

Secondary nanoparticle formation by a reaction of ozone and volatile organic compounds emitted from a commercial home cleaner liquid

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Abstract

In this study, the formation of nanoparticles by a reaction of ozone with the volatile organic compounds(VOCs) emitted from a commercial home cleaner liquid was investigated using a 1-m³ reaction chamber(1×1×1 m). The home cleaner liquid was found to contain many VOCs, particularly terpenes. Some of these VOCs are known to readily react with ozone, forming indoor secondary pollutants. The correlation of particle concentration and reacted ozone concentration was examined with injections of three different ozone concentrations; 50, 100 and 200 ppb. The secondary nanoparticles were formed faster, with their numbers and mass concentrations becoming higher on increasing the concentration of ozone injected.

Keywords : home cleaner liquid, Volatile organic compounds, Ozone, Secondary pollution, Nanoparticle

1. Introduction

Home cleaner liquid, is a popular consumer product used in homes. It usually contains surfactants and solvents to dissolve oily substances. However, these can cause low skin irritation. It has been reported that fragranced consumer products contain many volatile organic compounds(VOCs), none of which are listed on any product labels(Steinemann, 2009). The remaining traces of home cleaner liquids with VOCs dry fast and as yet, have not been shown to cause any human health, taste or smell problems.

Indoor VOC may be released from various materials, including paints, glues, resins, stored petrol, polishing materials, perfumes, spray propellants, building materials, personal care products and cleaning agents, and may be affected by the penetration of outdoor sources. Ventilation, with a high air exchange rate, is a good method to mitigate indoor VOC pollution, but it is difficult to maintain sufficient ventilation during winter and summer while heaters and air-conditioners, respectively, are continuously operating. Normally, the indoor concentrations of common organic pollutants are two to five times higher than those found outside(<http://www.epa.gov/iaq/voc.html>). The VOC concentrations are generally less than 50 µg/m³, with the mean concentration of a single VOC being below 10 µg/m³ in Europe and North

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America(Wolkoff and Nielsen, 2001). Many VOCs may cause cancer in human and animals, and most may cause irritation, nose and throat discomfort, headaches, allergic skin reactions, declines in serum cholinesterase levels, nausea and emesis. Some specific VOCs react with ozone to form secondary pollutants, such as particulates and intermediates.

Outdoor ozone is not a primary pollutants, which are emitted directly from emission sources, such as vehicles and industries, but is formed by photochemical reactions of air containing hydrocarbons and nitrogen oxides. Ozone can be formed nearby pollution sources or many kilometers down wind from a maximum distance of about 400 km(WHO, 2005). This means that outdoor ozone can affect the level of residential indoor ozone as a result of penetration. The predicted ozone concentration at the tropospheric level ranges between 5.1 and 18 ppb, with around 10 ppb predicted for the winters between 2000 and 2030(Stevenson, 2006). The US air quality standard for ozone is 75 ppb as an 8-h average(USA NAAQS, 2008). Besides of the effects of outdoor ozone, ozone may also be emitted from some office machines, such as photocopiers and laser printers. According to Weschler(2000), a photocopier could emit as much as 16–131 $\mu\text{g}/\text{copy}$ and 1–4 $\mu\text{g}/\text{copy}$ of ozone before and after maintenance, respectively, and a laser printer could generate an average rate of 1.2 mg/h ($<0.02\text{--}6.5 \text{ mg}/\text{h}$). The half-life of ozone is three days at 20 $^{\circ}\text{C}$, due to thermal decomposition, excluding wall effects, humidity, organic loading or other catalytic effects. Weschler(2000) reported that the half-life of indoor ozone was 7–10 min under normal surface removal and air exchange.

In this work, the formation of secondary nanoparticles was investigated during the reaction of ozone and VOCs emitted from a commercial home cleaner liquid, using a 1- m^3 reaction chamber. Three different ozone injections were set as the experimental variable. The VOCs contained in the home cleaner liquid were identified. The reacted ozone concentrations were compared with the amount of aerosols produced during the test period.

