



TNA User Report

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Project title	Atmospheric chemistry of unsaturated aldehydes
Name of the accessed chamber	QUAREC
Project objectives (max 100 words)	Unsaturated aldehydes are produced by a large number of plants and because of climate change and increasing stresses on vegetation, the emissions of these so-called Green Leaf Volatiles may significantly increase in the next years. The objectives of the project were to examine more deeply the atmospheric chemistry of two unsaturated aldehydes: trans-2-pentenal (T2P) and trans-2-hexenal (T2H), towards O ₃ and OH. Products and secondary organic aerosol (SOA) formation were especially investigated.
Description of work (max 100 words):	O ₃ - and OH-initiated chemistry of T2P and T2H have been investigated in the Quarec reaction chamber. The first week and half of the second one was dedicated to O ₃ chemistry (and various preliminary tests) while the rest of the second week was employed for OH chemistry. The products have been searched for using FTIR spectroscopy and on-line chemical ionization MS. Reference spectroscopic standard were used from the Quarec database as well as literature data. SOA formation have been measured by Scanning Mobility Particle Sizer.
Number of users in the project	2

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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 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: Alexandre TOMAS

Chamber name and location: QUAREC, Wuppertal, Germany

Campaign name and period: 9-20/04/2018

Text:

- Introduction and motivation

Unsaturated aldehydes belong to oxygenated volatile organic compounds (OVOCs) produced by a large number of plants like corn, tobacco, pine etc. Recent studies have shown that abiotic and biotic stress events can lead to strong emissions of unsaturated aldehydes for almost all plants; indeed, the emissions of unsaturated aldehydes are considered as a general response of plants to stress (Laothawornkitkul et al., 2009; Penuelas and Staudt, 2010). The main representative of this class of organic species is the C6 trans-2-hexenal (T2H). Because of climate change and increasing stresses on vegetation (temperature increase, drought periods, insect attacks etc.), the emissions of these so-called Green Leaf Volatiles may significantly increase in the next years and need to be taken into account in atmospheric chemistry models.

Surprisingly, the atmospheric chemistry of > C4 unsaturated aldehydes is poorly known (see review on OVOC atmospheric chemistry by (Calvert et al., 2011)). For T2H, the OH-initiated reaction is clearly the main degradation route (lifetime of about 10h) but the OH reaction products remain unknown. Davis et al. (Davis et al., 2007) suggested that nitrate organic species and dicarbonyls might be formed (without observing them), the latter being prone to photo-decompose under sunlight (impact on the radical budget). For O₃-initiated reaction, the two determinations in the literature differ by about 50% (Calvert et al., 2011) and only one

product study is available (Grosjean et al., 1996). For the C5 trans-2-pentenal (T2P), OH and O₃ reaction rate coefficients have been determined respectively twice (factor of 2 disagreement) and once, again with no data on reaction products. A better knowledge of the chemistry of these compounds is thus urgently needed.

We recently performed experiments on O₃ chemistry of T2P and T2H using a small Teflon simulation chamber and observed, for the first time, a significant formation of secondary organic aerosol (SOA) with aerosol yields of up to 14% for T2H. In the general context of inability to represent correctly the organic aerosol masses in the atmosphere, unsaturated aldehydes may constitute new precursors of SOA. Yet, much more organic aerosol (OA) masses were observed with T2H than with T2P (roughly a factor of 10). This last observation was quite surprising, since T2P and T2H have only one carbon atom difference. Reaction products were not observed. Besides, no data is available for SOA formation from OH-initiated reactions of T2P and T2P.

- Scientific objectives

The objectives of the project were thus to examine more deeply the atmospheric chemistry of T2P and T2H. The OH-initiated reaction being the major oxidation pathway of unsaturated aldehydes in the atmosphere, the OH chemistry was one of the main focuses of the project. O₃ reaction products were also investigated: indeed, although O₃ kinetics are much lower than OH ones, the O₃ initiated oxidation process may be significant in O₃ polluted areas and contribute to OA loadings. These experiments aimed also helping understanding the large differences observed in previous experiments in SOA masses between T2P and T2H.

