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

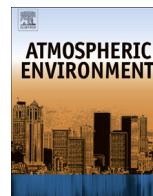2 **AUTHORS**, INCLUDING:

John C Wenger
University College Cork
125 PUBLICATIONS   **2,367** CITATIONS

SEE PROFILE

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

CrossMark

Shouming Zhou [a,b,*], John C. Wenger [a,b]

[a] Department of Chemistry, University College Cork, Cork, Ireland
[b] Environmental Research Institute, University College Cork, Cork, Ireland

HIGHLIGHTS

- Reactions with OH, O_3 and NO_3 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_3 and O_3 reactions.
- Acenaphthylene oxidation products are detected in both gas- and particle-phases.

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_3) and the nitrate (NO_3) radical. Using a relative rate technique the following rate coefficients (in cm^3 $molecule^{-1}$ s^{-1}) were determined at (293 ± 3) K in 1 atm of purified air: $(1.09 \pm 0.07) \times 10^{-10}$, $(3.99 \pm 0.15) \times 10^{-16}$ and $(4.42 \pm 0.32) \times 10^{-12}$ for the reactions with OH, O_3 and NO_3 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_3 and O_3 were predominantly oxygenated compounds arising from reaction at the C=C bond in the cylcopenta-fused ring of ace-naphthylene. 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_3. 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.

© 2013 Elsevier Ltd. All rights reserved.

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_3) 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.
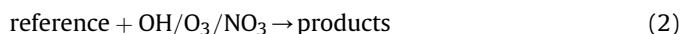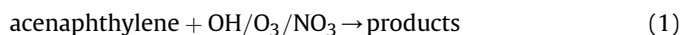E-mail address: szhou@chem.utoronto.ca (S. Zhou).

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 O₃ 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, O₃ and NO₃. 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, O₃ and NO₃ 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, O₃ or NO₃:

$$\text{acenaphthylene} + \text{OH/O}_3\text{/NO}_3 \rightarrow \text{products} \qquad (1)$$

$$\text{reference} + \text{OH/O}_3\text{/NO}_3 \rightarrow \text{products} \qquad (2)$$

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

$$\text{acenaphthylene} + \text{wall loss} + \text{h}\nu \rightarrow \text{products} \qquad (3)$$
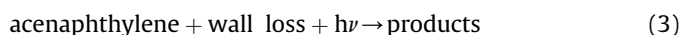
Test experiments showed that wall loss and the combination of wall loss and photolysis obeyed first order kinetics. No wall deposition or photolysis was observed for the reference compounds used in the experiments. The rate equations for reactions (1)–(3) were combined and integrated resulting in the following expression:

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

where $[\text{acenaphthylene}]_0$ and $[\text{reference}]_0$ are the initial concentrations of acenaphthylene and the reference compound; $[\text{acenaphthylene}]_t$ and $[\text{reference}]_t$ are the corresponding concentrations at time t; k_1 and k_2 are the rate coefficients for reactions of acenaphthylene and the reference compound with OH/O₃/NO₃ respectively; k_3 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 O₃ and NO₃ experiments, where lamps were not used. Plots in the form of Eq. (I) should give straight lines with slopes k_1/k_2 and a zero intercept. The value of k_1 can be derived from the rate coefficient ratios using the known value for k_2.

In OH experiments, the photolysis of H₂O₂ by mercury lamps (Philips TUV 40 W, $\lambda_{\max} = 254$ nm) was used as the source of OH radicals;

$$\text{H}_2\text{O}_2 + \text{h}\nu \rightarrow 2\text{OH} \qquad (4)$$
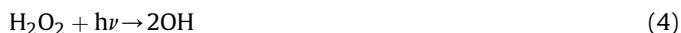
and isoprene was used as the reference compound. For the ozonolysis experiments, ozone was produced as a mixture in O₂ by an ozone generator and added to the chamber containing pre-mixed acenaphthylene, carbon monoxide (100 L to act as a scavenger for OH radicals) and the reference compound cyclopentene. NO₃ radicals were produced by the thermal dissociation of N₂O₅ prepared in solid form according to a literature method (Schott and Davidson, 1958):

$$\text{N}_2\text{O}_5 + \text{M} \leftrightarrow \text{NO}_3 + \text{NO}_2 + \text{M} \qquad (5)$$

N₂O₅ 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 N₂O₅ 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^{13} molecule cm⁻³ 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⁻¹; isoprene at 893.4 and 905.9 cm⁻¹; cyclopentene at 1048 cm⁻¹; 2,3-dimethyl-1,3-butadiene at 894.5 cm⁻¹.

2.2. Product studies

Product studies on the OH, O₃ and NO₃ 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, $\lambda_{\max} = 310$ nm) and 12 Philips TL 05 lamps (40 W, $\lambda_{\max} = 360$ nm). Photolysis of nitrous acid (HONO) under TL 05 lamps was used as the OH radical precursor:

$$\text{HONO} + \text{h}\nu \rightarrow \text{OH} + \text{NO} \qquad (6)$$

Nitrous acid was synthesized by adding a 1% NaNO₂ aqueous solution dropwise into a flask containing 30% sulfuric acid. Ozonolysis and NO₃ 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_x mixing ratio was monitored by a NO_x 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⁻¹ 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
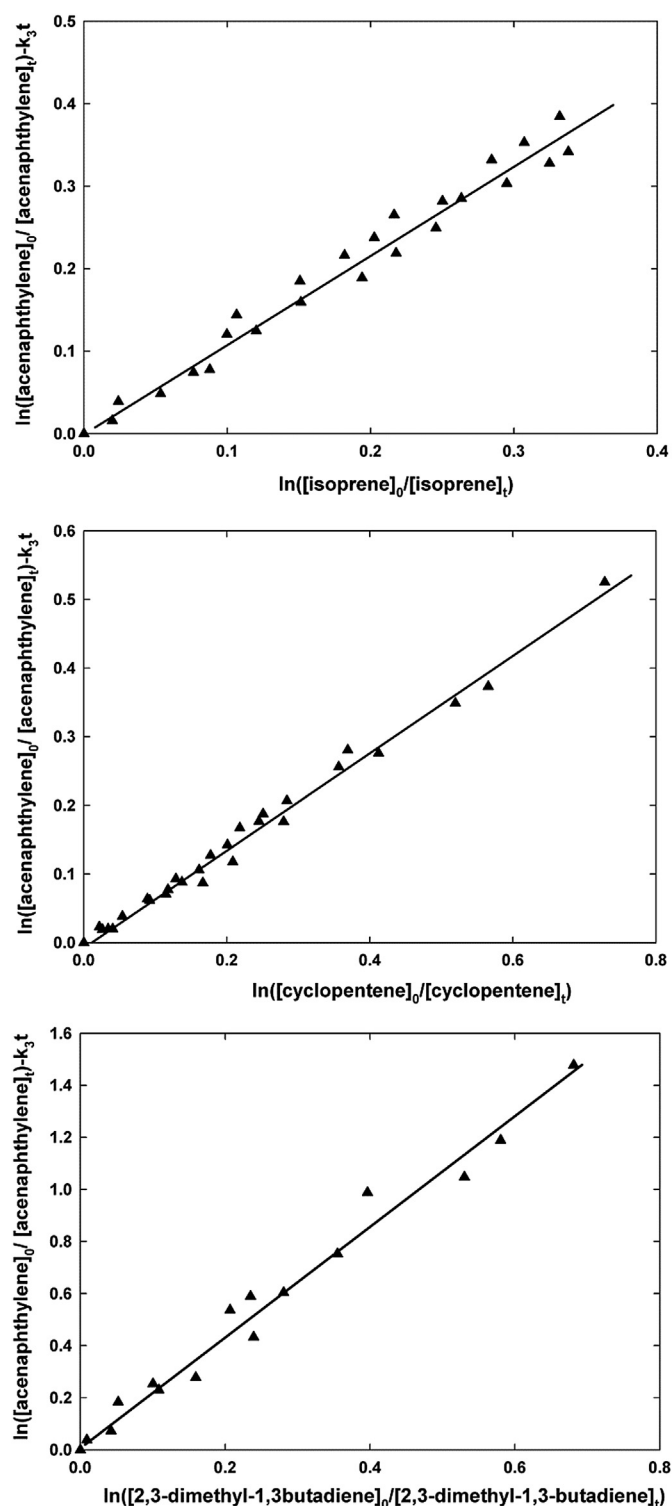
Fig. 1. Plots of the kinetic data according to Eq (I) for the gas phase reaction of OH radicals (top), ozone (middle) and NO₃ radicals (bottom) with acenaphthylene.

