

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.

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1. Introduction

The reactions of air pollutants often form products that pose greater health concerns than the reactants (Uhde and Salthammer, 2007; Weschler, 2006; Destailats 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 (Destailats 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 (Destailats 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-m³ 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 μ L (30 μ moles) 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 μ m) 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 10¹⁶ 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 cm³ 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 μ g m⁻³ and the mean particle diameter was 0.13 μ m. This is in agreement with reported mean diameters for SHS cigarette smoke (between 0.1 and 0.3 μ m) (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 O₃ 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. 1A)

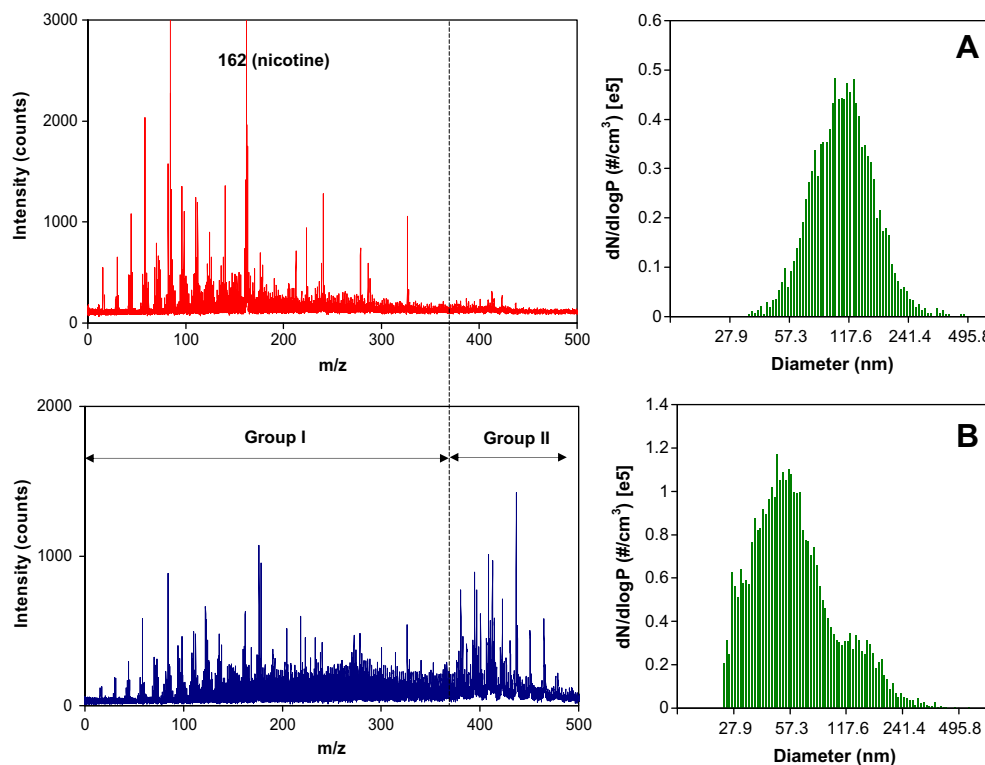


Fig. 1. VUV mass spectra (VUV energy: 10.4 eV) and SMPS size distribution of secondhand smoke (A) before and (B) after exposure to ozone.

whereas the peak at 60 nm reveals the formation of ultrafine particles (UFP, <100 nm). These changes were not observed when an identical bag, filled with similar SHS concentration ($120 \mu\text{g m}^{-3}$) and collected at the same time, was aged for more than an hour, without exposure to ozone. Thereby, the observed formation of UFP is caused only by the reaction of ozone with constituents of the SHS and not by other physical or chemical processes.

