TNA User Report

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Project title	Heterogeneous formation of organosulfates : towards a parameterisation of the kinetics - Part 1 : chamber experiments
Name of the accessed chamber	LEAK-LACIS
Number of users in the project	1
Project objectives (max 100 words)	The objective of this project is to get an in-depth insight into the kinetics of heterogeneous OS formation by documenting the influence of parameters such as aerosol acidity and water content, in order to better evaluate the contribution of this reaction pathway, in a wide range of atmospheric conditions, to OS formation and more broadly to organic carbon transfer from the gas phase the particulate phase.
Description of work (max 100 words):	Experiments focused on the reaction of alpha-pinene oxide (3 levels of concentration) with acidic and sulfated particles. Seed particle composition was modified from the initial mixture H_2SO_4/Na_2SO_4/HCl to control and vary particle acidity and sulfate content. Experiments were run under "dry" (RH<10%) and "wet" conditions (RH~80%). Similar experiments were performed in the second chamber but using nitrate instead of sulfate to investigate the heterogeneous processes of organonitrates formation and compare the reactivity of nitrated vs sulfated particles with alpha-pinene oxide. At the end of experiments, OH radicals were generated by photolysis of H_2O_2 to mimic atmospheric oxidative particle ageing.

Principal Investigator's and group's information	
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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.

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: Eric Villenave
Chamber name and location: LEAK
Campaign name and period: Heterogeneous formation of organosulfates : towards a parameterisation of the kinetics - Part 1 : chamber experiments (03.07.2019-12.07.2019)

Text:

Introduction and Motivation

Organosulfates (OSs) are part of the highly complex organic fraction of atmospheric aerosols and have been measured in ambient aerosols, rain and fogwater in a wide diversity of environments. These compounds have been shown to be of secondary origin and some of them are used as markers for biogenic secondary organic aerosols (BSOAs) enhanced in the presence of air masses from anthropogenic influences. OSs formation pathways have been investigated in laboratory experiments from the oxidation of biogenic volatile organic compounds (BVOCs) and the reactive uptake on acidic sulfate particles of various oxygenated products, amongst them epoxides (such as isoprene epoxydiols or alpha-pinene oxide (aPO)) are the most efficient precursors. However, the debate is still open on whether the OSs found in atmospheric aerosols are produced by ionic or radical mechanisms. Only few kinetic studies have been conducted yet on OS formation reactions and most of them were performed in bulk aqueous solutions and

even more at the gas-particle interface. Uptake coefficients of aPO on acidic aerosol were reported by Drodz et al. (2013) by measuring aerosol growth for different aPO gas concentration and aerosol acidity. More recently, rate constants were provided by Duporté et al. (2016) for heterogeneous OS formation. In these two studies, the crucial roles of acidity and humidity, closely related to the mixture state of the particles (i.e. the liquid-liquid phase separation, the core-shell structure…) on the kinetics of the reaction was strongly emphasized but finally not parameterized. However, the influence of parameters such as aerosol acidity and water content on OS formation kinetics is strongly needed to be implemented into atmospheric chemistry models (0D to 3D) and to properly evaluate the contribution of this reaction pathway, in a wide range of atmospheric conditions, to OS formation and more broadly to organic carbon transfer from the gas – to the particulate-phases.

Scientific objectives

In this context, the goal of this project was to get an in-depth insight into the kinetics of heterogeneous OS formation. We proposed to perform a series of well-selected chamber experiments combined to the time-resolved molecular analysis of the gas and particulate phases. The reaction of alpha-pinene oxide with sulfated particles was selected as (1) it was shown to be an efficient OS precursor and (2) its OS derived products are observed commonly in monoterpene-rich environments and (3) it was extensively studied by both the applicant (EPOC) and the host (TROPOS) groups. Although this reaction is not new, it was investigated here for the first time using a panel of complementary state-of-the art on-line and off-line instruments such as PTR-ToF-MS, CI-Api-ToF-MS, W-ToF-AMS, HPLC/(-)ESI-TOF-MS, allowing to comprehensively monitor the evolution of the gas and aerosol chemical composition and finally to unravel the complexity of this multiphasic reactions. The kinetic parameterization of OS heterogeneous formation will further be available for future implementation in chemical models and we expect it to be of wider interest to the atmospheric chemistry community as a « model » process for other heterogeneous reactions.

Reason for choosing the simulation chamber/ calibration facility

Experiments on organosulfate formation from monoterpene-derived compounds were successfully conducted in aerosol chamber at the atmospheric chemistry department (ACD-C) of TROPOS in the past. OS formation was also studied extensively by the applicant (EPOC) group.

More, a companion project was submitted simultaneously by Emilie Perraudin for a training at the Organic Tracers and Aerosol Constituents Calibration Center (OGTAC CC) in order to learn and apply the most adequate and up-to-date analytical techniques to gain insight in the detection and quantification of biogenic SOA markers and organosulfates in the studied particles.

