

Reaction of cyclopentadienyl and methyl radicals

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Abstract. Geometries and potential energies of reagents, products, and intermediate states for the reaction between cyclopentadienyl (C₅H₅) and methyl (CH₃) radicals are found by means of ab initio quantum mechanical methods CCSD(T)/cc-pVTZ-f12, B2PLYPD3/AUG-CC-PVDZ and B3LYP/6-311G. Basing on the analysis of the found energy, structural and kinetic characteristics of the compounds involved, the reaction paths leading to the formation of fulvene and benzene, the simplest aromatic compound, are determined. The reaction path begins from the formation of the intermediate compound, methylcyclopentadiene, followed by tearing-off a hydrogen atom from it: C₅H₅ + CH₃ → C₅H₅CH₃ → C₅H₄CH₃ + H. The subsequent monomolecular transformations of C₅H₄CH₃ are closed by the formation of either fulvene (via the loss of one hydrogen atom from the methyl group) or benzene (via the stages of transforming the pentamorous ring into a hexamorous one and tearing-off a hydrogen atom). The rate constants found in the paper using the software package MESS show that the rate of benzene formation is always higher than that for fulvene within the temperature interval 500-2250 K. Since fulvene can also isomerize into benzene, the reaction C₅H₅ + CH₃ is an important supplier of the initial bricks for building polycyclic aromatic hydrocarbons dangerous for living systems. © 2017 Journal of Biomedical Photonics & Engineering.

Keywords: Combustion, methyl, cyclopentadienyl, benzene, fulvene, PANs, quantum chemistry calculations, reaction pathways, rate constant.

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1 Introduction

Polycyclic aromatic hydrocarbons (PAH) comprise a considerable part of harmful emission from different fossil fuel power plants and serve as predecessors in soot formation [1-3]. They hugely affect the environment and human health. Appeared in the air and soil, they can be inhaled by humans or consumed with food, which leads to various health problems. PAH are very toxic by their nature, their prolonged effect is related to such diseases as skin allergy, immune deficit, asthma and other lung diseases, destruction of red blood cells, tumours, preterm birth, diseases of kidneys and liver, and valvular defect in neonates.

Methyl and cyclopentadienyl are among the key radicals in the PAH and soot formation. The methyl radical can be formed by partitioning of complex hydrocarbons or by their interaction with oxygen, while the cyclopentadienyl is turned out in the reactions of benzene and phenyl with atomic oxygen [6], in the pyrolysis of phenoxy radical [3-6], phenol [6], cyclopentadiene [7], etc. The reaction $\text{CH}_3 + \text{C}_5\text{H}_5$ is interesting because it yields the first aromatic compound, benzene, that is an initial brick in building more complex compounds, such as PAH, soot, carbon nanoparticles, fullerene, etc. There are strict standards on emission of these compounds for different power plants using hydrocarbon fuels [8]. At present, the search for hydrocarbon fuel burning regimes, in which the formation of aromatic compounds is suppressed basing on the detailed analysis or the processes that occur in the burning zone is carried out [9]. The reaction

between methyl radical and cyclopentadienyl occupies an important position among the kinetic reaction schemes of the formation of aromatic compounds.

The reaction of CH_3 with C_5H_5 was studied in theoretical papers [10-13]. Refs. [10, 11] show that the final products of this reaction are fulvene and benzene. Melius et al. [12] theoretically studied the isomerisation of fulvene using the method BAC-MP4. Jasper et al. [13] reported a detailed consideration of the fulvene-to-benzene isomerisation process catalysed by atomic hydrogen. However, in these papers, not all ways leading to the formation of benzene were considered, and no rate constants of elementary processes, depending on temperature and pressure, were presented.

In this paper, we present the geometries of the initial and final products involved in the reaction as well as of the intermediate and transition compounds, calculated by means of the density functional theory (DFT), B2PLYPD3 and B3LYP methods. For all found structures, the energy values are corrected using ab initio quantum chemistry calculations. Basing on the obtained data, we determine the optimal reaction paths for the system $\text{C}_5\text{H}_5 + \text{CH}_3$, leading to the formation of benzene and fulvene. Using the corrected energies and optimised geometries, we calculated the rate constants for a number of basin monomolecular reactions in the multistep process of interaction between the two radicals at the temperatures 500-2500K.