2. Experimental

2.1 Experimental specimen

A commercial home cleaner liquid (spray type) was chosen to test a daily consumer product. A headspace test using a solid-phase microextraction(SPME) method was performed for identification of VOCs emitted from the home cleaner liquid. The SPME is a very simple, efficient, and solventless sample preparation method with versatile and sensitive detection(Vas and Vekey, 2004). VOCs emitted from the home cleaner liquid of 20 μL contained in 20 mL glass vial were adsorbed on SPME fiber(75 μm thickness, Supelco, CAR/PDMS) for 1 h at 25 $^{\circ}\text{C}$ and analyzed via gas chromatography/mass spectrometry(GC/MS, Agilent, 6890N). A 30-m fused silica capillary column (internal diameter 0.25 mm; film thickness 0.25 μm , Agilent, HP-5MS) was used to separate the target analytes. The initial GC oven temperature was set at 40 $^{\circ}\text{C}$ for 2 min, and then programmed from 40 to 100 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ and from 100 to 250 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}/\text{min}$.

We found that the home cleaner liquid contained some VOCs such as α -pinene, camphene and cymene, as presented in Fig. 1. Among them, α -pinene is well known to rapidly react with ozone to form indoor secondary organic aerosols(Hoffmann *et al.*, 1997; Jang and Kamens, 1999; Liu *et al.*, 2004; Fan *et al.*, 2005). Camphene slowly reacts with ozone(Liu *et al.*, 2004). Assuming the ozone concentration was sufficient to react with VOCs, the formation of secondary aerosols would depend on the rate of VOC emissions. Liu *et al.*(2004) denoted the rates of limonene and α -pinene emissions in an air freshener using Eq. 1, as follows:

$$R(t) = R_0 e^{-kt} \quad \text{Eq. 1}$$

where $R(t)$ is the emission rate of a VOC($\mu\text{g}/\text{h}$) at time t , R_0 the initial emission rate($\mu\text{g}/\text{h}$), k the emission rate decay constant(h^{-1}), and t the elapsed time(h), with $0 < t \leq 120$. The values of R_0/k for limonene and α -pinene were 3678.5/0.01 and 2828.7/0.01, respectively. Thus, the VOC concentrations emitted from the specimen gradually decreased. The fraction of hydrocarbons

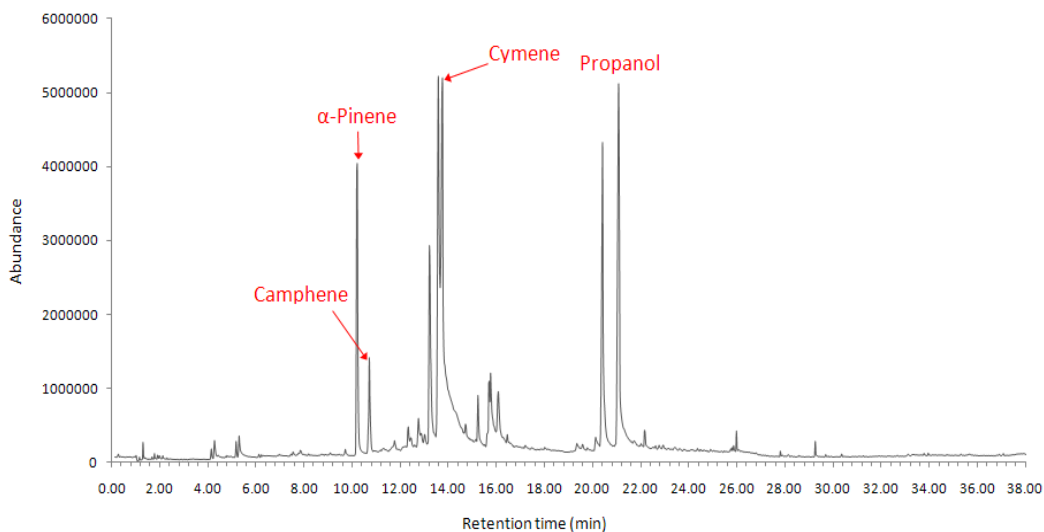


Fig. 1. Chromatogram of the volatile organic compounds emitted from the home cleaner liquid tested in this work.

converted to secondary aerosols increased with increasing initial hydrocarbon concentration. The reacted hydrocarbon concentration increased quickly at low aerosol mass concentrations, but was more stable at higher aerosol mass concentrations (Hoffmann *et al.*, 1997).

