Physical parameters effect on ozone-initiated formation of indoor secondary organic aerosols with emissions from cleaning products

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ABSTRACT

The effect of air exchange rate (ACH), temperature (T), and relative humidity (RH) on the formation of indoor secondary organic aerosols (SOAs) through ozonolysis of biogenic organic compounds (BVOCs) emitted from floor cleaner was investigated in this study. The total particle count (with D_p of 6–225 nm) was up to 1.2×10^3 # cm^{-3} with ACH of 1.08 h^{-1}, and it became much more significant with ACH of 0.36 h^{-1} (1.1×10^4 # cm^{-3}). This suggests that a higher ventilation rate can effectively dilute indoor BVOCs, resulting in a less ultrafine particle formation. The total particle count increased when temperature changed from 15 to 23 °C but it decreased when the temperature further increased to 30 °C. It could be explained that high temperature restrained the condensation of formed semi-volatile compounds resulting in low yields of SOAs. When the RH was at 50% and 80%, SOA formation (1.1–1.2×10^4 # cm^{-3}) was the more efficient compared with that at RH of 30% (5.9×10^3 # cm^{-3}), suggesting higher RH facilitating the initial nucleation processes. Oxidation generated secondary carbonyl compounds were also quantified. Acetone was the most abundant carbonyl compound. The formation mechanisms of formaldehyde and acetone were proposed.

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1. Introduction

Indoor uses of cleaning products and air fresheners lead building occupants of inhalation exposure to numerous airborne chemicals [1]. Singer and coworkers estimated that indoor concentrations of biogenic volatile organic compounds (BVOCs) can reach milligram per cubic meter levels associated with cleaning products consumption, while use of air fresheners can produce tens to hundreds of micrograms per cubic meter of BVOCs [2]. A few constituents in these household products can react with pre-existing indoor oxidants (e.g., ozone) to yield potentially harmful secondary pollutants including ultrafine particles and airborne chemicals [3]. Ozone is ubiquitous in indoor environment due to air-exchanges from outdoor air and generation from indoor sources such as photocopiers and laser printers [4]. Many proved the "burst" growth of secondary organic aerosols (SOAs) from reactions between indoor ozone and the BVOCs emitted from the household cleaning products [3,5,6].

In addition, it is noteworthy that the surfaces of those ultrafine particles are probably nitrated or acidic [7,8], of which if inhaled, they can pose adverse health risks.

The formation of indoor SOAs varied under certain conditions, for example, with particular physical parameters such as air exchange rates (ACH), relative humidity (RH), and temperature (T). Diurnal or seasonal variations of these physical parameters could dramatically influence the generation and growth of indoor SOAs [9]. Weschler et al. found that ACH can affect indoor chemistry through altering both reaction time and initial concentrations of reactive species involved in the SOAs formations [10]. The elevated ventilation rates not only enhance ozone infiltration from outdoor to indoor, but also boost the dilution of SOA derived from indoor chemistry [11]. A few chamber studies demonstrated that T has a pronounced influence on the mass and number concentrations of SOAs generated from the reactions between BVOCs and ozone [9,12–17]. With the semi-empirical thermodynamic approach done by Pankow and Odum et al., the productions of SOAs increased with a decreasing of T because of partitioning to condensed phase [12,18–20]. The T can affect complicatedly the SOAs reaction pathways and its degree of influences varied in different environmental

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systems. For example, Pathak et al. showed that the yields of SOAs from ozonolysis of α-pinene had a weak association with T between 15 and 40 °C while a much stronger T dependence was shown in the range of 0 and 15 °C [14]. Enthalpy of precursor vaporization was found to significantly impact T dependence on the SOAs formation [21]. The amount of SOAs formed at 17 °C was approximately 5–6 times higher than that at 45 °C during the ozonolysis of α-pinene [22]. RH is another critical physical parameter dramatically impacting the SOAs formations. Jonsson and co-workers reported that the water effect at a low $T(-30$ °C) could be ascribed to physical uptake and cluster stabilization, while at higher T (0 and 25 °C) chemical reaction mechanism could also be altered [12].

