



TNA User Report

*The completed and signed form below should be returned by email to
eurochamp2020@lisa.u-pec.fr*

Project title	The impact of structure on the stabilisation yields of atmospherically important Criegee Intermediates from alkene ozonolysis
Name of the accessed chamber	EUPHORE
Number of users in the project	3
Project objectives (max 100 words)	The project investigated the effect of the size and structure of the carbonyl co-product on the stabilisation of two SCI: CH ₂ OO, formed from all terminal alkenes; and (CH ₃) ₂ COO, likely one of the most abundant SCI in the atmosphere owing to its numerous sources and slow reaction rate with water (e.g. Vereecken et al., 2017). A systematic set of experiments on a homologous series of alkenes that produce these two SCI was performed.
Description of work (max 100 words):	Two experiments were performed for each alkene. In the first, the alkene (400 / 800 ppbv) and ozone (500 / 1000 ppbv) were added to the chamber in the dark. These experiments were then repeated in the presence of SO ₂ (~ 1800 ppbv), in order to scavenge any SCI produced. The difference in product yields between the two experiments was used to determine the stabilisation of each SCI produced. VOC products were determined mainly by FTIR. SO ₂ and O ₃ abundance were measured using conventional fluorescence UV absorption monitors respectively.

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

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

*The completed and signed form below should be returned by email to
eurochamp2020@lisa.u-pec.fr*

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 impact of structure on the stabilisation yields of atmospherically important Criegee Intermediates from alkene ozonolysis (13 days – 2/7/18 – 18/7/18)

Text:

Introduction and motivation

The reactions of alkenes with ozone (both ubiquitous throughout the tropospheric boundary layer and indoor environments) produce Criegee intermediates (CI). These short lived reactive species are an important non-photolytic source of radicals, including OH, can act as atmospheric oxidants, and participate in aerosol formation.

CI are produced together with a carbonyl co-product, from decomposition of the energy-rich primary-ozonide (POZ), formed in the initial ozonolysis reaction. The CI population is formed with a broad energy distribution: a fraction is formed chemically activated (CI*); another fraction is formed stabilised (SCI) (i.e. without enough internal energy to undergo prompt decomposition). A fraction of the initial CI* are then collisionally stabilised to add to the SCI population.

Total SCI yields have been determined for a number of alkenes. However, there is no apparent trend across size or structure of the parent alkene. Theoretical calculations have predicted that the stabilisation of a particular CI may increase with the size of the carbonyl co-product, because the larger the carbonyl, the more degrees of freedom it has to absorb the excess energy from the initial ozonolysis reaction, thus the lower the mean energy of the CI population (e.g. Vereecken and

Francisco, 2012). This hypothesis is tentatively confirmed by experiments on the ozonolysis of isoprene (Nguyen et al., 2016) and beta-pinene (Winterhalter et al., 2000), which suggest that CH₂OO Cl may be being formed close to 100 % stabilised in these systems, whereas the stabilisation yield of CH₂OO from ethene ozonolysis is ~40%.

Scientific Objectives

The EUPHORE chamber was used to investigate the effect of the size and structure of the carbonyl co-product on the stabilisation of three SCI: CH₂OO, formed from all terminal alkenes; and (CH₃)₂COO, likely one of the most abundant SCI in the atmosphere owing to its numerous sources and slow reaction rate with water (e.g. Vereecken et al., 2017). A systematic set of experiments on a homologous series of alkenes that produce these two SCI was performed.

In a second set of experiments, we aimed to determine the relative yields and stabilisation yields of *Z*- and *E*-CH₃CHOO in the ozonolysis of a series of 2-alkenes. These two isomeric forms of CH₃CHOO are expected to have different fates in the atmosphere owing to their very different reactivities (Sheps et al., 2014). These results may be more widely applicable to all systems forming mono-substituted Cl.

These experiments will provide, for the first time, systematic measurements of speciated Cl stabilisation yields (from non-symmetrical alkenes), crucial to accurately modelling the impacts of alkene ozonolysis chemistry in the atmosphere. Current models generally assume a fixed yield for a given Cl, based on the yield from its symmetrical parent alkene. If the stabilisation yields increase with carbonyl co-product size, this assumption would lead to underestimations of atmospheric concentrations of the Cls studied here of around a factor of three.