2.2 Experimental procedures

The experimental system consisted of a reaction chamber, ozone and pure air generators, and ozone and particle monitoring instruments (Vu *et al.*, 2011). The reaction chamber was made of 2-mil (about 51 μm) FEP Teflon film, with a volume and surface to volume ratio of 1 m^3 ($1 \times 1 \times 1 \text{ m}$) and 6.0 m^2 , respectively. The chamber was maintained under dark conditions by installing in a wooden box with a door. A pure air generation system (Aadco Instruments 737-15) was used to supply pure air into the reaction chamber in this study (Bae *et al.*, 2003). The impurities in the pure air were confirmed to consist of concentrations of O_3 , NO , NO_2 , NO_x and SO_2 of < 1 ppb, with the CO concentration < 0.05 ppm. Limonene, α -pinene, β -pinene and terpinene in the pure air were not detected by the gas chromatography/mass spectrometry system (GC-MS, Shimadzu QP2010) (Vu *et al.*, 2011). The chamber was flushed

twice with a mixture of pure air and ozone (200 ppb) for 4 h prior to each experiment to minimize the bag contamination effect. Thereafter, background ozone and particle mass concentrations of the chamber filled with pure air were < 1 ppb and < 0.06 $\mu\text{g}/\text{m}^3$, respectively, over a 4 h period.

During the experiments, the ozone concentration was monitored every minute using a U.V. photometric O_3 analyzer (TEI 49i), calibrated with 700-ppb span gas. The lower detection limit of the O_3 analyzer was 1.0 ppb. The particle number size distribution was measured with a scanning mobility particle sizer (SMPS, TSI 3936), which consisted of an electrostatic classifier (TSI 3081) and a condensation particle counter (CPC, TSI 3010), with a scanning time of 5 min. The flow rates of the aerosol and sheath flows in the electrostatic classifier were 0.3 and 3.0 L/min, respectively, with the detectable particle size range from 14 to 723 nm in diameter. A total number concentration of particles > 3 nm was also monitored using an ultrafine condensation particle counter (UCPC, TSI 3025), with a 1-sec response time. The air temperature and relative humidity in the Teflon chamber were monitored every 5 min, using a small sensor with a data logger (Sato Keiryoki SK-L200Th), with

a lower detection limit for relative humidity of 20% (Vu *et al.*, 2011), which was placed in the bottom of the chamber. One Teflon sampling line was used to connect the chamber to the O₃ analyzer, with particles sampled through another sampling line, made of SUS, to the SMPS and UCPC. The inflow and outflow controllers allowed an approximately air exchange rate of 0.24 h⁻¹.

A 0.5-mL test specimen of the home cleaner liquid was contained in a 50-mL petri dish, with a diameter of 65 mm and wall height of 25 mm, which was placed on the bottom of the chamber. The air temperature and relative humidity in the chamber were controlled at 20 ± 1 °C and < 20%, respectively. The diameter of the gate valve of the chamber was 114 mm. The time required for opening the chamber to place the petri dish was about 20 s. The injection of ozone into the center of the chamber, through a top surface using a photometric O₃ calibrator (API 401), was initiated 4 min after the test specimen was set. The ozone calibrator produced three different concentrations (50, 100 and 200 ppb), at a flow rate of 4.0 L/min. Each experiment lasted for about 4 h (Vu *et al.*, 2011).