It should be emphasized that previous studies only focused on individual BVOC and how physical parameters influencing its reaction with ozone in a small chamber (i.e., <1 m³ in volume). This may not fully reflect the reality for indoor environment because a mixture of different reactive BVOCs can be emitted from the household cleaning products. In this study, a large environmental chamber (18.26 m³ in volume) has been adopted to simulate a ventilated indoor environment. A popular floor cleaner sold in Hong Kong was selected which act as a BVOCs emission source. The physical parameters (ACH, T, and RH) affecting the SOAs formations in presence of ozone were investigated systematically. The ranges of these parameters are comparable to real indoor conditions in Hong Kong. Secondary reaction products of carbonyl compounds were also determined and their formation mechanism was tentatively discussed. A better understanding on those effects can assist occupants to choose an optimal abatement method for controlling indirect generation of SOAs while the household products are used.

2. Experimental

2.1. Environmental chamber

Experiments were conducted in a stainless-steel environmental chamber (3.2 m × 3.2 m × 2.5 m) with a effective volume of 18.26 m³ [23]. Its surface area to volume ratio is 2.87 (m²/m³). Fig. 1

shows the schematic diagram of the large environmental chamber set-up. 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 a central control system for adjustment of ACH, RH and 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 ACH was altered by controlling the airflow rate. The T of air was controlled by conditioning coils. RH was regulated by adding appropriate amount of deionized water into the air system. A Q-Trak monitor (Model 8550, TSI Inc., Shoreview, MN) recorded both T and RH continuously in a 1 min-sampling interval. 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.

2.2. Sample introduction

Table 1 summarizes the ACH, T, RH, ozone concentration, and floor cleaner dosage in each test. The background in the chamber air were kept <10 μg m⁻³ for total volatile organic compounds (TVOCs) and <2 μg m⁻³ for individual VOC [23,24]. A floor cleaner with lemon scent popularly used by Hong Kong households was selected as an emission source of BVOCs. A volume of 50 mL of the floor cleaner was transferred on a Teflon plate (38 cm × 32 cm × 4 cm) which was placed on the floor in 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 until a level of 45 ppbv was reached. The daily maximum 8 h mean ozone concentration is 50 ppbv as recommended by world health organization (WHO) in order to protect human health [25].
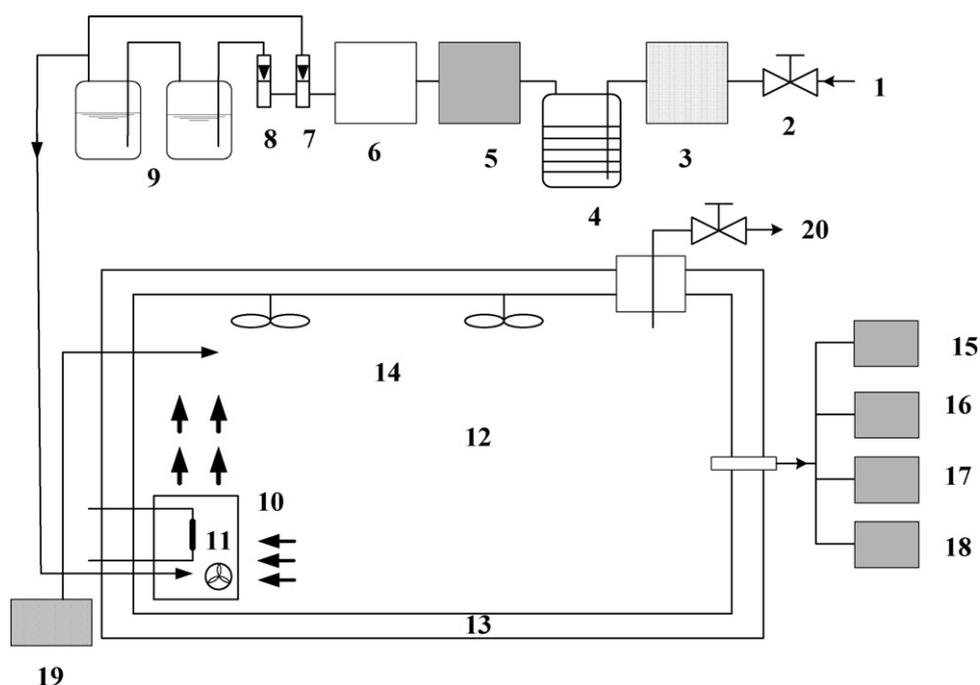
Fig. 1. Schematic diagram of the chamber study set-up: (1) air inlet; (2) valve; (3) blower; (4) active charcoal filters; (5) HEPA filters; (6) mass flow controllers; (7) flow controller dry air; (8) flow controller wet air; (9) humidifier; (10) rotating cylinder; (11) heating unit; (12) large environmental test chamber; (13) insulation layer; (14) mixing fan; (15) SMPS/CPC; (16) ozone monitor; (17) carbonyl sampling; (18) gas analyzer; (19) ozone generator; and (20) air outlet.

