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# Secondary organic aerosol formation from ozone reactions with single terpenoids and terpenoid mixtures

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#### ABSTRACT

Ozone reacts with indoor-emitted terpenoids to form secondary organic aerosol (SOA). Most SOA research has focused on ozone reactions with single terpenoids or with consumer products, and this paper reports the results from an investigation of SOA formation from ozone reactions with both single terpenoids and mixtures of p-limonene,  $\alpha$ -pinene, and  $\alpha$ -terpineol. Transient experiments were conducted at low (25 ppb) and high (100 ppb) initial concentrations of ozone. The three terpenoids were tested singly and in combinations in a manner that controlled for their different reaction rates with ozone. The SOA formation was assessed by examining the evolution in time of the resulting number sizedistributions and estimates of the mass concentrations. The results suggest that at higher ozone and terpenoid concentrations, SOA number formation follows a linear trend as a function of the initial rate of reaction. This finding was valid for both single terpenoids and mixtures. Generally speaking, higher ozone and terpenoid concentrations also led to larger geometric mean diameters and smaller geometric standard deviations of fitted lognormal distributions of the formed SOA. By assuming a density, mass concentrations were also assessed and did not follow as consistent of a trend. At low ozone concentration conditions, reactions with only p-limonene yielded the largest number concentrations of any experiment, even more than experiments with mixtures containing p-limonene and much higher overall terpenoid concentrations. This finding was not seen for high ozone concentrations. These experiments demonstrate quantifiable trends for SOA forming reactions of ozone and mixtures, and this work provides a framework for expanding these results to more complex mixtures and consumer products.

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#### 1. Introduction

Ozone  $(O_3)$  is common indoors and drives most indoor chemistry. Indoor sources of ozone are either due to outdoor-to-indoor transport of ozone-laden air (Sabersky et al., 1973; Weschler, 2000) or indoor emission from devices such as portable ion generators (Niu et al., 2001; Tung et al., 2005; Britigan et al., 2006; Waring et al., 2008; Waring and Siegel, in press) or office equipment (Lee et al., 2001). One of the more important types of indoor ozone gas-phase reactions are those with terpenoids. Terpenoids are often present indoors due to their emission from consumer products such as air fresheners, cleaning agents, and perfumes (Nazaroff and Weschler, 2004; Singer et al., 2006; Corsi et al., 2007) or wood products (Baumann et al., 1999; Saarela, 1999). The most common indoor

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terpenoids are the monoterpenes of p-limonene and  $\alpha$ -pinene (Brown et al., 1994). Also,  $\alpha$ -terpineol, a monoterpene alcohol, is emitted indoors as component of cleaners and pine oil (Nazaroff and Weschler, 2004). These terpenoids are often present at sufficient concentrations indoors that their ozone reaction rates compete with loss due to air exchange (Weschler and Shields, 1996; Wells, 2005).

Ozone/terpenoid reactions lead to the stable products of secondary organic aerosol (SOA), aldehydes, and carboxylic acids (Weschler and Shields, 1999; Kamens et al., 1999; Leungsakul et al., 2005). These reactions also yield unstable intermediates, such as hydroxyl radicals (OH), alkylperoxy radicals (RO<sub>2</sub>), and Criegee biradicals (Kamens et al., 1999; Leungsakul et al., 2005). The SOA formed is in the ultrafine (<0.1  $\mu$ m) and lower fine (0.1–2.5  $\mu$ m) particle size ranges, and it is composed of low vapor pressure, high molecular weight products. SOA formation occurs by both nucleation and partitioning mechanisms. Nucleation is responsible for SOA number formation, and its rate is hypothesized to be proportional to the formation of large secondary ozonides and hydroperoxides from





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stabilized Criegee intermediates (SCI) (Ziemann, 2003). Partitioning is primarily responsible for SOA mass formation, and the fraction of the products that partitions to the particle-phase increases with the mass of organic matter in the air (Odum et al., 1996). Most nucleation occurs near the commencement of the ozone/terpenoid reactions, while partitioning occurs during nearly the entire time of reaction.

Previous research on indoor SOA formation has focused either on ozone reactions with single terpenoids or consumer products. Weschler and Shields (1999) first showed that ozone reacted with D-limonene,  $\alpha$ -terpinene, or an  $\alpha$ -pinene-based cleaner to form SOA in an office setting. Other research has subsequently investigated SOA formation with single terpenoids at concentrations typical of indoor environments, with most of it focusing on ozone/p-limonene reactions (Wainman et al., 2000; Rohr et al., 2003; Weschler and Shields, 2003; Sarwar and Corsi, 2007; Vartiainen et al., 2006; Alshawa et al., 2007; Zuraimi et al., 2007; Langer et al., 2008; Fadeyi et al., 2009; Chen and Hopke, 2010) or  $ozone/\alpha$ pinene reactions (Rohr et al., 2003; Sarwar et al., 2003; Chen and Hopke, 2009). Regarding experiments with consumer products, SOA formation occurs when ozone reacts with lemon- and pinescented cleaners, air fresheners, and perfumes, both in laboratory chambers or rooms (Wainman et al., 2000; Sarwar et al., 2004; Destaillats et al., 2006; Singer et al., 2006; Corsi et al., 2007; Coleman et al., 2008; Lamorena and Lee, 2008; Waring et al., 2008) and in real indoor environments (Long et al., 2000; Hubbard et al., 2005; Waring and Siegel, in press).

