Mechanistic and kinetic studies on the OH-initiated atmospheric oxidation of fluoranthene

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HIGHLIGHTS

- We studied a comprehensive mechanism of OH-initiated oxidation of fluoranthene.
- We reported the formation pathways of fluoranthone, fluoranthenequinone and epoxide.
- The rate constants of the crucial elementary steps were evaluated.

ARTICLE INFO

ABSTRACT

The atmospheric oxidation of polycyclic aromatic hydrocarbons (PAHs) can generate toxic derivatives which contribute to the carcinogenic potential of particulate organic matter. In this work, the mechanism of the OH-initiated atmospheric oxidation of fluoranthene (Flu) was investigated by using high-accuracy molecular orbital calculations. All of the possible oxidation pathways were discussed, and the theoretical results were compared with the available experimental observation. The rate constants of the crucial elementary reactions were evaluated by the Rice–Ramsperger–Kassel–Marcus (RRKM) theory. The main oxidation products are a range of ring-retaining and ring-opening chemicals containing fluoranthols, fluoranthones, fluoranthenequinones, nitro-fluoranthenes, dialdehydes and epoxides. The overall rate constant of the OH addition reaction is 1.72×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and 1 atm. The atmospheric lifetime of Flu determined by OH radicals is about 0.69 days. This work provides a comprehensive investigation of the OH-initiated oxidation of Flu and should help to clarify its atmospheric conversion.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), an important fraction of semi-volatile organic compounds (SVOCs), are formed as byproducts of any incomplete combustion from traffic exhausts, industrial activities, domestic heating, forest fires and biomass burnings (Chen et al., 2013; Christie et al., 2012; Seinfeld and Pandis, 2006). The atmospheric emission of 16 priority PAHs in all Asian countries accounted for 53.5% of the total global emissions (504 Gg), with the highest emission from China (106 Gg) and India (67 Gg) during 2007 (Shen et al., 2013). PAHs are hydrophobic, stable, and sparingly soluble in water (Chaudhry, 1994). They can be metabolized to reactive electrophilic intermediates that can form DNA adducts, which may induce mutations and ultimately tumors (Ramírez et al., 2011). Due to the potential mutagenicity and carcinogenicity, their ubiquitous presence in air, water, soil

and vegetation is of major concern (Boström et al., 2002; Xue and Warshawsky, 2004). The European Union has set a target value of 1 ng m^{-3} of benzo[a]pyrene used as a main indicator of carcinogenic PAHs (EU, 2005).