Reaction of SHS with ozone decreased the concentration of most of the compounds with $m/z < 370$ (Group I) that were originally present in SHS, including nicotine. In this category of compounds, only cotinine (m/z 176) and nicotine-N-oxide (m/z 178) showed increased concentrations, which can be due to nicotine oxidation as discussed in the next paragraph (Section 3.3). The second group (Group II) shows the appearance of high molecular weight products in the range of m/z 370–470, at $m/z = 380, 394, 396, 408, 412, 422, 436$ and 450 . Similar products have been observed in other systems, including terpene ozonolysis (Bahreini et al., 2005; Gao et al., 2004; Tolocka et al., 2004). Although it is difficult to conclusively identify these products, the progressions of peaks spaced by 14 ($-\text{CH}_2$, $-\text{N}$) and 16 ($-\text{O}$, $-\text{NH}_2$) atomic mass units are characteristic of oligomer species (Denkenberger et al., 2007; Gross et al., 2006; Baltensperger et al., 2005), while the even mass-to-charge ratios suggest the presence of nitrogenated byproducts containing an even number of nitrogen atoms. Possible mechanisms of formation of these species include i) accretion reactions involving aldehydes, ketones, dicarbonyls or carboxylic acids (Barsanti and Pankow, 2004, 2005, 2006); ii) reactions of amines present in SHS with ozonolysis products (i.e. carboxylic acids, carbonyls) to form high molecular weight amides or imines (Malloy et al., 2009; Zahardis et al., 2008); iii) acid-catalyzed reactions to form oligomers via organic or inorganic acids produced from gas-phase oxidation (Kroll and Seinfeld, 2008; Murphy et al., 2007); and iv) acid–base reactions involving organic acids and NH_3 to produce condensable salts.

3.3. Ozone reactions with nicotine

As shown in Fig. 1, the formation of UFP particles was associated with nearly complete consumption of nicotine in SHS by reaction with ozone. To further examine the role of nicotine in the formation of UFP, experiments were carried out using pure nicotine exposed to ozone (1–110 ppbv) in dry and humidified air. Bags filled with nicotine alone showed no formation of particles via nucleation or condensation processes, whereas exposure to ozone led to formation of significant amounts of SOA, as illustrated in Fig. 2. This finding suggests that gas-phase nicotine, in the presence of ozone, could contribute significantly to the production of SOA during the aging of tobacco smoke. SOA was formed in both dry and humid air conditions. However, in presence of water vapor, SOA formation was enhanced and median particle size was increased from 76 nm to 200 nm. This may be related to an increase in water soluble organic carbon (WSOC) that partitions to the particle phase (Hennigan et al., 2008).

Total aerosol yield (Y) was determined using the equation defined by (Odum et al., 1996):

$$Y = \frac{\Delta M}{\Delta \text{ROG}} \quad (1)$$

where ΔM is the total aerosol mass concentration produced for a given amount of organic gas reacted, ΔROG . Using the SMPS data, ΔM was calculated to be $56 \mu\text{g m}^{-3}$ under dry conditions and $186 \mu\text{g m}^{-3}$ under humid conditions. Analysis of nicotine from the bags showed that ΔROG was 1.5 mg m^{-3} (220 ppbv) under dry conditions and 12 mg m^{-3} (1.77 ppmv) under humid conditions. Assuming that the formation of SOA was mainly due to gas-phase reactions between nicotine and ozone, we obtained $Y = 3.8\%$ and $Y = 9.2\%$ under dry and humid conditions, respectively. These values are close to aerosol yields reported by Murphy et al., (2007) for the ozonolysis of two tertiary amines, trimethylamine and

Table 1
AMS signals assigned to cigarette secondhand smoke constituents (no O₃ exposure).

<i>m/z</i>	Compounds
17	NH ₃
28	CO
30	HCHO, NO
31	Methylamine (CH ₃ NH ₂)
42	Propene
43	Carbohydrate fragment (C ₃ H ₇ ⁺), C ₂ H ₂ O ⁺
44	Acetaldehyde
45	Dimethylamine, ethylamine
54	1,3-butadiene
56	Acrolein, butene, 2-methylpropene
58	Acetone, propanal
68	Furan, isoprene, 1–3 pentadiene, cyclopentene
70	2-Butenal, methylethenylketone, 2-methyl-2-propenal
72	2-Methyl propenal, 2-butanone, butanal
74	Water-eliminated glycerol, tetrahydrofuran
82	Methylfuran, cyclohexene, 2-cyclopenten-1-one
84	Methyl pyrrolidine (nicotine fragment)
86	Methylbutanal, 3-methyl-2-butanone, 2,3-butanedione, 2-pentanone
94	Phenol, 2-ethenylfuran
95	Pyridinol, dimethylpyrrole
96	Dimethylfuran, furfural
97	Carbohydrate fragment
98	Furanemethanol, methyl-2-pentenal, 5-methyl-2(5H)-furanone, 1,3-cyclopentanedione
106	Xylene, ethylbenzene, benzaldehyde
108	Anisol, dimethylpyridine, methyphenol
109	3-Methoxypyridine
110	Dihydroxybenzene, 2-acetylfuran, methylfurfural, 3,4,5 trimethylpyrazole
111	Benzenediol
122	Benzoic acid, hydroxybenzaldehyde, ethylphenol, nicotinamide
123	Nicotinic acid
124	Dihydroxymethylbenzene, 2-methoxyphenol (guaiacol)
126	5-(hydroxymethyl)-furfural
128	Naphthalene
136	Limonene, methoxybenzaldehyde, 2-ethyl-5-methyl-phenol
138	1,4-dimethoxybenzene
140	Hexamethylentetramine
146	Myosmine
148	Normicotine
154	Acenaphthene
160	Anatabine
162	Nicotine
166	Fluorene
176	Cotinine
177	N-nitrosoanabine
178	Phenanthrene, Anthracene
191	NAB (N-nitrosoanabasine)
204	Fluoranthene
223	Nicotine-nitrate
240	Ambiguous
278	Dibenz[a,h]anthracene, Dibenz[a,h]anthracene, 9-Eicosine