The present project has thus benefited from the combined skills and expertise of the host group on OS formation, as well as from the unique analytical instrument panel for on-line and off-line aerosol chemical characterisation available at the Calibration centre for organic tracer and aerosol constituents (OGTAC CC).

Method and experimental set-up

8 days of experiments were conducted to focus on the reaction of alpha-pinene oxide with acidic and sulfated particles. An aqueous mixture of (either or all) H_2SO_4/Na_2SO_4/HCl was used to generate seed particles via nebulisation. The composition of this solution was modified in order to control and vary the particle acidity and the sulfate content. Experiments were run under "dry" (RH<10%) and "wet" conditions (RH~80%). At the end of each experiment, OH radicals were generated by photolysis of H_2O_2 in both chambers to mimic atmospheric oxidative particle ageing. In the second TROPOS chamber, similar experiments were conducted but using nitrated instead of sulfated particles, for a direct comparison.

Filter samples were generated in the aerosol chamber at TROPOS ACD by oxidizing alpha-pinene oxide under various conditions. Time-resolved filters were collected every 15 minutes throughout experiments. Two types of filters (i.e. PTFE and Fluoropore) were used.

Preliminary results

The following aspects will be considered during data analysis: the increase in organic mass throughout the experiments from SMPS and AMS, the consumption of alpha-pinene oxide, its fragmentation patterns under various conditions, and the formation and evolution of OS in the particle phase.

Organic mass production from MPSS

Figure 1 illustrates the organic mass production from two sets of experiments, A with sulfated seed and B with nitrated seed. In general, the mass production from nitrated seed seemed to be slightly higher than from sulfated seed. For most experiments, a long induction period could be observed, either caused by a delay in mass transfer or by the contribution of first-generation oxidation products (Ng et al., 2006).

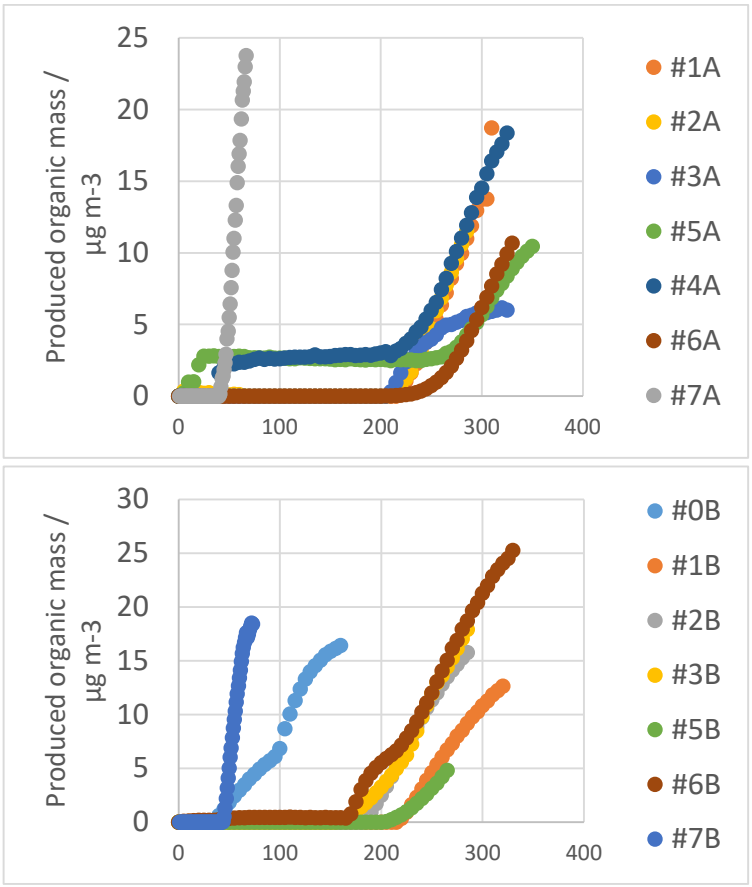

Figure 1. Evolution of organic mass during experiments set A and set B.

These results will be further evaluated by preparing yield and growth curves to gain more insights into particle growth processes.

Outcome and future studies

The main objectives of the proposed TNA activity were successfully completed. A huge set of experiments have been conducted throughout the TNA. Due to the size of the obtained data set, the analysis and data interpretation are still on-going.

In general, the findings of this project will provide new quantitative insights into organosulfate formation. The results obtained during this TNA project in combination with parallel TNA project at OGTAC CC, will solve few questions about the kinetics of OS formation. More time and work are needed to evaluate the findings of this project in combination with the huge online data set obtained during the respective TNA project at the aerosol chamber.

References

Ng, N. L., Kroll, J. H., Keywood, M. D., Bahreini, R., Varutbangkul, V., Flagan, R. C., Seinfeld, J. H., Lee, A., and Goldstein, A. H.: Contribution of First- versus Second-Generation Products to Secondary Organic Aerosols Formed in the Oxidation of Biogenic Hydrocarbons, Environmental Science & Technology, 40, 2283-2297, 10.1021/es052269u, 2006.