

ULTRA-FINE PARTICLES AND GASEOUS VOLATILE ORGANIC COMPOUND EXPOSURES FROM THE REACTION OF OZONE AND CAR-AIR FRESHENER DURING METROPOLIS TRAVEL

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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 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.

Key Words : Ozone, Volatile organic compounds, Monoterpenes, Particles, Air freshener

INTRODUCTION

The atmospheric oxidants (e.g., O₃, ·OH, NO₃) - initiated reactions with volatile organic compounds (VOCs) emitted from biogenic sources (e.g., vegetation, trees, etc.) significantly affect outdoor air environments. Ozone, one of the significant atmospheric oxidants, frequently exceeds the maximum threshold ambient level all the year round in many countries. Ambient

ozone can be easily introduced into indoor environments and confined spaces by opening windows and operating ventilation systems.¹⁾ Regulations for the restriction of toxic VOCs emission in indoor environments and confined spaces have recommended manufacturers to utilize environment-friendly natural products for their raw materials as alternatives to the toxic anthropogenic chemicals such as xylene and toluene. As an example, car air freshener contains the natural products such as extracts from essential oil and plant oil commonly found in scenting agents and solvents,^{2,3)} which could be

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a potential source of biogenic VOCs in a confined space (i.e., inside of the car). 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.⁴⁻⁷⁾ 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.^{8,9)} 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.^{10,11)} The ambient ozone concentration 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 the exposure and/or inhalation of toxic ultra-fine particles and secondary gaseous organic products. However, no significant study has been conducted to characterize the ozone-initiated oxidation with biogenic VOCs emitted from car air freshener during driving a car.

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 high condensable gases. The vapor pressures of organic compounds increases as well yielding a lower fraction of condensable gases.^{12,13)} 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.¹⁴⁾ Outdoor ground-level ozone is parti-

cularly significant during hot and sunny days. The health of passengers inside the vehicles could be affected by these organic secondary products formed during the ozone-initiated oxidation with biogenic VOCs emitted from car air freshener. We have investigated the effects of temperature as well as the ozone concentration on the formation of secondary organic products inside the vehicle during hot summer season in this research. Target biogenic VOCs emitted from the car air freshener and all gaseous products and particles have been monitored and identified during the ozone-initiated reactions.

MATERIALS AND METHODS

Chemicals

The car air freshener was purchased from an internet-based store in Seoul, Korea. It was an oil-based and a citrus scented air freshener. The air freshener was received in a glass container and the amount of emission could be controlled by adjusting the cover. It was chosen to best represent the 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), *p*-cymene (99%, Sigma-Aldrich); the carbonyl standard mixture (formaldehyde: 215 $\mu\text{g/mL}$, acetaldehyde: 190 $\mu\text{g/mL}$, acetone/acrolein: 122 $\mu\text{g/mL}$, and propionaldehyde: 122 $\mu\text{g/mL}$, Supelco). The solvents used as eluents and extractants in this research were HPLC or higher grade: acetonitrile (99.8%, J.T. Baker) and pure water (J.T. Baker).

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 Figure 1.

Ozone was produced in-situ using an ozone generator equipped with an ultraviolet 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 hour inside the chamber bag. The temperature was controlled at 30°C 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 hours, 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.

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 high performance liquid chromatograph (HPLC, Waters 600S, Waters) equipped with an ultraviolet (UV) 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) and an ultra-fine condensation particle cou-

