

Effect of ammonia on ozone-initiated formation of indoor secondary products with emissions from cleaning products

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HIGHLIGHTS

- ▶ We studied the effect of NH₃ on indoor secondary pollutants formation.
- ▶ The presence of NH₃ could significantly enhance SOAs formation.
- ▶ The consumptions of d-limonene in the reaction systems increased with NH₃ presence.
- ▶ The percent yields (%) of secondary carbonyl compounds were quantified.

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ABSTRACT

Biogenic volatile organic compounds (BVOCs) emitted from cleaning products and air fresheners indoors are prone to oxidation resulting in the formation of secondary pollutants that can pose health risks on residents. Ammonia (NH₃) is ubiquitous in ambient and indoor environments. In this study, we investigated the effect of ammonia (NH₃) on secondary pollutants formation from the ozonolysis of BVOCs emitted from cleaning products including floor cleaner (FC), kitchen cleaner (KC) and dishwashing detergent (DD) in a large environmental chamber. Our results demonstrated that the presence of NH₃ (maximum concentration is 240 ppb) could significantly enhance secondary organic aerosols (SOAs) formation from the ozonolysis of all the three categories of cleaning products. For example, for the FC sample, the maximum total particle concentration was up to $2.0 \times 10^4 \text{ # cm}^{-3}$ in the presence of NH₃, while it was $1.3 \times 10^4 \text{ # cm}^{-3}$ which was 35% lower without NH₃. However, it was found that the extent of NH₃ effect on SOAs formation from the ozonolysis of BVOCs emissions was component-dependent. The presence of NH₃ in the reaction systems could increase the consumptions of d-limonene that is the dominant BVOC species as identified in cleaning products. The percent yields (%) of secondary carbonyl compounds generated from the ozonolysis of BVOCs emitted from three categories of cleaning products were identified in the presence and absence of NH₃, respectively. The increase in SOAs particle number concentration can be attributed to the formation of condensable salts from reactions between NH₃ and organic compounds generated from the BVOCs ozonolysis processes. By investigating the NH₃ effect on the ozonolysis of BVOCs mixtures in contrast to the chemistry of individual compounds, a better assessment can be made of the overall impact cleaning products have on real indoor environments.

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1. Introduction

Ammonia (NH₃) is ubiquitous in ambient and indoor environments. Ambient NH₃ can be emitted by biogenic sources as well as anthropogenic sources, mainly including soil and vegetation, livestock operations, mobile exhaust, and fertilizer application

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(Na et al., 2007). Due to the possible health risks it causes, indoor NH_3 has attracted much more attention recently. The main indoor NH_3 source is concrete wall with addition of urea-based antifreeze admixtures, of which the continuous decomposition can release gaseous NH_3 (Bai et al., 2006; Tomoto et al., 2009). NH_3 is harmful to the human body and exposure to NH_3 can cause serious symptoms such as headaches, burns, and even permanent damage to eyes and lungs (Bai et al., 2006; Tuomainen et al., 2003). The reported NH_3 concentration was up to 3–6 ppmv in an office (Lindgren, 2010).

The gas-phase reaction between NH_3 and inorganic acids (e.g., sulfuric acid and nitric acid) leading to significant secondary particulate formation has been well characterized (Seinfeld and Pandis, 2003), while relatively few studies have been conducted on that with organic compounds indoors. Indoor chemistry dominated by ozone/terpene reactions has received most attention in the past two decades because of its substantial contribution to total human pollutant exposure (Weschler, 2004, 2011). Monoterpenes and oxygenated monoterpene species, which are the major components of biogenic volatile organic species (BVOCs), were determined at high concentration levels mainly due to the consumption of cleaning products and air fresheners indoors (Singer et al., 2006a, 2006b). These unsaturated BVOCs can react rapidly with ozone to form secondary pollutants, including secondary organic aerosols (SOAs), carbonyl compounds, and reactive hydroxyl radicals (Nazaroff and Weschler, 2004). The “burst” growth of SOAs which were generated from reactions between BVOCs emissions of household products and ozone has been observed in indoor environments (Coleman et al., 2008; Destailats et al., 2006; Lamorena and Lee, 2008). It should be noted that the surfaces of these generated ultrafine particles are probably nitrated or acidic (Carslaw, 2007; Carslaw et al., 2009), which can pose adverse health risks to building occupants. Furthermore, since gaseous organic compounds can be generated during BVOCs/ozone reactions, if NH_3 co-exists with these secondary products, the formation and growth of indoor aerosols could be possibly facilitated.

It was found that the aerosol number and volume concentrations rapidly increased in the α -pinene/ozone system when NH_3 was added due to the generation of new particles from reactions between NH_3 and oxidation-generated organic acids (Na et al., 2007). Conversely, after the addition of NH_3 to the styrene/ozone system, the aerosol yields were significantly reduced which could be probably ascribed to the rapid decomposition of intermediates (Na et al., 2006). Actually, in real indoor environments, the BVOCs are present in mixtures rather than a single compound. Forester and Wells reported that the BVOCs mixtures react differently with ozone in comparison with individual components (Forester and Wells, 2011). However, little work has been conducted with respect to NH_3 effect on indoor secondary pollutants formation resulting from reactions between ozone and BVOCs emitted from household cleaning products. The potential role of ammonia chemistry on indoor secondary pollutants formation is still poorly understood.

