



Characterization of the limonene oxidation products with liquid chromatography coupled to the tandem mass spectrometry



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HIGHLIGHTS

- Limonene SOA was generated under different conditions.
- Composition of the secondary organic aerosol (SOA) particles was studied.
- Structures for the several limonene oxidation products were proposed.
- Formation pathways for the detected oligomers were identified.

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ABSTRACT

Composition of the secondary organic aerosol (SOA) generated during ozonolysis of limonene was investigated with liquid chromatography coupled to the negative electrospray ionization (ESI), quadrupole tandem mass spectrometry (MS/MS) as well as high resolution Time-of-Flight mass spectrometry. Aerosol was generated in the flow-tube reactor. HR-MS/MS analysis allowed for proposing structures for the several up-to-date unknown limonene oxidation products. In addition to the low MW limonene oxidation products, significant quantities of oligomers characterized by elemental compositions: $C_{19}H_{30}O_5$, $C_{18}H_{28}O_6$, $C_{19}H_{28}O_7$, $C_{19}H_{30}O_7$ and $C_{20}H_{34}O_9$ were detected in the SOA samples. It was concluded that these compounds are most likely esters, aldol reaction products and/or hemiacetals. In addition to detailed study of the limonene oxidation products, the reaction time as well as initial ozone concentration impact on the limonene SOA composition was investigated. The relative intensities of the two esters of the limonic acid and 7-hydroxy limononic acid increased as a result of lowering the initial ozone concentration and shortening the reaction time, indicating that esterification may be an important oligomerization pathway during limonene SOA formation.

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1. Introduction

Biogenic volatile organic compounds (BVOC's): isoprene together with terpenes, account for approx. 90% of the global non-methane hydrocarbons emission (Guenther et al., 2000; Messina et al., 2016; Sindelarova et al., 2014). α -Pinene and β -pinene are the most abundant monoterpenes (Atkinson and Arey, 2003; Messina et al., 2016), followed by limonene (Messina et al., 2016; Sindelarova et al., 2014). It was proven that limonene has significantly higher SOA-forming potential as compared α and β -pinene when reacting with the common atmospheric oxidants (Jonsson et al., 2005; Leungsakul et al., 2005a; Youssefi and Waring, 2015).

In this work, SOA formation as a result of the ozone-initiated limonene oxidation in the flow-tube reactor was investigated. Limonene oxidation is important since it leads to the formation of ambient as well as indoor SOA (Athanasopoulou et al., 2013; Waring and Wells, 2015).

Although the initial stages of limonene ozonolysis are relatively well known (Leungsakul et al., 2005a, 2005b; Pathak et al., 2012), the data regarding structures and formation mechanisms of the high molecular weight (HMW) limonene SOA fraction is ambiguous (Heaton et al., 2007; Kundu et al., 2012; Nørgaard et al., 2013). There are a number of known association mechanisms for the first and second generation products leading to the formation of SOA oligomeric fraction (Camredon et al., 2010; Gao et al., 2010; Hall and Johnston, 2012; Jang et al., 2002). However, by studying the aerosol particles composition in the direct infusion (DI) mode by HR-ESI/

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MS, which is currently commonly used approach (Hall and Johnston, 2012; Kundu et al., 2012; Putman et al., 2012), it is very difficult to propose the structures as well as formation mechanisms for a specific compound (Hall and Johnston, 2012). In this work, high performance liquid chromatography coupled to the negative electrospray ionization mass spectrometry (HPLC(–)ESI/MS/MS) was used in order to characterize semi-volatile compounds formed during the ozone-initiated limonene oxidation in the flow-tube reactor. The use of this well-established SOA analysis method (Hallquist et al., 2009; Nozière et al., 2015) allowed for detailed characterization of the limonene oxidation products. In the past, a large number of important monoterpene SOA tracers were characterized using (–)ESI (Nozière et al., 2015; Putman et al., 2012; Tu et al., 2016; Yasmeeen et al., 2011). Still, this ionization method cannot be regarded as universal, since (–)ESI fails to directly ionize significant portion of oxidized molecules present in SOA particles (Nozière et al., 2015; Parshintsev and Hyötyläinen, 2015).

2. Experimental

2.1. Reagents

cis-Pinonic acid ($\geq 98.0\%$), 7-oxooctanoic acid ($\geq 98.0\%$), suberic acid ($\geq 99.5\%$), 8-hydroxyoctanoic acid ($\geq 99.5\%$), azelaic acid ($\geq 99.5\%$), sebacic acid ($\geq 98.0\%$), 10-hydroxydecanoic acid ($\geq 98.5\%$), *D*-limonene ($\geq 98.5\%$), as well as LC - MS hyper-grade solvents and eluent additives: acetonitrile ($\geq 99.9\%$), formic acid ($\geq 99.5\%$) were all purchased from Sigma - Aldrich (Schnelldorf, Germany). Deionized water ($18 \text{ M}\Omega \times \text{cm}^{-1}$) was prepared using Direct - Q3 Ultrapure Water System (Millipore). UHP gases: synthetic zero-air ($\leq 3 \text{ ppm}$ of H_2O , $\leq 0.1 \text{ ppm}$ of hydrocarbons), H_2 ($\geq 99.999\%$), He ($\geq 99.999\%$), and O_2 ($\geq 99.999\%$) was supplied by Multax (Stare Babice, Poland).

