



## TNA User Report

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Project title	Do Green Solvents Mean Cleaner Air?
Name of the accessed chamber	CERNESIM
Number of users in the project	2
Project objectives (max 100 words)	Objectives were to study the atmospheric degradation (reaction with OH and with Cl) of two new "green" solvents, namely 2,2,5,5-tetramethyloxolane (TMO) and cyclopentymethylether (CPME), for which no kinetic data was available. Apparatus (smog chamber), analytics (FTIR and PTR-MS) and kinetic methods (relative-rate and product yield) used at CERNESIM were to complement direct, absolute laser experiments conducted in York.
Description of work (max 100 words):	A day and a half of characterisation experiments (wall loss, VOC photolysis, spectral reference measurements) preceded the main study. For the bulk of the study, relative rate experiments were conducted where the target reactions (R1) were followed via FTIR alongside a well-characterised reference reaction for which the rate coefficient was known. $X + \text{VOC} \rightarrow (\text{products}) \quad (\text{R1})$ where X = OH or Cl; VOC = TMO or CPME or one of two breakdown products. These experiments were complemented by three days of studies focused on FTIR and PTR-MS measurements of the principal products formed in (R1).

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<sup>1</sup> **PLEASE CHOOSE ONLY ONE DOMAIN** Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

<sup>2</sup> 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.

<sup>3</sup> UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

<sup>4</sup> 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](http://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: Terry J. Dillon**

**Chamber name and location: CERNESIM, Iasi, Romania**

**Campaign name and period: Do Green Solvents Mean Cleaner Air? 9/12/2019 – 20/12/2019**

## 1. Introduction

Well-designed 'green' solvents such as TMO (2,2,5,5-tetramethyloxolane) are sustainable and less hazardous and harmful to health than the compounds they replace [1-2]. However, little to nothing is known of the air quality impacts of new green solvents. For gas-phase TMO, the only literature concerns a VUV absorption spectrum [3]. Accordingly, for this TNA activity, the principal objectives were to use the CERNESIM chamber facility to study the most likely atmospheric oxidation pathway for TMO, namely reaction (R1) with the hydroxyl radical, OH.



Rate coefficients,  $k_1(295 \text{ K})$  determined in this work using the relative rate technique complement direct laser-based determinations obtained at University of York. This previous work had indicated that  $k_1(295 \text{ K})$  was anomalously slow when compared to similar VOC and to calculated values from state-of-the-art structure activity relationships (SAR). Measurements of the products of (R1) using FTIR, PTR-MS and a carbonyl-derivatization method were to complement quantum-chemical calculations on the reaction mechanism of (R1). Experiments in York on the reaction of TMO with Cl-atoms were at best semi-quantitative, indicating a fast process. A secondary objective of this TNA was therefore to measure kinetics and products for (R2):



Further objectives were to use similar methods to study the atmospheric breakdown (R3-R4) of a second green solvent, cyclophenylmethylether (CPME).



Together with results from direct experiments and theoretical calculations [4] conducted in York, this information will enable construction of reliable atmospheric breakdown mechanisms for TMO and CPME and hence assessment of air quality impacts in a range of standard MCM scenarios [5].

## 2. Experimental

Experiments were conducted using the 780 dm<sup>3</sup> ESC-Q-UAIC environmental simulation chamber at Alexandru Ioan Cuza University, Iasi Romania. The 760 litre quartz chamber was equipped with inlet ports, sampling lines, UV lamps for photolysis (generation of OH or Cl-atoms) and FTIR and PTR-MS instrumentation for observation of reference VOC, TMO, CPME, and their oxidation products. In preliminary experiments, wall deposition and photolysis (360 nm and 254 nm) rates of were measured in order to correct the chemical reactions rate coefficients and product formation yields.

All experiments were conducted at  $p = 1 \text{ bar}$  and  $T = 295 \text{ K}$ . Choice of reference compound for kinetic experiments was informed by three factors:

(1) FTIR spectra. Experimental spectra (Figure 1), existing library data and calculated spectra [4] were all used to ensure that the spectrum of the target TMO or CPME contained strong features that did not overlap with that of the reference compound.

(2) Target TMO and CPME rate coefficient data. SAR calculations [6] and (for TMO) results from absolute studies conducted at University of York were used to predict rate coefficient values.

(3) Reference VOC rate coefficient data. Reference compounds that met criteria (1) and (2) also needed to have reliable  $k$ -values available in the literature (see Table 1).