In this study, we demonstrated the effect of NH_3 on the formation of indoor SOAs and secondary carbonyls from the ozonolysis of BVOCs emitted from different categories of household cleaning products. By investigating the NH_3 effect on the ozonolysis of BVOCs mixtures in contrast to the chemistry of individual compounds, a better assessment can be made of the overall impact cleaning products posed to the real indoor environments.

2. Experimental

2.1. Environmental chamber

Experiments were conducted in a stainless-steel environmental chamber (3.2 m \times 3.2 m \times 2.5 m) with an effective volume of

18.26 m³ (Lee and Wang, 2006). Its surface area to volume ratio is 2.87 (m² m⁻³). Clean air was supplied to the chamber by drawing outside air through an air cleaning system with activated charcoal particle filters to remove gaseous organics and High-Efficiency Particulate Air (HEPA) filters to remove particles. Mixing fans were installed at ceiling of the chamber to ensure a homogeneous mixing. The chamber system has its own a central control system for adjustment of air exchange rates (ACH), relative humidity (RH) and temperature (T). The ACH was pre-determined by the first-order decay of SF_6 , which was introduced to the chamber and continuously monitored with a Photoacoustic Field Gas Monitor (INNOVA 1412, Santa Clara, CA). The temperature of air was controlled by conditioning coils. RH was regulated by adding appropriate amount of deionized water into the air system. Prior to use, the chamber was fully cleaned by scrubbing the interior surfaces with a sponge mop. Before each experiment, the chamber was conditioned for 4 h at the desired physical conditions. The background in the chamber air were kept $<10 \mu\text{g m}^{-3}$ (<4.34 ppb) for total volatile organic compounds (TVOCs) and $<2 \mu\text{g m}^{-3}$ for individual VOC (Lee and Wang, 2006; USEPA., 1999b). All the experiments were conducted in the large environmental chamber with ACH of 0.36 h⁻¹, RH of 50% and T of 23 °C, which closely simulates real indoor environments as demonstrated in our previous studies (Huang et al., 2011a).

2.2. Sample introduction

Three categories of household cleaning products including floor cleaner (FC), kitchen cleaner (KC) and dishwashing detergent (DD) which are popularly used by Hong Kong households were selected as emission sources of BVOCs. For each study, a volume of 50 mL of one category of cleaning products was transferred onto a Teflon plate (38 cm \times 32 cm \times 4 cm) which was placed on the floor in the center of the chamber. After the complete vaporization of BVOCs in the cleaning agent (3 h), ozone was introduced into the chamber. Ozone was produced by a generator (Model, 2001; Jelight Company Inc., Irvine, CA) which was fed with purified air at a pressure of 20 psi. The ozone was introduced in the chamber at a constant flow rate. The daily maximum 8 h mean ozone concentration is 50 ppbv as recommended by World Health Organization (WHO) for the sake of human health (WHO, 2000). For NH_3 effect experiments, NH_3 was introduced to the chamber as soon as the dosage of cleaning products was completed. The NH_3 gas was supplied from a compressed gas cylinder at a concentration of 1000 ppm of NH_3 (N_2 balance, BOC gas). The temporal NH_3 concentration profile was shown in Fig. S4.

2.3. Sampling and analytical methods

The ozone concentration and particle number size distributions with diameters ranging from 6 to 225 nm were monitored continuously once the floor cleaner had been dosed. NH_3 was measured by flowing the chamber air through a thermal oxidizer (API thermal converter, Model 501) set to 825 °C and detecting the oxidized ammonia as NO (Chemiluminescent NH_3 Analyzer-Model 201A). The thermal oxidizer was calibrated using a certified cylinder of NH_3 .

Twelve of the BVOCs and seventeen of the carbonyl compounds were also quantified before and after ozone dosage. The ozone concentration was measured by a photometric ozone analyzer (Model 400E, Teledyne Instruments, San Diego, CA) and the data was record at a 1-min interval. Particle size distribution of SOAs was measured by a scanning mobility particle sizer (SMPS) system with a differential mobility analyzer (Model 3080, TSI Inc.) coupled to a condensation particle counter (Model 3022, TSI Inc.).

