



# The growth mechanism of polycyclic aromatic hydrocarbons from the reactions of anthracene and phenanthrene with cyclopentadienyl and indenyl



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## HIGHLIGHTS

- The PAH growth mechanism involves in six elementary steps.
- The smaller PAHs play an important role on the formation process of the larger PAHs.
- The cleavage of C–C bond is the rate-determining step due to the high barrier.

## ARTICLE INFO

### Article history:

Received 24 June 2017

Received in revised form

30 August 2017

Accepted 1 September 2017

Available online 5 September 2017

Handling Editor: R Ebinghaus

### Keywords:

PAH growth mechanism

Formation reactions

Anthracene

Phenanthrene

Cyclopentadienyl

Indenyl

## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are highly toxic, mutagenic and/or carcinogenic to humans. To reduce the emission of PAHs, it's significant and indispensable to explore the PAH formation mechanism. In the present work, the growth mechanism of PAHs from the reactions of anthracene and phenanthrene with cyclopentadienyl and indenyl radicals was investigated with the aid of high-accuracy quantum chemistry calculation. The rate constants of key elementary steps were calculated by meaning of the canonical variation transition-state (CVT) theory with the small curvature tunneling (SCT) correction over the temperature range of 400–1400 K. The mechanism of the PAH formation involves in six elementary steps, addition reaction, ring closure, intramolecular H-shift, cleavage of C–C bond, intramolecular H-shift and unimolecular elimination of CH<sub>3</sub> or H. The cleavage of C–C bond is the rate-determining step due to the high barrier. The formation of PAHs from the reactions of anthracene with cyclopentadienyl and indenyl radicals is easier than that from the reactions of phenanthrene.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds comprised of two or more aromatic rings. PAHs have attracted much attention in recent years because of their inherent toxicity (Shuttleworth and Cerniglia, 1995; Bruce et al., 2007; Mesquita et al., 2014). Some PAHs have potentially carcinogenic, teratogenic, and mutagenic effects (Boström et al., 2002). They have been regarded as persistent organic pollutants (POPs) (Katsoyiannis et al., 2011; Callen et al., 2013). Therefore, both the U.S. Environmental Protection Agency (EPA) and the European Environment

Agency regarded them as priority control pollutants (Ravindra et al., 2008; Ramirez et al., 2011). They are ubiquitous environmental pollutants presenting in air, water, soil and vegetation (Kim et al., 2013; Mah et al., 2013). The global total annual atmospheric emission of 16 priority PAHs was 504 Gg, and all Asian countries accounted for 53.5% of that, with the highest emission from China (106 Gg) and India (67 Gg) (Shen et al., 2013; Xu et al., 2016). PAHs are mainly formed by incomplete combustion of fossil fuels and biomass from natural and agricultural processes. In urban areas, vehicle emission also represents an important source (Baek et al., 1991; Nielsen et al., 1999; Ravindra et al., 2008). To reduce the emission of PAHs, it is significant and indispensable to explore the PAH formation mechanism.

The growth of PAHs from monocyclic aromatic hydrocarbons or small PAHs is an important source of PAHs, especially for large

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PAHs. With the increase in the molecular weight of PAHs, the carcinogenicity of PAHs generally increases. In other words, the larger PAHs may be more toxic (Ravindra et al., 2008; Kim et al., 2013; Hanedar et al., 2014). In addition, the large PAHs tend to be associated with particulate matter, especially PM<sub>2.5</sub> (particles with aerodynamic diameters less than 2.5 μm) (Ohura et al., 2005). Fine particulate matter with a relatively high content of large PAHs can penetrate deep into the lungs when inhaled, resulting in greater bio-accessibility than small PAHs (Kameda et al., 2005; Zhang et al., 2009; Kim et al., 2013). Thus, 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.

