TNA User Report

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Project title	The formation of beta-dicarbonyls, enols, and organic acids in the photo-oxidation of gamma-dicarbonyls
Name of the accessed chamber	EUPHORE
Number of users in the project	3
Project objectives (max 100 words)	The project investigated the photo-oxidation of a number of gamma- and beta-dicarbonyls. The goals were: (i) to look at the photolysis and OH reaction rates of these dicarbonyls; (ii) to look at the formation rates and photo-oxidation of the enol products expected to be formed from these dicarbonyls. The oxidation mechanisms will be elucidated by looking at the systems under a range of different conditions and comparing the observed products.
Description of work (max 100 words):	Unsaturated carbonyl precursors were reacted with ozone (initial concentrations 500 – 1000 ppbv) to form the dicarbonyl species of interest in-situ in the chamber. 3/4 experiments were performed with each precursor under different conditions (light / dark; presence / absence of OH scavenger; presence / absence of NOx) and conditions were varied through the experiment to allow elucidation of the chemical mechanisms. Products were measured by FTIR and PTR-MS.

Principal Investigator's and group's information	
First name	Mike
Family name	Newland
Nationality	British
Activity domain[1]	Chemistry
Home institution	University of York
Institution legal status[2]	UNI
Email	mike.newland@york.ac.uk
Gender	Male
User status[3]	PDOC
New user	No

User 1 Information[4]	
First name	Beth
Family name	Nelson
Nationality	British
Activity domain	Chemistry
Home institution	University of York
Institution legal status	UNI
Email	bsn502@york.ac.uk
Gender	Female
User status	PGR
New user	Yes

User 2 Information	
First name	Andrew
Family name	Rickard
Nationality	British
Activity domain	Chemistry
Home institution	University of York
Institution legal status	UNI
Email	andrew.rickard@york.ac.uk
Gender	Male
User status	ACA
New user	No

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[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 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: Mike Newland
Chamber name and location: EUPHORE, CEAM, Valencia, Spain
Campaign name and period: The formation of beta-dicarbonyls, enols, and organic acids in the photo-oxidation of gamma-dicarbonyls (15 days – 27/5/19 – 14/6/19)
Text:

Report on "The formation of β-dicarbonyls, enols and organic acids in the oxidation of γ-dicarbonyls" - EUPHORE-005-2019

Introduction and motivation

Combined measurement and global modelling studies have identified a large missing source of formic acid to the atmosphere (Millet et al., 2014). Formic and acetic acid, the two main organic acids found in the atmosphere, are key to determining atmospheric gas phase and aqueous phase acidity, which can affect processing particularly in the aqueous phase. One potential source of formic acid is the oxidation of enols by the hydroxyl radical (OH). This pathway has been highlighted in recent work with a focus on photoisomerization of acetaldehyde to the simplest enol, vinyl alcohol (Andrews et al., 2012;

Shaw et al., 2018). However, many other potential routes to enols in the atmosphere remain largely unexplored.

β-dicarbonyls, i.e. compounds in which two carbonyl groups are present separated by one carbon, have been shown to exist predominantly in the enol form in the gas phase (Holloway et al., 2005; Zhou et al., 2008). Gas-phase equilibria of > 95% (enol:carbonyl) for 2,4-pentanedione (Holloway et al., 2005) and 60 % for 3-methyl-2,4-pentanedione (Holloway et al., 2005) have been determined. OH reacts fast ($k > 8 \times 10^{-11}$ cm^3 s^{-1}) with enols at the carbon-carbon double bond to give organic acids in high yield (e.g. Zhou et al., 2008; So et al., 2014).

