

Supplementary Information:

Indoor secondary organic aerosol formation initiated from reactions between ozone and surface-sorbed d-limonene

Michael S. Waring^{a,*} and Jeffrey A. Siegel^{b,c}

^a Department of Civil, Architectural and Environmental Engineering, Drexel University, Philadelphia, PA, USA

^b Department of Civil Engineering, University of Toronto, Toronto, Ontario, Canada (current affiliation)

^c Department of Civil, Architectural and Environmental Engineering, University of Texas at Austin, Austin, TX, USA (previous affiliation)

* Corresponding author. Tel: +1 215 895 1502; fax: +1 215 895 1363.

E-mail address: msw59@drexel.edu (M.S. Waring)

This Supplementary Information contains the following sections:

1. Schematic of the small chamber system
 2. Method for analyzing d-limonene mass on Tenax GR focus liners with GC/FID
 3. Method to determine the aerosol mass fraction for SOA formed due to gas-phase reactions
 4. Deposition velocity calculation procedure
 5. Surface parameter results
 6. References in the Supplementary Information
-

1. Schematic of the small chamber system:

Figure S1 shows the schematic for the small chamber system used in the SOA formation experiments in this paper. The flow rates and chamber operation are described in the main text. The well-mixed condition was verified with tracer tests for both Chamber 1 and Chamber 2 conditions (i.e., without and with the added stainless steel screens).

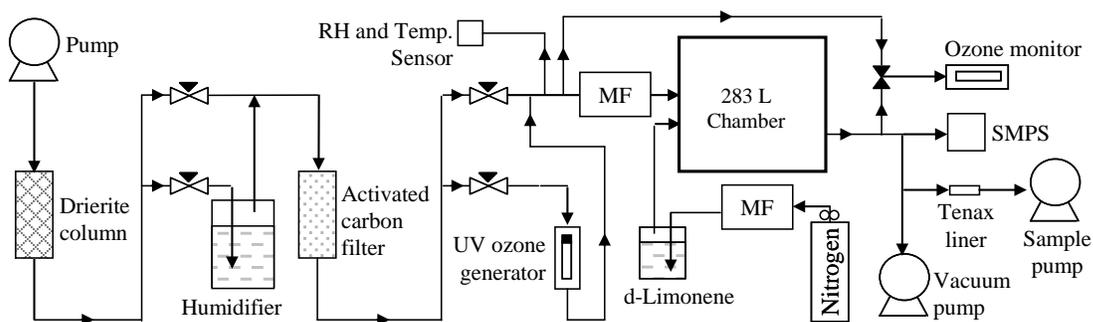


Figure S1. Experimental apparatus for measuring SOA formation due to chemical reactions with ozone and d-limonene. RH = relative humidity; Temp. = temperature; MF = mass flow controller; SMPS = scanning mobility particle sizer.

2. Method for analyzing d-limonene mass on Tenax GR focus liners with GC/FID:

The d-limonene was analyzed by thermal desorption, gas chromatography, with flame-ionization detection, TD/GC-FID (Agilent G1530A equipped with Atas Optic 2 thermal desorber), for a run time of 22 min. The focus liners were thermally desorbed by ramping at 10 °C/s from an initial temperature of 60 °C up to a holding temperature of 280 °C. The split ratio for the thermal desorber was 10:1, and a sample transfer pressure of 15 psi was held for 2 min before dropping to 14 psi and linearly increasing to 28.1 psi over the remainder of the run time. A Restek Rtx 5SilMS capillary column was used (30m length, 0.25mm internal diameter, 0.5 mm film thickness). The GC oven was held at the initial temperature of 40 °C for 2 min, after which it was ramped at 40 °C/min up to 95 °C and then 2 °C/min up to 125 °C then 60 °C/min from 125 to 270 °C, at which it was held for 1.2 min until the end of the run time. The FID was set at 250 °C with gas flows as follows: hydrogen, 35 mL/min; compressed air, 350 mL/min; and helium, 25 mL/min. Calibration standards for d-limonene were made from the same batch of d-limonene that was introduced into the chamber. Mass calibration was attained by injecting of methanol-diluted standards directly onto clean Tenax-filled tubes, which were purged with nitrogen at 20 mL/min for 20 min, and analyzed using TC/GC-FID.