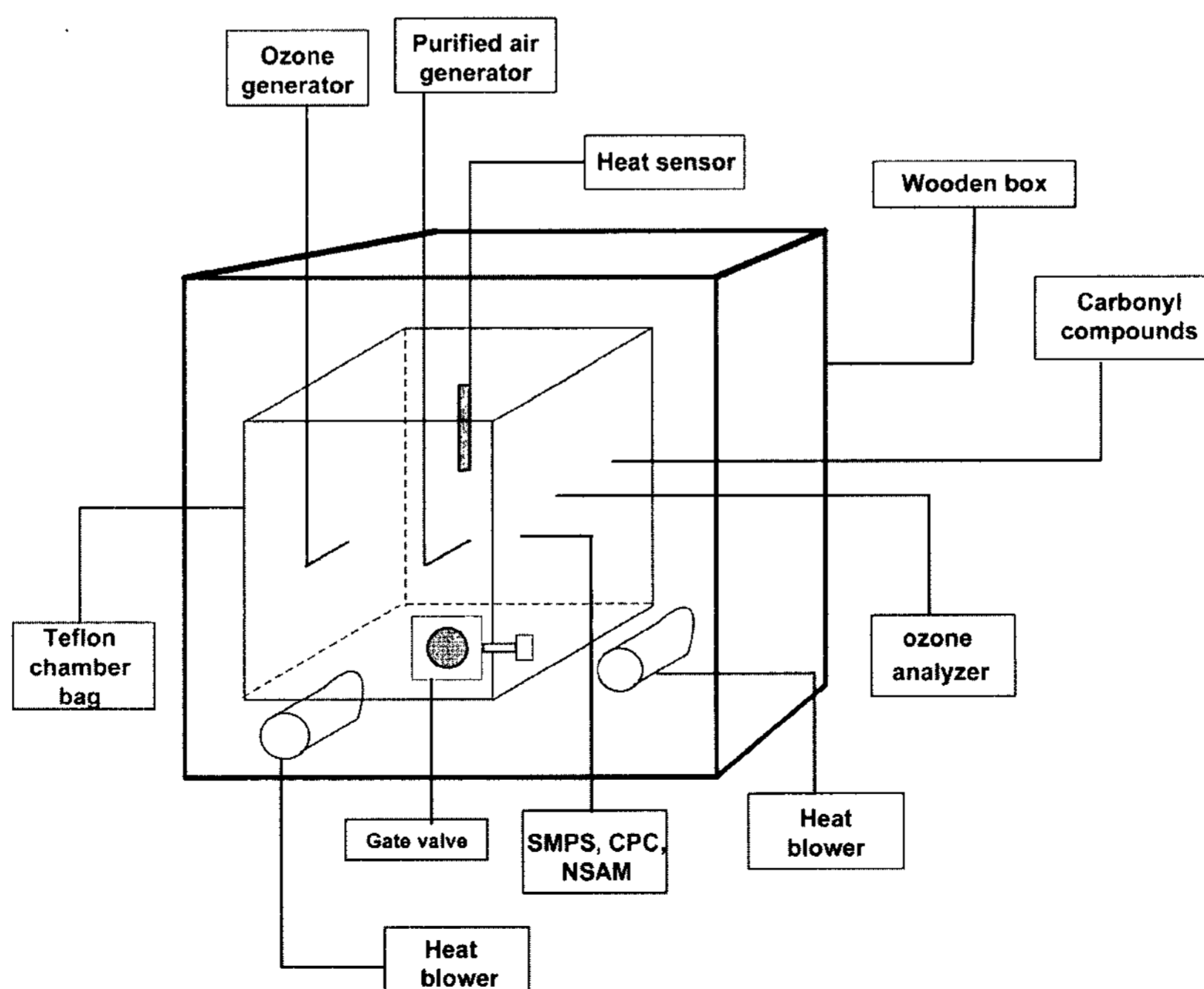


Figure 1. Schematic diagram of Teflon® film chamber.

nter (UCPC, TSI 3025). 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 nm to 160 nm were measured with the SMPS. The particles are assumed to have a sphere shape with a particle density of 1.0 g/cm^3 . 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 and alveolar regions of the human lung.

RESULTS AND DISCUSSION

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), ρ -cymene (0.001 ppm), and limonene (0.005 ppm). Air (carbon dioxide and nitrogen) was identified, which are mainly due to the contamination by impurities during the analysis. The chromatogram in Figure 2 confirmed that the biogenic VOCs emitted from the air freshener were mainly composed of the four monoterpenes identified above.

