TNA User Report

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Project title	Quantifying the Importance of Ketone Photolysis to Tropospheric Oxidation
Name of the accessed chamber	HELIOS
Number of users in the project	2
Project objectives (max 100 words)	The project objective was to study the rate of degradation of Methyl Ethyl Ketone (MEK) and Oxalyl Chloride $(ClCO)_2$ in surface-atmosphere conditions. The photolysis of MEK is a potentially important atmospheric source of hydroxyl radicals. We aimed to quantify both the rate and products of this important atmospheric reaction. The photolysis of $(ClCO)_2$ was investigated to characterize HELIOS chamber with the aim to evaluate the MEK photolysis studies under the same conditions.
Description of work (max 100 words):	A series of experiments were conducted to derive the rate of MEK photolysis under solar radiation in HELIOS. These investigations were complemented by studies on the photolysis of oxalyl chloride under same conditions. A large set of equipment was used to this aim (online PTR-Tof-MS, CIMS, HCHO and CO analyzers, UHPLC, FTIR spectrometer and a spectroradiometer to measure the solar flux). Data still under the process, however, a presentation is planned at the AGU fall meeting 2017 is planned.

Principal Investigator's and group's information	
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User status[3]	PGR
New user	Yes

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Gender	
User status	
New user	

[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; EXP= Expert; 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: Jared BREWER
Chamber name and location: HELIOS Atmospheric Simulation Chamber

Campaign name and period: June 13, 2017 – July 25, 2017

Text:

Introduction and Motivation

Methyl ethyl ketone (MEK) is a common carbonyl compound in the troposphere, but is currently poorly represented in global chemical transport models (CTMs). CTMs are used in atmospheric chemistry to test understanding of processes including emission, deposition, chemical reaction, and transport of atmospheric constituents. MEK, like its better-studied relative acetone, is a significant atmospheric species because it has a sufficiently long lifetime (estimated at 5 days) to be lofted into the upper troposphere. There, it plays an important role in atmospheric chemistry because it can be photolyzed, producing odd hydrogen (HOx = HO2 + OH) radicals. Odd hydrogen radicals are atmospheric detergents; most compounds are removed from the atmosphere via reaction with these radicals. Thus the photolysis of ketones like MEK impacts the concentrations and lifetimes of greenhouse gases and other atmospheric pollutants. Major uncertainties remain in the global MEK budgets. Processes that may be inadequately represented include the photolysis rates of MEK, the magnitude and distribution of biogenic and anthropogenic sources, and the specific reaction mechanisms which secondarily produce MEK in the troposphere.

We do not understand how much MEK contributes to upper tropospheric HOx because of crucial uncertainties remaining in the global MEK budget. When existing measurements of MEK are incorporated into CTMs, discrepancies between simulated and observed MEK abundances remain; ensuring that our CTMs accurately represent photolysis is the first step towards addressing this discrepancy. The rate of photolysis depends upon three factors: the actinic flux (incoming solar radiation), the absorption cross-section of the species in question (the probability of interaction between a single particle of the species of interest and a single photon), and the quantum yield (the number of times specific products are produced per photon absorbed by the molecule of interest). For MEK, both the quantum yield for a given reaction pathway and the absorption cross-section of the molecule depend on both temperature and pressure. Few measurements exist of MEK photolysis rates at surface pressure at wavelengths longer than 320 nm.

Scientific objectives:
In this project, we aimed to improve our understanding of MEK photolysis, and used the HELIOS atmospheric simulation chamber to study two scientific questions.

What is the rate of MEK photolysis at surface pressures in natural sunlight?
Which peroxide radicals result from MEK photolysis?

Why use HELIOS?
We needed to use HELIOS to perform this research because HELIOS is a unique facility that allowed experiments to be conducted under true solar light conditions, thus making its results more useful for incorporation into models. Additionally, measurements at large solar zenith angles at CNRS were beneficial. Quantum yields measured at atmospheric pressure with HELIOS will validate the parameterization. MEK is also primarily emitted at the surface, and therefore surface level photolysis determines that species' atmospheric lifetime and export to the upper troposphere. Finally, the large amount of equipment and breadth of expertise available at CNRS ICARE Orleans made it a uniquely ideal place for us to undertake our study.

