TNA User Report

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Project title	SOA formation from anthropogenic and biogenic precursors
Name of the accessed chamber	AIDA
Number of users in the project	2
Project objectives (max 100 words)	This project aims to study the physicochemical interactions of atmospheric oxidation products of toluene and α-pinene, major anthropogenic and biogenic precursors, respectively, for secondary organic aerosol (SOA) particles. Specific goals are the identification of molecular tracers for both compound categories, and the quantification of the potential impact of their physicochemical interactions on the total SOA yield. A better understanding of the contribution of anthropogenic and biogenic emissions to SOA will help developing more effective mitigation strategies for this climate active air pollutant.
Description of work (max 100 words):	During the course of 11 experiments in AIDA, we formed SOA via oxidation of toluene and/or α-pinene under temperature and relative humidity settings simulating conditions from the boundary layer to the free troposphere (293 – 243 K). For about half of the experiments, NO_x was added to investigate its influence on oxidation products and SOA yield. The chemical composition of the resulting SOA particles was analyzed in real time using advanced mass spectrometric techniques. For the lower temperatures in this study, also the (ice) cloud formation potential of the SOA particles was investigated.

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[1] Physics; Chemistry, Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

[2] UNI= University and Other Higher Education Organisation;
RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);
SME= Small and Medium Enterprise;
PRV= Other Industrial and/or Profit Private Organisation;
OTH= Other type of organization.

[3] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher EXP= Engineer; ACA= Academic; TEC= Technician.

[4] Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Claudia Mohr
Chamber name and location: AIDA Chamber, Karlsruhe, Germany
Campaign name and period: SOA17, 6.11. – 24.11.2017
Text:

Introduction and motivation

Atmospheric aerosols have adverse impacts on human health (Nel, 2005) and rank among the main drivers of anthropogenic climate change (IPCC, 2013). Organic compounds make up a large fraction (20−90 %) of submicron particulate mass (Jimenez et al., 2009). Secondary organic aerosol (SOA), formed via atmospheric oxidation of gaseous precursors (volatile organic compounds, VOC), dominates the global budget of organic aerosols (Shrivastava et al., 2015), can be of both biogenic and anthropogenic origin. Due to the wealth of precursors of both biogenic and anthropogenic origin, and formation mechanisms in both the gas and particle phase, SOA is very complex and can contain thousands of compounds with a wide range of functionalities, volatilities, and other physicochemical properties (Nozière et al., 2015). This leads to large uncertainties in estimates of both climate as well as health effects of SOA.

An important class of biogenic VOC are monoterpenes ($C_{10}H_{16}$). One of the most abundant monoterpenes is α-pinene. The fraction of total SOA mass from monoterpene oxidation products is estimated to be ~15 % globally (Heald et al., 2008). Toluene (C_7H_8) is the most abundant aromatic hydrocarbon in the atmosphere and is emitted primarily from anthropogenic sources. Photochemical oxidation of toluene plays an important role in tropospheric ozone and SOA formation. However, the detailed chemical mechanism of toluene oxidation in the atmosphere remains uncertain (Ng et al., 2007; Hildebrandt et al., 2009; Ji et al., 2017). Furthermore, the interaction of toluene and biogenic SOA precursors has only been studied in a few cases and still bears several uncertainties (Jaoui et al., 2008; Deng et al., 2017).

Scientific objectives

The project has the following scientific objectives:

- Identification of molecular tracers for atmospheric oxidation products in gas and particle phase of pure α-pinene, pure toluene, and mixed systems as a function of atmospherically relevant temperature and relative humidity conditions, as well as NOx concentrations (assessment of SOA fingerprints).
- Quantification of the potential impact of the physicochemical interaction of α-pinene and toluene oxidation products on the total SOA yield and comparison to SOA yield of the pure systems.
- For lower temperature conditions: Assessment of the (ice) cloud formation potential of the SOA particles.
- Long-term: Improve the interpretation (e.g. source apportionment) of mass spectroscopic studies of ambient aerosols with biogenic and anthropogenic influence.

Reason for choosing the simulation chamber/ calibration facility

The highly instrumented and well maintained AIDA facility is well suited for investigating chemical kinetics, aerosol chemistry (Saathoff et al., 2009), aerosol physics, and cloud microphysics in a wide range of atmospheric conditions, crucial for the scientific objectives of the study, e.g. pressure (1 to 1000 hPa), temperature (40 °C to -90 °C), and relative humidity (from extremely dry to super saturations).

Method and experimental set-up

We conducted two types of chamber experiments. In most experiments, SOA was directly formed in the dark AIDA chamber by reaction of precursors with OH radicals. Here, the ozonolysis of tetramethylethylene (TME) was used as an OH radical source. For the second type (Exp. 10, Table 1), SOA from α-pinene was first produced in an adjacent, smaller chamber (NAUA), and then introduced into the AIDA chamber and mixed with the SOA produced from toluene.