BVOCs were sampled with the solid-phase microextraction (SPME) method. A manual SPME sampling holder consists of a 75 μm Carboxen-PDMS fiber (Supelco, Bellefonte, PA). A new fiber was heated in a gas chromatography (GC) injection port (6890 GC, Hewlett–Packard, Santa Clara, CA) under continuous helium (He) gas flow at 300 °C for 1 h, aiming to thermally desorb any impurities. The conditioned fibers were stored properly inside a clean box in laboratory. Before sample collection, each fiber was re-conditioned in the GC injection port at 300 °C for 10 min. Experimental results showed that no significant amount of BVOCs remained on the fiber. For sample collection, the fiber was inserted through a sampling port and exposed for 5 min in the chamber. Once the sampling was completed, the fiber was stored (<5 min) and then inserted into the GC injection port at 280 °C for 4 min. During the desorption period, the GC oven temperature was kept at 50 °C. Such a temperature condition would allow the analytes released from the SPME fiber on the head of the GC column in a narrow band. The injector was kept in the splitless mode for the first 2 min and then switched to the split mode until the end of the GC oven temperature program. The GC oven temperature program was then started, which was initially set at 50 °C and was held at this temperature for 3 min, ramped at a rate of 5 °C min^{-1} to 95 °C and 10 °C min^{-1} to 130 °C and 55 °C min^{-1} to 290 °C, and then held at the final temperature of 290 °C for 3 min. A DB-5MS UI column (J&W, Agilent Technologies, Inc., Santa Clara, CA, 30 m \times 25 μm i.d. \times 25 μm film thickness) was adopted for the analytes separation. The GC injector temperature was kept at 280 °C throughout the analysis. The carrier gas was He (ultra-high purity grade) held at a constant flow of 1.0 mL min^{-1} . The analytes after the GC separation were detected using a mass spectrometry detector (5973 MSD, Hewlett–Packard), which was operated at an ion source temperature of 230 °C and 70 eV for electron-impact ionization (EI). The mass scan range was from 50 to 200 amu. Identification was achieved by comparing the mass spectra with NIST 08 MS library and retention time of the chromatographic peaks with those of calibration standards. The two or three most abundant ion fragments of each BVOC were selected as extraction ions for the quantification. High purity chemical standards including α -pinene, camphene, β -pinene, myrcene, 3-carene, *p*-cymene, d-limonene, eucalyptol, γ -terpinene, terpinolene, linalool and α -terpineol were purchased from Aldrich (Milwaukee, WI) and Fluka (Buchs, SG, Switzerland), which were used for calibration. The LODs of the target BVOCs ranged from 0.31 to 0.50 ppbv. In addition to BVOCs, 41 VOCs were collected in a pressurized canister and measured by a GC/mass spectrometer (MS) (6890 GC/5973MS, Hewlett Packard, Palo Alto, CA) with the U.S. EPA TO-14 method (USEPA, 1999a). However, no target VOCs were detectable in the series of experiments.

Carbonyls in the air were collected into silica cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH) (Sep-Pak DNPH-silica, 55–105 μm particle size, 125 Å pore size; Waters Corporation, Milford, MA) with a Desert Research Institute (DRI) standard carbonyl sampler at a flow rate of 1 L min^{-1} for 1 h (Ho and Yu, 2002). Collection efficiencies were measured under field conditions by sampling carbonyls into two identical cartridges connected in series. They were calculated as 100% $(1 - A_b/A_f)$, where A_f and A_b were the amounts of a carbonyl collected on the front and the back sampling tubes, respectively. No breakthrough was found at such sampling flow rates and sampling times. The flow rates were checked in the beginning and at the end of each sampling using a calibrated flow meter (Gilibrator Calibrator; Gilian Instruments, W. Caldwell, NJ). A Teflon filter assembly (Whatman, Clifton, NJ) and an ozone scrubber (Sep-Pak; Waters Corporation) were installed in front of the DNPH-silica cartridge in order to remove any particulate matters and prevent possible influence of ozone, respectively (Spaulding et al., 1999). The recovery of carbonyls collection was not

affected by the ozone trap (Ho and Yu, 2002). Collocated samples were collected to examine the sample collection reproducibility, which was >95% in field. A cartridge was reserved to serve as a field blank and was handled the same way as the sample cartridges. The amounts of carbonyls detected in the cartridges were corrected for the field blank when we computed the air concentrations of the carbonyls. The DNPH-coated cartridges were stored in a refrigerator at <4 °C after sampling and before analysis.

A total of 17 carbonyls was monitored, including formaldehyde, acetaldehyde, acetone, propionaldehyde, 2-butanone (MEK), *iso* + *n*-butyraldehyde, benzaldehyde, *iso*-valeraldehyde, *n*-valeraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, hexanal, 2,5-dimethylbenzaldehyde, glyoxal and methylglyoxal. Unsaturated carbonyls including acrolein and crotonaldehyde were detected but their abundances were not reported in the study. The unsaturated carbonyl DNP-hydrazones can react with excess reagent to form adducts, which could not be quantified accurately due to chromatographic and response factor issues (Ho et al., 2011; Schulte-Ladbeck et al., 2001).