methanol followed by gas chromatography–mass spectrometry (GC–MS) analysis using a Varian CP 3800 gas chromatograph interfaced to an ion trap mass spectrometer (Varian Saturn 2000). The GC was equipped with a fused silica capillary column (5% diphenyl, 95% dimethyl-polysiloxane, 0.25 μm film thickness, 0.25 mm internal diameter, and 30 m in length). Helium was used as carrier gas at 1 mL min⁻¹. The GC parameters have been detailed

in our previous work (Zhou and Wenger, 2013). The MS was operated in full scan mode over the range m/z 60–650 using both chemical ionization (CI) and electron ionization (EI). Methane was used as the CI gas at a flow rate of 1.8 mL min⁻¹. Blank denuders and filters were prepared, extracted and analyzed in the same manner.

2.3. Chemicals

Acenaphthylene (>99%, Sigma–Aldrich), isoprene (99%, Sigma–Aldrich), CO (99%, BOC Gases), methanol (HPLC grade, Sigma–Aldrich), H_2O_2 (50 wt.%, Sigma–Aldrich), cyclopentene (≥95%, Fluka), 2,3-dimethyl-1,3-butadiene (≥95%, Fluka), sodium nitrite (≥99%, Merck), sulfuric acid (Sigma–Aldrich) and NO_2 (≥98.5%, Fluka).

3. Results and discussion

3.1. Kinetic studies

The kinetic data obtained for the reactions of OH, O_3 and NO_3 with acenaphthylene were plotted according to Eq. (I). The plots, shown in Fig. 1 represent results obtained from three experiments and exhibit good linearity with near-zero intercepts. The following rate coefficient ratios (k_1/k_2) were obtained by least squares analysis of the data: 1.08 ± 0.07, 0.70 ± 0.03 and 2.10 ± 0.15 for reaction with OH, O_3 and NO_3, where the errors are twice the standard deviation arising from the linear regression analysis. The rate coefficients (k_1) for the reactions of acenaphthylene with OH, O_3 and NO_3 were placed on an absolute basis using the following rate coefficients (in cm^3 molecule⁻¹ s⁻¹) for the reference compounds; k_2 (OH + isoprene) = 1.01×10^{-10} (Atkinson, 1994), k_2 (O_3 + cyclopentene) = 5.7×10^{-16} (Atkinson and Arey, 2003) and k_2 (NO_3 + 2,3-dimethyl-1,3-butadiene) = 2.1×10^{-12} (Atkinson, 1997). The resulting rate coefficients are listed in Table 1 together with the available literature data. The indicated errors in k_1 do not include the uncertainties in the rate coefficients for the reference compounds (k_2), which may add up to a further 20% to the error reported in k_1.

As shown in Table 1, the rate coefficient for reaction with OH obtained in the present work is in very good agreement with the two previously reported values. There is also a reasonable level of agreement for the NO_3 reaction. It has been reported that the kinetics for NO_3 radical reactions with gas-phase PAHs including naphthalene (Atkinson et al., 1994), alkylnaphthalenes (Atkinson and Aschmann, 1988; Atkinson, 1991; Phousongphouang and Arey, 2003) and acenaphthene (Atkinson and Aschmann, 1988; Zhou and Wenger, 2013), are dependent on the NO_2 concentration.
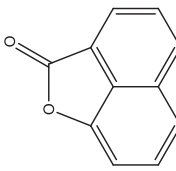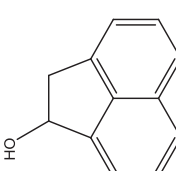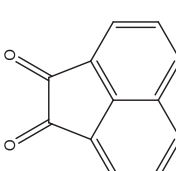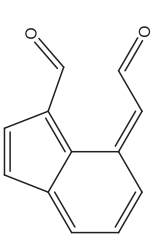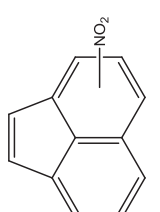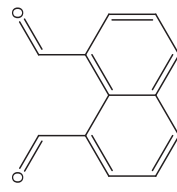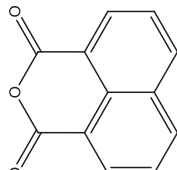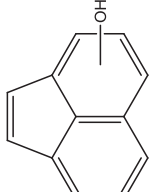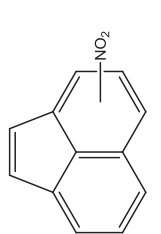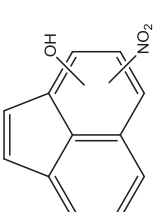
Table 1
Rate coefficients (k_1) for the gas-phase reactions of OH, O_3 and NO_3 with acenaphthylene.

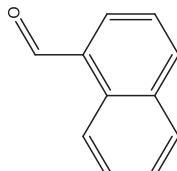|	k_1[a] (cm^3 molecule⁻¹ s⁻¹)	Temperature (K)	Reference
OH	$(1.09 \pm 0.07) \times 10^{-10}$	293 ± 3	This work
	$(1.10 \pm 0.11) \times 10^{-10}$	296 ± 2	Atkinson and Aschmann, 1988
	$(1.24 \pm 0.07) \times 10^{-10}$	296 ± 2	Reisen and Arey, 2002
O_3	$(3.99 \pm 0.15) \times 10^{-16}$	293 ± 3	This work
	5.5×10^{-16}	296 ± 2	Atkinson and Aschmann, 1988
	$(1.6 \pm 0.1) \times 10^{-16}$	296 ± 2	Reisen and Arey, 2002
NO_3	$(4.42 \pm 0.32) \times 10^{-12}$	293 ± 3	This work
	$(5.4 \pm 0.8) \times 10^{-12}$	296 ± 2	Atkinson and Aschmann, 1988

[a] The indicated errors in k_1 do not include the uncertainties in the rate coefficients for the reference compounds (k_2), which may add up to a further 20% to the error reported in k_1.

