

Nucleation and Growth of Freshly-Formed Particles from Limonene Ozonolysis

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1 Introduction

In building environments, oxidation reactions involving ozone and terpenoids lead to nano-sized particle formation [Jang et al. 1999]. Low volatility products of these reactions are important and add to particle mass concentrations in air through nucleation or condensation onto existing suspended particles [Lamorena and Lee 2008]. Several recent studies have focused on ozonolysis of monoterpenes (e.g. pinene, limonene, and terpineol) and shown that these reactions are major sources of indoor secondary organic aerosols (SOAs). Because of instrument limitations, there had been little information regarding freshly nucleated particles with diameters less than 10 nm until recently. Also, for secondary organic aerosols (SOAs), i.e., particles formed from gas-phase chemistry, information regarding the evolution of particle size distributions is lacking. To better understand the underlying processes of SOA formation, it is essential to evaluate particle nucleation (in terms of size and mode) and the associated evolution rate.

In this study, a series of experiments were conducted in both chambers and a residential room to characterize freshly nucleated particles ($d_p = 3\text{ nm}$ to 100 nm) generated from the gas-phase reaction of d-limonene and ozone. Influences of water vapor, reactant concentration, and OH-scavenger on ozone degradation of limonene and its particle formation were investigated.

2 Materials/Methods

A schematic of the experimental system is illustrated in Figure 1. A 60 L chamber, made of electro polished stainless steel, was used to host the ozone/terpene reaction. Both ozonated air and terpene-containing air were introduced into the flask through separate Teflon ports located

on the flask cap. The total flow rate of the two air streams were controlled at approximately 5 L/min (corresponding to an air change rate of 5 h^{-1}). Ozone was first added at realistic concentrations of 20 ppb_v to 25 ppb_v until the chamber reached steady state. Limonene (100 ppb_v to 400 ppb_v) was then continuously introduced to the chamber at a constant mass flow rate of 0.4 L/min.

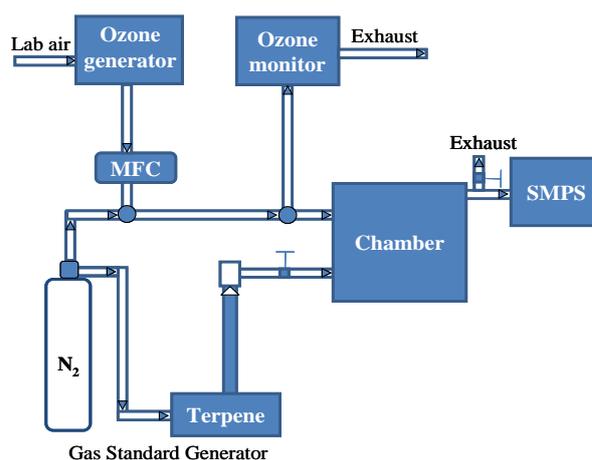


Figure 1: Environmental Chamber for Limonene and Ozone Reactions

Prior to each experiment, the chamber/flask was cleaned with deionized water followed by ethanol, and was also purged with a high concentration of ozone (2 ppm_v to 3 ppm_v) at a flow rate of 5 L/min until low particle number concentrations ($\sim 100\text{ per cm}^3$) were detected by the SMPS.

Experimental reproducibility was evaluated by repeating each experiment in duplicate or triplicate. Results are averaged and reported in the next section.

3 Results

Results indicated significant effects of reactant concentrations on particle mass and

size. With high limonene concentrations (400ppb_v), rapid particle production was observed in the first scan after limonene was introduced into the chamber [Figure 1]. A time delay (lasting a couple of 2.5 minute scans) for particle generation was found for lower concentrations; no or few particles formed at a limonene concentration of less than 100 ppb_v even though ozone was scavenged in the flask. This observation may indicate that low volatility oxidation products were generated and need some time to reach saturation before self-nucleating [Lamorena and Lee 2008].

