

DFT Study of Mechanism and Kinetics of Hydrogenolysis of Toluene

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Received Date: October 11, 2014 Accepted Date: November 13, 2014 Published Date: November 17, 2014

Citation: Luke Achenie, et al. (2014) DFT Study of Mechanism and Kinetics of Hydrogenolysis of Toluene. J Chem Proc Eng 1: 1-5.

Abstract

Interest in carbon nanotubes is mostly stimulated by their unique physical and chemical properties. One of the major steps in Chemical Vapor Deposition (CVD) of carbon nanotubes is pyrolysis of hydrocarbons at high temperature; in this reaction hydrogenolysis of toluene is important. The quality and yield of carbon nanotubes are the predominant considerations, thus the design and optimization of CVD reactors is necessary. Optimizing the reactor demands a good understanding and modeling of the chemical and physical phenomena inside the reactor. In this paper we propose the use of an ab initio method, namely DFT to study gas phase pyrolysis of xylene and toluene at high temperatures in a CVD reactor. The structure of gaseous species are optimized using the B3LYP/6-311(d,p) level of theory. Berny optimization is used to locate transition states structures. Our results compare very well with experimental data from the open literature.

Keywords: Carbon nanotube; Hydrogenolysis of toluene; Heat of reaction; CVD; DFT

Introduction

The past and current decades have seen high interest in carbon nanotubes due to the fact that they have unique physical and chemical properties. One of the major steps in chemical vapor deposition (CVD) of carbon nanotubes is pyrolysis of hydrocarbons at high temperature; in this reaction hydrogenolysis of toluene is important. The quality and yield of carbon nanotubes are the predominant considerations, thus the design and optimization of CVD reactors is critical. We posit that this demands a good understanding and modeling of the chemical and physical phenomena inside the reactor. Hydrogenolysis is a clean substitution process in which hydrogen reacts with a hydrocarbon to produce methane from the hydrocarbon in contrast to pyrolysis where no initial hydrogen is present. Benson and Shaw [1] proposed a mechanism for the hydrogenolysis of toluene whose overall kinetics is given as follows.



The authors described the hydrogenolysis as a three-step process, namely, decomposition of hydrogen molecule, reaction of hydrogen atom with the hydrocarbon to release a methyl radical, and reaction of methyl radical with the hydrocarbon to produce methane. Even though their model is in good agreement with experimental data for their desired temperature range (for the xylene and toluene system), it was based

on the assumption that the methyl radical addition reaction has the same barrier as hydrogen radical addition. Other researchers have performed more extensive studies that suggest different mechanisms for pyrolysis of toluene [2-7]. Most of the experimental work on toluene pyrolysis has been limited to specific operating conditions. Here there are uncertainties in the reported activation energies and subsequently the reaction mechanisms. Even though at high temperature the role of displacement and abstraction is important (taking into account the existence of relatively inert phenyl radical and highly reactive methyl radical), most researchers have relied predominantly on addition-type reaction mechanisms. These assumptions introduce errors, which may result in inconsistency of the reaction mechanism for specific operating conditions Kuwana et al. [8].

This ambiguousness in the reported activation barriers and lack of adequate reaction mechanism for the reactions involved in hydrogenolysis of toluene inspired the present work to estimate these reaction rates using Density Functional Theory [9]. DFT is a powerful tool for the theoretical investigation of reaction mechanisms with high accuracy in energy calculations. In the next section we briefly describe the computational method, followed by results, discussion, and summary.

Methods

The Beck [10] three-parameter and Lee Yang Par functional (B3LYP) [11] were used in our DFT calculations. These calculations involve geometry optimization, energy estimation, transition state search, and verification. A good trade-off be-

| Reaction | 6-311+g(d,p) | Gaussian G1 | Gaussian G2 | Gaussian G2MP2 | Experimental |
|---|--------------|-------------|-------------|----------------|--------------|
| $C_7H_8 + H_2 \xrightarrow{k_2} C_6H_6 + CH_4$ | -12.33 | -9.13 | -9.55 | -9.31 | -10.04 |
| $C_7H_8 + H \longrightarrow C_7H_7(MP) + H_2$ | 8.64 | 14.39 | 13.49 | 13.99 | 11.82 |
| $C_7H_8 + H \longrightarrow C_7H_7(Bz) + H_2$ | -12.14 | -10.27 | -10.80 | -10.26 | -10.04 |
| $C_7H_8 + CH_3 \longrightarrow C_7H_7(MP) + CH_4$ | 8.77 | 10.48 | 11.02 | 10.73 | 10.56 |
| $C_7H_8 + CH_3 \longrightarrow C_7H_7(Bz) + CH_4$ | -16.02 | -12.73 | -12.79 | -12.22 | -14.83 |

