EUROCHAMP 2020

TNA User Report

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Project title	**Formation and properties of secondary organic aerosol from the photooxidation of β-caryophyllene aged products**
Name of the accessed chamber	FORTH-ASC
Number of users in the project	1
Project objectives (max 100 words)	The proposed project is aimed at getting insights into the formation and properties of the aerosol particles formed through OH radical oxidation of selected β-caryophyllene SOA aged products, for example: β-caryophyllonic acid, β-norcaryophyllonic acid and β-caryophyllinic acid which are found as an important tracer compounds for β-caryophyllene secondary organic aerosol formation. Main goals of the proposed study are: (A) synthesis and purification of selected β-caryophyllene SOA aged products – as precursor compounds. (B) the OH radical-driven oxidation of selected β-caryophyllene SOA aged products using the 10 m3 FORTH/ICE-HT smog chamber, (C) physicochemical properties of fresh β-caryophyllene SOA aged products aerosol.
Description of work (max 100 words):	Synthesis of selected compounds was conducted, together with their purification. The selected compounds were introduced to the smog chamber FORTH, respectively. In first experiments chemical and physical properties were studied including: a thermodenuder, a Proton Transfer Reaction Mass Spectrometry (PTR-MS, Ionikon Analytik), an Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometry (HR-ToF-AMS) and Scanning Mobility Particle Sizer (SMPS, classifier model 3080, DMA model 3081, CPC model 3775, TSI). In the next experiments, HONO was introduced as a source of OH (UV lights are used for the HONO photolysis) and evolution of investigated compounds was studied.

Principal Investigator's and group's information	
First name	Agata
Family name	Kołodziejczyk
Nationality	polish
Activity domain[1]	Chemistry
Home institution	Institute of Physical Chemistry Polish Academy of Sciences
Institution legal status[2]	UNI
Email	agata.d.kolodziejczyk@gmail.com
Gender	female
User status[3]	PGR
New user	Yes

User 1 Information[4]	
First name	
Family name	
Nationality	
Activity domain	
Home institution	
Institution legal status	
Email	
Gender	
User status	
New user	

User 2 Information	
First name	
Family name	
Nationality	
Activity domain	
Home institution	
Institution legal status	
Email	
Gender	
User status	
New user	

[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: Agata Kołodziejczyk
Chamber name and location: FORTH-ASC, Patras, Greece
Campaign name and period: 10.06.2019 - 19.07.2019
Text:

Introduction and motivation

It is well established that exposure to ambient aerosols is associated with damaging effects on human respiratory and cardiovascular systems.[1-2] Secondary organic aerosol is formed through the oxidation of biogenic and/or anthropogenic volatile, intermediate volatility and semi-volatile organic compounds by atmospheric oxidants, including ubiquities OH (daytime) and NO_3 (nighttime) radicals. It is interesting that the global emission of biogenic volatile, which is estimated to be 500 – 1130 Tg/year, greatly exceeds emission from the anthropogenic sources that account for 100 – 150 Tg/year. The chemical analysis of ambient aerosol and/or smog chamber generated SOA showed thousands of organic compounds, of which far less than 20% was unambiguously identified.[3]

Recent studies have indicated that sesquiterpenes play an important role in the formation of SOA in the atmosphere.[4-5] The total emission of sesquiterpenes into the atmosphere is estimated to be about 29 Tg per year.[6] Sesquiterpenes were also found to have the high chemical reactivity towards atmospheric oxidants owing to the presence of unsaturated sites and complex ring architectures. The most abundant representative of the sesquiterpenes is β-Caryophyllene.[7] Consequently, the oxidation products of this compound were shown to play a significant role in the formation of SOA over boreal forests.[11] A few studies investigate the oxidation mechanisms of β-caryophyllene.[4] However, there is still a tremendous lack of the data regarding the aerosol particles formed through OH radical oxidation of selected β-caryophyllene SOA aged products.