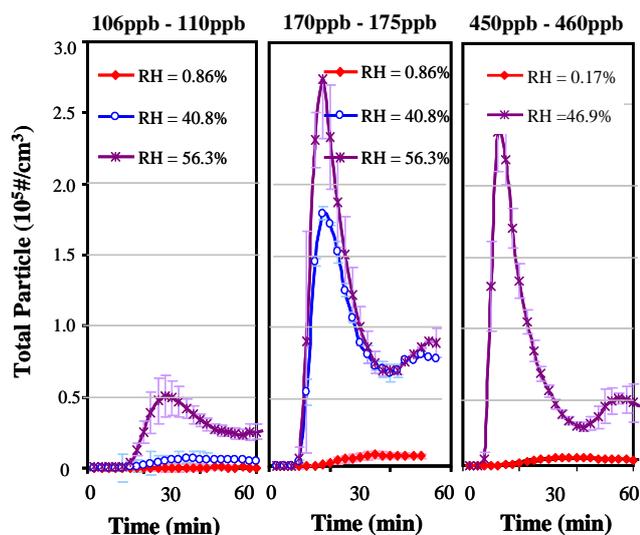


Figure 1. Effects of limonene concentration and relative humidity on particle concentration

Nucleation events were observable before particles started coagulating and low volatility compounds condensed on particle surfaces. During the first few 2.5-minute scans, the modes of newly-formed particles grew from 4 nm to 10 nm, suggesting nucleation. They then increased over time at different rates, depending on reactant concentrations and relative humidity [Figure 2, Figure 3].

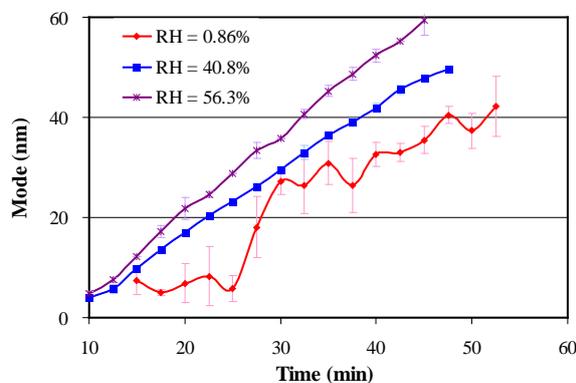


Figure 2. Mode growth with limonene concentration of 170 ppb_v to 175 ppb_v.

Relative humidity had a considerable effect during nucleation events, with a mode growth rate of 0.5 nm/minute to 1 nm/minute for increases in RH from 0 % to 60 %. Particles also grew faster at high limonene concentrations, a factor of 1.5 to 5 faster in the case of high and low humidity.

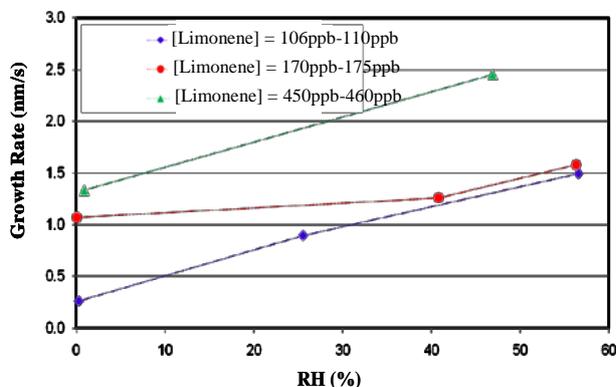


Figure 3. Mode growth rate versus RH for varying limonene concentrations.

4 Conclusions

Condensation and first and second generation oxidation processes had strong effects on the evolution of the particle size distribution. The study results can be used to estimate personal exposures and indoor concentrations of ultrafine particles due to ozone-limonene reactions. It is also important to develop an analytical model to predict secondary organic aerosol formation and growth.

5 References

Jang, M. and Kamens, R.M. 1999. Newly characterized products and composition of secondary aerosols from the reaction of α -pinene with ozone. *Atmospheric Environment*, 33 (3), 459-474.

Lamorena, R.B., and Lee, W. 2008. 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. *Journal of Hazardous Materials*, 158 (2-3), 471-477.