isomer and the associated NaH molecule. In this very case, the NaH molecule approximates the H atom bound to a metal surface. The exchange can be expressed in the following chemical

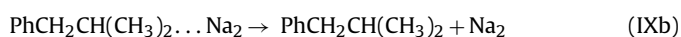
equations:



Thus, as a result of the return of the H atom from NaH molecule to the alkyl chain the proper product is formed and the Na<sub>2</sub> catalyst is re-constructed. The two molecules remain in a complex in which one of the Na atoms of the Na<sub>2</sub> molecule is approaching the  $\pi$ -electrons of the benzene ring. The barriers towards PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>...Na<sub>2</sub> (8a) and PhCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>...Na<sub>2</sub> (8b) are ca. 35 and 33 kcal/mol, respectively. Remark that, again, the barrier towards branched chain iso-butylbenzene (8b) is slightly smaller (Table 4). This is in good agreement with experimental findings [29] Moreover, the Gibbs free energy difference between products and reactants is slightly favoring the branched product as well: 22 and 19 kcal/mol for (8a) and (8b), respectively.

### 3.2.3. Dissociation of the complex

Isolation of the product, as well as return of the Na<sub>2</sub> molecule as the reactant/catalyst to the initial reaction, requires the PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>...Na<sub>2</sub> (8a) and PhCH<sub>2</sub>CH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>...Na<sub>2</sub> (8b) complexes to be dissociated.



As before, at 298.15 K the entropy term TS is large and the dissociation processes are endoergic in terms of  $\Delta G$ : a matter of ca. 7 and 5 kcal/mol for dissociation of (8a) and (8b), respectively (Table 4). However, when the reaction energetics is expressed in terms of

total energy or ZPE corrected energies, the two dissociations are exoergic and ca. 1–2 kcal/mol should be released from the system.

### 3.2.4. Summary of the energy changes at Path B

At Path B, we assume that the sodium toluenate ( $\text{PhCH}_2\text{Na}$ ) and  $\text{NaH}$  molecules, formed in the reaction between toluene and the  $\text{Na}_2$  molecule, remains in the complex which reacts further with propene. After insertion of propene into the C–Na bond, the H atom returns from the  $\text{NaH}$  molecule, and as a result of dissociation of the butylbenzene isomer complex with the  $\text{Na}_2$  molecule, the isolated butylbenzene is obtained and the  $\text{Na}_2$  catalyst can return to the initial step. As for Path A, the formation of the isobutylbenzene is slightly more favored than formation of *n*-butylbenzene both thermodynamically and kinetically. The barriers in the elementary stages are relatively high: 34–38 kcal/mol and 33–35 kcal/mol for the propene insertion and the Na/H exchange, respectively. However, at this path the every stationary point at the energy profile is always below the appropriate energy at Path A (Fig. 5). The highest TS energy at Path B connected with the Na/H exchange between sodium benzene butylenate, if referred to the energy of reactants, is equal to ca. 61 kcal/mol.

### 3.3. Comparison of energy profiles at Path A and B

The energy profiles for the two Paths are presented in Fig. 5. For the two Paths formation of the TS1, leading to sodium toluenate, is common. Then, at Path A there are two possibilities: either use the energy excess and go directly to the ( $R_A$ ) state, in which the  $\text{NaH}$  molecule is dissociated and propene is present, or go to (1), i.e., the same way as in Path B leading to the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex, and then dissociate the complex. Nevertheless, after the point (1) is reached, the energy profile at Path A is above the profile of Path B until completely separated products are obtained (Fig. 5). This indicates that Path A is thermodynamically disfavored, however, this is not the full truth.

Let us repeat our interpretation of the two Paths. Path A, where at the initial step the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex dissociates, models situation in the bulk gas phase. At this path  $\text{PhCH}_2\text{Na}$  plays the catalyst role: it is constituted after TS1 is formed and it is re-formed when the (5a) or (5b) are dissociated. Then, sodium toluenate returns to the catalytic cycle performed at Path A. The barriers at such a cycle, referred to ( $R_A$ ), do not exceed 30 kcal/mol, and the butylbenzenes are formed with a slight energy release (Fig. 5). When one of the reactants, propene or toluene, is exhausted, then  $\text{PhCH}_2\text{Na}$  exchanges the Na atom for the H atom in combustion with the  $\text{NaH}$  molecule yielding toluene and  $\text{Na}_2$ .