Table 1: Heat of reaction for various reactions involved in the hydrogenolysis of toluene. This is a comparison between theoretical and experimental values.

tween accuracy and computational cost was initially obtained by utilizing the structures optimized based on a medium size basis set instead of a larger basis set such as . Next we employed the approximate structures and the larger basis set to obtain improved structures. In several of our runs the improvement was not significant.

The geometry optimization was based on the Berny algorithm [12]; we considered only the minimum energy structures in the present work. The stability test and frequency calculation were performed and structures with no imaginary frequency were considered stable. The transition state search was performed using the transient guided Quasi Newton method (STQN). The transition state structures were determined by frequency calculation followed by the Intrinsic Reaction Coordinate (IRC) [13] calculations on the structures with only one imaginary frequency. The structures with only one imaginary frequency that connected the desired reactant and products on the reaction path coordinate were considered as transition state structures [14]. Once the desired structures were obtained, the reaction rate constants were calculated using Transition State Theory (TST) [14-16].

Various energy calculation methods were used in order to estimate the heat of reaction; these were B3LYP/6-311+g(d,p), Gaussian G1, Gaussian G2, and Gaussian G2MP2. The summarized results in Table 1 indicate that the B3LYP/6-311+g(d,p) method is a good choice that produces comparable results to the experimental data obtained from the literature [17].

Results and Discussion

All DFT calculations were performed using the Gaussian 03 program [12]. Initially the DFT calculations were performed on the reaction between toluene and molecular hydrogen (Eqn. 1), then other possible reactions between hydrogen radical and methyl radical with toluene were investigated.

Direct reaction between toluene and hydrogen

For the direct reaction pathway we postulated that a hydrogen molecule reacted directly with toluene in order to produce benzene and methane (Eqn. 1). Table 2 shows the transition state structure for this reaction optimized at the level of theory.

The transition state structure is a complex created by a loose connection of phenyl, methyl, and hydrogen radicals. The trajectories of the transition state structure show that the reaction initiates when a hydrogen molecule approaches the bond in

toluene. The hydrogen molecule decomposes when it comes within a distance of 2\AA of the bond, and the reaction leads to final products by addition of hydrogen atom to phenyl and methyl radicals to form benzene and methane molecules. The directional vectors pictured in Table 2 show the direction of hydrogen atom movement during the formation of transition state structure. The trajectories also show a very small movement of hydrogen atoms in the methyl radical towards forming a methane molecule.

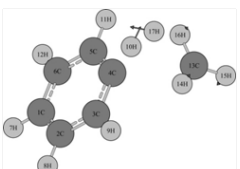
| Transition state structures | Bond length Angstrom () and angles (degree) | |
|--|--|---------------------------------------|
| Toluene + hydrogen  | $r_{4C-13C} = 2.465$ | $\angle_{3C-4C-5C} = 120.63^\circ$ |
| | $r_{4C-5C} = 1.391$ | $\angle_{4C-5C-6C} = 119.58^\circ$ |
| | $r_{5C-6C} = 1.396$ | $\angle_{6C-1C-2C} = 119.80^\circ$ |
| | $r_{6C-1C} = 1.394$ | $\angle_{1C-4C-13C} = 145.78^\circ$ |
| | $r_{4C-10H} = 1.34$ | $\angle_{16H-13C-15H} = 117.12^\circ$ |
| | $r_{13C-17H} = 2.05$ | |

Table 2: The B3LYP/6-311+g(d,p) optimized structures for the hydrogenolysis of toluene.

