EUROCHAMP 2020

TNA User Report

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Project title	**Chemistry of isoprene with NO_3 under various conditions**
Name of the accessed chamber	SAPHIR
Number of users in the project	8
Project objectives (max 100 words)	Specifically we wanted to investigate/measure the following: - isoprene peroxy radicals and their termination products (including HOM peroxy radicals) - HO_2 and NO_X (NO_3) as competitor to RO_2 in termination/radical chain propagation initiated by NO_3 addition - formation and ageing of isoprene derived SOA precursors and their SOA yields and properties - hydrolysis of particulate organic (di)nitrates and analysis of remaining products
Description of work (max 100 words):	With the planned setup of FIGAERO-I-HR-TOF-CIMS, Br-HR-TOF CIMS or NO3-HR-TOF CIMS, PTR-HR-TOF-MS (VOCUS, H+/NO+) and the direct OH-LIF, HO2-LIF, RO2-LIF, cavity ring down NO3 measurements, NO3 reactivity measurements and characterization of aerosol properties we will achieve new mechanistic understanding with innovative approaches applying state of the art methodology:

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User status[3]	ACA
New user	no

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User status	PGR
New user	yes

[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 ENG= Engineer; ACA= Academic; TEC= Technician.
[4] Reproduce the table for each user who accessed the infrastructure

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[5] Reproduce the table for each user who accessed the infrastructure
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User status	ACA
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[7] 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: Mattias Hallquist
Chamber name and location: SAPHIR, Julich Germany
Campaign name and period: NO3ISOP 2018, 23/7-2018 – 28/8-2018

• Introduction and motivation

Isoprene is the most abundant BVOC and its contribution to SOA is still under debate. Therein it is especially challenging to understand the role of NOX in the nighttime chemistry. This interesting since NO_2 regulation is one the most burning issues in air pollution and health, and its success may switch the atmospheric regime from NOX to VOC control.

Recent observations of enhanced organic nitrates in the particulate phase by aircraft in nighttime power plumes suggest a new and efficient source of secondary organic aerosols (SOA). Low concentrations of other VOC candidates, e.g. monoterpenens, substituted benzenes, suggested that isoprene should be the major organic driver, while the major oxidant was supposedly the NO_3 radical. Considering these formation conditions the SOA yield for NO_3 + isoprene reactions could be much higher, up to a factor of two or more, than thought before. However, it appeared difficult to bring the phenomenon in accordance with known mechanistic expectations. To be an efficient nighttime condensing SOA former, isoprene must be oxidized twice, at each double bond, i.e. requires some atmospheric ageing. Potential oxidants are NO_3, OH, and, as a minor, O_3. If ageing occurs via NO_3, formation of dinitrates is expected, but observations point to single nitrates. Organic dinitrates could be hydrolysed in the particle phase forming multifunctional single organic nitrates, that would still reside in the particulate phase. On the other hand nitrooxy-isoprene-RO_2 have substantial lifetimes in the nighttime atmosphere and autoxidation may lead the to highly oxidized single isoprene nitrates. Moreover, highly oxygenated peroxy radicals tend to recombine to form highly oxidized accretion products in the gas-phase, e.g. HOM (highly oxygenated molecules) dimers. As a third, oligomerization reactions of first generation isoprene nitrates could have happened in an acidic particle phase.

Solving this significant discrepancies requires a) revisiting the NO_3 + isoprene gas-phase chemistry for mechanistic considerations under the limits of HO_2, RO_2 (=VOC control) and NOX control b) revisiting the isoprene SOA formation triggered by the NO_3 + isoprene system in the presence of neutral (condensation, product vapor pressures) and acidic seed aerosols (acid catalized accretion reactions).

• Scientific objectives

Specifically we wanted to investigate/measure the following:

- isoprene peroxy radicals and their termination products (including HOM peroxy radicals)
- HO_2 and NO_X (NO_3) as competitor to RO_2 in termination/radical chain propagation initiated by NO_3 addition
- formation and ageing of isoprene derived SOA precursors and their SOA yields and properties
- hydrolysis of particulate organic (di)nitrates and analysis of remaining products

• Method and experimental set-up

With the planned setup of FIGAERO-I-HR-TOF-CIMS, Br-HR-TOF CIMS or NO3-HR-TOF CIMS, PTR-HR-TOF-MS (VOCUS, H+/NO+) and the direct OH-LIF, HO2-LIF, RO2-LIF, cavity ring down NO_3 measurements, NO_3 reactivity measurements and characterization of aerosol properties we will achieve new mechanistic understanding with innovative approaches applying state of the art methodology.

• Reason for choosing the simulation chamber/ calibration facility

The large SAPIRE chamber is were suitable to hosts these large numbers of instruments and scientists. The quality of support functions covering all aspects of instrumentations and the experiments are very high. Most important is that the chamber provides opportunities to work at low concentrations, option of plant emissions and investigating the transition from night to day-time chemistry. Furthermore, the investigation of isoprene nighttime chemistry, which likely includes chemical ageing requires long observation time. Indeed, often critics on too low isoprene SOA yields in general referred to too short observation times in too small laboratory devices. As can be seen from Figure 1 all instrument could be accommodated with reasonable access to sampling lines etc.

