



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

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### ARTICLE INFO

#### Article history:

Received 23 July 2010

Received in revised form

2 May 2011

Accepted 3 May 2011

#### Keywords:

Indoor chemistry

Ozone

D-limonene

$\alpha$ -Pinene

$\alpha$ -Terpineol

Particle formation

### 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 D-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 size-distributions 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 D-limonene yielded the largest number concentrations of any experiment, even more than experiments with mixtures containing D-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<sub>3</sub>) 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

terpenoids are the monoterpenes of D-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/*D*-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 pine-scented cleaners, air fresheners, and perfumes, both in laboratory chambers or rooms (Wainman et al., 2000; Sarwar et al., 2004; Destailats 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/*D*-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 *D*-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 M100XP-A Wide-Range Particle Spectrometer (WPS™) 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 time- and 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*,  $k_{O_3j}$  (ppb<sup>-1</sup> h<sup>-1</sup>), and the initial terpenoid *j* concentration,  $[terp_j]_i$  (ppb). Performing mixture experiments with equivalent  $k_{O_3j}[terp_j]_i$  (h<sup>-1</sup>) is an effort to ensure that the reaction rates of ozone with each terpenoid would be identical at the start of each experiment. The  $[terp_j]_i$  for each terpenoid are referred to as  $[d\text{-lim}]_i$  for *D*-limonene,  $[\alpha\text{-pin}]_i$  for  $\alpha$ -pinene, and  $[\alpha\text{-terp}]_i$  for  $\alpha$ -terpineol. The reaction rate constant for ozone reactions with *D*-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 ppb<sup>-1</sup> h<sup>-1</sup> (Wells, 2005). Thus, for example, reactions of ozone with  $[d\text{-lim}]_i = 50$  ppb,  $[\alpha\text{-pin}]_i = 118$  ppb, and  $[\alpha\text{-terp}]_i = 33$  ppb each yield  $k_{O_3j}[terp_j]_i = 0.9$  h<sup>-1</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

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