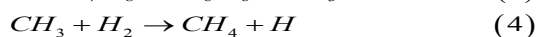
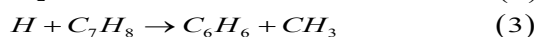
Within the transition state the bond extends to 2.46\AA and the methyl radical moves below the phenyl radical making an angle of 145.58° with and carbons in the phenyl radical. The atom in the phenyl radical shifts slightly towards the center of the ring; as a result the and bonds shrink to . In the transition state structure the hydrogen atom (10H) creates a loose bonding with the 4C carbon, which resembles a benzene molecule. Likewise the 17H atom loosely connects to the 13C carbon to resemble a methane molecule. The H-C-H angles in methyl radical of the transition state decrease to 117° degree that is 3° less than a planer methyl radical. This transition state structure has only one imaginary frequency (at -1400 Hz); an IRC calculation verified that this transition state connects toluene and hydrogen to benzene and methane. This reaction has activation energy of 118.3 kcal/mol with a pre-exponential coefficient of (calculated using frequencies obtained at $B3LYP-6311+g(d,p)$). The pre-exponent factor was calculated using partition functions of transition

state structure and reactants [18] as $A = \left(\frac{k_b T}{h} \right) \left(\frac{q_{TS}}{q_A q_B} \right) N_A$

. Here k_b is the Boltzmann constant, T is temperature, h is the Planck constant, q_{TS}, q_A, q_B are the partition functions for

transition state, reactant, and reactant, respectively. N_A is the Avogadro number. The partition function is the product of the translational, rotational, vibrational, and electronic partition functions.

The pre-exponential factor for this reaction has the same order of magnitude as that of the reaction between hydrogen radical and toluene. While the theoretical calculations confirm this transition state structure, the high activation barrier of 118.38 kcal/mol (calculated at) lead to competing radical mechanisms that involve reaction with lower activation barrier similar to the simple mechanism suggested by Benson and Shaw.



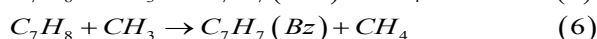
The suggested mechanism initiates by dissociation of hydrogen molecules into atomic hydrogen, and propagates by reaction of hydrogen radical and toluene, as well as reaction of methyl radical and hydrogen molecule to produce benzene and methyl radical, and methane and hydrogen radical, respectively.

Even though this mechanism seems reasonable and is consistent with a wide variety of experimental data, the simplifying assumption (the equal predilection of hydrogen radical for both methyl and benzene sites in toluene in the hydrogen addition step) provides a good reason for the development of other mechanisms, which considers various radical reactions. The more complicated mechanisms mostly obtained via experimental observations consider different hydrogen addition sites in toluene and the possibility of a variety of competing radical reactions in the system [6,7,19]. While most researchers agree on formation of methyl-phenyl or benzyl radical in the hydrogen addition step, the reported energy barriers vary in the range of 25 kcal/mol without considering the temperature power effect in the reaction rate.

In the next section we consider four major reactions of hydrogen and methyl radicals and toluene, which result formation of benzyl, methylphenyl, benzene, and methylcyclohexadienyl.

Reaction between methyl radical and toluene

Methyl radical is highly reactive and can easily react with various species in the gas phase. Depending on the way the methyl radical approaches toluene, the reaction between methyl radical and toluene produce methane and methyl-phenyl or methane and benzyl radical.



If the methyl radical approaches the toluene from the para position (1C) and react with it, the products are methyl-phenyl and methane. Table 3 shows the transition state structure for methyl substitution reactions. When the methyl radical approaches the 1C atom, toluene releases a hydrogen atom (19H), this atom moves towards the 16C atom in methyl to form methane molecule. Trajectories of this transition state show a linear movement of 19H atom between 1C and 16C atoms. The calculated activation energy for this reaction is

$$15.7 \frac{kCal}{mol} \text{ and the pre-exponent factor is } 10^{13}.$$

If the methyl radical approaches the 12C carbon in toluene, it can extract either of hydrogen atoms in CH₃ group of toluene