Anthracene and phenanthrene are typical PAHs with three aromatic rings and play an important role in air pollution. The concentration of anthracene observed can be ~40 ng/m<sup>3</sup>, accounted for 12.5% of the total concentration of PAHs in China (Wang et al., 2011; Zhou et al., 2013). The concentration range of anthracene was 15–31 ng/m<sup>3</sup> in the Shing Mun Tunnel, Hong Kong during the summer (Ho et al., 2009), and 6–19 ng/m<sup>3</sup> in Beijing-Tianjin region, North China (Wang et al., 2011). The concentration of phenanthrene observed in China can be ~100 ng/m<sup>3</sup>. The concentration range of phenanthrene was 48–138 ng/m<sup>3</sup> in Beijing-Tianjin region, North China, and 22–30 ng/m<sup>3</sup> in Dalian, a seaside city situated at the northeastern monsoonal area of China (Wang et al., 2011; Zhou et al., 2013; Zhao et al., 2016). During the combustion and pyrolysis process of many hydrocarbons, cyclopentadienyl radical, C<sub>5</sub>H<sub>5</sub>, is the most abundant product (Melius et al., 1996; Marinov et al., 1998; Richter and Howard, 2000; Lindstedt et al., 2001; Hansen et al., 2006; Qu et al., 2015; Chen et al., 2016). Its importance in the formation and growth of PAHs is well-known. The dimerization of the C<sub>5</sub>H<sub>5</sub> radicals can issue in immediately the formation of naphthalene (Melius et al., 1996; Marinov et al., 1998; Richter and Howard, 2000; Butler and Glassman, 2009; Xie et al., 2014). The addition of the C<sub>5</sub>H<sub>5</sub> moieties to PAHs can result in the growth of PAHs. The products from the pyrolysis of naphthalene and the C<sub>5</sub>H<sub>5</sub> radicals are anthracene and phenanthrene, which may react with the C<sub>5</sub>H<sub>5</sub> radicals further (Xu et al., 2016). Similarly, the role of the indenyl radical, C<sub>9</sub>H<sub>7</sub>, in the formation and growth of PAHs has been identified. For instance, the combination of the C<sub>9</sub>H<sub>7</sub> radicals with the C<sub>5</sub>H<sub>5</sub> radicals followed by rearrangement can issue in the formation of phenanthrene (McEnally and Pfefferle, 1998, 2000; Mulholland et al., 2000; Richter and Howard, 2000; Yu et al., 2016). Several experimental studies were reported about the growth of PAHs (Baek et al., 1991; Richter et al., 1999; Bauschlicher and Ricca, 2000; Frenklach, 2002; D'Anna, 2003; Roesler et al., 2003; Kislov et al., 2013; Xie et al., 2015). However, the detailed growth mechanism has still not been completely elucidated, largely due to the scarcity of efficient detection schemes for radical intermediate species. In such a situation, quantum chemical calculations can be an alternative. Currently, quantum chemistry calculations, as the supplement to experimental evaluation, has been successfully employed to elucidate the reaction mechanism and kinetics of PAHs pollutants in the environment (Qu et al., 2012). Thus, in the present work, firstly we have clarified the growth mechanism of PAHs from the reactions of anthracene and phenanthrene with the cyclopentadienyl and indenyl radicals at the atomic level. Secondly, we have described the configuration of short-lived reaction intermediates (IM) and transition states (TS). Thirdly, the rate constants of crucial elementary steps have been deduced by using the canonical variational transition-state theory (CVT) with the small curvature tunneling contribution.

## 2. Computational methods

By means of the Gaussian 09 (Frisch et al., 2015) programs, high-

accuracy molecular orbital calculations were carried out for the PAH growth mechanism. Geometries of the reactants, intermediates, transition states and products for the reaction system were optimized at the MPWB1K (Adamo and Barone, 1998; Zhao and Truhlar, 2004) level with a standard 6-31 + G(d,p) basis set. The MPWB1K/6-31 + G(d,p) level is an appropriate method for calculations due to the high accuracy of calculation with less computing resource. The vibrational frequencies were also calculated at the same 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. Moreover, the intrinsic reaction coordinate (IRC) analysis was performed to confirm that each transition state connects to the right minima along the reaction path (Fukui, 1981). For a more accurate evaluation of the energetic parameters, a large basis set, 6-311 + G(3df,2p), was employed to determine the single point energies of various species.

All the kinetic calculations were carried out with the aid of the POLYRATE 9.7 program (Corchado et al., 2007). The rate constants for the elementary steps involved in the reactions of anthracene and phenanthrene with the cyclopentadienyl and indenyl radicals were estimated by means of the canonical variational transition-state (CVT) theory with the small curvature tunneling (SCT) contribution (Garrett and Truhlar, 1979; Baldrige et al., 1989; Gonzalez-Lafont et al., 1991). The CVT rate constant for temperature  $T$  is given by:

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

where

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

where,  $k^{\text{GT}}(T, s)$  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,  $\Phi^{\text{R}}(T)$  is the reactant partition function per unit volume (excluding symmetry numbers for rotation) and  $Q^{\text{GT}}(T, s)$  is the partition function of a generalized transition state at  $s$  with a local zero of energy at  $V_{\text{MEP}}(s)$  and with all rotational symmetry numbers set to unity. For purpose of including the quantum effect for motion along the reaction coordinate, the CVT rate constant was multiplied by a ground-state transmission coefficient. In the present work, the small curvature tunneling (SCT) method, based on the centrifugal-dominant small-curvature semi-classical adiabatic ground-state approximation, was employed to calculate the ground-state transmission coefficient (Fernandez-Ramos et al., 2007).

## 3. Results and discussion

The geometric parameters and the vibrational frequencies of anthracene and phenanthrene were calculated at the MPWB1K/6-31 + G(d,p) level. The results were in accordance with the experimental data, and the maximum relative error remains within 2.0% for the geometrical parameters (McL Mathieson et al., 1950; Trotter, 1963; Martin et al., 1996) and less than 9.0% for the vibrational frequencies of anthracene, phenanthrene, cyclopentadienyl and indenyl (Castellucci et al., 1975; Klots, 1995; Martin et al., 1996). In order to check the reliability of the energy parameters, we calculated the reaction enthalpy for the reactions of anthracene and phenanthrene with cyclopentadienyl and indenyl at the MPWB1K/6-311 + G(3df,2p)//MPWB1K/6-31 + G(d,p) level and 298.15 K. For

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