Secondary Organic Aerosol from Ozonolysis of Biogenic Volatile Organic Compounds: Chamber Studies of Particle and Reactive Oxygen Species Formation

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Supporting Information

Particle development and evolution from BVOC ozonolysis

Particle size distributions evolve in a similar manner for each of these three terpenoid species studied. Figure S1 shows the typical evolution of the SOA size and volume concentrations as well as ozone concentration from the point at which terpenoids were added to the chamber containing a steady state ozone concentration. This point is defined as time zero in the figure. The number and volume concentration in Figure S1 are the sum over particle sizes from 14 to 700 nm. Figure S2 illustrates typical particle size distribution development. With an AER at 0.67 h^{-1}, it took around 7 hrs (except for linalool experiments that took about 8 hrs) to reach steady state concentrations for the number size distribution. The development of the number and volume size distributions for all of the experiments showed similar trends that consisted of four stages with regard to number size distribution (_1_, Figure 2; _2_, Figure 1). Upon adding terpenoids to the chamber, there was a sudden burst of small particles with a mode around 15-20 nm. Then the total number and volume concentrations increases but with a shift in size to larger particles until the number concentration started to decline defined the start of the second stage. The number concentration continued to decrease while the volume or mass concentration continued to increase. There was second nucleation burst that was smaller than the first burst in the number concentration. The number concentration increases represented the third stage in the process. Then both the number and mass concentrations approached steady-state values that represented the fourth stage. The volume concentrations followed a different pattern. There was an exponential increase in mass and eventually it reached steady state.

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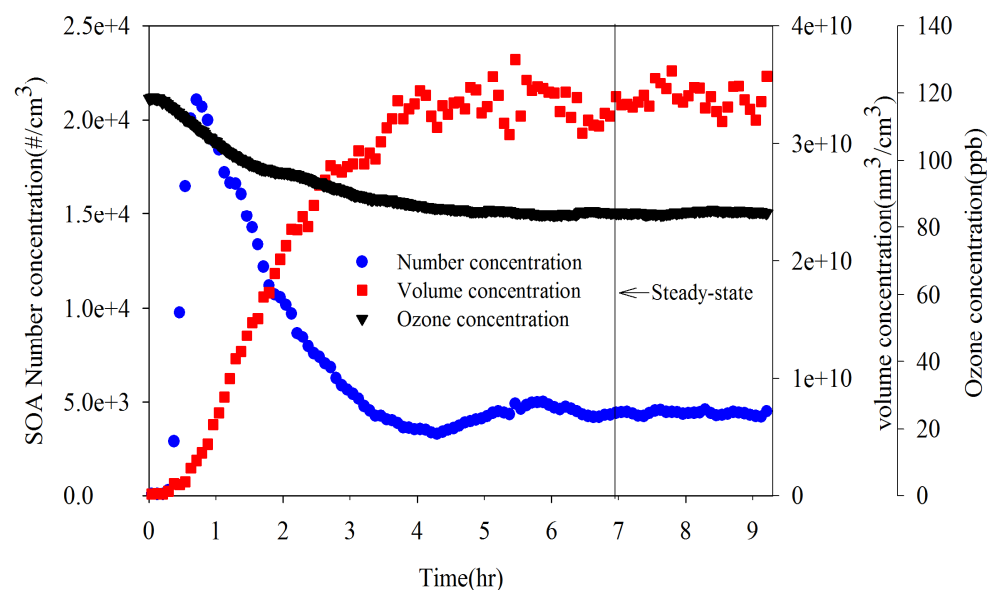
Figure S1. Typical time series of total number, volume and ozone concentration for terpenoids ozonolysis experiments.
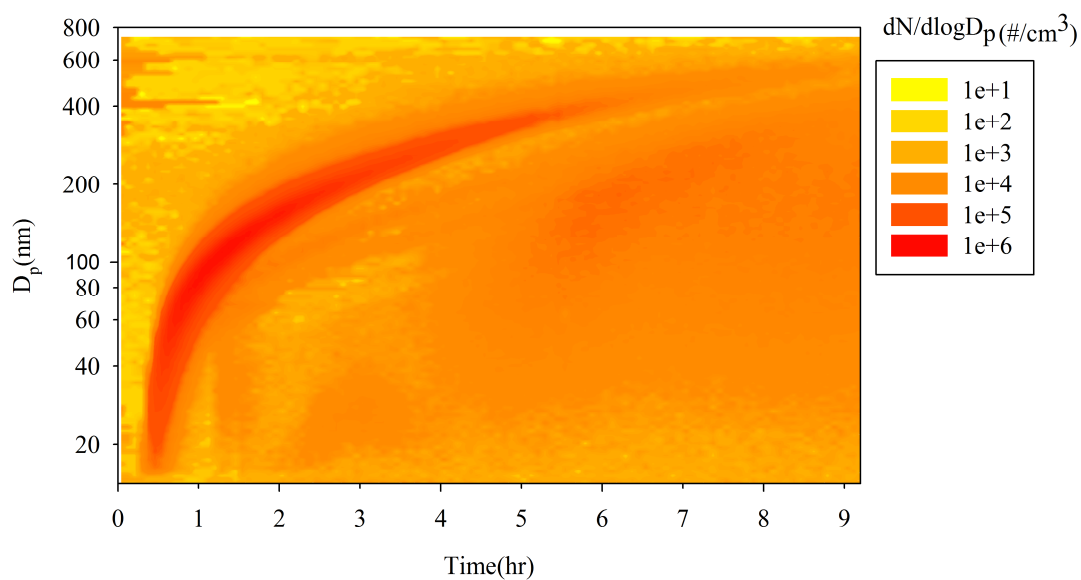

