Theoretical study on atmospheric reactions of fluoranthene and pyrene with N₂O₅/NO₃/NO₂

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**ABSTRACT**

It is complex to assign the products obtained from the gas-phase reactions of PAHs with NO₃/NO₂ and N₂O₅. For this purpose, theoretical calculations are performed. Results show that 2-nitrofluoranthenes and 2-nitropyrene are the dominant products for reactions of fluoranthene and pyrene with NO₃/NO₂, while 3-nitrofluoranthenes and 1-nitropyrene are the major nitration products of N₂O₅. S_n2 reaction mechanisms are elucidated and homolytic mechanisms are calculated for the first time. Rate constants for reactions of fluoranthene and pyrene with N₂O₅ are deduced for the first time, which are 2.50 × 10⁻²⁷ and 2.16 × 10⁻²⁴ cm³ molecule⁻¹ s⁻¹, respectively at 298 K.

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1. Introduction

Atmospheric polycyclic aromatic hydrocarbons (PAHs) and their nitrated derivatives (NPAHs) are worldwide pollutants and highly potent mutagens, which makes some of them carcinogetic to humans [1–3]. Certain NPAHs even exhibit increased mutagenicity at a concentration significantly lower than that of their parent PAHs [4]. Among them, nitrofluoranthenes (NFL) and nitropyrenes (NPY) isomers have attracted the most attention because they are typically considered as ubiquitous NPAH atmospheric pollutants [5–8]. These NPAHs can originate from primary emissions (e.g., diesel and power plant emissions) or by the atmospheric oxidation of their parent PAHs. For accurately tracing the source of NPAHs in the atmosphere, it is imperative to investigate the nitration mechanisms of fluoranthene (FL) and pyrene (PY).

Over the past few decades, extensive experimental and theoretical studies have been performed on gas-phase reactions of FL and PY with N₂O₅/NO₃/NO₂ [5,9–12]. As a thermal equilibrium exists in the N₂O₅/NO₃/NO₂ system, N₂O₅ also possibly contributes to nitration products even though NO₃ exhibits higher reactivity [12]. Moreover, in experimental studies, it is difficult to completely distinguish between PAH reactions with NO₃/NO₂ and those with N₂O₅. Previous studies have reported that the reactions of PAHs, such as naphthalene and methyl-naphthalene, with N₂O₅/NO₃/NO₂ air mixtures proceed via N₂O₅ direct reactions [13,14]. However, the latter studies have experimentally established that the reactions possibly proceed in the gas-phase by the initial addition of the NO₃ radical, followed by the subsequent addition of NO₂. These reactions initiated by NO₃ radical were thought to be kinetically equivalent to those reactions with N₂O₅ [15,16]. Theoretical calculations have been used to clarify the experimental results [17,18]. Ghigo et al. [17] have conducted a theoretical study on the reactions of naphthalene with N₂O₅/NO₃/NO₂ and determined that the previous kinetic value (~10⁻¹⁷ cm³ molecule⁻¹ s⁻¹) [13] should be the rate constant of the NO₃-initiated reaction rather than that of the N₂O₅ reaction. They have applied the S_n2 reaction mechanism to the reaction of naphthalene with N₂O₅, Ingold and co-workers [19] were the first to propose the S_n2 reaction mechanism in aprotic solvents. As for FL and PY, to the best of our knowledge, there is no complete computational study for illustrating the reaction mechanisms in N₂O₅/NO₃/NO₂ air mixtures thus far. Recently, Zhang et al. [11] have calculated and emphasized the role of water in the gas-phase formation of NPAHs, including NFL and NPY isomers; however, not all of the reaction channels have been calculated. In addition, it is still unclear whether N₂O₅ plays a direct role in the reactions with N₂O₅/NO₃/NO₂ and whether a particular NPAH isomer (such as 2-NFL, 3-NFL, 1-NPY, or 2-NPY) is derived from a direct N₂O₅ or NO₃-initiated reaction. Some researchers have considered that N₂O₅ directly reacts with FL to form 2-NFL in aprotic solvents [20]. Zielinska et al. [20] have investigated the reaction of N₂O₅ with FL in CCl₄ aprotic solvents and obtained 2-NFL in a high yield at room temperature, which was hypothesized to be formed by the homolytic mechanism. Atkinson et al. [9] have measured the products and kinetics of reactions with FL and PY by adding N₂O₅ to NO₃/PAH/air mixtures with the aim of minimizing the formation of NO₃ radicals. They have considered 2-NFL and
2-/4-NPY to be the products from the NO3-initiated reaction. In addition, the rate constants of the NO3-initiated reaction (in the order of \(10^{-17} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\)) were considered to be close to those of the N2O5 reaction. More recent studies [12,21] have also suggested that 2-NFL and 2-/4-NPY are generated from the gas-phase NO3-initiated reactions of FL and PY, respectively. Hence, the experimental results of the products and kinetics of FL and PY in the reaction with N2O5/NO3/NO2, as well as the postulated reaction mechanisms of N2O5 with PAHs, need to be further confirmed theoretically.