Despite this body of research on SOA formation, there has been limited research on ozone reactions with single versus mixtures of terpenoids. In the only investigation of controlled mixtures that we know of, Li et al. (2007) merged separate kinetic models for ozone/p-limonene and ozone/ $\alpha$ -pinene reactions and closely simulated the formation and timing for SOA mass concentrations in an outdoor smog chamber. Investigations of SOA formation due to ozone reactions with single versus mixtures of terpenoids are important because they help bridge the gap between research with single terpenoids and with consumer products, allowing further insight into indoor oxidative chemistry. To that end, this paper reports the results from a set of experiments investigating the SOA formed from ozone reactions with single terpenoids and mixtures of the terpenoids of p-limonene,  $\alpha$ -pinene, and  $\alpha$ -terpineol.

#### 2. Methodology

Experiments were performed in a 90 L Teflon-film reaction chamber (approximate dimensions of 0.3 m  $\times$  0.3 m  $\times$  1 m high) that was operated as a semi-batch reactor with a volume that decreased as samples were withdrawn. Diluent air at approximately 24 °C was introduced to the chamber and was passed through anhydrous CaSO<sub>4</sub> and molecular sieves to remove both moisture and organic contaminants. Low concentrations of 0.7 ppb NO and 1.3 ppb NO<sub>2</sub> were measured in this air stream (Thermo Environmental model 42-C), and their impact on ozone chemistry was neglected in our analysis. The filling system was equipped with a heated syringe injection port facilitating the introduction of liquid or gaseous reactants into the chambers with the flowing air stream, at amounts that would yield desired initial terpenoid concentrations. Ozone was introduced via a separate injection port at the opposite end of the reactor. Ozone was produced by photolyzing air with a mercury pen lamp in a separate Teflon-film ozone chamber. Ozone concentrations in the ozone chamber were determined with a UV photometric ozone analyzer (Thermo Environmental model 49-C). Aliquots of this ozone/air mixture were added to the reaction chamber using a gas-tight syringe, at amounts that would yield the desired initial ozone concentration in the 90 L reaction chamber, which was periodically verified. Particle samples were monitored continuously with an MSP Corporation M1000XP-A Wide-Range Particle Spectrometer (WPS<sup>TM</sup>) operated in the WPS mode, providing detection over the particle size range of 10–500 nm in 40 size bins (SMS portion), and 350–10,000 nm in 24 bins (LPS portion), every 2 min. Particles were not detected by the LPS portion of the device. The WPS was factory calibrated within six months of all experiments and had a flow rate of 1.0 L min<sup>-1</sup> in the WPS mode, according to the manufacturer.

Thirteen experiments were conducted that monitored the timeand size-resolved formation of SOA due to ozone reactions with single terpenoids and mixtures of terpenoids. Known amounts of a single terpenoid or a mixture of terpenoids were introduced via the heated syringe injection port with diluent air into the chamber. Once the chamber was filled, it was then connected to the particle counter. After one size-resolved particle count was taken (2 min) to establish the background particle concentration, a known amount of ozone was introduced into the chamber and 24 more particle counts were taken (48 min), for a total count time of 50 min. Number and mass concentrations are reported. Number concentrations from the WPS were converted to mass concentrations by multiplying the summed volume of each of the 40 bins by an assumed particle density of 1 g cm<sup>-3</sup>. Particle volume was estimated assuming that the formed particles were spherical, which is appropriate for liquid-phase SOA. Between all experiments, reaction chambers were cleaned by first ozonating them at high concentrations (>1 ppm) and then flushing at least six times. Analysis of both the treated, compressed air and the cleaned chamber by GC/MS revealed that any contaminants were below the part-per-trillion range.