Table 2
Products identified by GC–MS from the gas-phase reaction of acenaphthylene with OH, O_3 and NO_3.[a] Products 4, 5, 10 and 11 were identified from comparison of their retention times and mass spectra with those of authentic standards. All other products were tentatively identified based upon careful interpretation of the EI and CI mass spectra and comparison with previous studies.

2. Oxaacenaphthylen-2-one (OH,O_3,NO_3(g,p))

3. 1-Acenaphthenone (OH,NO_3(g,p))

4. 1-Acenaphthenol (OH(g))

5. Acenaphthenequinone (OH,NO_3(g,p))

6. Dialdehyde (OH,NO_3(g,p))

7. Nitroacenaphthylene (OH(p))

8. Naphthalene-1,8-dicarbaldehyde (OH,O_3,NO_3(g,p))

10. 1,8-Naphthalic anhydride (OH,NO_3(g,p))

11. 1-Naphthaldehyde (O_3(g,p))

12. Acenaphthylenol (NO_3(g,p))

14. Nitroacenaphthylene (NO_3(g))

15. Nitroacenaphthylenol (NO_3(g))

[a] Terms in brackets indicate that the product was identified in the OH, O_3 or NO_3 reaction, gas-phase (g), particle-phase (p).

This is explained by addition of NO_3 to the aromatic rings to form unstable NO_3-PAH adducts, which either decompose back to the reactants or combine with NO_2 or O_2 (Atkinson et al., 1994; Phousongphouang and Arey, 2003; Wang et al., 2009; Zhou and Wenger, 2013), with the reaction of NO_3-PAH adducts with NO_2 dominating at NO_2 mixing ratios greater than about 80 ppbv (Wang et al., 2009). In contrast, the kinetics of the NO_3 radical reaction with acenaphthylene is found to be independent of NO_2 mixing ratios (Atkinson and Aschmann, 1988) presumably because the reaction of acenaphthylene with NO_3 mainly proceeds via the addition of NO_3 to the unsaturated carbon–carbon double bond (C=C) in the cyclopenta-fused ring, with NO_3 addition to the aromatic ring being less important. This is confirmed in product studies of the NO_3 reaction and is discussed below.

From Table 1 it is clear that some discrepancy exists between the various determinations of the ozonolysis rate coefficient. In the first study of the reaction of acenaphthylene with O_3, Atkinson and Aschmann (1988) reported a rate coefficient of 5.5×10^{-16} cm^3 molecule^{-1} s^{-1} with an estimated overall uncertainty of a factor of 2. However, the reaction was performed without an OH radical scavenger and it is therefore likely that the measured loss of acenaphthylene included a contribution from the reaction with OH, i.e. the reported ozonolysis rate coefficient is likely overestimated. The observed difference between the values obtained in the present work and by Reisen and Arey (2002) is more difficult to explain since both studies employed a relative rate method and an OH scavenger. Although more detailed measurements may help to resolve this discrepancy, the observed level of agreement seems
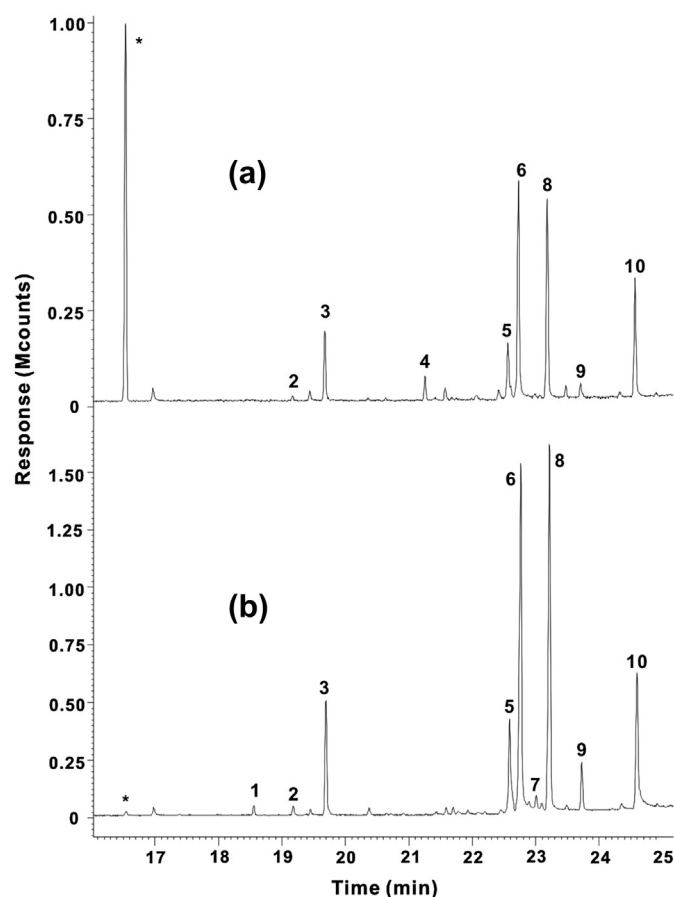
Fig. 2. GC–MS EI total ion chromatograms of denuder (a) and filter (b) samples from the OH-initiated oxidation of acenaphthylene (* denotes acenaphthylene).

fairly reasonable, given the difficulties associated with performing gas-phase kinetic experiments on compounds like acenaphthylene, which have low volatility.

3.2. Product studies

Gas- and particle-phase reaction products were determined by GC–MS analysis of the denuder and filter samples respectively. Representative total ion chromatograms are shown in Figs. 2–4. Wherever possible, reaction products were identified by comparing the mass spectra with those obtained from authentic standards.