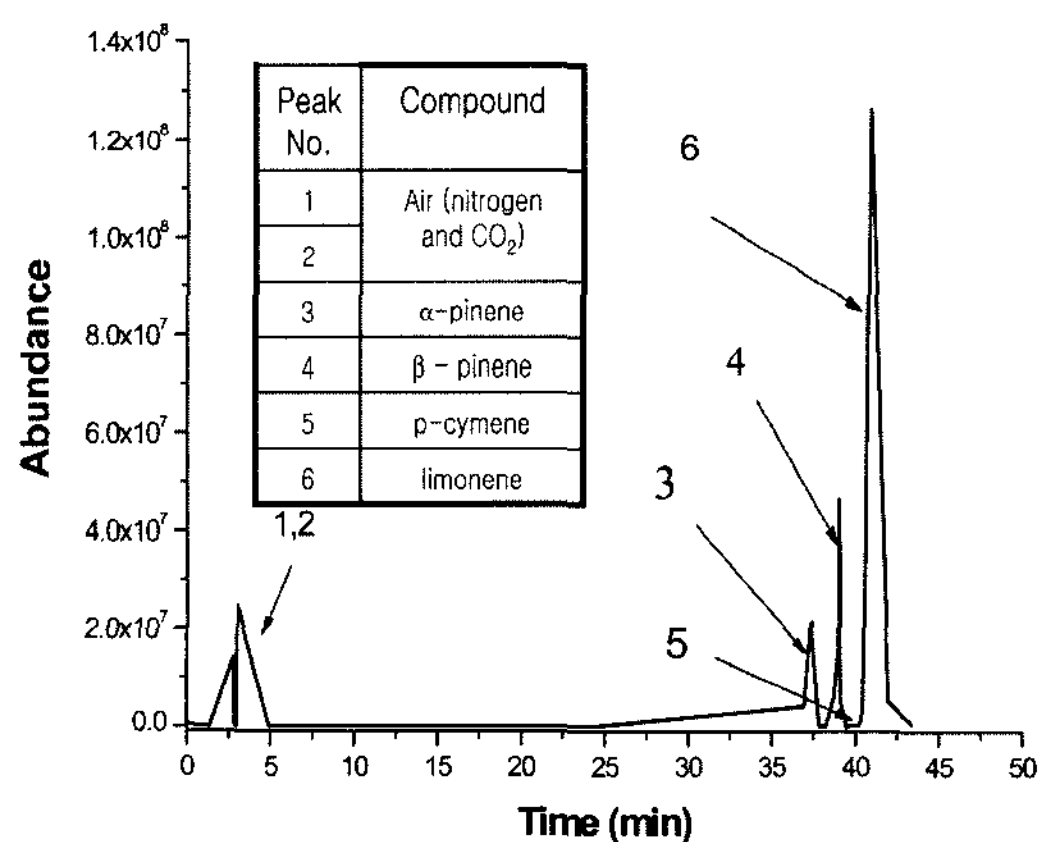


Figure 2. GC/MS chromatogram of biogenic VOCs emitted from car air freshener.

Effect of Ozone Concentration on the Particle Formation

It has been reported that particles can be

produced during the ozone-initiated oxidations with monoterpenes.¹⁵⁾ 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).¹⁶⁾ The formation and growth of particles from the reactions of ozone with the emitted terpenes from the car air freshener have been observed. In the ozone-initiated oxidations with air freshener, rapid particle production was observed in 15 min. Figure 3 shows the change of particle number concentration at 30°C under 50 and 100 ppb of ozone measured by UCPC. 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.¹⁷⁾ The observed time delay for the nucleation at low concentration indicates the time needed to reach the supersaturation points. 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 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.

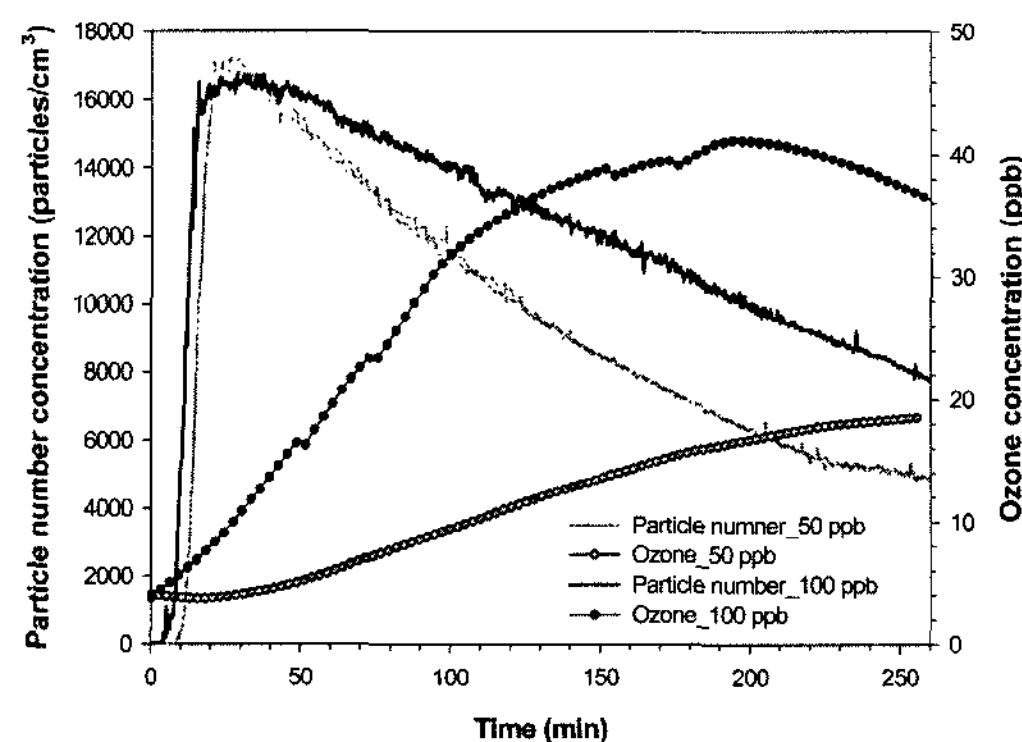


Figure 3. Particle number concentrations observed at 30°C with ozone concentrations at 50 ppb and 100 ppb measured by UCPC.

