TNA User Report

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Project title	"Gas-phase reactivity study and degradation mechanisms of selected hydrofluoroolefins: atmospheric implications and assessment as possible candidates of CFCs replacements".
Name of the accessed chamber	QUAREC
Number of users in the project	1
Project objectives (max 100 words)	- Product and mechanistic studies of reactions of OH/Cl with HFO, i.e. 2-fluoropropene, including its reactant and products calibrations. - Kinetic studies on the reactions of OH with fluorinated acrylates and methacrylates, e.g. 2,2,2-trifluoroethylacrylate (TFEA), 1,1,1,3,3,3-hexafluoroisopropylacrylate (HFIA), 2,2,2-trifluoroethylmethacrylate (TFEM) and 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (HFIM) as a function of temperature range 288-318 K. - Product and mechanistic studies of reactions of OH/Cl with fluorinated acrylates and methacrylates, e.g. TFEA, HFIA, TFEM and HFIM in the presence and absence of NOx. - Analysis of reactivity trends of these compounds and estimations of their atmospheric lifetimes. - Enviroment assessment of these atmospheric reactions and their products.
Description of work (max 100 words):	This work has been made, kinetic studies and degradation products of compounds of interest in atmospheric chemistry. The investigations were performed in the QUAREC installation using mainly in-situ FTIR spectroscopy to monitor the concentration-time profiles of reactants and products. The results could contribute to an improved representation of the degradation of the compounds under study in the atmospheric chemical models used to assess the environmental impact of chemicals and their contribution to the oxidizing capacity of the atmosphere.

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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

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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 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

Instructions

Name of the PI: Maria Sagrario Salgado
Chamber name and location: QUAREC Bergische Universität Wuppertal Physikalische und Theoretische Chemie
Campaign name and period: Eurochamp_2020 TNA since 06/02/2018 to 03/03/2018
Text:

Introduction and Motivation

For a long time, atmospheric chemistry is currently focused on a number of major environmental issues, special attention of a type of compounds like unsaturated halogenated esters. They present an important chemistry because are widely emitted into the atmosphere from high industrial production, processing and disposal. Therefore, it is interesting to study of compounds as unsaturated fluorinated acrylates and methacrylates (FAM), it is known that these fluorine-containing compounds could form polymers (fluoroelastomers), these have many industrial applications e.g. in protective coatings for the preservation of monuments, gaskets and in different automobile parts which requires higth temperature resistance property [1,2]. The widespread use of fluoropolymers could have a great impact on the quality of the air and consequently on the environmental ones, among them we can mention the climatic change [3].On the other hand, it is interesting to study other halogenated compounds, such as hydrofluoroolefins (HFOs) which are also currently being considered as viable replacements compounds because they have high gas-phase reactivities and consequently low global warming potentials (GWPs) resulting in a greatly reduced climate forcing compared to that of the hydrofluorocarbons (HFCs) which they replace[4]. The high reactivity of HFOs in the troposphere is due mainly to the presence of the double bond, which allows them to be much more rapidly degraded in the atmosphere compared to CFCs[5]. As for any new chemical, prior to their large-scale industrial production and application, a through assessment of their atmospheric chemistry and potential environmental impacts is necessary. In order to assess the environmental impact of these compounds mentioned above, it is necessary to perform kinetic and product studies of their degradation in air initiated by the main tropospheric oxidants at different atmospherically NOx levels.

Reason for choosing the simulation chamber

The INFIQC research group (Córdoba, Argentina) has extensive experience in kinetic and mechanistic studies of the reactions of unsaturated esters, halogenated acetates, oxygenated, sulfur and biogenic compounds with OH radicals, Cl atoms, using simulation chambers (collapsible Teflon bags) coupled to different detection systems (GC-FID, GC-MS). The installation QUAREC was chosen because the temperature dependent kinetic and product studies of the type to be performed in this reactor are not possible with experimental facilities available at our origin institute.

Methods and experimental setup

The kinetic and product studies were performed in a 1080 L quartz glass reaction chamber at a total pressure of 760 ± 10 Torr synthetic air. The reactor could be temperature regulated in the range of 288-318 K with a precision of ± 1 K. The IR spectra were recorded using a Nicolet Nexus FTIR spectrometer.

- OH radicals were generated by the photolysis of CH_3ONO/NO/air mixtures at 360 nm or by the photolysis of H_2O_2 at 254 nm.
- Cl atoms were generated by the photolysis of Cl_2 with the fluorescent lamps at 360 nm.

Preliminary results and conclusions

<u>Kinetic studies:</u> The kinetic studies on the reactions of OH radicals TFEA, HFIA, TFEM and HFIM presented here have been performed in an environmental chamber using the relative kinetic technique over the temperature range 288-318 K.

$CH_2{=}CHC(O)OCH_2CF_3$	$+ {}^{\bullet}OH \rightarrow k_1$	(1)
$CH_2{=}CHC(O)OCH(CF_3)_2$	$+ {}^{\bullet}OH \rightarrow k_2$	(2)
$CH_2{=}C(CH_3)\,C(O)OCH_2CF_3$	$+ {}^{\bullet}OH \rightarrow k_3$	(3)
$CH_2{=}C(CH_3)\,C(O)OCH(CF_3)_2$	$+ {}^{\bullet}OH \rightarrow k_4$	(4)

According to preliminary results, All the rate coefficients display a slight negative temperature dependence, which points to the importance of the reversibility of the addition mechanism for these reactions. There are no prior experimental determinations of the Arrhenius parameters, this is the first temperature dependence study for these reactions.