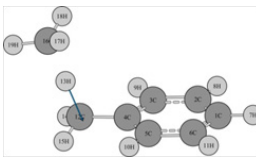
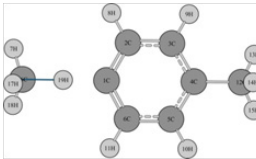
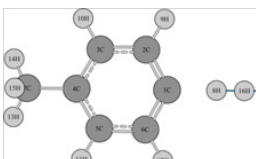
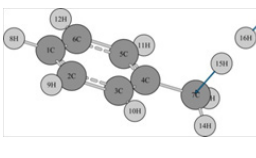
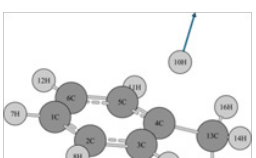
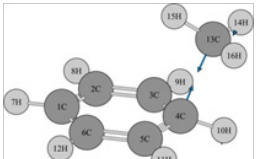
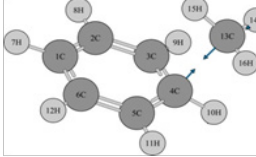
| Reaction | Bond measurements | Angle measurements |
|---|--|---|
| $C_7H_8 + CH_3 \rightarrow C_7H_7(Bz) + CH_4$  | $r_{4C-12C} = 1.477$ $r_{4C-5C} = 1.405$ $r_{5C-6C} = 1.391$ $r_{16C-12C} = 2.73$ $r_{12C-13H} = 1.27$ $r_{16C-13H} = 1.45$ | $\angle_{16C-13H-12C} = 178.1^\circ$ $\angle_{13H-12C-15H} = 102.8^\circ$ $\angle_{13H-12C-15H} = 102.8^\circ$ $\angle_{3C-4C-5C} = 117.91^\circ$ $\angle_{15H-12C-4C} = 114.54^\circ$ $\angle_{13H-12C-4C} = 109.5^\circ$ |
| $C_7H_8 + CH_3 \rightarrow C_7H_7(MP) + CH_4$  | $r_{4C-12C} = 1.510$ $r_{4C-5C} = 1.401$ $r_{5C-6C} = 1.398$ $r_{6C-1C} = 1.384$ $r_{1C-19H} = 1.380$ $r_{16C-13H} = 1.302$ $r_{16C-1C} = 2.685$ | $\angle_{3C-4C-5C} = 118.46^\circ$ $\angle_{4C-5C-6C} = 121.06^\circ$ $\angle_{6C-1C-2C} = 121.95^\circ$ $\angle_{16C-19H-1C} = 179.78^\circ$ $\angle_{17H-16C-19H} = 105.80^\circ$ |
| $C_7H_8 + H \rightarrow C_7H_7(MP) + H_2$  | $r_{4C-17C} = 1.511$ $r_{4C-5C} = 1.400$ $r_{5C-6C} = 1.399$ $r_{6C-1C} = 1.379$ $r_{1C-8H} = 1.506$ $8H \ 16H \ 0.847$ | $\angle_{3C-4C-5C} = 118.665^\circ$ $\angle_{4C-5C-6C} = 121.143^\circ$ $\angle_{6C-1C-2C} = 123.698^\circ$ $\angle_{4C-1C-8H} = 179.903^\circ$ $\angle_{16H-8H-1C} = 179.998^\circ$ $\angle_{13H-7C-15H} = 107.409^\circ$ |
| $C_7H_8 + H \rightarrow C_7H_7(Bz) + H_2$  | $r_{4C-7C} = 1.479$ $r_{4C-5C} = 1.404$ $r_{5C-6C} = 1.391$ $r_{6C-1C} = 1.394$ $r_{7C-15H} = 1.24$ $r_{15H-14H} = 1.06$ | $\angle_{3C-4C-5C} = 118.18^\circ$ $\angle_{4C-5C-6C} = 120.94^\circ$ $\angle_{13H-7C-4C} = 114.58^\circ$ $\angle_{15H-7C-13H} = 102.68^\circ$ $\angle_{15H-7C-4C} = 109.64^\circ$ $\angle_{15H-7C-4C} = 111.275^\circ$ |
| $C_7H_8 + H \rightarrow C_7H_9$  | $r_{4C-13C} = 2.465$ $r_{4C-5C} = 1.391$ $r_{5C-6C} = 1.396$ $r_{4C-10H} = 1.34$ $r_{13C-17H} = 2.05$ | $\angle_{3C-4C-5C} = 120.63^\circ$ $\angle_{4C-5C-6C} = 119.58^\circ$ $\angle_{6C-1C-2C} = 119.80^\circ$ $\angle_{1C-4C-13C} = 145.78^\circ$ $\angle_{16H-13C-15H} = 117.12^\circ$ |
| $C_7H_8 + H \rightarrow C_6H_6 + CH_3$  | $r_{4C-13C} = 2.465$ $r_{4C-5C} = 1.391$ $r_{5C-6C} = 1.396$ $r_{6C-1C} = 1.394$ $r_{4C-10H} = 1.34$ $r_{13C-17H} = 2.05$ | $\angle_{3C-4C-5C} = 120.63^\circ$ $\angle_{4C-5C-6C} = 119.58^\circ$ $\angle_{6C-1C-2C} = 119.80^\circ$ $\angle_{1C-4C-13C} = 145.78^\circ$ $\angle_{16H-13C-15H} = 117.12^\circ$ |
| $C_7H_9 \rightarrow C_6H_6 + CH_3$  | $r_{4C-13C} = 2.465$ $r_{4C-5C} = 1.391$ $r_{5C-6C} = 1.396$ $r_{6C-1C} = 1.394$ $r_{4C-10H} = 1.34$ $r_{13C-17H} = 2.05$ | $\angle_{3C-4C-5C} = 120.63^\circ$ $\angle_{4C-5C-6C} = 119.58^\circ$ $\angle_{6C-1C-2C} = 119.80^\circ$ $\angle_{1C-4C-13C} = 145.78^\circ$ $\angle_{16H-13C-15H} = 117.12^\circ$ |