# 3. Results and discussion

# 3.1. Initial concentrations in experiments

Table 1 lists the initial reactant concentrations for Experiments 1–13. Initial reactant concentrations were chosen to yield equivalent (or integer-factor) initial first-order loss rates of ozone with any terpenoid in the experiment. The initial first-order loss rate for ozone is the product of the reaction rate constant for ozone with terpenoid *j*,  $k_{O3/i}$  (ppb<sup>-1</sup> h<sup>-1</sup>), and the initial terpenoid j concentration, [terp<sub>i</sub>]<sub>i</sub> (ppb). Performing mixture experiments with equivalent  $k_{03/i}$ [terp<sub>i</sub>]<sub>i</sub>  $(h^{-1})$  is an effort to ensure that the reaction rates of ozone with each terpenoid would be identical at the start of each experiment. The [terp<sub>*i*</sub>]<sub>*i*</sub> for each terpenoid are referred to as [d-lim]<sub>*i*</sub> for D-limonene,  $[\alpha$ -pin]<sub>i</sub> for  $\alpha$ -pinene, and  $[\alpha$ -terp]<sub>i</sub> for  $\alpha$ -terpineol. The reaction rate constant for ozone reactions with p-limonene is 0.018 ppb<sup>-1</sup> h<sup>-1</sup>,  $\alpha$ pinene is 0.0076 ppb<sup>-1</sup> h<sup>-1</sup> (Atkinson et al., 1992), and  $\alpha$ -terpineol is  $0.027 \text{ ppb}^{-1} \text{ h}^{-1}$  (Wells, 2005). Thus, for example, reactions of ozone with  $[d-lim]_i = 50$  ppb,  $[\alpha-pin]_i = 118$  ppb, and  $[\alpha-terp]_i = 33$  ppb each yield  $k_{03/i}$  [terp<sub>i</sub>]<sub>i</sub> = 0.9 h<sup>-</sup>

Experiments 1–9 were conducted with various terpenoid concentrations and an initial ozone concentration,  $[O_3]_i$  (ppb), of 25 ppb. Experiments 10–13 were conducted with identical  $[terp_j]_i$  to Experiments 1, 3, 5, and 7, respectively, but with  $[O_3]_i = 100$  ppb. The experiments with  $[O_3]_i = 25$  ppb represent concentrations found indoors due to outdoor-to-indoor transport (Weschler, 2000) or from indoor sources such as office equipment (Britigan et al., 2006) or portable ion generators (Alshawa et al., 2007; Waring and Siegel, in press). The  $[O_3]_i = 100$  ppb are realistic in buildings with high air exchange rates in polluted urban environments (Weschler, 2000) or due to ozone generator use (e.g. Weschler and Shields, 1999; Hubbard et al., 2005). Terpenoid concentrations are in the lower range resulting from indoor use (Singer et al., 2006). Other ranges of reactants are possible indoors, and future work will

#### Table 1

For Experiments 1–13, initial concentrations of ozone  $([O_3]_i)$ , *p*-limonene  $([d-lim]_i)$ ,  $\alpha$ -terpineol  $([\alpha-terp]_i)$ , and  $\alpha$ -pinene  $([\alpha-pin]_i)$ , as well as the sum of the products of the rate constant for ozone reactions with each terpenoid *j* and the initial terpenoid *j* concentration  $(\sum_{i=1}^{n} (k_{O3/j} [terp_j]_i))$ . Also shown for the first peak and final SOA counts are the number (N), geometric mean diameter (GMD), and geometric standard deviation (GSD) of the size distributions and the resulting mass concentrations.

Exp.	Initial reactant concentrations					First peak ( $t = 10-16 \text{ min}$ )				Final ( $t = 50 \text{ min}$ )			
	[O <sub>3</sub> ] <sub>i</sub> (ppb)	[d-lim] <sub>i</sub> (ppb)	[α-terp] <sub>i</sub> (ppb)	[α-pin] <sub>i</sub> (ppb)	$\frac{\sum (k_{O3/j}[\text{terp}_j]_i)}{(h^{-1})}$	N (#/cm <sup>3</sup> )	GMD (nm)	GSD (-)	Mass (µg m <sup>-3</sup> )	N (#/cm <sup>3</sup> )	GMD (nm)	GSD (-)	Mass (µg m <sup>-3</sup> )
1	25	50	0	0	0.9	13,628	68.8	1.46	3.6	7430	94.5	1.33	4.2
2	25	0	0	118	0.9	4044	55.1	1.60	0.81	1985	115	1.34	2.1
3	25	0	33	0	0.9	547	48.8	1.65	0.071	486	97.2	1.44	0.33
4	25	0	33	118	1.8	9232	113	1.44	9.8	4406	129	1.39	6.6
5	25	50	33	0	1.8	8567	87.4	1.46	4.3	5991	104	1.35	4.6
6	25	0	67	0	1.8	7257	99.1	1.50	5.2	5626	124	1.39	7.2
7	25	50	33	118	2.7	12,854	91.1	1.45	7.1	7578	113	1.36	7.7
8	25	0	67	118	2.7	12,693	91.8	1.56	8.1	7982	124	1.38	11
9	25	50	67	0	2.7	11,284	98.6	1.45	8.1	9064	112	1.37	8.9
10	100	0	33	0	0.9	20,857	114	1.38	21	21,014	134	1.35	34
11	100	50	0	0	0.9	18,827	52.0	1.39	2.0	17,699	63.8	1.38	3.7
12	100	50	33	0	1.8	39,022	73.8	1.46	12	30,383	114	1.34	31
13	100	50	33	118	2.7	50,152	99.9	1.41	37	40,787	146	1.35	83

explore larger terpenoid concentrations that may result from consumer product use.