After the particle number concentrations have reached the maximum peak, it gradually decreased as the particles undergo condensation mechanisms and are deposited on chamber walls. The particle number concentration at the high ozone concentration decreased slowly, suggesting that more particles are being formed during the condensation stage. Figure 4 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 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 under 100 ppb and 30°C was 24.1 $\mu\text{g}/\text{m}^3$ at 35 min. This suggests that more semi-volatile products are formed at high initial 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.

Particles less than 10 nm were detected in all experimental conditions. The particles having ~

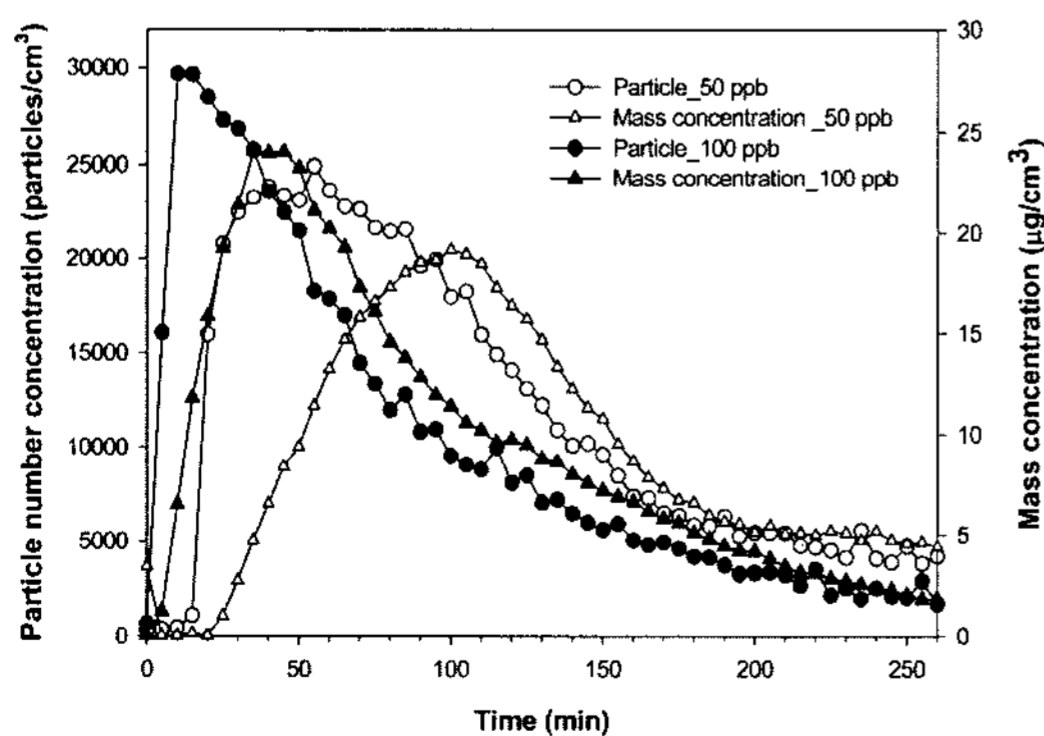


Figure 4. The variations of particle number concentration and mass concentrations at 30°C with low ozone (50 ppb) and with high ozone (100 ppb) measured by UCPC connected with SMPS.

20 nm diameter is 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 may be easily transported to other organs of the body.^{10,11)} Figure 5 shows the human lung-deposited surface area by particles which corresponds to the lung deposition of particles to a certain individual. This demonstrates the personal exposure to ultra-fine particles based on the measurement of particle surface area. Based on this measurements, passengers can have a maximum deposition of nanoparticles in their lungs around 40 min.