The results will enable the development of a structure activity relationship (SAR) which will allow a more accurate determination of stabilisation yields for all Cl. The resultant SAR will be made available to the community and incorporated into the MCM/GECKO-A automatic mechanism generator. This will greatly improve our ability to model the global effects of alkene ozonolysis chemistry on atmospheric composition and climate.

Method and Experimental setup

The experiments were performed at the EUPHORE chamber between 2/7/18 and 18/7/18.

The first set of experiments examined the stabilisation of CH₂OO and (CH₃)₂COO when formed from a range of different alkenes. Two experiments were performed for each alkene: firstly with no added SO₂, and secondly in the presence of 2000 ppbv of SO₂ to act as an SCI scavenger. At this mixing ratio, the SO₂ was calculated to scavenge >94% of (CH₃)₂COO and >99% of CH₂OO. The SO₂+SCI reaction has been shown to produce carbonyl+SO₃ in unit yield.

A list of the EUPHORE experiments performed are given in Table 1:

Date	Alkene	[Alkene] ₀ / ppb	[O ₃] ₀ / ppb	[SO ₂] ₀ / ppb
03/07	Myrcene	400	500	0
03/07	1-Heptene	800	1000	0
03/07	Myrcene	ca. 800	500	2000
03/07	1-Heptene	800	1000	2000
04/07	Cis-2-butene	400	500	0
04/07	Isobutene	800	1000	0
04/07	Cis-2-butene	400	500	2000
04/07	Isobutene	800	1000	2000
05/07	TME	400	500	0
05/07	2,4-Dimethyl-2-pentene	400	500	0
06/07	Trans-2-butene	400	500	0
06/07	Trans-2-butene	400	500	500
06/07	Trans-2-butene	400	500	1500
06/07	Trans-2-butene	400	500	500
09/07	2,3,4-Trimethyl-2-pentene	400	500	0
09/07	Propene	800	1000	0
09/07	2,3,4-Trimethyl-2-pentene	400	500	1800
09/07	Propene	800	1000	1800
10/07	2-Methyl-2-butene	400	500	0
10/07	Styrene	800	1000	0
10/07	2-Methyl-2-butene	400	500	1800
10/07	Styrene	800	1000	1800
11/07	Trans-2-pentene	400	500	0
11/07	2-Methyl-1-butene	800	1000	0
11/07	Trans-2-pentene	400	500	1800
11/07	2-Methyl-1-butene	800	1000	1800
12/07	Cis-2-pentene	400	500	0
12/07	\beta-pinene	800	1000	0
12/07	Cis-2-pentene	400	500	1800
12/07	\beta-pinene	800	1000	1800
13/07	Isobutene	800	1000	1800
13/07	TME	400	500	4500
13/07	TME	400	500	1800
13/07	TME	400	500	9000
16/07	Isobutene	800	1000	4500
16/07	Ethene	800	1000	1800
17/07	Cis-2-hexene	400	500	0
17/07	1-Heptene	800	1000	1800
17/07	Cis-2-hexene	400	500	1800
17/07	2-Methyl-2-butene	800	1000	4500
18/07	Myrcene	800	500	0
18/07	Propene	800	1000	0
18/07	Myrcene	800	500	1800
18/07	Trans-2-butene	400	500	9000

Table 1. Ozone + alkene experiments carried out in EUPHORE in July 2018

The difference between the measured carbonyl yields in the excess SO₂ and zero SO₂ experiments generally represents the total amount of SCI formed. The stabilisation of each individual CI is then its SCI yield divided by its CI yield (i.e., 1 - carbonyl co-product yield). For certain systems (e.g. propene), the smaller carbonyl is expected to also be formed as a decomposition product of the larger CI, hence the measured smaller carbonyl at zero SO₂ is not representative of the primary carbonyl yield. However, this can still be determined as (1 - larger carbonyl yield). The sum of the two determined SCI yields using the method above will also be compared to the total SCI yield determined from SO₂ vs. O₃ loss rates (as done in Newland et al., 2015a,b).

The second set of experiments were performed to determine the relative yields and stabilisation of *Z*- and *E*-CH₃CHO from the ozonolysis of a range of 2-alkenes (*Z*-but-2-ene, *E*-but-2-ene, *Z*-pent-2-ene, *E*-pent-2-ene, and *E*-hex-2-ene). The total stabilised yield of each isomer will be constrained from both measurements of the changing yield of products, and the changing loss rate of SO₂. The [*Z*-CH₃CHO]* yield will be determined by the ratio of measurements of the expected decomposition products, glyoxal and glycolaldehyde, under zero SO₂ and excess SO₂. The [*E*-CH₃CHO]* yield, from total CI* yield - [*Z*-CH₃CHO]* yield.