However, most of the reaction products were not commercially available and their tentative identification was therefore based upon careful interpretation of the EI and CI mass spectra and the use of mass spectral libraries, whilst taking into account the results from previous studies (Arey et al., 1989; Banceau et al., 2001; Reisen and Arey, 2002). The identified products are listed in Table 2 and their corresponding mass spectra are shown in Figs. S1–S13 (Supporting information). It should be noted that a small amount of acenaphthylene was always observed in the particle-phase in the OH and NO₃ radical reactions (Figs. 2 and 4), presumably due to its partitioning from the gas-phase after aerosol was formed. Although
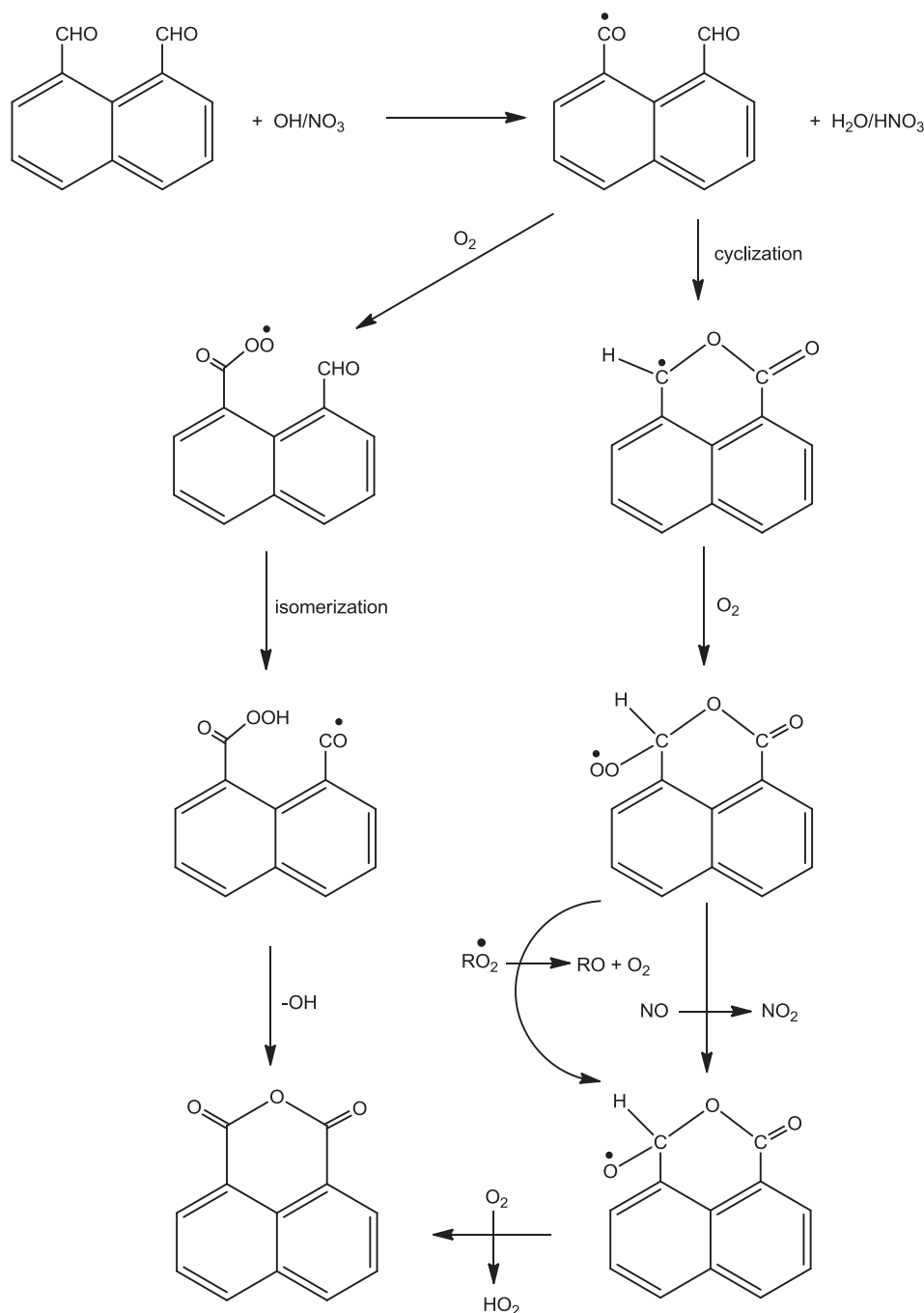
Scheme 1. Proposed mechanism for the formation of 1,8-naphthalic anhydride from the reaction of naphthalene-1,8-dicarbaldehyde with OH and NO₃ radicals. Under the experimental conditions in this work, the peroxy radicals (RO₂) react with NO during the OH initiated oxidation, but undergo self- or cross-reactions during the NO₃ initiated oxidation.

particle-phase reaction of acenaphthylene is also possible within the chamber, at such small amounts it is unlikely to influence the distribution of the products to a significant extent.

3.3. OH radical reaction

A total of eight products were identified in the total ion chromatograms obtained for the OH radical reaction (Fig. 2 and Table 2). Prominent peaks were observed for products **6** and **8**, which, based on their mass spectra (Figs. S6 and S9), are structurally similar isomers with molecular weight (MW) 184. The loss of 29 amu (CHO) in the EI mass spectra suggests the presence of an aldehyde or aromatic −OH group and a further loss of 28 amu (CO) is also indicative of a carbonyl group. The mass spectra are consistent with the two products of MW 184 identified by Reisen and Arey (2002): a dialdehyde formed by OH radical addition to the six-membered ring of acenaphthylene and naphthalene-1,8-dicarbaldehyde. As described below, product **8** was also observed as one of the major products in the ozonolysis of acenaphthylene, where reaction occurs only at the C=C bond. Product **8** is thus identified as naphthalene-1,8-dicarbaldehyde and product **6** is attributed to a dialdehyde (Table 2).

Products **3**, **5**, **9** and **10** showed reasonably intense peaks in the chromatograms (Fig. 2). The mass spectra of product **3** (Fig. S3) indicate a MW 168 and the loss of 28 amu (CO) suggests the presence of a carbonyl moiety. The same compound was observed as one of the major products in the reactions of acenaphthene with OH and NO$_3$ performed in the same chamber (Zhou and Wenger, 2013) and is identified as 1-acenaphthenone. Banceau et al. (2001) also reported 1-acenaphthenone formation in the reaction of acenaphthylene with OH and although Reisen and Arey (2002) identified a product with MW 168, it was attributed to an epoxide, which was also observed using API-MS in their study. However, the chromatograms presented in the latter work clearly show that this product was also generated in the reaction of acenaphthene with OH. The authors did not provide an explanation for this observation, but noted that the GC−MS results for the acenaphthylene/OH reaction were somewhat inconsistent (Reisen and Arey, 2002). The mass spectra of product **5** (Fig. S5) suggest a MW 182 and show successive losses of 28 amu (CO) indicating the presence of two carbonyl groups. Based on the mass fragmentation patterns (Fig. S5) and previous studies (Calvert et al., 2002; Banceau et al., 2001), product **5** is thus identified as acenaphthenequinone. Product **9** is difficult to identify since the CI mass spectrum (Fig. S8) does not provide a clear indication of the MW; while the CI and EI mass spectra for product **10** (Fig. S9) suggest a MW 198 with loss of 44 amu (CO$_2$) and 28 amu (CO), consistent with that of 1,8-naphthalic anhydride, also identified in previous studies (Banceau et al., 2001; Reisen and Arey, 2002; Lee and Lane, 2010).

The other identified products, **1**, **2**, **4** and **7**, have relatively small peaks in the chromatograms (Fig. 2). **1** and **2** are major products of the reactions of acenaphthylene with O$_3$ and NO$_3$ respectively, and details concerning their identification are provided below. Product **4** is also observed in the reaction of acenaphthene with OH, where it is identified as acenaphthenol, formed by OH radical attack on the aromatic ring of acenaphthene (Reisen and Arey, 2002; Zhou and Wenger, 2013). The mass spectra of product **7** reveal that its MW is 197 and, based on previous studies (Arey et al., 1989; Reisen and Arey, 2002), is attributed to an isomer of nitroacenaphthylene, probably 4-nitroacenaphthylene (Arey et al., 1989).