Figure S2. Typical time series of particle size distribution for terpenoids ozonolysis experiments.

Steady state OH radical concentrations estimation

The OH radical concentrations in the chamber at steady state are calculated as follows. The OH source reaction is ozone/ biogenic VOC, and the sinks include reaction with biogenic VOC and its dominant primary ozonolysis products as well as physical loss pathways.

$$[OH] = \frac{y_{OH} k_{O_3-BVOC}[O_3][BVOC]}{AER + k_d \frac{A}{V} + k_{OH-BVOC}[BVOC] + \sum k_{OH-POP}[POP]} \tag{S1}$$

where BVOC=biogenic VOC, POP=primary ozonolysis products from BVOC; y_{OH} is molar yield of OH from ozone/ BVOC reaction; k_d is OH deposition velocity (0.0007 m/s)(3); A/V is chamber surface to volume ratio (4.5 m^{-1}); $k_{O_3\text{-}BVOC}$ is second order rate constant for reaction of BVOC with ozone; $k_{OH\text{-}BVOC}$ is second order rate constant for reaction of BVOC with OH; $k_{OH\text{-}POP}$ is second order rate constant for reaction of primary BVOC ozonolysis products with OH. Comparing the reaction of OH with BVOC and its primary ozonolysis products, the OH losses resulting from ventilation and deposition are negligible. All of the concentrations for species in equation S1 refer to their steady-state values.

Steady-state POP concentrations were not measured. Thus, it is estimated from the stoichiometric or experimental molar yields reported in literature, detailed parameters and reaction rate constants were given previously elsewhere (1,2,3). It was assumed that POP production was solely from ozone oxidation and further decomposition by OH or ozone was neglected for rough estimation. These assumptions might produce an overestimation of POP concentrations. However, for the [OH] estimation, the dominant term (in eq S1) was the reaction with BVOC. Therefore, this approach to the estimation of the POP concentrations should not introduce significant error into these calculations. However, the estimation of [OH] is based on a number of assumptions and uncertain yields adopted. Thus, it is hard to consider propagating uncertainties into a firm number. Rough estimation of uncertainty associated with the calculated [OH] is to a factor of 2.

Steady state SOA mass yields

A model developed by Odum et al. (4) related SOA yield that is defined as the mass of SOA formed per mass of VOC consumed, with SOA mass loading.

