

Influence of ozone concentration and temperature on ultra-fine particle and gaseous volatile organic compound formations generated during the ozone-initiated reactions with emitted terpenes from a car air freshener

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Abstract

Experiments were conducted to identify the emissions from the car air freshener and to identify the formation of ultra-fine particles and secondary gaseous compounds during the ozone-initiated oxidations with emitted volatile organic compounds (VOCs). The identified primary constituents emitted from the car air freshener in this study were α -pinene, β -pinene, *p*-cymene, and limonene. Formation of ultra-fine particles (4.4–160 nm) was observed when ozone was injected into the chamber containing emitted monoterpenes from the air freshener. Particle number concentrations, particle mass concentrations, and surface concentrations were measured in time dependent experiments to describe the particle formation and growth within the chamber. The irritating secondary gaseous products formed during the ozone-initiated reactions include formaldehyde, acetaldehyde, acrolein, acetone, and propionaldehyde. Ozone concentration (50 and 100 ppb) and temperature (30 and 40 °C) significantly affect the formation of particles and gaseous products during the ozone-initiated reactions. The results obtained in this study provided an insight on the potential exposure of particles and irritating secondary products formed during the ozone-initiated reaction to passengers in confined spaces.

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1. Introduction

Automobiles, which usually have confined space, have potentially higher concentrations of air pollutants than those in urban troposphere. The toxic air pollutants at the indoor of automobiles mostly consist of gasoline and diesel exhausts. These pollutants (i.e., carbon monoxide (0.7–83.7 ppm) [1,2], ozone (2–86 ppb) [1,3], nitrogen oxides (NO_x: 1.6–548.5 ppb) [1,3], particulate matter, and other volatile organic compounds (VOCs: 1999–5373 $\mu\text{g}/\text{m}^3$) [4]) can easily accumulate inside the automobile and provide a chance of fatal exposure to the passengers as observed in several studies. A host of other volatile organic chemicals could also be emitted from the car interior materials such as cabin components and accessories. As an example, car air fresheners are commonly found inside the automobiles to improve and refresh the indoor atmosphere. Air fresheners usually contains the natural products such as extracts from essential

oil and plant oil commonly found in scenting agents and solvents [5,6], which could be a potential source of biogenic VOCs in a confined space. It is well known that biogenic VOCs such as monoterpenes have an exceptional capacity to generate condensable products as a result of oxidation with ozone in early stage. The ozone-initiated oxidation subsequently forms ultra-fine particles and potentially irritating gaseous organic products such as formaldehyde, hydrogen peroxide, hydroxyl radicals, and other low volatile oxygenated compounds [7–10]. It has been reported that ultra-fine (less than 100 nm) and fine (less than 1000 nm) particles can be produced during the oxidation of terpenes with ozone. They are mostly in the range of 67–397 nm, which is very appropriate for the deposition in respiratory tracts. Therefore, they can easily cause harmful effects (e.g., irritations) on human and animals [11,12]. The ultra-fine particles have a high alveolar deposition fraction and larger surface area, which could increase the possibility to react with a living body and/or to play a role as the carrier of toxic gas [13,14]. The ozone concentration inside the automobile could be high enough to initiate chemical oxidations with monoterpenes emitted from car air freshener so that the use of car air freshener under the condition can lead to

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the exposure and/or inhalation of toxic ultra-fine particles and secondary gaseous organic products.

Smog chamber studies have shown that temperature significantly affects the distribution of secondary gaseous products and particles. The reaction kinetic rate increased as the temperature increased producing volatile or highly condensable gases. The vapor pressures of organic compounds increases as well yielding a lower fraction of condensable gases [15,16]. It has been shown that the increase of temperature considerably affects the gas-particle equilibrium and favors the formations of high concentrations of gas-phase products and low concentrations of particle-phase products [17]. Outdoor ground-level ozone is particularly significantly high during hot and sunny days. The health of passengers inside the vehicles could be significantly affected by these secondary organic products formed during the ozone-initiated oxidation with biogenic VOCs emitted from car air freshener. The exposures could pose more harmful occupational hazards to the heavily exposed group (e.g., taxi and truck drivers, car patrol officers, etc.).

