TNA User Report

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Project title	Oxidation of organo-silicone compounds in the atmosphere
Name of the accessed chamber	FORTH-ASC
Number of users in the project	3
Project objectives (max 100 words)	The scientific objective of the project was to probe the evolution of organosilicon compounds under different oxidative conditions, and their potential to form new particles or secondary organic aerosols.
Description of work (max 100 words):	We used the FORTH-ACS chamber at Patras for conducting a series of experiments using vapors from commonly used organosilicons under different oxidizing conditions (i.e., different concentration of OH radicals and when they are irradiated with UV light). The size distributions and chemical composition of the aerosol particles were constantly monitored during the course of the experiments in order to detect and classify potential new particle formation events and/or secondary organic aerosol formation.

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[1] *PLEASE CHOOSE ONLY ONE DOMAIN* 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

Trans-National Access (TNA) Scientific Report

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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

Instructions

Name of the PI: George Biskos
Chamber name and location: FORTH-ASC, Patras, Greece
Campaign name and period: Oxidation of organo-silicone compounds in the atmosphere (13/06/2019 - 05/07/2019).

1. Introduction and motivation

Extremely low vapor pressure organic compounds have been recognized to play an important role in the first stages of nucleation in the troposphere. Organic species containing silica molecules (e.g., siloxanes), released in the atmosphere from various industrial processes as well as from products (silicone oils, sealants, anti-foaming agents, biogas, etc.) that are widely used around the globe, have been found in the atmosphere in concentrations that vary from a few tens of ng/m^3 in remote locations (Buser et al., 2013) to a few μg/m^3 indoors (Tang et al., 2015).

The potential significance of organosilicone compounds lies in the fact that atmospheric oxidation leads to a series of product molecules of decreasing volatility, at the end of which practically zero-vapor-pressure solid particles of SiO_2 are expected. The scientific objective of this project was to probe the evolution of these compounds under different, atmospheric-relevant, oxidative conditions and observe the resulting newly formed particles. The FORTH-ACS chamber at

Patras was employed for conducting a series of experiments using vapors from the most common organosilicons under different conditions (i.e., different concentration of OH, and when they are irradiated with UV light). The scientific team operating the specific chamber has excellent experience in simulating oxidation of organic species of atmospheric relevance.

2. Method and experimental setup

The experiments conducted were divided in two main categories, namely seeded and unseeded experiments. During the unseeded experiments, the oxidation of organosilicon compounds took place in the chamber with the UV lights turned on and in the presences of OH radicals. The scope of these experiments was to test the ability of certain organosilicon compounds to cause new particle formation (NPF) upon oxidation by OH radicals, as suggested in other studies (Wu and Johnston, 2017). In addition, we conducted experiments where polydipserse ammonium sulfate particles were introduced in the chamber before the introduction of organosilicon and oxidative agent (i.e., seeded experiments). The purpose of introducing the ammonium sulfate particles was to act as condensation sink, mainly for condensing gas species (which were expected to form upon oxidation of the organosilicon compounds), thus more realistically simulating the actual atmospheric conditions. Two organosilicon compounds were used in both seeded and unseeded experiments: decamethylcyclopentasiloxane, that according to the available literature may lead to the formation of particles (Wu and Johnston, 2017), and hexamethyldisiloxane that has a lower molecular weight and higher vapor pressure. The concentrations of the OH radicals were high but realistic for photochemically active environments, and the seed concentrations were also realistic at a few micrograms per cubic meter.

It should be noted that we also conducted a blank experiment was conducted (i.e., without any organosilicon compound but with seed aerosol, oxidative agent and UV light) for verifying clean conditions in the chamber (i.e., no nucleation induced by impurities in the chamber). Aggregated information about the experiments conducted can be found in Table 1, whereas more details can be provided upon request.

Table 1: Aggregate information relevant to the organosilicon compounds used and the experiments conducted

Compound	**Seeds (Ammonium Sulfate), (μgm^{-3})**	**Organosilicon Concentration Range (ppb)**
Hexamethyldisiloxane	25	100
Hexamethyldisiloxane	80	250
Hexamethyldisiloxane	-	250
Decamethylcyclopentasiloxane	10	200
Decamethylcyclopentasiloxane	-	250
Blank	10	-

The experimental setup included the FORTH-ACS environmental chamber (12-m^3 indoor chamber with temperature control and artificial UV light), in which the organosilicon, the seed particles (for the seeded experiments only), and HONO were introduced. The latter, produces OH radicals upon illumination with UV light. The physicochemical properties of the particulate phase were probed by two scanning mobility particle sizers (SMPSs; Wang and Flagan 1989) and one high resolution, time of flight, aerosol mass spectrometer (HR-TOF-AMS; DeCarlo et al., 2006). The instruments which had a temporal resolution of 3-5 minutes, sampled continuously (during the duration of the experiments) from within the chamber at a total flow rate of ca. 2.2 Lpm. The two SMPS systems were employed for providing full cover in the size range from ca. 2.5 to 700 nm (i.e., Nano-DMA SMPS: 2.5-51.4 nm; Long-DMA SMPS: 14-700 nm) thus facilitating the detection and evolution of any NPF event.