# 3.2. First peak number and final number and mass concentrations

For the first peak and final count of the measured SOA for Experiments 1–13, Table 1 also lists the number concentrations, the associated unimodal lognormal parameters for the number sizedistribution (Seinfeld and Pandis, 1998), and the mass concentrations calculated using the assumed density. Experiments are first grouped by  $[O_3]_i$  and then by their  $\sum (k_{O3/i} [terp_i]_i)$  (h<sup>-1</sup>), which is the total initial first-order loss rate for ozone that includes the summed effects of all terpenoids present in the chamber. For the lognormal parameters, the geometric mean diameter (GMD) and geometric standard deviation (GSD) were fit to minimize the sum of the squared difference between measured and modeled distributions. More accurate fits could be obtained by using two or three modes, as in Coleman et al. (2008). However, we chose to use the unimodal distribution since it is easier to identify trends in the formed size-distributions (see Section 3.5). To establish the background particle concentration for each experiment, one particle count was taken prior to ozone introduction. For all experiments. the maximum measured background particle number concentration was 51  $\#/cm^3$ .

Ozone reactions with terpenoids yield OH, which can react with any terpenoids still present or other reaction products (Atkinson et al., 1992; Weschler and Shields, 1996). Our experiments did not scavenge formed OH, and our results exhibit the combined effects of terpenoid oxidation via both ozone and formed OH, as is common in a real indoor environment. The chemistry due to OH is expected to increase the mass of SOA formed but not the nucleation of SOA (Colville and Griffin, 2004). Though the contribution to formed SOA of OH versus ozone has been estimated with kinetic models for  $\alpha$ -pinene (e.g. Chen and Hopke, 2009) and p-limonene (e.g. Chen and Hopke, 2010), we have not made similar estimations due to the potential differences arising from mixture chemistry.

# 3.3. Effect of decreasing volume of the reaction chamber

Since the chamber was operated as a semi-batch reactor, the chamber volume steadily decreased as samples were withdrawn from the initial 90 to 40 L at the end of each 50 min experiment. For a semi-batch reactor, the change in the SOA mass concentration,  $C_{\text{SOA}}$  (µg m<sup>-3</sup>), with time, *t* (h), is as shown in Eq. (1):

$$\frac{\mathrm{d}C_{\mathrm{SOA}}}{\mathrm{d}t} = r_{\mathrm{SOA}} - \left(v_d \frac{A}{V} - \frac{Q}{V}\right) C_{\mathrm{SOA}} \tag{1}$$

where  $r_{SOA}$  (µg m<sup>-3</sup> h) is the rate of formation of SOA due to the ozone/terpenoid reactions;  $v_d$  (m h<sup>-1</sup>) is the deposition velocity of SOA to the chamber surfaces; A (m<sup>2</sup>) is the chamber surface area; Q (m<sup>3</sup> h<sup>-1</sup>) is the flow rate of air out of the chamber; and V (m<sup>3</sup>) is the chamber volume, which is decreasing according to V = 0.09-0.06t. The number balance for  $C_{SOA}$  (i.e., units of #/cm<sup>3</sup>) would be the same as in Eq. (1), except there would be an extra loss term for coagulation effects.

Eq. (1) shows that deposition to chamber surfaces will decrease  $C_{\text{SOA}}$  while the flow rate out of the reactor will increase  $C_{\text{SOA}}$ , and the magnitude of both of these effects will increase with time as the volume of the chamber decreases. We estimated the magnitude of  $v_d \cdot A/V$  with the model of Lai and Nazaroff (2000) and Eq. (1) from Coleman et al. (2008). The model inputs are the chamber surface area and volume and the friction velocity of the air,  $u^*$  (cm s<sup>-1</sup>), which is an empirical parameter that describes the level of turbulence intensity near a surface and has typical values ranging from 0.3 to 3 cm s<sup>-1</sup> indoors.  $v_d$  is particle size-dependent, and for the peak and final size-distributions, their corresponding volumes and surface area, and the typical range of  $u^*$ , we estimated a range of integrated  $v_{d} \cdot A/V$  of 0.023–0.59 h<sup>-1</sup> for peak and 0.042–0.75 h<sup>-1</sup> for final distributions. In the term Q/V, the Q is the flow rate of the WPS (i.e., 1 L min<sup>-1</sup> = 0.06 m<sup>3</sup> h<sup>-1</sup>). So at the time of the peak and final distributions, Q/V = 0.77 and 1.5 h<sup>-1</sup>, respectively. Thus, the difference in the two terms,  $(v_d \cdot A/V - Q/V)$  ranges from -0.75 to -0.18 h<sup>-1</sup> and -1.5 to -0.75 h<sup>-1</sup> for the peak and final distributions, respectively, and the net effect would increase  $C_{SOA}$ . We have not corrected our SOA concentrations for these effects given the large uncertainty associated with the  $v_d \cdot A/V$  term, which is almost as large as the net effect of  $(v_d \cdot A/V - Q/V)$ . Neglecting surface reactions to the Teflon chamber walls and terpenoid adsorption, the decreasing volume is not expected to affect SOA concentrations in other ways.