Studies have been conducted to monitor the existing air pollutant concentrations inside automobiles [1–4], however no significant studies have been conducted to characterize the potential ozone-initiated oxidation with biogenic VOCs emitted from car air fresheners. We have investigated the potential effects of temperature as well as the ozone concentration on the formation of secondary organic products using a chamber test in this research. Target biogenic VOCs emitted from the car air freshener and several gaseous products and particles have been monitored and identified during the ozone-initiated reactions.

2. Experimental

2.1. Chemicals

The car air freshener was purchased from an internet-based store in Seoul, Korea. An oil-based liquid car freshener type with a citrus scent was chosen to best represent its terpene source and ozone was used as a representative atmospheric oxidant in confined environments. The air freshener does not necessarily represent all different types of car air fresheners.

The chemicals used for the analyses of target compounds and products were ACS grade or higher: α -pinene (98%, Sigma–Aldrich), β -pinene (99%, Sigma–Aldrich), limonene (97%, Sigma–Aldrich), and *p*-cymene (99%, Sigma–Aldrich); the carbonyl standard mixture (formaldehyde: 215 $\mu\text{g}/\text{mL}$, acetaldehyde: 190 $\mu\text{g}/\text{mL}$, acetone/acrolein: 122 $\mu\text{g}/\text{mL}$, and propionaldehyde: 122 $\mu\text{g}/\text{mL}$, Supelco). The solvents used as eluents and extractants in this research were high-performance liquid chromatograph (HPLC) or higher grade: acetonitrile (99.8%, J.T. Baker) and pure water (J.T. Baker).

2.2. Experimental procedures

A Teflon[®] film batch bag (~5 L) was used to identify the biogenic VOCs emitted from the car air freshener. A Teflon[®] film chamber (1 m³) was used to investigate and monitor the effects of ozone concentrations and temperature on the formation of secondary products such as aldehydes and ketones and ultra-fine particles. The schematic diagram of experimental setup used for the chamber experiments is shown in Fig. 1.

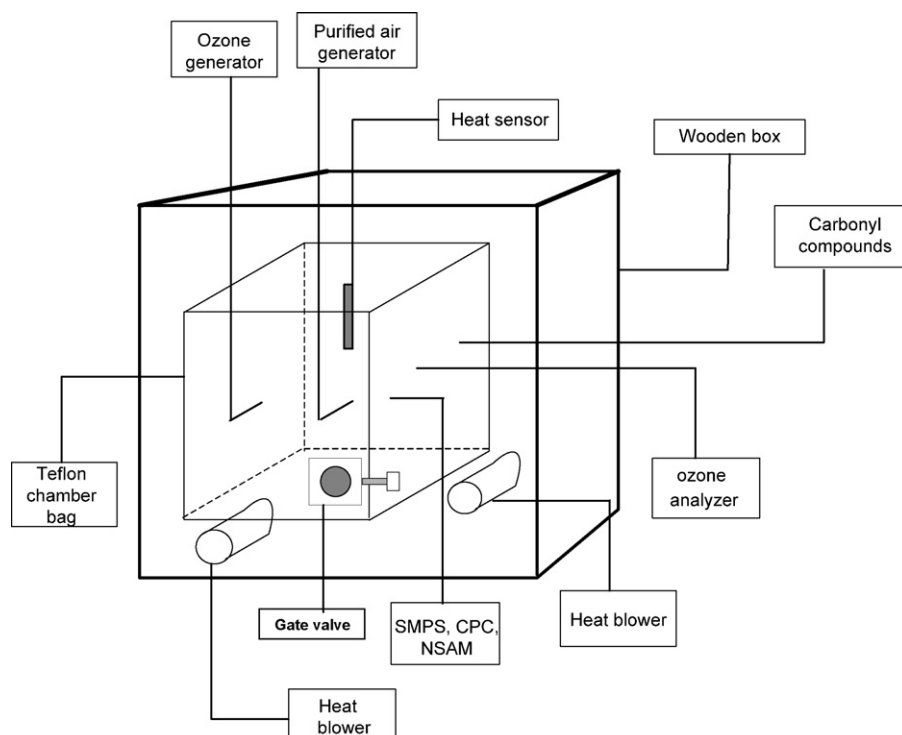


Fig. 1. Schematic diagram of Teflon[®] film chamber.