Sources of β-dicarbonyls to the atmosphere include photo-oxidation of γ-dicarbonyls (and larger dicarbonyls), both via photolysis (Norrish Type I process), and OH reaction. The γ-dicarbonyl 4-oxo-pentanal has been identified as a major VOC in indoor air, coming from the ozonolysis of squalene on human skin (Wisthaler and Wechsler, 2010). Other major sources of the β-dicarbonyls proposed for study here include: photo-oxidation of the 'green leaf volatile' cis-3-hexenal, released by plants in response to wounding; and the hydroperoxyaldehyde compound, HPALD1, formed in isoprene photo-oxidation which has been predicted to yield the β-dicarbonyl 3-oxo-butanal (Wennberg et al., 2018).

To the authors' knowledge there is only one study looking at the equilibration time of a β-dicarbonyl / enol system in the gas phase: Holloway et al. (2005) determined the equilibration time of 3-methyl-2,4-pentanedione to have a half life of 10 hours, a rate of ~2 x 10^{-5} s^{-1} – this is competitive with the expected rate of [OH] reaction / photolysis of the β-dicarbonyl in the atmosphere.

Scientific Objectives

This project aimed to determine (i) the atmospheric fate of the γ-dicarbonyls: butanedial and 4-oxo-pentanal (i.e. photolysis rates and products, and OH reaction rates and products); and (ii) the fate of the β-dicarbonyls / enols formed during oxidation of butanedial and 4-oxo-pentanal, namely 3-oxo-butanal, and propanedial (i.e. OH reaction rates and products, rate of conversion to enol, fate of enols).

The chemistry of enols is currently almost entirely absent from atmospheric mechanisms – e.g. MCMv3.3.1. We aimed to determine formation rates of enols from β-dicarbonyl isomerisation and their oxidation pathways and products, to determine the importance of these processes in the atmosphere and to include them in future versions of atmospheric mechanisms.

Method and Experimental setup

The work was performed at the EUPHORE chamber, Valencia.

Neither the γ-dicarbonyls nor the β-dicarbonyls used in this study could be purchased directly. We used a novel approach – making use of gas phase ozonolysis of available precursors to create these species in-situ in the chamber. The basic formation mechanism of primary carbonyl products from ozonolysis is well understood. From ozonolysis of non-symmetrical alkenes, two primary carbonyls are formed with a sum yield of 1. So, although calibrated FTIR spectra do not exist for the γ-dicarbonyls or β-dicarbonyls, we could determine the yield of the unknown carbonyl by measuring the yield of the known carbonyl.

The first set of dark ozonolysis experiments (performed in the presence of an OH scavenger) thus allowed the determination of calibrated FTIR spectra for the two γ-dicarbonyls: butanedial and 4-oxo-pentanal; and the two β-dicarbonyls: 3-oxobutanal and propanedial.

To determine photolysis products of the dicarbonyls, when the alkene has been consumed, NO was added to the chamber (to ensure conversion of peroxy radicals to alkoxy radicals) and the chamber was opened.

To determine OH reaction products of the dicarbonyls, experiments were performed without an OH scavenger. The major product of the OH + alkene precursor was the dicarbonyl (the same as for ozonolysis). When the alkene had been consumed, NO and an OH tracer were added to the chamber, and the chamber was opened.

To determine the rate of dark isomerisation of the β-dicarbonyls to the enols, experiments were performed with the chamber left dark for several hours, followed by opening the chamber to monitor the isomerisation rate in sunlight.

Reaction rates of enols with OH determined from a similar set of experiments, adding NO and an OH tracer to the chamber after several hours in the dark and then opening the chamber.

Hydrocarbon, carbonyl and enol products were detected with FTIR and PTR-MS. O_3 was monitored by UV absorption monitor and FTIR. The EUPHORE chamber is outdoors and hence provides photolysis rates directly relevant to the atmosphere. Initial concentrations of alkene precursors and ozone were 400 – 1000 ppbv. RH was < 10 %.

Preliminary results

Three unsaturated carbonyl systems were explored in detail: cis-3-hexenal, cis-4-heptenal, and 6-methyl-5-hepten-2-one. The ozonolysis of the precursors produced the species of interest: propanedial, butanedial, and 4-oxo-pentanal respectively.