$$Y = \frac{\Delta M}{\Delta HC} = M \sum \frac{\alpha_i K_{p,i}}{1 + MK_{p,i}} \tag{S2}$$

where Y is SOA mass yield, $K_{p,i}$ and α_i are partitioning coefficient and mass yield of compound i, respectively. Overall the SOA yield from a given precursor can be calculated by summing equation (S2) for all semi-volatile species produced. SOA mass yields for the three BVOC studied were analyzed using eq S2 characterizing with "one hypothetical product" yield model (Figure S3). Previous analyses indicated that "one-hypothetical product" yield model is adequate to represent the range of SOA produced (1,2,3).
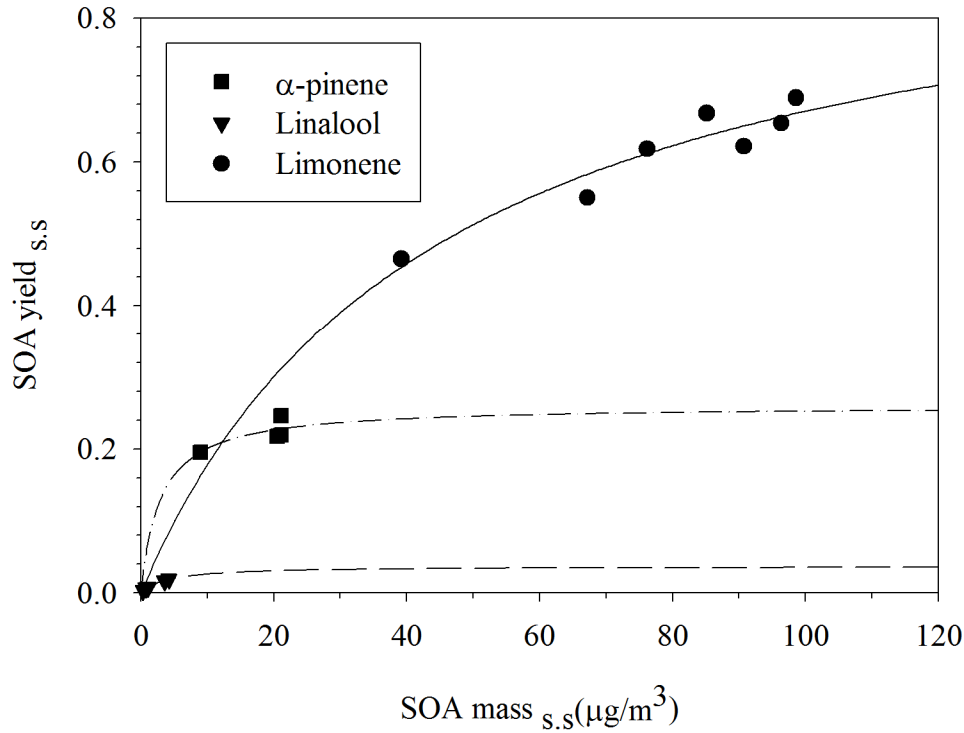

Figure S3. SOA yields plots for BVOC ozonolysis experiments. Parameters: α-pinene, α=0.26, K_p=0.34; Linalool, α=0.037, K_p=0.24; Limonene, α=0.97, K_p=0.023.

Steady state BVOC concentrations estimation

BVOC concentrations in the chamber at steady state are calculated as follows. BVOC source is from continuous input, and the sinks include reaction with ozone and its ozonolysis by-product hydroxyl radicals as well as physical loss pathways. Physical loss pathways here refer to removal by air exchange and wall deposition. Wall deposition coefficients of BVOC were not measured in this study and only dominant removal by air exchange is used for calculation. Simplified calculation is given as:

$$\frac{d[BVOC]}{dt} = IR_{BVOC} - AER[BVOC] - k_{O_3-BVOC}[O_3][BVOC] - k_{OH-BVOC}[OH][BVOC] \quad \text{(S3)}$$

where IR_{BVOC} is the input rate of BVOC from diffusion vessel.
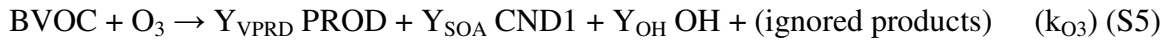
At steady state, eq S3 can be solved to estimate $[BVOC]_{s.s}$ as follows:

$$[BVOC]_{S.S} = \frac{IR_{BVOC}}{AER + k_{O_3-BVOC}[O_3] + k_{OH-BVOC}[OH]} \quad \text{(S4)}$$

Steady state BVOC concentrations are estimated using eq S4, based on which $\Delta[BVOC]$ is calculated to compared with experimentally measured consumed BVOC at steady state. The estimation of [OH] is based on a number of assumptions and uncertain yields adopted and uncertainty associated with the calculated [OH] is up to a factor of 2. Given the fact that [OH] is with high uncertainty, hence calculations of $\Delta[BVOC]$ are conducted to both include and exclude [OH] term in eq S4. The comparisons of experimental and calculated fractions of BVOC reacted are shown in Figure 1.