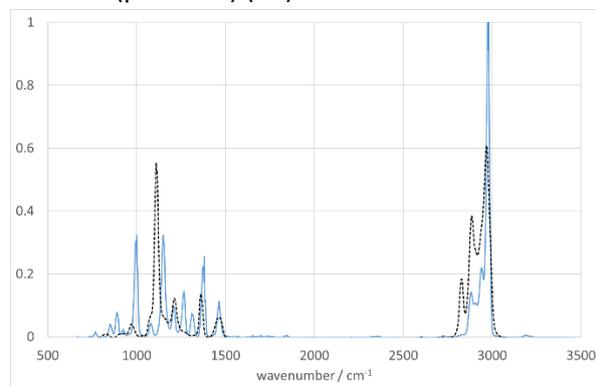
**Table 1** – summary of kinetic data for reference compounds used in this work.

Reference VOC	$k_{\text{ref}}$ (OH + VOC)	Lit.	$k_{\text{ref}}$ (OH + VOC)	Lit.
c-C <sub>6</sub> H <sub>12</sub> (cyclohexane)	6.97	[7]	330	[10]
CH <sub>3</sub> OCH <sub>3</sub> (dimethylether)	2.86	[8]	173	[11]
C <sub>3</sub> H <sub>6</sub> (propene)	26.3	[9]	223	[12]

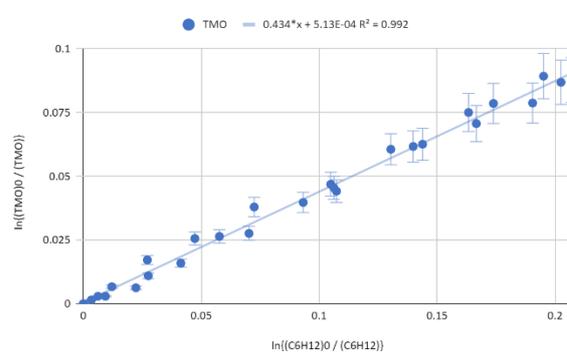
Notes:  $k_{\text{ref}}$  values (in  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) are for conditions of  $p = 1$  bar and  $T = 298$  K unless stated otherwise.

### 3. Preliminary Results and Discussion

Fig. 1 shows FTIR spectra of TMO and CPME recorded at the outset of this TNA activity. Neither TMO nor CPME were significantly impacted by wall or photolytic removal indicating that corrections to subsequent kinetic data were unnecessary. Qualitatively, the spectra compared well to predictions [4] thus allowing for use of pre-planned reference compounds (Table 1) in relative rate experiments. An example of the results from one such relative rate study is displayed in Figure 2. Here, the reaction of TMO with OH was studied alongside the well characterised reference reaction OH + c-C<sub>6</sub>H<sub>12</sub> → (products) (R7).



**Figure 1** – FTIR spectra of TMO (blue solid line) and CPME (black dashed line) used in kinetic experiments.



**Figure 2** – typical relative rate plot showing consumption of TMO by OH (R1) versus the reference reaction of c-C<sub>6</sub>H<sub>12</sub> + OH (R7)

**Table 2** describes preliminary results from all relative rate experiments to determine  $k_1(295\text{ K})$  for OH + TMO. Direct, absolute laser-based experiments conducted at University of York had indicated that (R1) proceeds surprisingly slowly, a factor of three slower than the state-of-the-art SAR calculation. AR calculations indicated that the reaction would proceed much faster than (R1), hence the choice of different reference VOC. The provisional average result from this TNA of  $k_1(295\text{ K}) = 3.1 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (full error analysis still in progress) is in excellent agreement with results from the (unpublished) laser-based experiments. The close agreement between results from two complementary experimental techniques is pleasing and lends confidence to our assertion that the 3-D structure of TMO is too complex for accurate kinetic analysis by SAR. To the best of our knowledge no values of  $k_1$  have been published elsewhere.

