TNA User Report

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Project title	Aerosol particle organic analytical training course
Name of the accessed chamber	OGTAC CC
Number of users in the project	2
Project objectives (max 100 words)	Project working title: Nitration of aromatic compounds under atmospheric nighttime conditions The main objective of this project was to confirm and understand dark gas-phase nitration of aromatic precursors in the absence of $NO_3^{\bullet}$ leading to secondary nitroaromatic formation in the atmosphere.
Description of work (max 100 words):	A series of chamber experiments was performed to study the reactivity of semi-volatile biomass-burning pollutant guaiacol (2-methoxyphenol) towards gaseous NOy species (NO, NO_2 and HNO_2) in the presence and absence of sodium nitrite particles under dry conditions. Experimental data collected online (NOx analyzer, NO2-CAPS, PTR-MS, SMPS) were combined with the offline analyses of adsorption tube, denuder and filter samples by GC/MS and HPLC/(-)ESI-TOFMS.

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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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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: Ana Kroflič
Chamber name and location: LEAK-LACIS, TROPOS, Leipzig, Germany
Campaign name and period: /
Text:

INTRODUCTION

Nitrated aromatic compounds are of special interest due to their atmospheric abundance and important impacts to the ecosystem and climate change. There have been strong evidences that nitrated aromatic pollutants secondarily form in the atmosphere (Wang et al. 2019 and others). In the respective paper, nighttime formation of nitrocatechols is closely related to the atmospheric aqueous phase, whereas photooxidation is the proposed pathway of other nitrophenols formation in the polluted environment.

Kroflič et al. (2015 and 2018) have extensively studied aqueous-phase nitration of aromatic precursors from biomass burning under mild conditions. In collaboration with TROPOS, they have also performed complementary LEAK Aerosol Chamber experiments to verify the results of pure laboratory studies in a multiphase system (yet unpublished data). There have been strong indications that dark gas-phase chemistry other than by $NO_3^{\bullet}$ may lead to secondary nitroaromatic formation in the atmosphere. Similar has already been speculated by Yee et al. 2013. However, additional experiments were needed to support these findings.

The aim of this study is to confirm and understand dark gas-phase chemistry leading to nitroaromatic formation in the absence of $NO_3^{\bullet}$.

METHODS

Experiments were performed in aerosol chamber LEAK. The experimental setup was different to those typically applied in such experiments (such as in the study of Yee et al. 2013). Reactive NaNO2/H2SO4 seed solution was used for the generation of aerosol in the chamber, resulting in the combination of NO, NO_2 and HONO in the gas phase (beside $NaNO_2$ particles). Blank experiments were also performed.

Online NOx, NO_2 and O_3 monitors as well as PTR-TOFMS were used to follow the concentrations of NO, NO_2, O_3 and guaiacol (GUA) as well as its cumulative nitrated products (i.e., nitroguaiacols, NG) in the chamber. Particle mass and size distribution were obtained with use of SMPS.

At the end of experiment, gaseous and particulate phases were additionally sampled for offline analysis. Tenax adsorption cartridges and glass denuders coated with XAD4 polymer were used for the offline determination of gas-phase guaiacols by GC-MC and LC-MS, respectively. Filter samples were also collected (where applicable), extracted with methanol and analyzed by LC-MS.

RESULTS

Online data collected during the original experiment are shown in Figure 1. Immediately after the injection of GUA (MM[GUA-H^+] = 125.0602), a slight increase of NO_2 and a slight decrease of NO signal are observed (interference). Following nebulization of a slightly acidic $NaNO_2/H_2SO_4$ solution pH 4.5 causes a rapid increase in NO and NO2 (note slower response of SMPS).