Each DNPH-coated cartridge was eluted with 2.0 mL of acetone-free acetonitrile (HPLC/GCMS grade, Mallinckrodt Laboratory Chemicals, Phillipsburg, NJ) to a volumetric flask. Test has been done to demonstrate that there was no DNPH and its derivatives remained in the cartridge after elution. Certified calibration standards of the monocarbonyl DNP-hydrazones were purchased from Supelco (Bellefonte, PA) and diluted into concentration ranges of 0.015–3.0 mg mL^{-1} . Calibration standards of the dicarbonyls were prepared by mixing glyoxal and methylglyoxal from Sigma (St. Louis, MO) in acetonitrile with 1 mL of 100 $\mu\text{g mL}^{-1}$ DNPH in an acidic aqueous solution. The mixtures were allowed to react at room temperature at least 6 h for a complete derivatization. The final volume of each calibration mixture was made to be 2.0 mL with 8:2 (v/v) of acetonitrile/pyridine (HPLC/GCMS grade; Sigma). Concentrations of the dicarbonyl DNP-hydrazones in the calibration standards ranged from 0.01 to 2.0 $\mu\text{g mL}^{-1}$. Linearity was indicated by a correlation of determination (r^2) of at least 0.999. The cartridge extracts and calibration standards were analyzed by injecting 20 μL of the samples to a high-pressure liquid chromatography (HPLC) system (Series 2000, PerkinElmer, Norwalk, CT) equipped with an ultra-violet (UV) detector. The column for separation was a 4.6 \times 250 mm Spheri-5 ODS 5 μm C-18 reversed-phase column (PerkinElmer, Norwalk, CT) operated at room temperature. The mobile phase consisted of two solvent mixtures: mixture A, 60:30:10 (v/v) of water/acetonitrile/tertbutylhydrofuran; mixture B, 40:60 (v/v) of water/acetonitrile. The gradient program was 80% A/20% B for 1 min, followed by linear gradients to 50% A/50% B for next 8 min and then to 100% B for next 10 min, and finally 100% C for next 5 min. The flow rate was 2.0 mL min^{-1} throughout the run. The absorbance at 360 and 420 nm were used for identification of the aliphatic and aromatic carbonyls (benzaldehyde and tolualdehydes) and dicarbonyls, respectively. Identification and quantification of carbonyl compounds were based on retention times and peak areas of the corresponding calibration standards, respectively. The Limit of Detection (LOD) was done by analyzing a minimum of seven replicates of a standard solution containing the analytes at a concentration of 0.02 mg mL^{-1} (25.45 ppm). It is estimated using the equation:

$$\text{LOD} = t_{(n-1, 1-\alpha=99\%)} \times S, \quad (1)$$

where $t_{(n-1, 1-\alpha=99\%)}$ is the T-distribution value at $n-1$ degrees of freedom, and S is the standard derivation of the replicates. The LODs of the target carbonyls ranged from 0.002 to 0.010 mg mL^{-1} . The measurement precision ranges from 0.5 to 3.2% and 1.7–4.6% for monocarbonyls and dicarbonyls, respectively.

3. Results and discussion

3.1. NH_3 effect on secondary organic aerosols (SOAs) formation

Fig. 1 presents the SOAs particle size distributions from the ozonolysis of BVOCs emitted from FC in the absence and presence of NH_3 . With the introduction of ozone, the “burst” growth of ultrafine particles (with $D_p < 100$ nm) was observed in the absence of NH_3 .

This finding is consistent with recent reports on the formation of SOAs that were generated from household product emissions in the presence of ozone (Destailats et al., 2006; Singer et al., 2006a). With the coexistence of NH_3 , the initial ultrafine particle formation was analogous to that in the absence of NH_3 . However, particle formation was much significant in the presence of NH_3 compared with that in the absence of NH_3 , especially with particle diameter ranging from 50 to 130 nm (Fig. 1b). The number concentration of