To examine both physical and chemical characteristics of the formed SOA, three different mass spectrometers were used:

- a high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne) for determining SOA and seed aerosol mass concentrations;
- a laser ablation single particle mass spectrometer (LAAPTOF, AeroMegt) for studying the mixing state of the aerosol particles;
- a chemical ionization time of flight mass spectrometer (FIGAERO-CIMS, Aerodyne) for identifying the characteristic molecules formed from the different precursors, using Iodide as reagent ion.

Data description

During the three-week measurement campaign we conducted three series of experiments, including the SOA formation from the mixture of toluene and α-pinene; from toluene, α-pinene and NO_x with $NaNO_3$ seed; and from α-pinene and NO_x. For each series, three different temperatures (T = ~243, ~272 and ~293 K) were chosen to study the temperature dependence of the interaction of the oxidation products. Initial NO_2 levels ranged between 30-35 ppb and relative humidities between 3 and 97, keeping the water concentration nearly constant. For the lowest temperature (~243 K), the (ice) cloud formation potential of the SOA particles was investigated. In addition, two more experiments concerning the impacts of external vs. internal mixing of SOA from toluene and α-pinene were conducted. The details of the experiment design are listed in Table 1.

The data available from the campaign include mass spectra from gaseous oxidation products (one second time resolution) and particulate phase (hourly time resolution) oxidation products on molecular level (FIGAERO-CIMS), total organic aerosol mass (HR-ToF-AMS), and particle mixing state, as well as particle number concentration and size. The data provide detailed information about yields, physical properties, and chemical composition of SOA, as well as the ice nucleation abilities of the SOA particles.

Table 1: Experiment design.

	Exp. No.	Precursor(s)	T [K]	RH [%]	Cloud activation
Series 1	1	toluene + α-pinene	243	97	√
	2		272	14	
	3		293	3	
Series 2	4	toluene + α-pinene + NO_x + $NaNO_3$ seed	243	97	√
	5		272	14	
	6		293	3	
Series 3	7	α-pinene + NO_x	243	97	√
	8		272	13	
	9		293	3	
	10	α-pinene SOA (from NAUA) + toluene SOA on $NaNO_3$ seed (in AIDA)	293	3	
	11	Conversion of $NaCl/NO_2/O_3$ to $NaNO_3$ aerosol	293	3	

Preliminary results and conclusions

Figure 1 presents a comparison of particle-phase example mass spectra for SOA from the oxidation of mixtures of toluene and α-pinene by OH radicals at three different temperatures (Series 1). These preliminary data indicate that the temperature has a significant impact on the chemical composition for these mixed SOA.

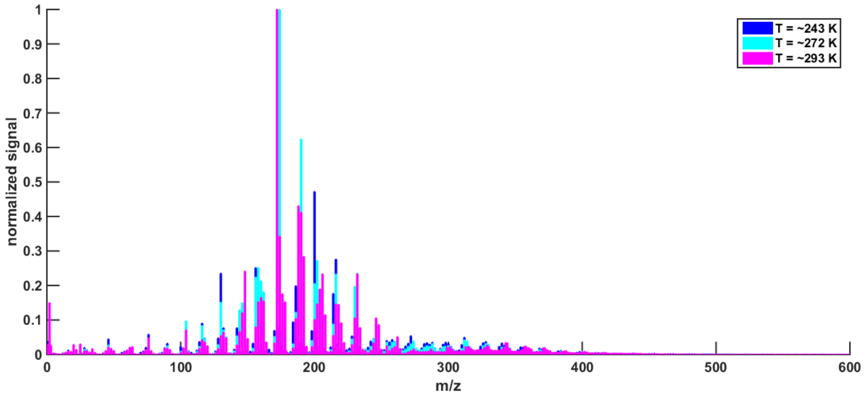

Figure 1: FIGAERO-CIMS particle-phase mass spectra of SOA from the oxidation of a mixture of toluene and a-pinene by OH radicals for three different temperatures.

Figure 2 presents a comparison of particle-phase example mass spectra for SOA from the oxidation of pure toluene and of toluene/NO_x mixtures by OH radicals at 243 K (Series 2). In the presence of NO_x a clear reduction of the SOA yield was observed, especially for compounds with higher masses.

