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Secondary organic aerosol formation from ozone-initiated reactions with nicotine and secondhand tobacco smoke

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ABSTRACT

We used controlled laboratory experiments to evaluate the aerosol-forming potential of ozone reactions with nicotine and secondhand smoke. Special attention was devoted to real-time monitoring of the particle size distribution and chemical composition of SOA as they are believed to be key factors determining the toxicity of SOA. The experimental approach was based on using a vacuum ultraviolet photon ionization time-of-flight aerosol mass spectrometer (VUV-AMS), a scanning mobility particle sizer (SMPS) and off-line thermal desorption coupled to mass spectrometry (TD-GC-MS) for gas-phase byproducts analysis. Results showed that exposure of SHS to ozone induced the formation of ultrafine particles (<100 nm) that contained high molecular weight nitrogenated species (m/z 400–500), which can be due to accretion/acid–base reactions and formation of oligomers. In addition, nicotine was found to contribute significantly (with yields 4–9%) to the formation of secondary organic aerosol through reaction with ozone. The main constituents of the resulting SOA were tentatively identified and a reaction mechanism was proposed to elucidate their formation. These findings identify a new component of thirdhand smoke that is associated with the formation of ultrafine particles (UFP) through oxidative aging of secondhand smoke. The significance of this chemistry for indoor exposure and health effects is highlighted.

1. Introduction

The reactions of air pollutants often form products that pose greater health concerns than the reactants (Uhde and Salthammer, 2007; Weschler, 2006; Destaillats et al., 2006a; Singer et al., 2006a; Mauderly and Chow, 2008). Cigarette smoke and ozone are two pollutants frequently encountered in indoor and outdoor environments. Secondhand tobacco smoke (SHS) contains several thousand compounds that are distributed as particles and gases (Jenkins et al., 2000). SHS is a major source of human exposure to fine particles (Klepeis et al., 2003) and hazardous air pollutants indoors (Charles et al., 2007; Nazaroff and Singer, 2004) which are linked to adverse health effects such as chronic asthma, coronary heart disease, lung cancer, and chronic obstructive pulmonary disease (DHHS, 2006).

Ozone is also a pervasive pollutant in outdoor air. Although it is highly reactive, the atmospheric lifetime of ozone is long enough to allow for its transport to the indoor environment (Weschler, 2000). Ozone may also be generated indoors in substantial concentrations (100–300 ppbv) from devices marketed as "air purifiers" to remove odors related to SHS (Boeniger, 1995), and ozone is occasionally produced by copiers and laser printers (Destaillats et al., 2008). Epidemiological and toxicological studies have shown that atmospheric ozone and particulate matter induce synergistic harmful effects on the respiratory system (Bosson et al., 2007; Kleinman and Phalen, 2006). Ozone is known to react with acidic aerosols and form strongly oxidizing species such as ozonides that may be responsible for these effects (Enami et al., 2008). Similarly, synergistic effects have been observed from combinations of SHS pollutants and ozone that were more severe than the sum of the effects of individual pollutants (Yu et al., 2002; Wu et al., 1997).

We reported recently that nicotine – a major and lingering constituent of cigarette smoke – reacts on surfaces with atmospheric species such as ozone (Destaillats et al., 2006b) and nitrous acid (Sleiman et al., 2010) to form "thirdhand smoke" hazards in the

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form of irritant gas-phase products and carcinogenic sorbed species, respectively. In the current study, our aim was to explore the formation of secondary organic aerosols from the ozonolysis of not only nicotine but also the full mixture of SHS, under realistic conditions. Special attention was devoted to real-time monitoring of the particle size distribution and chemical composition of SOA because these two attributes are believed to be key factors influencing the toxicity of SOA (Chow et al., 2006; Donaldson et al., 2001). The approach utilized real-time monitoring of the number size distribution of the aerosol, off-line thermal desorption coupled to mass spectrometry (TD-GC-MS) and vacuum ultraviolet photon ionization time-of-flight aerosol mass spectrometry (VUV-AMS). The tunable VUV light is a “soft ionization” technique which reduces the fragmentation of organic molecules compared to other methods (Morrical and Zenobi, 2002; Yadav et al., 2004), allowing for a better characterization of complex aerosols such as SHS.

2. Experimental

2.1. Sample generation

SHS was generated in an 18-m^3 environmental chamber by smoldering 10 cigarettes from a leading US brand. After the first 15 min after smoking started, the diluted smoke was pumped into evacuated 100-L tedlar bags to about 40% capacity. In separate experiments, 5 μL (30 μmoles) of liquid nicotine (Sigma Aldrich, purity 99%) was injected into two 20-L tedlar bags, one with 10-L dry air (RH~0%) and the other with 10-L humidified air (RH~50%).

