Gas and Particle Phase Chemistry of Linalool Ozone Reactions and Analysis of Resulting Reactive Oxygen Species

Meera A. Sidheswaran and Lawrence L Tavlarides,

Department of Biomedical and Chemical Engineering,
Syracuse University, Syracuse, NY 13244
Corresponding email: smeeraan@syr.edu

SUMMARY
Linalool ozone reactions were conducted in two stainless steel chambers (100L and 54 m3) and the gas and particle phase chemistry have been studied. A preliminary analysis of the gas and particle phase products have been performed and a number of intermediates including 2-ethenyl-2-methyl-5-hydroxytetrahydrofuran, 2(3H)-furanone-5-ethenyldihydro-5-methyl-, tetrahydro-1-methyl-5-oxo2-furancarboxylic acid and 2-hydroxy-2,3-dimethylsuccinic acid have been identified. Further, reactive oxygen species have been identified as produced during the reaction process. Fluorescence techniques will be employed in identifying and quantifying these species in the sub-micron particles. The reaction rate constant for the oxidation of linalool by ozone was found to be 3.49×10^{-16} cm3/molecules-sec. The particle size distributions of the particles produced due to these reactions has been obtained. It was concluded that the concentration of linalool and the concentration of ozone play a vital role in the formation and growth of particles. Yield of the products in the particle phase has also been obtained to study the partition of organics produced in the gas and particle phase.

KEYWORDS
Linalool – ozone chemistry, particle size distribution

INTRODUCTION
It has been found that much pollution occurs indoors due to the extensive use of chemicals like fragrances, air fresheners, laundry detergent, air spray, hard wood boards, etc. It has also been found that the occupant themselves cause pollution while indoors. Although photochemistry is not very important indoors, the ozone terpene - reactions play an important role in deciding the quality of air. The presence of oxidants such as hydroxyl radicals, ozone, and NO_x radicals cause oxidation reaction of the volatile organic compounds to produce biradicals and oxygen species. Hubbel et al., 2005, summarized the relation between ozone and respiratory related diseases. The oxidation reactions of terpenes produce volatile and semi volatile organics that are capable of condensing on particulate matter. These organics are yet to be identified and their toxicity is yet to be determined. Work by Seinfeld and Pandis, 1998; indicates that the organics produced from the reaction of terpenes, terpenoids and terepene alcohols condense to form fine particulate matter which grows. Such particulate matters are called secondary organic aerosols and they affect human and ecological health, visibility, and indoor air quality.

Linalool, a natural substance of the terpene alcohol family is biosynthesized by a host of plants specifically many herbs, species and fruits. Linalool has been produced for many years in high volume from natural precursors or through total chemical synthesis. It is used in vitamin E synthesis and is added to processed food beverages, perfumes, costumes, soaps, household detergents, waxes for stored food and pest control (Linalool, UNEP Publications). It has been found previously that in the troposphere, linalool reacts with hydroxyl radicals, nitroxide radicals and ozone (Atkinson 1997) and has a reaction time of less than one hour.

Presently, linalool is widely used indoors in indoor spray and perfumes and as a disinfectant and thereby causing unwanted indoor reaction products due to its reaction with the radicals and ozone present indoors. This study focuses on the linalool ozone reactions and the identification of particles and gas phase products. Reaction mechanisms along with yield models have also been studied.

MATERIALS AND METHODS

Linalool (97%) was purchased from Alfa Aesar and injected using a syringe. Ozone was generated using an API Ozone generator 400, and monitored using an API Ozone monitor 440. Gas samples were collected using Tenax Tubes with the help of a hand pump (Socket), and analyzed using chromatographic techniques (GC-MS, Trace-DSQ from Thermo Electron and Auto thermal desorption unit Turbomatrix 300 from Perkin Elmer). Particle samples were collected using a Nano-aerosol sampler from TSI instruments Model 3086, and analyzed using GC-MS techniques after dissolving the particles and extracting them with methanol using the Soxhlet extraction technique.