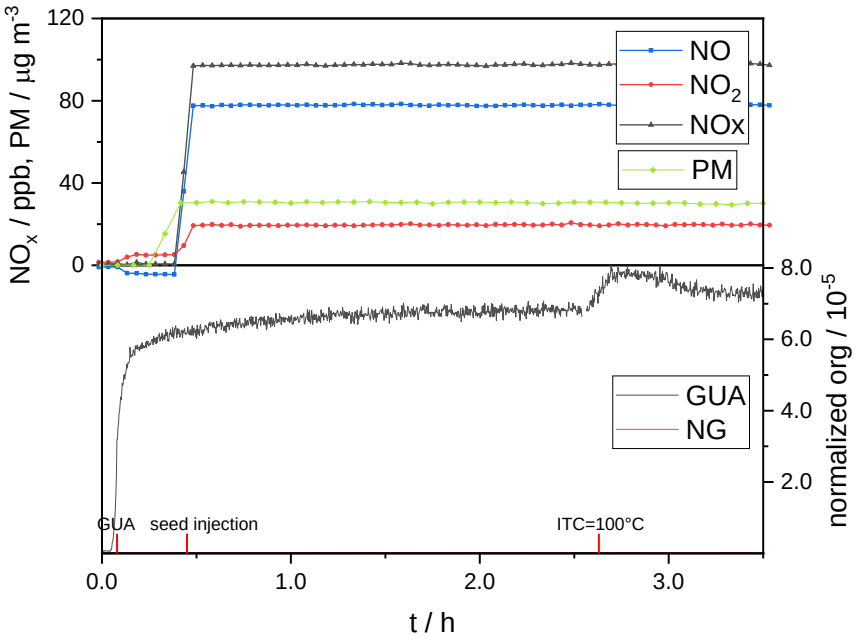

Figure 1 : online data of the original experiment – slightly acidic $NaNO_2/H_2SO_4$ seed solution was injected by nebulization producing PM mass, NO and NO_2 (and total NOx); guaiacol (GUA, normalized signal by m21) was injected in the gaseous phase and no nitroguaiacols (NG) were detected.

A disproportionation reaction is well known, especially for concentrated aqueous solutions of HNO_2 producing NO and NO_2 in equal amounts:

$$2HNO_2(aq) \rightarrow NO + NO_2 + H_2O \qquad \text{(R-1)}$$

However, the measured concentration of NO is about four times that of NO_2. Therefore, additional experiment (Figure 2) was performed simultaneously using different NOx monitors (i.e. APNA-370, Horiba and Model 42*i*-TL, Thermo Scientific) and CAPS NO_2 monitor (Aerodyne Research) to check

their interferences. As assumed, the used NOx monitors give different results for the levels of NOx species in the chamber. The cumulative concentration of NO and NO_2 (i.e. NOx signal) measured each time is about the same. However, NO and NO_2 signals seem to be interfered in both cases, presumably by HONO and/or $NaNO_2$. As CAPS determines NO_2 directly, measured APNA-370 NO_2 concentrations seem to be alright (the observed shift is due to the GUA interference, see above).

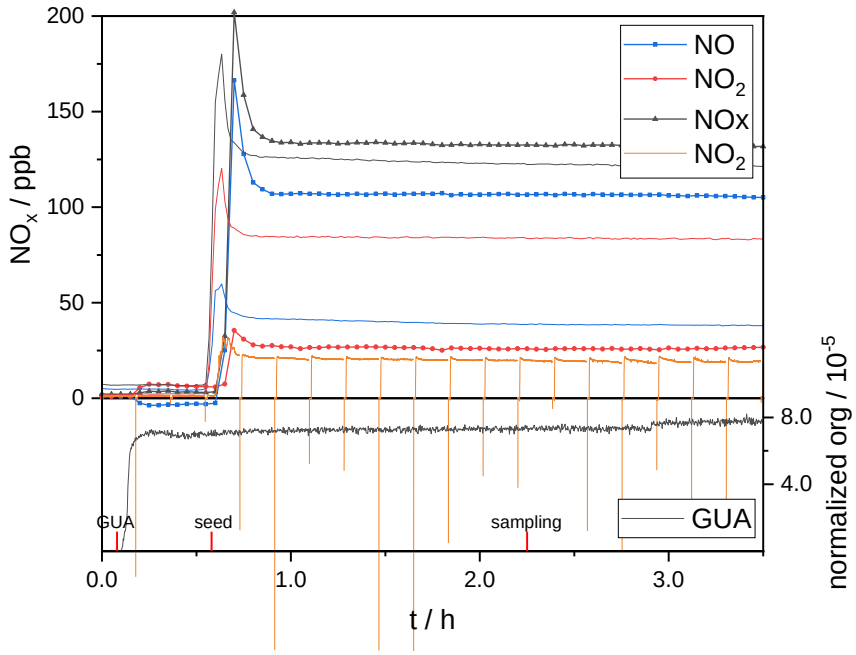

Figure 2 : the repeated experiment with additional online monitors - APNA-370 Horiba (dotted black, blue and red lines), Model 42i-TL Thermo Scientific (solid black, blue and red lines), CAPS NO_2 monitor Aerodyne Research (orange line).

