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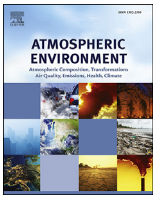

Gas- and particle-phase products from the photooxidation of acenaphthene and acenaphthylene by OH radicals

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HIGHLIGHTS

- Identification of competitive pathways for the OH-initiated oxidation of Acenaphthene.
- Formation of ring-opening products favored from the OH oxidation of Acenaphthylene.
- Impact of NOx on product distributions and SOA formation have been observed.
- Proposition of identified secondary chemistry in the extended mechanisms.
- SOA yields in the range 46–68% have been measured.

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ABSTRACT

This work is focused on the gas-phase oxidation of acenaphthylene and acenaphthene by OH radicals and associated secondary organic aerosol (SOA) formation under low and high-NO_x conditions. Experiments were carried out 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) to chemically characterize the gas- and particle-phase products, respectively. Due to the structures of these two aromatic compounds, the proposed chemical mechanisms exhibit some differences. In the case of acenaphthene, H-atom abstraction from the saturated cyclopenta-fused ring was found to be competitive with the OH-addition to the aromatic rings. During the photooxidation of acenaphthene using nitrous acid (HONO), aromatic ring-opening products such as indanone and indanone carbaldehyde, generated through OH addition to the aromatic ring, were formed in higher yields compared to low-NO_x conditions. In the case of acenaphthylene, OH addition to the unsaturated cyclopenta-fused ring was strongly favored. Hence, ring-retaining species such as acenaphthenone and acenaphthenequinone, were identified as the main reaction products in both gas- and particle-phases, especially under high-NO_x conditions. Subsequent SOA formation was observed in all experiments and SOA yields were determined under low/high-NO_x conditions to be 0.61/0.46 and 0.68/0.55 from the OH-initiated oxidation of acenaphthylene and acenaphthene, respectively.

1. Introduction

Atmospheric fine particulate matter ($PM_{2.5}$, aerosol with aerodynamic diameters less than 2.5 μm) plays a key role in air quality and climate change, and is associated with damaging effects on human health (Pope III and Docherty, 2006; Hallquist et al., 2009). Globally, the largest mass fraction of $PM_{2.5}$ is organic (up to 90% in some locations) and is dominated by secondary organic aerosol (SOA). Formation of SOA mainly results from the formation of gas-

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phase products with low vapor pressures from the oxidation of volatile organic compounds (VOCs) (Hallquist et al., 2009). The anthropogenic contribution to global SOA formation is estimated to be small, actually around 10% (Kroll and Seinfeld, 2008). SOA formation from anthropogenic sources is, however, suggested to be higher than currently predicted (Volkamer et al., 2006; Hallquist et al., 2009). In order to explain the current discrepancy between the mass of aerosols measured in different atmospheres and the mass predicted by atmospheric models, some studies have suggested that other sources of SOA are not yet identified or well characterized (Kroll and Seinfeld, 2008; Hallquist et al., 2009). Among them, heterogeneous chemistry (formation of oligomers and organosulfates) (Surratt et al., 2008; Pye and Pouliot, 2012) and the contribution of intermediate volatility organic compounds (IVOCs) to SOA formation have been proposed (Robinson et al., 2007; Tkacik et al., 2012). It is worth noting that recent studies have also underlined that reactive uptake and/or multiphase chemistry of water-soluble volatile organic compounds, such as glyoxal, in wet acidic aerosols or cloud droplets could be an important source of SOA (Galloway et al., 2009; Ervens et al., 2011; Pye et al., 2013; Marais et al., 2016). Nevertheless, a large part of the underestimation in urban areas, due to the non-considered IVOC contribution to SOA formation, comes from the involvement of alkanes and polycyclic aromatic hydrocarbons (PAHs) (Tkacik et al., 2012). Much of the current efforts in the research community are focused on trying to identify these missing or mis-represented SOA sources.