Formation of the major products from the OH radical reaction can be explained by the reaction mechanism proposed by Reisen and Arey (2002). Addition of the OH radical to the aromatic ring followed by subsequent reactions can account for the ring-opening dialdehyde and nitroacenaphthylene. It is interesting to note that

another expected product from this reaction pathway, acenaphthylenol, was not identified in this work or by Reisen and Arey (2002). This observation is also consistent with the low yields of naphthols produced from reaction of OH with naphthalene (Sasaki et al., 1997) and confirms that production of phenolic compounds from the OH-initiated oxidation of PAHs is much less important than for the monoaromatics (Calvert et al., 2002). The other main reaction pathway is addition of the OH radical to the unsaturated cyclopenta-fused ring of acenaphthylene followed by reaction with O$_2$ to yield naphthalene-1,8-dicarbaldehyde as the principal product (Reisen and Arey (2002, 2002) suggested that the other main product detected by GC−MS, 1,8-naphthalic anhydride, was an artifact generated from more labile species during sampling and analysis. Here, it is proposed that this product could be formed from further reaction of naphthalene-1,8-dicarbaldehyde, as outlined in Scheme 1. The reaction pathways are analogous to those of the structurally similar compound phthaldialdehyde, which produces phthalic anhydride during reaction with OH (Wang et al., 2006). The formation of the remaining products is more difficult to explain. It should be noted that acenaphthene was present as a low-level impurity during the reactions and may contribute to several of the observed products, *i.e.* product **2** (oxaacenaphthylen-2-one), **3** (1-acenaphthenone) and **4** (acenaphthenol) (Zhou and Wenger, 2013). However, the moderate intensity of product **3** in Fig. 2 cannot be explained by reaction of OH with small amounts of acenaphthene impurity, suggesting that 1-acenaphthenone mainly originates from the OH-initiated oxidation of acenaphthylene. Moreover, co-production of acenaphthenequinone (product **5**), which is observed in the OH and NO$_3$ reactions (Fig. 4) could be due
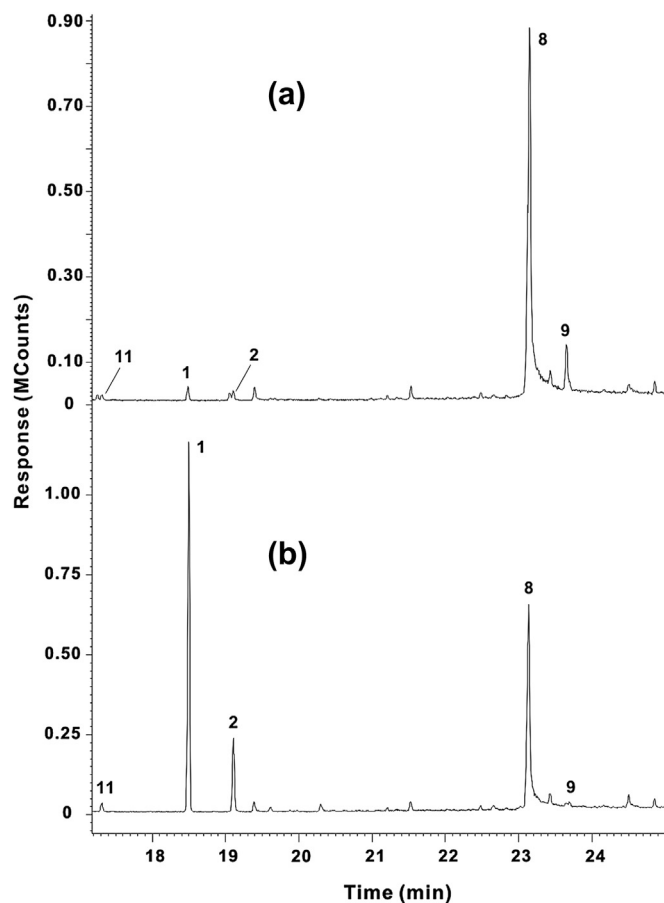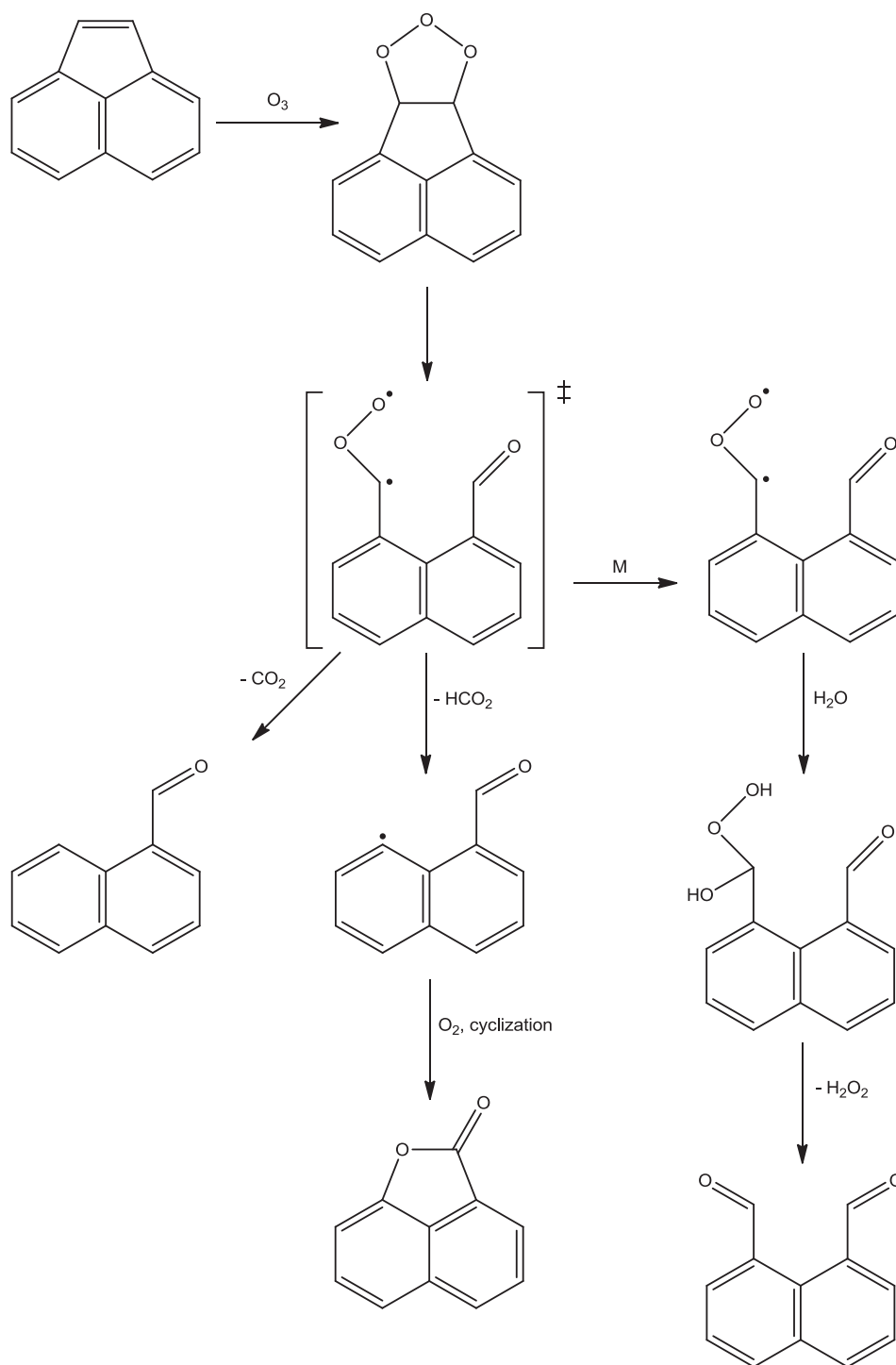

Fig. 3. GC−MS EI total ion chromatograms of denuder (a) and filter (b) samples from the O$_3$-initiated oxidation of acenaphthylene.