The ozonolysis experiments were all performed in the dark, reducing the effects of wall photochemistry, and dry (< 1% RH). They were performed with excess cyclohexane as an OH scavenger (to minimise effects of OH + alkene chemistry). Initial concentrations of alkene and ozone were 400 – 1000 ppbv. Hydrocarbon precursors and carbonyl products were detected with FTIR and PTR-MS. SO₂ and O₃ were monitored by conventional fluorescence and UV absorption monitors respectively.

Results

Eighteen different alkene systems were explored. Six of these produced CH_2OO (propene, iso-butene, 2-methyl-but-1-ene, 1-heptene, beta-pinene, styrene), six produced $(\text{CH}_3)_2\text{COO}$ (iso-butene, 2-methyl-2-butene, 2,3-dimethyl-but-2-ene, 2,4-dimethyl-2-pentene, 2,3,4-trimethyl-2-pentene, myrcene), and seven produced CH_3CHOO (propene, *Z*-but-2-ene, *E*-but-2-ene, *E*-pent-2-ene, *Z*-pent-2-ene, *Z*-hex-2-ene, 2-methyl-2-butene).

The final data is still being processed. Preliminary O_3 and SO_2 data is presented in this report. The data has not been corrected for chamber dilution effects.

Figure 1 shows the SO_2 and O_3 measurements from an experiment on 3/7/18 in which ~ 1000 ppbv O_3 and ~ 1900 ppbv of SO_2 was added to the chamber. A model fit to the ozone loss, using $k(\text{iso-butene}+\text{O}_3)$ from the MCMv3.3.1 (mcm.leeds.ac.uk/MCM), is also shown. The model slightly underestimates ozone loss but this is to be expected as the data is not currently corrected for dilution. 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 2 shows the relationship between change in SO_2 and change in O_3 during the experiment shown in Figure 1. The gradient of this plot gives the total SCI yield from iso-butene (Equation E1).

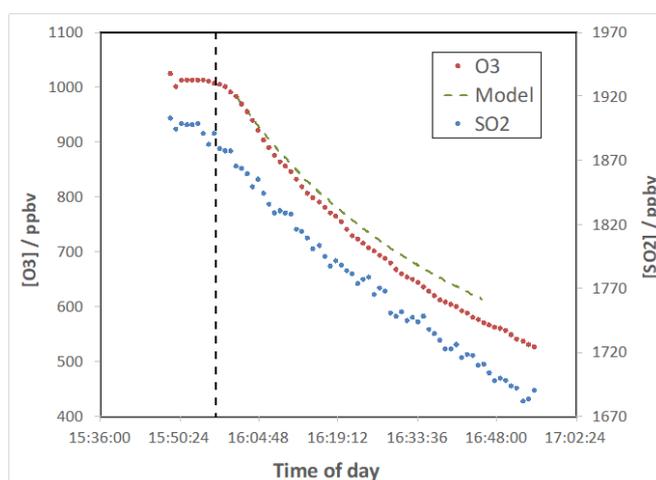


Figure 1: Preliminary O_3 (red) and SO_2 (blue) measurements with time during ozonolysis of iso-butene performed on 3/7. O_3 measurements are compared to model output (green dashed line) using $k(\text{iso-butene}+\text{O}_3)$ from the MCMv3.3.1.

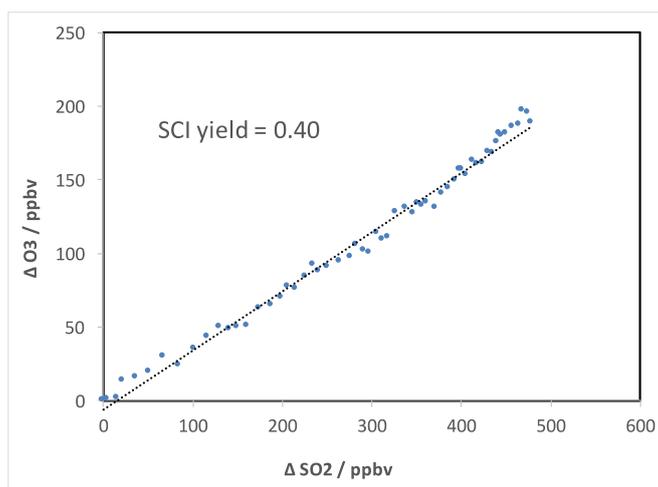


Figure 2: Loss of SO₂ against loss of O₃ from the same experiment as shown in Figure 1. The gradient of the plot gives the total SCI yield (Equation E1).

