



Chemical characterization of secondary organic aerosol constituents from isoprene ozonolysis in the presence of acidic aerosol



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HIGHLIGHTS

- Acidified sulfate aerosol enhances production of SOA from isoprene ozonolysis.
- Isoprene ozonolysis in the presence of acidic aerosol yields 2-methyltetrols.
- Unique organosulfates (OSs) are characterized from isoprene ozonolysis.
- 2-Methyltetrols and OSs may originate from heterogeneous reaction of peroxides.
- Isoprene ozonolysis yields on average 14% of isoprene-derived OSs in field samples.

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ABSTRACT

Isoprene is the most abundant non-methane hydrocarbon emitted into Earth's atmosphere and is predominantly derived from terrestrial vegetation. Prior studies have focused largely on the hydroxyl (OH) radical-initiated oxidation of isoprene and have demonstrated that highly oxidized compounds, such as isoprene-derived epoxides, enhance the formation of secondary organic aerosol (SOA) through heterogeneous (multiphase) reactions on acidified sulfate aerosol. However, studies on the impact of acidified sulfate aerosol on SOA formation from isoprene ozonolysis are lacking and the current work systematically examines this reaction. SOA was generated in an indoor smog chamber from isoprene ozonolysis under dark conditions in the presence of non-acidified or acidified sulfate seed aerosol. The effect of OH radicals on SOA chemical composition was investigated using diethyl ether as an OH radical scavenger. Aerosols were collected and chemically characterized by ultra performance liquid chromatography/electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS) and gas chromatography/electron impact ionization-mass spectrometry (GC/EI-MS). Analysis revealed the formation of highly oxidized compounds, including organosulfates (OSs) and 2-methyltetrols, which were significantly enhanced in the presence of acidified sulfate seed aerosol. OSS identified in the chamber experiments were also observed and quantified in summertime fine aerosol collected from two rural locations in the southeastern United States during the 2013 Southern Oxidant and Aerosol Study (SOAS).

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1. Introduction

The largest mass fraction of fine particulate matter (PM_{2.5}, aerosol with aerodynamic diameters $\leq 2.5 \mu\text{m}$) is generally organic, dominated by secondary organic aerosol (SOA) formed from the gas-phase oxidation of volatile organic compounds (VOCs).

Although SOA contributes a large portion (20–90%) of the total PM_{2.5} mass, for the most part current models under-predict SOA mass (Kroll and Seinfeld, 2008; Hallquist et al., 2009). Biogenic VOCs (BVOCs), such as isoprene and monoterpenes, are typically the most abundant SOA precursors, especially in regions of dense terrestrial vegetation (Guenther et al., 2006).

Isoprene (2-methyl-1,3-butadiene, C₅H₈) is the most abundant non-methane hydrocarbon emitted into the troposphere with emissions exceeding 500 Tg yr⁻¹ (Guenther et al., 2006). The principal atmospheric degradation pathway of isoprene is

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oxidation by hydroxyl (OH) radical (Atkinson, 1997; Edney et al., 2005; Kroll et al., 2006), which along with oxidation by nitrate (NO_3) radical and ozone (O_3), accounts for up to 50% of the SOA budget (Henze and Seinfeld, 2006). Before 2004, SOA formation from atmospheric oxidation of isoprene was considered insignificant (Kamens et al., 1982; Pandis et al., 1991) because of the low molecular weight and high volatility of its known oxidation products and as a consequence, isoprene was not included in SOA models. However, the identification by Claeys and coworkers of 2-methyltetrols (Claeys et al., 2004a) and C_5 -alkene triols (Wang et al., 2005) in ambient $\text{PM}_{2.5}$ collected in the Amazon caused a re-examination of the potential for isoprene oxidation to yield SOA. Since the 2-methyltetrols and C_5 -alkene triols contain the isoprene skeleton, isoprene was proposed as their source, although the mechanisms and environmental conditions leading to these products as well as the formation of isoprene SOA were not evident. Research over the last decade has established that relative humidity (RH) (Nguyen et al., 2011; Zhang et al., 2011), levels of nitrogen oxides (NO_x) (Kroll et al., 2006; Chan et al., 2010) and aerosol acidity (Surratt et al., 2007a, b) have pronounced effects on isoprene SOA formation. Recent studies show that increased aerosol acidity is a key variable in enhancing SOA formation through the acid-catalyzed reactive uptake and multiphase chemistry of the OH radical-initiated oxidation products of isoprene, particularly the isomeric isoprene epoxydiols (IEPOX) (Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2012; Gaston et al., 2014). Acid-catalyzed particle-phase reactions of IEPOX have been shown to yield the 2-methyltetrols and C_5 -alkene triols as well as IEPOX-derived dimers observed in the Amazonian $\text{PM}_{2.5}$ (Surratt et al., 2010; Lin et al., 2012). Epoxides generated by OH radical oxidation of isoprene have also been shown to explain the formation known organosulfates (OSs) and oligomers measured in ambient $\text{PM}_{2.5}$ samples (Surratt et al., 2007a, 2008; Lin et al., 2014). Although research over the last decade has focused principally on OH radical-initiated oxidation of isoprene, some work has also demonstrated significant SOA formation from the NO_3 radical-initiated oxidation of isoprene (Ng et al., 2008).