2 Methodology

We used ab initio quantum mechanical methods of high level to study the possible products of the reaction $\text{CH}_3 + \text{C}_5\text{H}_5$. The optimised structures and energies of the reagents, products, intermediate and transient states involved in the reaction were found at the first stage using the widespread hybrid method of density functional theory B3LYP with the basis set 6-311G**. Using the same method, we calculated the vibrational frequencies and zero-point energies (ZPE) for all the structures.

At the second stage the energies, the optimised geometries and vibrational frequencies for all structures were found using more up-to-date density functional method B2PLYPD3 with the basis set AUG-CC-PVDZ in order to compare the two methods applied to the system $\text{CH}_3 + \text{C}_5\text{H}_5$.

At the last stage the total energies of the involved structures were corrected using the method of couple clusters with the single and double excitations taken into account (CCSD(T)) with the basis set cc-pVTZ-f12. The used method allows the energy calculations with the accuracy to 1-3 kcal/mole. The B3LYP and B2PLYPD3 calculations were carried out using the Gaussian software packages [14-16], while the CCSD(T) calculations were performed using the Molpro software package [17].

Basing on the corrected total energies and geometry of reagents, products, intermediate and transient states, we calculated the rate constants at different pressures and temperatures, using the software package MESS, based on the Rice-Ramsperger-Kassel-Marcus statistical theory [18].

3 Results and discussion

Figure 1 presents the reaction paths of interaction between the CH_3 and C_5H_5 radicals. The energies of the transient states TS_i , the intermediate states and the products, calculated using three methods, are presented relative to the total energy of the initial reagents in the kcal/mole units. As a result of the interaction at the first stage the methylcyclopentadiene $\text{C}_5\text{H}_5\text{CH}_3$ molecule is formed. Further transformations are related to the possible transition to the initial products or with the hydrogen atom tearing-off and the formation of $\text{C}_5\text{H}_4\text{CH}_3$ or $\text{C}_5\text{H}_5\text{CH}_2$ molecules. In Ref. [10] it was shown that the first path is less energy-consuming, therefore, below we will consider the path with the formation of the molecule $\text{C}_5\text{H}_4\text{CH}_3$ (1). Then the path via the transient state (barrier) TS_6 with the decay into fulvene $\text{C}_5\text{H}_4\text{CH}_2$ (2) and the hydrogen atom. An alternative path from the structure $\text{C}_5\text{H}_4\text{CH}_3$ is related to regrouping the atoms into the molecule $\text{C}_5\text{H}_5\text{CH}_2$ (3) with the activation barrier TS_5 of 54.1 kcal/mole. In further transformations either the structure $\text{C}_5\text{H}_5\text{CH}_2$ yields a fulvene molecule and a hydrogen atom with the transient barrier TS_1 of 61.1 kcal/mole, or the expansion

of the ring begins leading to the formation of the $\text{C}_5\text{H}_5\text{CH}_2\text{RE}$ (4) structure with the transient barrier TS_2 of 37.9 kcal/mole. After passing the barrier TS_3 of 40.99 kcal/mole the bond between carbon atoms is broken and the cyclohexadienyl structure $\text{C}_6\text{H}_6\text{H}$ (5) is formed. Finally, the hydrogen atom tearing-off leads to the formation of the benzene ring C_6H_6 (6) after passing the barrier TS_4 (31.1 kcal/mole). The relative energy of the final state of this chain in the form of fulvene amounts to 56.1 kcal/mole, while in Ref. [10] it was equal to 54.2 kcal/mole. The ab initio method chosen here, providing higher precision as compared with G2M (rcc, MP2) used in Ref. [10], allowed higher accuracy of relative energies of the structures, involved in the reaction (Table 1).

Table 1 Relative corrected energies of reagents, transient states, and reaction products obtained using the method CCSD(T)/cc-pVTZ-f12.