triethylamine (15% and 5%, respectively). Sorbed nicotine was also found to react with ozone (Destailats et al., 2006b) and therefore could be a source of SOA. However, the semivolatile and non-volatile ozonolysis byproducts of sorbed nicotine are less likely to partition to airborne particles and would not reach the AMS. Also, as gas-phase nicotine reacts, its levels may be partially restored by desorption from the bag surfaces. For these reasons, the yields calculated here are considered upper limits to the aerosol yield.

The mass spectra of SOA formed during nicotine ozonolysis included main peaks at *m/z*: 17, 30, 58, 60, 79, 84, 107, 119, 122, 123, 136, 148, 149, 161–164, 176, 178, 190, 192, 206, 208 and 223. The distribution of the mass spectra shown in Fig. 2A and B differ, indicating that different products were formed in the presence and absence of water vapor. The peaks at *m/z* 17, 30 and 45 disappear under humid conditions. These peaks could be attributed to ammonia (NH₃), formaldehyde and formamide, respectively, but

could also result from dissociative photoionization of larger species. Moreover, assuming that the photoionization efficiencies of nicotine and its products are equal, cotinine (*m/z* 176), one of the most prevalent oxidation byproducts, accounted for ≈8% of the products under dry conditions and 19% in presence of water vapor.

The mass spectra of SOA shown in Fig. 2 and Fig. 1B include common peaks such as *m/z* 176 (cotinine), *m/z* 223, and some high molecular weight (HMW) species (*m/z* > 400). The HMW species were less abundant in SOA produced by ozonolysis of only nicotine (Fig. 2) than in SOA produced by ozone reaction with SHS (Fig. 1B). This difference suggests that additional SHS components such as carboxylic acids, amines or NH₃ and/or oxidation products participate in the formation of non-volatile salts, polyfunctional compounds, oligomers and condensation products.

3.4. Reaction products and mechanisms of ozone–nicotine reactions

Proposed molecular structures for the main peaks observed in Fig. 2 and their formation mechanisms are shown in Scheme 1. Several of the tentatively identified products were reported by (Destailats et al., 2006b): cotinine (*m/z* 176), nicotine–aldehyde (*m/z* 107), formaldehyde (*m/z* 30) and formamide (*m/z* 45). Also shown are previously unidentified multifunctional and dicarbonyl products corresponding to peaks *m/z* 136, 149, 178, 190, 192 and 208. These products are expected to partition to the particle phase. The peak at 223 may correspond to an alkyl nitrate that could be formed through acid–base reaction of protonated nicotine and nitrate (NO₃[−]), from the oxidation of an amino group (Murphy et al., 2007).



Several studies have shown that the attack of ozone on tertiary amines occurs mainly at the nitrogen atom (Angelino et al., 2001, Munoz and von Sonntag, 2000, Tuazon et al., 1994, von Gunten, 2003). The two possible primary products for nicotine are an alkylamine-N-oxide and an amine radical cation ⁺NR₃. The detection of an alkylamine-N-oxide in the aerosols produced from the reaction of secondary and tertiary amines with ozone was first reported by (Angelino et al., 2001). In the current study, the presence of an nicotine-N-oxide was corroborated by the detection of both its molecular ion (*m/z* 178) and its main fragment at *m/z* 119. A rearrangement of the nicotine-N-oxide, preferably at site 5' and subsequent loss of OH• leads to an alkoxy radical that could react with O₂ to form cotinine, a known metabolic product of nicotine oxidation. Subsequent oxidation of cotinine at the 2' carbon and the methyl group in the α position to the pyrrolidine nitrogen leads to the formation of dicarbonyl products **1** and **2** which correspond to *m/z* 192 and 190, respectively. Due to the electron-attracting effect of the CO–NH functional group, it follows that intermediate **1** can undergo an oxidation at position 4' giving rise to product **3** with a molecular weight of *m/z* 208. Product **3** further decomposes to form product **5** (*m/z* 149). On the other hand, intermediate **2** can be further oxidized at the aldehyde group to form product **4**, which corresponds to *m/z* 206.