Scheme 2. Possible mechanism for the formation of 1-naphthaldehyde, oxaacenaphthylen-2-one and naphthalene-1,8-dicarbaldehyde from the gas-phase ozonolysis of acenaphthylene.

to further reaction of 1-acenaphthenone or thermal decomposition of nitroacenaphthylene as discussed below, for the NO_3 reaction.

3.4. O_3 reaction

A total of five products have been identified in the total ion chromatograms obtained for the reaction with ozone (Fig. 3 and Table 2). Three of them, oxaacenaphthylen-2-one (product **2**), naphthalene-1,8-dicarbaldehyde (product **8**), and naphthaldehyde

(product **11**), were also reported by Reisen and Arey (2002), who attributed these products to decomposition of a secondary ozonide generated in the reaction, which was observed by API-MS but absent in GC–MS analyses. Although a similar explanation may be offered here, it should be noted that these products could also be formed from reactions of the Criegee Intermediate generated from ozone addition to the C=C bond in the unsaturated cyclopentafused ring of acenaphthylene, as shown in Scheme 2. Product **9** was also observed as a significant gas-phase product, and

although its identity remains unknown, the fact that it is observed in the ozonolysis reaction indicates that it is produced from reaction at the C=C bond in the unsaturated cyclopentafused ring of acenaphthylene. The mass spectra of product 1 (Fig. S1), which is much more abundant in the particle phase, indicate a MW 186 and show losses of 15 amu (CH$_3$) and 31 amu (OCH$_3$). A detailed search of mass spectral databases suggests two possibilities for the identity of this product, methyl-1-naphthoate or 8-methoxy-1-naphthaldehyde. Neither of these compounds is likely to be produced in the chamber during the reaction process and following Sauret-Szczepanski and Lane (2004), it is proposed that product 1 is an artifact generated from the reaction of a labile product with the extraction reagent, methanol. Possible candidates for the identity of the labile product includes the secondary ozonide or a hydroperoxide.

3.5. NO$_3$ radical reaction

A total of nine products have been identified in the total ion chromatograms obtained for the NO$_3$ reaction (Fig. 4). In the gas-phase, prominent peaks were observed for 1-acenaphthenone (product 3), acenapthenequinone (product 5), product 9 and 1,8-naphthalic anhydride (product 10). The GC–MS data shows two major products in the particle-phase, 2 and 12. CI and EI mass spectra for product 2 (Fig. S2) indicate a MW 170 with two successive losses of 28 amu (CO), suggesting the presence of two carbonyl groups or an aromatic pyranone similar to dibenzopyranone formed from OH reaction with phenanthrene (Lee and Lane, 2010). A plausible dicarbonyl compound with MW 170 does not

Fig. 4. GC–MS EI total ion chromatograms of denuder (a) and filter (b) samples from the NO$_3$-initiated oxidation of acenaphthylene (* denotes acenaphthylene).

exist and product 2 is thus attributed to oxaacenaphthylen-2-one, which was also identified as a significant particle-phase product during the ozonolysis reaction. The mass spectra of product 12 indicate a MW 168 and the loss of 29 amu (HCO) suggests the presence of an aldehyde or −OH group attached to the aromatic ring (Fig. S10). The difference in MW between acenaphthylene and product 12 is 16 suggesting addition of an oxygen atom to the acenaphthylene molecule and product 12 is therefore identified as acenaphthylenol. Two nitro-PAHs were identified among the other products. Product 14 has a MW of 197 and exhibits fragments corresponding to loss of 30 amu (NO), 47 amu (HNO$_2$), suggesting an isomer of nitroacenaphthylene as the likely identity of this product. The CI and EI mass spectra of product 15 indicate the presence of an OH group (loss of 17 from the molecular ion in the CI mass spectrum) and NO$_2$ (loss of 46 from the molecular ion in the EI mass spectrum) (Fig. S12) and is therefore attributed to nitro-acenaphthylenol, MW 213. In addition, naphthalene-1,8-dicarbaldehyde was observed as a minor product in the gas- and particle-phases while products 13 and 16 remain unidentified (CI and EI mass spectra of these two products are given in Figs. S11 and S13, respectively).

In the only previous product study of the reaction of NO$_3$ with acenaphthylene, Arey et al. (1989) observed trace levels of nitroacenaphthylene isomers and concluded that the major products were oxygenated compounds. These results are in good agreement with those obtained here. The reaction pathways leading to the formation of acenaphthylenol, nitroacenaphthylene and nitroacenaphthylenol, are likely to be analogous to those proposed for the reaction of NO$_3$ with naphthalene (Sasaki et al., 1997), where the initial step involves addition of NO$_3$ to the aromatic ring followed by subsequent reaction with NO$_2$, O$_2$ or decomposition.

However, kinetic studies indicate that addition of NO$_3$ to the aromatic ring is of minor importance and the principal pathway is NO$_3$ addition to the C=C double bond in the cyclopenta-fused ring. A simplified reaction mechanism, based on the current understanding of NO$_3$ reactivity toward alkenes (Atkinson and Arey, 2003), is proposed in Scheme 3. Organo-nitrates are among the expected reaction products, however, they were not detected by GC–MS, suggesting that either the GC–MS has low sensitivity to these species or that they may have undergone thermal decomposition during the analytical procedure yielding some of the other identified products such as acenaphthenequinone, oxaacenaphthylen-2-one and 1-acenaphthenone. The decomposition of nitrates could also possibly account for the formation of 1,8-naphthalic anhydride, however, it seems more likely that this is a secondary product arising from the reaction of naphthalene-1,8-dicarbaldehyde with NO$_3$, as outlined in Scheme 1. Finally, the formation of acenaphthenequinone from further reaction of 1-acenaphthenone cannot be excluded.