3. Method to determine the aerosol mass fraction for SOA formed due to gas-phase reactions:

SOA formation due to the gas-phase oxidation of reactive organic compounds (ROG) is parameterized with the aerosol mass fraction (AMF), ξ_g , which is the ratio of the mass of organic aerosol formed, ΔC_{SOA} ($\mu\text{g}/\text{m}^3$), to the mass of the ROG reacted, ΔROG ($\mu\text{g}/\text{m}^3$):

$$\xi_g = \frac{\Delta C_{SOA}}{\Delta\text{ROG}} = \sum_i \left(\frac{\alpha_i}{1 + (c_i^*/C_{SOA})} \right) \quad (\text{S1})$$

where the right-most side of Equation S1 expresses the ξ_g as a multi-product model; α_i is the mass-based yield of product i ; c_i^* ($\mu\text{g}/\text{m}^3$) is the effective gas-phase saturation concentration of species or group i (Odum et al., 1996; Presto and Donahue, 2006); and C_{SOA} ($\mu\text{g}/\text{m}^3$) is the concentration SOA. For the d-limonene AMF, we use the volatility basis set (VBS) approach, which constrains the c_i^* at logarithmically spaced intervals and describes formation results with fits of α_i at those c_i^* . For the c_i^* of {0.01, 0.1, 1, 10, 100, 1000 $\mu\text{g}/\text{m}^3$ }, we used the α_i of {0, 0.020, 0.19, 0.20, 0.20, 0.39}, which are the d-limonene ozone-excess values from Zhang et al. (2006), reduced to account for ozone-limited conditions in our chamber.

4. Deposition velocity calculation procedure:

We performed SOA formation experiments in two chambers. Chamber 1 was the empty stainless-steel chamber (volume = 283 L, surface area = 2.60 m^2) and Chamber 2 was that chamber plus 14 stainless-steel woven wire screens. The addition of the stainless-steel screens increased the surface area by 460% and decreased the volume by 2%, which changed the total surface area to volume ratio from Chamber 1 to Chamber 2 by 469%. Please see the text of the main article for more details. In this discussion, any subscript “1” or “2” refers to Chamber 1 or Chamber 2, respectively, “1w” are the wall surfaces in Chamber 1, “2w” are the walls in Chamber 2, and “2s” are the stainless-steel screens in Chamber 2.

First, before any SOA formation experiments and before any d-limonene was injected into the chamber, the deposition velocities of ozone to the surfaces in Chamber 1 and Chamber 2, which are $v_{d,o,1}$ (m/h) and $v_{d,o,2}$ (m/h), respectively, were determined. All experiments to determine $v_{d,o}$ were performed until steady-state was reached, allowing $v_{d,o}$ for Chamber 1 and Chamber 2 to be determined with Equation S2:

$$v_{d,o,1 \text{ or } 2} = \frac{\lambda(C_{O3,m,inlet} - C_{O3,m})}{C_{O3,m}(A/V)_{1 \text{ or } 2}} \quad (\text{S2})$$

where λ (h^{-1}) is the air exchange rate; $C_{\text{O}_3,\text{m}}$ and $C_{\text{O}_3,\text{m,inlet}}$ (ppb) are the mole fractions of ozone in the chamber air and entering with the inlet air, respectively; A (m^2) is the surface area of Chamber 1 or Chamber 2; and V (m^3) is the volume of air in the chamber.

For Chamber 1, Equation S2 yields $v_{\text{d},\text{o},1}$, the deposition velocity of ozone to the only surface in the chamber, which are the stainless-steel chamber walls. However, for Chamber 2, Equation S1 yields $v_{\text{d},\text{o},2}$, the total deposition velocity to both the chamber walls and the 14 stainless-steel screens. By assuming that the deposition velocity calculated for Chamber 1 is equivalent to the deposition velocity for Chamber 2 to the chamber walls (i.e., $v_{\text{d},\text{o},1} = v_{\text{d},\text{o},2\text{w}}$), the deposition velocity of ozone to the added stainless-steel screens in Chamber 2, $v_{\text{d},\text{o},2\text{s}}$, can be determined with Equation S3, which is a surface-to-volume ratio weighted average:

$$v_{\text{d},\text{o},2\text{s}} = \frac{(A/V)_2}{(A/V)_{2\text{s}}} v_{\text{d},\text{o},2} - \frac{(A/V)_{2\text{w}}}{(A/V)_{2\text{s}}} v_{\text{d},\text{o},2\text{w}} \quad (\text{S3})$$

A total of twelve experiments (O1–O12) were conducted to determine the $v_{\text{d},\text{o},1}$, $v_{\text{d},\text{o},2\text{w}}$, and $v_{\text{d},\text{o},2\text{s}}$ for the different chamber conditions, at the different RH of 20, 50, and 70%. Multiple $v_{\text{d},\text{o}}$ experiments were performed with different steady state values for C_{O_3} for Chamber 1 and Chamber 2 at RH = 50% to ascertain how $v_{\text{d},\text{o}}$ changes with $C_{\text{O}_3,\text{m}}$.

