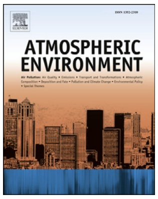
Atmospheric Environment xxx (2015) 1–9

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv



Monoterpene SOA – Contribution of first-generation oxidation products to formation and chemical composition

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HIGHLIGHTS

- SOA formation potential of β-pinene/OH > α-pinene/OH > limonene/OH.
- Oxidation of first-generation oxidation products enables insights into the formation of secondary organic aerosol (SOA).
- New reaction channels yielding SOA marker compounds.
- First analytical evidence for homoterpenylic acid – a SOA marker compound.

ARTICLE INFO

Article history:
Received 27 May 2015
Received in revised form
27 October 2015
Accepted 28 October 2015
Available online xxx

Keywords:
Secondary organic aerosol (SOA)
Monoterpene
Carbonyl compounds
Chemical characterization

ABSTRACT

Investigation of the consecutive reactions of first-generation terpene oxidation products provides insight into the formation of secondary organic aerosol (SOA). To this end, OH radical reactions with α-pinene, β-pinene, and limonene were examined along with the OH-oxidation of nopinone as a β-pinene oxidation product and pinonaldehyde and myrtenal as α-pinene oxidation products. The SOA yield of β-pinene (0.50) was much higher than that of α-pinene (0.35) and the limonene/OH system (0.30). This is opposite to the ozonolysis SOA yields described in the literature. The growth curve of SOA from β-pinene shows the contribution of secondary reactions, such as further reaction of nopinone. This contribution (17%) and the high SOA yield of nopinone (0.24) might lead to the high SOA formation potential observed for β-pinene. The majority of the C_9 oxidation products observed from β-pinene can be attributed to the consecutive reaction of nopinone, whereas in the case of pinonaldehyde, only a few α-pinene oxidation products were identified. Nopinone contributes significantly to the formation of pinic acid (51%), homoterpenylic acid (74%), and 3-methyl-1,2,3-butane-tricarboxylic acid (MBTCA, 88%) during β-pinene oxidation. The oxidation of pinonaldehyde was expected to produce important SOA markers, but only negligible amounts were identified. This indicates that their formation by oxidation of α-pinene must proceed via different pathways from the further oxidation of pinonaldehyde. Only pinonic acid and MBTCA were found in considerable amounts and were formed in α-pinene oxidation with 57% yield, while that for the pinonaldehyde/OH reaction was 33%. The lack of important SOA marker compounds might cause the low SOA yield (0.07) observed for pinonaldehyde. Based on the low SOA yield, pinonaldehyde contributes only 4.5% to α-pinene SOA. Myrtenal was identified among the gas-phase products of α-pinene oxidation. A majority of α-pinene SOA marker compounds was indeed formed by myrtenal oxidation, especially terebic acid (84%), pinic acid (76%), and diaterpenylic acid acetate (DTAA; 40%). In general, the contribution of myrtenal to α-pinene SOA is estimated to be as high as 23%. Among the detected compounds, homoterpenylic acid was positively identified as a new SOA marker compound, which was formed from β-pinene/OH and nopinone/OH but not from α-pinene/OH. A new reaction pathway yielding MBTCA was also identified in the β-pinene/OH system formed by the oxidation of nopinone, while in the case of α-pinene, the oxidation of pinonaldehyde yielded MBTCA.

1. Introduction

Large amounts of volatile organic compounds (VOC) are emitted into the atmosphere by both biogenic and anthropogenic sources.

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http://dx.doi.org/10.1016/j.atmosenv.2015.10.080
1352-2310/

Please cite this article in press as: Mutzel, A., et al., Monoterpene SOA – Contribution of first-generation oxidation products to formation and chemical composition, Atmospheric Environment (2015), http://dx.doi.org/10.1016/j.atmosenv.2015.10.080

Although highly uncertain, the global VOC emissions are estimated to be about 1300 TgC yr^{-1} (Goldstein and Galbally, 2007), and the emissions from biogenic sources (BVOC) are thought to account for 500–1150 TgC yr^{-1}. Once VOCs are emitted into the atmosphere, they undergo gas-phase reactions with ozone (O_3), hydroxyl (OH), or nitrate (NO_3) radicals. Those reactions can result in the formation of oxygenated products with a lower vapor pressure than the parent hydrocarbons. The products formed can partition into a particle phase, leading to the formation of secondary organic aerosol (SOA).

Recent top-down estimations by Goldstein and Galbally (2007) give a broad range of the global SOA burden with 140–910 TgC yr^{-1}, which is equivalent to a conversion of 11–70% of the overall emitted BVOC mass into SOA. Such a high conversion is inconsistent with SOA yields obtained from aerosol chamber experiments, which typically lead to lower global SOA loadings than the estimated burden from field measurements. This underestimation is thought to be due to additional SOA formation pathways, such as (i) further oxidation of first-generation products that are formed in the earlier oxidation steps, (ii) oxidative and non-oxidative particle phase reactions, including aqueous phase processes leading to aqSOA (so called aqueous SOA), and (iii) processing of pre-existing SOA (Kroll and Seinfeld, 2008).

