



Secondary organic aerosol formation by limonene ozonolysis: Parameterizing multi-generational chemistry in ozone- and residence time-limited indoor environments



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HIGHLIGHTS

- Secondary organic aerosol (SOA) formation due to limonene ozonolysis indoors is parameterized.
- SOA formation is quantified with the aerosol mass fraction, $AMF = \Delta(SOA)/\Delta(\text{limonene})$.
- Limonene is doubly unsaturated, so its AMF varies by a factor of 4 if one or both bonds are ozonated.
- The 'resultant AMF' depends on ozone and limonene concentrations and air exchange rate (AER).
- Framework predicts 'resultant AMF' based on reactants and AER using volatility basis set (VBS).

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ABSTRACT

Terpene ozonolysis reactions can be a strong source of secondary organic aerosol (SOA) indoors. SOA formation can be parameterized and predicted using the aerosol mass fraction (AMF), also known as the SOA yield, which quantifies the mass ratio of generated SOA to oxidized terpene. Limonene is a monoterpene that is at sufficient concentrations such that it reacts meaningfully with ozone indoors. It has two unsaturated bonds, and the magnitude of the limonene ozonolysis AMF varies by a factor of ~4 depending on whether one or both of its unsaturated bonds are ozonated, which depends on whether ozone is in excess compared to limonene as well as the available time for reactions indoors. Hence, this study developed a framework to predict the limonene AMF as a function of the ozone $[O_3]$ and limonene $[\text{lim}]$ concentrations and the air exchange rate (AER, h^{-1}), which is the inverse of the residence time. Empirical AMF data were used to calculate a mixing coefficient, β , that would yield a 'resultant AMF' as the combination of the AMFs due to ozonolysis of one or both of limonene's unsaturated bonds, within the volatility basis set (VBS) organic aerosol framework. Then, β was regressed against predictors of $\log_{10}([O_3]/[\text{lim}])$ and AER ($R^2 = 0.74$). The β increased as the $\log_{10}([O_3]/[\text{lim}])$ increased and as AER decreased, having the physical meaning of driving the resultant AMF to the upper AMF condition when both unsaturated bonds of limonene are ozonated. Modeling demonstrates that using the correct resultant AMF to simulate SOA formation owing to limonene ozonolysis is crucial for accurate indoor prediction.

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1. Introduction

Ambient air quality is impacted by oxidative reactions of the hydroxyl radical (OH), nitrate radical (NO_3), ozone (O_3) with reactive organic gases (ROG) in the atmosphere (Seinfeld and Pandis, 2012). The hydroxyl radical strongly and nitrate radical less

strongly react with saturated and unsaturated ROGs, and ozone reacts with unsaturated ROGs, such as terpenes (Atkinson, 2000, 1990; Atkinson and Arey, 2003). Indoors, oxidative reactions are also key chemistry drivers, and the relative influence of different oxidative reactions may be characterized by comparing indoor lifetimes of different ROGs to residence times of air in buildings. Lifetime analyses indicate that ozone/terpene reactions are among the most important reactions indoors (Waring and Wells, 2015; Weschler, 2000). The residence time of indoor air, τ_{res} (h), is

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governed by the building air exchange rate, λ or AER (h^{-1}), which is the frequency with which indoor air is replaced by outdoor air, and so $\tau_{\text{res}} = \lambda^{-1}$. The AER can include unintentional infiltration and/or intentional mechanical or natural ventilation. For instance, AERs range from 0.2 to 1.5 h^{-1} for infiltration in residences (Murray and Burmaster, 1995) and from 0.26 to 4.2 h^{-1} for mechanical ventilation in offices (Persily and Gorfain, 2008), between the 10th and 90th percentiles of measured distributions.

Ozone typically occurs at indoor/outdoor (I/O) ratios of 0.2–0.7 owing to outdoor-to-indoor transport (Weschler, 2000), though indoor emissions from some appliances are sometimes active (Lee et al., 2001; Waring et al., 2008). Indoor terpenes have I/O ratios higher than unity (Rackes and Waring, 2015, 2013; Weisel et al., 2005), so indoor sources are chief concentration drivers. Wooden building materials emit terpenoids (Uhde and Salthammer, 2007), though stronger indoor emissions correspond to usage of consumer products such as general-purpose cleaners and air fresheners (Nazaroff and Weschler, 2004). About a decade ago, a set of articles (Coleman et al., 2008; Destailats et al., 2006; Singer et al., 2006a, 2006b) characterized cleaner and air freshener emissions and their secondary emission potentials. Singer et al. (2006a, 2006b) conducted 'typical use experiments' with products identified as customer preferred by surveys in a 50 m^3 room at an AER = 1 h^{-1} . Some of the terpenoids (e.g. limonene) reached 1-hr integrated concentrations of 100s of ppb. Also, in the Relationship of Indoor, Outdoor and Personal Air (RIOPA) study, which measured a set of pollutants in 310 occupied homes, 48-hr time-averaged limonene indoor concentrations reached a 99th percentile of ~50 ppb (Weisel et al., 2005).

The oxidation of ROGs initiates reactions that generate myriad semivolatile organic compounds (SVOC) that can partition or nucleate to the condensed phase to form secondary organic aerosol (SOA), which may comprise a large fraction of the global aerosol budget (Kanakidou et al., 2005; Robinson et al., 2007). Over time in the atmosphere, 'fresh' SOA that is composed of early generation products 'ages' due to later generation reactions (e.g. oxidation, oligomerization) that make it more hydrophilic while also lowering the overall aerosol volatility, such that it may be less volatile than much of that from primary organic aerosol (POA) emissions (Donahue et al., 2009; Jimenez et al., 2009). The focus of this article is indoor SOA formation due to terpenoid ozonolysis. Waring (2014) modeled SOA formation over the RIOPA dataset and concluded that SOA comprised a large amount of indoor organic aerosols and $\text{PM}_{2.5}$ (total mass with aerodynamic diameter $\leq 2.5 \mu\text{m}$) for a subset of the results (e.g., more than 47% of indoor organic aerosol and 30% of $\text{PM}_{2.5}$ for 10% of the modeled cases).

