Mechanical and kinetic study on gas-phase formation of dinitro-naphthalene from 1- and 2-nitronaphthalene

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HIGHLIGHTS

- Formation of dinitro-naphthalene via both OH and NO_3 were investigated firstly.
- Water molecule plays an important role during the formation of dinitro-naphthalene.
- The overall rate constants were calculated for 1- and 2-nitronaphthalene at 298 K.
- The Arrhenius formulas were fitted for the OH addition.

ARTICLE INFO

ABSTRACT

Nitrated polycyclic aromatic hydrocarbons have received an increasing number of considerations because of their higher mutagens than parent PAHs. In this paper, the formation of dinitro-naphthalene was investigated mechanistically using 1- and 2-nitronaphthalene as precursors with the aid of high-accuracy quantum chemistry calculation. The geometrical parameters, as well as vibrational frequencies, were calculated at the BB1K/6-31+G(d,p) level. Water molecule plays an important role in the formation of dinitro-naphthalene. The rate constants were deduced by canonical variational transition-state theory with small curvature tunneling contribution over the temperature range of 273−333 K. Meanwhile, the Arrhenius formulas were fitted for the OH addition of both 1- and 2-nitronaphthalene. The calculated overall rate constants for 1-nitronaphthalene and 2-nitronaphthalene at 298 K and 1 atm are 7.43×10^{-13} and 7.48×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively. The rate constants of NO_3 addition to 1-nitronaphthalene and 2-nitronaphthalene by RRKM method at 298 K and 1 atm are 3.55×10^{-15} and 3.47×10^{-15} cm^3 $molecule^{-1}$ s^{-1}, respectively. This study provides a comprehensive investigation of the formation process of dinitro-naphthalenes, initiated by OH and NO_3 radicals and should facilitate to illuminate its atmospheric source. Oxygen may probably be competitive with the second NO_2 addition step when the concentration of NO_2 is at low level.

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1. Introduction

Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs), as derivatives of parent PAHs, have been recognized as the toxic air pollutants (Schauer et al., 2003; Perrini et al., 2005; Hien et al., 2007; Albinet et al., 2008; Kawanaka et al., 2008; Benbrahim-Tallaa et al., 2012). Though the concentration of nitro-PAHs is generally lower than that of parent PAHs at 1−2 orders of magnitude, these atmospheric pollutants have been at the forefront of public concern because of their known 100,000 times more mutagenic and 10 times more carcinogenic than PAHs (Durant et al., 1996). Nitro-PAHs have been demonstrated to account for over 50% of the total direct-acting mutagenicity and the total carcinogenicity activity of ambient air (Pitts et al., 1978; Salmeen et al., 1984; Finlayson-Pitts and Pitts, 1999; Lu et al., 1999). Among nitro-PAHs, 5 dinitro-PAHs (3,7- and 3,9-dinitro-fluoranthene, 1,6-, 1,8-dinitro-pyrene, and 3,6-dinitro-benzo[a]pyrene) are found extremely high mutagenic potency ($\geq$100,000 revertants $nmol^{-1}$) in the *Salmonella typhimurium* microsome test(Tokiwa et al., 1994). This result elaborates some kind of dinitro-PAHs more mutagenic to bacterial assays, compared with mononitro-PAHs. Furthermore, the mutagenicity of PAHs and their oxo- and nitro-derivatives has also been modelled by means of Quantitative Structure-Activity Relationships (QSAR) in human cells (Papa et al., 2008). However, in

the aspect of carcinogenicity, nitro-PAHs and parent PAH are not totally similar depending on the route of administration (Organization, 2003). In addition, nitro-PAHs occur in a wide range of global environment (Finlayson-Pitts and Pitts, 1999), even have been detected in the Antarctic air particulate (Vincenti et al., 2001).

Nitro-PAHs can be formed in the atmosphere by both direct emission, primarily by diesel engines through electrophilic nitration process, and secondary formation of the atmospheric reaction of parent PAHs (Ringuet et al., 2012). Secondary formation has been revealed a significant contribution to various nitro-PAHs through the observation of specific isomers for nitro-PAHs in ambient air (Arey et al., 1986; Gibson et al., 1986; Atkinson and Arey, 1994; Bamford and Baker, 2003; Reisen and Arey, 2005). Nitro-PAHs can be generated via homogeneous reactions of PAHs with OH at daytime and NO_3 radicals at night-time in the presence of NO_2 (Nielsen, 1984; Ramdahl et al., 1986; Atkinson et al., 1987; Atkinson and Arey, 1994). In addition, nitro-PAHs can also be produced by the heterogeneous reactions of parent PAHs in particles with N_2O_5 or HNO_3 molecule (Nielsen, 1983; Kamens et al., 1990). The previous research indicates that the homogeneous reactions are generally faster contrasted with the heterogeneous reactions (Esteve et al., 2006). Thus, the formation process in gas phase has been recognized as a significant source of nitro-PAHs in the atmosphere. However, to our best knowledge, previous researches mostly focused on the atmospheric formation of mononitro-PAHs, and few studies on the atmospheric formation of dinitro-PAHs.

