

# Gas and particle phase characterization of limonene ozonolysis products and their role in SOA formation

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## Introduction

Low vapor pressure products from the oxidation of volatile organic compounds (VOC) contribute significantly to atmospheric aerosol particle formation and growth (Hallquist et al., 2009). Limonene is a doubly unsaturated VOC with lower emission rates than other monoterpenes (e.g.  $\alpha$ -pinene) and shows high reactivity in the presence of ozone. This can subsequently lead to the formation of secondary organic aerosol (SOA) in both the atmosphere and indoor environments. Detailed gas phase mechanisms of limonene oxidation are available through the master chemical mechanism (MCM) and present a framework against which observed product distributions can be compared.

Carboxylic acids are one major class of products from limonene oxidation. They have been shown to play an important role in SOA formation due to their low vapor pressure (Salo et al., 2009). A previous modelling study assessed the relative contribution of carboxylic acids from limonene oxidation to SOA formation (Pathak et al., 2012). According to their model, limonene-ozonolysis produces significant amounts of carboxylic acids and the distribution is affected by changes in both OH and ozone concentrations. Beside carboxylic acids, other classes of compounds with low volatilities (e.g. aldehydes, alcohols, ketones, peroxides or multifunctional compounds) are formed during the oxidation process and their contribution to SOA formation is one focus of the current study.

## Material and Methods

Oxidation studies of limonene in the presence of ozone have been performed under a variety of experimental conditions in the Gothenburg Flow Reactor for Oxidation Studies at Low Temperatures (G-FROST), described in a previous study (Jonsson et al., 2008). In our study, limonene was added through a characterized diffusion source and concentrations were increased stepwise (15, 40, 150 ppb). Temperature (20°C), ozone concentrations (400, 1000 or 5000 ppb) and relative humidity (dry or 25% RH) were kept constant during the run of the experiments. Experiments were performed with and without 2-butanol as an OH scavenger. The oxidation product distribution in the gas and particle phase was measured with an acetate High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS) coupled to a Filter Inlet for Gases and AEROSols (FIGAERO) and analyzed for their chemical composition. SOA mass based on particle size

distribution was derived with a Scanning Mobility Particle Sizer (SMPS).

## Results

Identified products are reported in terms of relative ratios between the gas and particle phase. It was evident that some of these relative ratios for selected carboxylic acid and aldehyde oxidation products (figure 1) are in agreement with the volatility bin calculations from Pathak et al. (2012). However, there were also some that deviated significantly. To further elucidate the source of these discrepancies a comparison of the product distribution with MCM will be discussed.

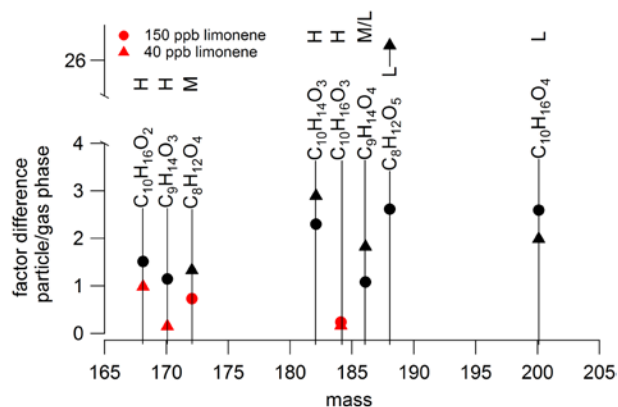


Figure 1. Relative ratios between gas and particle phase data for high (circles) and medium (triangles) limonene concentrations with 1000ppb O<sub>3</sub>, humid conditions and OH scavenger. Ratios <1 (red) indicate a higher gas phase signal for the respective compound and ratios >1 (black) indicate a higher particle phase signal. High (H), Medium (M) and Low (L) indicate volatility bins according to Pathak et al. (2012).

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