<u>Products studies</u>: fluorinated acrylates and methacrylates

The mechanisms of the initiated oxidation of fluoroesters, mixtures of CH_3ONO/NO/FAM/air or H_2O_2/FAM/air and Cl_2/FAM/air have been studied, the samples (reactants and radical precursors in air) were irradiated for periods of 15−20 min during the course of which infrared spectra were recorded with the FTIR spectrometer. In this work we have studied the atmospheric degradation pathways of the reaction of FAM with OH radicals and Cl atoms, in presence and absence of NOx:

$CH_2{=}CHC(O)OCH_2CF_3$	$+ {}^{\bullet}OH \rightarrow$ Products	(1)
$CH_2{=}CHC(O)OCH(CF_3)_2$	$+ {}^{\bullet}OH \rightarrow$ Products	(2)
$CH_2{=}C(CH_3)\,C(O)OCH_2CF_3$	$+ {}^{\bullet}OH \rightarrow$ Products	(3)
$CH_2{=}C(CH_3)\,C(O)OCH(CF_3)_2$	$+ {}^{\bullet}OH \rightarrow$ Products	(4)
$CH_2{=}CHC(O)OCH_2CF_3$	$+ {}^{\bullet}Cl \rightarrow$ Products	(5)
$CH_2{=}CHC(O)OCH(CF_3)_2$	$+ {}^{\bullet}Cl \rightarrow$ Products	(6)
$CH_2{=}C(CH_3)\,C(O)OCH_2CF_3$	$+ {}^{\bullet}Cl \rightarrow$ Products	(7)

$CH_2=C(CH_3)\,C(O)OCH(CF_3)_2 \quad + {}^{\bullet}Cl \rightarrow \text{Products} \quad (8)$

The following reaction products have been identified:

$HC(O)CH_2OH$, $HC(O)H$ (1)

$HC(O)CH_2OH$, $HC(O)H$, $CF_3C(O)CF_3$ (2)

$CH_3C(O)CH_2OH$, $HC(O)OH$ (3)

$CH_3C(O)CH_2OH$, $HC(O)H$, $CF_3C(O)CF_3$ (4)

$HC(O)CH_2Cl$, $HC(O)Cl$ (5)

$HC(O)CH_2Cl$, $HC(O)Cl$, $CF_3C(O)CF_3$ (6)

$CH_3C(O)CH_2Cl$, $HC(O)Cl$ (7)

$CH_3C(O)CH_2Cl$, $HC(O)Cl$, $CF_3C(O)CF_3$ (8)

Regarding to FAM, these result are in agreement a previous work performed by analysis of the chromatogram obtained by CG-MS for reaction of fluoromethacrylates with Cl atoms [6].

Products studies: **OH/Cl- initiated degradaction of 2-fluoropropene (2-FP)** .

The mechanisms of the OH/Cl initiated oxidation of 2-fluoropropene (2-FP), mixtures of H_2O_2/2-FP/air and Cl_2/2-FP/air have been studied, the samples (reactants and radical precursors in air) were irradiated for periods of 15−20 min during the course of which infrared spectra were recorded with the FTIR spectrometer. In this work we have studied the atmospheric degradation pathways of the reaction of 2-FP with OH radicals and Cl atoms, in absence of NOx:

$CH_3CF=CH_2 \quad + {}^{\bullet}OH \rightarrow \text{Products} \quad (9)$

$CH_3CF=CH_2 \quad + {}^{\bullet}Cl \rightarrow \text{Products} \quad (10)$

The following reaction products have been identified:

$CH_3C(O)F$, $HC(O)H$ (9)

$CH_3C(O)F$, $HC(O)Cl$ (10)

In addition, the calibration of the reactant 2-FP ($CH_3CF=CH_2$) and acetyl fluoride ($CH_3C(O)F$) degradation product of the reaction of 2-FP with OH / Cl has been made. No quantitative products studies are currently available for OH-radical and Cl atoms initiated degradation of 2-fluoropropene. The results mentioned above are the main products of these reactions. The results indicates that the products proceed of the alcoxy intermediate of the reactions of OH radicals and Cl atoms with fluorinated compounds like FAM or HFOs by initial addition of OH/Cl to the >C=C< bond.

Outcome and future studies

The studies of quantification of products in presence and absence of NOx will continue, additionally reactivity trends and atmospheric implications will be discussed. Furthermore, it would be interesting to continue on the kinetic studies of temperature dependence for the reactions of FAM with Cl atoms, furthermore these results form part of the PhD work and will be submit to reviews scientific journals in the area of physical chemistry and environment, as well as being to send to scientific meetings.

References

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5- Tovar, C. M.,Blanco M.B.,Barnes I.,Wiesen P., &Teruel M.A. 2014. Atmos. Environ.t 88:107–14.
6- Rivela, C. B., Blanco, M. B., & Teruel, M. A. (2018). Atmos. Environ., 178, 206-213.