Therefore, in order to fill the gap in the knowledge about the formation and properties of secondary organic aerosol formed by the photooxidation of β-caryophyllene aged products, we decided to conduct a series of smog chamber experiments with selected β-caryophyllene SOA aged products, for example: β-caryophyllonic acid, β-norcaryophyllonic acid and β-caryophyllinic acid. The implementation of this proposal will extend the knowledge about the formation mechanism and growth of atmospheric aerosols, which influence not only on many environmental processes but also on our health and the quality of our life.

Scientific objectives

The main objective of our experiments was to study the formation and properties of the aerosol particles formed through OH radical oxidation of selected β-caryophyllene SOA aged products. Main goals of the proposed study were: (A) synthesis and purification of selected β-caryophyllene SOA aged products – as precursor compounds, (B) execution of a series of the OH radical-driven oxidation of the above mentioned β-caryophyllene SOA aged products using the 10 m^3 FORTH/ICE-HT smog chamber, (C) determination of the properties of fresh β-caryophyllene SOA aged products aerosol, including the product volatility, density etc..

Reason for choosing the simulation chamber/ calibration facility

The FORTH-ASC facility has produced significant results in respect to the physical and chemical properties of an important markers of α-pinene aerosol, such as 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), diaterpenylic acid acetate (DTAA), terebic acid.[8] Moreover, the chamber facility operating for the last several years yielded in a number of important publications.[8-9] The most important argument for choosing the experimental location was well-equipped FORTH smog chamber (HR-tof-AMS, PT-RMS, SMPS, thermodenuder, gas monitors, etc.).

Method and experimental set-up

The indoor smog chamber facility located in FORTH is a 30 m^3 temperature controlled room. Teflon smog chamber (~10 m^3) is placed in the chamber room with aluminum coated walls and is equipped with a series of black light lamps that emit in the wavelength range between 300 and 450 nm and have the ability to simulate sunlight conditions that range from a very sunny day (JNO_2 = 0.6 min^{-1}) to a partially cloudy day (J_{NO2} = 0.2 min^{-1}). A suite of state-of-the-art instrumentation is used to follow both the gas and aerosol phase processes inside the smog chamber. To the gas-phase following instruments are used: a PTR-MS (Ionicon Analytik), an ozone monitor (API Teledyne, model 400E) and a NO_X monitor (API Teledyne, model T201), while to the aerosol phase an HR-ToF-AMS (Aerodyne Research Inc.), a Scanning Mobility Particle Sizer (SMPS, classifier model 3080, DMA model 3081, CPC model 3787, TSI) are used. Details on the instrumentation used can be found elsewhere.[10]

