

Yields of Secondary Organic Aerosol from Reactions between Ozone and Surface-Adsorbed d-Limonene

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1 Introduction

Nearly all previous studies on secondary organic aerosol (SOA) formation focused on gas-phase reactions between ozone and terpenes. However, terpenes can adsorb onto building materials, and Springs et al. (2011) determined that ozone did, in fact, react with terpenes adsorbed to surfaces. The purpose of this work was to determine the yield of ozone reactions with surface-adsorbed d-limonene on gas-phase SOA concentrations.

2 Background

The framework we used to design experiments starts with the deposition velocity of ozone to an “original” surface (without terpene adsorption), $v_{d,o}$ (m/h), which is the ratio of the ozone flux to the original surface and its bulk concentration. We defined a deposition velocity of ozone to an original surface with terpenes (of a single type) adsorbed to it as $v_{d,(o+terp)}$ (m/h) (Coleman, 2009):

$$v_{d,(o+terp)} = \left(\frac{1}{v_t} + \frac{4}{\gamma_{(o+terp)} \langle v \rangle} \right)^{-1} \quad (1)$$

where v_t (m/h) is the transport-limited deposition velocity; $\langle v \rangle$ (m/h) is the Boltzmann velocity; and $\gamma_{(o+terp)}$ (-) is the reaction probability of the surface that now includes the reactivity of the original surface and adsorbed terpenes, which is:

$$\gamma_{(o+terp)} = (1 - r_{terp})\gamma_o + r_{terp}\gamma_{terp} \quad (2)$$

where γ_o (-) is the reaction probability of the original surface without terpene adsorption; γ_{terp} (-) is the reaction probability of the terpene; and r_{terp} (m² terpene/m² intrinsic surface area) is the fractional coverage of terpenes on the surface. The fraction of ozone that reacts on the surface with the adsorbed terpenes, $f_{O3,terp}$ (-), is thus:

$$f_{O3,terp} = \frac{r_{terp}\gamma_{terp}}{\gamma_{(o+terp)}} \quad (3)$$

The deposition velocity of ozone to the adsorbed terpenes, $v_{d,terp}$ (m/h), may be calculated with:

$$v_{d,terp} = f_{O3,terp}v_{d,(o+terp)} \quad (4)$$

Using only deposition velocity terms, $v_{d,terp}$ is:

$$v_{d,terp} = \left(1 - \frac{v_{d,o}}{v_{d,(o+terp)}} \right) v_{d,(o+terp)} \quad (5)$$

The SOA concentration, C_{SOA} (μg/m³), is a sum of the contributions of reactions of ozone and terpenes on the surface, $C_{SOA,s}$ (μg/m³), and in the gas-phase, $C_{SOA,g}$ (μg/m³). At steady state, assuming well-mixed air, isothermal conditions, and no resuspension, $C_{SOA,s}$ is:

$$C_{SOA,s} = \frac{Y_{s,m} \left(C_{O3} v_{d,terp} \frac{A}{V} \right) \left(\frac{MW_{SOA}}{MW_{O3}} \right)}{\lambda + \beta} \quad (6)$$

where $Y_{s,m}$ (-) is the molar surface yield, which is the ratio of moles of SOA formed and moles of ozone consumed by ozone/terpene reactions that occur on the surface; C_{O3} (μg/m³) is the mass concentration of ozone; A (m²) is the area of the surface; V (m³) is the gas volume; MW_{SOA} and MW_{O3} (g/mol) are the molecular weights of SOA and ozone, respectively; λ (h⁻¹) is the rate of air exchange; and β (h⁻¹) is the surface loss rate of SOA. Additionally, making the same assumptions as for Equation 6, $C_{SOA,g}$ (μg/m³) is:

$$C_{SOA,g} = \frac{Y_{g,m} k C_{terp,m} C_{O3,m}}{\lambda + \beta} \quad (7)$$

where $Y_{g,m}$ (-) is the molar yield of SOA for gas-phase reactions, which is defined as ratio of the moles of SOA formed and terpene consumed; k ($\text{ppb}^{-1} \text{h}^{-1}$) is the gas-phase reaction rate constant between ozone and the terpene; and $C_{\text{O}_3,m}$ and $C_{\text{terp},m}$ (ppb) are molar concentrations of ozone and the terpene, respectively.