In this study, to elucidate in detail the formation mechanism of NFL and NPY isomers from the reactions of FL and PY in N2O5/NO3/NO2 air mixtures, respectively, a comprehensive investigation is conducted by density functional theory (DFT). Schemes 1 and 2 show the major reaction pathways for FL and PY with NO3/NO2 and N2O5, respectively. The reaction mechanisms and reaction rates are also explored. The process of the addition of NO3 was found to be highly exothermic with an energy barrier significantly lower than that of the direct reaction with N2O5. Kinetic results rule out N2O5 as an effective reactant in gas-phase reactions. Thus, isomers associated with N2O5 reactions such as 3-NFL and 1-NPY observed in the atmosphere possibly originate from heterogeneous reactions or primary emissions.

2. Computational methods

Electronic structure calculations were conducted by DFT theory using the GAUSSIAN09 program [22]. The geometrical parameters and vibrational frequencies of all stationary points on the reaction potential energy surface (PES) were calculated using the B3LYP [23,24] functional with the standard 6-31G(d,p) basis set. The widely used B3LYP method has proven to be an economic and accurate computational model for predicting electronic structure [25–27]. The minima were confirmed to have positive frequencies, and each transition state had only one imaginary frequency, confirming their location as the maxima (i.e. first-order saddle point) along a single reaction coordinate. In addition, intrinsic reaction coordinate (IRC) paths were calculated to ensure that the given transition states connected the correct minima along the reaction path. A more flexible basis set, 6-311++G(3df,2p), was employed for single-point energy calculations for acquiring more reliable energetic values. The energy derivatives, including gradients and Hessians at geometries of some selected points (30 points on each side) along the minimum energy path (MEP) from \(s = -9.216\) to \(9.836\) (amu)^{1/2} Bohr, were also calculated. The enthalpy of the reaction and Gibbs free energy values were calculated at 298.15 K and 1.0 atm. Figure 1 shows the structures of FL and PY, with atomic numbering indicated for convenience.

Theoretical rate coefficients were calculated by the canonical variational transition state theory (CVT) [28,29] with a small-curvature tunneling (SCT) [30] correction using the initial DFT calculations. The rate constant for a bimolecular reaction is expressed by the formula:

\[
k^{CVT}(T) = \min_{s} k^{CT}(T, s)
\]

where

\[
k^{CT}(T, s) = \frac{\sigma}{\beta h} \frac{Q^{CT}(T, s)}{\phi^{R}(T)} e^{-\beta V_{\text{MEP}}(s)}
\]

In these equations, \(k^{CT}(T, s)\) is the generalized-transition-state-theory rate constant at the dividing surface \(s\), \(\sigma\) is the symmetry factor, \(\beta\) is \((k_{B}T)^{-1}\) where \(k_{B}\) is the Boltzmann constant and \(h\) is the Planck constant. \(Q^{CT}(T, s)\) is the internal partition function of the generalized transition state at \(s\), and \(\phi^{R}(T)\) is the reactant partition function per unit volume. \(V_{\text{MEP}}(s)\) is the classical potential energy along the MEP with its zero of energy at the reactants. Note that
the energy zeroes for $Q^T(T, s)$ and $\phi^R(T)$ are at the saddle point and the bottom of the reactant potential well, respectively. The PES, gradients, and Hessians of the electronic structure at the B3LYP/6-31G(d,p) level were directly used to calculate the rate constants over a suitable temperature range (178–398 K). All kinetic calculations were performed using the online VQLAB program package [31].