**Table 2 – determinations of  $k_1(295\text{ K})$  for OH + TMO**

Precursor	$\lambda$ / nm	Ref. VOC	$k_1 / k_{\text{ref}}$	$k_1(295\text{ K})^a$	Mean
CH <sub>3</sub> ONO + NO	365	c-C <sub>6</sub> H <sub>12</sub>	0.4353	3.03	
CH <sub>3</sub> ONO + NO	365	c-C <sub>6</sub> H <sub>12</sub>	0.4454	3.10	
CH <sub>3</sub> ONO + NO	365	CH <sub>3</sub> OCH <sub>3</sub>	1.1416	3.26	
H <sub>2</sub> O <sub>2</sub>	254	CH <sub>3</sub> OCH <sub>3</sub>	1.0053	2.88	
H <sub>2</sub> O <sub>2</sub>	254	CH <sub>3</sub> OCH <sub>3</sub>	under	evaluation	
CH <sub>3</sub> ONO + NO	365	CH <sub>3</sub> OCH <sub>3</sub>	under	evaluation	<b>3.1</b>

Notes: experiments conducted at  $p = 1$  bar and  $T = 295$  K unless stated otherwise; a =  $k_1(295\text{ K})$  reported in  $10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$

**Table 3** describes preliminary results from relative rate experiments to determine  $k_2(295\text{ K})$  for Cl + CPME. The provisional average result of  $k_2(295\text{ K}) = 1.2 \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (error analysis still in progress) agreed well with results from a semi-quantitative laser-based experiment conducted at University of York. No previously published values were found in the literature. Reaction (R2) with Cl-atoms may be an important atmospheric loss process for TMO under certain conditions, given the large value for  $k_2(295\text{ K})$  reported here and the anomalously slow reaction (R1) with OH.

**Table 3 – determinations of  $k_2(295\text{ K})$  for Cl + TMO**

Precursor	$\lambda$ / nm	Ref. VOC	$k_2 / k_{\text{ref}}$	$k_2(295\text{ K})^a$	Mean
Cl <sub>2</sub>	365	CH <sub>3</sub> OCH <sub>3</sub>	0.7591	131	
Cl <sub>2</sub>	365	c-C <sub>6</sub> H <sub>12</sub>	0.3709	122	
		C <sub>3</sub> H <sub>6</sub>	0.551	123	
Cl <sub>2</sub>	365	CH <sub>3</sub> OCH <sub>3</sub>	0.682	118	
		c-C <sub>6</sub> H <sub>12</sub>	0.349	115	
		C <sub>3</sub> H <sub>6</sub>	0.425	94.7	<b>120</b>

Notes: experiments conducted at  $p = 1$  bar and  $T = 295$  K unless stated otherwise; a =  $k_2(295\text{ K})$  reported in  $10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$

Two series of experiments were conducted to record the products of TMO oxidation from both (R1) and (R2). These experiments were distinct from the kinetic experiments outlined above, in that no reference compounds were present and the conditions were controlled to allow for consumption of a larger proportion of TMO. Products were monitored by time-resolved FTIR and PTR-MS. Further end-product analysis was via a carbonyl-derivatization technique. At the time of writing, data from each of these experiments is awaiting analysis and no provisional results are presented here.

**Table 4** describes preliminary results from relative rate experiments to determine  $k_3(295\text{ K})$  for OH + CPME. SAR calculations indicated that the reaction would proceed much faster than (R1), hence the choice of different reference VOC. The provisional average result of  $k_3(295\text{ K}) = 1.6 \times 10^{-11}\text{ cm}^3$

molecule<sup>-1</sup> s<sup>-1</sup> is, to our knowledge the first such determination. The value is slightly larger than the SAR prediction of  $1 k_3(295 \text{ K}) = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , though likely to be within combined uncertainties (full error analysis of these experiments is still a work in progress).

**Table 4 – determinations of  $k_3(295 \text{ K})$  for OH + CPME**

Precursor	$\lambda / \text{nm}$	Ref. VOC	$k_3 / k_{\text{ref}}$	$k_3(295 \text{ K})^a$	Mean
H <sub>2</sub> O <sub>2</sub>	254	c-C <sub>6</sub> H <sub>12</sub>	2.2399	15.6	<b>16</b>
		CH <sub>3</sub> OCH <sub>3</sub>	4.2582	12.2	
H <sub>2</sub> O <sub>2</sub>	254	c-C <sub>6</sub> H <sub>12</sub>	2.6104	18.2	
		C <sub>3</sub> H <sub>6</sub>	0.6726	17.7	
CH <sub>3</sub> ONO + NO	365	c-C <sub>6</sub> H <sub>12</sub>	under	evaluation	
		C <sub>3</sub> H <sub>6</sub>	under	evaluation	
CH <sub>3</sub> ONO + NO	365	c-C <sub>6</sub> H <sub>12</sub>	1.9100	13.3	
		C <sub>3</sub> H <sub>6</sub>	0.6521	17.2	

Notes: experiments conducted at  $p = 1 \text{ bar}$  and  $T = 295 \text{ K}$  unless stated otherwise; a =  $k_3(295 \text{ K})$  reported in  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

**Table 5** describes preliminary results from relative rate experiments to determine  $k_4(295 \text{ K})$  for Cl + CPME. The reaction was anticipated to be fast, close to the collision limit, hence the choice of two highly reactive reference VOC (see **Table 1**).

