

# Kinetics and products of the gas-phase reactions of acenaphthylene with hydroxyl radicals, nitrate radicals and ozone



Shouming Zhou<sup>a,b,\*</sup>, John C. Wenger<sup>a,b</sup>

<sup>a</sup> Department of Chemistry, University College Cork, Cork, Ireland

<sup>b</sup> Environmental Research Institute, University College Cork, Cork, Ireland

## HIGHLIGHTS

- Reactions with OH, O<sub>3</sub> and NO<sub>3</sub> all contribute to the atmospheric removal of acenaphthylene.
- Atmospheric oxidation products are mainly ring-retaining compounds.
- The formation of hydroxylated and nitro-PAHs is only a minor reaction pathways.
- Addition to the C=C bond is the major reaction pathway for NO<sub>3</sub> and O<sub>3</sub> reactions.
- Acenaphthylene oxidation products are detected in both gas- and particle-phases.

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## ABSTRACT

A series of simulation chamber experiments has been performed on the gas-phase atmospheric oxidation of acenaphthylene with the hydroxyl (OH) radical, ozone (O<sub>3</sub>) and the nitrate (NO<sub>3</sub>) radical. Using a relative rate technique the following rate coefficients (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were determined at (293 ± 3) K in 1 atm of purified air: (1.09 ± 0.07) × 10<sup>-10</sup>, (3.99 ± 0.15) × 10<sup>-16</sup> and (4.42 ± 0.32) × 10<sup>-12</sup> for the reactions with OH, O<sub>3</sub> and NO<sub>3</sub> respectively. The results indicate that all three oxidants effectively contribute to the removal of acenaphthylene from the atmosphere. A denuder-filter sampling system coupled with off-line analysis by gas chromatography – mass spectrometry (GC–MS) was used to determine the gas- and particle-phase products of these reactions. The major products identified in the reaction with OH were naphthalene-1,8-dicarbaldehyde, 1,8-naphthalic anhydride and a 10 carbon ring-opened dialdehyde. The products identified in the reaction with NO<sub>3</sub> and O<sub>3</sub> were predominantly oxygenated compounds arising from reaction at the C=C bond in the cyclopenta-fused ring of acenaphthylene. The formation of hydroxylated and nitro-PAHs appears to be a very minor reaction pathway. Acenaphthenequinone, a compound known to generate reactive oxygen species at the cellular level, was formed from the reactions of acenaphthylene with OH and NO<sub>3</sub>. The majority of the oxidation products were found to be distributed between the gas and particle phases, with only acenaphthylenol and oxaacenaphthylen-2-one, relatively more abundant in the particle phase.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous air pollutants released into the atmosphere as a by-product of combustion processes. In the atmosphere, PAHs containing two and three rings are found predominantly in the gas-phase, whilst those containing six or more rings principally adsorb to particles. PAHs with four or five rings are found in both phases (Finlayson-Pitts and

Pitts, 2000; Calvert et al., 2002; Ravindra et al., 2008). In the gas-phase, PAHs can be chemically transformed *via* reaction with the hydroxyl (OH) radical, ozone and nitrate (NO<sub>3</sub>) radical (Calvert et al., 2002; Atkinson and Arey, 2007) to produce a range of products, including nitro-PAHs and quinones (Sasaki et al., 1997; Calvert et al., 2002; Reisen and Arey, 2002; Atkinson and Arey, 2007; Lee and Lane, 2010), known to have adverse effects on human health (Atkinson and Arey, 1994), and other pollutants such as ozone and secondary organic aerosol (SOA) (Chan et al., 2009; Shakya and Griffin, 2010). Despite their obvious importance in polluted environments, our knowledge of the rates, products and mechanisms for the atmospheric degradation of many PAHs is far from complete (Calvert et al., 2002; Atkinson and Arey, 2007).

\* Corresponding author. Current address: Department of Chemistry, University of Toronto, Toronto, Canada. Tel./fax: +1 416 946 7359.

