



# Mechanism for the growth of polycyclic aromatic hydrocarbons from the reactions of naphthalene with cyclopentadienyl and indenyl



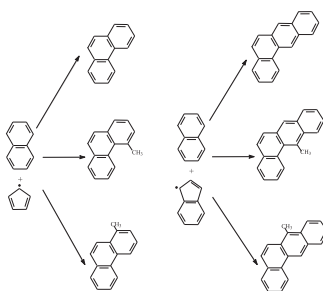
Fei Xu, Xiangli Shi, Qingzhu Zhang\*, Wenxing Wang

Environment Research Institute, Shandong University, Jinan, 250100, PR China

## HIGHLIGHTS

- Several energetically feasible pathways were revealed to compare the formation potential of PAH products.
- The rate constants for the elementary steps were deduced.
- The C-C cleavage steps are the rate determining steps due to the extremely high barrier.
- The formation of PAHs from naphthalene with indenyl is slightly more difficult than from naphthalene and cyclopentadienyl.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 14 February 2016

Received in revised form

11 June 2016

Accepted 13 July 2016

Handling Editor: Caroline Gaus

### Keywords:

PAHs  
Growth mechanism  
Naphthalene  
Cyclopentadienyl  
Indenyl  
Reaction pathway  
Rate constants

## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are globally concerned atmospheric particle-bound pollutants due to their toxicities. A mechanistic understanding of their formation from other environmental sources is of crucial importance for successful prevention of PAH. In the present work, the formation and growth mechanism of PAHs from the reactions of naphthalene with the cyclopentadienyl and indenyl radicals was investigated by using the hybrid density functional theory (DFT) at the MPWB1K/6-311+G(3df,2p)//MPWB1K/6-31+G(d,p) level. The rate constants for the crucial elementary steps were deduced with the aid of the canonical variational transition-state (CVT) theory with the small curvature tunneling (SCT) contribution. The formation of PAHs was involved in six elementary processes including: the addition reaction, ring closure, intramolecular H-shift, C-C cleavage, intramolecular H-shift and unimolecular elimination of CH<sub>3</sub> or H. The C-C cleavage steps were revealed as the rate determining steps due to the extremely high barrier. At high temperature conditions like the combustion and pyrolysis of many hydrocarbons, the main products are phenanthrene, 4-methyl-phenanthrene and 1-methyl-phenanthrene from the reactions of naphthalene and cyclopentadienyl, and benzo(*a*)anthracene, 12-methyl-phenanthrene and 7-methyl-phenanthrene from the reactions of naphthalene and indenyl radicals. The reaction of naphthalene with indenyl radical is slightly more difficult than the reaction of naphthalene with cyclopentadienyl radical because of the bigger HOMO-LUMO orbital energy difference of naphthalene with indenyl relative to that of naphthalene with cyclopentadienyl.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a constant concern due to their association with human lung cancer (Finlayson-Pitts and Pitts, 1997; Zhang et al., 2009; Abedi-Ardekani et al., 2010;

\* Corresponding author.

E-mail address: [zqz@sdu.edu.cn](mailto:zqz@sdu.edu.cn) (Q. Zhang).

Motorykin et al., 2013). PAHs have been listed as priority pollutants by the U.S. Environmental Protection Agency (EPA) (Environmental Protection Agency, 1999; Levinson et al., 2005). They are formed as byproducts of the incomplete combustion from traffic exhausts, industrial activities, domestic heating, forest fires and biomass burnings (Christensen and Bzdusek, 2005; Moon et al., 2006). The atmospheric emission of 16 priority PAHs in all Asian countries accounted for 53.5% of the global inventory (504 Gg), with the largest data from China (106 Gg) and India (67 Gg) (Shen et al., 2013). In China, lung cancer is emerging as the dominant cause of cancer deaths, accounting for approximately 23% (Wang et al., 2012; Beijing Municipal Government, 2014). Studies on the PAH formations are of interest because they can serve as a basis for minimizing PAH emissions.

The monocyclic aromatic hydrocarbons or smaller PAHs can enhance their toxicity by two patterns. On the one hand, smaller PAHs play a vital role in generations of persistent organic pollutants (POPs). Lots of experimental and theoretical studies show that polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), considering as typical POPs, can be formed from naphthalene, fluorine, phenanthrene and pyrene via oxidative pathways at high temperature (Wilhelm et al., 2001; Imagawa and Lee, 2001; Weber et al., 2001; Hajizadeh et al., 2001; Jansson et al., 2011; Li and Zhang, 2015; Cosentino et al., 2012). Polychlorinated naphthalenes (PCNs), which have recently been proposed for listing under the priority controlling roster of the Stockholm Convention on POPs, are reported to be formed from naphthalene via chlorination effect (Williams et al., 1994; Ryu et al., 2013). On the other hand, the growth of monocyclic aromatic hydrocarbons or smaller PAHs is an important source of larger PAHs. Under the general atmospheric conditions, PAHs with two or three aromatic rings are present in the vapor phase, while PAHs with four or more aromatic rings exist in particulate phase (Hanedar et al., 2014; Masiol et al., 2012). Hence, larger PAHs are more likely to incept soot particles. In addition, larger PAHs may be more toxic. The increased carcinogenicity and bio-accessibilities of PAHs was reportedly related to the higher molecular weight of large PAHs (Hanedar et al., 2014; Ravindra et al., 2008; Ohura et al., 2005). It was proposed that large PAHs in the particulate phase might pose a greater adverse health effect on the human body than small PAHs in the gaseous phase (Li et al., 2005; Zhang et al., 2009). Therefore, a detailed description of the growth mechanism of large PAHs is important.