- Reason for choosing the simulation chamber

Quarec is a middle-size simulation chamber enabling many experiments per day to be carried out, thus optimizing the experimental time. The availability of long-path IR spectroscopy and the chemical ionization mass spectrometry (CIMS) was also decisive, as well as the aerosol measurement device (SMPS).

- Method and experimental set-up

A typical experiment proceeded as follow: after evacuating the chamber for at least 30 min, synthetic air was introduced up to 760 Torr and background scans were taken (FTIR, CIMS and SMPS). The chamber was then partly pumped down to ~500 Torr and the compound injected (target concentration about 2 ppm) under a flow of air and fans on and let homogenize for about 20 min. The oxidant (O₃ or CH₃ONO+NO – OH precursor) was finally injected and, in the case of CH₃ONO, the UV-lamps were switched on. The reaction lasted from 45 min to 1.5 h. FTIR spectra (5 min time resolution) were continuously recorded together with SMPS analysis (5 min time resolution). Note that (1) the SMPS was available from 12/4 to 20/4 only; (2) CIMS analysis were only available from 9/4 to 16/4 and for short periods, since the lifetime of the filament (ionizing source) painfully reached 4 h of functioning before burning (!).

An ozone analyzer was brought from our lab to double-check the O₃ concentration measured by FTIR. DNPH and Carbotrap cartridges were also brought and samples were taken at time zero and final reaction time for almost all experiments. The cartridges are currently analyzed at IMT Lille Douai, SAGE department.

- Data description

The O₃- and OH-initiated oxidation of trans-2-pentenal and trans-2-hexenal have been investigated. 16 ozonolysis experiments (one with an OH scavenger) and 7 OH experiments were performed. FTIR and SMPS data are the main data available for all the experiments, while CIMS data are scarce due to lack of functioning of the material. Other data from HPLC and GC-MS analysis will be obtained after analysis of the samples at IMT Lille Douai.

- Preliminary results and conclusions

The decrease of the reactants due to reaction with O₃ or OH is clearly observed, as well as formation of products (FTIR analysis). For example, the glyoxal IR features have been detected in the ozonolysis of both compounds as well as the complementary primary carbonyl (propanal and butanal in the present case). The

formation of secondary organic aerosol is also observed in all experiments, confirming the first experiments carried out in our lab with significant aerosol yields.

- Outcome and future studies

All the data have to be carefully analyzed to provide rigorous and consistent results. We plan to submit a paper before the end of the year including the results obtained in our lab.

- References

Calvert, J.G., Mellouki, A., Orlando, J.J., Pilling, M.J., Wallington, T.J., 2011. The mechanisms of atmospheric oxidation of the oxygenates. Oxford University Press, New York.

Davis, M.E., Gilles, M.K., Ravishankara, A.R., Burkholder, J.B., 2007. Rate coefficients for the reaction of OH with (E)-2-pentenal, (E)-2-hexenal, and (E)-2-heptenal. Phys. Chem. Chem. Phys. 9, 2240-2248.

Grosjean, E., Grosjean, D., Seinfeld, J.H., 1996. Gas phase reaction of ozone with trans-2-hexenal, trans-2-hexenyl acetate, ethylvinyl ketone, and 6-methyl-5-hepten-2-one. Int. J. Chem. Kin. 28, 373-382.

Laothawornkitkul, J., Taylor, J., Paul, N.D., Hewitt, C.N., 2009. Biogenic volatile organic compounds in the Earth system: Tansley review. New Phytologist 183, 27-51.

Penuelas, J., Staudt, M., 2010. BVOCs and global change. Trends in Plant Science 15, 133-144.

Prof. A. TOMAS