Table 1
Summary of the physical parameters investigated on the reaction between BVOCs emitted from the floor cleaner and ozone in the chamber study.

Floor cleaner dosage (mL)	ACH (h^{-1})	T (°C)	RH (%)	Maximum ozone concentration (ppbv)
ACH effect				
50	1.8	23	80	45
50	1.08	23	80	45
50	0.36	23	80	45
T effect				
50	0.36	30	80	45
50	0.36	23	80	45
50	0.36	15	80	45
RH effect				
50	0.36	23	80	45
50	0.36	23	50	45
50	0.36	23	30	45

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. Twelve of BVOCs and seventeen of 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 recorded 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 solid-phase microextraction (SPME) method. A manual SPME sampling holder consists of a 75 μm Carboxen-PDMS fiber (Supelco, Bellefonte, PA). New fiber was heated in a gas chromatography (GC) injection port 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 show that no BVOCs of interest remained on the fiber. For sample collection, the fiber was inserted through sampling port and exposed for 20 min in the chamber. The SPME sample was once measured with a GC/flame ionization detector (FID) system (GC-17A, Shimadzu, Tokyo, Japan) by desorbing it in the injection port at 280 °C for 5 min. During the desorption period, the GC oven temperature was kept at 40 °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 program was initially set at 40 °C and held for 5 min, increased to 150 °C at a rate of 10 °C min^{-1}, then increased to 250 °C at a rate of 25 °C min^{-1}, and held at the final temperature for 2 min. A DB-5MS UI column (30 m × 25 mm i.d. × 25 μm film thickness, J&W, Agilent Technologies, Santa Clara, CA) was adopted for the analytes separation. The flow of hydrogen and air for FID were 30 and 300 mL min^{-1}, respectively. The detector temperature was 280 °C. Identification was achieved by comparing the retention times of the chromatographic peaks with those of calibration standards. The high purity of 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) were used for calibration. The LODs of the targeted BVOCs ranged from 2 to 5 ppbv. P-cymene, d-limonene and α-terpineol were

quantified from the floor cleaner with chemical compositions of 60.4 ± 5.25, 575.0 ± 19.0 and 135.8 ± 36.1 μg g^{-1}, respectively, of which d-limonene was the most abundant species accounting up to 74.6%. In addition to BVOCs, 41 VOCs were collected in pressurized canister and measured by a GC/mass spectrometer (MS) (6890 GC/5973MS, Hewlett Packard, Palo Alto, CA) with the US EPA TO-14 method [26]. However, no any targeted VOCs were detectable in the series of experiment.

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 [27]. 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 [28]. The recovery of carbonyls collection was not affected by the ozone trap [29]. 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 methyglyoxal. 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 [30,31].

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 no any DNPH and its derivatives remained in the cartridge after the 2.0 mL 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 μg mL^{-1} DNPH in an acidic aqueous solution. The mixtures were allowed to standard 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 μg 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 mm × 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/tertahydrofuran; 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}. It is estimated using the equation:

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

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 μg mL^{-1}. The measurement precision ranges from 0.5–3.2% to 1.7–4.6% for monocarbonyls and dicarbonyls, respectively.