3.6. Atmospheric implications

The rate coefficients determined in this study can be used to estimate the atmospheric lifetime of acenaphthylene. Assuming typical tropospheric concentrations (in molecule cm^{-3}) of OH (12 h daytime average = 2×10^6 (Prinn et al., 1995)), O$_3$ (24 h average = 7×10^{11} (Logan, 1985)) and NO$_3$ (12 h night-time average = 5.4×10^8 (Shu and Atkinson, 1995)), the atmospheric lifetimes of acenaphthylene with respect to gas-phase reaction with OH, O$_3$ and NO$_3$ are estimated to be 1.3 h, 1 h and 7 min, respectively. These short lifetimes indicate that, following emission into the atmosphere, acenaphthylene will react quickly and contribute to the formation of secondary pollutants, such as ozone, nitrates and SOA, on the local to regional scale. The atmospheric degradation products of the OH-initiated oxidation of acenaphthylene are naphthalene-1,8-
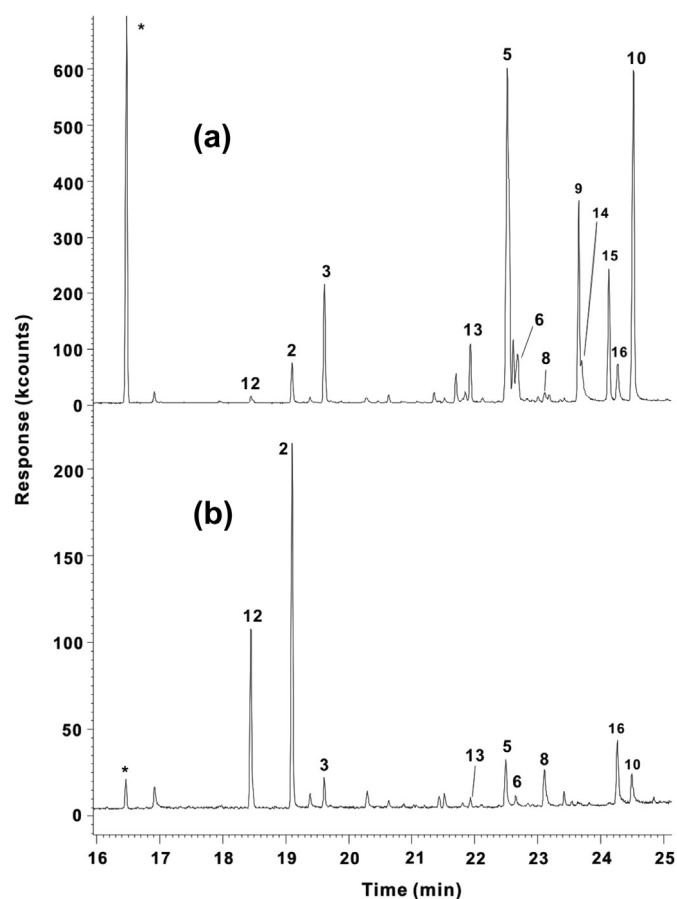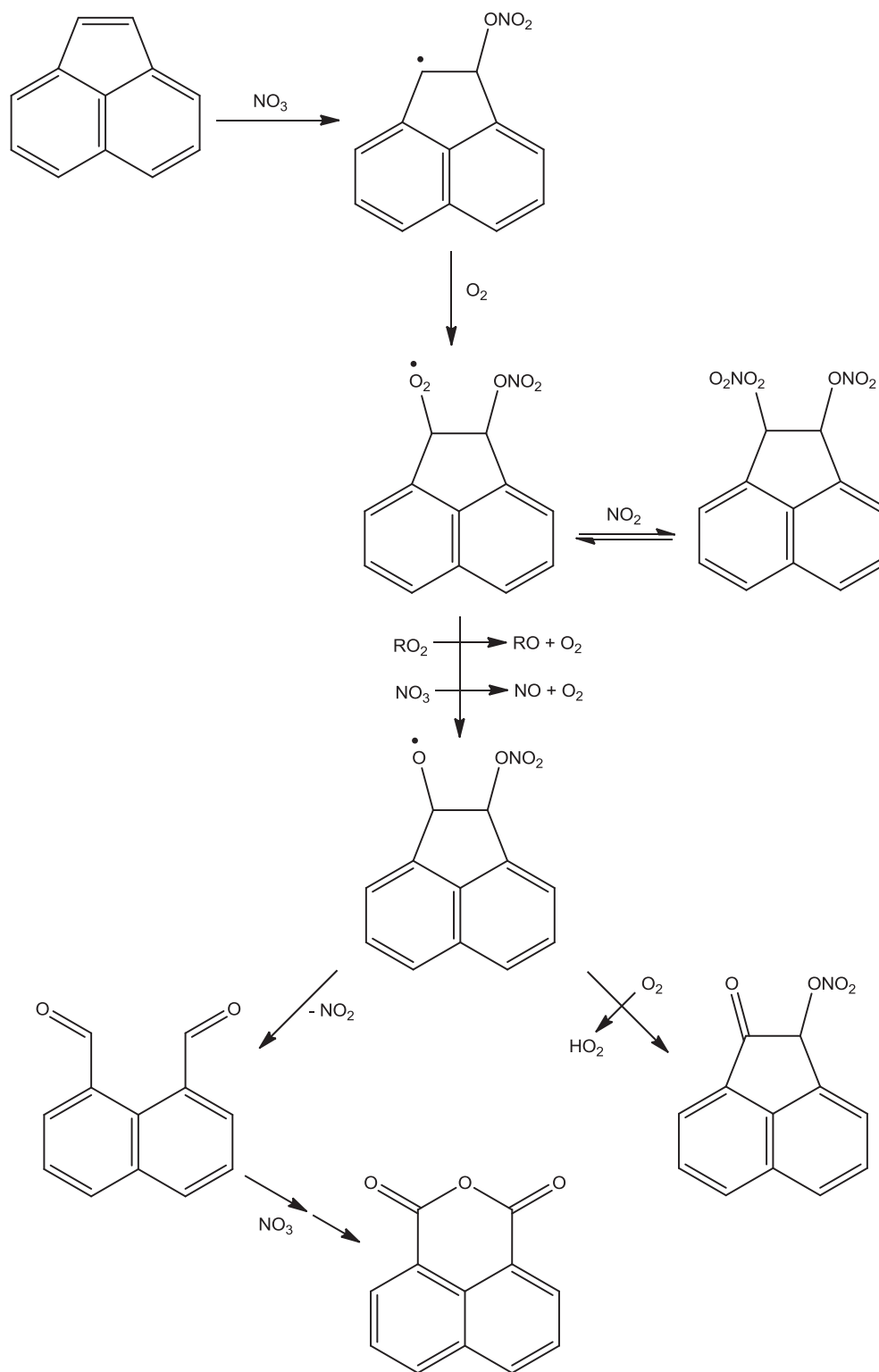
Scheme 3. Proposed mechanism for the addition of NO$_3$ to the unsaturated cylcopenta-fused ring of acenaphthylene.

dicarbaldehyde, 1,8-naphthalic anhydride and a 10 carbon ring-opened dialdehyde. The products arising from the reaction with NO$_3$ and O$_3$ are predominantly oxygenated compounds arising from reaction at the C=C bond in the cylcopenta-fused ring. Under atmospheric conditions, these products are expected to react further with OH or NO$_3$ radicals and some may also undergo photolysis by sunlight (Atkinson and Arey, 2003). Reaction at the aromatic ring

and subsequent formation of hydroxylated and nitro-PAHs appears to be a very minor reaction pathway. Nevertheless, nitro-PAHs are known to be mutagenic and carcinogenic (Atkinson and Arey, 1994) indicating that acenaphthylene emissions could affect human health. The potential toxicity of the oxidation products is further enhanced by the presence of acenaphthenequinone, which has been shown to generate reactive oxygen species (ROS) at the cellular level

and might play a role in human lung inflammatory disease (Chung et al., 2006, 2007).

The results from this study indicate that most of the acenaphthylene oxidation products are semi-volatile and will be distributed between the gas and particle phases, according to variations in temperature and the availability of existing particle mass. A small number of products, e.g. acenaphthylenol and oxaacenaphthylen-2-one, are relatively more abundant in the particle phase, and may thus be involved in SOA formation and growth. However, it remains uncertain whether or not some of these species are genuine oxidation products or generated from thermal decomposition of more labile compounds during GC—MS analysis. Further experimental work using alternative techniques, such as PTR-TOF-MS and LC-MS for analysis of the gas- and particle-phase products respectively, should help to clarify this issue and also possibly provide information on the yields of the various products.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.04.049.