First-generation oxidation products are usually semivolatile organic compounds and are thus suitable candidates for SOA formation. Important biogenic first-generation oxidation products are pinonaldehyde, nopinone, and limonaketone, which originate from α-pinene, β-pinene, and limonene, respectively. They are formed in high yields of 6–87%, 15–79%, and 5–39% from their respective precursor compounds (Hakola et al., 1994; Hatakeyama et al., 1991; Jaoui and Kamens, 2001; Larsen et al., 2001; Lee et al., 2006a,b). Furthermore, semivolatile first-generation oxidation products usually contain one or more carbonyl groups, so they are highly reactive towards OH radical reactions (Calogirou et al., 1999). However, the further oxidation and resulting oxidation products of first-generation oxidation products have been rarely investigated (Calogirou et al., 1999). Furthermore, only few studies have reported the ambient mixing ratio of pinonaldehyde and nopinone (Hellen et al., 2004; Kavouras et al., 1998).

Consequently, first-generation oxidation products are i) atmospherically relevant, ii) formed in high yields from the oxidation of their respective precursor compounds, iii) highly reactive towards OH radicals, and iv) suggested to play an important role in SOA formation. The present study addresses the oxidation of first-generation oxidation products, their influence on the SOA formation, and the resulting composition obtained from the reaction of their precursor compounds. The results are of high interest since they provide insights into the SOA formation processes.

2. Materials and methods

Experiments were conducted in the Leipziger aerosol chamber (LEAK). The Supplementary material (SI) provides a detailed description. All experiments were carried out in the presence of ammonium hydrogensulfate particles (78 mM in water) at 0% RH by the photolysis of hydrogen peroxide as an OH radical source. H_2O_2 was injected constantly over the entire run of the experiments using a peristaltic pump at 120 μL h^{-1} with 5 L min^{-1} of bypass air. Precursor compounds were injected into the aerosol chamber using a micro-syringe. The consumption of the precursor compounds (ΔHC) was measured by a proton-transfer-reaction mass spectrometer (PTR-MS), while the volume size distribution was measured with a scanning mobility particle sizer (SMPS). An average density of 1 g cm^{-3} was used to covert the SMPS measurement data into the increase in organic mass (ΔM). An overview of the experiments can be found in Table S1.

At the end of each experiment, 1.8 m^3 of the chamber content was collected on a PTFA filter (borosilicate glass fiber filter coated with fluorocarbon, 47 mm in diameter, PALLFLEX T60A20, PALL, NY, USA). For the collection of gas-phase products and to avoid sampling artefacts, a denuder (URG-2000-30B5, URG Corporation, Chapel Hill, NC, USA) was connected in front of the filter (Kahnt et al., 2011).

2.1. Sample preparation

Half of the filter was cut into small pieces and extracted in 500 μL of methanol using an orbital shaker for 15 min. To remove insoluble material, the extract was filtered through a syringe filter (0.2 μm, Acrodisc Pall, USA). Afterwards, the filter residue was extracted again with 500 μL of MeOH. The combined extracts were dried under a gentle stream of nitrogen and reconstituted in 250 μL of CH_3OH/H_2O (50/50, v/v). Denuder samples were prepared as described by Kahnt et al. (2011). Chamber-generated SOA and denuder samples were analyzed by High-performance liquid chromatography electrospray ionization coupled to time-of-flight mass spectrometry (HPLC/(-)ESI-TOFMS) according to the methods described by Mutzel et al. (2013) and Kahnt et al. (2011).

2.2. Chemicals

The following chemicals were used as received: α-pinene, limonene, nopinone, myrtenal, terebic acid, and pinic acid (Sigma–Aldrich, St. Louis, USA). 2,4-dinitrophenylhydrazine (DNPH, Fluka, St. Louis, USA) was recrystallized twice. The following compounds were synthesized according to procedures in the literature: norpinonic acid, terpenylic acid (Claeys et al., 2009), 3-methyl-1,2,3-butanetricarboxylic acid (Szmigielski et al., 2007), diaterpenylic acid acetate (DTAA; Iinuma et al., 2009), and pinonaldehyde (Glasius et al., 1997). The synthesis of homoterpenylic acid is described in the supplementary material.

3. Results and discussion

3.1. Oxidation of α-pinene, β-pinene and limonene

In the present study α-pinene, β-pinene, and limonene were oxidized with OH radicals. Table 1 shows that the SOA yield of β-pinene (50 ± 5%) was much higher than those of α-pinene (35.5 ± 2.5%) and the limonene/OH system (30 ± 4%). The difference between the SOA yield of α-pinene and limonene are small, so the variance is in the range of the experimental error. Notably, the opposite SOA formation potential is described in the literature for the ozonolysis of these compounds (limonene > α-pinene > β-pinene; Lee et al., 2006b; Chen and Hopke, 2010). Furthermore, small discrepancies were observed for the calculated SOA yields for the OH radical initiated oxidation in comparison to the literature data.

The SOA yield of the β-pinene/OH radical reaction was slightly higher than the values reported by Hatakeyama et al. (1991), whereas the SOA yield calculated for α-pinene agrees reasonably well with the data reported by Eddigsaas et al. (2012) and Ng et al. (2007). Smaller discrepancies are most likely a result of different reaction conditions. However, it is worth noting that only little data are available for SOA yields of the OH radical oxidation of α- and β-pinene and limonene in low NO_x conditions (Hatakeyama et al., 1991; Ng et al., 2007; Eddigsaas et al., 2012), which highlights the importance of the presented study.

VOC-dependent SOA yields were also observed by Ng et al. (2006), which was attributed to the chemical structures of the

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