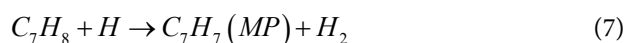
Table 3: Transition state structures for various toluene reactions obtained at B3LYP-6-311+g(d,p) level of theory.

and produce benzyl radical and methane. Table 3 shows the transition state structure for this reaction. The trajectories of this transition state show that as the 13H atom moves away from the 12C atom, other hydrogen atoms connected to the 12C atom move toward forming a planer CH₂ in benzyl radical. This transition state has an activation barrier of $8.85 \frac{\text{kcal}}{\text{mol}}$ and pre-exponent factor $10^{13.5}$.

Reactions of hydrogen radical and toluene

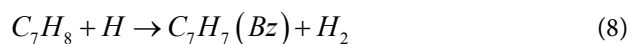
Like methyl, hydrogen atom can react with toluene and produce hydrogen, methylphenyl, benzyl, and methylcyclohexadienyl depending on the reaction site.

Formation of Methylphenyl radical



When the hydrogen atom approaches toluene from the para position in the benzene ring, toluene releases one hydrogen atom at its para position, this hydrogen reacts with the atomic hydrogen to form hydrogen molecule. The final products of this reaction are methyl-phenyl and hydrogen molecule. Table 3 shows the transition state structure for this reaction. As the 16H atom approaches the 8H atom in toluene, the 8H atom moves away from the 1C carbon in toluene. The trajectories of this transition state show a reciprocal movement of 8H atom in between 16H and 1C atoms. This movement follows the directional vector as pictured in Table 3. The IRC calculation and frequency calculations confirmed this transition state, the activation barrier for this reaction is $12 \frac{\text{kcal}}{\text{mol}}$ the calculated pre-exponent factor of 10^{14} at B3LYP/6-311+g(d,p) level of theory.

Formation of benzyl radical



Like methyl radical, when hydrogen atom approaches the methyl in toluene, it extracts one of the hydrogen atoms in the methyl group and forms hydrogen molecule. Table 3 shows the transition state structure for this reaction, trajectories of this reaction shows a linear reciprocal movement between the hydrogen atoms. The directional vector pictured on the transition state structure ensemble this linear movement. The IRC calculation connects toluene and hydrogen through this transition state to benzyl radical and hydrogen molecule. Frequency calculation at B3LYP/6-311+g(d, p) shows only one negative frequency at -1156.88 Hz which confirms that this structure is a transition state.

