

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



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HIGHLIGHTS

- ▶ Gas-phase reactions with OH and NO₃ radicals are important degradation processes.
- ▶ Atmospheric oxidation yields a range of ring-retaining and ring-opening products.
- ▶ H-atom abstraction and OH addition are important reaction pathways in OH reactions.
- ▶ Acenaphthene 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 atmospheric oxidation of acenaphthene at (293 ± 3) K in 1 atm of purified air. Rate coefficients for reaction with hydroxyl (OH) radicals, nitrate (NO₃) radicals and ozone have been determined using the relative rate technique. The values obtained for reaction with OH and O₃ were (in units of cm³ molecule⁻¹ s⁻¹) $(9.89 \pm 0.51) \times 10^{-11}$ and $(1.79 \pm 0.10) \times 10^{-19}$ respectively. The rate coefficient for reaction with NO₃ was found to be dependent on NO₂ concentration and is given by $(4.16 \pm 0.70) \times 10^{-13} + (3.45 \pm 1.73) \times 10^{-27}[\text{NO}_2]$ cm³ molecule⁻¹ s⁻¹. A denuder-filter sampling system coupled with off-line GC–MS analysis was used to collect and identify gas- and particle-phase products of the OH and NO₃ initiated oxidation of acenaphthene. For the OH reaction, a range of ring-retaining and ring-opening products were identified in both phases, although some species, including nitroacenaphthene and 1,8-naphthalic anhydride, were found exclusively in the particle phase. In particular, the identification of 1-acenaphthenone and naphthalene-1,8-dicarbaldehyde amongst the products indicates that H-atom abstraction from the cyclopenta-fused ring is an important reaction pathway, along with OH addition to the aromatic ring. For the NO₃ reaction, 1-acenaphthenone and nitroacenaphthene were identified as the major gas- and particle-phase products respectively. Possible reaction mechanisms for the formation of these products are proposed.

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1. Introduction

Acenaphthene, with three rings in its chemical structure, is one of the simplest polycyclic aromatic hydrocarbons (PAHs). It is emitted into the atmosphere from vehicle exhaust and other combustion sources (Finlayson-Pitts and Pitts, 2000; Calvert et al., 2002; Ravindra et al., 2008). Under typical ambient temperatures, acenaphthene is found predominantly in the gas-phase (Finlayson-Pitts and Pitts, 2000; Cousins and Mackay, 2001), and can be

chemically transformed via reaction with the hydroxyl (OH) radical, the nitrate (NO₃) radical and ozone to produce a range of secondary pollutants (Calvert et al., 2002; Atkinson and Arey, 2007), including secondary organic aerosol (SOA) (Shakya and Griffin, 2010). Detailed information on the kinetics and products of the atmospheric degradation of acenaphthene are therefore required in order to fully assess its environmental impact.

A number of previous studies of the atmospheric oxidation of acenaphthene have been reported in the literature. The rate coefficient for reaction with OH radicals has been measured by several research groups (Klöpffer et al., 1986; Atkinson and Aschmann, 1988; Brubaker and Hites, 1998; Banceu et al., 2001; Reisen and Arey, 2002), however, the results are not in good agreement. Rate coefficients for the reactions of acenaphthene with ozone and NO₃

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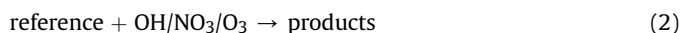
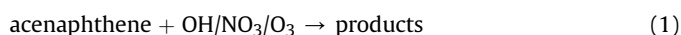
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radicals have only been reported once (Atkinson and Aschmann, 1988). In the first product study of the OH-initiated oxidation of acenaphthene, Banceu et al. (2001) identified a number of products which originated from attack of OH on the cyclopenta-fused ring. However, contrasting results were obtained in subsequent studies (Reisen and Arey, 2002; Sauret-Szczepanski and Lane, 2004), where it was proposed that the reaction proceeds mainly via OH radical addition to the aromatic ring, followed by the formation of ring-opening products. Information on the products of the NO₃ initiated oxidation of acenaphthene is very limited, with nitro-acenaphthene being identified as the only product to date (Arey et al., 1989) and several possible products proposed in the theoretical study of Qu et al. (2008). Clearly, there is a considerable degree of uncertainty concerning the gas-phase atmospheric degradation of acenaphthene. In this work, kinetic studies of the reactions of acenaphthene with OH, NO₃ and ozone have been performed using a relative rate technique and the gas- and particle-phase products of the OH and NO₃ initiated oxidation reactions have been investigated using gas chromatography–mass spectrometry (GC–MS).