Ozone was produced in situ using an ozone generator equipped with an ultraviolet (UV) lamp (Advanced Pollution Instrumentation) and a flow meter. The concentration of ozone was monitored during the reactions with monoterpenes using a photometric ozone analyzer (Thermo Environmental Instruments Inc.) at a wavelength of 254 nm.

An aliquot amount of liquid air freshener (0.5 mL) was placed in the bottom of 50 mL beaker. It was allowed to emit the biogenic VOCs for 1 h inside the chamber bag. The temperature was controlled at 30 and 40 °C. Ozone was injected at two different concentrations (50 and 100 ppb) with a flow rate of 2.0 L/min at each temperature. The total reaction time was approximately 4 h, which is slightly more than the average travel time in a metropolitan area. The chamber was flushed with ozone and purified air for several hours before and after each experimental run.

2.3. Sampling and analysis

The analytical procedures for the identification and quantification of VOCs in the experimental part were well described in an earlier paper [18]. Briefly, identification and quantification of the monoterpenes were determined using Fourier transform infrared spectrometer (FT/IR, Model 1400-1F, MIDAC) and a gas chromatograph with mass spectrometer (GC-MS, Varian Model Saturn 2000) equipped with a DB-1 column (60 m × 0.32 mm i.d. × 1.8 μm film thickness, J&W Scientific).

The carbonyl samples in the chamber were collected before ozone addition and during the ozone-initiated reactions using 2,4-dinitrophenylhydrazine coated cartridges (Supelco) for 10 min under the flow rate of 0.6 L/min. Carbonyl compounds in the atmosphere were adsorbed in the cartridge during the sampling and then eluted by adding 5 mL of acetonitrile. An aliquot of extractant (20 μL) was introduced into the injection port of a HPLC (Waters 600S, Waters) equipped with an ultraviolet detector and Nova-Pak C18 column (3.9 mm × 300 mm, Waters).

Particle number concentrations were monitored by a scanning mobility particle sizer (SMPS, TSI 3085) with a scanning time of 5 min and an ultra-fine condensation particle counter (UCPC, TSI 3025) with a response time of 1 s. The total particle number concentrations for diameters larger than 3 nm were measured with the UCPC, while the particle number size distributions from 4.4 to 160 nm were measured with the SMPS. The particles are assumed to have a spherical shape with a particle density of 1.0 g/cm³. The human lung-deposited surface area of particle was measured by a nano-particle surface monitor (Model 3550, TSI). The measured surface area corresponds to tracheobronchial or alveolar regions of the human lung.

3. Results and discussion

3.1. Identification of biogenic VOCs emitted from car air freshener

The biogenic VOCs identified from the emission of liquid car air freshener were monoterpenes including α-pinene

(0.046 ppm), β-pinene (0.023 ppm), *p*-cymene (0.001 ppm), and limonene (0.005 ppm). Air (carbon dioxide and nitrogen) was identified, which was mainly due to the contamination by impurities from the sample preparation procedure. The gas chromatographic analysis showed and confirmed that the biogenic VOCs emitted from the air freshener were mainly composed of the four monoterpenes identified above.