PAHs are emitted into the atmosphere from incomplete combustion processes of organic materials and have been identified as major components in traffic and wood burning emissions. The PAHs with less than four aromatic rings exist mainly in the gaseous phase and can undergo photooxidation processes with different atmospheric oxidants (Atkinson and Aschmann, 1988; Sasaki et al., 1998; Keyte et al., 2013; Zhou and Wenger, 2013a,b; Riva et al., 2014). When oxidized, these compounds have been shown to produce large range of oxygenated and nitro compounds with high molecular weights (Sasaki et al., 1998; Reisen and Arey, 2002; Lee and Lane, 2009; Kautzman et al., 2010; Kleindienst et al., 2012; Zhou and Wenger, 2013a,b; Riva et al., 2015a,b,c; 2016). Although PAHs are potentially carcinogenic and mutagenic (Atkinson and Arey, 1994) some of their oxidation products present a larger toxicity than their parent hydrocarbons (Lin et al., 2005). Gas-phase products can partition to the particle phase and participate in SOA formation (Chan et al., 2009; Kautzman et al., 2010; Shakya and Griffin, 2010; Kleindienst et al., 2012; Riva et al., 2015a, 2016; Chen et al., 2016). A few studies have previously reported the importance of naphthalene gas phase photooxidation in SOA formation (Chan et al., 2009; Kleindienst et al., 2012). Other gaseous PAHs have, however received less attention. Acenaphthylene and acenaphthene are fairly unique among PAHs in that they contain a carbon-carbon double bond and a saturated carbon-carbon bond, respectively, in their structure that enables them 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, 2013a,b; Riva et al., 2014). Acenaphthylene and acenaphthene were identified in both indoor and outdoor atmospheres and in large concentrations in certain areas (Chang et al., 2006; Ho et al., 2009). The concentration of both PAHs (greater than 20–30 ng m^{-3}) could be even comparable to that of naphthalene in certain urban atmospheres (Dejean et al., 2009; Hanedar et al., 2014) suggesting that acenaphthylene and acenaphthene might contribute to SOA formation in such areas. Large rate constants for the reaction of acenaphthene $((7.69 \pm 1.91) \times 10^{-11})$ and acenaphthylene $((1.14 \pm 0.08) \times 10^{-10})$ in cm^3 $molecule^{-1}$ s^{-1}) with OH radicals have been previously reported (Atkinson and Aschmann, 1988; Zhou and Wenger, 2013a,b). These previous efforts underline the potential importance of the OH initiated oxidation of acenaphthylene and acenaphthene in the atmospheric chemistry of PAHs. Indeed, it has been shown that the reactivity of aromatic hydrocarbons is dominated by their reactions with the OH radicals in the atmosphere (Calvert et al., 2002; Estève et al., 2003; Atkinson and Arey, 2007). Although the OH-initiated oxidation of PAHs has been studied previously, the impact of NO_x concentration on the reactivity of PAHs remains poorly documented. Only two studies on the oxidation of naphthalene performed under high- and low-NO_x conditions, have been reported hitherto (Kautzman et al., 2010; Kleindienst et al., 2012). Previous works have determined the rate constants and oxidation products for the photooxidation of acenaphthene and acenaphthylene in the presence of NO_x (Atkinson and Aschmann, 1988; Reisen and Arey, 2002; Zhou and Wenger, 2013a,b). In addition, Shakya and Griffin (2010) have, for the first time, reported the SOA yields arising from these reactions. These results highlight the propensity for both PAHs to participate in SOA formation and only partial mechanisms were proposed in these previous studies. However, some discrepancies remain and further work is needed to clarify the reaction products as well as the chemical mechanisms leading to SOA formation.

In this work, we performed a series of simulation chamber experiments to identify products arising from the photooxidation of acenaphthylene and acenaphthene under low- and high-NO_x conditions using state-of-the-art mass spectrometry techniques for online analysis of both gaseous (proton transfer reaction time-of-flight-mass spectrometer) and particulate (aerosol time-of-flight-mass spectrometer) phases. Based on these approaches, extended and improved reaction mechanisms for the OH-initiated oxidation of acenaphthylene and acenaphthene are now proposed. SOA growth and yields are determined in both cases to evaluate the importance of the photooxidation of acenaphthene and acenaphthylene in SOA formation.

2. Experimental section

Experiments were performed at room temperature (293 ± 2 K) and atmospheric pressure 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 and is surrounded by 16 lamps (Philips TL12, 40W) with an emission maximum at 310 nm and 12 lamps (Philips TL05, 40 W) with an emission maximum at 360 nm (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 non-methane 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). The temperature and water concentration in the chamber were monitored by a dew point meter (Vaisala DM70). The relative humidity in the chamber was typically less than 1% for the experiments with HONO and less than 5% for experiments carried out with H_2O_2.

Acenaphthylene (Sigma-Aldrich, 99%) and acenaphthene (Sigma-Aldrich, 99%) were introduced into the chamber by flowing dry purified air throughout a heated Pyrex glass bulb containing a known amount of the solid compound sufficient to produce PAH mixing ratios around 300 ppb (Table S1). The PAHs and gas-phase oxidation products were monitored during the experiments using a proton transfer reaction - time of flight - mass spectrometer (PTR-TOF-MS, Kore Technology Ltd.). Details of the instrument and its operating principle are given in Cappelin et al. (2012). Briefly, H_3O^+