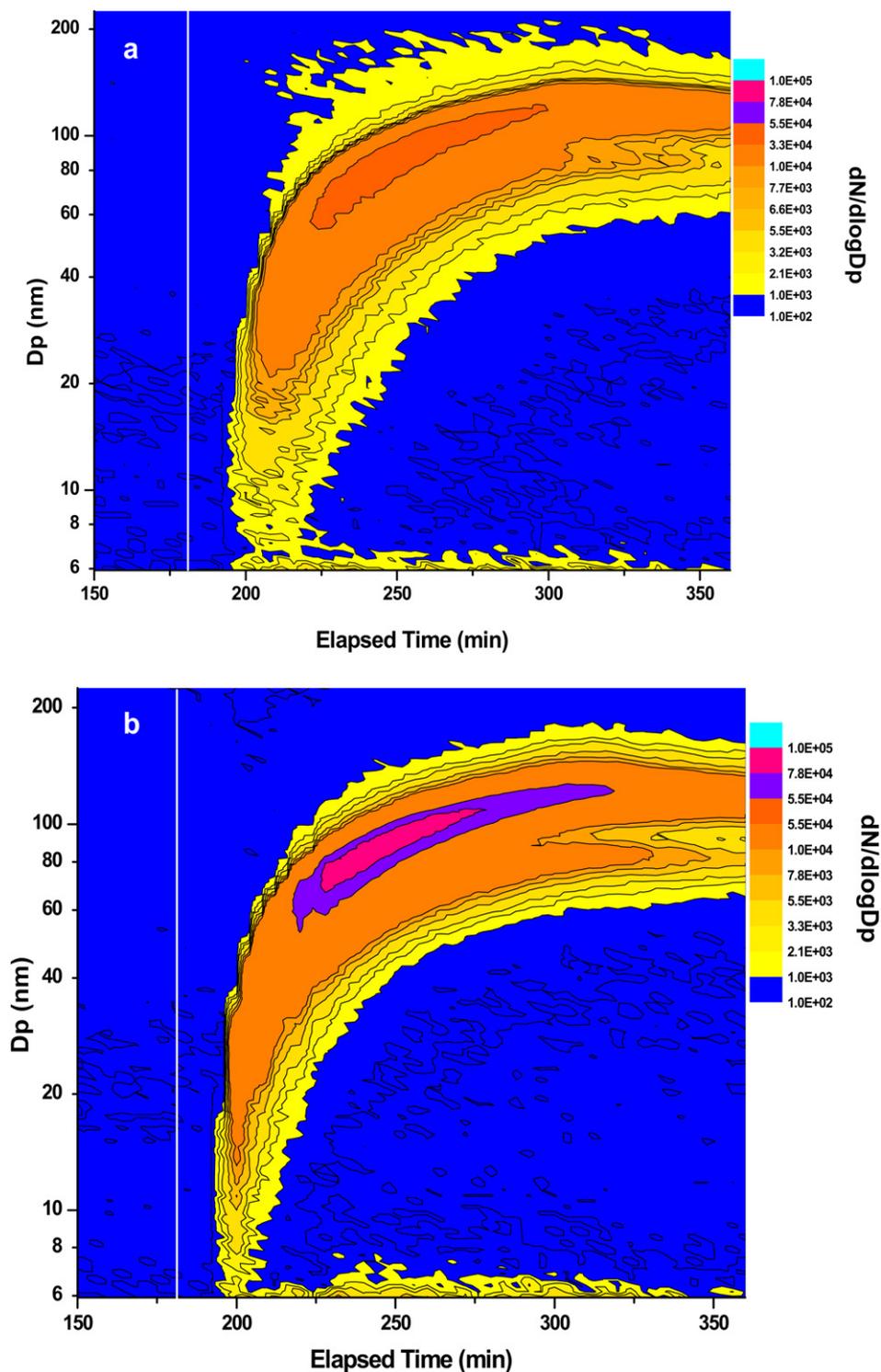


Fig. 1. Temporal evolutions of particle size distributions with a diameter of 6–225 nm measured with the SMPS equipment (a) without NH_3 presence, and (b) with NH_3 presence in the initial chamber atmosphere, respectively.

these nuclei mode particles was dominant relative to the total particle number concentration in the chamber atmosphere. The maximum total particle concentration was up to $2.0 \times 10^4 \text{ # cm}^{-3}$ in the presence of NH_3 (average maximum total particle concentration: $(2.0 \pm 0.01) \times 10^4 \text{ # cm}^{-3}$), but it was $1.3 \times 10^4 \text{ # cm}^{-3}$ without NH_3 which was 35% lower (Fig. 2a) (average maximum total particle concentration: $(1.3 \pm 0.006) \times 10^4 \text{ # cm}^{-3}$). This suggests that the new particles formation ability resulting from gas-to-particle conversion is stronger in the presence of NH_3 . The formed particles upon ozone dosage enlarged in diameter which can be attributed to the coagulation of particles in the nuclei mode and to the condensation of vapors onto existing particles resulting in the formation of particles in larger size range eventually (Seinfeld and Pandis, 1998). Our experimental results demonstrate that the coexistence of NH_3 pollutant has significant influence on indoor ozone chemistry, specifically ultrafine particles formations. Fig. 2a shows the typical ozone concentration profile during the whole experimental processes. The variations of particles geometric mean diameters before and after ozone introduction with and without NH_3 presence are compared in Fig. 2b. Before ozone introduction, the geometric mean diameters were ca. 70 nm either with or without NH_3 presence. However, after ozone dosage, the geometric mean particle diameters were reduced to less than 10 nm rapidly and then enlarged to ca. 110 nm. The nuclei coagulation and condensation resulted in the growth of SOAs. As shown in Fig. 2b, the presence of NH_3 slightly enlarges the mean particle diameter.

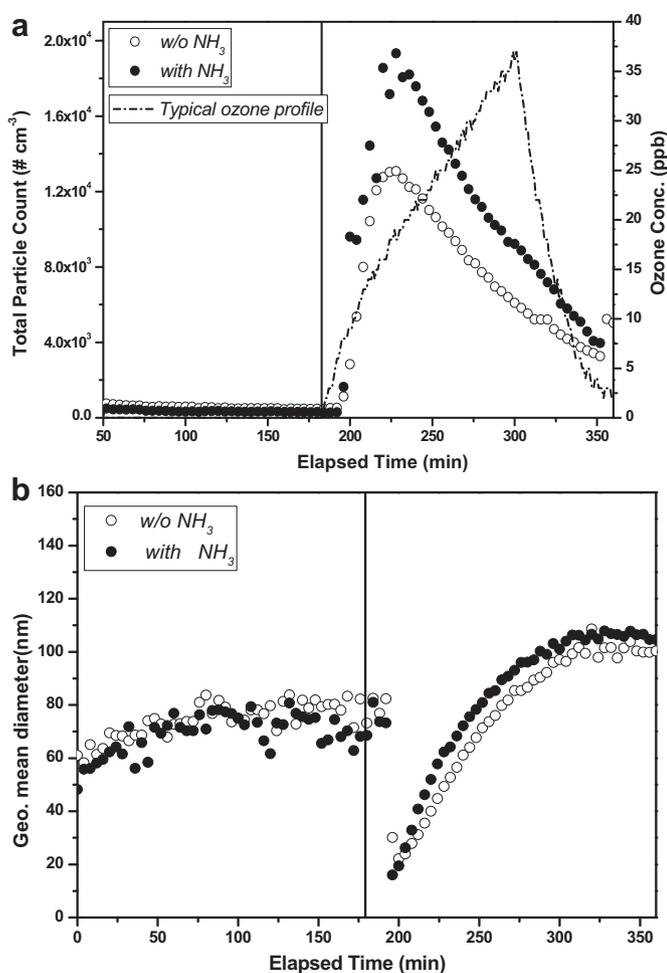


Fig. 2. (a) Ozone concentration, total particle number concentration, and (b) geometric mean diameters of particles without and with NH_3 presence in the initial chamber atmosphere.