3. Results and discussion

3.1. Reactions of FL and PY with NO$_3$ radicals

NO$_3$ radicals are mainly formed via the oxidation of NO$_2$ by O$_3$, with nighttime concentrations from less than 10 to 400 ppt, as reported by field observations [32–35]. The first step in the reaction between NO$_3$ and PAHs is either the abstraction of hydrogen or the addition of NO$_3$ to the aromatic ring, the corresponding reaction pathways of which are presented in Figure 2, showing potential barriers ($\Delta E^\ddagger$) and reaction enthalpies ($\Delta H$). Table S1 (Supporting information) lists the detailed thermodynamic data. Figures S2 and S3 (Supporting information) show the optimized structures of the transition states involved in these pathways, where the main bond distances have been labeled.

Five transition states for FL (FL-TS1, FL-TS2, FL-TS3, FL-TS7, and FL-TS8 in Figure S1) and three transition states for PY (PY-TS1, PY-TS2, and PY-TS4 in Figure S2) were located for the H-abstraction channels. The corresponding products are HNO$_3$ with fluoranthryl (FL-1, FL-2, FL-3, FL-7, or FL-8) and pyrenyl (PY-1, PY-2, or PY-4), respectively, as depicted in Figure 2a and c. All H-abstraction channels are endothermic by 15.2–15.9 kcal mol$^{-1}$ with barrier heights of 13.1–14.8 kcal mol$^{-1}$. The presence of a product complex (PC) explains the slightly lower barriers than its reaction endothermicity, as the processes from PCs to the isolated products are also endothermic. As shown in Table S1, the reaction profile from the reactants to the PCs is endothermic of 9.8–11.0 kcal mol$^{-1}$. The generated fluoranthryl and pyrenyl isomers may react with NO$_2$ radicals to form NPAHs in the atmosphere. Considering that the reaction barriers of H-abstraction processes are significantly higher than those of NO$_3$.
addition processes, H-abstraction and subsequent reactions are not likely to be the dominant pathways for the reactions of NO3 with FL and PY under ambient atmosphere.

For the addition of NO3, seven different reaction sites on FL and three different reaction sites on PY were revealed. NO3 radicals attack the C1, C2, C3, C7, C8, C1a, and C7a atoms in FL and the C1, C2, and C4 atoms in PY to form NO3-FL (FL-IMx, x = 1, 2, 3, 7, 8, 1a, and 7a) and NO3-PY (PY-IMx, x = 1, 2, and 4) adducts, respectively, via their corresponding transition states, as shown in Figure 2b and d. The addition of NO3 radicals to the C1a and C3a atoms in PY is strictly hindered as C1a and C3a are inside the bend of the PY molecule. The energies of most of the transition states are lower than the total energies of the isolated reactants. In particular, prior to the generation of FL-TS1′, FL-TS3′, FL-TS7′, FL-TS8′, PY-TS1′, and PY-TS4′, the existence of a reactant complex (RC) is verified through geometry optimization by the steepest descent method from the end point on the IRC. Figure S3 shows the configurations of the hydrogen-bonded RCs. The barrier heights of the initial reaction steps are derived from the energy difference between the transition states and the RCs (if they exist) or reactants. Both processes, i.e., the formation of RCs from the isolated reactants and formation of NO3-PAH adducts from the RCs, are exothermic, releasing energies of 4.6–7.5 and 4.7–13.3 kcal mol⁻¹, respectively.

