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Gas and particulate phase products from the ozonolysis of acenaphthylene

Matthieu Riva [a, b, d], Robert M. Healy [c, 1], Sophie Tomaz [a, b], Pierre-Marie Flaud [a, b], Emilie Perraudin [a, b], John C. Wenger [c, **], Eric Villenave [a, b, *]

[a] Univ. Bordeaux, EPOC, UMR 5805, F-33405 Talence Cedex, France
[b] CNRS, EPOC, UMR 5805, F-33405 Talence Cedex, France
[c] Department of Chemistry and Environmental Research Institute, University College Cork, Cork, Ireland
[d] Now at the Department of Physics, PO Box 64, 00014, University of Helsinki, Finland

HIGHLIGHTS

- Eight oxygenated naphthalene derivatives are among the reaction products.
- The major reaction products are detected in both gas and particle phases.
- Hydroxyl radical formation appears to be negligible.
- SOA yields in the range 23–37% have been measured.

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are recognized as important secondary organic aerosol (SOA) precursors in the urban atmosphere. In this work, the gas-phase ozonolysis of acenaphthylene was investigated in an atmospheric simulation chamber using a proton transfer reaction time-of-flight-mass spectrometer (PTR-TOF-MS) and an aerosol time-of-flight-mass spectrometer (ATOFMS) for on-line characterization of the oxidation products in the gas and particle phases, respectively. SOA samples were also collected on filters and analyzed by ultra performance liquid chromatography/electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS) and gas chromatography/electron impact ionization-mass spectrometry (GC/EI-MS). The major gas-phase products included a range of oxygenated naphthalene derivatives such as 1,8-naphthalic anhydride, naphthalene 1,8-dicarbaldehyde and naphthaldehyde, as well as a secondary ozonide. Possible reaction mechanisms are proposed for the formation of these products and favoured pathways have been suggested. Many of these products were also found in the particle phase along with a range of oligomeric compounds. The same range of gas and particle phase products was observed in the presence and absence of excess cyclohexane, an OH scavenger, indicating that OH radical production from the ozonolysis of acenaphthylene is negligible. SOA yields in the range 23–37% were determined and indicate that acenaphthylene ozonolysis may contribute to part of the SOA observed in urban areas.

1. Introduction

Aerosols play a major role in many atmospheric processes which impact on regional and global climate (Stevens and Boucher, 2012). They can also participate in heterogeneous chemical reactions thus affecting the abundance and distribution of atmospheric trace gases (Hallquist et al., 2009). From an exposure perspective, atmospheric particulate matter impacts upon human health and is associated with respiratory and cardiovascular diseases (Elder and

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[*] Corresponding author. Univ. Bordeaux, EPOC, UMR 5805, F-33405 Talence Cedex, France.

[**] Corresponding author.

E-mail addresses: j.wenger@ucc.ie (J.C. Wenger), e.villenave@epoc.u-bordeaux1.fr (E. Villenave).

[1] Now at Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment and Climate Change, Toronto, Canada.

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Oberdorster, 2006). A significant fraction of atmospheric aerosol is organic in nature and often dominated by secondary organic aerosol (SOA) formed from the oxidation of volatile organic compounds (VOCs). Although SOA represents a major mass fraction (20–90%) of ambient fine particulate matter ($PM_{2.5}$), current models still predict less SOA than is typically observed during field measurements (Kroll and Seinfeld, 2008; Hallquist et al., 2009). An important part of this underestimation is due to the incomplete consideration of some intermediate volatility organic compounds (IVOCs) as SOA precursors, such as alkanes (Tkacik et al., 2012) and polycyclic aromatic hydrocarbons (Chan et al., 2009).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous compounds in the environment, mainly emitted into the atmosphere from combustion of diesel, gasoline, coal and wood (Ravindra et al., 2008). They are recognized as potential carcinogenic and mutagenic compounds (Atkinson and Arey, 1994) and can be found in the atmosphere, distributed between the gaseous and particulate phases. PAHs existing in the particle phase can undergo heterogeneous oxidation processes (Estève et al., 2003; Perraudin et al., 2007; Miet et al., 2009). However, PAHs with less than four aromatic rings mainly exist in the gas phase and can undergo oxidative degradation via reaction with the different atmospheric oxidants (Keyte et al., 2013) to produce oxygenated and nitro-containing compounds (Lee and Lane, 2009; Kautzman et al., 2010) which can partition to the particle phase and participate in SOA formation (Chan et al., 2009; Shakya and Griffin, 2010; Zhou and Wenger, 2013a,b; Riva et al., 2015a,b).