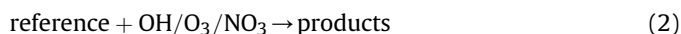
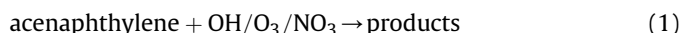
E-mail address: [szhou@chem.utoronto.ca](mailto:szhou@chem.utoronto.ca) (S. Zhou).

Acenaphthylene is a PAH generated from a variety of sources including diesel exhaust and solid fuel combustion (Ravindra et al., 2008). It contains three rings in its chemical structure and primarily exists in the gas-phase under typical atmospheric conditions (Cousins and Mackay, 2001). To date, there have been two kinetic studies of the gas-phase atmospheric reactivity of acenaphthylene reported in the literature (Atkinson and Aschmann, 1988; Reisen and Arey, 2002). A number of gas-phase products of the OH and O<sub>3</sub> initiated oxidation of acenaphthylene were reported by Reisen and Arey (2002), while nitroacenaphthylene (Arey et al., 1989), oxygenated PAHs (Banceau et al., 2001) and glyoxal (Nishino et al., 2009) have also been identified as products from reaction with OH. There is no published information on the particle phase products of the atmospheric oxidation of acenaphthylene despite being recently identified as a potential source of SOA (Shakya and Griffin, 2010). In this study we have performed a series of simulation chamber experiments to determine rate coefficients, gas- and particle-phase oxidation products of the reactions of acenaphthylene with OH, O<sub>3</sub> and NO<sub>3</sub>. The results provide new information on the gas-phase atmospheric chemistry of acenaphthylene and help to further our understanding of its potential impact on the environment.

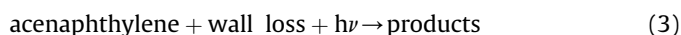
## 2. Experimental section

### 2.1. Kinetic studies

Experiments were performed in a 3910 L cylindrical chamber at (293 ± 3) K and atmospheric pressure of purified air. The chamber consists of a FEP Teflon foil tube surrounded by UV lamps and is equipped with *in situ* FTIR spectroscopy for chemical analysis of gaseous species (Thüner et al., 2004; Kourtchev et al., 2009). Rate coefficients for the reactions of OH, O<sub>3</sub> and NO<sub>3</sub> with acenaphthylene were determined using a relative rate method in which the relative disappearance rates of acenaphthylene and a reference compound, whose rate coefficient for reaction with the reactive species is well known, were measured in the presence of either OH, O<sub>3</sub> or NO<sub>3</sub>:



Acenaphthylene was also lost by deposition to the reactor walls in all experiments and additionally by photolysis during the OH experiments:



Test experiments showed that wall loss and the combination of wall loss and photolysis obeyed first order kinetics. No wall deposition or photolysis was observed for the reference compounds used in the experiments. The rate equations for reactions (1)–(3) were combined and integrated resulting in the following expression:

$$\ln \left\{ \frac{[\text{acenaphthylene}]_0}{[\text{acenaphthylene}]_t} \right\} - k_3 t = \frac{k_1}{k_2} \ln \left\{ \frac{[\text{reference}]_0}{[\text{reference}]_t} \right\} \quad (1)$$

where [acenaphthylene]<sub>0</sub> and [reference]<sub>0</sub> are the initial concentrations of acenaphthylene and the reference compound; [acenaphthylene]<sub>t</sub> and [reference]<sub>t</sub> are the corresponding concentrations at time *t*; *k*<sub>1</sub> and *k*<sub>2</sub> are the rate coefficients for reactions of acenaphthylene and the reference compound with OH/O<sub>3</sub>/NO<sub>3</sub> respectively; *k*<sub>3</sub> is the rate coefficient for combined wall loss and photolysis of acenaphthylene in the OH experiments and

simply the rate coefficient for wall loss in the O<sub>3</sub> and NO<sub>3</sub> experiments, where lamps were not used. Plots in the form of Eq. (1) should give straight lines with slopes *k*<sub>1</sub>/*k*<sub>2</sub> and a zero intercept. The value of *k*<sub>1</sub> can be derived from the rate coefficient ratios using the known value for *k*<sub>2</sub>.