The final data is still being processed. Preliminary FTIR data is presented in this report. The data has not been corrected for chamber dilution effects.

Figure 1 shows measurements from an experiment on 4/6/19 in which ~ 500 ppbv O_3 and of cis-4-heptenal was added to the chamber, in the presence of 1000 ppbv of CO as an OH scavenger. Figure 2 shows a model fit to the ozone loss, using k(cis-4-heptenal+O_3) = 7.5×10^{-17} cm^3 s^{-1}. The data is not currently corrected for dilution, or the minor reaction of the alkene with OH. This correction will be available when the time profiles of the SF_6 tracer added to the chamber becomes available from the FTIR measurements.

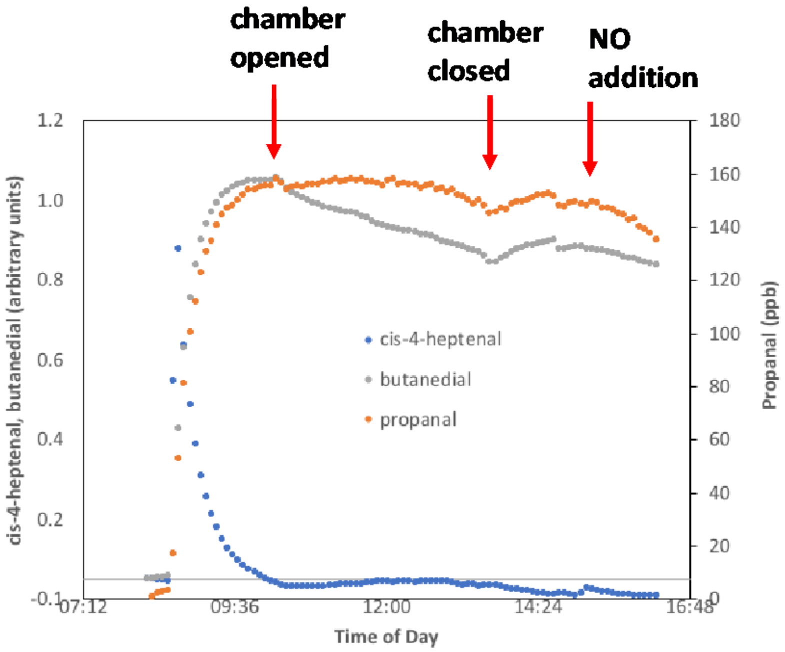

Figure 1: Preliminary measurements of the primary products butanedial and propanal during ozonolysis of cis-4-heptenal performed on 4/6/19.

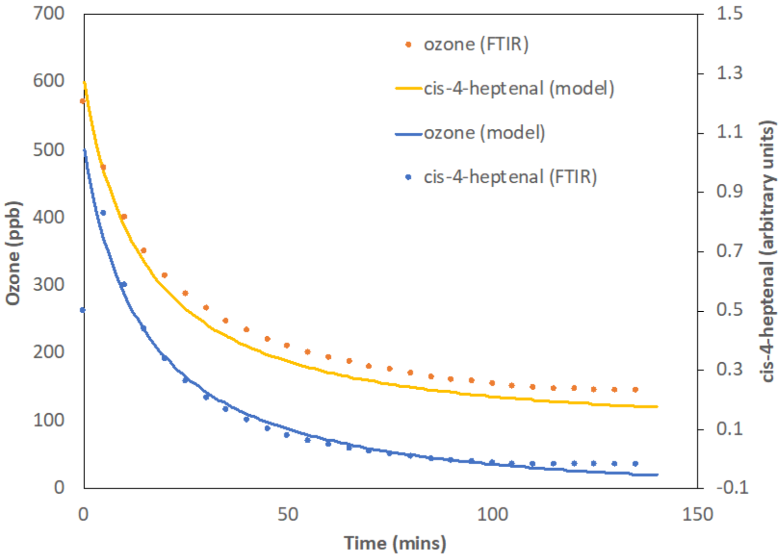

Figure 2: Preliminary modeling of the ozonolysis of cis-4-heptenal performed on 4/6/19 using a reaction rate of *k*(cis-4-heptenal+O_3) = 7.5x10^{-17} cm^3 s^{-1}.