Not all of the products generated by ROG oxidation have low enough volatility to partition to generate SOA (Kroll and Seinfeld, 2008). SOA formation strength is most often parameterized with what is known as the aerosol mass fraction (AMF), also called the SOA yield. The AMF is the mass ratio of the SOA formed to reactive organic gas (ROG) consumed (Odum et al., 1996). Because SOA formation is predominately an absorptive phenomenon, AMFs for ROGs span a range of values and increase with organic aerosol (OA) concentrations over 2 to 3 orders of magnitude, depending on the particular ROG oxidized (Griffin et al., 1999; Hoffmann et al., 1997). To recreate this behavior, AMF frameworks lump the numerous products generated by ROG reactions into n -bins of like products, where each lumped product bin has an effective saturation concentration and formation strength associated with it (Donahue et al., 2006; Kanakidou et al., 2005; Odum et al., 1996; Presto and Donahue, 2006).

Fig. 1 displays the structures for some monoterpenes ($\text{C}_{10}\text{H}_{16}$, 136.24 g/mol) and a few monoterpene alcohols ($\text{C}_{10}\text{H}_{18}\text{O}$, 154.25 g/mol) likely to be meaningfully present indoors, based on

measurements of consumer product emissions (Singer et al., 2006a, 2006b). Moreover, the monoterpenes α -pinene, β -pinene, and limonene are routinely measured indoors (Brown et al., 1994; Hodgson and Levin, 2003; Weisel et al., 2005). Table 1 lists ranges of some measured AMFs for ozonolysis of α -pinene, β -pinene, limonene, α -terpineol, and linalool; other than for these ROGs, ozonolysis-dominated AMFs have been measured in limited numbers for the terpenoids in Fig. 1 (e.g. one measured AMF for α -terpinene and terpinolene, from Ng et al., 2006), though fuller sets of photochemical AMF chamber experiments exist for them (Griffin et al., 1999; Hoffmann et al., 1997).

While indoor residence times are short enough that indoor SOA is unlikely to age appreciably as compared to ambient SOA, multi-generational chemistry can still impact SOA formation strength indoors. One reason for this is because alkene ozonolysis reactions produce hydroxyl and other radicals (Atkinson and Arey, 2003; Kroll and Seinfeld, 2008). A second reason is because many of the terpenoids in Fig. 1 are doubly unsaturated and may react with ozone at multiple locations. This article focuses on parameterizing the impact of limonene's multigenerational ozone reactions on SOA formation within the context of indoor environments. Limonene has one methyl-substituted endocyclic double bond in a six-member ring and an exocyclic terminal unsaturation. The endo bond may react 10–50 \times faster than the exo bond (Zhang et al., 2006), so ozone reactions with the endo bond yield most first generation SOA forming products. Following this reaction, the SOA formation strength can increase further for the same reacted limonene mass as the second double bond in first generation products are further ozonated (Ng et al., 2006), likely with ozone in the aerosol phase (Maksymiuk et al., 2009; Zhang et al., 2006).

For limonene, details have emerged regarding its SOA formation owing to first- and second-generation ozonolysis chemistry. Zhang et al. (2006) measured AMFs from limonene ozonolysis at strong ozone excess conditions so that both bonds were fully oxidized. Conversely, Donahue et al. (2007) estimated limonene AMFs at ozone limited conditions so that the endo bond only would be oxidized, using a surrogate compound having a single endo unsaturated bond, limonene ketone ($\text{C}_9\text{H}_{14}\text{O}$, 138.21 g/mol), as also shown in Fig. 1. Over a large OA concentration range of 0.1–1000 $\mu\text{g}/\text{m}^3$, the AMFs for endo only oxidation range from 0.0092 to 0.31 and are a mean (standard deviation) factor of 0.25 (0.0082) lower than those for endo and exo ozonolysis, which range from 0.034 to 1.2. To explore conditions when ozone is neither in excess or limited, Leungsakul et al. (2005), Chen and Hopke (2010), and Youssefi and Waring (2014) measured AMFs for limonene ozonolysis over conditions when ozone and limonene were similar in magnitude, and those AMFs existed between the endo only and endo + exo boundaries.

Besides ozone/limonene ratios, conditions differed among these experiments according to their residence times. Zhang et al. (2006), Leungsakul et al. (2005), and Donahue et al. (2007) conducted batch experiments without air exchange, while Chen and Hopke (2010) conducted steady state flow through experiments at AER = 0.67 h^{-1} , while Youssefi and Waring (2014) conducted transient flow through experiments at AERs = 0.28–0.97 h^{-1} . Since they varied residence times, Youssefi and Waring (2014) observed that the AMF decreased linearly with the logarithm of the ratio of the heterogeneous ozone oxidation rate and chamber residence times. The work herein improves upon that earlier work by parameterizing limonene formation within the volatility basis set (VBS) framework (Donahue et al., 2006; Presto and Donahue, 2006), while also incorporating more limonene AMF data into the parameterization itself. Using this study, one can predict indoor SOA formation due to limonene ozonolysis at various ozone, limonene, and AER conditions within a broader VBS organic aerosol

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