3. Results and discussion

3.1. Effect of air exchange rate (ACH)

Experiments were conducted with three different ACHs of 0.36, 1.08 and 1.8 h^{-1} at constant T of 23 °C and RH of 80% (Table 1). The formation of SOAs was not observed with the ACH of 1.80 h^{-1} in the presence of ozone (Fig. 2a). However, while the ACH was reduced 40% to 1.08 h^{-1}, the generation of SOAs was seen after the introduction of ozone (Fig. 2b). Such "burst" growth phenomenon is much obvious with the lowest testing ACH of 0.36 h^{-1} (Fig. 2c). Fig. 3 demonstrates the increase of total particle number concentrations (particle diameter D_p, ranging from 6 to 225 nm) when ozone was input in the chamber with the three ACHs. The maximum particle count ($N_{6-225nm}$) reached 1.1×10^4 # cm^{-3} with the ACH of 0.36 h^{-1} which is one order of magnitude higher than that with the ACH of 1.08 h^{-1} (1.2×10^3 # cm^{-3}). This suggests that a higher ventilation rate can effectively dilute the BVOCs in the indoor environment, resulting in a less ultrafine particle formation in the presence of ozone. Our results are agreed with the observation by Weschler et al. [10]. Their study showed that the concentrations of indoor pollutants increased from both unimolecular and bimolecular reactions while the ventilation rate decreased. Our finding is informative for indoor environmental conservation because usual residential ACH is typically <1 h^{-1}. The average ACH was 0.71 h^{-1} at residential homes in US metropolitan urban areas [32] and was below 0.5 h^{-1} at Swedish homes [33]. The average ACH is expected to be even lower than these values in high-density cities such as Hong

Fig. 2. Particle size distributions of SOAs generated from the reaction between BVOCs emitted from the floor cleaner and ozone with (a) ACH = 1.80 h^{-1}, (b) ACH = 1.08 h^{-1} and (c) ACH = 0.36 h^{-1} at T of 23 °C and RH of 80%. Number indicated in boxes corresponds to the particle distribution dN/dlogD_p (# cm^{-3}) for each contour line. Ozone supply started at t = 120 min and ended at t = 240 min.
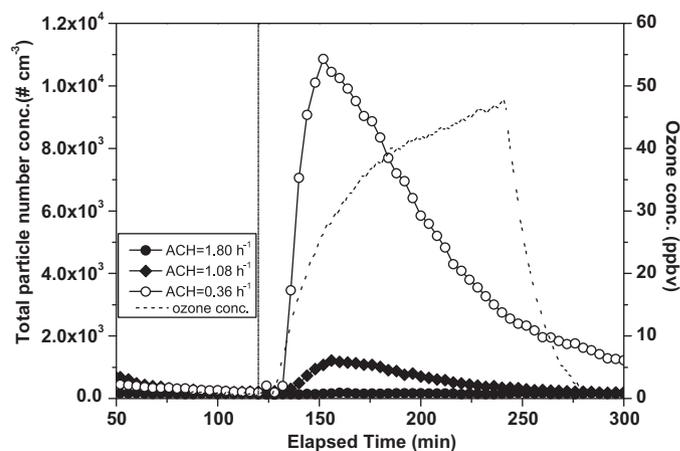
Fig. 3. Profiles of total particle count and ozone concentration with particle diameter (D_p) ranging from 6 to 225 nm at T of 23 °C and RH of 80%.

Kong. Our observation suggests that the SOAs formation from the use of cleaning products is possibly favor in real residential homes.