Analysis

Photolysis and OH reaction rates of the two γ-dicarbonyls: butanedial and 4-oxo-pentanal; and the two β-dicarbonyls: 3-oxobutanal and propanedial will be determined from FTIR and PTR-MS measurements.

Box modelling, using the AtChem2 model combined with mechanisms from the MCM, will be used to constrain the intermediate chemistry of products that cannot be measured such as hydroperoxides.

Outcome and future studies

The campaign was successful with all of the planned experiments achieved during the 15 day period. The data is currently being processed by the team at EUPHORE and hence is not yet available. However, preliminary PTR-MS data and some FTIR data is available.

Analysis of the data will be performed and analysed by the University of York (UoY) staff with the support of the permanent EUPHORE staff. The data will be analysed and written into a publication in a high impact peer review journal by UoY with support from EUPHORE.

The modelling of the results will inform the mechanisms in the MCMv3.3.1 (Master Chemical Mechanism – Jenkin et al., 1997).

The results of this campaign will hopefully highlight currently undescribed chemistry pointing the way toward future areas of study.

References

Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, Atmos. Environ., 31, 81–104, 1997.

Andrews, D. U., Heazlewood, B. R., Maccarone, A. T., Conroy, T., Payne, R. J., Jordan, M. J., and Kable, S. H.: Photo-tautomerization of acetaldehyde to vinyl alcohol: a potential route to tropospheric acids, Science, 337, 1203-1206, 2012.

Millet, D. B., Baasandorj, M., Farmer, D. K., Thornton, J. A., Baumann, K., Brophy, P., Chaliyakunnel, S., de Gouw, J. A., Graus, M., Hu, L., Koss, A., Lee, B. H., Lopez-Hilfiker, F. D., Neuman, J. A., Paulot, F., Peischl, J., Pollack, I. B., Ryerson, T. B., Warneke, C., Williams, B. J., and Xu, J.: A large and ubiquitous source of atmospheric formic acid, Atmos. Chem. Phys., 15, 6283–6304, https://doi.org/10.5194/acp-15-6283-2015, 2015.

Shaw, M. F., Osborn, D. L., Jordan, M. J. T., and Kable, S. H.: Infrared Spectra of Gas-Phase 1- and 2-Propenol Isomers, J. Phys. Chem. A, 121, 3679–3688, 2017.

Holloway, A. L., Treacy, J., Sidebottom, H., Mellouki, A., DaeÏe,V., LeBras,G., and Barnes, I.: Rate coefficients for the reactions of OH radicals with the keto/enol tautomers of 2, 4-pentanedione and 3- methyl-2, 4-pentanedione, allyl alcohol and methyl vinyl ketone using the enols and methyl nitrite as photolytic sources of OH. J. Photochem. Photobiol. A., 176, 183-190, 2005.

Zhou, S., Barnes, I., Zhu, T., Bejan, I., Albu, M., and Benter, T.: Atmospheric chemistry of acetylacetone. Environ. Sci. Technol., 42, 7905–7910, 2008.

So, S., Wille, U., and da Silva, G.: Atmospheric Chemistry of Enols: A Theoretical Study of the Vinyl Alcohol + OH + O_2 Reaction Mechanism, Environ. Sci. Technol., 48, 6694-6701, 2014.

Wennberg, P. O., Bates, K. H., Crounse, J. D., et al.: Gas-phase reactions of isoprene and its major oxidation products, Chem. Rev., 118, 3337-3390, 2018.

Wisthaler, A., and Wechsler, C. J.: Reactions of ozone with human skin lipids: Sources of carbonyls, dicarbonyls, and hydroxycarbonyls in indoor air, Proc. Nat. Acad. Sci. USA, 107, 6568-6575, 2010.