Ozone was generated by UV irradiation (UVP Inc.) of pure air, diluted with dry or humidified air and introduced into the tedlar bags previously filled either with SHS or pure nicotine. The ozone concentration in the supply air was 1.2 ppmv as measured using a calibrated UV monitor (API 400). One liter of ozone (1.2 ppmv) was introduced into each nicotine bag, corresponding to an initial concentration of ozone inside the bag (in the absence of reactive losses) of 110 ppb, or a total of 45 nmoles of ozone available (ratio ozone/nicotine of 0.0015). For SHS, the bag previously filled with 40 L was supplied with 5 L of ozone-containing air (1.2 ppmv), corresponding to ~250 nmoles of total ozone available for the reaction and an initial concentration of 150 ppbv. Ozone was not monitored during the reaction as smoke could interfere with the measurement of ozone concentration. Considering the very low initial ratio ozone/nicotine (0.0015) and the relatively high initial SHS concentration, we assume that ozone was completely consumed during reaction.

2.2. Particle characterization

Tedlar bags containing fresh or ozonated SHS and nicotine were connected without further dilution to a scanning mobility particle sizer (SMPS, see below) and to a custom-built aerosol mass spectrometer (Gloaguen et al., 2006) whose ionization source was the VUV beam line of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Copper tubing was used to connect the Tedlar bags to the AMS, except for a few cm of conductive silicone tubing at the inlet to the spectrometer, to minimize possible artifacts associated with the silicone tubing (Timko et al., 2009).

2.2.1. Particle sizing

Particles were sized in the range of 20–700 nm and counted using a scanning mobility particle sizer (SMPS, model 3936, TSI, Shoreview, MN). The SMPS consisted of an electrostatic classifier (TSI model 3080) coupled to an ultrafine condensation particle counter (butanol CPC, TSI model 3025A). The sample and sheath air flow rates of the SMPS were set to 0.3 L m^{-1} and 3 L m^{-1}, respectively. We converted the SMPS measured particle number concentrations to particle mass concentrations for each particle size range by assuming that SHS particles have a density of 1.1 g cm^{-3} (Lipowicz, 1988), that the logarithm of the particle mass concentration is uniformly distributed within each size range, and that SHS particles are spherical.

2.2.2. Particle composition

The particle composition was characterized using a custom-built orthogonal extraction time-of-flight mass spectrometer. The basic principles of VUV-AMS and the instrumental set-up at the ALS were described previously (Gloaguen et al., 2006). Particles were introduced into the vacuum through an aperture (200 μm) at a flow rate of 0.27 L min^{-1}. The particle beam was focused by an aerodynamic lens into a narrow beam that was transported to a 3 mm heated copper tip surface (temperature set at 150 °C) where particles were vaporized upon impact and then photoionized by the synchrotron’s tunable VUV radiation (ALS, Chemical Dynamics Beam line), if their ionization energies (IE) were less than the photon energy (7.7–11.2 eV, nominal flux of 10^{16} photons s^{-1}). Most small organic molecules have IE of less than 10.5 eV and were thus easily ionized by the VUV beam.

2.2.3. Gas-phase analyses

Gas-phase nicotine and ozone reaction products were sampled from the Tedlar bags into Tenax-TA sorbent tubes at a flow rate of 100 cm^3 min^{-1} for 1 h. The Tenax tubes were analyzed by thermal desorption/gas chromatography with mass spectrometry (TD-GC-MS) as described previously (Singer et al., 2006b).

3. Results and discussion

3.1. Characterization of SHS

Figure 1A shows the VUV-AMS mass spectra (left panel) and the size distribution (right panel) for diluted SHS smoke. The particle concentration was approximately 130 μg m^{-3} and the mean particle diameter was 0.13 μm. This is in agreement with reported mean diameters for SHS cigarette smoke (between 0.1 and 0.3 μm) (Kleeman et al., 1999; Klepeis et al., 2003).

The mass spectrum of SHS shows a large number of peaks because it is chemically complex. The most intense signal is assigned to nicotine at m/z 162. This is consistent with the high levels of this alkaloid in tobacco as well as with its room-temperature vapor pressure of 42.5 mTorr (Norton et al., 1940) and previous observations of its partitioning between the gas and particle phases (Pankow, 2001; Pankow et al., 2003). A list of the observed mass signals assigned to cigarette smoke constituents is given in Table 1. Identification was based on the mass calibration of the AMS and prior studies (Adam et al., 2006; Pieraccini et al., 2008; Charles et al., 2007; Hearn and Smith, 2006; Borgerding and Klus, 2005; Mitschke et al., 2005; Lu et al., 2004; Yadav et al., 2004; Baek and Jenkins, 2004; Silva and Prather, 2000). Fifty compounds were detected including carbonyls, dimethylfuran, phenolic compounds, N-nitrosamines, nitrogen-containing species and PAHs (Table 1).

3.2. Ozone reactions with secondhand smoke

Figure 1B illustrates the size distribution and mass spectrum of SHS particles after 1-h exposure to ozone (initially 110 O_3 ppbv) in the tedlar bag. Compared to fresh SHS shown in Fig. 1A, the mass concentration of ozonated SHS particles increased by a factor of 1.8 and the particle size distribution became bimodal. The peak at 130 nm is similar to that observed in the absence of ozone (Fig. 1 A)