Figure 6 shows the size distribution and growth of particles in the chamber at 30°C after 10

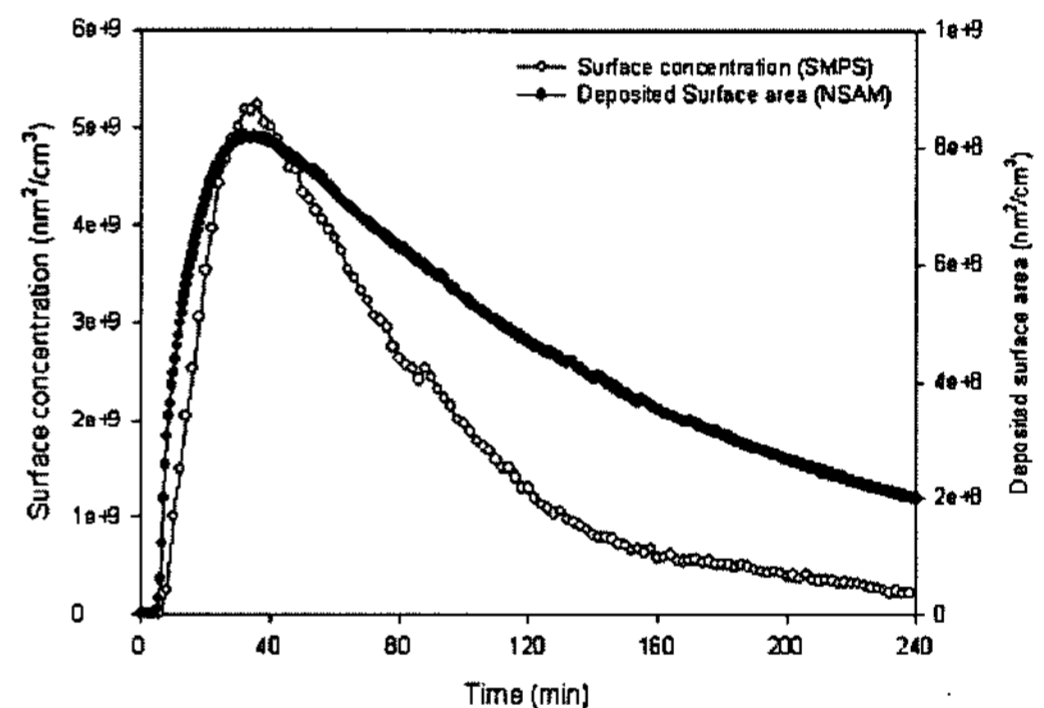


Figure 5. Measurement of particle surface concentration and its correlation with the deposited surface area in human lung.

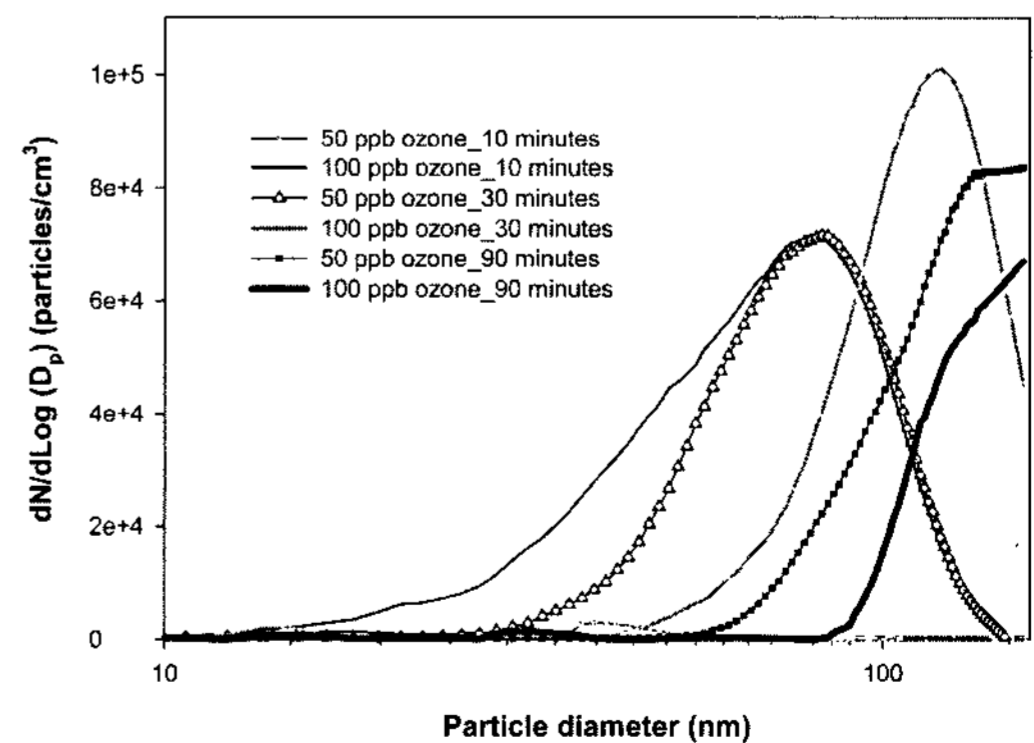


Figure 6. The variation of particle size distribution at 30°C with low ozone (50 ppb), and with high ozone (100 ppb) after 10 min, 30 min, and 90 min.

min, 30 min and 90 min. The particle diameters increased as reactions proceeded but the particle number concentrations 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.