Then, for the SOA formation experiments, all deposition velocities of ozone to surfaces with surface-adsorbed d-limonene in the chamber, $v_{\text{d},(\text{o}+\text{terp})}$, were calculated with Equation S4, which is similar to Equation S2 but with an additional loss term for ozone due to gas-phase reactions with d-limonene:

$$v_{\text{d},(\text{o}+\text{terp}),1 \text{ or } 2} = \frac{\lambda C_{\text{O}_3,\text{m,inlet}} - (\lambda + kC_{\text{terp},\text{m}})C_{\text{O}_3,\text{m}}}{C_{\text{O}_3,\text{m}}(A/V)_{1 \text{ or } 2}} \quad (\text{S4})$$

Similarly to experiments for $v_{\text{d},\text{o}}$, for Chamber 1 $v_{\text{d},(\text{o}+\text{terp}),1}$ is the deposition to the chamber walls and for Chamber 2 $v_{\text{d},(\text{o}+\text{terp}),2}$ is the total deposition velocity to the chamber walls and the 14 stainless-steel screens. Again, by assuming that the deposition velocity calculated for Chamber 1 is equivalent to the deposition velocity for Chamber 2 to the chamber walls (i.e., $v_{\text{d},(\text{o}+\text{terp}),1} = v_{\text{d},(\text{o}+\text{terp}),2\text{w}}$), the deposition velocity for the 14 stainless-steel screens in Chamber 2, $v_{\text{d},(\text{o}+\text{terp}),2\text{s}}$, can be determined with Equation S5:

$$v_{\text{d},(\text{o}+\text{terp}),2\text{s}} = \frac{(A/V)_2}{(A/V)_{2\text{s}}} v_{\text{d},(\text{o}+\text{terp}),2} - \frac{(A/V)_{2\text{w}}}{(A/V)_{2\text{s}}} v_{\text{d},(\text{o}+\text{terp}),2\text{w}} \quad (\text{S5})$$

The assumption that $v_{\text{d},(\text{o}+\text{terp}),1} = v_{\text{d},(\text{o}+\text{terp}),2\text{w}}$ is reasonable if there are similar d-limonene concentrations in experiments with Chamber 1 and Chamber 2.

5. Surface parameter results:

Results from experiments O1–O12. Experiments O1–O7 were performed in Chamber 1 and O8–O12 were performed in Chamber 2 to determine the original deposition velocities of ozone without d-limonene adsorption in those chambers. The full results are listed in Table S1, and Figure S2 plots the Chamber 1 and Chamber 2 deposition velocities versus $C_{\text{O}_3,\text{m}}$. For experiments at RH = 50%, $C_{\text{O}_3,\text{m}}$ was varied to demonstrate its effect on deposition velocities. As $C_{\text{O}_3,\text{m}}$ increased, the deposition velocity decreased. Since different chamber concentrations of ozone would be present during the SOA formation experiments, power law fits were applied values of $v_{\text{d},\text{o},1}$ or $v_{\text{d},\text{o},2}$ versus $C_{\text{O}_3,\text{m}}$ at RH = 50% to use in calculations of ζ_{s} , which were $v_{\text{d},\text{o},1} = 0.38(C_{\text{O}_3,\text{m},1})^{-0.35}$ ($R^2 = 0.97$) and $v_{\text{d},\text{o},2} = 0.30(C_{\text{O}_3,\text{m},2})^{-0.48}$ ($R^2 = 0.81$). The experiments at lower RH resulted in slightly lower deposition velocities and those at higher RH in slightly higher deposition velocities, at comparable $C_{\text{O}_3,\text{m}}$. This difference was neglected in our calculations since it was small and there were not enough data to determine its effect in a robust manner.

Table S1. Results from steady state experiments O1–O12. Values in parentheses are uncertainty for the ozone mole fractions and deposition velocities.