Estimation of SOA with a simplified empirical model

A simplified empirical model was developed to simulate the SOA produced in the chamber runs. The reactions in the chamber system are simplified and the chemistry is represented as:

$$BVOC + O_3 \rightarrow Y_{VPRD}\ PROD + Y_{SOA}\ CND1 + Y_{OH}\ OH + \text{(ignored products)} \qquad (k_{O3})\ \text{(S5)}$$

$$BVOC + OH \rightarrow Y_{VPRD1}\ PROD + Y_{SOAOH}\ CND1 + \text{(ignored products)} \qquad (k_{OH})\ \text{(S6)}$$

$$PROD + OH \rightarrow \text{(ignored products)} \qquad (k_{PROD-OH})\ \text{(S7)}$$

$$O_3 + WALL \rightarrow \text{(wall loss)} \qquad (k_{O3\text{-wall}})\ \text{(S8)}$$

$$CND1 + PMmass \rightarrow PM\text{-}CND1 + \text{mass factor PMmass} \qquad (k_{cnd})\ \text{(S9)}$$

$$PM\text{-}CND1 \rightarrow CND1 + \text{mass factor PMmass} \qquad (k_{evap})\ \text{(S10)}$$

$$PMmass \rightarrow \text{(wall loss)} \qquad (k_{PM\text{-}wall})\ \text{(S11)}$$

where CND1 is the gas-phase condensable product, represented as primary products either from O_3 or OH reactions; Y_{SOA} and Y_{SOAOH} are the molar yields of these products; Y_{OH} is the molar OH yield in the O_3 reaction (Table S2); PROD is the reactive volatile product produced, Y_{VPRD} and Y_{VPRD1} are the yields of such product in the OH and O_3 reactions; $k_{O3\text{-wall}}$ is the O_3 wall loss rate, set at 6.67×10^{-6} min^{-1} based on measurements of O_3 loss rates in the reactor; PM-CND1 is the condensed phase condensable product; PMmass is the mass of SOA formed per unit volume (same as PM-CND1 in these calculations except in mass units); "mass factor" is the conversion factor from molar PM-CND1 to PMmass (depends on molecular weight); k_{cnd} is the rate constant used for condensation of CND1 onto the particle phase (set to an arbitrary value that is sufficiently high so that calculated PMmass is insensitive to this value); k_{evap} is the rate constant for evaporation of the condensable product from the particle phase, which is given as k_{cnd} / $K_{p,CND1}$, where $K_{p,CND1}$ is the partitioning coefficient in Equation (S2); and $k_{PM\text{-wall}}$ is the particle wall loss rate, set at 1.33×10^{-3} min^{-1}, based on measurements of particle loss rates in the reactor.

Y_{SOA} and Y_{SOAOH} used in the simplified model are derived from Odum one-hypothetical yield model in Figure S3. However, the mass yields from Odum yield model in this study are overall SOA yields from both O_3 and OH reactions together. In order to incorporate the derived single overall SOA yields into the model as Y_{SOA} and Y_{SOAOH}, for each BVOC, up to four simulation scenarios were conducted. Simulation "1" through "3" used maximum reactive product yields ($Y_{VPRD} = Y_{VPRD1} = 1$), calculation "4" used zero reactive product yields ($Y_{VPRD} = Y_{VPRD1} = 0$), and simulations "2" and "3" varied the SOA yields from the OH and O_3 reactions. For α-pinene and linalool, simulations "2" assumed zero CND1 (SOA precursor) yields from the O_3 reactions, and simulations "3" assumed zero CND1 from the OH reaction, and the yield from the other reactions increased so that the overall yield, weighed by the fraction reacting with OH and O_3 at the experiments with maximum SOA, would be the same as the α values derived using Odum one-product yield model in Figure S3. For limonene the overall SOA yield is too high to set either one to zero and vary the other and still keep the same overall yield as experiments without the yield exceeding 1.0, so simulation "2" just simulated the effect

of assuming no SOA from OH reactions. The specific parameters of different simulations are listed in Table S1.