# 3.4. Temporal development of the number concentration and sizedistribution

Additional insight into the potential effect of the decreasing volume on the SOA size-distribution can be gleaned with Figs. 1 and 2. Fig. 1 displays the temporal development of the total number concentrations for Experiments 1, 3, 5, and 7, and 10–13, which are four pairs of experiments with identical  $[terp_i]_i$  but at low



Fig. 1. Temporal development of the SOA number concentration for 8 experiments. Ozone was injected at 2 min. Italicized numbers on the plot correspond to the experiment number. Initial experimental conditions are listed in the legend.

 $[O_3]_i = 25$  ppb and high  $[O_3]_i = 100$  ppb. The initial detection of the SOA formation and the time of peak number formation depended on the initial reaction rate for ozone and any terpenoids present, which is  $[O_3]_i \sum (k_{O3/j}[\text{terp}_j]_i)$  (ppb/h). For Experiments 11–13 with higher values of  $[O_3]_i \sum (k_{O3/j}[\text{terp}_j]_i)$ , SOA formation was detected 6 min after ozone was introduced into the chamber, but for Experiments 1, 3, 5, 7, and 10 with lower values of  $[O_3]_i \sum (k_{O3/j}[\text{terp}_j]_i)$ , SOA formation was detected 8–14 min after ozone injection.

This detection time is a function of the time-scales of two processes: the SOA nucleation and the mixing of the air between the ozone injection and particle counting ports (which were at the top and bottom of the approximately-rectangular chamber). These two processes occur in parallel, so the detection time for Experiments 11–13 implies that the mixing time in the chamber may be less than 6 min. For all experiments, the first peak number concentration occurred 10–16 min after the ozone injection, after which particle number concentrations eventually converged to a near-constant value. For Experiments 1–9 with low  $[O_3]_i = 25$  ppb, the first peak concentration was the highest observed particle number concentration. For Experiments 10–13 with high  $[O_3]_i = 100$  ppb, the first peak was not always the highest observed number concentration.

Fig. 1 shows that the SOA number concentrations were nearconstant by the end of each 50 min experiment. When coupled with the theoretical analysis in Section 3.3, this stability in the sizedistributions implies that the gain in  $C_{SOA}$  from the decreasing volume and the loss in C<sub>SOA</sub> due to any wall deposition may have nullified each other, thus not substantially affecting the sizedistributions over the time scale for most experiments. However, Fig. 1 shows that experiments with high  $[O_3]_i = 100$  ppb did yield enough particle mass that deposition slightly reduced the number concentration over time, but this effect is minimal and does not substantially change the trends discussed in the next section. Fig. 2 displays the temporal development of the SOA size-resolved number distribution for minutes 12-50 of Experiment 10, which had initial concentrations of  $[\alpha$ -terp]<sub>i</sub> = 33 ppb and  $[O_3]_i = 100$  ppb. For Experiment 10, SOA formation was detected at the particle count taken at minute 10. From minutes 12-24, shown in Fig. 2(a), each successive count displays an increasing size-distribution and increasing geometric mean diameter until minute 20. Each successive count in Fig. 2(b) shows the size-distribution stabilizing around the final size-distribution, shown for minutes 44-50 in Fig. 2(c).

## 3.5. SOA formation trends from single terpenoids and mixtures

For the first peak and final count, Fig. 3(a-h) displays SOA number, GMD and GSD of the number size-distributions, and mass concentrations versus  $[O_3]_i \sum (k_{O3/j} [terp_j]_i)$  for all experiments thus plotting the results as a function of the initial reaction rate for ozone and the terpenoids in the chamber. Hollow white circles signify Experiments 1–9, and gray circles signify Experiments 10–13. Linear fits were applied to all results, and these were forced



**Fig. 2.** Temporal development of the SOA number size-distribution for Experiment 10 with  $[\alpha$ -terp]<sub>i</sub> = 33 ppb and  $[O_3]_i = 100$  ppb (total time = 50 min). SOA size-distributions are displayed in (a) for minutes 12–24, (b) for minutes 28–40, and (c) for minutes 44–50.



**Fig. 3.** For Experiments 1–13, characteristics of formed SOA as a function of  $[O_3]_i \sum (k_{O3/j}[terp_j]_i)$ , where the *y*-axes show (a) first peak and (b) final number concentrations, (c) first peak and (d) final geometric mean diameters (GMD) of the number size-distributions, (e) first peak and (f) final geometric standard deviation (GSD) of the number size-distributions, and (g) first peak and (h) final mass concentrations. Italicized numbers correspond to experiment number. Light gray circles are for low initial ozone experiments, and dark gray circles are for high initial ozone experiments.

through zero for the first peak and final concentrations of SOA number and mass. Fig. 3(a, b) shows that first peak and final number concentrations are reasonably predicted with knowledge of  $[O_3]_i \sum (k_{O3/j} [terp_j]_i)$  for both single and mixtures of terpenoids. Peak number has a steeper slope than final number, with the linear fits being y = 0.020x ( $R^2 = 0.94$ ) and y = 0.016x ( $R^2 = 0.93$ ), respectively, which reflects the tendency of formed SOA particles to coagulate after nucleation. (Note that fits are for the number concentrations divided by 10,000, as in Fig. 3.)