The chemical composition of sampled aerosol particles in the range of ca. 70-1000 nm was provided by the HR-TOF-AMS, sampling at ca. 0.1 Lpm. The concentration of basic trace gases (i.e., SO_2, NO_x, NH_3) was measured at the beginning and at the end of each experiment for verifying that the chamber was clean (i.e., before starting each experiment) and for indirectly verifying the production of OH radicals, through the concentration increase of NO_x.

It should be noted here that a PTR-MS was also planned to be used in the experiments, but unfortunately this was not operational during our experiments.

For visual characterization of the fine/ultrafine aerosol particles we used Transmission Electron Microscopy (TEM) with samples collected on grids during some of the experiments. For this purpose, we employed a TEM grid sampler coupled with a vacuum pump, the flow of which was controlled via a mass flow controller.

3. Data Description

Data from both SMPS systems were merged/analyzed in order to obtain the size distribution of particles from 2.5-700 nm, aiming to detect NPF event and study its evolution through time. The data from the HR-ToF-AMS were treated in order to obtain the mass concentration of organic species in the aerosol phase, which would denote either new particles formed from the oxidation of organosilicones and/or condensation of the oxidation products on seed particles (i.e., ammonium sulfate). By combining the size distribution (i.e., SMPS data) and mass concentration of the organics (i.e., HR-ToF-AMS data) the yield of the organisilicons in forming new particles or condensing species can be accurately assessed. Data from HR-ToF-AMS regarding inorganic species were also used for detecting proper injection and evolution of inorganic seeds inside the chamber and also for verifying an inert/clean chamber during the blank experiment. Imaging data from the TEM were used for verifying the existence of ultrafine particles and for conducting individual assessment on their sizes and shapes (e.g., fractal-like particles).

4. Preliminary results and conclusions

No experimental artefacts were observed during the blank experiment. In brief all the instruments detected the injection of seed particles, while no NPF event or condensation of organic species on the seed particles were observed when the oxidative agent (i.e., HONO) was inserted and the UV lights were operational (cf. supplement for more details). Seeded experiments with both organosilicons did not exhibit any NPF event but resulted in the detection of a few sub- 15 nm particles, not forming a distribution however, as shown for example in figure 1. The existence of these particles was verified by TEM images as for instance shown in figure 2. The same experiments resulted in an increase in the detected by the HR-ToF-AMS mass of organic aerosols from ca. 0.1 to 0.8 $\mu g/m^3$, depending on the organosilicon substance (i.e., higher for the Decamethylcyclopentasiloxane) and on its initial concentration, indicating the formation of secondary organic aerosol (SOA; cf. figure 3 as an example). Most interestingly no NPF events were detected during the unseeded experiments, although some particles (i.e., not a forming a distribution and with low number concentration) were detected after the injection of the oxidative agent and the illumination of the chamber with UV light (cf. figure 4 as an example). Our results suggest that these organosilicon compounds do not contribute to NPF events at common/atmospheric relevant oxidative conditions, however part of the compounds and/or their oxidation products were detected in the aerosol phase at lower yields than the available literature suggests cf. Wu and Johnston, 2017, Janechek et al., 2019 for more details).

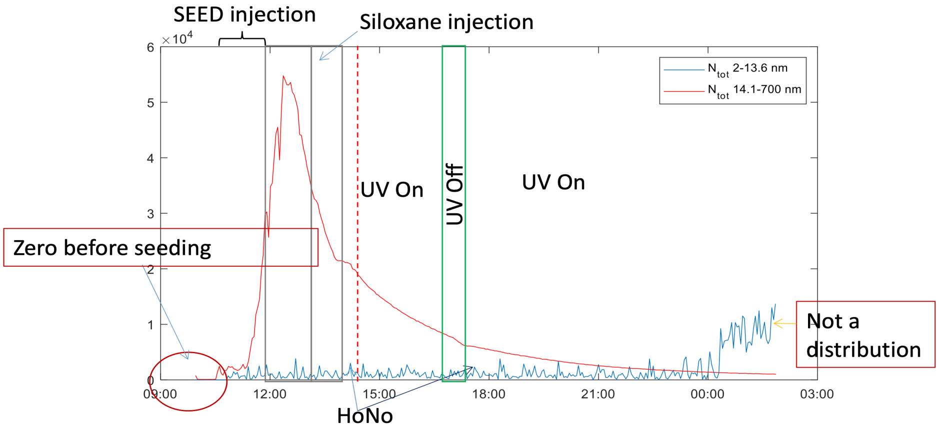

Figure 1: Number concentration of particles residing in the ranges 2-14 and 14-700 nm measured by the two SMPS systems, during a seeded experiment (80 μgr/m^3 ammonium sulfate) and 250 ppb of Hexamethyldisiloxane.