Exp.	Chamber condition	RH (%)	$C_{O_3, \text{inlet}}$ (ppb)	C_{O_3} (ppb)	$v_{d,0,1}$ or $v_{d,0,2}$ (m/h)
O1	Chamber 1	20	214 (5.5)	117 (3.0)	0.069 (0.006)
O2	Chamber 1	50	27.1 (2.0)	8.26 (1.7)	0.19 (0.06)
O3	Chamber 1	50	52.1 (1.6)	20.9 (1.7)	0.12 (0.02)
O4	Chamber 1	50	104 (2.8)	50.1 (1.7)	0.089 (0.007)
O5	Chamber 1	50	203 (5.1)	100 (2.9)	0.085 (0.007)
O6	Chamber 1	50	400 (10)	242 (6.1)	0.054 (0.005)
O7	Chamber 1	70	203 (5.1)	88.6 (2.4)	0.11 (0.007)
O8	Chamber 2	20	182 (4.9)	70.5 (2.6)	0.029 (0.002)
O9	Chamber 2	50	104 (3.0)	18.7 (1.7)	0.085 (0.010)
O10	Chamber 2	50	157 (4.3)	55.3 (1.8)	0.034 (0.002)
O11	Chamber 2	50	394 (9.9)	141 (3.6)	0.033 (0.002)
O12	Chamber 2	70	197 (4.9)	32.9 (1.6)	0.09 (0.006)

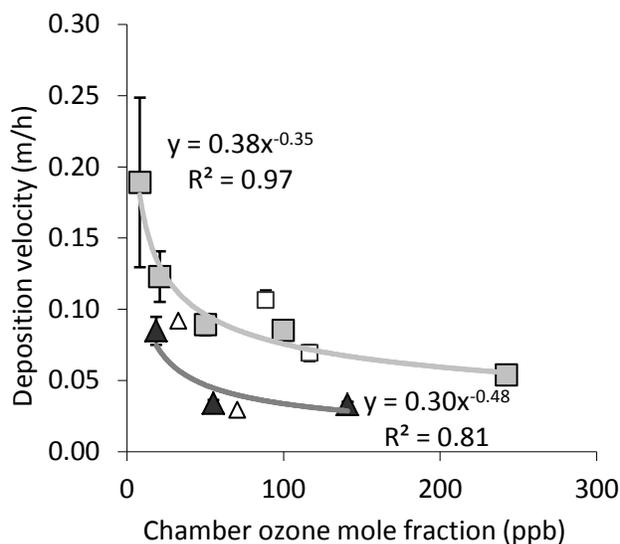


Figure S2. Plot of $v_{d,0,1}$ or $v_{d,0,2}$ versus $C_{O_3,m}$, the chamber ozone concentration. Squares are for Chamber 1 and triangles for Chamber 2. Filled symbols are experiments at RH = 50%. Hollow symbols are at RH = 20 or 70%. Power law fits are for RH = 50% only.

Specific values for surface parameters. Table S2 lists the deposition velocities, fractions of ozone reacting with the adsorbed terpenoids, fractional coverage of the sorbed terpenoids, and aerosol mass fractions of SOA.

Table S2. Deposition velocities, fractions of ozone reacting with the adsorbed terpenoids, fractional surface coverage of the adsorbed terpenoids, and aerosol mass fractions of SOA.

Parameter	RH = 20%	RH = 50%	RH = 70%
Deposition velocity (m/h)			
$V_{d,o,1w}$	0.21 (0.031)	0.21 (0.032)	0.23 (0.035)
$V_{d,o,2w}$	0.20 (0.030)	0.21 (0.032)	0.22 (0.033)
$V_{d,o,2s}$	0.10 (0.031)	0.11 (0.033)	0.12 (0.035)
$V_{d,(o+terp),1w}$	0.53 (0.14)	0.59 (0.19)	1.1 (0.43)
$V_{d,(o+terp),2w}$	0.53 (0.14)	0.59 (0.19)	1.1 (0.43)
$V_{d,(o+terp),2s}$	0.37 (0.12)	0.55 (0.16)	0.66 (0.25)
$V_{d,terp,1w}$	0.61 (0.33)	0.64 (0.41)	0.79 (0.51)
$V_{d,terp,2w}$	0.63 (0.34)	0.65 (0.41)	0.81 (0.52)
$V_{d,terp,2s}$	0.73 (0.46)	0.80 (0.46)	0.82 (0.55)
Fraction of ozone reacting on surface with adsorbed terpenoids			
$f_{O_3,terp,1w}$	0.32 (0.15)	0.38 (0.21)	0.87 (0.45)
$f_{O_3,terp,2w}$	0.33 (0.15)	0.38 (0.21)	0.88 (0.45)
$f_{O_3,terp,2s}$	0.27 (0.15)	0.44 (0.21)	0.54 (0.30)
Fractional coverage			
$r_{terp,1w}$	0.010 (0.0047)	0.012 (0.0063)	0.027 (0.014)
$r_{terp,2w}$	0.010 (0.0047)	0.012 (0.0063)	0.027 (0.014)
$r_{terp,2s}$	0.0084 (0.0046)	0.014 (0.0066)	0.017 (0.0092)
AMF for SOA formation			
ξ_s	0.91 (0.87)	0.84 (0.70)	0.70 (0.65)
$\xi_{s,terp}$	0.32	0.29	0.25
ξ_g	0.60–0.62	0.60–0.62	0.59–0.62