Alternatively, the amine radical cation undergoes an H-abstraction, either at the CH₃ group or at the 5' carbon, to form two amino alkyl radicals which then produce two Schiff-base intermediates **6** and **7** (*m/z* 161), respectively. Subsequently, compound **6** is hydrolyzed to produce formaldehyde (*m/z* 30) and normicotine (**8**, *m/z* 148). Abstraction of hydrogen from the 5' carbon followed by formation of imine and subsequent hydrolysis lead to formation of an amino-aldehyde intermediate (**9**, *m/z* 164). In

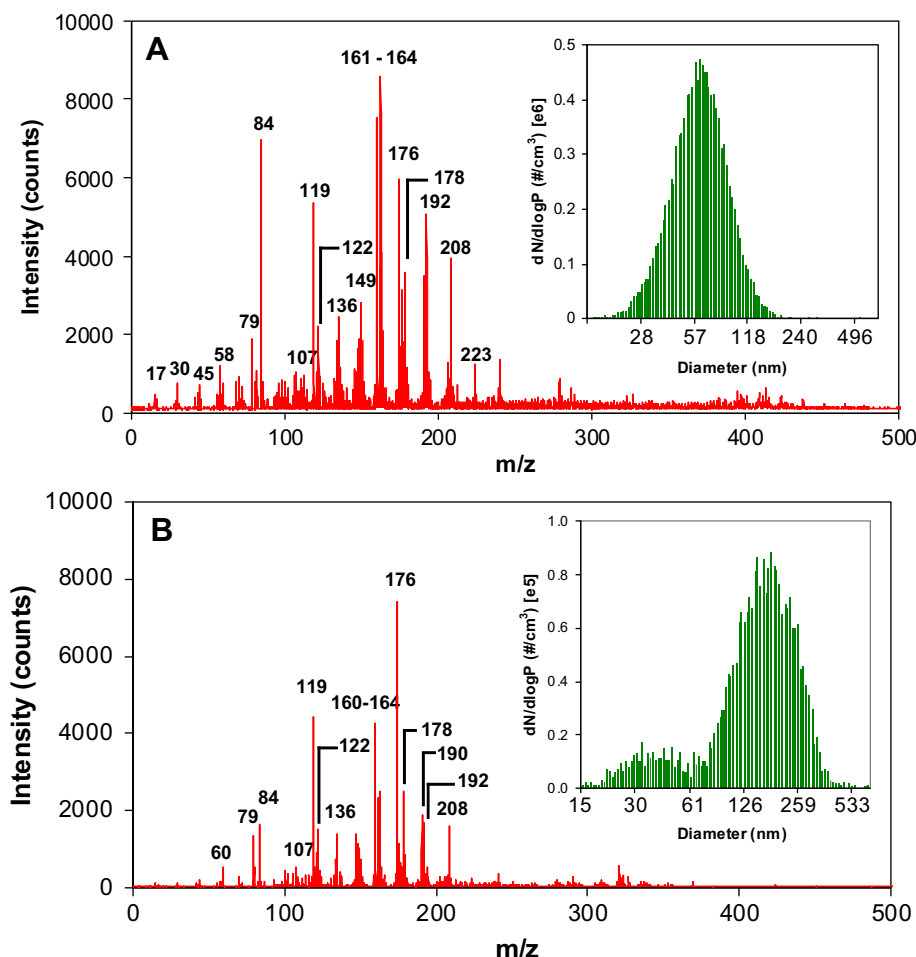


Fig. 2. VUV mass spectra (VUV energy: 10.4 eV) and SMPS size distribution of secondary organic aerosol generated during nicotine reaction with ozone in (A) dry and at 50% RH (B).