3.2. Effect of ozone concentration on the particle formation

It has been reported that particles can be produced during the ozone-initiated oxidations with monoterpenes [19]. The particles have been known to form from a self-nucleation process with the subsequent condensation of new particles and/or from a thermodynamic equilibrium distribution between the gas and particle-phases leading to the gas-particle partitioning of semi-volatile organic compounds (SVOCs) [20]. The formation and growth of particles from the reactions of ozone with the emitted terpenes from the car air freshener have been observed. Particle parameters were monitored during ozone injections into the chamber bag to determine the effect of ozone concentration on the particle formations. Fig. 2 shows the change of particle number concentration at 30 °C under 50 and 100 ppb of ozone measured by UCPC. UCPC was used for the experiment because it can give better measurements by the continuous monitoring of particle formation (every 1 s) than UCPC with SMPS did (every 5 min). Rapid particle production was observed in 15 min after the ozone injection. Nucleation started earlier at high concentration of ozone (100 ppb) suggesting that ozone concentration significantly affects the nucleation rate of particle formation. This is very similar to the result observed from the ozone-initiated oxidation with biogenic VOCs emitted from natural paint [18,21]. The observed time delay for the nucleation at low concentration indicates the time needed to reach the supersaturation of vapor pressures of the SVOCs. After reaching the supersaturation point, the concentrations of semi-volatile products started to increase to sufficient levels to form particles or to condense on the pre-existing smaller particles. The peak number particle concentrations at two ozone concentrations were

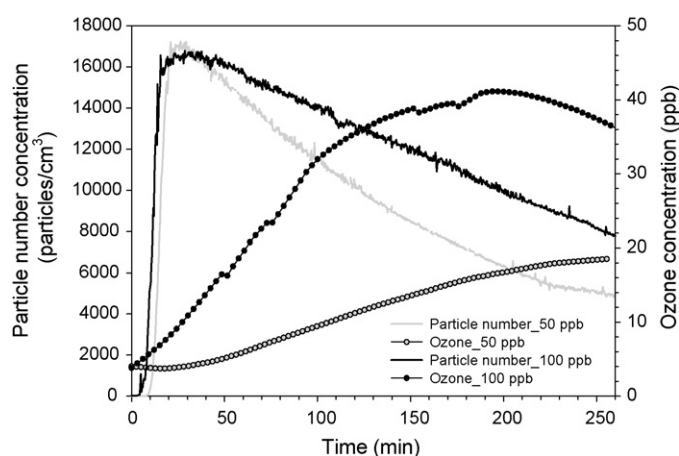


Fig. 2. Particle number concentrations observed at 30 °C with ozone concentrations at 50 and 100 ppb.

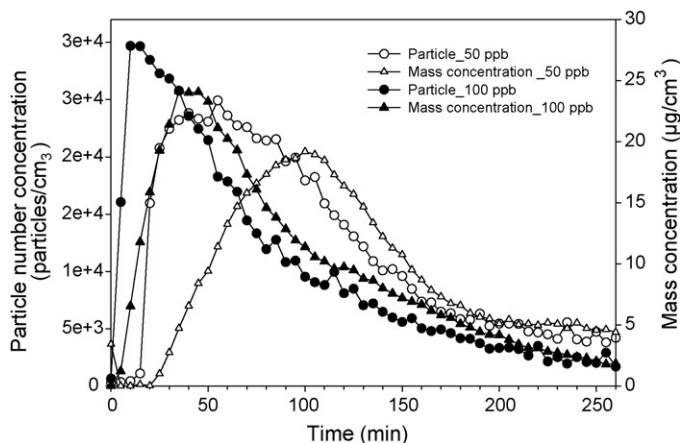


Fig. 3. The variations of particle number concentration and mass concentrations at 30 °C with low ozone (50 ppb) and with high ozone (100 ppb).

almost similar: $1.7 \times 10^4 \text{ cm}^{-3}$ at 50 ppb and $1.67 \times 10^4 \text{ cm}^{-3}$ at 100 ppb ozone injections.