EXPERIMENTAL SETUP

Experiments were conducted in 100L and 54 m^3 stainless steel chambers, each operated in batch mode. Linalool was injected inside each chamber using the micro syringe (Hamilton Co.) into the chambers through a septum sealed inlet. The humidity inside the system was kept at 25% RH and room temperature was maintained. Samplings for the gas and particle phase were made possible through outlet ports situated at the diagonal end of the inlet ports. Gas and particle phase samples were collected at regular intervals and analyzed to identify gas and particle phase compounds formed due to the reaction. Further, the growth and decay of these compounds were monitored.

RESULTS
Gas Phase Analysis

Linalool ozone reactions proceed through two possible routes due to the presence of the two double bonds in its chemical structure. The reaction of ozone with linalool is expected to proceed through the initial addition of ozone in the $>C=C<$ of the $C_5 - C_6$ group (probability $\sim 97\%$), leading to the reaction pathway on the left (Atkinson, 1994, Atkinson, 1997, and Calogirou et al., 1995). The reaction initially proceeds through the addition of ozone to the $>C=C<$ bond of $(CH_3)_2C=CH-$ to form acetone and a Criegee biradical. These Criegee biradicals are extremely reactive and they form stable intermediates as the reaction sequence (Scheme 1) suggests. Further acetone and acetaldehyde were also formed as expected. It should be noted that the major products formed from the biradicals, 2-ethenyl-2-methyl-5-hydroxytetrahydrofuran and 2(3H)-furanone-5-ethenyldihydro-5-methyl-, are in agreement with the previous study by Shu et al., 1997. In this study, ozone reactions involves the elimination of hydroxyl radicals, however, we chose not to use cyclohexene or any other hydroxyl scavenger as this hinders the reaction mechanism and alters the particle formation and number. The primary reaction sequence of the $[(CH_3)_2COO]^*$ biradical is by the formation and decomposition of hydroperoxide leading to the formation of formaldehyde. Formaldehyde was observed in the samples measured by using PFPH derivitized Tenax sorbents and derivitizing the collected gas samples. The yield of formaldehyde however was

not significant. Hence quantitative analysis of the formation of formaldehyde was not performed. This is in concurrence with the results obtained by Shu et al., 1997, where they report that the overall formaldehyde yield was less than 3%. Additionally, the formation of tetrahydro-1-methyl-5-oxo2-furancarboxylic acid and 2-hydroxy-2,3-dimethylsuccinic acid shows that the major products of the linalool ozone reaction system undergo further reaction with ozone due to the presence of the double bond to give rise to secondary Criegees as suggested by Shu et al., 1997, Atkinson et al., 1995, and Calogirouet al., 1995. The formation of these compounds suggests that the biradical $[CO_2HCH_2CH_2C(OH)(CH_3)CH^*OOH]^*$ cyclizes with the loss of water molecule, a behavior similar to formation of the second major product 2(3H)-furanone-5-ethenyldihydro-5-methyl-. The double bond of $(CH_3)_2C=CH-$ can also produce 2-ethenyl-2-methyl-5-methyltetrahydrofuran. The Criegee biradicals formed due to the ozonlysis reaction react with stable intermediates to undergo nucleation to form particles. These nucleates condense and adsorb volatile organics present in the surrounding to grow in size and form particles. Scheme 1 shows the reaction sequence of the oxidation of linalool with ozone. The other intermediates formed subsequently are listed in Table 1. The identified intermediates were quantified using chromatographic techniques. The concentrations of organics showed in the Table 1 are for samples collected after 30 minutes of linalool injection.

Figure 1 shows the concentration decay of linalool and the increase and decrease of the products of linalool ozone reaction in the gas phase. The increase in the concentrations of the products in the gas phase show the initial burst of intermediates and the process of the formation of nucleates. These nucleates condense to form particles and they adsorb the organics present in the surrounding environment. Hence the concentrations of these organic products decrease.

The reaction rate constants were computed according to the methods established by Atkinson et al., 1995 taking propene as the reference compound. The reaction rate constant for the ozonation of linalool from these experiments were estimated to be 210.2 m^3/mole-sec ($3.49x10^{-16}$ cm^3/molecule-sec). These values are in concurrence with the works by Atkinson et al., 1995 and Shu et al., 1997 (rate constants reported are in the order of 10^{-16}).