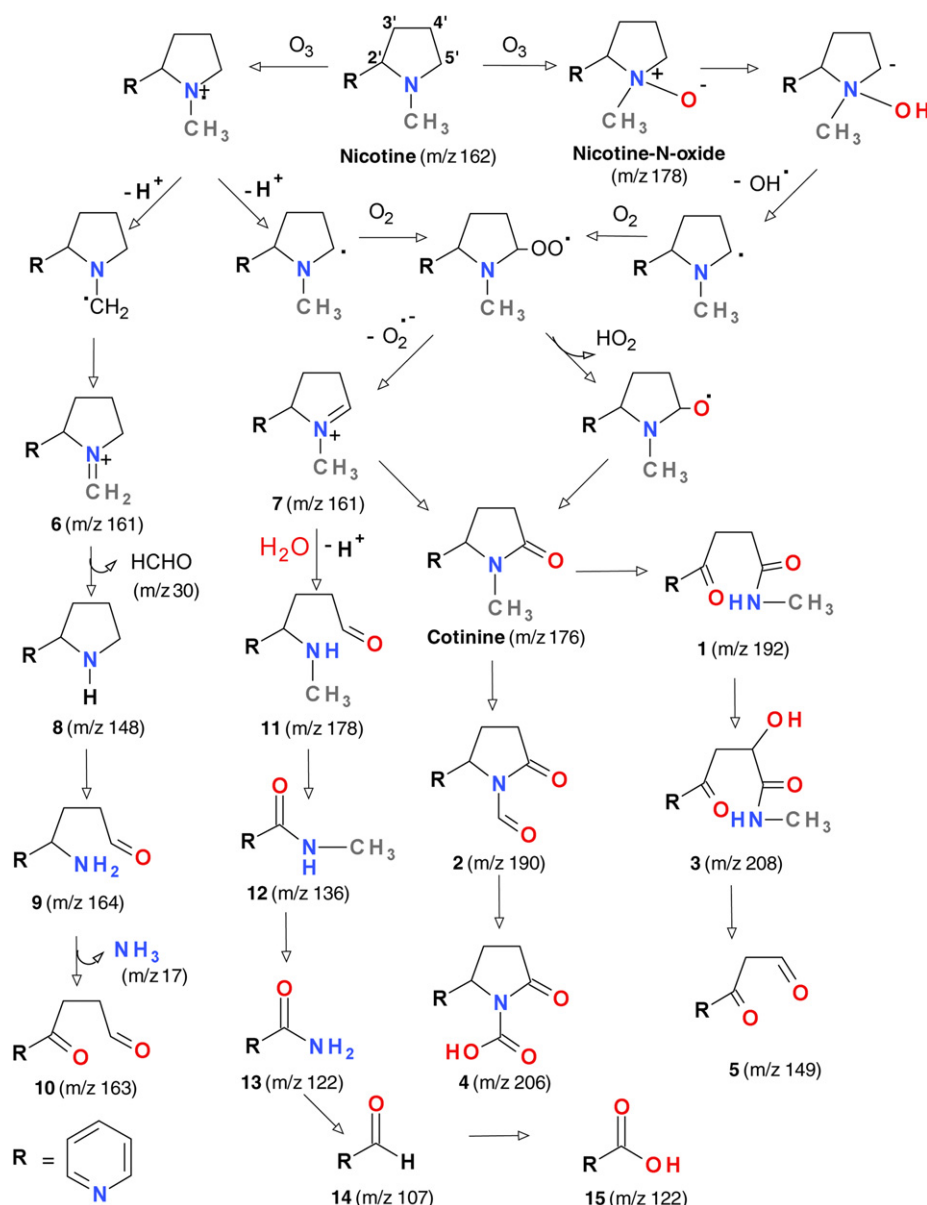
a similar manner, intermediate **7** gives rise to an amino-aldehyde (**11**, m/z 178), which is further oxidized in the α position of $-N$ to yield an amide intermediate (**12**, m/z 136). Subsequent analogous oxidation at the α position to $-N-$ of intermediates **9** and **12** leads to the generation of products **10** (m/z 163) and **13** (m/z 122). Finally, the nicotine-amide (**13**) can be converted to nicotine-aldehyde (**14**, m/z 107) and subsequently to nicotinic acid (**15**, m/z 122). The proposed reaction scheme is consistent with the experimental results and identified products. Nevertheless, its verification requires further investigation of the evolution of reaction intermediates.