These results suggest a stepwise mechanism, which involves the formation of a PC in the exit channel for all the H-abstraction and the formation of an RC in the entrance channel for some NO3 addition paths. The complex mechanism may be significant for the NO3-initiated reactions of PAHs. The roles of such complexes were examined in the reactions of OH radicals with glycolaldehyde [36], glyoxal, and methylglyoxal [37], which exhibited a notable effect on the dynamics.

The reaction Gibbs free energies range from −1.5 to 16.0 kcal mol⁻¹ for NO3 addition pathways. Among these pathways, the values of the Gibbs free energies are negative for the formation of FL-IM3 and PY-IM1, implying that these two pathways possibly occur spontaneously at 298.15 K and 1.0 atm. In addition, the two processes are exothermic by 13.3 and 13.0 kcal mol⁻¹, demonstrating that the position of the highest electron density (the 3-position in FL and 1-position in PY) is readily attacked by electrophilic or oxidizing reagents. These results indicate that the most favorable pathways are the formation of FL-IM3 and PY-IM1, and their subsequent products 2-NFL and 2-NPY are the dominant oxidation products for the gas-phase reactions of NO3 with FL and PY, respectively.

Secondary reactions of FL-IMx and PY-IMx with NO3 radicals were also calculated. Figure 3 shows the relevant energies of the stationary points along the reaction profile for the most favorable pathways (reactions of FL-IM3 and PY-IM1 to form 2-NFL and 2-NPY, respectively); Figures S4 and S5 show the other pathways and configuration of corresponding transition states, respectively. NO3-PAH adducts further react with NO2 without a barrier to form NO3−NO2−PAH intermediates. The energy decrease for the formation of FL-IM3-2 and PY-IM1-2 is 27.3 and 16.9 kcal mol⁻¹, respectively. These intermediates decompose via transition states FL-TS3-2 and PY-TS1-2 with barrier heights of 24.7 and 20.5 kcal mol⁻¹, respectively, generating 2-NFL and 2-NPY with HNO3. The mechanism is summarized as the addition of NO3 and NO2 radicals and elimination of HNO3, which has been reported previously [11,18,38,39]. The facile generation of RCs may also lead to the production of 7-8-NFL and 4-NPY. In fact, low amounts of 4-NPY have been observed in the reactions of FL and PY in N2O5/NO3/NO2 air mixtures [9,12].

3.2. Reactions of FL and PY with N2O5

Tropospheric N2O5 is also an important gas-phase oxidant, which forms upon the recombination of NO2 and NO3. Typical concentrations of N2O5 varying from approximately 100 ppb to 10 ppb have been observed [33,34,40–42]. In our study, two different mechanisms were determined for the reactions of N2O5 with FL and PY. Mechanism (a): an S02-type reaction mechanism in which...
the covalent N2O3 molecule serves as an electrophile, and mechanism (b): a homolytic mechanism in which the homolysis of N2O3 generates a radical pair consisting of ONO2 and NO2, which adds to the reactive positions.

In the S8-2-type mechanism for the reactions of FL and PY with N2O5, eight 6-membered transition states denoted as FL-TS1a, FL-TS2a, FL-TS3a, FL-TS7a, FL-TS8a, PY-TS1a, PY-TS2a, and PY-TS4a were located successively, producing 1-, 2-, 3-, 7-, and 8-NFL and 1-, 2-, and 4-NPY, respectively. The superscript indicates the data from the reaction mechanism (a). Table S2 summarizes the energy barrier $\Delta E^+$, enthalpy $\Delta H$, Gibbs free energy $\Delta G$, and free-energy barrier $\Delta G^+$ for the reactions of FL and PY with N2O5. The results show that all eight processes are strongly exothermic with $\Delta H$ values ranging from $-36.8$ to $-31.7$ kcal mol$^{-1}$. In particular, the pathways involved in the formation of 3-NFL and 1-NPY were found to be the most favorable because of the small barriers of 19.4 and 16.3 kcal mol$^{-1}$, respectively. By contrast, the formation of 2-NFL and 2-NPY is not facile because of their increased barrier heights of 24.7 and 24.9 kcal mol$^{-1}$, respectively. The corresponding free energy barriers are in the range of 30.3–35.6 and 26.8–35.1 kcal mol$^{-1}$ for FL and PY in reactions with N2O5, the maximum of which are close to those of benzene (38 kcal mol$^{-1}$) and naphthalene (36.1 kcal mol$^{-1}$) calculated by Ghigo et al. [17]. Figure S6 shows the structures of the reactive species corresponding to the most favorable pathways, and Figure S7 shows the configurations of other transition states.

