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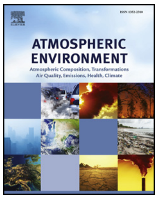

SOA and gas phase organic acid yields from the sequential photooxidation of seven monoterpenes

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A B S T R A C T

We investigate secondary organic aerosol (SOA) and gas phase organic acid yields from the sequential photooxidation of seven monoterpene isomers (α-pinene, β-pinene, limonene, sabinene, terpinolene, α-terpinene, and γ-terpinene) using an Oxidative Flow Reactor under dry conditions. SOA yields were highest for terpinolene (33% at 5.7 days of aging), followed by sabinene, β-pinene, α-pinene, limonene, γ-terpinene, and α-terpinene. Isomers with exocyclic double bonds (i.e. immediately adjacent to a ring) had higher SOA yields than those with endocyclic double bonds, or with double bonds that are unattached to a ring structure. SOA yields increased with OH exposure, highlighting the limitation of using single values for SOA yield in modeling studies, and the need for isomer-specific SOA parameterizations. SOA yields were adequately fit by a one-product model and in broad agreement with previous studies. SOA yields linearly increased with organic aerosol mass concentration, possibly the result of high OH loading and short residence times in the flow reactor. Gas phase yields of formic, acetic, butyric, and methacrylic acid (or their isomers) followed very different patterns as a function of OH exposure from SOA yields, and were poorly correlated with OH rate constants. These observations suggest that higher volatility (fragmentation) products of monoterpene photooxidation were produced and lost on different timescales from the production and condensation of lower-volatility (functionalization) products. Formic acid yields ranged from 0.06 to 9.3% across all OH exposures. Formic acid yields from γ-terpinene (0.36–3%) monotonically increased with OH exposure, unlike the other monoterpene isomers, which exhibited initial increases in formic acid yields with OH exposure, followed by decreases at higher OH concentrations. This difference in organic acid yield trends is consistent with the distribution of carbon-containing species identified by chemical ionization mass spectrometry.

1. Introduction

Biogenic monoterpene emissions from vegetation comprise a significant fraction of total volatile organic compound (VOC) emissions to the atmosphere. Monoterpenes have the chemical formula $C_{10}H_{16}$, and are estimated to contribute up to 162 Tg per year and 15% of the estimated total biogenic VOC emissions globally (Guenther et al., 2012). α-Pinene, β-pinene and limonene have the highest abundances in the atmosphere, although many more monoterpene isomers are present, varying widely in structure (Geron et al., 2000; Guenther et al., 2012). These isomers can have one to three double bonds and multiple ring structures. Monoterpenes dominate emissions from coniferous forests, but depend on plant species, sunlight exposure and temperature, resulting in regional scale differences in the relative abundance of different isomers. For example, biogenic emissions in the Southeast US are dominated by α- and β-pinene (Geron et al., 2000). However, α-terpinene, which comprises a small fraction of total monoterpene emissions in the US, can contribute up to 10% of monoterpene emissions in the Rocky Mountain and Great Plains regions. Similarly, sabinene is a minor monoterpene in terms of national emissions, but contributes up to 10% of total monoterpene emissions on the west coast, lower Mississippi River basin, and Great Plains (Geron et al., 2000). These monoterpene emissions impact atmospheric chemistry in important ways: (1) as parent hydrocarbons for the formation of secondary organic aerosol (SOA), (2) as VOCs that can react with hydroxyl (OH) radicals to form peroxy radicals (RO_2), which participate in tropospheric ozone (O_3) production, and (3) as VOCs that can react with ozone at night to produce OH radicals.