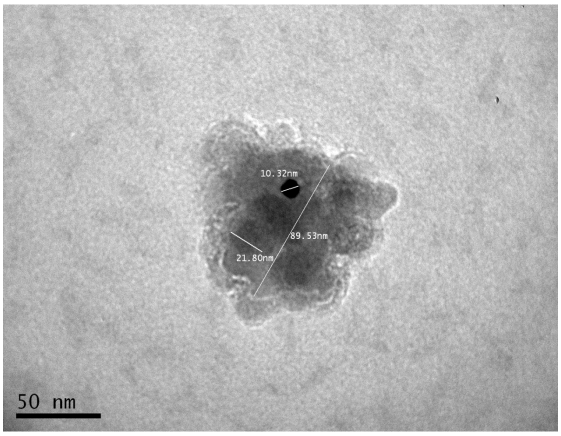

Figure 2. Image of an aggregated particle obtained by the TEM during a seeded experiment (80 μgr/m^3 ammonium sulfate) and 250 ppb of Hexamethyldisiloxane. The light shadowed aggregate probably consists of ammonium sulfate particles while a ca. 10 nm particle can be also recognized (darker in color).

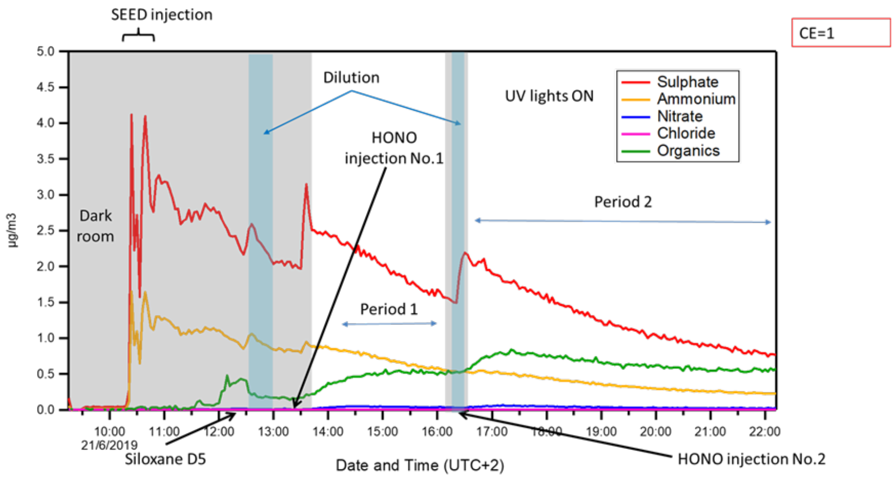

Figure 3. Mass concentration of inorganic and organic species measured by the HR-TOF-AMS during the seeded (i.e., 10 μg/m^3 of ammonium sulfate) and 200 ppb of Decamethylcyclopentasiloxane experiment.

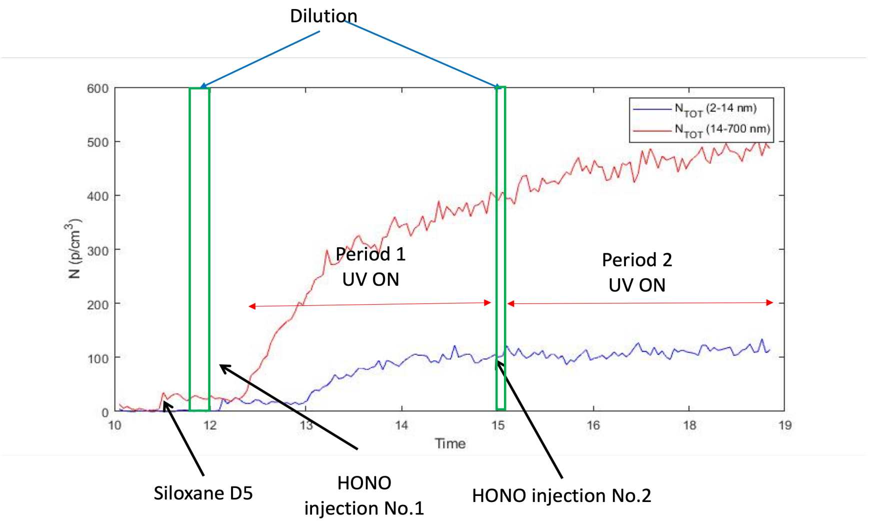

Figure 4: Number concentration of particles residing in the ranges 2-14 and 14-700 nm measured by the two SMPS systems, during an unseeded experiment with 250 ppb of Decamethylcyclopentasiloxane.

5. Outcome and future studies

Unseeded and seeded (i.e., with ammonium sulfate polydisperse aerosol particles) experiments on the oxidation of two siloxanes (namely hexamethyldisiloxane and decamethylcyclopentasiloxane) with OH radicals, at levels resembling atmospheric oxidative conditions, did not provide any evidence that these substances can act as NPF agents, while their SOA yield upon oxidation with OH radicals was limited. Our results are in contrast to similar experiments reported in the literature thus far, where substantially higher concentrations of organosilicons and oxidative agents were employed. This warrants for further investigation to explore the concentration limits above which the tested siloxanes cause NPF under typical atmospheric conditions.

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