On the contrary, Path B, for which the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex is not dissociated, models situation at the surface metal catalyst. The metal catalyst is here simplified to the  $\text{Na}_2$  molecule. Structure of the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex (1) can be interpreted as molecule  $\text{PhCH}_2\text{Na}$  attached to the surface at which the H atoms are settled, too. Then, Path B goes through barriers which are quite high, the largest, referred to ( $R_B$ ) where propene is present, is ca. 50 kcal/mol. Moreover, each barrier at Path B is higher than the analogous barrier at Path A. Thus, kinetically, Path A is not favored. At Path B, the  $\text{Na}_2$  molecule plays the catalyst role. The  $\text{Na}_2$  catalyst appear at the very beginning, the ( $R_0$ ) point, and is re-formed after (8a) or (8b) is dissociated. Then, it returns to the first step to participate again in the next catalytic cycle.

In our opinion the two Paths are possible as they proceed in different regions: Path A occurs in the bulk gas phase and Path B occurs at the surface. In this point it is very important the ratio of the number of molecules that are present in the bulk gas phase and at the surface. Usually, the ratio is high, i.e., number of molecules in the bulk gas phase is much greater than the number of those at the

surface. Therefore, we think that the mechanism described by Path A is describing majority of processes running in the gas phase in the reactors. In the Path A, where sodium toluenate plays a catalyst role (i.e., is desorbing and then is participating in multiple turnovers in the gas phase) is practically the same as that described by Pines et al. fifty years ago. However, Path B, where  $\text{Na}_2$  plays a catalyst role, represents situations when the molecules in the bulk are deactivated at the metal catalyst surface and can further proceed according to this very scheme.

## 4. Conclusions

In this paper we present a computational study on the toluene side chain alkylation by propene over a basic catalyst. In the modeling, the basic catalyst is represented by the  $\text{Na}_2$  molecule. The process starts by formation of the sodium toluenate molecule ( $\text{PhCH}_2\text{Na}$ ) in complex with the  $\text{NaH}$  molecule. The complex is formed in the reaction of toluene with the  $\text{Na}_2$  molecule. Then, the two reaction Paths are considered: Path A at which the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex is dissociated, and Path B at which the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex is not dissociated. The following reaction steps are considered at the two paths: insertion of the propene double bond into the C–Na bond of sodium toluenate and the Na/H exchange leading to one of the isomers of butylbenzene. At Path A, the  $\text{PhCH}_2\text{Na}$  molecule is re-formed in the last stage and can return to the propene insertion step. Thus, for Path A, the  $\text{PhCH}_2\text{Na}$  molecule plays role of a catalyst. At Path B, the  $\text{Na}_2$  molecule is re-constructed in the last stage and can return to the beginning formation of the  $\text{PhCH}_2\text{Na}$  molecule. At the two paths isobutylbenzene is favored over *n*-butylbenzene by both thermodynamic and kinetic factor. This is in good agreement with experimental findings [29]. The energy levels at Path A are always above those of Path B, whereas energy barriers at the essential steps of Path A are always significantly lower than the appropriate ones at Path B. Thus Path A seems to be preferred kinetically while Path B thermodynamically. However, our interpretation goes further. If we accept that the  $\text{Na}_2$  molecule represents the metal surface, then Path A at which the  $\text{PhCH}_2\text{Na}$  molecule is dissociated out from the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex, can be understand as dissociation of the sodium toluenate molecule from surface to the bulk gas phase. On the contrary, the  $\text{PhCH}_2\text{Na} \dots \text{NaH}$  complex undissociated throughout the entire Path B can be interpreted as remaining of the  $\text{PhCH}_2\text{Na}$  molecule and its products at the metallic surface rich in hydrogen (represented by the  $\text{NaH}$  molecules). Then, Path A describes the reaction in the bulk gas phase whereas Path B describes the reaction at the metal surface. If one assume that the number of molecules is greater in the bulk than in the surface then 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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