Scheme 1. Linalool Ozone Reaction Sequence.

Sl.no	Type of Chamber	Type of Experiments	Linalool [ppb]	O$_3$ [ppb]	2-Ethenyl-2-methyl-5-hydroxytetrahydrofuran x10^4 µg/m^3	2(3H)-Furanone-5-ethenyldihydro-5-methyl- x10^4 µg/m^3	Acetaldehyde x10^4 µg/m^3	Acetone x10^4 µg/m^3	Acetic acid x10^4 µg/m^3	Tetrahydro-1-methyl-5-oxo2-furancarboxylic acid x10^4 µg/m^3	2-hydroxy-2,3-dimethylsuccinic acid x10^4 µg/m^3	6-methyl-5-heptene-2-one x10^4 µg/m^3	Un-reacted Linalool x10^4 µg/m^3
1	Small Chamber (100L)	Batch	75	75	2.58	0.97	0.798	0.46	0.21	-	-		0.65
2		Batch	150	150	4.87	1.84	1.19	0.81	0.55	0.04	0.02		1.47
3		Batch	200	200	7.22	1.94	0.963	1.17	0.79	0.06	0.01		3.1
4		Continuous	100	100	4.04	1.37	0.954	0.523	1.45	0.0083	0.052	0.26	
5		Continuous	200	200	8.23	2.82	1.976	0.942	3.98	0.019	0.086	0.55	
5	Big Chamber (54m^3)	Batch	35	39	1.21	0.3	0.013	0.16	0.019	0.01	0.01		0.31
6		Batch	46	42	1.55	0.34	0.012	0.24	0.014	0.03	0.03		0.48
7		Continuous	55	50	2.1	0.72	0.62	0.35	0.25	0.023	0.082	0.13	

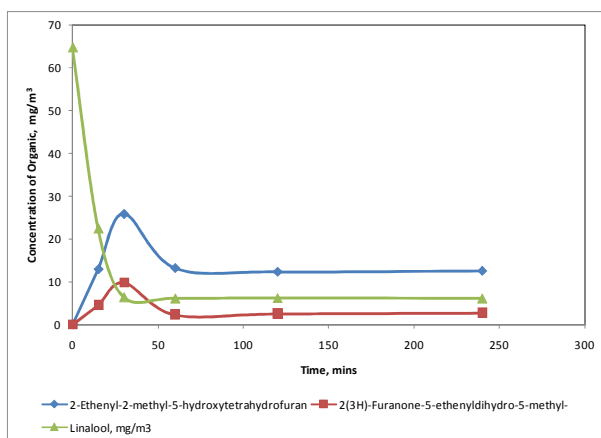Table 1. Products of Linalool Ozone Reaction

Figure 1. Concentration Of Linalool And Products Of Linalool Ozone Reaction For Initial Linalool Concentration Of 75ppb

Particle Size Distribution and Particle Phase Analysis

The particle phase analysis was performed using partition models developed by Kamens et al., 1999. The partition coefficients of three major components in the particle phase were determined using these models and they are shown in Table 2.

Sl. No	Compound	Activity Coefficient	Vapor Pressure (Torr)	K_p $(\mu g/\mu g)_{particle}/(\mu g/m^3)_{gas}$
1	2-Ethenyl-2-methyl-5-hydroxytetrahydrofuran	2.71	0.0316	1.29
2	2(3H)-Furanone-5-ethenyldihydro-5-methyl-	2.53	0.244	0.18
3	Acetone	1.73	348.0	4×10^{-4}

Table 2. Activity Coefficient, Vapor Pressure and Partition Coefficient of the Major Compounds Present in the Particle Phase

The particle size distributions were obtained using Scanning Mobility Particle Sizer (TSI SMPS) system using the long Differential Mobility Analyzer (DMA). It was found that as time progressed, the number of particles in the larger size range increased significantly. Figure 2 shows the particle formation in the 100 L chamber for 100 ppb of linalool and ozone. As the system was purged the particle number in the system decreased gradually. No particular trend was observed in this phase of the experiment.