SOA impacts cloud formation and lifetime, reduces visibility, and negatively impacts human health (IPCC, 2013; Lim et al., 2012; Hallquist et al., 2009). The present impact of biogenic SOA on the radiative balance of the planet is uncertain, with one estimate suggesting

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an indirect effect of -0.22 to $-0.77\,W/m^2$, and a direct effect of -0.08 to $-0.78\,W/m^2$, with the large range due to uncertainty in the yield of SOA from biogenic VOCs (Scott et al., 2014). While numerous studies have made strides to understand SOA composition, abundance, and distribution in the atmosphere, high uncertainty still exists in global models (Hodzic et al., 2010; M. Shrivastava et al., 2011; Heald et al., 2011; Carlton et al., 2010), largely due to treatment of SOA formed from biogenic VOCs (Scott et al., 2014). In a top-down estimate of organic aerosol sources, Spracklen et al. (2011) estimated that monoterpenes are approximately half (i.e. 6.5 Tg/yr) of the global biogenic SOA source. Monoterpene emissions contribute to biogenic SOA production following reaction with OH, nitrate radicals (NO_3), and O_3. This reaction forms an array of oxidized organic products, some of which are lower in volatility than their parent monoterpene. These lower volatility products can homogeneously nucleate to form new particles (Kirkby et al., 2016; Riipinen et al., 2012) or partition to existing condensed phase to grow organic particles to larger sizes (Donahue et al., 2012).

The reactivity and SOA formation potential of monoterpenes varies by isomeric structure (Griffin et al., 1999; Zhao et al., 2015; Lee et al., 2006b). For example, Lee et al. (2006a) reported SOA yields from ozonolysis of monoterpenes to range from 17% for β-pinene to 41% for α-pinene. The trends in yields also varies by oxidant. For example, Draper et al. (2015) reported that SOA yields from α-pinene + O_3 decreased in the presence of NO_2, while other monoterpene isomers including β-pinene and Δ^3-carene increased, presumably due to the competition between O_3 and NO_3 oxidation. Friedman et al. (2016) further noted that the gas-phase products of α- and β-pinene can vary substantially as a function of SO_2, indicating that monoterpene isomers may follow different chemical pathways during oxidation. Thus, regional- and canopy-scale models of biogenic SOA production may be highly sensitive to isomeric distribution of parent monoterpenes and their associated properties. However, due to computational expense, many atmospheric chemistry models use a single representative monoterpene to capture monoterpene emissions and SOA. α-Pinene is often used as the model compound due to its dominant atmospheric abundance, despite the fact that α-pinene chemistry can be quite different from other isomers.

While monoterpenes are dominant precursors for SOA in the western US and boreal forests (Berg et al., 2013), the isomeric distribution of these precursors may vary as a function of abiotic and biotic stress. The impact of environmental stress and land use changes on SOA formation, and the resulting climate feedbacks, may impact climate and air quality predictions (Mentel et al., 2013; Unger, 2014). However, the changes in monoterpene isomer distributions are rarely taken into account, despite their potential impact on SOA predictions. During bark beetle attack on pine trees, not only are monoterpene emissions elevated relative to normal conditions, but the relative distribution of monoterpene isomers can also vary (Berg et al., 2013). Land use and species distributions are predicted to change under future climate conditions, and increases in temperature, CO_2 and drought stress are expected to alter biogenic VOC emission rates. Understanding the impact of monoterpenes on atmospheric chemistry – and SOA formation potential in particular – is important for predicting aerosol loading under future climate conditions. However, previous studies of SOA formation and product yields from monoterpenes have largely focused on oxidation by O_3; these studies also typically focus on only one or two of the dominant monoterpenes – typically α- and β-pinene (e.g. Lee et al., 2006a; Lee et al., 2006b; Eddingsaas et al., 2012b; Zhao et al., 2015; Draper et al., 2015). Fewer studies have focused on OH oxidation or a larger suite of monoterpenes (e.g. Lee et al., 2006b; Zhao et al., 2015; Griffin et al., 1999; Larsen et al., 2001; Stirnweis et al., 2017; Sarrafzadeh et al., 2016; Ng et al., 2007; McVay et al., 2016; Henry et al., 2012).

