The study of rearrangement of 3-phenyl-1-propyl radical by ab initio method

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Introduction

The emission of aromatics via commercial fuels is due to their intrinsic toxicity, also, the formation of the other toxics from aromatics oxidation in troposphere [1]. n-propylbenzene is an aromatic component that can be found in some commercial fuels like Gasoline, diesel fuel and kerosene [2]. The oxidation of n-propylbenzene produce some radical component that can make corrosion in cylinders, have toxicity and so dangerous effects in nature with emission in troposphere and stratosphere and ozone layer and also creating changes in some component of organic systems. One of them is 3-phenyl-1-propyl radical (Fig.1) [2]. In a consideration to its structure, a rearrangement is possible for stabilizing of radical. And these stabilized radicals damage cylinders and also this created radical is more stable and it can be more harmful than primary radical in nature. This rearrangement produces benzyl radical and ethylene (Fig. 2) [2]. So in this article, we investigated this rearrangement in calculation aspect. We used Gaussian 98 [3] software to calculate some properties of this rearrangement such as OH, OS and also bound-lengths and angles in reactant and products. In this calculation, we use B3LYP level of theory with the 6-311++G** basis set for optimized geometry.

In addition we suggest a transition state for this rearrangement (Fig. 3). We reported its properties such as OH, OS and bound-lengths, angles. In this calculation, we use QST2 and QST3 methods with 6-311++G** basis set.

Keywords: 3-phenyl-1-propyl radical; radical rearrangement; ab initio methods; Gaussian 98.

Computational method

DFT calculations were carried out using the Gaussian 98 suite of programs [3].
Optimization of geometries were performed using the density functional theory (DFT) calculations with B3LYP level and the standard basis set of 6-311++G**. To evaluate the optimized structures for the molecules, frequency calculations were carried out using analytical second derivative.

The EFG and chemical shielding tensors of Reactant, transition state and products were calculated at level of DFT method including B3LYP with the 6-311++G** basis set for optimized geometry.

Results and discussion

It was found that the structure of transition state is planar. In the other word, dihedral angle is 180° (C14-C13-C12-C6 in Fig. 2), in the results, benzyl group left easily transition state molecule. We determined NQR parameters for reactant, transition state and products. The results show that Nuclear Quadrupole Coupling Constant (NQCC) and asymmetric parameter have changed in molecule reactivity sites. These changes confirmed the formed transition state. Table.1 shows the obtained thermodynamical data for the formation of 3-phenyl-1-propyl radical and benzyl radical by ab initio method. These results were compared experimental data [2]. The agreement of theoretical and experimental data shows that the calculated thermodynamical data for transition state is correct. Therefore, we determined thermodynamic properties for the suggested transition state. Also, we investigated the mechanism of the change of 3-phenyl-1-propyl radical to 1-phenyl-3-propyl radical via benzyl shift.

![Figure 1. The optimized structure of 3-phenyl-1-propyl radical, B3LYP/6-311++G**](image)
Table 1. Thermodynamical data for species involved in the rearrangement of 3-phenyl-1-propyl radical, $\Delta H^\circ_j$ in kcal mol$^{-1}$ and $S^\circ_j$ in cal mol$^{-1}$K$^{-1}$ and $C_p$ in cal mol$^{-1}$K$^{-1}$. The data obtained in 298K.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H^\circ_j$</th>
<th>$S^\circ_j$</th>
<th>$C_p$</th>
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</thead>
<tbody>
<tr>
<td>C6H5CH2</td>
<td>49.85(50.31)$^a$</td>
<td>77.21(76.75)</td>
<td>25.38(26.23)</td>
</tr>
<tr>
<td>C6H5C3H6</td>
<td>49.74(50.09)</td>
<td>97.31(96.33)</td>
<td>35.11(36.21)</td>
</tr>
<tr>
<td>C6H5C3H6 (TS)</td>
<td>55.46</td>
<td>101.22</td>
<td>38.89</td>
</tr>
</tbody>
</table>

$^a$ Results in parentheses obtained by Experiment [2].
References
