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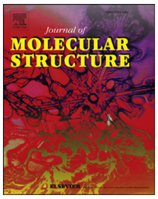

Theoretical investigation on the mechanism of NO_3 radical-initiated atmospheric reactions of phenanthrene

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ABSTRACT

Phenanthrene is a polycyclic aromatic hydrocarbon from fossil fuel combustion with toxic properties. The products arising from atmospheric reaction can be more mutagenic and carcinogenic compared to unmodified phenanthrene, and are therefore important to be studied. The products of the specific NO_3-radical reactions with phenanthrene where therefore investigated in this study by means of Density Functional Theory (DFT). The results show that the main products are proposed to be 10-(nitrooxy)-10-hydro-phenanthrene-9-one, 2,2′-diformylbiphenyl, 9,10-phenanthrenequinone, 9-fluorenone and dibenzopyranone. 10-(nitrooxy)-10-hydro-phenanthrene-9-one and 2,2′-diformylbiphenyl are classified as first-generation products which are subject to secondary reactions to produce 9,10-phenanthrenequinone, 9-fluorenone and dibenzopyranone. The rate constants of elementary reactions were assessed by Rice-Ramsperger-Kassel-Marcus (RRKM) theory. The atmospheric lifetime of Phe determined by the gas-phase reaction with NO_3 is estimated to be 1.8 h, based on the calculated overall rate constant of 3.04×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K and 1 atm. Combined with available experimental observation, this work should help to clarify the transformation and potential health risk of Phe in the atmosphere.

1. Introduction

Phenanthrene (Phe), which exists mainly in the gas-phase due to its vapor pressure under ambient conditions, is one of the most abundant polycyclic aromatic hydrocarbons (PAHs) in the atmosphere [1–4]. Phe has been frequently detected in field observation at concentrations higher than those of PAHs containing 4 aromatic rings or more [4–7]. Donateo et al. reported that in summer 2012, the average Phe concentration in Brindisi (South Italy) was approximately 1 ng m^{-3} [4]. Zhou revealed that the Phe concentration in Dalian was 22–30 ng m^{-3} from November 2009 to October 2010 [6]. Gaseous Phe can be removed from the atmosphere by oxidants such as OH, NO_3 and O_3. The reaction between Phe and nitrate radicals (NO_3) is suggested to be the most significant nocturnal removal process [8–11]. Several laboratory studies reported the formation of oxygenated-PAHs (OPAHs) and nitro-PAHs (NPAHs) from NO_3-initiated atmospheric reactions of Phe in the presence of O_2/NOx. Arey et al. detected trace amounts of nitro-phenanthrene from the gas-phase degradation of Phe initiated by NO_3 [9]. Wang and coworkers identified nitrodibenzopyranones, 9,10-phenanthrenequinone and some other oxygenated products from the gas-phase reaction between Phe and NO_3 in the presence of O_2/NOx [10]. As reported, nitro-phenanthrene can be more mutagenic and carcinogenic in comparison with Phe [12]. Nitro-dibenzopyranones were revealed to be highly mutagenic in bacteria [13]. 9,10-phenanthrenequinone could contribute to the toxicity of diesel exhaust particles, which have adverse effects on human lungs [14]. The observed 9,10-phenanthrenequinone concentration on urban atmospheric particulates was up to 1 ng m^{-3} [15]. OPAHs and NPAHs derived from Phe are more hydrophilic relative to Phe, due to the high electronegativity of N and O atoms. However, hydrophilic molecules are easily reabsorbed in the alveolus [16]. Therefore these Phe derivatives can be more toxic in comparison with Phe. OPAHs and NPAHs also contribute to secondary organic aerosol (SOA) formation in the atmosphere [17] and further exacerbate the carcinogenic potential of particulate organic matter. Though nitro-phenanthrene, nitro-dibenzopyranones and

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9,10-phenanthrenequinone, have been monitored in the atmosphere due to their toxicity, their formation mechanism remains to be revealed.

Literature on gas-phase reactions between Phe and NO_3 mainly focuses on rate constant determination [8] and product analyses [9,10]. To the best of our knowledge, systemic reports on the reaction mechanism of gas-phase reactions between Phe and NO_3 are sparse, possibly due to lack of efficient detection methods for intermediate species and standard spectra for reaction products [18]. With this concern, theoretical calculation can be an alternative to specification of reaction mechanisms, determination of the reaction products and assessment of the reaction kinetics. Qu et al. studied NO_3-initiated atmospheric reactions of benzene [19], naphthalene [20] and acenaphthene [21] by density functional theory (DFT). The calculated results were in well agreement with the available experimental observation.

In this work, we theoretically investigated the possible products and mechanism of the gas-phase reactions of Phe initiated by NO_3 in the presence of O_2/NO using DFT. Additional investigations were contributed to the formation mechanisms of nitrodibenzopyranones and 9,10-phenanthrenequinone. The rate constants of elementary reactions of interest were calculated by Rice-Ramsperger-Kassel-Marcus (RRKM) theory [22]. Several new reaction pathways were revealed. The obtained theoretical results were discussed combined with available experimental observation to assess the atmospheric implication of NO_3 radical-initiated reaction of Phe.