Due to the limitation of experiment condition, some short-lived reaction intermediates and transition states are difficult to be detected. Therefore, as a supplement to the experiment, quantum chemical calculation can be of considerable help in identifying the mechanism of specific reaction route. In this paper, we investigated the formation of dinitro-naphthalene arising from the OH-initiated and NO_3-initiated atmospheric reaction of 1- and 2-nitronaphthalene by quantum chemical calculation. Recent years, researches with density functional theory have yielded satisfying results in PAH derivatives (Bekbolet et al., 2009; Dang et al., 2015a,b; Onchoke et al., 2016). The atmospheric model places a high demand on accurate kinetic parameters (Feilberg et al., 1999). So, the rate constants of key elementary reactions initiated by OH radical were evaluated by using canonical variational transition-state (CVT) theory with small curvature tunneling (SCT) contribution on the basis of the electronic structure calculations. Because the reactions initiated by NO_3 radical are barrierless, the rate constants initiated by NO_3 radical were carried out by Rice-Ramsperger-Kassel-Marcus (RRKM) theory.

2. Computational methods

Utilizing Gaussian 09 program (Frisch et al., 2009), high-accuracy molecular orbital calculations were performed on a supercomputer. The geometries of the reactants, intermediates, transition states (Qu et al., 2009; Xu et al., 2010b, 2010c) and products were carried out at the BB1K level with the 6-31+G(d,p) (Zhao et al., 2004), which has an excellent results in the previous study (Zhang et al., 2014). The vibrational frequencies were calculated at the same level to verify whether the structures obtained are true minima or first-order saddle points. To confirm each transition state connecting to the right minima along the reaction path, the intrinsic reaction coordinate (IRC) calculations were further carried out at the 6-31+G(d,p) level. Single-point energy calculations were performed at a more flexible basis set, 6-311+G(3df,2p), to obtain a more accurate evaluation of the energetic parameters.

The rate constants initiated by OH radical were performed by the means of POLYRATR 9.3 program (Steckler et al., 2002). This program is based on the canonical variational transition-state (CVT)

theory. The CVT rate constant for temperature T is given by:

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

where

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

where, $k^{GT}(T,s)$ is the generalized transition state theory rate constant at the dividing surface s, σ 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 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 transmission coefficient.

The rate constants initiated by NO_3 radical were carried out with the aid of Rice-Ramsperger-Kassel- Marcus (RRKM) theory (Robinson and Holbrook, 1972). The RRKM rate constant is given by:

$$k(E) = \frac{W(E)}{h\rho(E)} \tag{3}$$

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

$$k(T) = \frac{1}{Q(T)} \int k(E)\rho(E)\exp(-\beta E)dE \tag{4}$$

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

3. Results and discussion

It is difficult to directly compare the theoretical results with experimental values because of the lack of the experimental data of present reaction. Therefore, we optimized geometries and calculated vibrational frequencies of nitro-benzene, 1-nitron-aphthalene and 1,5-dinitro-naphthalene at the BB1K/6-31+G(d,p) level, for the sake of verifying the reliability of our computational results. The relative deviation remains within 3% for bond length and 8% for the vibrational frequencies (Johnson, 2005; Arivazhagan et al., 2009; Govindarajan and Karabacak, 2012).

To describe the results conveniently, the carbon atoms in naphthalene are numbered as follows:
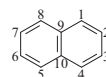
C−H and C=C bonds exist in 1- and 2-nitronaphthalene, which makes it possible for both H abstraction from C−H bonds and OH addition to C=C bonds. Obviously, both 1- and 2-nitronaphthalene have seven H abstraction positions. The potential barrier and reaction heat were calculated at BB1K/6-311+G(3df,2p) level. Results show that the potential barriers spread from 5.17 to 9.26 kcal mol^{-1}. Moreover, the reaction heats of H abstraction are from −5.29