After the particle number concentrations have reached the maximum peak, it gradually decreased as the particles undergo condensation mechanisms, deposited on chamber walls and other loss processes such as chamber air dilution and ventilation in the chamber by evacuation of particle counter and ozone analyzer. The particle number concentration at the high ozone concentration decreased slowly, suggesting that more particles are being formed during the condensation stage. Fig. 3 shows the change of the particle number concentration as well as particle mass concentration with respect to reaction time under different ozone concentration which were measured by UCPC connected with SMPS. The analytical equipments used for measuring the particle number concentrations in Fig. 3 was different from that to the particle number concentration monitoring in Fig. 2, thereby the results of each experiment can have some variations. The mass concentration reached its peak value higher and earlier at high ozone concentration (100 ppb) at 30 °C and the particle number concentration shows the same trend under the same experimental conditions. The peak mass concentration under 50 ppb ozone and 30 °C was $19.1 \mu\text{g}/\text{m}^3$ at 90 min, while that of 100 ppb and 30 °C was $24.1 \mu\text{g}/\text{m}^3$ at 35 min. This demonstrates that more semi-volatile products are formed at 100 ppb ozone concentration and have significant influence on the growth of the particles. Ozone was continuously introduced into the chamber but the particle number concentration continuously decreased. This indicates that the emitted monoterpenes from the air freshener was consumed by ozone after approximately 50 min. In this study, we focused on the formation of nano-sized particles (1–100 nm) and limited the measurement range of particle size of equipments. The particles greater than 160 nm were not considered for the measurement of mass concentration.

Particles less than 10 nm were detected in all experimental conditions. The particles having ~ 20 nm diameter are very appropriate for alveolar deposition in the human lung. It has been further investigated that deposited ultra-fine particles are rendered less available during phagocytosis by alveolar macrophages. Thus, they are not phagocytosized efficiently and

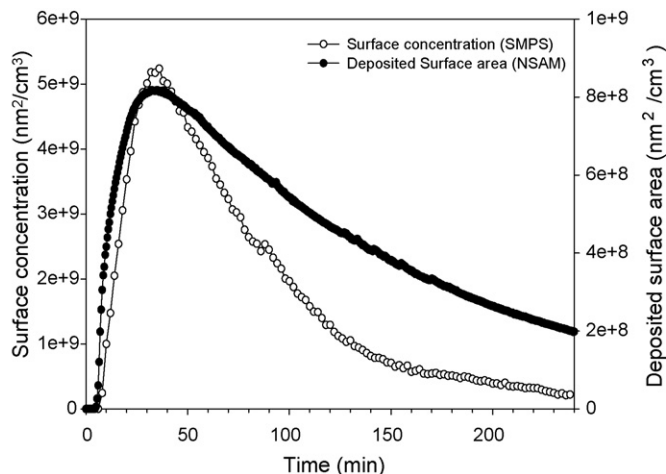


Fig. 4. Measurement of particle surface concentration and its correlation with the deposited surface area in human lung.

may be easily transported to other organs of the body [13,14]. One approach to assess the quantity of particle surface area that deposits in the lung is to correlate the surface area size distributions with a lung-deposition model. The value obtained from this determines the extent of impact of inhaled ultrafine particles [22]. The nano-particle surface area measurement we have used in this experiment corresponds to the lung deposition of particles for a reference worker as given by the human lung-deposition model developed by the International Commission on Radiological Protection [23]. Fig. 4 shows the human lung-deposited surface area by particles which corresponds to the lung deposition of particles in the tracheobronchial region of a certain individual. This demonstrates the personal exposure to ultra-fine particles based on the measurement of particle surface area. Based on these measurements, nano-particles inhaled per 1 cm^3 air by exposed passengers within 40 min could occupy approximately $8.0 \times 10^8 \text{ nm}^2$ of surface area in the lung.

