

# Characterization of organic nitrates from biogenic and anthropogenic SOA: dimer formation and relation to volatility

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The formation and processing of Secondary Organic Aerosol (SOA) has effects on the global atmosphere, such as impacts on climate (Kanakidou et al., 2005). Previous studies have emphasized the importance of investigating the mechanisms of SOA formation from VOC oxidation (Hallquist et al., 2009). Toluene and Limonene have high potentials for SOA formation (Hildebrandt et al., 2009; Pathak et al., 2012), and organic nitrate formation has been observed for both species (Cao and Jang, 2008; Hallquist et al., 1999). To further characterize the formation and partitioning of these organic nitrates, a series of flow tube reactor experiments were performed under varied  $[\text{NO}_x]/[\text{Toluene}]$  and  $[\text{NO}_x]/[\text{Limonene}]$  ratios.

Limonene experiments were performed in the Gothenburg Flow Reactor for Oxidation Studies at Low Temperatures (G-FROST). A characterized limonene source was used to add concentrations of 15, 40 and 100 ppb in a step-wise pattern. A low flow (10 – 80 sccm) from a  $\text{N}_2\text{O}_5$  diffusion source (at  $-28^\circ\text{C}$ ) was added to generate  $\text{NO}_3$ , similar to previous studies (Hallquist et al., 1999). Reactions were allowed to proceed in the dark.

For toluene experiments, a Potential Aerosol Mass (PAM) flow reactor was used. Dry and humidified air were mixed with  $\text{O}_3$  and irradiated using two Phillips TUB 30 W bulbs with peak emissions at 254 nm. Varied concentrations of  $\text{NO}_x$  (~10-100 ppb, as  $\text{NO}$ ) were added throughout the experiments to facilitate nitrate formation.  $\text{OH}$  was generated by irradiation of the mixture to drive toluene oxidation.  $\text{OH}$  exposure in the chamber at a residence time of 45 s was equivalent to approximately 3.5 days of atmospheric oxidation.

Characterization of both gas and particle phase organic species was performed using a High Resolution-Time-of-Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS) coupled to a Filter Inlet for Gases and AEROSOLS (FIGAERO). Gases were sampled via  $\frac{1}{4}$ " Teflon tubing and particles were collected through 12 mm copper tubing onto a Zefluor filter. The filter was cyclically heated  $200^\circ\text{C}$ , followed by a temperature soak for at least 10 minutes to ensure full desorption of particle phase organics. Sample and desorption times varied 30-60 and 30-60 minutes, respectively. Aerosol size distributions and total mass were measured using a SMPS (TSI Inc., DMA 3081, CPC 3775, and  $\text{NO}_x$  concentrations were monitored (Teledyne, model 42i).

Several hundred organic species were observed to be present in the SOA generated from both Toluene and Limonene. In addition to species present in the Master Chemical Mechanism (v3.3.1), elevated signals from

many other ions were identified during SOA desorptions. A comparison of dominant VOCs and particle phase species, including organic nitrates, formed from both sets of experiments will be made. Additionally, relative volatilities of species in the particle phase, as determined by the timing of the peak ion signal during desorption from the FIGAERO-HR-ToF-CIMS, will be discussed. For example, several compounds were detected in the Limonene experiments at high masses where dimers of known species could exist. Figure 1 shows a comparison of the thermal desorption of several of these ions relative to those of ions at lower masses which desorb significantly earlier.

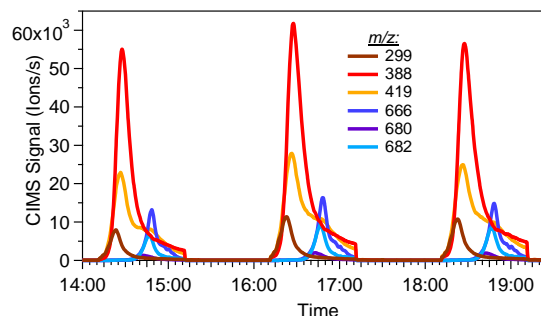


Figure 1. Desorption profiles for selected mid- and high-mass ions detected during a Limonene experiment.

Analysis of the most important organic species contributing to SOA mass, and potential identities of the very high masses detected will be discussed.

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