



TNA User Report

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Project title	Photolysis of oxygenated compounds under natural irradiation
Name of the accessed chamber	EUPHORE
Project objectives (max 100 words)	The main objective is to assess the importance of the photolysis degradation pathway of carbonyl compounds in the atmosphere. Measurements of photolysis frequencies under natural sunlight are rather scarce and often concern simple carbonyl species. For most of the carbonyls, in the absence of direct measurements, photolysis frequencies may be calculated from the solar actinic flux and the absorption cross sections assuming quantum yields of 1, but this leads (often) to an overestimation of the photolysis rates. Measurements under real sunlight conditions are thus clearly necessary to improve the consistency and robustness of atmospheric chemistry models.
Description of work (max 100 words):	The measurement of the photolysis rates of multifunctional carbonyls under natural irradiation will be carried out. 4 multifunctional compounds have been selected: an alpha-dione: 2,3-pentanedione and 3 hydroxyketones: 3-hydroxy-3-methyl-2-butanone, 4-hydroxy-4-methyl-2-pentanone and 4-hydroxy-3-hexanone. These compounds present relatively high photolysis rates that could make the photolysis pathway non-negligible in the atmosphere. The present work will allow confirming (or not) the significance of the photolysis pathway for these compounds. These experiments should also allow determining photolysis products (and possible secondary organic aerosol formation) to get a global view of the process.
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: EUPHORE, Valencia, Spain

Campaign name and period: 12-21/07/2017

• Introduction and motivation

Photolysis of carbonyls is known to be a significant source of radicals, impacting the budget of HOx and NOx on regional to global scales. Yet, measurements of photolysis frequencies under natural sunlight are rather scarce and often concern simple species like formaldehyde, acetaldehyde and acetone (Calvert et al., 2011). For most of the carbonyls, in the absence of direct measurements, photolysis frequencies can be estimated from the solar actinic flux and the absorption cross sections assuming quantum yields of 1, but this leads to upper limit values and (often) to an overestimation of the photolysis rates. Indoor simulation chambers with actinic lamps may be used more easily, but high uncertainties result in the photolysis frequencies due to the different irradiation spectrum. Accurate photolysis frequencies are one of the main uncertainties in atmospheric chemistry models like MCM or GECKO-A, especially for larger and multifunctional carbonyl compounds. Measurements under real sunlight are thus clearly necessary to improve the consistency and robustness of atmospheric chemistry models.

A range of recent studies (Aslan et al., 2017a; Bouzidi et al., 2015a; Bouzidi et al., 2015b; Bouzidi et al., 2014a; Bouzidi et al., 2014b; Messaadia et al., 2015; Messaadia et al., 2012) have indicated that the atmospheric photolysis of multifunctional carbonyls could be significant. The compounds investigated in these studies are dicarbonyls and hydroxycarbonyls that may either be directly emitted into the atmosphere or be produced in

the degradation of hydrocarbons and oxygenated compounds, as suggested by detailed atmospheric chemistry models (Aumont et al., 2005). While rather rarely measured in the atmosphere, the assumed presence of these organic species may partly explain the lack of OH radical reactivity observed in various environments. In the above-mentioned studies, the atmospheric photolysis rates were either calculated based on solar actinic flux and absorption cross sections or measured using indoor simulation chamber with actinic lamps. Thus, significant uncertainties still remained on the importance of the photolysis channel for these species and photolysis rate measurements under natural sunlight are required in order to correctly assess the atmospheric significance of the photolysis pathway for these compounds.

• Scientific objectives

The project aims at measuring photolysis rates of multifunctional carbonyls under natural irradiation. Dicarbonyl and hydroxycarbonyl compounds have been chosen, based on the above-mentioned literature data. The effective atmospheric quantum yields and the photolysis products are also expected to be determined to extent literature data and to get a global view of the photolytic process.

• Reason for choosing the simulation chamber/calibration facility

We needed a facility enabling photolysis experiments under natural sunlight conditions to be carried out. In addition, as we expected rather low kinetic rates, rather high actinic fluxes were required. Thus, we choose the Euphore simulation chamber in summer.

• Method and experimental set-up

Euphore simulation chamber B has been used with a broad range of analytical techniques. A typical experiment proceeded as follow: the compound was first injected (target concentration about 500 ppb) and let homogenize for about 30 min, then SF₆ was injected (tracer for dilution) as well as, for some experiments, cyclohexane as OH scavenger. After 30 min homogenization, the chamber was open and exposed to sunlight. FTIR spectra were continuously recorded together with PTR-MS analysis. Other analytical techniques were: LC-MS, GC-MS, HPLC. Potential formation of aerosols was checked by SMPS and TEOM analysis.