Plotting the GMD and GSD of the size-distributions for peak and final number formation as a function of  $[O_3]_i \sum (k_{O3/j}[\text{terp}_j]_i)$  reveals trends as well. Though Fig. 3(c, d) shows much scatter, the GMDs do tend to increase as  $[O_3]_i \sum (k_{O3/j}[\text{terp}_j]_i)$  increases, for both peak and final number formation. Moreover, the slope of the GMDs for final number is steeper than for peak number because partitioning of products over time shifts the mean diameter positively. In Fig. 3(e, f), the fits to the GSDs of the peak and final size-distributions have negative slopes; thus the GSDs tend to become smaller as  $[O_3]_i \sum (k_{O3/j}[\text{terp}_j]_i)$  increases. The GSDs for the final size-distributions in Fig. 3(f) show a converging of the GSDs around a common value of between 1.3 and 1.4. This potential finding

warrants more attention in future work, since it implies that reactant concentrations and types of terpenoids may not impact the final GSD of the size-distribution in a meaningful way.

From a mass perspective, all experiments exhibited a steady concentration by the end of the sampling time, except for Experiment 13, which was still slightly increasing. Relative to peak formation, the SOA mass increased at the end of the experiments (though the number decreased), which reflects the tendency of SOA formation to occur by partitioning of products to existing particles following the increase of particle number due to nucleation and the subsequent much smaller decrease in number due to coagulation. Peak mass has a less steep slope than final mass, with the linear fits being y = 0.12x ( $R^2 = 0.73$ ) and y = 0.24x ( $R^2 = 0.80$ ), respectively. As shown in Fig. 3(g, h), peak and final mass concentrations are less well-predicted as a function of  $[O_3]_i \sum (k_{O3/j}[terp_j]_i)$  than number concentrations. Additionally, the mass formation is better predicted by  $[O_3]_i \sum (k_{O3/j}[terp_j]_i)$  for Experiments 1–9 with  $[O_3]_i = 25$  ppb than Experiments 10–13 with  $[O_3]_i = 100$  ppb.

Other researchers have noted similar relationships among initial reactant concentrations and SOA number formation. Langer et al. (2008) plotted maximum SOA number concentration as a function of the product of the initial ozone and D-limonene concentrations, and results show linear trends (Fig. 4 in their paper). Also, Chen and Hopke (2009) plotted the particle formation rate as a function of the product of the initial ozone and  $\alpha$ -pinene concentrations, and results show a linear trend for the lower range of reactants (Fig. 6 in their paper). Our results are novel in that they illustrate that number formation relationships hold not only for ozone reactions with single terpenoids but *also* with mixtures, so long as the reaction rate constants are taken into account with the independent variable, which was  $[O_3]_i \sum (k_{03/j}[terp_j]_i)$  in our case. This is an important finding, as it implies that the nucleation rate may be at least moderately independent of the particular terpenoids present, at least for the studied terpenoids of D-limonene,  $\alpha$ -pinene, and  $\alpha$ -terpineol in our experiments with larger initial reactant concentrations.

Though for values of  $[O_3]_i \sum (k_{O3/i} [terp_i]_i) \ge 45 (ppb/h)$  first peak formation followed a near linear trend as a function  $[O_3]_i \sum (k_{O3/i} [terp_i]_i)$ , results from Experiments 1–3 were less well predicted by this relationship. (The R<sup>2</sup> for the linear fit increases to 0.98 if the first three experiments are excluded.) Experiments 1-3 illustrate differences in SOA formation among ozone reactions with single terpenoids of D-limonene,  $\alpha$ -pinene, and  $\alpha$ -terpineol at equivalent  $k_{O3/i}$  [terp<sub>i</sub>]<sub>i</sub> with low  $[O_3]_i = 25$  ppb. Experiment 1 with  $[d-lim]_i = 50$  ppb yielded a peak number concentration one order of magnitude larger than Experiment 2 with  $[\alpha$ -pin]<sub>i</sub> = 118 ppb and two orders of magnitude larger than Experiments 3 with  $[\alpha$ -terp]<sub>i</sub> = 33 ppb. Moreover, for Experiments 1–9 with low  $[O_3]_i = 25$  ppb, Experiment 1 yielded the largest peak total number concentration, higher than any of the other experiments with single terpenoids or mixtures, though Experiments 4–6 had two times the total  $\sum (k_{O3/i}[terp_i]_i)$  and Experiments 7–9 had three times the total  $\sum (k_{03/j} [terp_j]_i)$ . The final number concentrations for Experiment 1 were the third largest observed for the experiments with low  $[O_3]_i = 25$  ppb.