2. Materials and methods

2.1. Kinetic studies

Experiments were performed in a 3910 L cylindrical FEP Teflon chamber at (293 ± 3) K and 1 atm of purified air at a relative humidity of 1–3%. The chamber is equipped with fans to ensure rapid mixing of reactants, ports for the introduction of reactants and sampling of products, and a variety of lamps for photolysis. A detailed description of the chamber can be found elsewhere (Thüner et al., 2004; Kourtchev et al., 2009). Rate coefficients for the reactions of OH, NO₃ and O₃ with acenaphthene were determined using a relative rate method in which the decay rate of acenaphthene was measured relative to that of a reference organic compound in the presence of OH, NO₃ or O₃:



During the experiments, acenaphthene was also lost by deposition on the walls of the chamber:



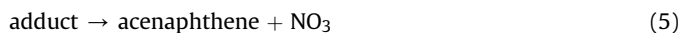
The wall loss rate for acenaphthene was determined by monitoring its decay in the dark over a period of 1–2 h. Similar test experiments showed that the wall loss of the reference compounds was negligible over the timescale of the experiments (2–3 h). The rate equations for reactions (1)–(3) can be combined and integrated to yield the following equation:

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

where [acenaphthene]₀ and [reference]₀ are the concentrations of acenaphthene and reference compound at the start of the reaction; [acenaphthene]_t and [reference]_t are the corresponding concentrations at time *t*; *k*₁, *k*₂ and *k*₃ are the rate coefficients for reactions (1)–(3) respectively. A plot in the form of Eq. (1) is expected to give a straight line with gradient *k*₁/*k*₂, and if *k*₂ is well-known, the value of *k*₁ can therefore be determined.

However, the kinetic analysis for the NO₃ radical reaction is more complicated because the measured rate coefficient is dependent on

the concentration of NO₂ (Atkinson and Aschmann, 1988). Recent studies on other alkylnaphthalenes (Phouongphouang and Arey, 2003; Wang et al., 2009) have shown that addition of NO₃ to the aromatic rings proceeds via the formation of a NO₃-PAH adduct that can decompose to reform the reactants or react with O₂ and/or NO₂ to give products:



For NO₂ mixing ratios up to 50 ppmv, the back-decomposition reaction dominates and the partial rate coefficient for NO₃ addition, *k*_{add}, is:

$$k_{\text{add}} = k_4(k_6[\text{O}_2] + k_7[\text{NO}_2])/k_5 \quad (II)$$

where *k*₄ to *k*₇ are the rate coefficients for reactions (4)–(7) respectively (Atkinson and Aschmann, 1988; Phouongphouang and Arey, 2003; Wang et al., 2009). H-atom abstraction from the cyclopenta-fused ring can also occur and the overall measured rate coefficient, *k*₁, is therefore given by:

$$k_1 = k_{\text{abs}} + k_{\text{add}} = k_{\text{abs}} + k_4(k_6[\text{O}_2] + k_7[\text{NO}_2])/k_5 \quad (III)$$

where *k*_{abs} is the partial rate coefficient for the H-atom abstraction pathway. The reaction of NO₃-PAH adducts with NO₂ dominates at mixing ratios greater than about 80 ppbv (Wang et al., 2009) and, under these conditions, the kinetic treatment is simplified further:

$$k_1 = k_{\text{abs}} + k_4 k_7 [\text{NO}_2] / k_5 \quad (IV)$$

Thus, if *k*₁ is determined using the relative rate technique outlined above, a plot of *k*₁ versus [NO₂] is expected to give a straight line with gradient *k*₄*k*₇/*k*₅ and an intercept *k*_{abs}.

Acenaphthene and the reference compounds were introduced into the reaction chamber using an inlet system in which measured amounts of the reactants were gently heated in a small flow of purified air. Initial mixing ratios of 1.0–2.5 ppmv were employed for the organic compounds in all experiments (1 ppmv = 2.46 × 10¹³ molecule cm⁻³ at 298 K). Isoprene was selected as the reference compound for the OH and NO₃ reactions; methacrolein was used during the ozonolysis reaction. The photolysis of hydrogen peroxide at 254 nm and thermal decomposition of N₂O₅ (Schott and Davidson, 1958) were used as the precursors of OH and NO₃ radicals respectively. Ozonolysis was performed in the presence of CO (7000–7500 ppmv) to act as a scavenger for any OH radicals produced in the reaction system.

The organic compounds were measured throughout the reactions using in situ FTIR spectroscopy. Quantitative analysis was performed by linear subtraction of calibrated reference spectra and subsequent integration of selected absorption bands: acenaphthene (784 cm⁻¹), isoprene (893 and 906 cm⁻¹), methacrolein (934 cm⁻¹). Prior to the start of the experiments, the wall loss rate for acenaphthene was monitored for at least 1 h. FTIR spectroscopy was also used to measure the concentration of NO₂ during the NO₃ relative rate experiments.

2.2. Product studies

Product studies on the OH and NO₃ radical initiated oxidation of acenaphthene were performed at (298 ± 5) K and 1 atm of purified

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