



TNA User Report

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Project title	ISOPOOH and IEPOX photochemistry
Name of the accessed chamber	SAPHIR
Number of users in the project	4
Project objectives (max 100 words)	The goal of this project is to investigate the photochemistry of ISOPOOH and its first generation product IEPOX in separate experiments. Time series of trace gas and radical concentrations are compared to predictions by model calculations using the Master Chemical Mechanism and literature suggestions. Separate experiments were done with ISOPOOH and IEPOX to distinguish the outcome caused by RO ₂ from ISOPOOH and the oxidation of its major first-generation product IEPOX. Reference experiments looking at known chemistry ensure the quality of experiments.
Description of work (max 100 words):	The PTR of the Harvard group was installed at SAPHIR and people from Harvard were trained to do experiments at the chamber. Injection of IEPOX and ISOPOOH were done via a Liquid-Calibration-Unit (LCU) into the clean chamber in the dark. Time series of trace gases and radicals were measured during photooxidation of these species by the Harvard PTR and instrumentation provided by the host. Several reference experiments with injections of MVK, isoprene and CO were conducted to compare results from different instruments detecting the same compounds and results from model calculations.

Principal Investigator's and group's information	
First name	Frank
Family name	Keutsch
Nationality	German
Activity domain ¹	Chemistry
Home institution	Harvard University
Institution legal status ²	University
Email	keutsch@seas.harvard.edu
Gender	Male
User status ³	RES
New user	yes

User 1 Information ⁴	
First name	Alexander
Family name	Zaytsev
Nationality	Russian
Activity domain	Chemistry
Home institution	Harvard University
Institution legal status	University
Email	zaytsev@g.harvard.edu
Gender	Male
User status	PGR
New user	yes

User 2 Information	
First name	Martin
Family name	Breitenlechner
Nationality	Austrian
Activity domain	Chemistry
Home institution	Harvard-University
Institution legal status	University
Email	martinb@seas.harvard.edu
Gender	Male
User status	PDOC
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 EXP= Engineer; ACA= Academic; TEC= Technician.

⁴ Reproduce the table for each user who accessed the infrastructure

User 3 Information	
First name	Jean C
Family name	Rivera
Nationality	US
Activity domain	Chemistry
Home institution	Harvard-University
Institution legal status	University
Email	jeanrivera@g.harvard.edu
Gender	Male
User status	PGR
New user	yes

Trans-National Access (TNA) Scientific Report

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Name of the PI: Frank Keutsch

Chamber name and location: SAPHIR, Forschungszentrum Jülich GmbH

Campaign name and period: ISOPOOH and IEOPX photochemistry (10 April 2017 to 27 June 2017)

Introduction and motivation:

The understanding of the chemical transformation of organic compounds in the atmosphere is of great importance for the mitigation and prediction of air quality and of climate change. The majority of organic compounds is released by plants. Measurements in forested environments show that our current knowledge is incomplete to bring model calculations and measurements into agreement (see Review Whalley, Top. Curr. Chem, 2012). The simulation chamber SAPHIR is ideal to investigate these processes, because the chemical processes can be investigated at realistic conditions for both concentration ranges and oxidant levels. Isoprene is the most abundant biogenic organic compound (Guenther et al., Geosci. Model Dev., 2012). It is primarily oxidized by the hydroxyl radical (OH) producing organic peroxy radicals (RO₂). In biogenic environments, nitrogen oxide concentrations are typically very low, so that a large fraction of RO₂ either undergoes isomerization reactions (Peeters et al, PCCP, 2014) or reacts with hydroxyperoxy radicals (HO₂) forming isoprene hydroxy peroxides (ISOPOOH). The photochemical fate of ISOPOOH and its first-generation product IEPOX has not been investigated in detail specifically regarding radical regeneration and OH reactivity. Model calculations using the Master-Chemical- Mechanism suggest a fast reformation of OH radicals. This part of the isoprene chemistry is of particular importance for the formation of aerosol in the isoprene oxidation scheme (see for example Liu, Environ. Sci. & Technol., 2016).

Scientific objectives

The goal of this project is to investigate the photochemistry of ISOPOOH and its first generation product IEPOX in separate experiments. Time series of trace gas and radical concentrations are compared to predictions by model calculations using the Master Chemical Mechanism and suggestions in literature. Separate experiments will be done with ISOPOOH and IEPOX to distinguish the outcome caused by RO₂ from ISOPOOH and the oxidation of its major first-generation product IEPOX. In addition, the variation of chemical conditions (change of the NO concentration) will allow determining details of the fate of organic peroxy radicals which potentially reform OH by isomerization and decomposition reactions as predicted by the Master Chemical Mechanism. The direct measurements of all relevant radical species (OH, HO₂ and RO₂) and trace gases which are available in SAPHIR in combination with the quantification of organic compounds by the Harvard PTR instrument allow testing if the predictions are correct. Adjustments in the mechanism will be worked out in sensitivity studies of the model to bring measured and modelled time series in agreement, if disagreement is observed. Organic compounds are measured by several experiments applying different ionization schemes. It is explored, how results of the different instruments compare. Experiments in SAPHIR allow specifically quantifying the OH radical budget so that sources of OH can

be identified which are not included in current models. In addition, total measured OH reactivity can be compared with calculations using OH reactant measurements in order to quantify missing reactivity due to either products that cannot be detected or reactions rate constants which may not be accurately known for higher oxidized products that are formed within the oxidation chain of ISOPOOH. Results will reduce the uncertainties in current chemical models used for predictions of air pollutant concentrations.

Reason for choosing the simulation chamber

The SAPHIR chamber provides accurate radical and OH reactivity measurements that are essential for the goal of the experiments. In addition, trace gases that are relevant for the analysis of the radical budget are measured as well as organic compound that complement the capabilities of the Harvard PTR instrument.

Method and experimental set-up

All instruments were connected to sample chamber air and for each experiment initially chamber backgrounds were collected. The different precursors to be studied (both VOC and oxidant) were introduced with a Liquid Calibration Unit, allowing known amounts to be injected into the chamber. The concentrations of the precursors were however also observed with different types of instrumentation, including and especially the Harvard PTR instrument. Photooxidation was initiated by opening the chamber to introduce sunlight. The concentrations of precursors were measured as well as oxidation products, oxidants and intermediates. The PTR instrument was calibrated overnight after each experiment to ensure quality assurance and control.

Data description

The Harvard PTR recorded time series of high resolution mass spectra. The detector signal was converted to mixing ratios via calibrations for specific precursors. As not all of the many mass to charge ratios correspond to compounds for which calibrations are possible, the other compounds are being estimated using known methods using polarity and size of the species. With this approach time series of the concentrations of many species are derived.

Preliminary results and conclusions

The experiments were conducted successfully. Experiments for all target species were conducted and time traces of the precursors, their reaction products and reaction conditions, such as irradiation intensity, oxidant (OH, ozone) and other reactant concentrations (HO₂, NO, ...), and total OH reactivity were recorded.

Outcome and future studies

The analysis of the experiments, which involves working with extensive datasets, will provide new insights into the details of the overall oxidation mechanism of isoprene. This will greatly improve the understanding of how fast reactive carbon from isoprene is processed and what oxidation products are formed, especially, which ones are the most important ones for aerosol formation and reactivity. This will allow a better understanding of the impact of isoprene oxidation on the fate of reactive carbon and oxidative capacity.