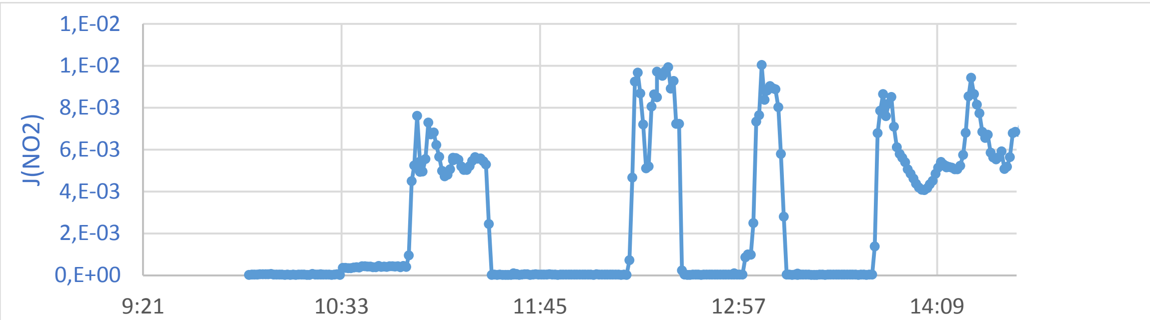
Methods and Experimental Setup
MEK photolysis and subsequent radical generation measurements: we used the HELIOS chamber and its attendant instrumentation, specifically the API-ToF-CIMS, FTIR, PTR-ToF-MS, SAMU-CIMS (Spectromètre de masse Aéroporté MULti-espèces par réactions ion-molécule) and spectroradiometers. We performed several experiments under various conditions to address questions 1) and 3). In each experiment, the chamber was filled with filtered zero-air (N2, O2, and CO2 only) for a day in order to remove any traces of past experiments. On the day of the experiment, the chamber was exposed to natural sunlight for a half-hour with no MEK or other species added, to ensure that no contamination was present. This control run completed, the chamber was closed and a predetermined volume of MEK was added to the chamber in order to achieve a target mixing ratio within the chamber itself. Once the target mixing ratio was achieved, we monitored the loss rate of MEK in the chamber without exposing it to sunlight for a half-hour, in order to monitor the loss of MEK to dilution. After a half-hour of dilution, the HELIOS was exposed to natural sunlight. This exposure lasted between 3-6 hours, depending upon the instrumentation used and the heat of the

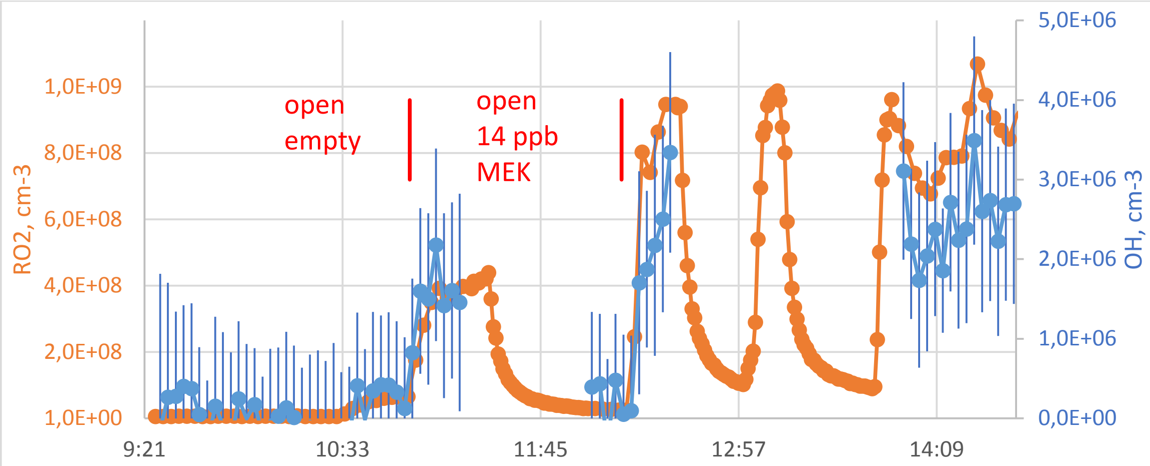
day, in order to avoid overheating sensitive instrumentation while still taking the maximum data possible.