References

Arey, J., Zielinska, B., Atkinson, R., Aschmann, S.M., 1989. Nitroarene products from the gas-phase reactions of volatile polycyclic aromatic hydrocarbons with the OH radical and N_2O_5. Int. J. Chem. Kinet. 21, 775—799.

Atkinson, R., 1994. Gas-phase tropospheric chemistry of organic compounds. J. Phys. Chem. Ref. Data Monogr. 2, 1—216.

Atkinson, R., 1997. Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes. J. Phys. Chem. Ref. Data 26, 215—290.

Atkinson, R., Arey, J., 1994. Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: formation of atmospheric mutagens. Environ. Health Perspect. 102, 117—126.

Atkinson, R., Arey, J., 2003. Atmospheric degradation of volatile organic compounds. Chem. Rev. 103, 4605—4638.

Atkinson, R., Arey, J., 2007. Mechanisms of the gas-phase reactions of aromatic hydrocarbons and PAHs with OH and NO_3 radicals. Polycycl. Aromat. Comp. 27, 15—40.

Atkinson, R., Aschmann, S.M., 1988. Kinetics of the gas phase reactions of acenaphthene and acenaphthylene and structurally-related aromatic compounds with OH and NO_3 radicals, N_2O_5 and O_3 at 296 ± 2 K. Int. J. Chem. Kinet. 20, 513—539.

Atkinson, R., Tuazon, E.C., Bridier, I., Arey, J., 1994. Reactions of NO_3-naphthalene adducts with O_2 and NO_2. Int. J. Chem. Kinet. 26, 605—614.

Banceau, C.E., Mihele, C., Lane, D.A., Bunce, N.J., 2001. Reactions of methylated naphthalenes with hydroxyl radicals under simulated atmospheric conditions. Polycycl. Aromat. Comp. 18, 415—425.

Calvert, J.G., Atkinson, R., Becker, K.H., Kamens, R.M., Seinfeld, J.H., Wallington, T.J., Yarwood, G., 2002. The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons. Oxford University Press, Oxford.

Cousins, I.T., Mackay, D., 2001. A critical review of gas-particle partitioning of organic compounds and its interpretation using relative solubilities. Environ. Sci. Technol. 35, 643—647.

Chan, A.W.H., Kautzmanm, K.E., Chhabra, P.S., Surratt, J.D., Chan, M.N., Crounse, J.D., Kürten, A., Wennberg, P.O., Flagan, R.C., Seinfeld, J.H., 2009. Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs). Atmos. Chem. Phys. 9, 3049—3060.

Chung, S.W., Chung, H.Y., Toriba, A., Kameda, T., Tang, N., Kizu, R., Hayakawa, K., 2007. An environmental quinoid polycyclic aromatic hydrocarbon, acenaphthenequinone, modulates cyclooxygenase-2 expression through reactive oxygen species generation and nuclear factor kappa B activation in A549 cells. Toxicol. Sci. 95, 348—355.

Chung, M.Y., Lazaro, R.A., Lim, D., Jackson, J., Lyon, J., Rendulic, D., Hasson, A.S., 2006. Aerosol-borne quinones and reactive oxygen species generation by particulate matter extracts. Environ. Sci. Technol. 40, 4880—4886.

Finlayson-Pitts, B.J., Pitts, J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, San Diego.

Healy, R.M., Wenger, J.C., Metzger, A., Duplissy, J., Kalberer, M., Dommen, J., 2008. Gas/particle partitioning of carbonyls in the photooxidation of isoprene and 1,3,5-trimethylbenzene. Atmos. Chem. Phys. 8, 3215—3230.

Kourtchev, I., Bejan, I., Sodeau, J.R., Wenger, J., 2009. Gas phase reaction of (E)-beta-farnesene with ozone: rate coefficient and carbonyl gas phase products. Atmos. Environ. 43, 3182—3190.

Lee, J., Lane, D.A., 2010. Formation of oxidized products from the reaction of gaseous phenanthrene with the OH radical in a reaction chamber. Atmos. Environ. 44, 2469—2477.

Logan, J.A., 1985. Tropospheric ozone: seasonal behavior, trends, and anthropogenic influence. J. Geophys. Res. 90, 10463—10482.

Nishino, N., Arey, J., Atkinson, R., 2009. Yields of glyoxal and ring-cleavage co-products from the OH radical-initiated reactions of naphthalene and selected alkylnaphthalenes. Environ. Sci. Technol. 43, 8554—8560.

Phousongphouang, P.T., Arey, J., 2003. Rate constants for the gas-phase reactions of a series of alkylnaphthalenes with the nitrate radical. Environ. Sci. Technol. 37, 308—313.

Prinn, R.G., Weiss, R.F., Miller, B.R., Huang, J., Alyea, F.N., Cunnold, D.M., Fraser, P.J., Hartley, D.E., Simmonds, P.G., 1995. Atmospheric trends and lifetime of CH_3CCl_3 and global OH concerns. Science 269, 187—192.

Ravindra, K., Sokhi, R., Grieken, R.V., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42, 2895—2921.

Reisen, F., Arey, J., 2002. Reactions of hydroxyl radicals and ozone with acenaphthene and acenaphthylene. Environ. Sci. Technol. 36, 4302—4311.

Sasaki, J., Aschmann, S.M., Kwok, E.S.C., Atkinson, R., Arey, J., 1997. Products of the gas-phase OH and NO_3 radical-initiated reactions of naphthalene. Environ. Sci. Technol. 31, 3173—3179.

Sauret-Szczepanski, N., Lane, D.A., 2004. Smog chamber study of acenaphthene: gas-particle partition measurements of the products formed by reaction with the OH radical. Polycycl. Aromat. Comp. 24, 161—172.

Schott, G., Davidson, N., 1958. Shock waves in chemical kinetics: the decomposition of N_2O_5 at high temperatures. J. Am. Chem. Soc. 80, 1841—1853.

Shakya, K.M., Griffin, R.J., 2010. Secondary organic aerosol from photooxidation of polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 44, 8134—8139.

Shu, Y., Atkinson, R., 1995. Atmospheric lifetimes and fate of a series of sesquiterpenes. J. Geophys. Res. 100, 7275—7281.

Temime, B., Healy, R.M., Wenger, J.C., 2007. A denuder-filter sampling technique for the detection of gas and particle phase carbonyl compounds. Environ. Sci. Technol. 41, 6514—6520.

Thüner, L., Bardini, P., Rea, G.J., Wenger, J.C., 2004. Kinetics of the gas-phase reactions of OH and NO_3 radicals with dimethylphenols. J. Phys. Chem. A 108, 11019—11025.

Wang, L., Arey, J., Atkinson, R., 2006. Kinetic and products of photolysis and reaction with OH radicals of a series of aromatic carbonyl compounds. Environ. Sci. Technol. 40, 5465—5471.

Wang, L., Aschmann, A.M., Atkinson, R., Arey, J., 2009. Effect of NO_2 concentration on product yields of the gas-phase NO_3 radical-initiated reaction of ethyl- and dimethyl-naphthalenes. Environ. Sci. Technol. 43, 2766—2772.

Zhou, S., Wenger, J.C., 2013. Kinetics and products of the gas-phase reactions of acenaphthene with hydroxyl radicals, nitrate radicals and ozone. Atmos. Environ. 72, 97—104.