Fig. 5 shows the size distribution and growth of particles in the chamber at 30 °C after 10, 30, and 90 min. The particle diameters increased as reactions proceeded but the particle number concen-

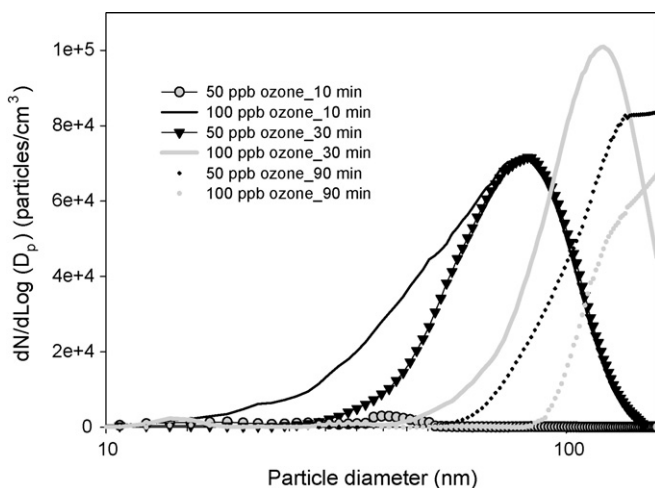


Fig. 5. The variation of particle size distribution at 30 °C with low ozone (50 ppb), and with high ozone (100 ppb) after 10, 30, and 90 min.

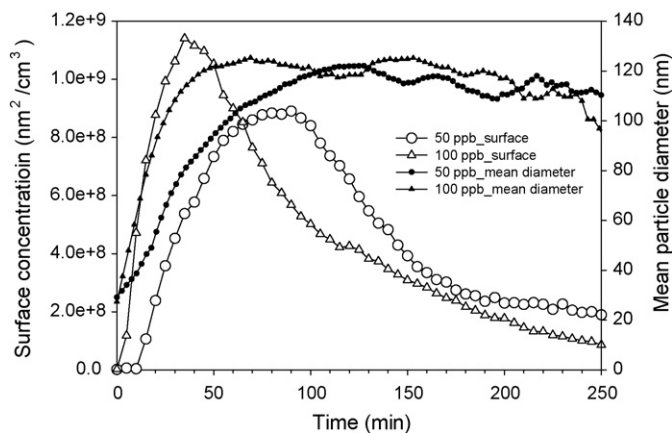


Fig. 6. The variations of surface concentration and mean particle diameter at 30 °C with low ozone (50 ppb) and with high ozone (100 ppb).

trations consequently decreased. This implies that the particle growth mechanisms were carried out via condensation and then subsequent gas-to-particle partitioning of the reaction products. At high ozone concentration (100 ppb), the growth of particles was accelerated and the number of large particles increased as the reactions proceeded. Particle growth was observed to proceed even until 90 min. The *x*-axis was cut-off due to the limitation of detection range of the SMPS.

Fig. 5 additionally shows particle parameters to support the growth of particles in the chamber. The initial mean particle diameter was in the range of 10–30 nm, increased to 120 nm, and showed the tendency of saturation at 30 °C. Because of the limitation of measurement range of SMPS, the particles greater than 160 nm cannot be counted for the measurement of mean particle diameter. This can significantly affect the tendency of saturation at 120 nm. Particle diameter grew faster at high ozone concentration as shown in Fig. 6. The high particle surface concentration at 30 °C and high ozone concentration (100 ppb) in Fig. 6 explains the observed rapid particle growth in 10 min at Fig. 5. This result further supports the fact that semi-volatile products form rapidly at initial high ozone concentration, continue to condense, and grow through adsorbing onto existing particles.

3.3. Temperature effects on particle formation

According to an indoor chemistry and exposure model, indoor secondary organic aerosol number concentrations are expected to increase by a factor of two for every 10 °C decrease in indoor temperatures [16]. This is anticipated because lower temperature decreases a chemical reaction rate. The chosen temperatures were assumed to be similar to that of the hot summer seasons especially in tropical regions and possibly in populated cities. Fig. 7a–c shows the effect of temperature on the particle growth and its property. Fig. 7a shows that under 100 ppb ozone and 40 °C, the mass concentration reached its peak value earlier (30 min), which is 4–6 times lower than those under the experimental conditions above. The particle number concentration seems to increase continuously.