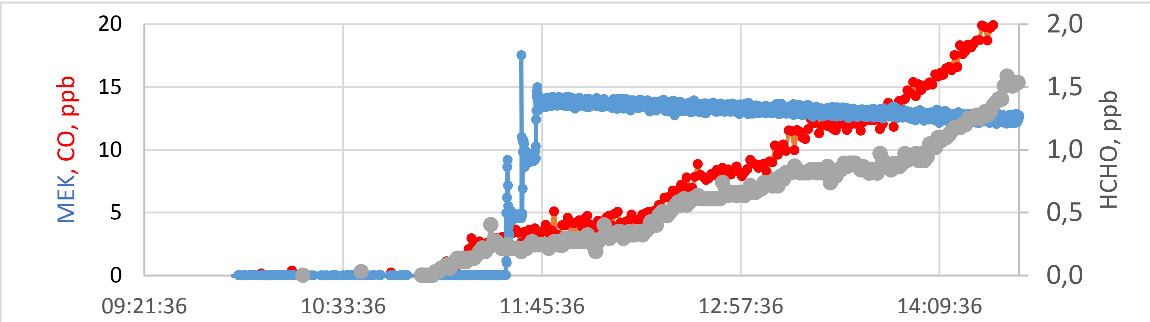
In order to fully characterize the HELIOS chamber, we also performed chamber studies with oxalyl chlorate (ClCO)2. This compound was chosen because its photolysis is both simple and well understood. When photolyzed, oxalyl chlorate dissociates fully to yield 2Cl atoms and 2CO molecules, which the suite of instruments at HELIOS can measure. Furthermore, atomic chlorine is highly reactive, and will react with any contaminants in the chamber, yielding HCHO among other compounds. Thus, we have run multiple experiments tracking the photolysis of oxalyl chlorate using both filtered air and pure N2, and will use the difference between the HCHO concentrations in these two runs to characterize the contaminants in the chamber itself as well as in the filtered air fed in during the MEK experiments.

Data Description and preliminary results

Each HELIOS experiment output continuous irradiance data as well as MEK, hydroxyl radical (OH), formaldehye (HCHO), peroxy radical (RO2), and carbon monoxide (CO) concentrations. Additionally, each experiment provided a wealth of mass spectrometry data that we can use to examine the precise speciation of the RO2 produced. An example HELIOS run is shown below, from our experiment performed on the 28th of June. The following graphs are as yet unpublished data and should be kept confidential.







The first of these figures plots J(NO2) – the photolysis rate of NO2, a proxy for whether HELIOS was open or shut. The second figure plots the concentration of OH and RO2 radicals, which increase rapidly as the chamber opens and then decrease when it closes. Finally, the third plot shows the gradual photochemical loss of MEK into two of its near-end products, CO and HCHO. The differences in this slope between the open and closed periods will be used to identify the precise loss of MEK to photolysis. In this way, we can examine the rate of MEK loss and the production of the resulting products.

Outcome and future studies

With the support of EUROCHAMP, I was able to spend twenty-five days in Orleans studying MEK and Oxalyl Chloride photolysis. In the course of this research, we used the HELIOS Atmospheric simulation chamber and its attendant instrumentation to measure 1) the photolysis rate of MEK under real-sunlight conditions and 2) the products which result from this photolysis. The results of these analyses are novel and important, and will be integrated into a published scientific paper in the immediate future. Additionally, once these results are published, I will incorporate these new MEK photolysis measurements into the chemical scheme of the GEOS-Chem CTM, Fast JX, and publish the resulting findings as appropriate. The Fast JX photolysis scheme is implemented in many other global models, and so my work with CNRS will benefit the broader atmospheric research and modeling community.