Naphthalene, the smallest PAH, accounts for approximately 50% of the airborne concentration of total PAHs in vapor and particle phases. In flames, naphthalene is believed to be the gas phase molecular precursors of soot particles through the formation of large PAHs. The reactions of naphthalene with resonantly stabilized radicals play an important role in the growth of large PAHs (Frenklach et al., 1983; Melius et al., 1996; Marinov et al., 1998; Colket and Seery, 1994; McEnally and Pfefferle, 2000; Lindstedt et al., 2001; Frenklach, 2002). The cyclopentadienyl radical,  $C_5H_5$ , is among the most abundant radicals formed during the combustion and pyrolysis of many hydrocarbons (Melius et al., 1996; Marinov et al., 1998; Richter and Howard, 2000; Lindstedt et al., 2001; Hansen et al., 2006). The dimerization of the cyclopentadienyl radicals can result in directly the formation of naphthalene (Melius et al., 1996; Marinov et al., 1998; Ikeda et al., 2000; Richter and Howard, 2000; Butler and Glassman, 2009). The insertion of the cyclopentadienyl moieties to the aromatic rings can result in the growth of PAHs (Gomez et al., 1984; Manion and Louw, 1989; Marinov et al., 1998; Melius et al., 1996; Lamprecht et al., 2000; Mulholland et al., 2000; Lu and Mulholland, 2001). The indenyl radicals,  $C_9H_7$  also play a vital role in the formation and growth of PAHs (McEnally and Pfefferle, 1998; Mulholland et al., 2000; Lu and Mulholland, 2001). For example, the combination of

the  $C_5H_5$  with  $C_9H_7$  followed by rearrangement can result in the formation of phenanthrene (Marinov et al., 1997).

Despite of a lot of experimental studies about the formation and growth mechanisms of PAHs with other initiators (such as acetylene, ally, propargyl and propenyl addition to benzene or PAHs) (Frenklach et al., 1983, Frenklach, 2002; Colket and Seery, 1994; Melius et al., 1996; Marinov et al., 1997, 1998; D'Anna and Kent, 2003, 2008; Hansen et al., 2012; Kislov et al., 2013), the current understanding of the formation and growth mechanisms of PAHs with cyclopentadienyl and indenyl radicals in the combustion environment are still insufficient and need to be improved. Furthermore, the accuracy of the models used to predict the formation of PAHs is still limited by lack of kinetic data of reactions involving aromatic intermediates under relevant conditions of pressures and temperatures. Hence, in the present work, we report the quantum chemical and kinetic studies on the formation and growth of PAHs from the reactions of naphthalene with the cyclopentadienyl and indenyl radicals.

## 2. Computational methods

The high-accuracy molecular orbital calculations were performed for the reaction mechanism section using Gaussian 09 programs (Frisch et al., 2009). Geometrical optimizations of the reactants, intermediates, transition states and products were conducted at the MPWB1K/6-31+G(d,p) level (Zhao and Truhlar, 2004). The basis set 6-31+G(d,p) was chosen in consideration both computational time and accuracy. The vibrational frequencies were also computed at the MPWB1K/6-31+G(d,p) level in order to determine the nature of the stationary points, the zero-point energy (ZPE), and the thermal contributions to the free energy of activation. The minimum energy path (MEP) was obtained by the intrinsic reaction coordinate (IRC) theory in mass-weighted Cartesian coordinates to confirm that the transition state really connects to minima along the reaction path (Fukui, 1981). The rate constant calculations are most sensitive to the energies. All the relative energies were calibrated by ZPE with unscaled frequencies obtained at the MPWB1K/6-31+G(d,p) level.

The rate constants of the elementary reaction steps involved in the formation of PAHs from the reactions of naphthalene with the cyclopentadienyl and indenyl radicals were calculated with the aid of canonical variational transition-state (CVT) theory (Baldridge et al., 1989; Gonzalez-Lafont et al., 1991; Garrett and Truhlar, 1979) by means of the Polyrate 9.7 program (Fernandez-Ramos et al., 2007; Corchado et al., 2007). The CVT rate constant for temperature  $T$  is given by:

$$k^{CVT}(T) = \min_s k^{GT}(T, s) \quad (1)$$

where

$$k^{GT}(T, s) = \frac{\sigma k_B T}{h} \frac{Q^{GT}(T, s)}{\Phi^R(T)} e^{-V_{MEP}(s)/k_B T} \quad (2)$$

where,  $k^{GT}(T, s)$  is the generalized transition state theory rate constant at the dividing surface  $s$ ,  $\sigma$  is the symmetry factor accounting for the possibility of more than one symmetry-related reaction path,  $k_B$  is Boltzmann's constant,  $h$  is Planck's constant,  $\Phi^R(T)$  is the reactant partition function per unit volume (excluding symmetry numbers for rotation) and  $Q^{GT}(T, s)$  is the partition function of a generalized transition state at  $s$  with a local zero of energy at  $V_{MEP}(s)$  and with all rotational symmetry numbers set to unity. To include quantum tunneling effects for motion along the reaction coordinate, the CVT rate constants were multiplied by a

Download English Version:

<https://daneshyari.com/en/article/6306181>

Download Persian Version:

<https://daneshyari.com/article/6306181>

[Daneshyari.com](https://daneshyari.com)