3. Results and Discussion

Fig. 2 shows the differences between the un-reacted ozone concentrations under pure air and the remaining ozone concentrations when the specimen was added into the chamber. The reacted ozone concentration at each injected ozone concentration was estimated by this difference. The reacted ozone concentrations were 7.4, 13.5 and 37.8 ppb at 240 min for injected ozone concentrations of 50, 100 and 200 ppb, respectively. Here, the elapsed time was calculated just after the ozone injection.

Fig. 3 shows the particle formation phenomenon for the ozone reaction with VOCs emitted from the home cleaner liquid at three different ozone concentrations. Nanoparticles were formed at 20, 18 and 12 min for ozone concentrations of 50, 100 and 200 ppb, respectively, as presented in Fig. 3a. The maximum nano-

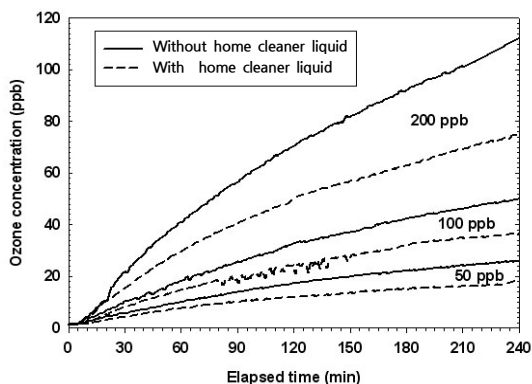


Fig. 2. The variations in the un-reacted ozone concentrations without a specimen and ozone remaining with a specimen.

particle number concentrations were 45600, 57500 and 76300 particles/cm³ at 60, 55 and 39 min for the injected ozone concentrations of 50, 100 and 200 ppb, respectively. Note: the higher nanoparticles were more quickly formed at higher injected ozone concentrations. The particle number concentration initially increased very quickly (within 60 min), and reached a peak concentration. Thereafter, the particle number concentration notably decreased due to both coagulation and wall loss for the particle number concentration of about 76,000 particles/cm³ (Hinds, 1999; Lee *et al.*, 2004; Vu *et al.*, 2011). The decrease in the particle number concentration can be well explained only by the wall loss rates of particles of < 50,000 particles/cm³ (Lee *et al.*, 2004).

VOCs were still emitted from the home cleaner liquid and ozone continuously injected during the experimental period. As shown in Fig. 3b, the particle mean diameters increased continuously during the experimental period. The particle growing phenomenon might be caused by nanoparticle coagulation or the condensation of condensable vapors onto pre-existing nanoparticles. The larger particles were formed at higher ozone concentrations. The mean particle diameters gradually increased up to 54, 67 and 70 nm at 240 min for the injected ozone concentrations of 50, 100, and 200 ppb, respectively.

The particle mass concentrations increased during the experimental period, as presented in Fig. 3c, and were