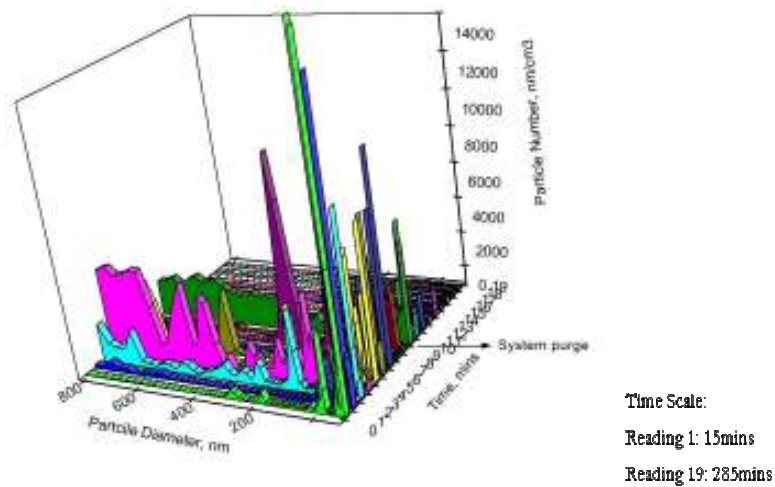Time Scale:

Reading 1: 15mins

Reading 19: 285mins

Figure 2. Particle Size Distribution of Linalool (100ppb) And Ozone (100ppb) Reaction

Figure 3 shows the total concentration of particles formed for different concentrations of linalool and ozone in different chambers. The ozone linalool concentrations were maintained almost at a 1:1 ratio. It should be noted that the number of particles in the system depended on the concentration of linalool and ozone present in the system.
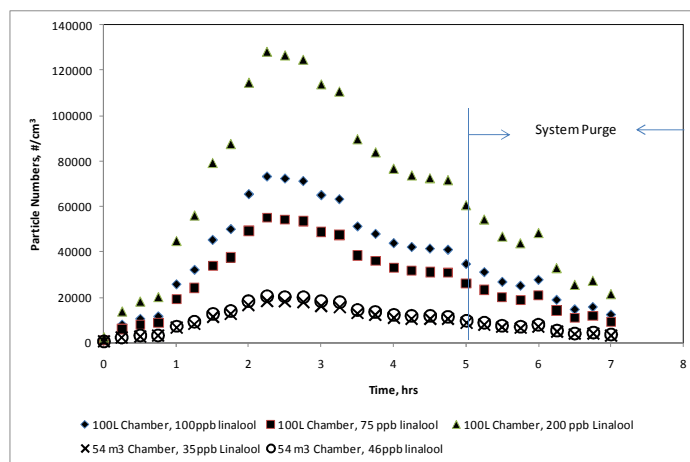

Figure 3. Total Particle Number Count for Different Concentrations of Linalool and Ozone

The number of particles starts to decrease after about 2 hours due to the increase in the particle size as seen from Figure 2. This behavior shows that particles grow by coagulating and absorbing organics present in the surrounding. The concentration of organics present in the particles however reaches a steady state and this can be found from the yield computed for the system shown in Figure 4.

Yield of secondary organic aerosol can be defined as the ratio of the organics produced due to the ozone reactions of linalool present in the particle phase to that of the initial amount of organics present in the system. It can be defined as follows:

$$Y = \frac{M_o}{\Delta \text{HC}}$$

(1)

where, Y is the yield, M_0 is the mass of secondary organic aerosols produced from the gaseous hydrocarbons ΔHC. Yield was calculated based on the above given formula, and the yield graph is presented in Figure 4. In the graph the solid lines are the model predictions obtained from the models developed by Kamens et al., 1999. For obtaining the model fit of the yield of organics in the particle phase, it was assumed that only three major organics were present in the particle phase. This assumption was validated by the chromatography results of the particle phase. Partition coefficients were calculated and their values are listed in Table 2.
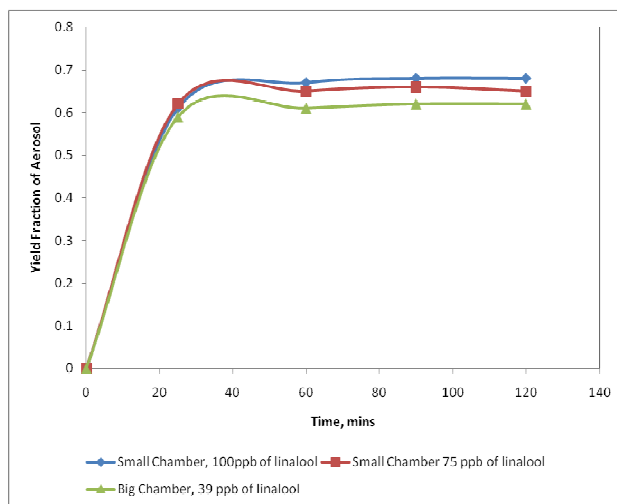