Table S1. Parameters for different model simulation scenarios

Parameter	Simulation1	Simulation2	Simulation3	Simulation4
α-Pinene				
Y_{VPRD}	1	1	1	0
Y_{VPRD1}	1	1	1	0
Y_{SOA}	19%	30%	0%	19%
Y_{SOAOH}	19%	0%	52%	19%
Limonene				
Y_{VPRD}	1	1		0
Y_{VPRD1}	1	1		0
Y_{SOA}	72%	72%		72%
Y_{SOAOH}	72%	0%		72%
Linalool				
Y_{VPRD}	1	1	1	0
Y_{VPRD1}	1	1	1	0
Y_{SOA}	2.8%	4.2%	0%	2.8%
Y_{SOAOH}	2.8%	0%	8.8%	2.8%

Table S2. Reaction rate constants and parameters

Compound	k_{O3}[a] $(ppb^{-1}s^{-1})$	k_{OH}[a] $(ppb^{-1}s^{-1})$	y_{OH}[b]	$k_{PROD-OH}$ $(ppb^{-1}s^{-1})$	MW^{*}_{CND1}
α-Pinene	$2.1×10^{-6}$	1.32	0.77±0.10	0.98[c]	184.24
Linalool	$1.1×10^{-5}$	3.98	0.66±0.10	1.49[d]	204.27
Limonene	$4.9×10^{-6}$	4.23	0.67±0.10	2.55[e]	184.24

MW^{*}_{CND1} : Molecular weight of condensable products(use BVOC+3O for calculation)
[a] Ref 5 and references therein.
[b] Ref 6.
[c] Ref 7, PROD:use pinonaldehyde for calculation.
[d] Ref 8,PROD:use 2-ethenyl-2-methyl-5-hydroxyterahydrofuran and
  5-ethenyldihydro-5-methyl-2(3H)-furanone weighted for calculation.
[e] Ref 9, PROD:use limonaldehyde and keto-limonene weighted for calculation.

Fractions of OH+PROD reaction for limonene reactions simulations

The fraction of OH reacted with PROD (primary reactive volatile product produced) is defined as the portion of OH radicals reacted with PROD among all OH reactions occurred, which in this empirical modeling include OH reactions with BVOC and PROD:

$$f_{OH+PROD} = \frac{(OH + PROD)}{(OH + PROD) + (OH + BVOC)} \qquad\qquad (S12)$$

In Figure S4, curves for simulation 1 and 2 are the same, while simulation 4 assumed $Y_{VPRD} = Y_{VPRD1} = 0$, hence the resulting zero-fraction under simulation scenario 4.
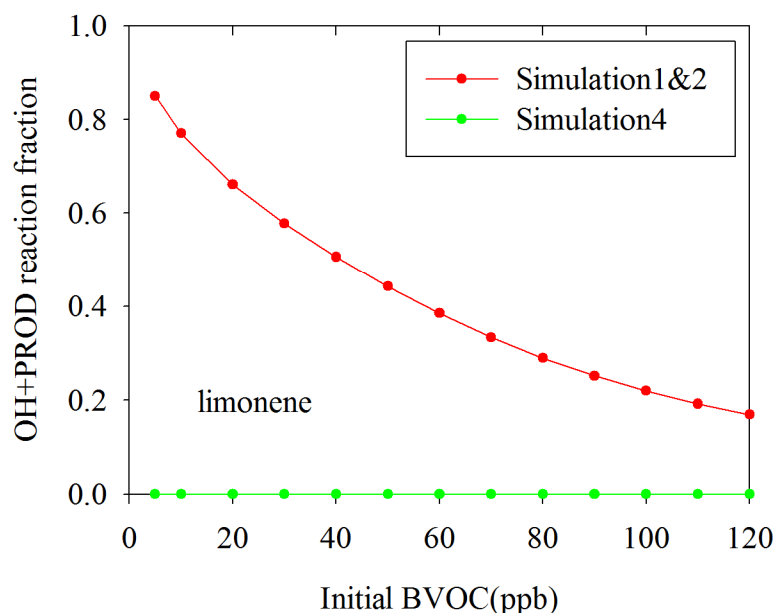

Figure S4. Fractions of OH reactions with primary products at different initial limonene concentrations.

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