Acenaphthylene is fairly unique among PAHs as it contains a carbon-carbon double bond in its structure which enables it to react quickly with all atmospheric oxidants including OH and NO_3 radicals, Cl atoms and O_3 (Atkinson and Aschmann, 1988; Reisen and Arey, 2002; Zhou and Wenger, 2013b; Riva et al., 2014). It has been reported that the concentration of acenaphthylene (greater than 20–30 ng m^{-3}) could be comparable to that of naphthalene in certain urban atmospheres (Dejean et al., 2009; Hanedar et al., 2014) suggesting that acenaphthylene might contribute to SOA formation in such areas. Reisen and Arey (2002) performed the first detailed study of the gas phase products arising from ozonolysis of acenaphthylene using both on-line and off-line methods and also reported a preliminary SOA yield of 13%. More recently, Zhou and Wenger (2013b) identified gas and particle phase products using off-line methods, while Dang et al. (2015) performed a computational study to investigate the various reaction pathways for this chemical system. However, some discrepancies exist between the products identified in these studies and further work is needed to clarify the products and reaction mechanisms.

In this work, we have performed a series of simulation chamber experiments to identify products arising from the gas-phase ozonolysis of acenaphthylene using state-of-the-art mass spectrometry techniques for on-line analysis of both gaseous and particulate phases. In addition, filters collected from the chamber experiments were analyzed by ultra performance liquid chromatography/electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS) and gas chromatography/electron impact mass spectrometry (GC/EI-MS). Based on these approaches, an extended and improved reaction mechanism for the ozone-initiated atmospheric oxidation of acenaphthylene is proposed. SOA yields in the presence and absence of an OH radical scavenger are also reported.

2. Experimental section

2.1. Simulation chamber experiments

Experiments were performed in the 3910 L atmospheric simulation chamber at University College Cork, which is described in detail elsewhere (Thüner et al., 2004). Briefly, it is a cylinder consisting of a Teflon FEP foil tube closed with aluminum plates covered with Teflon FEP foil. The chamber is equipped with fans to ensure rapid mixing of reactants (Kourtchev et al., 2009). Before each experiment, the chamber is cleaned by flushing with dried purified air and photolysis of added ozone (ca. 1 ppmv) until the particle number concentration is below 200 cm^{-3}. The flushing also reduces the levels of NO_x and nonmethane hydrocarbons to <10 ppbv. The mixing ratios of NO_x and O_3 are measured using standard automated gas analyzers (Thermo Model 42i and 49i respectively).

Experiments were performed in darkness at room temperature (293 ± 2 K) and atmospheric pressure with relative humidity less than 1%. Acenaphthylene (Sigma-Aldrich, 99%) was introduced into the chamber by passing dry purified air over a heated Pyrex glass bulb containing a known amount of the solid compound. Ozone was generated by flowing oxygen at 2.5 L min^{-1} through an ozone generator (Ozone Services GE60/FM5000). Five experiments were performed using initial mixing ratios of ca. 300 ppbv for both acenaphthylene and ozone. In three of the experiments, 80 ppmv of cyclohexane (Sigma-Aldrich 99.9%) was added as a scavenger for any OH radicals produced during the ozonolysis reaction. Initial conditions and SOA yields are summarized in Table 1.

2.2. On-line chemical characterization

The decay of acenaphthylene and formation of gaseous oxidation products was measured using a proton transfer reaction-time of flight-mass spectrometer (PTR-TOF-MS, Kore Technology Ltd.). The instrument generates H_3O^+ which reacts with analyte organic compounds (M) to form positively charged ions $(M + H)^+$, that are detected using a time of flight mass spectrometer. Sampling frequency during the experiments was fixed at 1 min and the operating range of the mass spectrometer was m/z 0–300. The PTR-TOF-MS was directly connected to the chamber via a Teflon tube heated to 298–303 K to prevent condensation.

The formation and growth of secondary organic aerosol was monitored using a scanning mobility particle sizer (SMPS, TSI model 3034): size distribution, number and mass concentrations were determined for all experiments, assuming an SOA density of 1.4 g cm^{-3} (Chan et al., 2009; Shakya and Griffin, 2010). SOA

Table 1
Experimental conditions and SOA formation yields for the ozonolysis of acenaphthylene. In all experiments the initial concentration of ozone was around 300 ppbv.

Experiment	[Cyclohexane] (ppmv)	[HC] (mg m^{-3})	ΔHC (mg m^{-3})[a]	ΔM_0 (mg m^{-3})[a,b]	Yield (Y)[a,c]
1a	0	2.00	1.83 ± 0.04	0.68 ± 0.01	0.37 ± 0.02
1b	0	2.10	2.01 ± 0.03	0.58 ± 0.04	0.28 ± 0.03
2a	80	2.13	1.74 ± 0.04	0.43 ± 0.01	0.25 ± 0.02
2b	80	2.00	1.86 ± 0.04	0.43 ± 0.03	0.23 ± 0.05
2c	80	2.10	1.95 ± 0.02	0.53 ± 0.05	0.27 ± 0.05

[a] Stated uncertainties (2σ) are from scatter in particle volume measurements.
[b] Assuming an SOA density of 1.4 g cm^{-3}.
[c] Yields determined at the point of maximum SOA concentration.