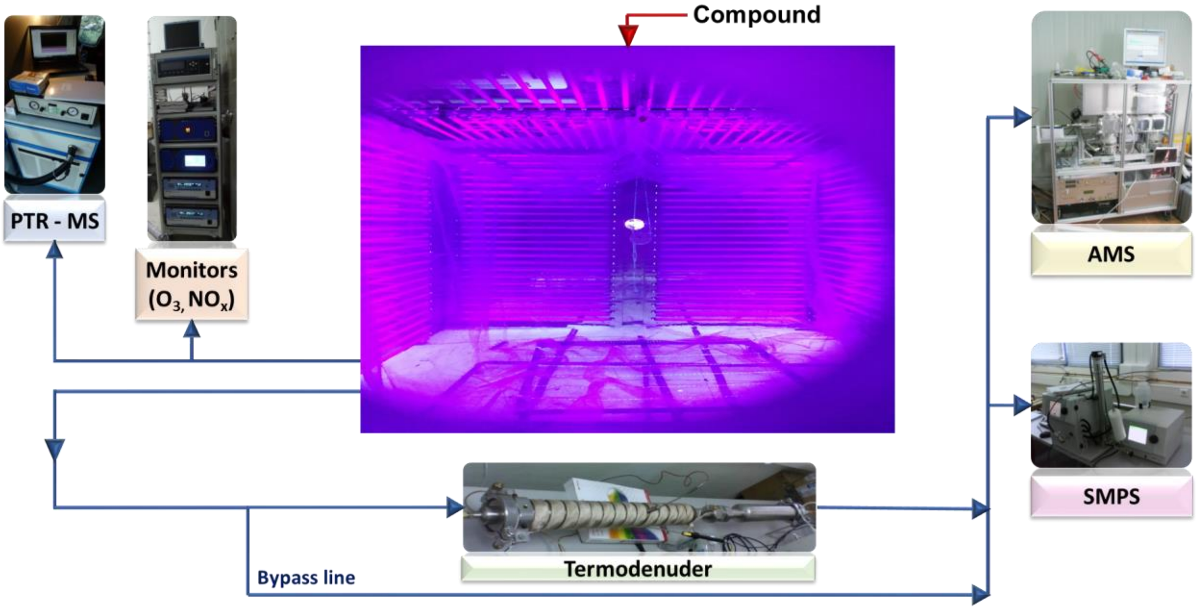


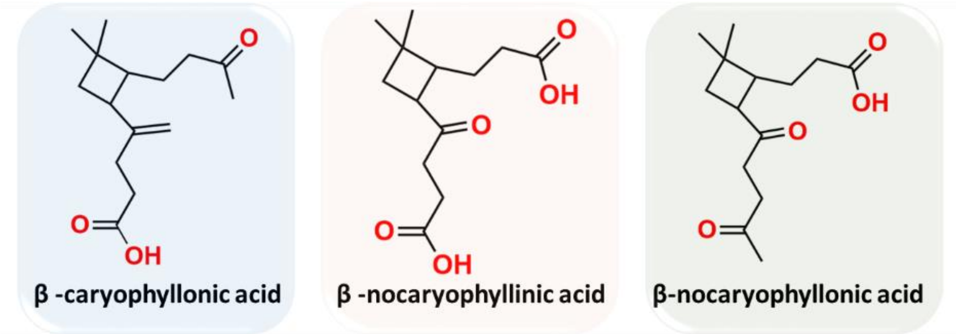
Figure 1. Scheme of the FORTH-ASC facility.

Data description

Synthesis and purification of selected β-caryophyllene SOA aged products was conducted successfully. The purity of investigated compounds was found higher than 96% for each compound. A few preliminary experiments were conducted in FORTH smog chamber. All available in LAQS group instrument were used, including a PTR-MS, an HR-ToF-AMS and a SMPS. An HR-ToF-AMS was used to examined the particulate mass (μm/m^3) and size distributions (nm), as well as the AMS mass spectra and O:C ratio of the organic mass. A SMPS was used to studied the mass (μm/m^3), number (#/cm^3) and volume of the particules (nm^3/cm^3), as well as the particules size distributions. A PTR-MS was used to measure the chemical composition in the gas-phase.

Preliminary results and conclusions

Synthesis of the β-nocaryophyllonic acid, β -caryophyllonic acid and β-nocaryophyllinic acid were carried out successfully (see structures below).



First experiments have shown that selected β-caryophyllene SOA aged products have limited solubility in water. Injection of the investigated compound to the smog chamber using an atomization of water/investigated compound solution is not an effective method for this group of compounds. Therefore, a few next tasks were focused on building the flash vaporization system to inject the studied compounds to the smog chamber. It was proven that using the flash vaporization system to inject the studied compounds to the smog chamber is effective method. The conducted experiments have provided a number of interesting data, such as the AMS mass spectra of selected β-caryophyllene SOA aged products, O:C ratio of the organic mass generated in reaction with OH radicals, as well as a number o physicochemical properties of OA enerated from investigated compounds (e.g. volatility, density).

Outcome and future studies

The presented proposal have provided new data about the formation and properties of secondary organic aerosol from the photooxidation of β-caryophyllene aged products. Obtained results will lead to better understanding of the impact of the β-caryophyllene and their aged products to the ambient SOA formation. The future work includes the conduction of a few more experiments to clarified obtained results and also publication of the crucial observations.

References

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