2. Computational methods

All theoretical calculations reported herein were performed employing the Gaussian 09 program [23]. The reactants, intermediates, transition states and products were optimized using hybrid M06-2X [24] functional with the 6-311+G(d,p) basis set. Frequency calculations were conducted at the same level of theory to obtain zero-point energy corrections and to identify the stationary points obtained as true minima or first-order saddle points. Minima were confirmed with no imaginary frequency. Each saddle point was ensured to have single imaginary frequency and further confirmed by intrinsic reaction coordinate (IRC) calculations [25]. Single point energies were calculated by using 6-311+G(2df,2p) at the optimized M06-2X/6-311+(d,p) geometry. All the activation enthalpies (ΔE) and reaction enthalpies (ΔH) are reported with zero-point correction at 298.15 K. The reliability of the chosen method has been validated in our previous work [26].

Rate constants of elementary reactions were calculated by RRKM theory [22] using the MESMER package [27]. According to the RRKM theory, the rate constant of a given reaction is given by:

$$k(E) = \frac{W(E - E_0)}{h\rho(E)} \tag{1}$$

where $W(E - E_0)$ is the sum of states at the transition state, $\rho(E)$ is density of states of reactants, and h is Planck's constant. The canonical rate constant $k(T)$ is assessed by:

$$k(T) = \frac{1}{Q(T)}\int k(E)\rho(E)\exp(-\beta E)dE \tag{2}$$

where $Q(T)$ is the partition function of reactants, $k(E)$ is the rate constant in a microcanonical ensemble with energy E, $\beta = (k_B T)^{-1}$, and k_B is Boltzmann's constant. The collisional parameters are estimated according to Gilbert and Smith [28].

3. Results and discussion

3.1. Preliminary reactions of NO_3 and Phe

3.1.1. Hydrogen abstraction

The Phe molecule belongs to C_{2v} symmetry group, and each C atom in the Phe molecule is labeled in Fig. 1. In the atmosphere, NO_3 can react with gaseous Phe via H abstraction and NO_3 addition reactions. NO_3 can abstract H atoms from C1–H, C2–H, C3–H, C4–H and C10–H bonds, leading to the formation of phenanthrenyl radicals and HNO_3 molecules. The reaction schemes are displayed in Fig. S1 in the Supplementary material. The H abstraction reactions are endothermic by 1.79–3.84 kcal/mol with activation enthalpies of 5.41–6.56 kcal/mol.

3.1.2. NO_3 addition

NO_3-Phe adduct isomers can be formed through NO_3 addition to C1, C2, C3, C4, C9, C11 and C13 atoms of Phe, as depicted in Fig. 1. The scan profiles of the potential energy surface varying the C–O bond length show that the formation reactions of IM1-IM5 are exothermic without activation enthalpies. In contrast, the activation enthalpies for the formation of IMb1 and IMb2 are 2.00 and 0.77 kcal/mol, respectively. As shown in Table 1, the rate constants of IMb1 and IMb2 formation are much lower than those of other NO_3 addition pathways. Therefore these two NO_3 addition pathways are of minor importance and will not be further discussed.

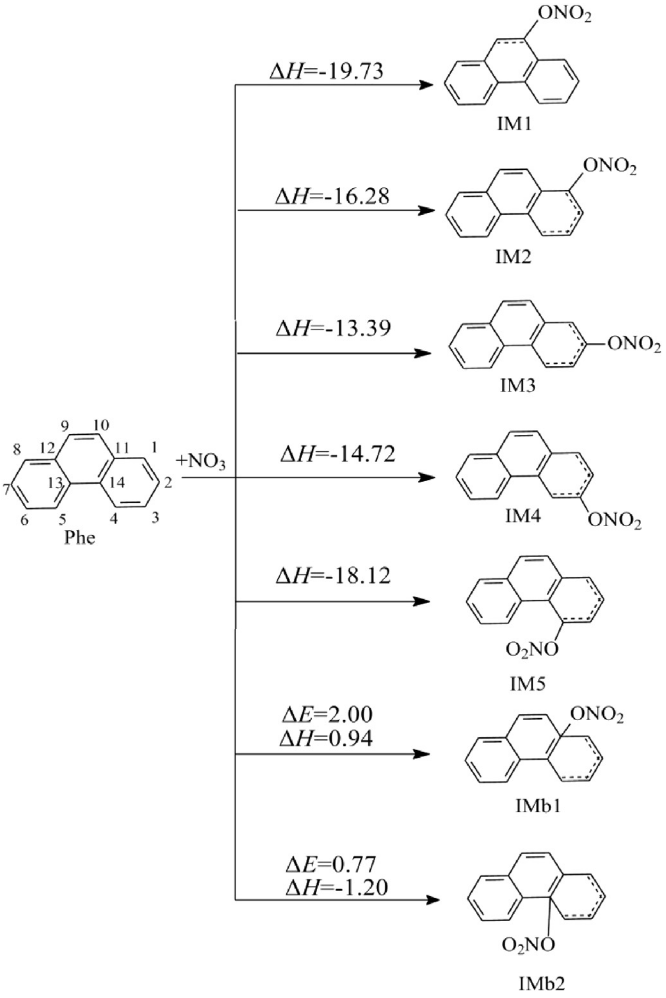

Fig. 1. Phe numbering system and NO_3 addition pathways embedded with the activation enthalpy ΔE and reaction enthalpy ΔH (all in kcal/mol, 298.15 K).