Fluoranthene (Flu), a member of non-alternant PAHs, is one of the most abundant PAHs in the environment (Monte et al., 2012; Wetzel et al., 1994). Because of its high concentration in ambient air and potential carcinogenicity, it is suggested as a complementary indicator to benzo[a]pyrene (Boström et al., 2002). During spring of 1994–2000, the measurement in Stockholm has shown ambient air concentrations of Flu ranging from 8 to 25 ng m^{-3} (Boström et al., 2002). Air samples collected from eight locations in the Laurentian Great Lakes region revealed that the maximum concentration of Flu is up to 9350 pg m^{-3} (Galarneau et al., 2006). Atmospheric monitoring in Eordea Basin, west Macedonia, Greece and Kurashiki City has also detected Flu and other PAHs, the gas phase concentration of Flu scattered over the range of 0.623–30.3 ng m^{-3} (Terzi and Samara, 2004). On account of its prevalent presence in air, it is critical to understand the fate of gaseous Flu. In general, the tropospheric removal of Flu involves wet and dry deposition, and oxidation reactions with OH, NO$_3$ and O$_3$. The
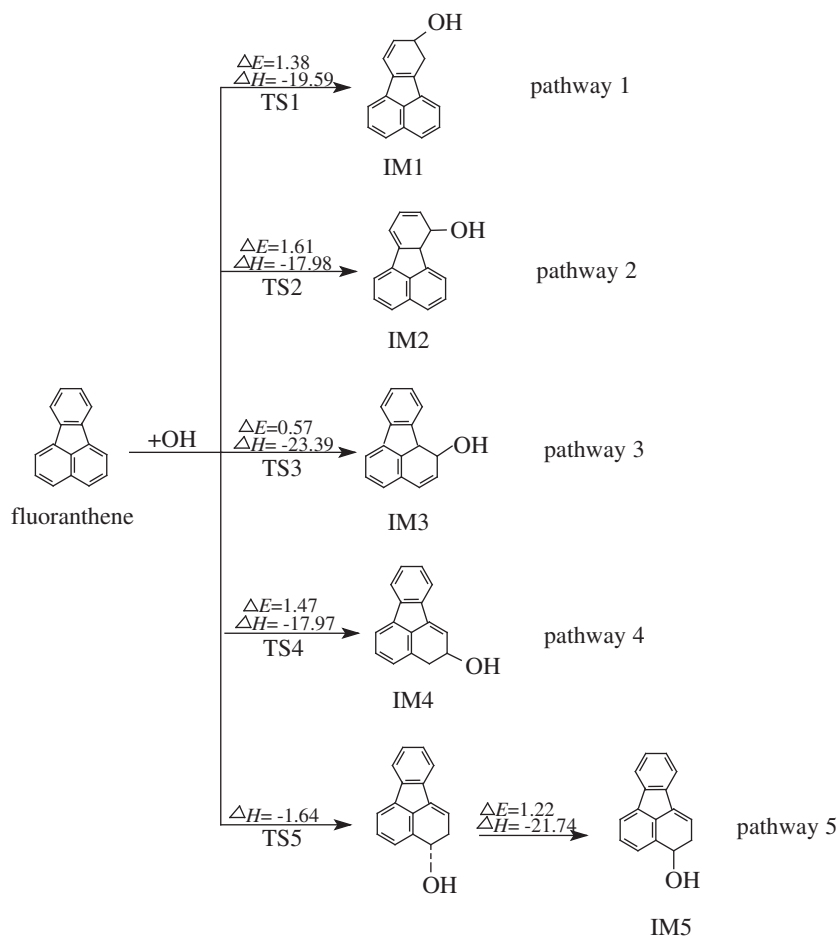
Fig. 1. The OH addition reaction scheme of Flu embedded with the potential barrier ΔE (in kcal/mol) and reaction heat ΔH (in kcal/mol). ΔH is calculated at 0 K.

wet and dry deposition of gaseous Flu is relatively insignificance as a removal pathway. Among the various oxidants, OH radicals play the most essential role in determining the oxidation power of the atmosphere (Keyte et al., 2013). The reaction with OH radicals is considered to be a dominant removal process for gaseous Flu. However, there exists a notable absence of direct experimental data concerning the reaction mechanism, largely due to the lack of efficient detection schemes for intermediate radical species. In this paper, using quantum mechanics and the RRKM theory, we carried out a theoretical study on the OH-initiated atmospheric oxidation reaction of Flu in the presence of O_2/NO and HO_2, which is helpful to clarify the atmospheric fate of Flu.

2. Computational method

The electronic structure calculations were performed with the Gaussian 03 software package (Frisch et al., 2003). Geometries of the reactants, intermediates, transition states, and products were optimized at the BB1K/6-31 + G(d,p) level, which has yielded satisfying results in the previous research (Qu et al., 2006). The harmonic frequency calculations were also performed at the same level in order to determine the nature of the stationary points, the zero-point energy (ZPE), and the thermal contribution to the free energy of activation. Besides, the intrinsic reaction coordinate (IRC) analysis was carried out to confirm that each transition state connects to the right minima along the reaction path. For a more accurate evaluation of the energetic parameters, a more flexible basis set 6-311 + G(3df,2p), was employed to determine the single point energies of various species.

By means of the MESMER program (Glowacki et al., 2012), the rate constants of the crucial elementary reactions were deduced by using Rice–Ramsperger–Kassel–Marcus (RRKM) theory (Robinson and Holbrook, 1972). The RRKM rate constant is given by:

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

where, $W(E)$ is the rovibrational sum of states at the transition state, $\rho(E)$ is the density of states of reactants, and h is Planck's constant. Then, canonical rate constant $k(T)$ is determined by using the usual equation:

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

where, Q(T) is the reactant partition function.

3. Results and discussion

Due to the lack of experimental information on the thermochemical parameters for the present reaction system, it is difficult to compare the calculated results with experimental data directly. To verify the reliability of the computational results, we optimized the geometries and calculated the vibrational frequencies of benzene, phenol and naphthalene. The results agree well with the available experimental values, and the maximum relative errors are less than 3.0% for geometrical parameters and less than 7.2% for vibrational frequencies