Analysis

The change in concentration of O₃ and SO₂ allows for the determination of the total SCI yield, ϕ_{SCI} , formed from the ozonolysis of each alkene. The CI* will quickly decompose or stabilise by loss of energy through collisions. All SCIs are thought to react with SO₂ only in dry conditions, producing a range of products. Thus, we can use both the loss of SO₂, along with the change in ozone to determine the yield of SCIs formed, where f is the fraction of SCIs scavenged by the SO₂ (>94% of (CH₃)₂COO and >99% of CH₂OO for the conditions employed) (Equation E1).

$$\frac{\Delta SO_2}{\Delta O_3} = f \cdot \phi_{SCI} \quad (E1)$$

For the alkenes producing CH₂OO or (CH₃)₂COO, the difference in measured concentration-time profiles of products between the zero and high SO₂ runs will reveal how much of each specific CI formed in the ozonolysis reaction was stabilised.

For a given 2-alkene, comparing the measured concentration-time profiles of products, will reveal the amount of the chemistry that has proceeded via either the vinylhydroperoxide mechanism or the 'hot acid' mechanism. This provides information on the Z:E CI ratio from the initial alkene ozonolysis.

Outcome and future studies

The campaign was successful with all of the planned experiments achieved during the 13 day period. The raw measurement data is currently being processed by the team at EUPHORE and hence is not yet available. However, preliminary data for O₃ and SO₂ measured and recorded during the campaign suggest that the experiments worked as planned.

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. Modelling of the results will inform the mechanisms in future updated versions of the MCM (Master Chemical Mechanism – Jenkin et al., 1997). The results of this campaign will hopefully highlight trends in CI stabilisation that will allow further development of the current ozonolysis SARs.

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.
- Newland, M. J., Rickard, A. R., Alam, M. S., Vereecken, L., Muñoz, A., Ródenas, M., and Bloss, W. J.: Kinetics of stabilised Criegee intermediates derived from alkene ozonolysis: reactions with SO₂, H₂O and decomposition under boundary layer conditions, *Phys. Chem. Chem. Phys.*, 17, 4076, 2015.
- Newland, M. J., Rickard, A. R., Sherwen, T., Evans, M. J., Vereecken, L., Muñoz, A., Ródenas, M., and Bloss, W. J. The atmospheric impacts of monoterpene ozonolysis on global stabilised Criegee intermediate budgets and SO₂ oxidation: experiment, theory and modelling, *Atmos. Chem. Phys.*, 18, 6095-6120, 2018.
- Nguyen, T. B., Tyndall, G. S., Crouse, J. D., Teng, A. P., Bates, K. H., Schwantes, R. H., Coggon, M. M., Zhang, L., Feiner, P., and Milller, D. O.: Atmospheric fates of Criegee intermediates in the ozonolysis of isoprene, *Phys. Chem. Chem. Phys.*, 18, 10241– 10254, 2016.
- Sheps, L., Scully, A. M., and: UV absorption probing of the conformer-dependent reactivity of a Criegee intermediate CH₃CHOO *Phys. Chem. Chem. Phys.*, 16, 26701-26706, 2014.
- Vereecken, L., and Francisco, J. S.: Theoretical studies of atmospheric reaction mechanisms in the troposphere, *Chem. Soc. Rev.*, 41, 6259-6293, 2012.
- Vereecken, L., Novelli, A., and Taraborrelli, D.: Unimolecular decay strongly limits the atmospheric impact of Criegee intermediates, *Phys. Chem. Chem. Phys.*, 19, 31599–31612, 2017.
- Winterhalter, R., Neeb, P., Grossmann, D., Kolloff, A., Horie, O., and Moortgat, G.: Products and mechanism of the gas phase reaction of ozone with B-pinene, *J. Atmos. Chem.*, 35, 165-197, 2000.