The contribution of isoprene ozonolysis to the SOA budget had been concluded to be negligible (Hasson et al., 2001; Kleindienst et al., 2007; Sato et al., 2013) on the basis of a large number of studies reporting only volatile and semivolatile products, such as methyl vinyl ketone (MVK), methacrolein (MACR) or low molecular weight acids. However, the potential importance of isoprene ozonolysis as a pathway for SOA formation is supported by recent studies documenting the formation of highly oxidized products, including oligomers, in both gas and particulate phases (Nguyen et al., 2010; Inomata et al., 2014). Initial formation of isoprene primary ozonides leads to stabilized Criegee intermediates (sCIs), which can react to form OH radicals, undergo further oxidation or condense to form higher molecular weight products. The total yield of sCIs, including CH_2OO radical and higher molecular weight fragments, was determined to be 0.26 (Hasson et al., 2001), and the yield of OH radicals to be 0.25–0.27 (Atkinson et al., 1992). Formation of highly oxidized compounds, such as oligomeric hydroperoxides identified in recent studies (Nguyen et al., 2010; Inomata et al., 2014), was proposed by the reaction of sCIs with organic ozonolysis products (e.g. carboxylic acids) of isoprene. Multiphase reactions of the oxidized products could thus make significant contributions to the yield of SOA from isoprene ozonolysis. With the exception of reports by Jang et al. (2002) and Czoschke et al. (2003), effects of varying composition and acidity of sulfate aerosols and the presence of OH scavengers on SOA generated from isoprene ozonolysis have not been systematically investigated, nor have efforts have been reported to identify products unique to isoprene ozonolysis in ambient $\text{PM}_{2.5}$ samples collected from

isoprene-rich areas.

In this study we investigate isoprene ozonolysis in the presence of sulfate seed aerosol of varying acidity and composition with a focus on the formation of OSs and highly oxidized compounds. Because of the high yield of OH radicals from isoprene ozonolysis, experiments were performed both in the presence and absence of an OH radical scavenger in order to identify SOA constituents derived directly from ozonolysis. Filters collected from indoor smog chamber experiments were analyzed by ultra performance liquid chromatography/electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS) and gas chromatography/electron impact mass spectrometry (GC/EIMS). $\text{PM}_{2.5}$ samples collected from ground sites at Look Rock, TN, and Centerville, AL, during the 2013 Southern Oxidant and Aerosol Study (SOAS) were also analyzed to identify OSs present in both field and chamber studies and quantify their contribution to ambient $\text{PM}_{2.5}$. Comparison of lab and field data supports the potential importance of isoprene ozonolysis in the isoprene-derived SOA budget.

2. Experimental section

2.1. Smog chamber experiments

Ten experiments were performed in the indoor environmental smog chamber at the University of North Carolina. The experimental setup and analysis techniques used in this work were described in detail previously (Lin et al., 2012; Zhang et al., 2012). Briefly, experiments were carried out under dark and dry conditions ($3.3 \pm 0.25\%$, RH) at 296 ± 1 K in a 10-m^3 Teflon chamber. Experimental conditions are summarized in Table 1. Prior to each experiment, the chamber was flushed continuously with clean air for ~24 h until the particle mass concentration was $<0.01 \mu\text{g m}^{-3}$ to ensure that there were no pre-existing aerosol particles prior to injection of isoprene. Aerosol size distributions were continuously measured using a differential mobility analyzer (DMA, BMI model 2002) coupled to a mixing condensation particle counter (MCPC, BMI model 1710) in order to monitor aerosol number, surface area, and volume concentration within the chamber. Chamber flushing also reduced O_3 and VOC concentrations below the detection limit (<1 ppb for ozone and isoprene). Temperature and RH in the chamber were continuously monitored using a dew point meter (Omega Engineering Inc.).

A known quantity of isoprene (Sigma–Aldrich, 99%) was introduced into the chamber by passing a heated nitrogen (N_2) stream through a heated glass manifold. In some experiments, diethyl ether was injected by the same procedure to serve as an OH scavenger. Concentrations of isoprene and diethyl ether were measured every 10 min using an online gas chromatography/flame ionization detector (GC-FID, Model CP-3800, Varian), which was calibrated using multiple injections of isoprene and diethyl ether. Approximately 100 ppb of isoprene was injected for each experiment, while 3.5 ppm of diethyl ether was introduced in the experiments performed in the presence of OH scavenger. Approximately 1 h after isoprene injection, 120–150 ppb of O_3 was introduced into the chamber using an O_3 generator (Model L21, Pacific ozone). O_3 concentration was monitored over the course of experiments using an UV photometric analyzer (Model 49P, Thermo-Environmental).

Non-acidified or acidified ammonium or magnesium sulfate seed aerosols were introduced two hours after O_3 injection. Non-acidified seed aerosol was generated from 0.06 M magnesium sulfate (MgSO_4) or ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) (aq) solutions and acidified seed aerosol from 0.06 M MgSO_4 (aq) or $(\text{NH}_4)_2\text{SO}_4$ (aq) + 0.06 M H_2SO_4 (aq) solutions. Once aerosol volume concentrations stabilized (~1 h after reaction), aerosols were collected

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