3.5. Significance for indoor exposure and health implications

The chemistry described here could increase the hazards associated with exposure to SHS by increasing the likelihood of adverse respiratory and cardiovascular health effects that are linked to formation of ultrafine particles, as well as exposure to newly-formed ozonolysis byproducts.

The particles in the SHS measured in this study are of the size that can deposit deep within the lungs (Nazaroff et al., 1993). Many of the chemical constituents identified in the SHS are potentially toxic or carcinogenic (Fowles and Dybing, 2003), such as acetaldehyde (m/z 44), butadiene (m/z 54), acrolein (m/z 56), fluoranthene (m/z 204) and N-nitrosonicotine (m/z 177). In addition, α,β -unsaturated aldehydes, in particular acrolein and crotonaldehyde, are major mediators of cigarette smoke-induced macrophage

activation and pulmonary inflammation (Facchinetti et al., 2007). Although the signal intensities of the majority of small molecular weight constituents of fresh SHS were reduced after ozonation, new HMW products were formed. These products are likely to contain multifunctional groups and particularly nitrogen and oxygen. According to (Jarvis et al., 2005), molecules that include nitrogen or oxygen functional groups were associated with an occupational asthma hazard, particularly when the functional group was present twice or more in the same molecule. In addition, the concentrations of UFP formed via SHS ozonolysis were 8-times higher than those measured in fresh SHS and 10-times higher than those found in typical urban environments ($16\text{--}28\text{ }\mu\text{g m}^{-3}$ vs. $1.7\text{--}3.6\text{ }\mu\text{g m}^{-3}$, (EPA, 2002)). While these levels are based on measurements in tedlar bags, the mass concentrations of both SHS and ozone used in this work are representative of indoor environments where tobacco smoking is regularly occurring and where ozone purifiers are used to remove smoke odors. We expect that even under more realistic conditions (ozone concentration of $20\text{--}50$ ppbv, SHS particle concentration of $50\text{ }\mu\text{g m}^{-3}$ and air exchange rate of 1 h^{-1}), the formation of UFP through reaction of SHS with ozone would be significant. UFP pose a health concern because of their very high alveolar deposition fraction, large surface area, chemical composition, ability to induce inflammation, and potential to translocate into the circulatory system (Loft et al., 2005; Oberdorster et al., 2004; Pope et al., 2002; Donaldson et al., 2001; Oberdorster, 2001).



Scheme 1. Reaction products and proposed mechanism for nicotine reaction with ozone.

Furthermore, based on the hazard prediction model developed by (Jarvis et al., 2005), most of the identified reaction products of nicotine ozonolysis have a hazard index between 0.7 and 1 (with 0 corresponding to no hazard and 1 to maximum hazard), which are summarized in Table 2. In several cases, the hazard index is higher than that corresponding to nicotine, the parent compound, suggesting that ozonolysis byproducts are more likely to cause or exacerbate asthma.

These findings raise concerns about residual secondhand smoke that can lead to new generation of pollutants (*thirdhand smoke*) through oxidative reactions. As a consequence, interaction between indoor pollutants such as SHS or residual nicotine and ozone needs to be taken into account for better exposure assessment. Moreover, further work needs to be undertaken to establish clear links between the properties (size, composition) of SOA formed and synergistic health effects.

Table 2

Asthma hazard index for nicotine and its ozonolysis products.

Product ^a	Hazard index
Nicotine	0.64
Cotinine	0.76
Nicotine-N-oxide	0.57
1	0.87
2	0.85
3	0.99
4	0.94
5	0.83
9	0.92
10	0.86
11	0.94
12	0.61
13	0.53
14	0.59
15	0.92

^a Product numbers refer to structures shown in Scheme 1

4. Conclusions

This study found that the reaction between secondhand smoke from cigarettes (SHS) and a common air pollutant (ozone) generates ultrafine particles containing nitrogenated species. In addition, nicotine contributed significantly (yields 4–9%) to the formation of secondary organic aerosol through reaction with ozone. Water vapor was shown to influence the formation and/or partitioning of some products formed during ozonolysis (i.e. cotinine). The main constituents of the resulting SOA were tentatively identified and a reaction mechanism to elucidate their formation was proposed. Some of the products (nicotine-N-oxide, dicarbonyl/multifunctional products, etc.), have not been reported previously, and are likely to be associated with a high asthma hazard index. These findings highlight the significant role that ozone can play in the aging of cigarette smoke and raise concerns about the health effects of UFP in thirdhand smoke.

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