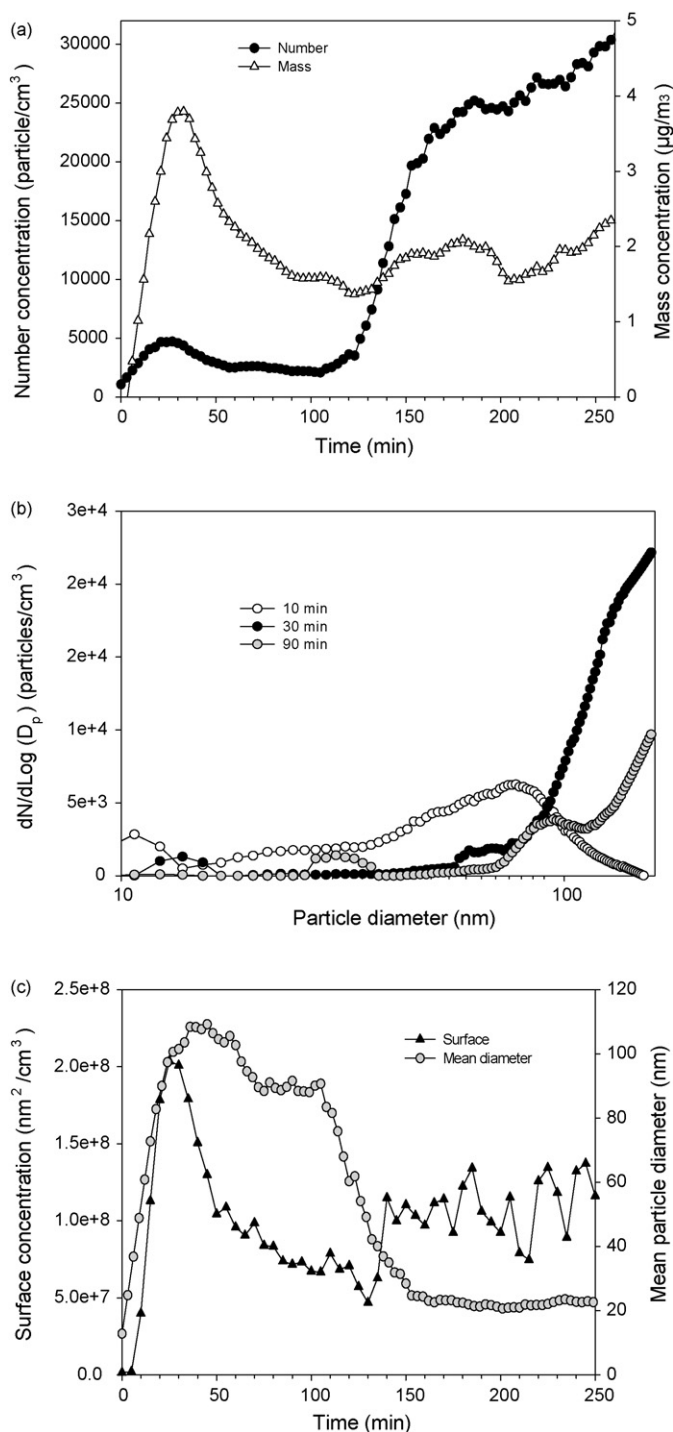


Fig. 7. The variations of particle parameters at 40 °C and with 100 ppb of ozone concentrations (a). The variations of particle number concentration and mass concentrations (b). The variation of particle size distribution after 10, 30, and 90 min (c). The variations of surface concentration and mean particle diameter.