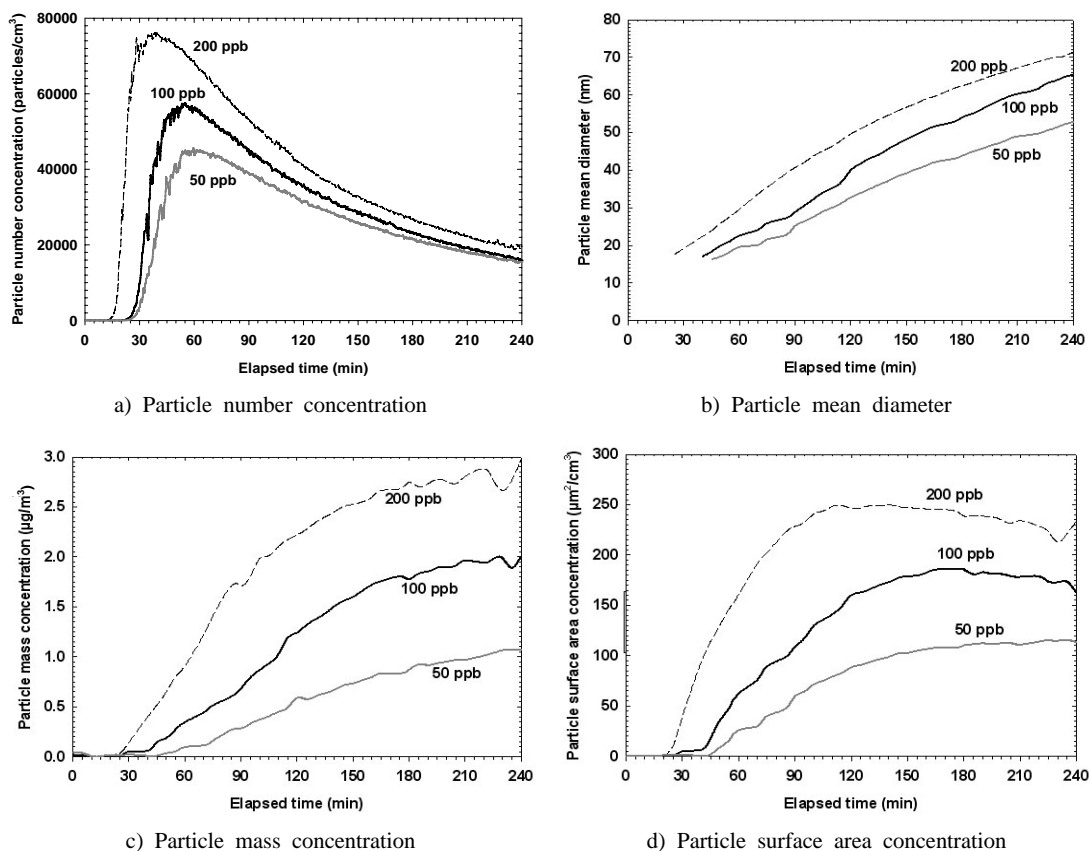


Fig. 3. Effects of injected ozone concentration on the particle formation.

1.1, 2.0 and 2.9 $\mu\text{g}/\text{m}^3$ at 240 min for the injected ozone concentrations of 50, 100 and 200 ppb, respectively. Considering the reacted ozone concentrations were 7.4, 13.5 and 37.8 ppb at 240 min for the injected ozone concentrations of 50, 100 and 200 ppb, respectively, the formation of nanoparticles might be associated with the reacted ozone concentration. The ratios of reacted ozone concentration and formed particle mass concentration for the three injected ozone concentrations of 50, 100 and 200 ppb were all different 2.6:1.8:1.0 for particle mass concentration and 5.1:1.8:1.0 for reacted ozone concentration at 240 min. The reacted ozone concentration showed a good linear correlation with the particle mass concentration produced, with a determination coefficient of more than 0.9 for injected ozone concentrations of 50 and 100 ppb, as shown in Fig. 4. In the case of the

200-ppb injected ozone concentration, the reacted ozone concentration exhibited a curvature in the relationship, with a particle mass concentration of approximately 20 ppb that of the reacted ozone concentration. The linear slope between the reacted ozone concentration and particle mass concentration produced before a 20-ppb reacted ozone concentration was 0.15, which was similar to those found in other experiments. This implies that some VOCs having a high potential of secondary aerosol formation were not sufficiently emitted from the home cleaner liquid to react with the 200 ppb ozone injected. In addition, ozone could react with other substances, such as secondary reactive intermediates, but not produce particles. The particle mass concentrations produced from the reactions in this work were significantly lower than those from the reactions of ozone and VOCs

emitted from a commercial air freshener(Vu *et al.*, 2011). These differences might have been caused by the different VOCs contained in the test specimens.