Figure 7 shows particle properties to support the growth of particles in the chamber. The initial mean particle diameter was in the range of 10 to 30 nm and increased to 120 nm at 30°C. Particle diameter grew faster at high ozone concentration as shown in Figure 7. The high particle surface concentration at 30°C and high ozone concentration (100 ppb) in Figure 7 explains the observed rapid particle growth in 10 min at Figure 6. 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.

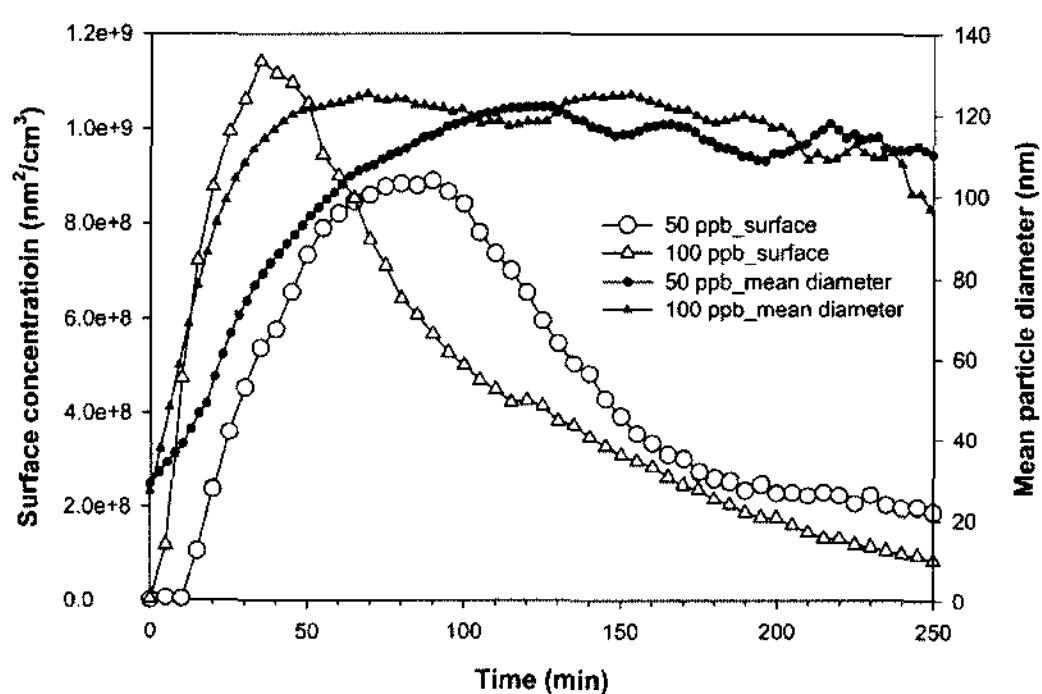


Figure 7. The variations of surface concentration and mean particle diameter at 30°C with low ozone (50 ppb) and with high ozone (100 ppb).

Temperature Effects on Particle Formation

According to an indoor chemistry and exposure model, indoor secondary organic aerosol concentrations are expected to increase by a factor of two for every 10°C decrease in indoor temperatures.¹⁴⁾ This is anticipated because lower tempe