Thus, Experiment 1 results may reflect a large nucleation potential of ozone/p-limonene reaction products at these low ozone conditions of  $[O_3]_i = 25$  ppb and particular terpenoid concentrations. For experiments with  $[d-lim]_i = 50$  ppb, the addition of one of the other terpenoids appears to lessen the nucleation potential of the reactants, which is illustrated by the results of Experiments 5, 7, and 9 exhibiting lower peak number formation than Experiment 1. The reason for the large nucleation potential of products of ozone/ D-limonene reactions at low ozone conditions appears to be more complicated than simply that less ozone is available to react with plimonene in a mixture, since the same trend was not observed with Experiment 11, which had equivalent  $[d-lim]_i = 50$  ppb to Experiment 1 but at high  $[O_3]_i = 100$  ppb and yielded peak number formation very near to that predicted by the linear fit. Thus, the ozone-limited reaction with p-limonene yielded a set of byproducts with higher nucleation potential than those that occur with ozonelimiting or-excess reactions with mixtures of terpenoids or ozone-excess reactions with p-limonene. In accordance with this observation, Nøjgaard et al. (2007) found that ozone-limiting reactions with D-limonene favored the formation of the secondary ozonides, which could explain the large observed nucleation event during Experiment 1.

However, though the peak and final number formed for Experiment 11 is well-predicted by the linear fit, the mass formed is not. Experiment 11 with  $[d-lim]_i = 50$  ppb and  $[O_3]_i = 100$  ppb has much lower peak and final mass formed than Experiment 10, which had  $[O_3]_i = 100$  ppb and  $[\alpha$ -terp]\_i = 33 ppb, and thus an equivalent  $\sum (k_{O3/j} [\text{terp}_j]_i)$  to Experiment 11. Conversely, the mass predicted by the fit for Experiment 1 falls very near the fitted line, though the number formed is much larger than the number predicted.

This study is the first we know of to examine the SOA formation from ozonolysis of  $\alpha$ -terpineol. Results from Experiments 1–9

reveal SOA formation trends of  $\alpha$ -terpineol reacting with ozone at low concentrations of  $[O_3]_i = 25$  ppb, both as a single terpenoid and as part of a mixture of terpenoids. Ozone reactions with  $\alpha$ -terpineol led to low number and mass formation at low  $\sum (k_{O3/i}[terp_i]_i)$ = 0.9 h<sup>-1</sup>. Experiment 3, with  $[O_3]_i$  = 25 ppb and  $[\alpha$  $terp]_i = 33 ppb$ , yielded the least amount of formed number and mass concentrations of any experiment, an order of magnitude lower than Experiment 2, which had  $[\alpha-pin]_i = 118$  ppb and was very near the linear fit to peak number formation. Also, Table 1 shows experiments grouped by  $\sum (k_{03/i}[\text{terp}_i]_i) = 0.9$ , 1.8, or 2.7 h<sup>-1</sup>, and within each group, the experiments with  $\alpha$ -terpineol comprising a majority of the  $\sum (k_{03/i} [terp_i]_i)$  led to the least amount of peak number SOA formation. However, reactions from these same experiments yielded the largest amounts of final number and mass formation. These findings, coupled with the D-limonene number/mass formation relationships discussed above in the context of Experiments 1 and 11, imply that the nucleation and partitioning potential of products from mixture reactions should not be inferred from each other.

#### 3.6. Extrapolation of results to other environments

As stated above, the air in our chamber system was at approximately 24 °C, was dry, and contained negligible amounts of nitrogen oxides (NO<sub>x</sub>) and background particles. Indoor temperature in the US typically ranges between 18 and 27 °C and relative humidity between approximately 20 to near 60 or 70%, depending on the type of building, set-point temperature, season, and climatic zone. Decreasing temperatures are expected to increase the number of nucleated particles (Lamorena and Lee, 2008), as well as the mass of SOA formed (Leungsakul et al., 2005; Sarwar and Corsi, 2007; Warren et al., 2009) due to an increase in gas-to-particle partitioning resulting from lower product vapor pressures. At typical indoor concentrations of terpenoids, increasing the water vapor concentration decreases both the SOA number and mass formation (Bonn et al., 2002; Leungsakul et al., 2005). The presence of NO and NO<sub>2</sub> reduces the magnitude of SOA formation from terpenoid ozonolysis because it provides an additional loss mechanism for ozone (Nøjgaard et al., 2006). Finally, background particles could increase the mass of formed particles, since the SOA mass yield is a function of the amount of organic material in the air (Odum et al., 1996).