3.2. Effect of temperature (T)

Fig. 4 shows the T effects on the SOAs formation from the reaction of BVOCs and ozone with constant ACH of $0.36\,h^{-1}$ at RH of 80%. The total particle count increased when T rose from 15 to 23 °C but then decreased at 30 °C (Fig. 5). While the T reached to 30 °C (Fig. 4c), the formation of ultrafine particles was delayed in comparison with that at 15 and 23 °C (Fig. 4a and b). Furthermore,
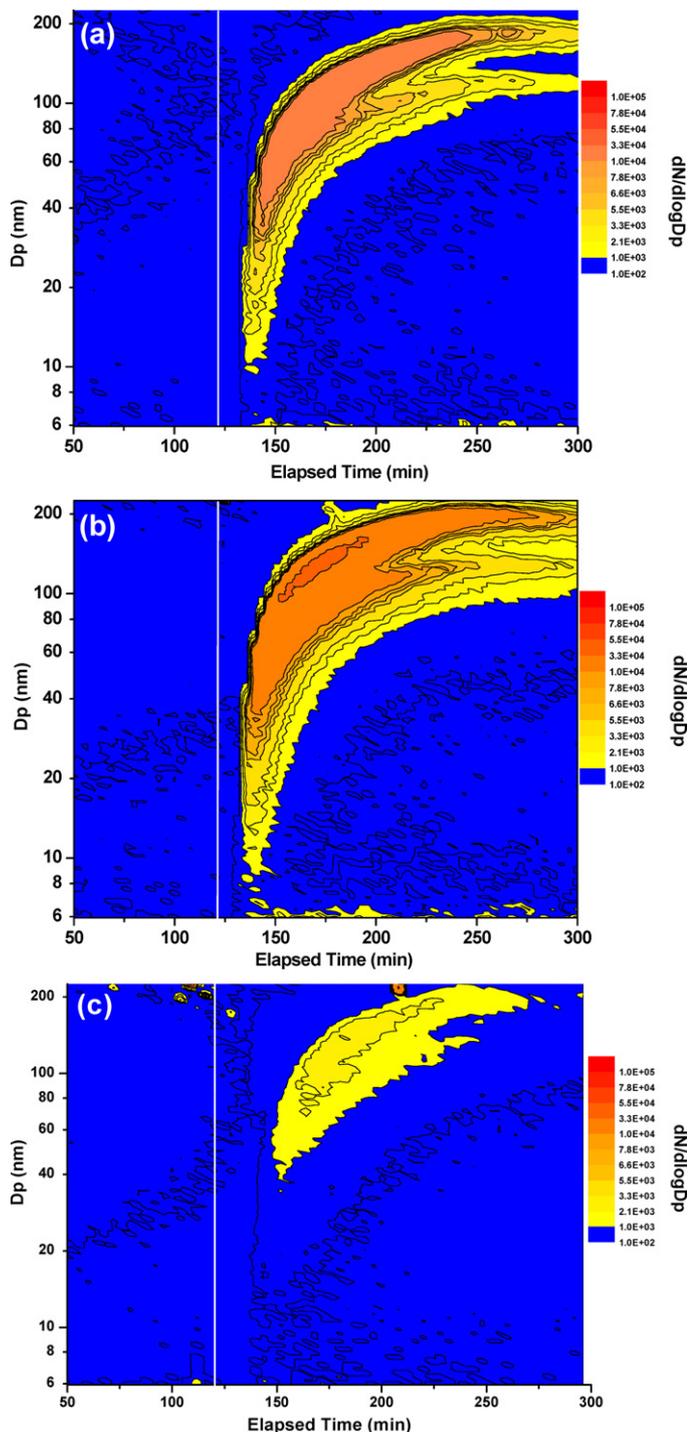
the formation of ultrafine particles with $D_p < 40\,nm$ was extremely suppressed at 30 °C. This can be attributed to the volatilization of semi-volatile products at a high T inhibiting the nuclei formation and products condensation [13]. After the ozone introduction, rapid formations of large numbers of ultrafine particles occurred, followed by particle growth. Fig. 4a and b shows uniform bimodal particle size distributions with the reaction time elapsed, reflecting the growth of particles after initial nucleation processes. When the T increased from 15 to 23 °C, the total particle number concentration ($N_{6-225nm}$) increased significantly from 6.32×10^3 to $1.08 \times 10^4\,\#\,cm^{-3}$. This observation was different from a few previous studies demonstrating that a lower T facilitates the formation and growth of SOAs through ozonolysis [9,12,13,17] because intermediate reaction products should be more stable [15]. In contrast, Pathak and coworkers showed that the yields of SOAs from ozonolysis of α-pinene at atmospherically relevant concentrations had a weak dependence on T in the range of 15 and 40 °C but the influence became stronger between 0 and 15 °C [14]. Jonsson et al. also observed that the ozonolysis of limonene was the most efficient in production of SOAs at 25 °C evidenced by both number and mass of particles formed [12]. In our study, it is understandable that a higher T is more favorable for the evaporation and dispersion of BVOCs from liquid floor cleaner sample. However, if T is too high (e.g., >30 °C), it can inhibit the condensation of semi-volatile organic compounds (SVOCs) formed in the reactions, resulting in less SOAs generations.