The individual and overall rate constants for the S8-2 reactions of N2O5 with FL and PY were computed (Tables S2 and S3). The overall rate constant for the reaction of FL with N2O5 is denoted as $k_{FL} = k_{FL-NFL} + k_{FL-NPY}$, where $k_{FL-NFL}$ and $k_{FL-NPY}$ are the corresponding individual rate constants for the generation of 1-NFL, 2-NFL, 3-NFL, 7-NFL, and 8-NFL, respectively. Similarly, the overall rate constant for the reaction of PY with N2O5 is denoted as $k_{PY} = 4k_{PY-NFL} + 4k_{PY-NPY}$, where $k_{PY-NFL}$ and $k_{PY-NPY}$ are the corresponding individual rate constants at 298 K for FL and PY with N2O5 are $2.50 \times 10^{-27}$ and $2.16 \times 10^{-24}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively.

For the homolytic mechanism, the transition state FL-TS3b (Figure S8) is obtained for the initially formed radical pair (FL-IM3b, FL-ONO2...NO2 radical pair). The radical pair undergoes recombination to generate the nitro–nitrato intermediate FL-IM3-2, which subsequently proceeds via FL-TS3-2 to form 2-NFL. Other transition states, FL-TS1b, FL-TS2b, FL-TS7b, FL-TS8b, PY-TS1b, PY-TS2b, and PY-TS4b, were also verified by IRC analysis. The superscript indicates the data from the reaction mechanism (b). However, these directly dissociate to form free NO2 radicals and FL-IM1, FL-IM2, FL-IM7, FL-IM8, PY-IM1, PY-IM2, and PY-IM4, respectively. Then, the re-addition of NO2 to FL-IMx ($x = 1, 2, 7, 8$) and PY-IMx ($x = 1, 2, 4$) leads to the generation of the nitro–nitroto intermediates, followed by the elimination of HNO3 to formNFL and NPY isolomers, respectively. The first step in the homolytic mechanism requires overcoming very high barriers of 32.5–43.2 kcal mol$^{-1}$ (Table S4). For the favorable pathway through FL-TS3b, the kinetic constant ($k(T)$) = $3.58 \times 10^{-15}$ T$^{-0.16}$ e$^{-1394/K}$ is 7.9 $\times 10^{-30}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K. In contrast with the kinetic results obtained for the S8-2 reaction, those obtained for the reaction of N2O5 with PAHs tend to rule out the possibility of a homolytic mechanism. Thus, the homolytic mechanism postulated by Zielinska et al. [20] for the formation of 2-NFL is not possible either thermodynamically or kinetically in the gas phase.

The calculated reaction rate constants of N2O5 with FL and PY ($2.50 \times 10^{-27}$ and $2.16 \times 10^{-24}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively, at 298 K) are approximately 10 and 7 orders of magnitude less than the experimental values measured by Atkinson et al. [9] Thus, it can be concluded that the NO3-initiated reaction products are actually 2-NFL and 2/4-NPY, but the kinetic values ($10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) of N2O5/NO3/NO2 air systems may be assigned to an incorrect nitrating agent between N2O5 and the NO3 radical [9].

In fact, this result is also consistent with observations reported in a recent study by Zimmermann et al.’s [12] in which they reported that the formations of 2-NFL and 2/4-NPY are significantly greater in the NO3 reaction than in the N2O5/NO3 reaction.