Particles within this size range are small enough to penetrate deeply into the human lung and have been always linked to severe short- and long-term health effects such as asthma, cardio-respiratory disease, and lung cancer (De Gouw and Jimenez, 2009).

For the household samples of KC and DD, the presence of NH_3 in the initial atmosphere had a positive relationship with particles formation (see supporting information, Fig. S1 and S2). For KC sample, the maximum total particle concentration was up to $2.7 \times 10^4 \text{ # cm}^{-3}$ in the presence of NH_3 , while it was only $1.4 \times 10^4 \text{ # cm}^{-3}$ without NH_3 existence (Fig. S1 c). The NH_3 influence on KC sample was much stronger compared with that of FC sample. For DD sample, the maximum total particle concentration was up to $1.1 \times 10^5 \text{ # cm}^{-3}$ in the presence of NH_3 , while it was $3.2 \times 10^4 \text{ # cm}^{-3}$ without NH_3 (Fig. S2 c). The NH_3 influence on DD sample was the strongest among the three categories of household cleaning products. For KC and DD sample, as shown in Fig. S1d and Fig. S2d, the geometric mean particle diameters were reduced significantly in the presence of NH_3 compared with that in the absence of NH_3 . This indicates that the formation rates of new ultrafine particles resulting from gas-to-particle conversions were much faster than those of particle growths.

The above experimental results conclude that the extent of NH_3 effect on SOAs formation from the ozonolysis of BVOCs emissions from cleaning products is different among different cleaning products. This can be rationalized by considering the characteristics of BVOCs components in cleaning product and associated reaction byproducts with ozone. The reaction rates between ozone and different BVOCs are different (Huang et al., 2011b). Additionally, characteristics of the reaction byproducts are expected to affect the nucleation process (Destailats et al., 2006). As a result, different BVOCs emission components with a variety of ozone reaction constants can alter SOAs formation ability and result in the formation of different oxidation byproducts. For instance, linalool in the FC sample would react with ozone that fragments its carbon backbone yielding products with fewer carbon atoms. These products are therefore less likely to nucleate or condense (Destailats et al., 2006). Part of these oxidation-generated byproducts are organic acids that can experience gas-to-particle conversion if NH_3 is present (Na et al., 2007).

3.2. Effect on the consumption of BVOCs

Fig. 3 presents the consumption of BVOCs from FC, KC and DD in the presence of ozone with and without NH_3 . Before ozone introduction, the total quantified BVOCs concentrations in the chamber atmosphere after the complete evaporation of loaded cleaning products for FC, KC and DD were 395.2 ± 60.9 ppbv, 433.0 ± 11.3 ppbv and 491.4 ± 70.0 ppbv, respectively. The BVOCs component fractions for the three categories of household product were shown in Fig. S3 (see supporting information). d-Limonene, linalool, eucalyptol, camphene and p-cymene contributed 51%, 27%, 17%, 3.7% and 1.3% respectively, to the total BVOCs for the FC sample. d-Limonene was the most abundant species in KC with a composition of 94.5%, followed by terpineolene of 3.9% and p-cymene of 1.6%. Only d-limonene was detected in the DD sample. Remarkably, d-limonene was the most abundant compound in all the three cleaning products. For the five BVOC quantified in FC sample, p-cymene was consumed completely under the conditions either with or without the presence of NH_3 . Camphene was consumed completely in the absence of NH_3 , while 87% of it was consumed in the presence of NH_3 . The consumption percentages of d-limonene, eucalyptol, and linalool in the absence and presence of NH_3 were 87.0% and 91.0%, 73.0% and 68.0%, and 71.0% and 72.0%, respectively. p-Cymene, camphene and eucalyptol are relatively inert to the other BVOCs because of their low bimolecular rate constants with ozone ($<1.5 \times 10^{-19}$, $<5 \times 10^{-20}$ and $9 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,