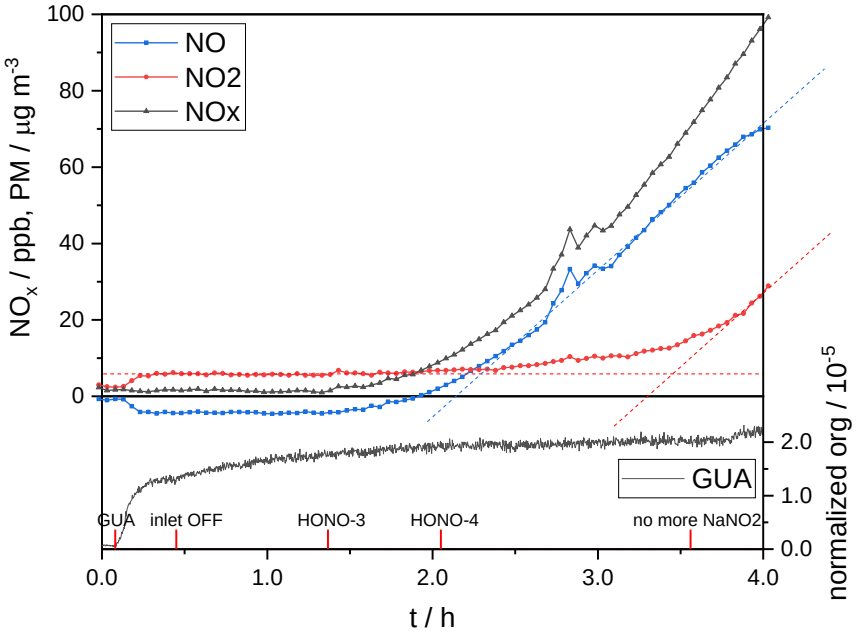

Figure 3 : HONO injection from the headspace above the solution of H_2SO_4 to which NaNO2 solution was being added dropwise.

This explanation is supported by another experiment (Figure 3), in which HONO was directly introduced in the chamber from the headspace above 1% H_2SO_4 to which 0.1% $NaNO_2$ was being added dropwise by i) 3 mL h^{-1} (HONO-3) and afterwards ii) 4 mL h^{-1} (HONO-4). No $NaNO_2$ was in the

chamber and only APNA-370 monitor was used. Initially, only NO is increasing, must be due to the interference with HONO. At the increased speed of $NaNO_2$ dropping into the acid, a slight increase in NO_2 can also be observed and it starts increasing rapidly after all $NaNO_2$ has been completely consumed. Again, comparable evolution of both nitrogen oxides is expected in this phase of experiment (due to the disproportionation reaction R-1), which is confirmed by the same slopes of NO and NO_2 traces at the end of experiment. This indicates that HONO interferes with the NO signal in APNA-370, whereas NO_2 channel gives reasonable values.

To confirm the assumed organic gas-phase chemistry leading to NG formation, the first experiment was repeated with using PM filter in the inlet of injected seed solution (Figure 4). The aim was to filter out particles and only inject gaseous species of the produced aerosol, presumably HONO. This is confirmed by the rapid increase of NO signal, while only a very tiny step in the NO_2 level can be observed. Note that both NOx monitors respond comparably this time.

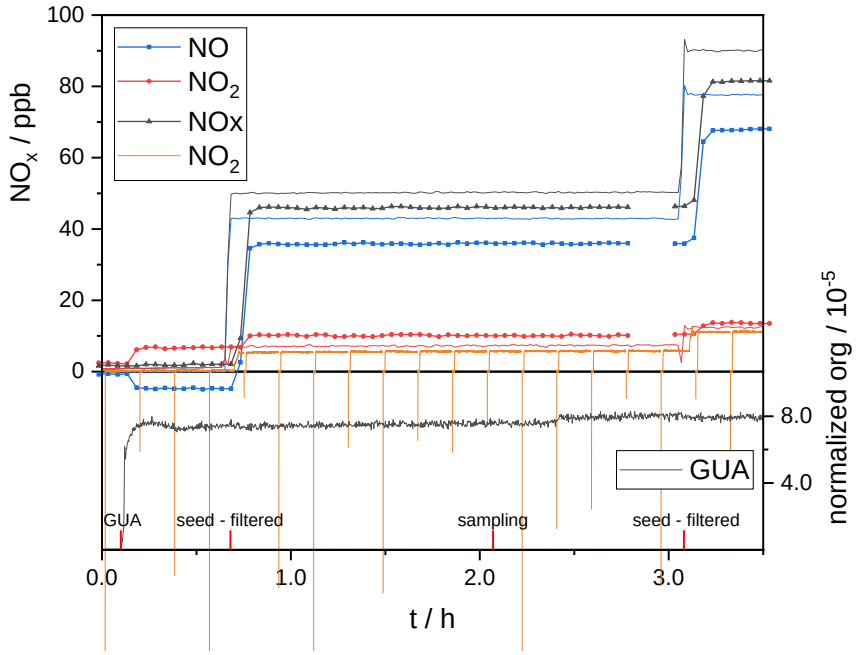

Figure 4 : the experiment without PM injected.

NG formation was observed online in neither of the experiments, although the original experiment in Figure 1 was repeated from the past when increasing MM[NG-H^+] = 170.0453 signal had been detected. Offline analyses of gas-phase products were thus also performed and showed that NG indeed formed from GUA in the presence of NO/NO_2/HONO and HONO only (with possible traces of NO/NO_2), although in very low yields (estimated in the order of a few %).

OUTCOME AND FUTURE PERSPECTIVE

It has been shown that HONO efficiently oxidizes catechol (1,2-dihydroxy benzene) in aqueous solution (Vidović et al. 2018). We now provide a strong evidence for its gas-phase oxidizing capabilities, but the extent to which it is able to react with different phenols remains a challenge for future studies, as well as the atmospheric consequences it may cause (i.e. impacts on air quality and radiative forcing).

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