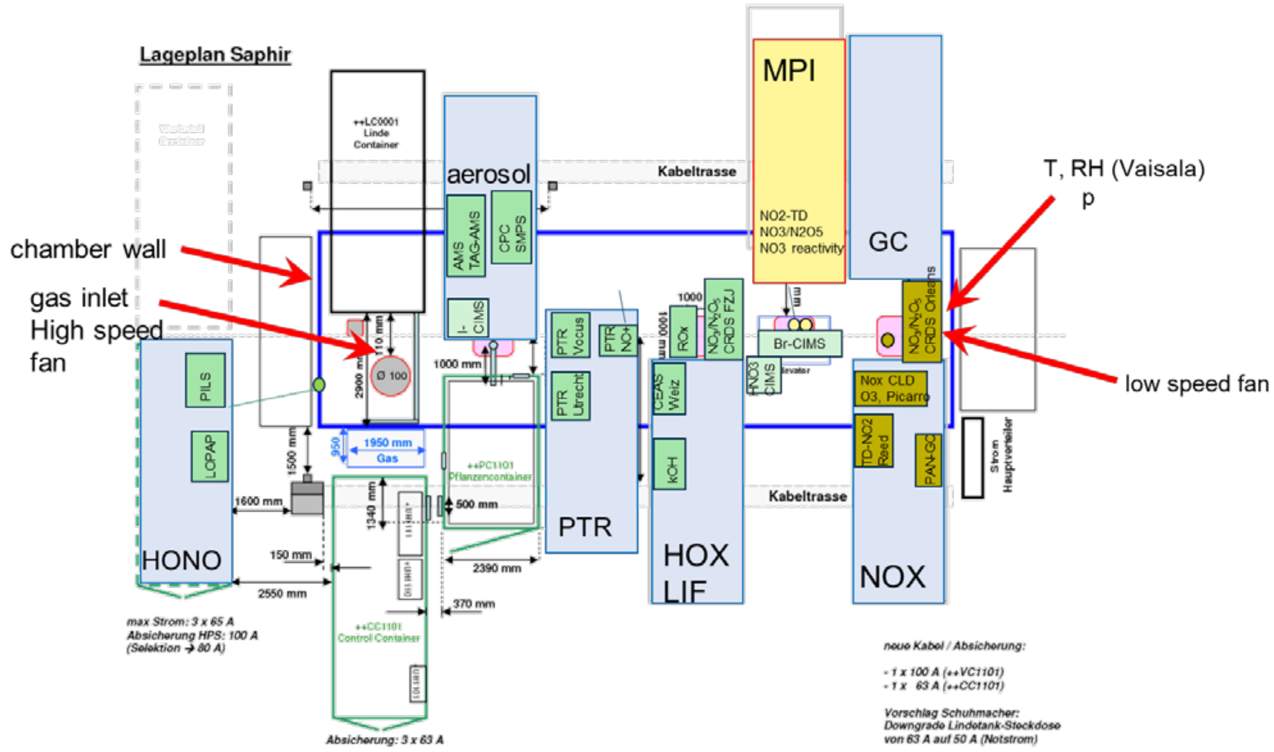

***Figure 1.** The-set up of instruments etc at the SAPHIR chamber.*

• Data description

The number of instrument creates a big and rather complex matrix of various measurements and corresponding data. We have used the Eurochamp data format to report most of our data. Final data will be made public on the Eurochamp database. We are only requesting data from users for the core of the campaign, not including calibrations and test days using the chamber before and after the core days. The current situation on preliminary data availability is shown in Table 1.

***Table 1.** Preliminary data availability. Green-data exist and quality is good; Yellow- quality unsure or data are missing; Red - no data available due to instrument had malfunction or was not in use-.*

NO3ISOP 2018	31.07	01.08	02.08	03.08	06.08	07.08	08.08	09.08	10.08	12.08	13.08	14.08	15.08	16.08	17.08	18.08	19.08	20.08	21.08	22.08	23.08	24.08
Instruments																						
NOX																						
O3																						
CO/CO2/H2O/CH4																						
Radiation																						
GC																						
PTR NO+																						
VOCUS PTR H3O+																						
ROX																						
k(OH)																						
Br CIMS																						
HONO																						

CPC																						
SMPS																						
AMS																						
TAG-AMS																						
NO3/N2O5 CRDS																						
I-CIMS																						
PTR-MS																						
CO3 CIMS																						
NO3/N2O5 CRDS																						
SCRDS AN PN																						
TDNO2																						
NO3 Lifetime	no VOC																					
TDNO2																						
NO3/N2O5 CRDS																						
PILS																						
CEAS																						

• Preliminary results and conclusions

Some selected preliminary data were presented at the Atmospheric Chemical Mechanisms meeting on Dec. 5-7-2018 in Davis, US mostly with the aim to promote the TNA activity. During a two days meeting, 21-22 January 2019, all groups presented their first findings, based on their contribution to the measurement. This enabling formation of groups that got either of two types of tasks. 1) Further data analysis or 2) a scientifically task including data interpretation and publication of results. As one can expect the complexity of the experimental matrix and the need to interact in groups could make preliminary conclusions illusive. However, to illustrate some preliminary results I-CIMS data from one experiment is presented in Figure 2.