#### 3.7. Application of formation trends to consumer products

Consumer products range from simple to complex mixtures that contain one or many terpenoids. Singer et al. (2006) assessed emissions resulting from the simulated normal use of a pine oil cleaner (POC) and an air freshener (AFR). The POC and AFR each emitted a complex mixture of reactive terpenoids into the air. The POC emitted p-limonene, terpinolene,  $\alpha$ -terpineol, and to a lesser extent three other terpenes and four other terpene alcohols. The AFR emitted dihydromyrcenol, linalool, linalyl acetate, p-limonene, and two other terpenoids at very low concentrations. We used the concentrations measured by Singer et al. (2006) and rate constants from the literature (Atkinson et al., 1992; Grosjean and Grosjean, 1997; Wells, 2005) and estimated that the POC had a  $\sum (k_{03/i}[\text{terp}_i]_i) = 28 \text{ h}^{-1}$  and the AFR a  $\sum (k_{03/i}[\text{terp}_i]_i) = 0.32 \text{ h}^{-1}$ . For their initial ozone concentration of 60 ppb, the POC and AFR had a  $[O_3]_i \sum (k_{O3/i}[terp_i]_i)$  of 1680 and 19.2 ppb  $h^{-1}$ , respectively, and we used our linear fits for peak number and mass concentrations with these  $[O_3]_i \sum (k_{O3/i}[terp_i]_i)$  from Singer et al. (2006). The POC would yield a peak number concentration of 70,000 #/cm<sup>3</sup> and mass concentration of 91  $\mu$ g m<sup>-3</sup>. These values are approximately double the peak measured number concentration and approximately 30%

lower than the peak measured mass concentration. The AFR would yield a peak number concentration of 3800 #/cm<sup>3</sup> and mass concentration of 2.5  $\mu$ g m<sup>-3</sup>, approximately 3.3 times greater and 34% lower than the measured values, respectively. There are a number of reasons that could lead to these discrepancies including profound differences in the number of seed particles present (about 10× greater in Singer et al. (2006)), higher deposition and air exchange loss in Singer et al. (2006), and differences in particle instrumentation, particularly for particles smaller than 150  $\mu$ m and larger than 500  $\mu$ m. Despite these differences, there is some evidence of being able to predict SOA formation from consumer products using  $[O_3]_i \sum (k_{O3/j} [terp_j]_i)$ , although more controlled experiments are warranted to fully explore this hypothesis.

#### 4. Conclusions

We investigated the time- and size-resolved number and mass concentrations of SOA that resulted from ozone reactions with single and mixtures of terpenoids, which included the monoterpenes, D-limonene and  $\alpha$ -pinene, and the monoterpene-alcohol,  $\alpha$ -terpineol. To identify trends, we plotted the peak and final SOA number, GMD, GSD, and mass as a function of  $[O_3]_i \sum (k_{O3/i} [terp_i]_i)$ , which is the initial reaction rate for ozone and the terpenoids. Most generally, our results showed that peak and final number formation can be reasonably well-predicted with linear fits of formation versus  $[O_3]_i \sum (k_{O3/j}[terp_j]_i)$ . Regarding the GMDs, there was much scatter in the plots, but increasing  $[O_3]_i \sum (k_{O3/i}[terp_i]_i)$  led to higher GMDs overall. The GSDs for all experiments exhibited a negative slope, implying that the GSD decreases as  $[O_3]_i \sum (k_{O3/i} [terp_i]_i)$ increases. Additionally, the results showed a tightening of the GSDs around a common value of between 1.3 and 1.4, regardless of the terpenoids or initial concentrations of reactants. Mass formation results were not as well predicted by  $[O_3]_i \sum (k_{O3/i}[terp_i]_i)$ , especially for experiments with higher initial ozone concentrations.

When  $[O_3]_i \sum (k_{O3/i}[terp_i]_i) \ge 45 \text{ ppb/h}$  (i.e., all but the first three experiments), the nucleation rate was largely independent of the types of terpenoids present for both single and mixtures of terpenoids, for our reactants and concentrations. However, two experiments with  $[O_3]_i = 25$  ppb deviated from this trend, those with  $[d-lim]_i = 50$  ppb and  $[\alpha$ -terp]<sub>i</sub> = 33 ppb. Reactions of  $[O_3]_i = 25$  ppb with  $[d-lim]_i = 50$  ppb yielded the largest initial nucleation of all experiments with low ozone, even larger than those with three times the  $\sum (k_{03/i} [\text{terp}_i]_i)$ , and its peak formation was much above the linear fits in Fig. 3(a). On the contrary, high  $[O_3]_i = 100$  ppb and  $[d-lim]_i = 50$  ppb yielded SOA number concentrations very near the linear fits, but the mass formed was lower than the predicted fit. A different trend was observed for  $[O_3]_i = 25$  ppb with  $[\alpha$ -terp]<sub>i</sub> = 33 ppb, which exhibited very low number and mass formation, much less than the predicted fits. However, for experiments when  $[O_3]_i \sum (k_{O3/i}[terp_i]_i) \ge 45 \text{ ppb/h}$ , those experiments with  $\alpha$ -terpineol as the majority of the mixture yielded the largest amounts of final number and mass formation. These findings thus imply that the nucleation and mass formation potential of products may not be related. A limited number of experiments were performed in this study to highlight interesting trend in SOA formation from ozone reactions with mixtures. This work highlights the need for further experiments that investigate SOA formation from ozone reactions with both terpenoid mixtures and  $\alpha$ -terpineol itself.

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