Fig. 3d shows the particle surface area concentrations that were estimated from SMPS data for the three levels of the injected ozone. The particle surface area concentration is associated with lung disease(Wang *et al.*, 2008). It was reported that nearly spherical particles may cause lung damage, and these particles can be deposited on the surfaces in different regions of the human respiratory system(Fissan *et al.*, 2007). The large surface areas provided by ultrafine particles and nanoparticles in contact with the lung provide the opportunity for the surface chemistry of the particles to have a damaging effect. Ultrafine particles and nanoparticles penetrate interstitial macrophages and other sensitive cells in lungs, which leads to the development of subsequent diseases in the lungs(Donaldson *et al.*, 1997). The deposited surface area in a human lung per hour was found to be 12–30% of the particle surface concentration in indoor environments(Lamorena and Lee, 2008). The deposited surface area rate was also found to depend on the particle surface area concentration in indoor environments. The higher the particle surface area concentration produced, the greater the increase in the rate of the deposited surface area. In this investigation, the particle surface area concentration quickly increased at 45, 25 and 20 min for ozone concentrations of 50, 100 and 200 ppb, respec-

tively. It was assumed that the deposited surface area was 20% of particle surface area concentration per hour. The maximum deposited surface areas were 23, 36 and $50 \mu\text{m}^2/\text{cm}^3$ during the period from 180 to 240 min for ozone concentrations of 50, 100 and 200 ppb, respectively. Thus, the higher ozone concentration present, the higher the particle surface area concentration produced, leading to higher rates of the deposited surface areas in the lungs.

As analyzed above, the higher the injected ozone concentration, the higher the particle concentration produced. The produced particle mass concentrations were directly proportional to the reacted ozone concentrations, as presented in Fig. 4. There were good correlations between the injected ozone concentrations of 50 and 100 ppb with the particle mass concentrations produced. In these cases, the average ratio of the reacted ozone concentrations(ppb) to the produced mass concentrations($\mu\text{g}/\text{m}^3$) was 9:1. The average ratio of the reacted ozone concentrations(ppb) to the particle mass concentrations produced($\mu\text{g}/\text{m}^3$) was 11:1 for an injected ozone concentration of 200 ppb. The correlations of the reacted ozone concentrations with the particle mass concentration produced with injected ozone levels of 50 and 100 ppb were better than that at an injected ozone concentration of 200 ppb.

4. Conclusions

In this work, experiments were carried out on the formation of secondary nanoparticles, using a home cleaner liquid, which is a popular daily consumer product. The home cleaner liquid contained many VOCs, such as hexane, n-butanol, propyl acetate, toluene, ethyl benzene, xylene, α -pinene, limonene, linalool and benzyl acetate. These VOCs might contribute to the formation of nanoparticles within the three different ozone-containing environments. The nanoparticle formation phenomena were characterized in terms of the particle number, mass, surface area and mean diameter.

The nanoparticle formation phenomena were heavily

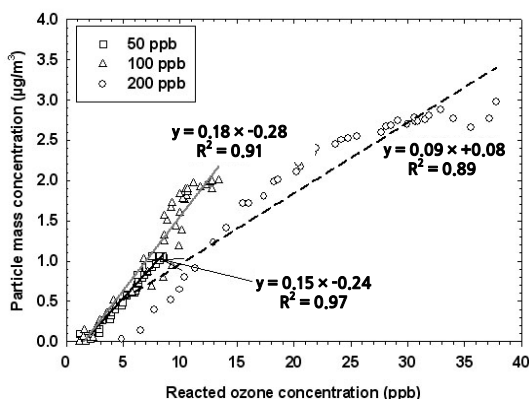


Fig. 4. Correlation between the reacted ozone concentration and produced particle mass concentration.

dependent on the injected ozone concentration. The higher nanoparticles were quickly formed at higher injected ozone concentrations, with higher particle masses. The particle mass formed by the ozone-VOCs reaction was reasonably proportionate to the reacted ozone with injected ozone concentrations of 50 and 100 ppb.

These results imply that the VOCs emitted from the home cleaner liquid have the potential to produce secondary nanoparticles at low ozone concentration; an issue relating to human exposure to nanoparticles within indoor environments.

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