Formation of Methylcyclohexadienyl



The other possibility for a hydrogen atom to approach Toluene is to approach the carbon atom on the benzene ring, which is connected, to the methyl group of toluene—the 4C carbon. While the final products of this reaction are benzene and methane, our DFT calculations show that this reaction could proceed through two different pathways. One of the pathways directly connects the reactants and products together, while the other pathway proceeds through formation of methylcyclohexadienyl. As Table 3 shows, except for the formation of methylcyclohexadienyl both pathways have similar transition

state structures. The trajectories of the transition state for the formation of methylcyclohexadienyl shows the movement of the hydrogen atom (10H) towards the 4C carbon and the movement of the methyl group under the benzene ring.



Methylcyclohexadienyl is 22 kcal/mol more stable than the reactants (toluene and hydrogen); the molecule can decompose into benzene and methyl radical. The transition state for this reactions, shows movement of methyl radical above and the away from the 12C carbon in toluene until the C-C bond breaks and toluene releases the methyl group. The activation energy for this reaction is $18.7 \frac{\text{kcal}}{\text{mol}}$ with a pre-exponent factor of 10^{14} .

Comparison with experimental data

A potential application of hydrogenolysis of toluene is in the CVD growth of carbon nanotubes where a substantial amount of hydrogen gas is used as a scavenging agent in the reactor. At high temperatures, the majority of the reactions in the CVD reactor involve hydrogenolysis of hydrocarbons. We performed DFT calculations in order to estimate the reaction rate for hydrogenolysis of toluene. Our DFT calculation verifies Benson and Shaw's assumption. Table 4 shows the comparison between our calculated rate of reaction and the experimental values reported in the literature (3Pamidimukkala et al., 1987). For methylphenyl formation, the reaction of toluene with hydrogen or methyl radical Our calculated rates show very good agreement with the experimental rates reported at the temperature range between 700-1300 which is well suited for simulation of carbon nanotubes production using Computational Fluid Dynamics.

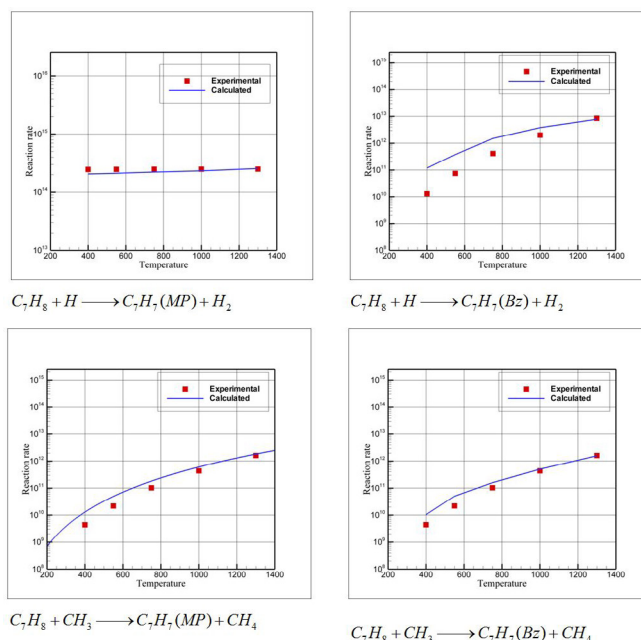


Table 4: Comparison of experimental reaction rate constants [3] with the calculated rate constants at B3LYP-6-311(d,p)

Summary and Conclusions

One of the major steps in the CVD of carbon nanotubes is pyrolysis of hydrocarbons at high temperature; in this reaction hydrogenolysis of toluene is important. Optimizing the

CVD reactor demands a good understanding and modeling of the chemical and physical phenomena inside the reactor. To this end, in this paper we have employed a DFT technique to study the gas phase pyrolysis of xylene and toluene at high temperatures. The structure of gaseous species have been optimized using the B3LYP/6-311(d,p) level of theory. Our results compare very well with experimental data from the open literature. The results from the DFT study can be used to develop other CVD configurations and to predict the yield of carbon nanotube.

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