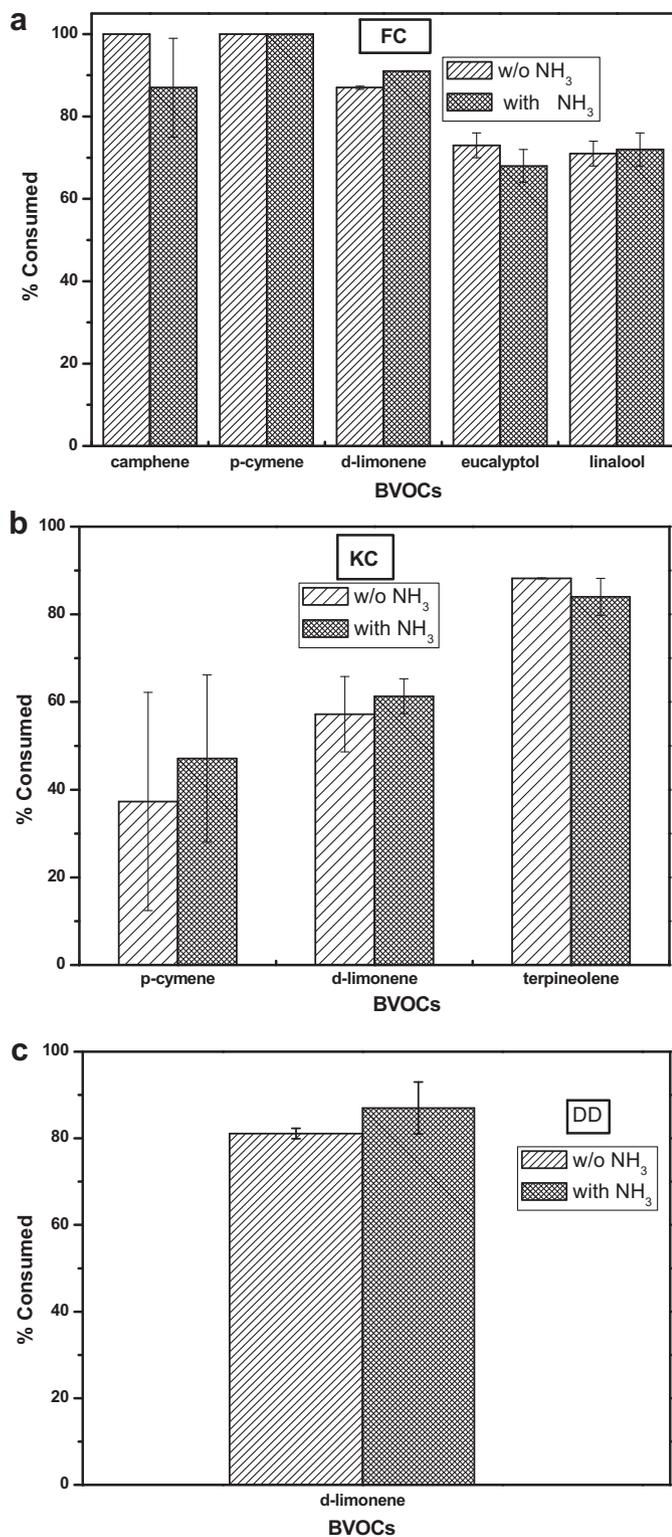


Fig. 3. Consumption of BVOCs from floor cleaners (FC), kitchen cleaners (KC) and dishwashing detergents (DD) in the presence and absence of NH₃. Error bars indicated SD (n = 3).

respectively) (Atkinson et al., 1990a, 1990b). For terpineolene, linalool, and d-limonene, the reaction rate constants with ozone in descending order were 1.9×10^{-15} , 4.3×10^{-16} , and 2.1×10^{-16} cm³ molecule⁻¹ s⁻¹, respectively (Atkinson and Arey, 2003; Atkinson et al., 1995). For the KC sample, the consumption percentages of p-cymene, d-limonene, and terpineolene were 37.3% and 47.1%,