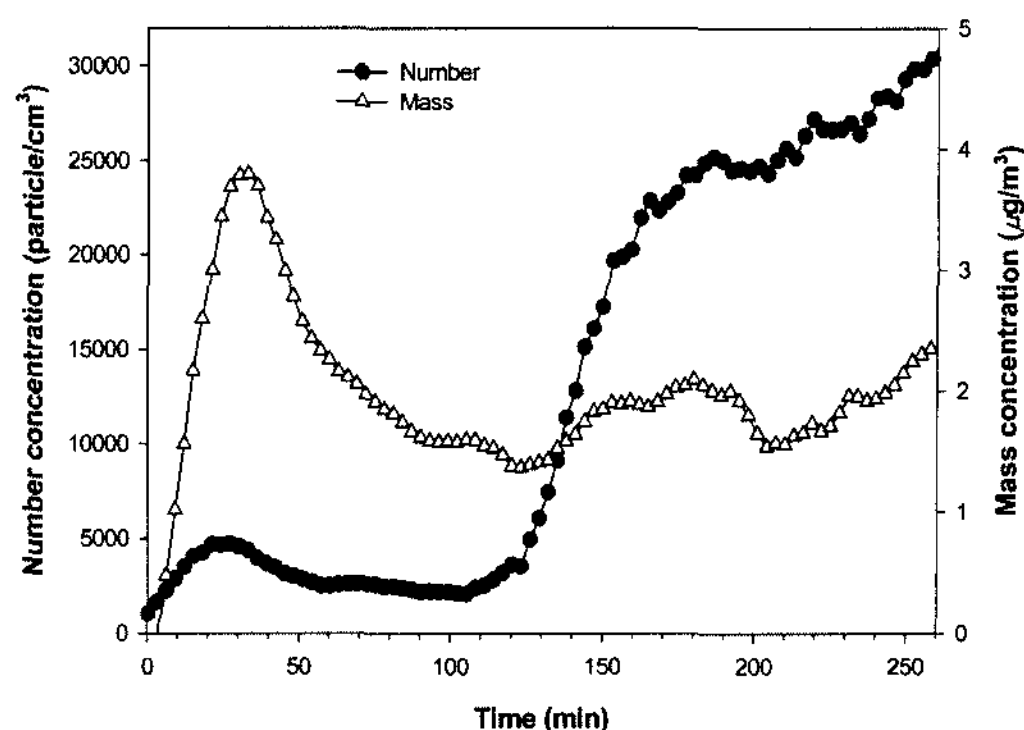


Figure 8. The variations of particle number concentration and mass concentrations at 40°C with high ozone (100 ppb).

perature decreases a chemical reaction rate. Figures 8 - 10 show the effect of temperature on the particle growth and its property. Figure 8 shows that the mass concentration reached its peak value earlier (30 min) under 100 ppb ozone and 40°C, which is 4 - 6 times lower than those under the experimental conditions above. The particle number concentration seems to increase continuously.

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 (Figure 8). This is due mainly to the volatilization of semi-volatile species and subsequent formation of gas-phase products by the increase of temperature.¹⁸⁾ The particle number concentrations at each particle size under high temperature (40°C) were low compared to those under low temperature (30°C) (Figure 6).

The increase of particle number concentration at 40°C was slow and there was a long delay for 120 min (Figure 8). 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 (Figures 9 and 10). These results imply that daytime temperatures (or high summer temperatures) tend to decrease particle concentrations, while cooler night-