• Data description

Four multifunctional compounds have been selected: an α -dione: 2,3-pentanedione (C₅H₁₀O₂) and 3 hydroxyketones: 3-hydroxy-3-methyl-2-butanone (C₅H₁₀O₂), 4-hydroxy-4-methyl-2-pentanone (C₆H₁₂O₂) and 4-hydroxy-3-hexanone (C₆H₁₂O₂). Two experiments for each compound were performed, one with OH scavenger, the other without. Recorded data concern: actinic flux ($J(\text{NO}_2)$), pressure, temperature, humidity, CO, NO_x and O₃ concentrations, gas sampling on C18 and DNPH cartridges for organic acid and carbonyl analysis, stripping for peroxide analysis, in situ FTIR spectra and sampling on SPME fibers (with and without derivatisation).

• Preliminary results and conclusions

In general, we benefited from sunny days, especially the first three days (see Figure 1); we experimented more cloudy days from the 17th July. The average J_{NO_2} was around 0.5 min⁻¹. No aerosol formation was observed. The photolysis frequency was determined for each compound from an average of the FTIR and GC-MS-SPME data (experiments with scavenger) taking into account the dilution and wall losses using the FTIR data before opening the chamber. Preliminary kinetic results show that i) 2,3-pentanedione is readily photolysed in the atmosphere, with a photolysis frequency around 0.9 h⁻¹, in reasonable agreement with (Bouzidi et al., 2014a) who found 0.42 h⁻¹ using artificial irradiation and actinometry ii) photolysis rates of 4H4M2P, 3H3M2B and 4H3H are much lower (roughly an order of magnitude); in addition, more than 80% of the observed decays are due to dilution and wall losses of the compound. Therefore, the uncertainties on the photolysis frequencies are high, probably a factor of 2-3. The 4H4M2P, 3H3M2B and 4H3H photolysis frequencies are estimated to around 6×10⁻³ h⁻¹ for all three compounds, representing a factor of 3 lower than the frequencies estimated using

artificial irradiation under overhead sun conditions (22nd June, 40°N) (Aslan et al., 2017a; Aslan et al., 2017b; Bouzidi et al., 2014b).

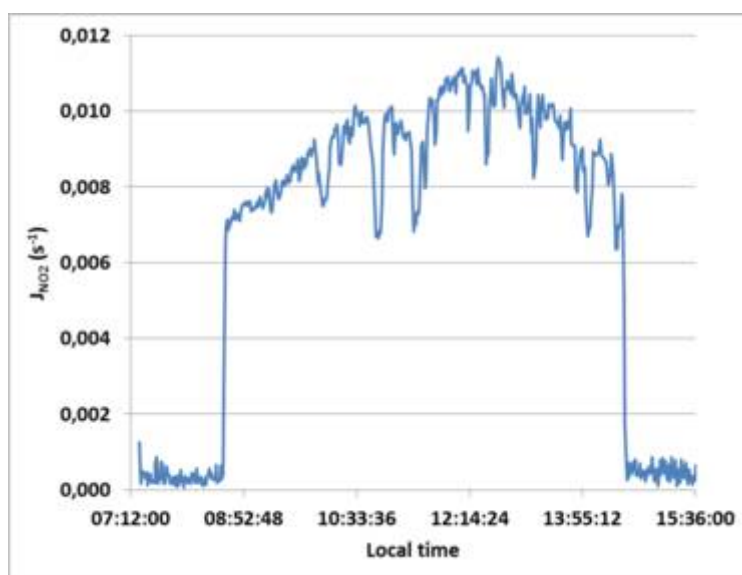


Figure 1: NO₂ photolysis frequency in s⁻¹ as a function of local time (12th July)

Note that these are preliminary results and deeper analysis will be carried out to better evaluate the wall losses and dilution terms. Regarding the products, the whole analytical results are not yet available. A range of different oxygenated products like aldehydes, dicarbonyls, hydroxyl- and dihydroxy-carbonyls have been observed and quantified. OH production was also deduced from the observation of cyclohexanone (from cyclohexane + OH) in the experiments with cyclohexane as OH-scavenger.

• Outcome and future studies

This campaign presents new data on the significance of atmospheric photolysis for multifunctional oxygenated compounds. The analyses already show that hydroxyketones photolyze at a much lower rate than α -dicarbonyls. The range of products observed together with a comparison of the experiments with and without OH-scavenger will allow a better understanding of the on-going processes.

It may be interesting to use a chamber facility equipped with a solar simulator in order to increase the ratio between photolysis rate and wall loss and dilution rate. This will enable more accurate photolysis frequencies to be obtained; moreover, the primary quantum yields could also be determined.

• References

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- Aslan, L., Laversin, H., Roth, E., Coddeville, P., Fittschen, C., Chakir, A., Tomas, A., 2017b. Gas-phase UV absorption cross-sections and photolysis kinetics of 4-hydroxy-3-hexanone: Atmospheric implications. *Chem. Phys. Lett.* in revision.
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Messaadia, L., El Dib, G., Ferhati, A., Roth, E., Chakir, A., 2012. Gas phase UV absorption cross-sections for a series of hydroxycarbonyls. *Chem. Phys. Lett.* 529, 16-22.

Prof. A. TOMAS