Molecule	Relative energy, kcal/mole
$\text{CH}_3 + \text{C}_5\text{H}_5$	0.0
$\text{C}_5\text{H}_5\text{CH}_3$	-70.4
$\text{C}_5\text{H}_4\text{CH}_3$ (1)	1.4
TS_5	54.1
$\text{C}_5\text{H}_5\text{CH}_2$ (3)	29.6
TS_1	61.1
TS_2	37.9
$\text{C}_5\text{H}_5\text{CH}_2$ RE (4)	31.5
$\text{C}_5\text{H}_4\text{CH}_2$ (2)	56.1
TS_3	41.0
$\text{C}_6\text{H}_6\text{H}$ (5)	4.3
TS_4	31.1
C_6H_6 (6)	24.7

Table 2 Rate constants for the reactions $\text{C}_5\text{H}_4\text{CH}_3 \rightarrow \text{C}_5\text{H}_4\text{CH}_2$, $\text{C}_5\text{H}_4\text{CH}_3 \rightarrow \text{C}_6\text{H}_6$ under the pressure of 1 atm.

T (K)	k (s ⁻¹)	
	$\text{C}_5\text{H}_4\text{CH}_3 \rightarrow \text{C}_5\text{H}_4\text{CH}_2$	$\text{C}_5\text{H}_4\text{CH}_3 \rightarrow \text{C}_6\text{H}_6$
500	6.01×10^{-13}	3.10×10^{-11}
600	9.51×10^{-9}	2.64×10^{-7}
700	9.73×10^{-6}	1.64×10^{-4}
800	1.79×10^{-3}	1.97×10^{-2}
900	0.11	0.87
1000	2.76	16.76
1125	72.74	318.91
1250	981.79	3.29×10^3
1375	7.94×10^3	2.11×10^4
1500	4.26×10^4	9.36×10^4
1650	2.07×10^5	3.76×10^5
1800	6.93×10^5	1.08×10^6
2000	2.29×10^6	3.02×10^6
2250	6.62×10^6	7.39×10^6