3.3. Effect of relative humidity (RH)

Fig. 6 shows the effects of RH on the formation and growth of SOAs with the constant ACH of $0.36\,h^{-1}$ at 23 °C. When the RH was >50%, the initial rate of SOA formation was higher than that at RH of 30%. This suggests that higher RH facilitates the initial nucleation processes, which is essential for ultrafine particles formation. Additionally, a 20-min delay of the SOA formation was observed at RH of 30%. As shown in Fig. 7, with an increase of RH, the total particle number concentration ($N_{6-225nm}$) also increased obviously. The maximum total particle number concentration ($1.1–1.2 \times 10^4\,\#\,cm^{-3}$) was similar at the RH of 50 and 80%. The results indicate that the increases of RH can enhance the SOAs production during the ozonolysis. Jonsson et al. [34] found that an increase of RH from <2% to 85% can promote more SOAs productions from the ozone-initiated oxidation of limonene, Δ^3-carene, and α-pinene. Their later study also reported that water at a low temperature (i.e., −30 °C) could be ascribed to physical uptake and cluster stabilization, while at higher temperatures (i.e., 0 and 25 °C)

Fig. 4. Particle size distributions of SOAs generated from the reaction between BVOCs emitted from the floor cleaner and ozone with ACH of $0.36\,h^{-1}$ at RH of 80% and (a) T = 15 °C, (b) T = 23 °C, and (c) T = 30 °C.
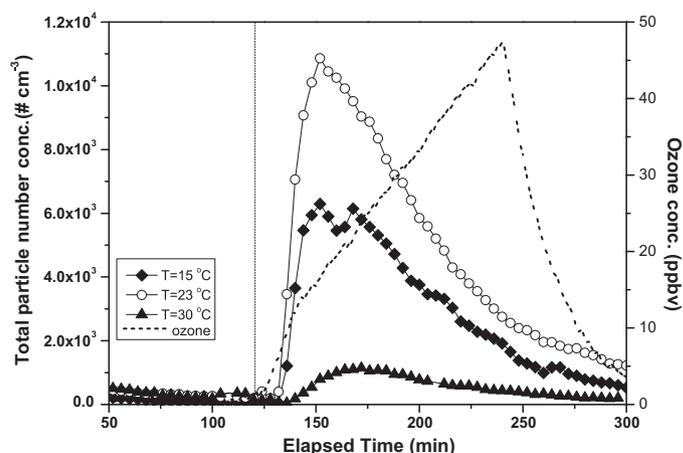
Fig. 5. Profiles of total particle count and ozone concentration with particle diameter (D_p) ranging from 6 to 225 nm with ACH of $0.36\,h^{-1}$ at RH of 80%.

Fig. 7. Profiles of total particle count and ozone concentration with particle diameter (D_p) ranging from 6 to 225 nm with ACH of 0.36 h^{-1} at T of 23 °C.

cally unfavorable reactions to take place [36]. We also believe that higher RH (>50%) can alter chemical reaction pathways in this study based on our experimental results. The excellent and good classes of Hong Kong indoor air quality (IAQ) objectives for offices and public places of RH are 40–70% and 70%, respectively [37]. However, such range of RH can supply favorite conditions for indoor SOA formations after the uses of household cleaning products if ozone presents.

3.4. Formation of secondary carbonyl compounds

Fig. 8 shows the percent yields of secondary carbonyl compounds during ozonolysis of BVOCs emitted from the floor cleaner sample. Percent yield is defined as the molar ratio of carbonyl compounds generated from the ozonolysis to the total quantified BVOCs consumed.

Acetone, followed by formaldehyde and methyl ethyl ketone (MEK), were the most three dominant carbonyls produced in the reaction. The concentrations of other monocarbonyls and dicarbonyls were below LOD. Formaldehyde and acetone are air toxics and can pose public health risks [38–40]. Only acetone was detected which had a yield of 7.9% with the ACH of 1.80 h^{-1}. When the ACH was reduced to 1.08 h^{-1}, Formaldehyde was additionally detected. The percent yield of these two secondary carbonyls was 6.3%. MEK, in addition to formaldehyde and acetone, were detected when the