3 Materials/Methods

Steady-state experiments were performed in a well-mixed 283 L stainless steel chamber with ozone and d-limonene (“terp” in our equations) to quantify $Y_{s,m}$ for ozone and surface adsorbed d-limonene. Clean air at ~ 24 °C at different relative humidity (RH) values of 20, 50, and 70% was delivered to the chamber at air exchange rates of 0.76 – 0.78 h^{-1} . Inlet RH and temperature, inlet and outlet ozone, and outlet d-limonene and particle concentrations were measured during each experiment.

SOA formation was measured while varying the A/V in the chamber for different experiments to isolate the impact of surface reactions on C_{SOA} . To vary A/V , we conducted experiments with the empty chamber (Ch1) and the empty chamber plus 14 stainless-steel wire screens (Ch2). The stainless-steel screens increased the A by 460% and decreased V by 2%, which changed the total A/V by 469%. Before experiments with d-limonene, $v_{d,o}$ was determined in both Ch1 and Ch2 with a steady-state mass balance, and during the SOA formation experiments, $v_{d,(o+terp)}$ was similarly determined (accounting for the gas-phase reaction term as well). As a result, $v_{d,terp}$ could be calculated with Equation 5. β was estimated using the theory of Lai and Nazaroff (2000) for Ch1 and Ch2 as 0.03 and 0.14 h^{-1} , respectively, $Y_{g,m}$ as 0.38–0.42 (depending on the SOA concentration), MW_{SOA} as 180 g/mol, and k as $0.018 \text{ ppb}^{-1} \text{ h}^{-1}$ (Atkinson et al., 1992). Thus, all the parameters in Equations 6 and 7 were either measured or estimated, except for $Y_{s,m}$. By subtracting C_{SOA} for Ch1 from that for Ch2 and accounting for the contribution from the gas-phase reactions with Equation 7, $Y_{s,m}$ could be calculated directly with Equation 6.

4 Results

Twelve formation experiments were conducted. Six with Ch1 had concentrations of inlet ozone of 120–409 ppb and outlet ozone of 4.2–29 ppb, d-limonene of 413–671 ppb, and SOA number of 9,575–15,656 $\#/\text{cm}^3$ and SOA mass of 187–359 $\mu\text{g}/\text{m}^3$. Additionally, six with Ch2 had

concentrations of inlet ozone of 221–251 ppb and outlet ozone of 4.4–7.1 ppb, d-limonene of 388–483 ppb, and SOA number of 17,447–25,616 $\#/\text{cm}^3$ and SOA mass of 227–266 $\mu\text{g}/\text{m}^3$.

The higher A/V in Ch2 yielded larger number and mass formation than in Ch1, providing evidence of SOA formation from surface reactions. One experiment was performed with Ch1 at ~ 5 times higher ozone concentrations, and this one had a size distribution with a larger geometric mean diameter than seen with Ch2, thus providing evidence that the increased SOA in Ch2 was due to surface reactions and not an artifact of higher ozone concentrations.

For RH = 20–70%, $Y_{s,m}$ ranged from 0.16–0.20. The ratios of the SOA number concentration ($\#/\text{cm}^3$) and the mass ($\mu\text{g}/\text{m}^3$) concentration formed for gas-phase (χ_g) and surface-phase (χ_s) reactions were also determined, and χ_s ranged from 126–339 ($\#/\text{cm}^3$)/($\mu\text{g}/\text{m}^3$) and χ_g ranged from 51.1–60.2 ($\#/\text{cm}^3$)/($\mu\text{g}/\text{m}^3$). We observed that lower RH led to higher number formation from surface reactions but not from gas-phase reactions. We also used the model framework to predict that building materials on which ozone/d-limonene surface reactions lead to SOA formation are those with initially low surface reactivity with ozone, such as glass, sealed materials, or smooth metals.

5 Conclusions

Products of adsorbed d-limonene and ozone reactions can potentially influence airborne SOA concentrations. SOA formation from surface reactions must be taken into account to fully understand particle formation indoors.

6 References

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