SOA is not the only fate of the biogenic organic carbon emitted as monoterpenes. A substantial fraction of the carbon is oxidized and remains in the gas-phase. In the absence of NO_x ($= NO + NO_2$), the RO_2 radicals produced from OH + hydrocarbon reactions can react with HO_2 or other RO_2 species to eventually produce an array of oxidation products, including aldehyde, ketone, alcohol, peroxide, and carboxylic acid functionality – or combinations thereof. The exact product distribution obviously depends on the structure of the parent monoterpene and oxidation conditions. In the presence of NO_x, these RO_2 radicals can instead react with NO radicals, typically resulting in carbonyl and organic nitrate functionality. Of course, primary oxidation products can be repeatedly oxidized, and the multigenerational products typically have multiple functional groups. This multigenerational chemistry can lead to either functionalization and the formation of lower volatility products, which can contribute to SOA growth, or fragmentation and the formation of smaller, higher volatility products. Small organic acids are known fragmentation products of monoterpene oxidation. In particular, formic and acetic acids are the two most abundant carboxylic acids in the atmosphere, and are produced from gas phase oxidation of alkenes, including isoprene and monoterpenes (Orzechowska and Paulson, 2005; Chebbi and Carlier, 1996; Glasius et al., 2000). However, observed formic acid concentrations are typically larger than those predicted from models, suggesting a gap in our understanding of formic acid sources (Paulot et al., 2011; Stavrakou et al., 2012; Millet et al., 2015; Schobesberger et al., 2016). Inversion modeling schemes coupled with satellite observations constrained the potential biogenic source of formic acid, suggesting that photochemical oxidation of unidentified VOCs is a substantial global formic acid source, on the order of 90–110 Tg/yr, as compared to the total atmospheric formic acid source of 102–120 Tg/yr (Stavrakou et al., 2012). Previous studies have suggested that monoterpene oxidation by OH can be a substantial, but highly uncertain, source of formic acid. Reported formic acid yields from photooxidation of α-pinene range from 7% to 28%; formic acid from limonene photooxidation have been reported as high as 50% (Larsen et al., 2001; Orlando et al., 2000). Due to the likely multiple pathways for production, yields of organic acids and other gas-phase products are likely to depend on OH exposure, and single product yields may be inadequate for describing products of monoterpene photooxidation.

This study aims to investigate SOA formation and organic acid production from oxidation of an array of monoterpenes over a range of OH concentrations under dry conditions. Specifically, we report a series of oxidative flow reactor photooxidation experiments on seven different monoterpenes (α-pinene, β-pinene, limonene, sabinene, terpinolene, α-terpinene, and γ-terpinene) at low-NO_x conditions and a range of OH concentrations. The associated gas-phase chemistry provides insight into the variability of SOA yields across monoterpene isomers. We also report gas-phase yields of small organic acids for each monoterpene as a function of OH to aid in more accurately assessments of the atmospheric budgets of carboxylic acids, and the extent to which fragmentation products correlate with functionalization products.

2. Methods

2.1. Oxidative flow reactor

The Oxidative Flow Reactor (OFR) is a 13.3 L cylindrical continuous flow chamber that allows for oxidant exposure on the order of hours to weeks. The OFR is described in detail elsewhere (Kang et al., 2007; Lambe et al., 2011; Li et al., 2015; Peng et al., 2015; Friedman et al., 2016). Briefly, one UV lamp ($\lambda = 185$ nm and 254 nm) is mounted in the chamber; 40 ppb O_3 is introduced into the chamber and photolyzed, and OH is produced via the reaction of $O(^1D)$ with H_2O. The amount of OH produced is controlled by changing the intensity of the UV lamp. No NO_x was introduced to the chamber, allowing $RO_2 + HO_2$ reactions to dominate. The residence time in the OFR was 130 s. OH concentrations were determined offline by observing the decay of SO_2, and ranged from 4.7×10^{10} to 7.4×10^{11} molec cm^{-3} s, corresponding to