4. Conclusion

A comparison of the gas-phase reactions of NO3 and N2O5 with PAHs shows that both NO3 and N2O5 initially act as electrophilic reagents and attack the position of the highest electron density (the 3-position of FL and 1-position of PY). Then, the NO3-initiated reaction generates the dominant products 2-NFL and 2-NPY (7-, 8-NFL, and 4-NPY are the possible minor products) through the addition of a NO3 radical to the ortho position accompanied by the elimination of HNO3. By contrast, N2O5 directly reacts with PAHs by electrophilic substitution to form the dominant products 3-NFL and 1-NPY. NO3 addition is highly exothermic with an energy barrier lower than that for the direct reaction with N2O5, leading to a calculated rate constant of $10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the NO3 reaction [11], which is significantly higher than that of the N2O5 reaction calculated in this study.

By using the theoretical method, this study identifies the different NFL/NPY isolomers produced from NO3-initiated and N2O5 reactions as well as the mechanism and kinetics of the N2O5 reaction.
reaction, which have not been confirmed before. The obtained results can offer new assistant information for recognizing the source of NPAH pollutants. First, the product assignments show that gas-phase NO3-initiated and N2O5 reactions with FL/PY have their individual specific products. The dominant products for NO3-initiated reactions are 2-NFL/2-NPY, while those for N2O5 reactions are 3-NFL/1-NPY. The kinetic data reveal that N2O5 is not expected to be an effective reactant in gas-phase reactions with PAHs. This result indicates that 2-NFL and 2-NPY can be produced as the major degradation products in the gas-phase reaction of FL and PY in the N2O5/NO3/NO2 air system. 3-NFL and 1-NPY observed in the atmosphere possibly originate from primary emissions or heterogeneous reactions. In addition, because of the different reaction processes, the heterogeneous reactions of FL and PY with N2O5/NO3/NO2 are quite different from the gas-phase reactions under atmospheric conditions, which produces 3-, 8-, 7-, 1-NFL, and 1-NPY as the major particulate nitration products [21]. However, 2-NFL is considered as the dominant particle-bound NPAH measured in ambient atmospheres, which possibly originates mainly from the gas-phase NO3 reaction and condensation on the aerosol surface. The reaction mechanism illustrated in this study may also help to interpret the atmospheric transformation of other PAHs toward N2O5/NO3/NO2.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2015.06.056