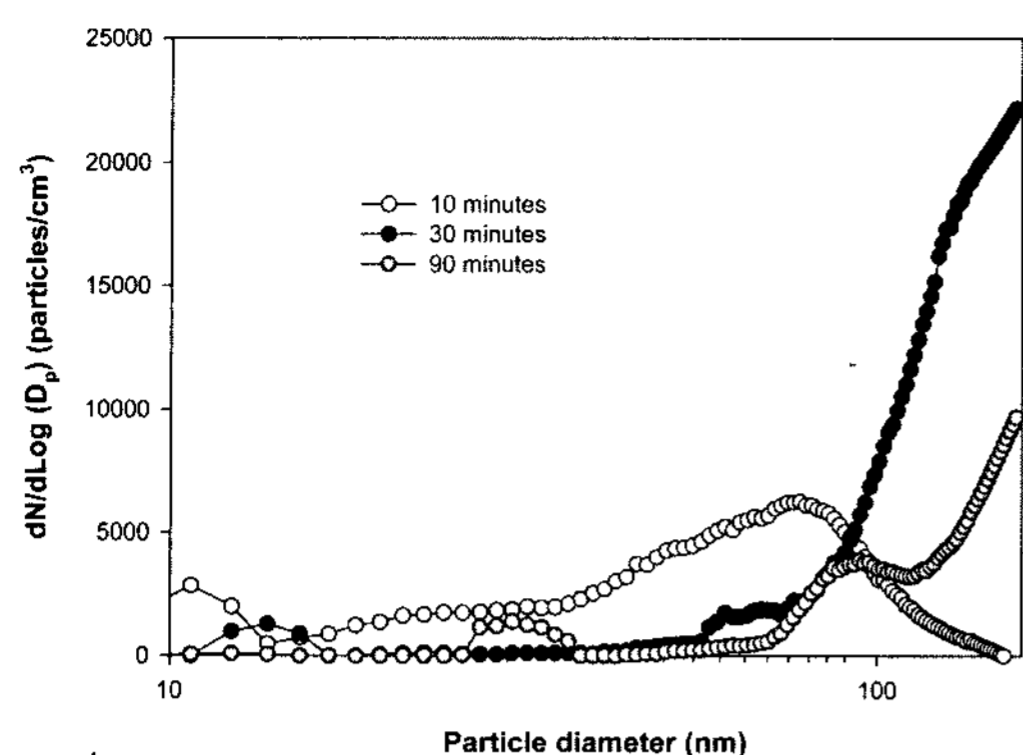


Figure 9. The variation of particle size distribution at 40°C with high ozone (100 ppb) after 10 min, 30 min, and 90 min.

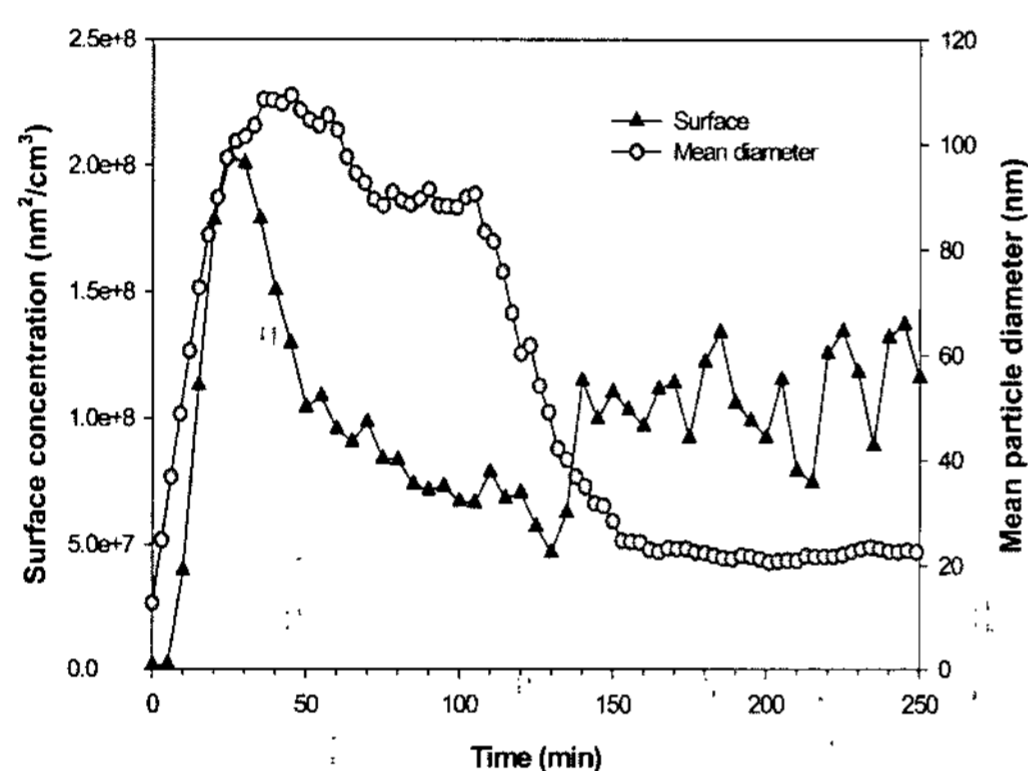


Figure 10. The variations of surface concentration and mean particle diameter at 40°C with high ozone (100 ppb).

time temperatures lead to significantly increased yields.

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.⁴⁾ 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. Other chemicals (such as formaldehyde at 30°C and 120 min and acetone at 40°C and 120 min) also deviated substantially. Sampling artifacts might contribute to these results. Further investigations may be undertaken to confirm the irregularity with propionaldehyde, formaldehyde at 30°C and 120 min and acetone at 120 min and 40°C. The observed increase of concentrations of formaldehyde in other cases, acetaldehyde and acrolein shows that they are secondary products of the oxidation process and accumulates in the chamber.

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

Table 1. Gaseous products (aldehydes and ketone) during the ozone-initiated oxidation. Concentrations are in ppm

| Time (min) | Condition | Form | Ace | Acro | Acn | Prop |
|------------|----------------|-------|-------|-------|-------|-------|
| 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 |

Form - formaldehyde
Prop - propionaldehyde

Acn - acetone
Acro - acrolein

Ace - acetaldehyde
ND - not detected

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 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 affect the health of passengers in the vehicle. Relative humidity and air exchange rate 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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