Confirming our experiments were in the reaction rate limited regime. Using our experimental data and the theory of Morrison and Nazaroff (2002), we estimated $u^* = 3$ cm/s and the transport limited deposition velocity as $v_t = 8.1$ m/h, and we have plotted the deposition velocities as a function of the surface reaction probabilities in Figure S3. All values are less than the critical point that separates the reaction rate limited from the transport limited regime (Morrison and Nazaroff, 2002), confirming the appropriateness of Equation 9 (see main text for details).

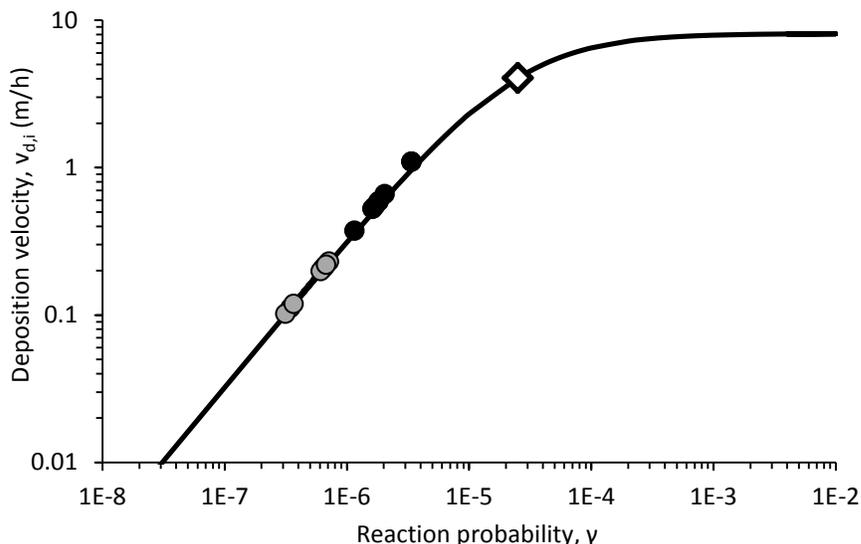


Figure S3. Plot of deposition velocities as a function of surface reaction probability, using experimental data and the theory of Morrison and Nazaroff (2002), for $u^* = 3$ cm/s and $v_t = 8.1$ m/h. Gray circles are experiments O1–O12, black circles are experiments SOA1–SOA12, and the hollow diamond is the critical point that separates the reaction rate limited from the transport limited regime (Morrison and Nazaroff, 2002).

6. References in the Supplementary Information:

Morrison, G.C.; Nazaroff, W.W. 2002. The rate of ozone uptake on carpet: Mathematical modeling. *Atmos. Environ.* 36: 1749-1756.

Odum, J.R.; Hoffmann, T.; Bowman, F.; Collins, D.; Flagan, R.C.; Seinfeld, J.H. 1996. Gas/particle partitioning and secondary organic aerosol. *Environ. Sci. Technol.* 30: 2580-2585.

Presto, A.A.; Donahue, N.M. 2006. Investigation of α -pinene + ozone secondary organic aerosol formation at low total aerosol mass. *Environ. Sci. Technol.* 40: 3536-3543.

Zhang, J.; Hartz, K.E.H.; Pandis, S.N.; Donahue, N.M. 2006. Secondary organic aerosol formation from limonene ozonolysis: Homogeneous and heterogeneous influences as a function of NO_x. *J. Phys. Chem. A* 110: 11053-11063.