References

[1] S.-C. Chen, C.-M. Liao, Sci. Total Environ. 366 (2006) 112.
[2] H. Lu, L. Zhu, S. Chen, Environ. Pollut. 152 (2008) 569.
[3] P.-J. Tsai, H.-Y. Shieh, W.-J. Lee, S.-O. Lai, Sci. Total Environ. 278 (2001) 137.
[4] J.L. Durant, W.F. Busby Jr., A.L. Lafleur, B.W. Pennman, C.L. Crespil, Mutat. Res. Genet. Toxicol. 371 (1996) 123.
[5] J.N. Pitts Jr., J.A. Sweetman, B. Zielinska, A.M. Winer, R. Atkinson, Atmos. Environ. 19 (1985) 1601.
[6] J.N. Pitts, J.A. Sweetman, B. Zielinska, R. Atkinson, A.M. Winer, W.P. Harger, Environ. Sci. Technol. 19 (1985) 1115.
[7] T. Ramdahl, B. Zielinska, J. Arey, R. Atkinson, A.M. Winer, J.N. Pitts, Nature 321 (1986) 425.
[8] H.A. Bamford, J.E. Baker, Atmos. Environ. 37 (2003) 2077.
[9] R. Atkinson, J. Arey, B. Zielinska, S.M. Aschmann, Int. J. Chem. Kinet. 22 (1990) 999.
[10] R. Atkinson, J. Arey, Environ. Health Perspect. 102 (1994) 117.
[11] Q. Zhang, R. Gao, F. Xu, Q. Zhou, G. Jiang, T. Wang, J. Chen, J. Hu, W. Jiang, W. Wang, Environ. Sci. Technol. 48 (2014) 5051.
[12] K. Zimmermann, R. Atkinson, J. Arey, Y. Koijma, K. Inazuh, Atmos. Environ. 55 (2012) 431.
[13] J.N. Pitts, R. Atkinson, J.A. Sweetman, B. Zielinska, Atmos. Environ. 19 (1985) 701.
[14] B. Zielinska, J. Arey, R. Atkinson, P.A. McElroy, Environ. Sci. Technol. 23 (1989) 723.
[15] R. Atkinson, E.C. Tuazon, J. Arey, Int. J. Chem. Kinet. 22 (1990) 1071.
[16] L. Wang, R. Atkinson, J. Arey, Environ. Sci. Technol. 44 (2010) 2381.
[17] C. Ghigo, M. Causa, A. Maranzana, G. Tonachini, J. Phys. Chem. A 110 (2006) 13270.
[18] X. Qu, Q. Zhang, W. Wang, Chem. Phys. Lett. 432 (2006) 40.
[19] V. Gold, E. Hughes, C. Ingold, G. Williams, J. Chem. Soc. (1950) 2452 (resumed).
[20] B. Zielinska, J. Arey, R. Atkinson, T. Ramdahl, A.M. Winer, J.N. Pitts, J. Am. chem. Soc. 108 (1986) 4126.
[21] K. Zimmermann, N. Jariyasopit, S.L. Masssey Simonich, S. Tao, R. Atkinson, J. Arey, Environ. Sci. Technol. 47 (2013) 8434.
[22] M.J. Frisch, et al., Gaussian09, Revision A02, Gaussian, Inc., Wallingford, CT, 2009.
[23] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[24] G. Lee, W. Yang, R.C. Parr, Phys. Rev. B 37 (1988) 785.
[25] Y. Pan, R. Wang, Chem. Phys. Chem. 367 (2010) 48.
[26] L. Sandhiya, P. Kolandavel, K. Senthil Kumar, J. Phys. Chem. A 117 (2013) 4611.
[27] L. Sandhiya, P. Kolandavel, K. Senthil Kumar, Can. J. Chem. 90 (2012) 384.
[28] B.C. Garrett, D.G. Truhlar, J. Am. Chem. Soc. 101 (1979) 4534.
[29] B.C. Garrett, D.G. Truhlar, R.S. Grev, A.W. Magnuson, J. Phys. Chem. 84 (1980) 1730.
[30] J.P. Liu, D.H. Lu, A. Gonzalez-Lafont, D.G. Truhlar, B.C. Garrett, J. Am. Chem. Soc. 115 (1993) 7806.
[31] S.-W. Zhang, T.N. Truong, V. Klavariotis, J. Phys. Chem. A 110 (2006) 72851.
[32] A. Galano, J.R. Alvarez-Idaboy, M.E. Ruiz-Santoyo, A. Vivier-Bunge, J. Phys. Chem. A 105 (2005) 169.
[33] A. Galano, J.R. Alvarez-Idaboy, M. Ruiz-Santoyo, A. Vivier-Bunge, ChemPhysChem 5 (2004) 1379.
[34] X. Qu, Q. Zhang, W. Wang, Can. J. Chem. 86 (2008) 129.
[35] C.E. Jessen, A. Gross, J. Kongsted, S. Jorgensen, Chem. Phys. 389 (2011) 39.
[36] R. Atkinson, A.M. Winer, J.N. Pitts, Atmos. Environ. 20 (1986) 331.
[37] J. Stutz, B. Alcicek, R. Ackerman, A. Geyer, A. White, E. Williams, J. Geophys. Res. Atmos. 109 (2004) D12306.
[38] S.S. Brown, H. Stark, T.B. Ryerson, E.J. Williams, D.K. Nicks, M. Trainer, F.C. Fehsenfeld, A. Ravishankara, J. Geophys. Res. Atmos. 108 (2003) D94299.
[39] K.K. Onschoke, Polycycl. Aromat. Comp. 28 (2008) 193.