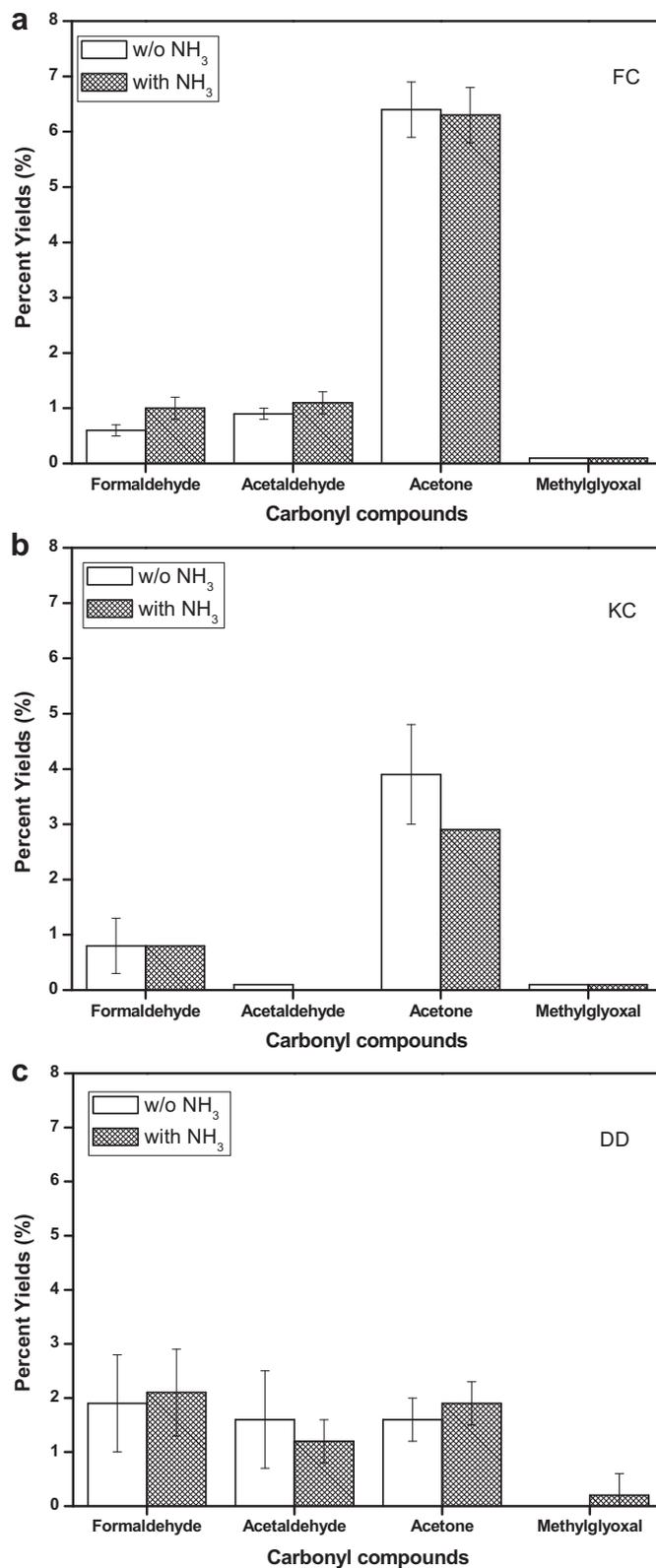


Fig. 4. Yields of carbonyl compounds to BVOCs consumption (ppbv/ppbv) in the absence and presence of NH₃.

57.2% and 61.3%, and 88.2% and 84.0% respectively in the absence and presence of NH₃. For DD, the consumption percentages of d-limonene were 81.1% and 87.0% in the absence and presence of NH₃, respectively. These results suggest that the presence of NH₃ in the

reaction systems can increase the consumption of d-limonene which is the most dominant BVOC compound in the cleaning products.

3.3. Effect on the formation of secondary carbonyl compounds

The percent yields (%) of secondary carbonyl compounds generated from the ozonolysis of BVOCs emitted from three categories of cleaning products were identified in the presence and absence of NH_3 . The percent yields are defined as the ratio of carbonyl compounds generated to the total quantified BVOCs reacted (ppbvppbv^{-1}). Fig. 4 shows the yields of carbonyl compounds from the ozonolysis of BVOCs emitted from FC, KC and DD samples in the presence and absence of NH_3 , respectively. As shown in Fig. 4a, acetone, followed by formaldehyde and acetaldehyde, were the three most dominant carbonyls produced in the reaction. The dicarbonyl compound, methylglyoxal, was also quantified. In the presence of NH_3 , the yields of formaldehyde and acetaldehyde were slightly higher than those with NH_3 absent. However, the yields for acetone and methylglyoxal were almost unchanged under the same conditions. For the KC and DD samples (Fig. 4b and c), the yields of acetone were not as high as those for FC sample under the same experimental conditions. In the presence of NH_3 , acetaldehyde was below LOD (Fig. 4b). For the DD sample, of which only d-limonene was quantified, the yields of formaldehyde and acetaldehyde were the highest among all the three categories of cleaning products. Formaldehyde can be generated as a primary carbonyl compound during ozonation of terminal alkenes such as d-limonene (Atkinson and Arey, 2003; Destailats et al., 2006).

According to our experimental results, the presence of NH_3 in the reaction system can significantly enhance the generation of ultrafine SOAs for all of the cleaning products. As reported by Na et al., condensable salts could be formed in the α -pinene ozonolysis system while NH_3 was present (Na et al., 2007). It was generally accepted that low volatility organic acids such as pinic acid and pinonic acid would be generated during the oxidation of biogenic hydrocarbons (Kavouras et al., 1999; Yu et al., 1999). In our chamber reaction system, organic acids were also expected to be the major byproducts. These generated organic acids can react with NH_3 to form the condensable salts of low volatility, which can probably contribute to the increase of SOAs particle number concentration.

4. Conclusions

This laboratory investigation illustrates the potential impact of NH_3 on ozone-initiated indoor chemistry involving constituents of common household cleaning products regarding the formation of SOAs and secondary carbonyl compounds. The SOAs formation ability resulting from gas-to-particle conversion becomes stronger in the presence of NH_3 , and the influence is BVOCs component-dependent. The NH_3 influence on DD sample was the strongest among the three categories of household cleaning products regarding to SOAs formation. The consumption of d-limonene, which is the most dominant BVOC compound in the cleaning products, was increased in the presence of NH_3 in the reaction systems that can partially contribute the enhancement of SOAs formation ability. The formation of secondary carbonyl compounds were also quantified in the presence and absence of NH_3 . By investigating the NH_3 effect on the ozonolysis of BVOCs mixtures in contrast to the chemistry of individual compounds, a better assessment can be made of the overall impact cleaning products have on real indoor environments.

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Appendix A. Supporting information

Supplementary data related to this article can be found online at doi:10.1016/j.atmosenv.2012.04.059.

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