Fig. 6. Particle size distributions of SOAs generated from the reaction between BVOCs emitted from the floor cleaner and ozone with ACH of 0.36 h^{-1} at T of 23 °C and (a) RH = 30%, (b) RH = 50%, and (c) RH = 80%.

the chemical mechanism or reaction rates would be altered [12]. Tobias and coworkers also demonstrated that RH offers a considerable influence on the chemical formations of SOAs from the reaction of 1-tetradecene and ozone [35], suggesting the water vapor can possibly alter the chemical reaction pathways. It has recently been shown that water can alter the kinetics of radical-molecule reactions because of reduced reaction barrier heights for the complexes, thereby possibly allowing additionally energeti-

Fig. 8. Yields of carbonyl compounds to BVOCs consumption (ppbv/ppbv).

ACH was further decreased to 0.36 h^{-1}. The total carbonyl yields also rose to 16.1%. Even though the particle number concentration was lower at 15 °C than that at 23 and 30 °C, the total carbonyl yield was the highest of 22.8%. RH had influences on the secondary carbonyl formation as well. For the RH of 30%, the yield was >30%, which was the highest among the three testing RHs.

Acetone is formed in the reaction between •OH and α-terpineol but was not detected when •OH scavenger (e.g., cyclohexane) of ozone is present [42,45]. Summarizing the observations from those studies, an increase in concentration of acetone can be partially ascribed to the oxidation of α-terpineol by •OH. Here concludes potential chemical pathways for the oxidation of α-terpineol by •OH radicals to form acetone [42,46]:

α-Terpineol

Formaldehyde

Acetone

Acetone

4-Oxopentanal

Glyoxal
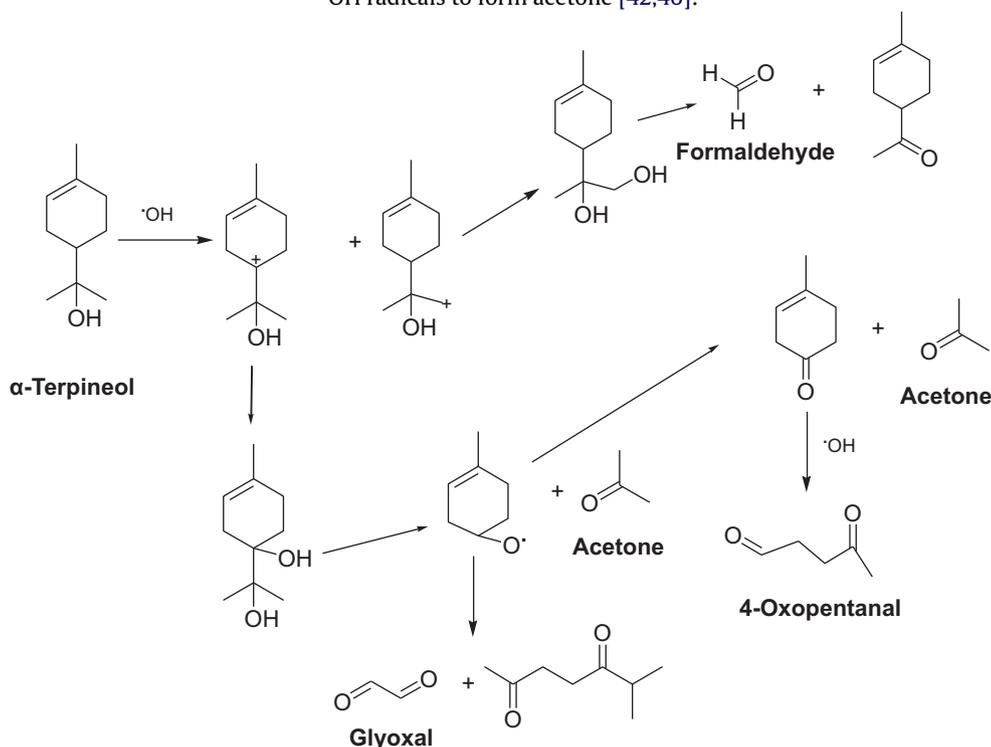
p-Cymene, d-limonene and α-terpineol were quantified in the floor cleaner sample adopted in this study with mass concentrations of 60.4 ± 5.25, 575.0 ± 19.0 and 135.8 ± 36.1 μg of BVOC in 1 g of floor cleaner sample (μg g^{-1}), respectively. Their molecular structures are shown as follows:

p-Cymene   d-Limonene   a-Terpineol
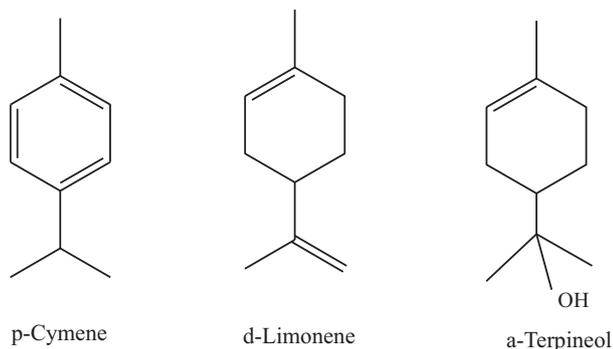
Apparently, these compounds all contain at least one endocyclic double bonds, especially for d-limonene with a terminal double carbon bond. Hydroxyl radicals (•OH) can be generated from the terpene/O$_3$ reactions in indoor environment [41,42]. It was shown that the yield of •OH radical from the gas-phase reactions of O$_3$ with limonene was 67 ± 10% [43]. The concentration of •OH strongly depends on the dynamic balance between the rate of its production and the rate of consumption by chemical reactions [3]. The average •OH concentration in a typical office was approximately 7×10^5 molecule cm^{-3} under natural conditions [44]. Besides, those generated •OH radicals can react with BVOCs by either addition to the carbon–carbon double bond in cyclic ring or by hydrogen abstraction.

Formaldehyde, acetone, and glyoxal can be possibly generated. However, the concentrations of glyoxal were below LOD in this study, representing that its formation may be limit under our defined conditions. 4-Oxopentanol can be formed potentially but it could not be quantified with the DNPH/HPLC-UV method.

Formaldehyde can be produced as a primary carbonyl in the ozonolysis of the terminal alkenes such as d-limonene [47]. Moreover, •OH generated from the ozone/terpene reactions plays an important role in chemical transformations, which is responsible for approximately 56–70% of the total formaldehyde production [41]. Therefore, the increase in concentrations of formaldehyde in this study could be ascribed to both the ozonolysis (primary) and •OH oxidation reactions (secondary). Unfortunately, their contributions could not be encountered accurately without knowledge on all formation mechanisms and quantification of all potential precursors and reaction products.

Even through MEK was one of the three important carbonyls in this study, there is a lack of information showing it can be generated by either primary and/or secondary pathway. We assume that its production pathway should be similar to acetone owing to their similarity in chemical structures and properties of ketone. Further study is thus needed to elucidate its role in the ozonolysis.

4. Conclusion

Environmental parameters including ACH, T, and RH have significant influences on the formation and growth of SOAs from reactions between BVOC emissions from floor cleaner and ozone. With high ACH of 1.8 h^{-1}, the formation of SOA was unnoticeable after ozone dosing. However, when the ACH was reduced to 1.08 h^{-1} and 0.36 h^{-1}, the generation and growth of SOA particles was observed. High ACH can effectively dilute the BVOCs in the

indoor environment, resulting in a less ultrafine particle formation in the presence of ozone. Although a higher T is more favorable for the evaporation and dispersion of BVOCs from liquid floor cleaner sample, the T may influence reversely the condensation of semi-volatile organic compounds (SVOCs) formed in the reactions if T is too high (e.g., >30 °C). Higher RH (>50%) facilitates the initial nucleation processes compared with that at lower RH (30%). However, the excellent and good classes of Hong Kong indoor air quality (IAQ) objectives for offices and public places of RH are 40–70% and 70%, respectively. Therefore, it can supply favorite conditions for indoor SOA formations, leading to a hidden issue for the uses of household cleaning products if ozone presents. Acetone, followed by formaldehyde and methyl ethyl ketone (MEK), were the most three dominant carbonyls produced in the ozonolysis reaction. The carbonyl yields also varied with the physical parameters variation. The results obtained in this study are meaningful for occupants to select proper control method over indoor SOAs formations in real indoor environments.

Acknowledgements

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