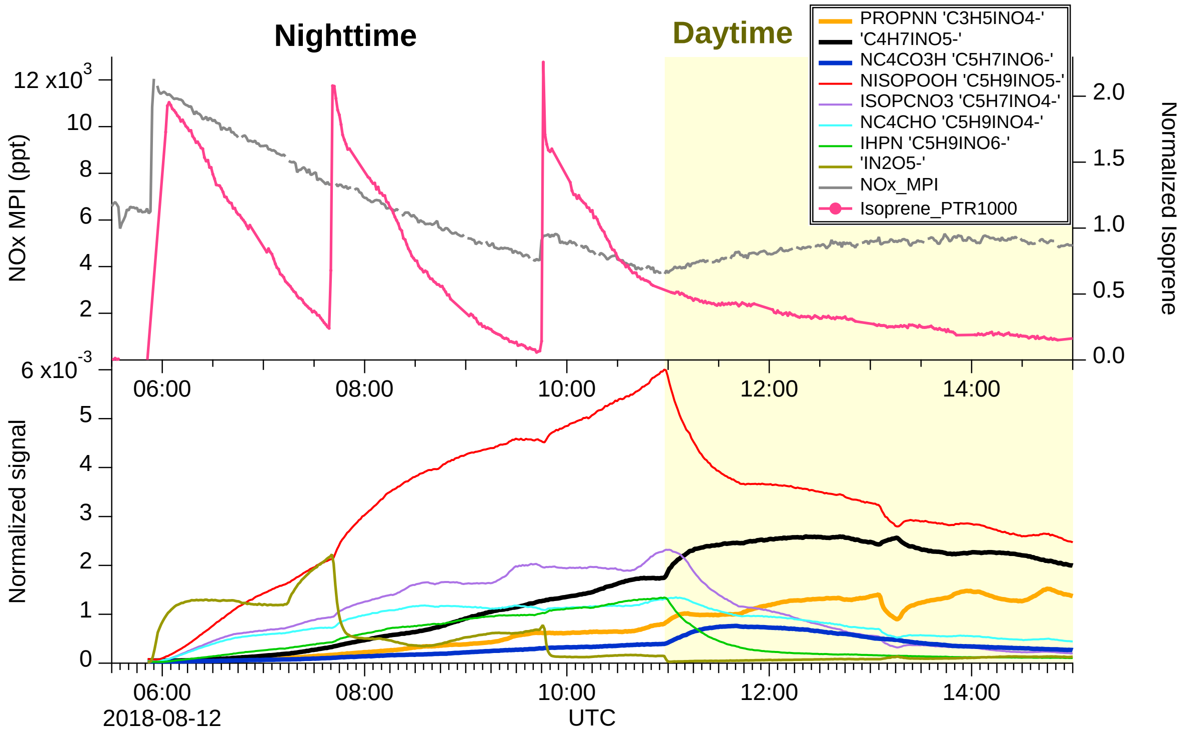

Figure 2. *Experiment with three additions of isoprene during night-time condition followed by daytime conditions initiating photochemistry of the isoprene products.*

Based on exact molecular mass and previous knowledge in suggested mechanism enabled us to assign peaks in our mass-spectra to a number of isoprene products, Figure 2 shows 7 selected products and how they are increasing while being either primary or secondary products fromnNO_3 initiated oxidation of isoprene. When the source, i.e. isoprene or NO3 is consumed the loss processes, such as chemical reaction, deposition, photolysis or dilution, becomes larger than the production terms and the signals decreases. Thus, the evolution of the observed product signal is dictated by the formation and removal processes. From these one the products can be classified and then relate to any explicit chemical mechanism. However, the detailed extraction of mechanistic data from the experiments is depending on a complex evaluation process including modelling of the chamber condition that just has been initated.

• Outcome and future studies

The next step in the evaluation, interpretation and further understanding of our data are focused on the following areas.

- Characterization of chemical composition of aerosol, gas-particle partitioning, vapour pressure of organic compounds, total organic compounds vs individual compounds
- Modelling of gas-phase chemistry, test of chemical mechanism and NO_3 reactivity
- Chemical mechanisms – Pattern analysis of product species, Quantum-chemical calculations
- Connecting field results with chamber work
- NOx linked to NOy budget including e.g. NO3 / N2O5 /HONO /HNO3 alkyl nitrates