Figure 4. Yield of Aerosol in for Different Concentration of Linalool in Different Chambers

It should be noted that the yield of the particles are in the same range for different concentrations of linalool and ozone, showing that the concentration of organic produced is in the same ratio although the concentration of the particles decreases with the concentration of linalool.

CONCLUSION
The linalool ozone reaction system has been studied with two chamber systems. The small chamber was used to study large concentrations and the large chamber was used to study smaller concentrations more typical of the indoor air. Different intermediates were identified both in the gas and particle phase and a gas phase reaction pathway has been developed based on chromatographic results. 2-Ethenyl-2-methyl-5-hydroxytetrahydrofuran and 2(3H)-furanone-5-ethenyldihydro-5-methyl-, acetone, acetaldehyde, formaldehyde, acetic acid, tetrahydro-1-methyl-5-oxo2-furancarboxylic acid and 2-hydroxy-2,3-dimethylsuccinic acid were identified as the stable intermediates in the linalool – ozone reaction system. The rate constant for the ozonolysis of linalool was found to be 3.49×10^{-16} cm^3/molecule-sec. Sampling of particle phase led to the identification of two main products of the linalool ozone reaction, 2-ethenyl-2-methyl-5-hydroxytetrahydrofuran and 2(3H)-furanone-5-ethenyldihydro-5-methyl-. Further it was found that the particle size distribution depends on the concentration of linalool and ozone. The higher the concentration of the ozonide and ozone, the higher the number of particles formed in the system. Partition coefficients for three

major compounds of gas and particle phase have been calculated and the yields of these organics in the particle phase, based on the partition coefficient, have been developed.

REFERENCES
Atkinson R. 1997. "Atmospheric reactions of alkoxy and β-hydroxyalkoxy radicals", International Journal of Chemical Kinetics , Volume 29, Issue 2, 99-111.

Atkinson, R. 1994. J. Phys. Chem. Ref. Data Monograph *2*, 1-216.

Atkinson, R.; Arey, J.; Aschmann, S. M.; Corchnoy, S. B.; Shu, Y., Rate constant for the gas phase reactions of cis-3-hexen-1-ol, cis-3-hexenylacetate, trans-2-hexenal, and linalool with OH, NO_3 radicals and O_3 at $298 \pm 2K$ and OH radicals formation yields from the O_3 reactions Int. J. Chem. Kinet. **1995**, 27, 941-955.

Calogirou, A.; Kotzias, D.; Kettrup, A. 1995. Naturwissenschaften 82, 288-289.

Hubbell BJ, Hallberg A, McCubbin DR, Post E. 2005. Health related benefits of attaining the 8-hr ozone standard. Environ Health Perspect 113:73–82.

Kamens R., Jang M., Chien C J., and Leach K. 1999. Aerosol formation from reaction of α-pinene and ozone using a gas-phase kinetics – aerosol partitioning model, Environmental Science and Technology, 33, 1430 – 1438.

Seinfeld J.H and Pandis S.N. 1998. Chemistry of the troposphere. In Atmospheric chemistry and physics. From air pollution to climate change. John Wiley & Sons, Inc., New York. 234-336.

Shu YH, Kwok ESC, Tuazon EC, Atkinson R, Arey J. 1997. Products of the gas-phase reactions of linalool with OH radicals, NO_3 radicals, and O_3. Environ Sci Technol 31(3): 896–904.