2.2. Flow reactor

A diagram of the flow reactor used in this study is shown in Fig. 1. This is a newly constructed experimental setup and a more sophisticated version of the flow-tube reactor than the one used in our previous study (Witkowski and Gierczak, 2014).

The reaction vessel was 1.5 m long and 12 cm ID Pyrex glass tube. As shown in Fig. 1 several instruments were connected to the reactor, including: four mass flow-meters (Sierra, TopTrack series), UV ozone generator (Ultra-Violet Products Ltd, SOG-2 Ozone Generator), thermo hygrometer (model 701, LAB-EL), capacitance manometer (model MP 221, Elvac) and UV-Vis ozone analyzer (EcoSensors, UV-100 Ozone Analyzer). Limonene concentration was monitored off-line, with GC-17A gas chromatograph (Shimadzu) equipped with the flame-ionization detector; details of the calibration procedure were described previously (Witkowski and Gierczak, 2014). All experiments were carried out under laminar flow conditions and the total flow rate of gasses added to the reactor, including zero-air (carried gas, humidified air and limonene/air mixture) and UHP oxygen (supplied to the ozone generator) was 3.3 LPM, yielding Reynolds number of approx. 40 (Young et al., 2011). Pressure inside the reactor was 1 atm., temperature was $298 \pm 2 \text{ K}$ and the flow-tube was shielded from the outside irradiation. RH was adjusted to $\approx 5\%$ by bubbling air through the deionized water. No OH radical's scavenger was used.

Initially, humidified air and ozone were added to the reactor. After stabilizing the ozone concentration, the line connecting the reactor with the ozone analyzer was shut-off (Fig. 1). Limonene was added to the flow-tube by passing a stream of air over the pure

liquid. Samples for the GC/FID analysis were taken from the sampling port connected with the ozone-free section as shown in Fig. 1. After stabilizing the limonene concentration, the airflow from the reactor was directed through the sampling assembly. This experimental setup allows for independent and very precise adjustment of the initial ozone and precursor concentrations, thus SOA formation conditions were readily reproducible. Initial ozone concentration was varied between 0.15 and 4.0 ppm. The average reactants residence time was also varied between approx. 1 and 4 min by adjusting the movable mixing plunger position. After each experiment, very high amount of ozone (between 500 and 1 000 ppm) was added to the reactor (generated by a high-output electric discharge ozone generator). Afterwards, zero-air was added and the reactor was flushed for 2–3 h after shutting down the high-output ozone generator to remove the excess ozone and any products of limonene oxidation leftover from the previous experiment. The effectiveness of this procedure was confirmed by analyzing blank filters obtained before and after the ozonolysis experiments.

2.3. SOA collection and sample preparation

Particles were collected on 47 mm filter (EMFAB TX40H120-WW, Pall Corporation) using in-line filter holder. Before SOA collection, filters were heated for 3 h at $50 \text{ }^\circ\text{C}$ to remove absorbed volatiles and kept in low-humidity environment prior to the aerosol collection. After sufficient amount of SOA was collected, ultrasound-assisted extraction was carried out for 10 min and 1.5 ml of ACN/ H_2O mixture (1:1, v/v), was used as the extraction solvent. Afterwards, the filter extract was filtered through PTFE syringe filter (pore size $0.22 \text{ }\mu\text{m}$) and subjected to the chromatographic analysis under the experimental conditions described in section 2.4.

2.4. Apparatus

2.4.1. HPLC/MS analysis conditions (triple quadrupole mass spectrometer)

Low resolution - HPLC/MS analysis was carried out with LC20A liquid chromatograph (Shimadzu) coupled to the QTRAP 3 200 (Sciex) triple quadrupole mass spectrometer. Separation was carried out with reverse phase Luna (Phenomenex) C18 column ($100 \text{ mm} \times 2.1 \text{ mm}$, $3 \text{ }\mu\text{m}$, 100 \AA) kept at $30 \text{ }^\circ\text{C}$, equipped with the security guard cartridge with a 2 mm ID C18 pre-column. The mobile phase, consisting of eluent A - aqueous solution of formic acid (pH 2.8) and eluent B - acetonitrile (ACN) was delivered at a flow rate of 0.2 mL/min and the sample volume was 5 μl . Gradient elution was used according to the following program: 0–4 min 5% B, 4–30 min linear gradient to 60% B, 30–36 min linear gradient to 95% B, 36–42 min 95% B, 42–42.5 min linear gradient to 5% B. Afterwards, the column was equilibrated at 5% B for 12.5 min and the analysis was completed in 55 min. Mass spectra in the negative ionization mode were acquired in both total ion current (TIC) in the mass range 50–700 m/z and selected reaction monitoring (SRM) modes. The ESI conditions were as follows: capillary voltage was -4.5 kV , source temperature $450 \text{ }^\circ\text{C}$ and nitrogen was used as curtain ($3 \times 10^5 \text{ Pa}$), auxiliary gas ($3 \times 10^5 \text{ Pa}$) and collision gas. Analyst 1.4.2 Software (Sciex) was used for data acquisition and processing.

2.4.2. HPLC/MS analysis conditions (time-of-flight mass spectrometer)

HPLC-HR-MS/MS analysis was carried out with Q-TOF 6 540

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