Two series of experiments were conducted to record the products of CPME oxidation from both (R3) and (R4). As outlined for TMO products above, experiments used no reference compounds were and featured a high proportion of CPME consumption. Preliminary analysis by FTIR allowed for identification of cyclopentanone as a major product of both (R3) and (R4). Products were monitored by time-resolved FTIR and PTR-MS. Further end-product analysis was via a carbonyl-derivatization technique. At the time of writing, data from each of these experiments is awaiting analysis and no provisional results are presented here.

Preliminary experiments were conducted on the reactions of breakdown products, cyclopentanone (from CPME) and dihydro-2,2,5,5-tetramethyl-3(2H)-furanone (from TMO). The data from these experiments is awaiting evaluation.

**Table 5 – determinations of  $k_4(295\text{ K})$  for Cl + CPME**

Precursor	$\lambda / \text{nm}$	Ref. VOC	$k_4 / k_{\text{ref}}$	$k_4(295\text{ K})^a$	Mean
Cl <sub>2</sub>	365	c-C <sub>6</sub> H <sub>12</sub>	0.9418	311	<b>310</b>
		C <sub>3</sub> H <sub>6</sub>	1.2845	286	
Cl <sub>2</sub>	365	c-C <sub>6</sub> H <sub>12</sub>	1.0987	363	
		C <sub>3</sub> H <sub>6</sub>	1.4197	317	
Cl <sub>2</sub>	365	c-C <sub>6</sub> H <sub>12</sub>	0.9666	319	
		C <sub>3</sub> H <sub>6</sub>	1.2775	285	

Notes: experiments conducted at  $p = 1$  bar and  $T = 295$  K unless stated otherwise; a =  $k_4(295\text{ K})$  reported in  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

#### 4. Conclusions and Outlook

Instrumentation and other technical aspects of the project worked well throughout the two weeks and a large number of experiments were successfully performed. Preliminary assessment of the kinetic data indicates that, for OH + TMO (R1), results agree with those from previous York-based experiments and will contribute to a strong publication. The results obtained for (R2 – R6) in this study appear robust and will be complemented by direct, laser-based experiments at York. At the time of writing, analysis of the products from (R1 – R4) is very much a work in progress.

Preliminary results from this work form the basis for a poster presentation at the forthcoming Faraday joint interest group conference, in Sheffield, April 2020. We will further disseminate these results at the 26<sup>th</sup> International Symposium on Gas Kinetics in Karlsruhe, September 2020. The success of this TNA has allowed for the estimate of outputs to be revised upwards; we now anticipate the publication of three high-impact publications from this and related work.

#### 5. Literature:

- [1] Byrne, F. et al. (2017), *Green Chem.*, 19, 3671, DOI: 10.1039/c7gc01392b ;
- [2] Bossaert, G. et al. (2018), Patent filing WO 2018/033635 A1
- [3] Kizilkilic, H.-P. et al. (1980), *Can. J. Chem.* 58, 2819-2826, DOI: 10.1139/v80-452
- [4] Frisch, M.J. et al. (2016), Gaussian 16, Gaussian, Inc., Wallingford CT ; [5] mcm.york.ac.uk
- [6] Jenkin, M.E., et al. (2018), *Atmos. Chem. Phys.*, 18, 9297-9328 ; [7] Atkinson, R. *Atmos. Chem. Phys.*, 86 (1986), 2233 – 2307 ; [8] DeMore, W.B., Bayes, K.D. *J. Phys. Chem. A*, 103 (1999), 2649 – 2654 ; [9] Atkinson, R. *Chem. Rev.*, 86 (1986) ; [10] Anderson, R.S. et al. *J. Phys. Chem. A*, 111 (2007), 495 – 504 ; [11] Giri, B.R., Roscoe, J.M. *J. Phys. Chem. A*, 114 (2010), 8369 – 8375
- [12] Ceacero-Vega, et al. *Chem. Phys. Lett.*, 484 (2009) 10–13