The temperature change from 30 to 40 °C produced a lower particle mass concentration. The mass concentration maximum at 40 °C and 100 ppb is 3.80 μg/m³ at 30 min (Fig. 7a). This is due mainly to the volatilization of semi-volatile species and subsequent formation of gas-phase products by the increase of temperature [24]. The particle number concentrations at each particle diameter size under high temperature (40 °C)

Table 1
Identified gaseous products (aldehydes and ketone) during the ozone-initiated oxidation

Time (min)	Condition	Compounds				
		Form (0.002)	Ace (0.004)	Acro (0.001)	Acn (0.001)	Prop (0.005)
60	30 °C, 100 ppb	0.003	0.015	0.153	ND	ND
120		0.084	ND	0.211	ND	ND
300		0.005	ND	0.264	ND	0.056
60	40 °C, 100 ppb	0.004	0.675	ND	ND	ND
120		0.024	0.742	ND	0.183	ND
300		0.055	ND	0.336	ND	0.008

Detection limits are given in parentheses. Concentrations are in ppm. Form: formaldehyde; Acn: acetone; Ace: acetaldehyde; Prop: propionaldehyde; Acro: acrolein; ND: not detected.

were low compared to those under low temperature (30 °C) (Fig. 5).

The increase of particle number concentration at 40 °C was slow and there was a long delay for 120 min (Fig. 7a). The delay period may be caused by volatilization of semi-volatile products by high temperature. Therefore, it took time for the semi-volatile products to reach to their satisfactory concentrations for the particle nucleation. Although some particle formation has been observed, it does not seem to significantly affect the growth to larger particles (Fig. 7b and c). These results imply that daytime temperatures (or high summer temperatures) tend to decrease particle concentrations, while cooler nighttime temperatures lead to significantly increased yields. Temperatures used in the experiment seemed to be relatively hot during normal conditions. However, tropical regions and densely populated urban cities have been set to high temperatures caused by the tendencies of concrete, buildings and roads to heat up especially in peak summer seasons. These conditions could potentially lead to our monitored results.

3.4. Gaseous products

Low molecular carbonyls, i.e., acetone, formaldehyde, and acetaldehyde were also observed during the ozone-initiated reactions with emitted monoterpenes (Table 1). The increase of temperature could allow the chemical species to leave the particle phase and re-establish the gas-particle equilibrium. Formaldehyde was detected in all experimental conditions, while acetone was detected only at 40 °C at 100 ppb ozone. Formaldehyde was easily detected in all experimental conditions since it formed as a primary carbonyl compound during the ozonation of biogenic VOCs [7]. The concentration of acrolein was high compared to other compounds. Higher concentrations of acetaldehyde were detected at the higher temperature which supports the fact that semi-volatile compounds remain in the gaseous phase. However, a curious deviation from the trend was observed with propionaldehyde which showed a lower concentration at 40 °C. The observed increase of concentrations of formaldehyde, acetaldehyde, and acrolein shows that they are secondary products of the oxidation process and accumulates in the chamber. It has been revealed in several studies that VOCs concentrations inside automobiles are usually higher than the roadside measurements [1,4]. Generation of the additional secondary organic products from atmospheric

oxidant-initiated secondary reactions, such as those detected in this study (0.001–0.742 ppm) poses further potential health risks to passengers, particularly the occupational group with long working hours in road travel.

4. Conclusions

We demonstrated the formation and growth of particles as well as the gaseous products during the ozone-initiated reactions with biogenic VOCs emitted from a car air freshener. The effects of temperature and ozone concentration on the formation of the reaction products were investigated in this study.

Over the course of a typical metropolis travel, ozone concentrations (2–86 ppb) [1,3] and VOCs (1999–5373 $\mu\text{g}/\text{m}^3$) [4] may vary depending on the dynamic ambient conditions. Based on the experimental results obtained here, the formation of particles and gaseous products can be expected to occur during the ozone-initiated oxidations with monoterpenes from the car air freshener inside the vehicle. This can significantly affects the health of passengers in the vehicle. Several other factors such as relative humidity and air exchange rate or ventilation were not considered in the study. Therefore, the results might be overestimated. The results are not intended as direct representations of specific ambient conditions. Nevertheless, it will serve as useful background information to assess the importance of temperature and ozone concentration fluctuations. The results can be used to better understand the potential exposures of irritating or toxic reaction products to passengers that could be easily found in confined spaces with high ozone content and high temperature during hot summer seasons.

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