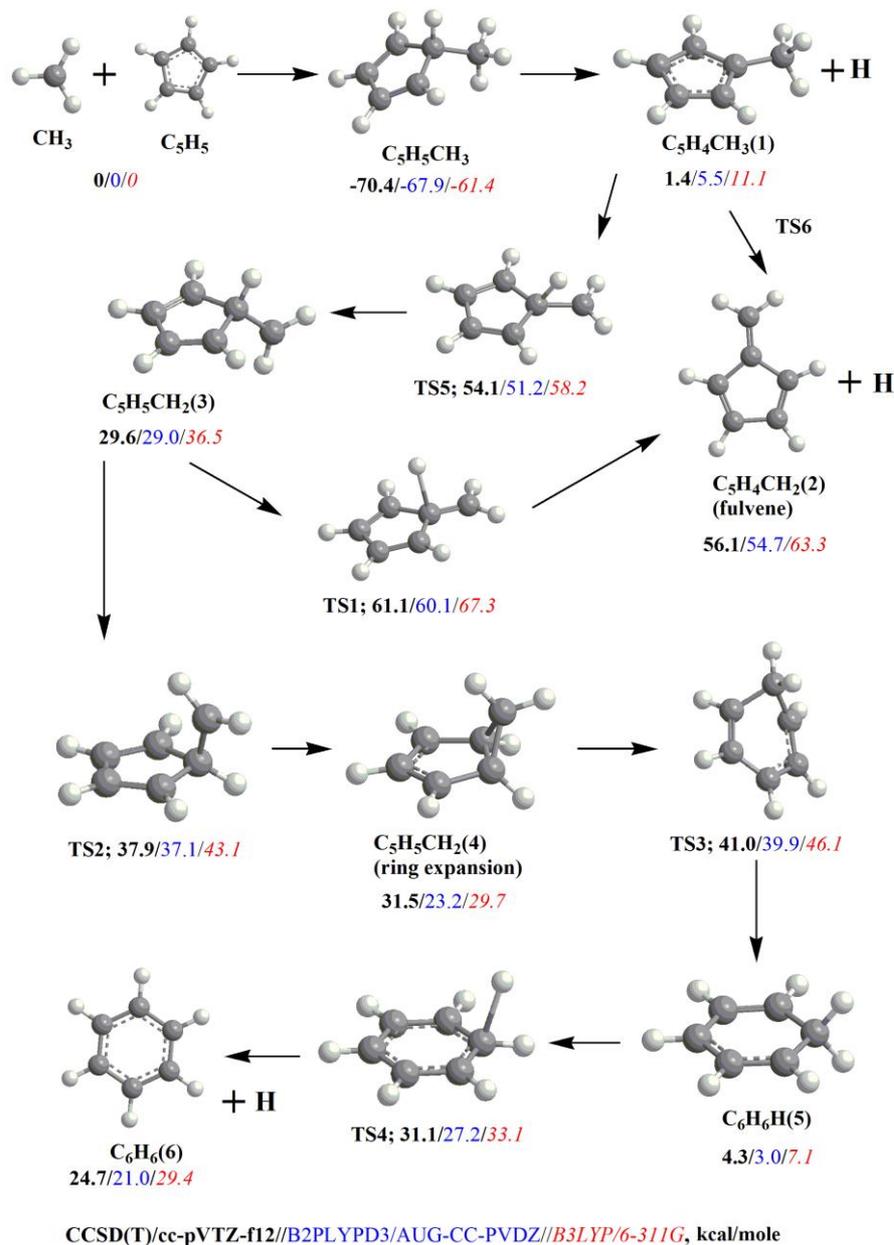


Fig. 1 Reaction paths, structures and relative energies for the reaction of interaction between methyl and cyclopentadienyl radicals. The figures below each structure indicate the relative energy, calculated using the methods CCSD(T) with the basis set cc-pVTZ-f12 (boldface type), B2PLYPD3 with the basis set AUG-CC-PVDZ (normal type, blue colour), B3LYP with the basis set 6-311G** (italic type, red colour), respectively.

Table 2 presents the rate constants for the sequence of monomolecular transformations from $\text{C}_5\text{H}_4\text{CH}_3$ to $\text{C}_5\text{H}_4\text{CH}_2$ and from $\text{C}_5\text{H}_4\text{CH}_3$ to C_6H_6 under the pressure of 1 atm., calculated using the software package MESS [16] that provides kinetic accuracy. From the obtained values, one can see that under the increase of temperature the rates of formation of fulvene and benzene molecules grow exponentially. Under the pressure of 1 atm. the rate of benzene formation exceeds that of the fulvene at all temperatures, considered in the present work. At the temperatures below 1000 K the rate of monomolecular transformations in the chain $\text{C}_5\text{H}_4\text{CH}_3 \rightarrow \text{C}_6\text{H}_6$ is higher by more than an order of magnitude, while in the temperature interval 1000-2250

K the rate constants for both reaction paths have the same order of magnitude.

4 Conclusion

As a result of the present work, the $\text{CH}_3 + \text{C}_5\text{H}_5$ reaction paths are found, the energies of the compounds are determined with higher accuracy, the general picture of fulvene and benzene formation is considered, and the rate constants for the reactions $\text{C}_5\text{H}_4\text{CH}_3 \rightarrow \text{C}_5\text{H}_4\text{CH}_2$, $\text{C}_5\text{H}_4\text{CH}_3 \rightarrow \text{C}_6\text{H}_6$ at different temperatures and the pressure of 1 atm. are calculated for the first time. Basing on the analysis of the obtained energy and kinetic characteristics, three reaction paths were

revealed, two of them leading to the formation of fulvene and one to the formation of benzene. The rate of benzene formation is always higher than that of fulvene over the entire temperature range implemented in combustion chambers. Fulvene is known to be capable of further isomerisation into benzene [13], which makes the reaction $\text{CH}_3 + \text{C}_5\text{H}_5$ a potential source of PAH in combustion chambers of different power plants using hydrocarbon fuel.

The balance between the accuracy and the available computation facilities is commonly achieved by using two-level calculations, where the geometry of reagents, transient and intermediate states are found using the DFT and their energies in optimised geometries are calculated using the CCSD(T) method. The DFT method B3LYP is most frequently used to find the

structural parameters of the compounds at the first level. However, the DFT methods developed in recent years allow the calculation of geometry and vibrational frequencies with the similar or somewhat better accuracy than B3LYP, in particular, the method B2PLYPD3 that allows for the dispersion corrections and, therefore, describes distant interactions better than B3LYP. As follows from our data, presented in Fig. 1, the values of energies calculated using B2PLYPD3 are in much better agreement with those calculated using the ab initio method than the results of B3LYP. Thus, our data show that the DFT method B2PLYPD3 has successfully passed the test in application to the particular system $\text{CH}_3 + \text{C}_5\text{H}_5$.

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