In OH experiments, the photolysis of H<sub>2</sub>O<sub>2</sub> by mercury lamps (Philips TUV 40 W, λ<sub>max</sub> = 254 nm) was used as the source of OH radicals;



and isoprene was used as the reference compound. For the ozonolysis experiments, ozone was produced as a mixture in O<sub>2</sub> by an ozone generator and added to the chamber containing pre-mixed acenaphthylene, carbon monoxide (100 L to act as a scavenger for OH radicals) and the reference compound cyclopentene. NO<sub>3</sub> radicals were produced by the thermal dissociation of N<sub>2</sub>O<sub>5</sub> prepared in solid form according to a literature method (Schott and Davidson, 1958):



N<sub>2</sub>O<sub>5</sub> was added to the chamber containing a mixture of acenaphthylene and the reference compound 2,3-dimethyl-1,3-butadiene, by passing dry purified air over the surface of solid N<sub>2</sub>O<sub>5</sub> stored in a cold trap at –50 °C. The initial mixing ratios of acenaphthylene and reference compounds in all experiments were 1.0–2.5 ppmv (1 ppmv = 2.46 × 10<sup>13</sup> molecule cm<sup>–3</sup> at 298 K) and 1.0–2.0 ppmv, respectively. The changes in concentration of the reactant and reference compounds were determined by spectral subtraction procedures using the following infrared absorption peaks; acenaphthylene at 773.0 and 832.8 cm<sup>–1</sup>; isoprene at 893.4 and 905.9 cm<sup>–1</sup>; cyclopentene at 1048 cm<sup>–1</sup>; 2,3-dimethyl-1,3-butadiene at 894.5 cm<sup>–1</sup>.

### 2.2. Product studies

Product studies on the OH, O<sub>3</sub> and NO<sub>3</sub> initiated oxidation of acenaphthylene were performed at (298 ± 5) K and atmospheric pressure of purified air in a 6500 L rectangular FEP Teflon chamber (Temime et al., 2007). The chamber is equipped with 12 Philips TL12 lamps (40 W, λ<sub>max</sub> = 310 nm) and 12 Philips TL 05 lamps (40 W, λ<sub>max</sub> = 360 nm). Photolysis of nitrous acid (HONO) under TL 05 lamps was used as the OH radical precursor:



Nitrous acid was synthesized by adding a 1% NaNO<sub>2</sub> aqueous solution dropwise into a flask containing 30% sulfuric acid. Ozonolysis and NO<sub>3</sub> radical reactions were performed in a manner analogous to the kinetic studies, however, without addition of reference compounds. In all experiments, the initial mixing ratio of acenaphthylene was 1.0–2.0 ppmv.

The decay of acenaphthylene was measured using gas chromatography-flame ionization detector (GC-FID) and the NO<sub>x</sub> mixing ratio was monitored by a NO<sub>x</sub> analyzer (Thermo Model 42i). A denuder-filter sampling technique (Temime et al., 2007; Healy et al., 2008) was employed to collect the gas- and particulate-phase products. The denuder consisted of 5 concentric glass tubes coated with absorbent XAD-4 resin. The products were collected at 10 L min<sup>–1</sup> for 30 min and the denuder was extracted twice with 10 mL methanol followed by sonication for 15 min, while the filter was extracted by sonication for 15 min in 10 mL methanol. 2 mL of the extracts from the denuder and filter were passed through a 0.45 μm pore size PTFE membrane syringe filter and dried under a gentle stream of nitrogen. The residue was dissolved in 200 μL

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