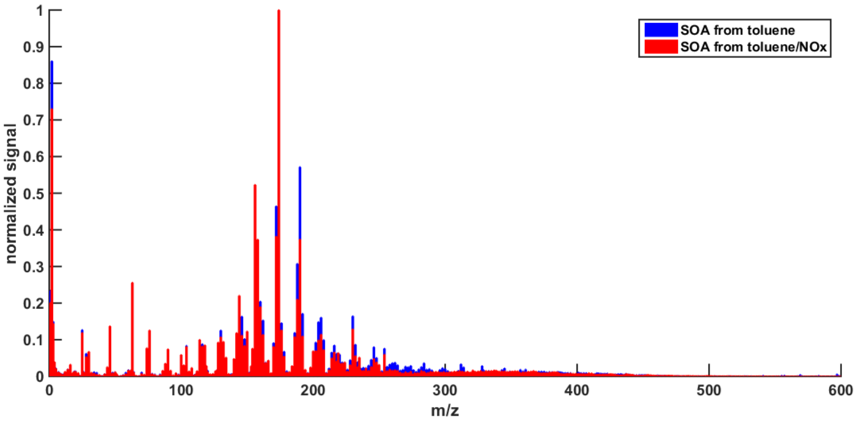

Figure 2: FIGAERO-CIMS particle-phase mass spectra of SOA from the OH radical induced oxidation of pure toluene (blue) and a mixture of toluene and NO_x (red) both at 243 K.

Among the main components (ions with highest signal intensity) identified are $C_7H_{10}O_6$ in the pure toluene spectrum, and $C_7H_{10}O_6$ and $C_{10}H_{16}O_5$ in the spectrum of the mix of SOA particles from α-pinene and toluene formed separately. Mixing the particles after they have been formed thus seems not to drastically change the nature of the organic compounds. This is a somewhat expected result, as the time scales of particle mixing and potential subsequent chemical reaction between particle-phase compounds likely lie beyond the time scales of our few-hour-experiments. However, when gaseous compounds of the two precursors are already mixed during the oxidation process before particle formation takes place, different compounds such as e.g. $C_8H_{12}O_4$ exhibit high signal.

Figure 3 shows averaged mass spectra for 3489 single particles formed by coagulation in an initially external mixture of $NaNO_3$ particles coated with toluene SOA and of $(NH_4)_2SO_4$ particles coated with α-pinene SOA (Exp. 10).

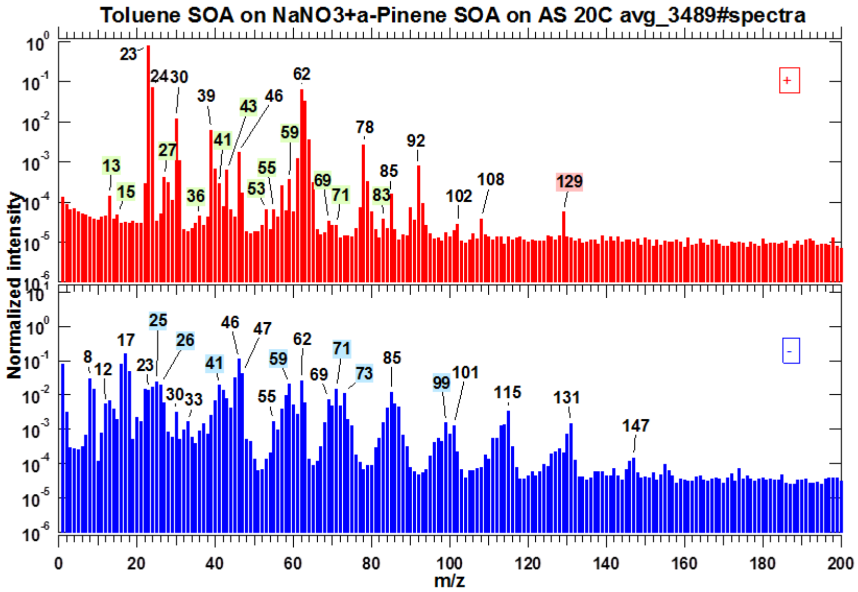

Figure 3: LAAPTOF averaged mass spectra for 3489 single particles formed by coagulation of α-pinene SOA on $(NH_4)_2SO_4$ seed (from NAUA) and toluene SOA on $NaNO_3$ seed (in AIDA). Green labels represent the fragments from α-pinene; the red label represents the fragment from toluene; and blue labels represent the fragments most likely from toluene.

Outcome and future studies

The measurements at AIDA have provided a unique dataset of the interactions between anthropogenic and biogenic precursors and their influence on SOA physicochemical properties at a wide range of temperature and relative humidity values that simulate conditions from the Earth´s surface to altitudes where cloud formation can take place. This dataset will also serve as a complement to field measurements with the FIGAERO-CIMS that will be undertaken in spring 2018 at the GAW station Chacaltaya in the Bolivian Andeas (5240 m a. s. l.). This high-altitude site is impacted by both anthropogenic emissions from the nearby city of La Paz, and biogenic emissions from Eucalyptus forests (close to the station) and the Amazon region (long-range transport).

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