



TNA User Report

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Project title	Kinetic and mechanistic study of tropospheric degradation of a series of furanones derived from: 2(3H)-Furanone and 3(2H)-furanone initiated by Cl atoms and OH radicals at 298 K, and their atmospheric implications.
Name of the accessed chamber	QUAREC CHAMBER
Number of users in the project	1
Project objectives (max 100 words)	<ul style="list-style-type: none"> - Kinetic studies on the reaction of 3 (2H) -furanone, 2-methyl-3 (2H) -furanone, 5-methyl-3 (2H) -furanone, 2,2-Dymethyl-3 (2H) -furanone with Cl atoms and OH radicals at 298 K. - Mechanistic study of products formed in the OH radicals and Cl atoms reactions of 3 (2H) -furanone, 2-methyl-3 (2H) -furanone; 2,2- Dymethyl-3 (2H) -furanone. - Kinetic studies on the reaction of ethyl-dihydro-2 (3H) -furanone and 5-propyl-dihydro-2 (3H) -furanone initiated by Cl atoms and OH radicals at 298 K. - Mechanistic study of products of the reaction of OH radicals and Cl atoms with ethyl-dihydro-2 (3H) -furanone and 5-propyl-dihydro-2 (3H) – furanone.
Description of work (max 100 words):	<p>The kinetic coefficient of the reaction initiated by Cl atoms of the furanone family was determined: 2-methyl-3 (2H) -furanone, 2,2-Dimethyl-3 (2H) -furanone, $(1.35 \pm 0.11) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $(1.87 \pm 0.17) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. In addition, the kinetic coefficients with Cl atoms of a second family of furanones were also determined: 5-propyldihydro-2 (3H) - $(1.36 \pm 0.12) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and ethyl-dihydro-2 (3H) - furanone $(1.02 \pm 0.11) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively. All the furanones studied have been reported in previous studies [1], [2] in the cellulose-hemicellulose pyrolysis, pine wood pyrolysis and as volatile compounds in edible oil. The relative kinetic in Quarec Chamber method with detection FT-IR was used, using the kinetic coefficients obtained the atmospheric implications of these compounds were determined.</p>

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¹**PLEASE CHOOSE ONLY ONE DOMAIN** 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.

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

⁴Reproduce the table for each user who accessed the infrastructure

User status	
New user	

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: Kinetic and mechanistic study of tropospheric degradation of a series of furanones derived from: 2(3H)-Furanone and 3(2H)-furanone initiated by Cl atoms and OH radicals at 298 K, and their atmospheric implications.

Chamber name and location: QUAREC CHAMBER, Universität Wuppertal, Gaußstraße 20, 42119 Wuppertal, Alemania

Introduction.

Furans and their derivatives, such as furanones, are of atmospheric importance since reactions in the troposphere of these compounds initiated by Cl atoms and OH radicals generate much more polluting compounds than furanone itself. Furans and furanones are not intentionally manufactured by man, they derive as by-products of uncontrolled reactions that involve high temperatures, or also by the degradation of other compounds such as isoprene. [2]. At present, not much is known about the reactions with OH and Cl of furanones, this is one of the main motivations of this project. Previous work have identified some furanones by burning biomass or cellulose pyrolysis [1], products such as 5-chloro-4-methyl-2 (5H) -furanone and methyl-2 (3H) -furanone have been identified in reactions of furans with oxidants such as Cl and OH [2].

In this work, the reactions with OH and Cl radicals of the following compounds were studied: 3 (2H) -furanone, 2-methyl-3 (2H) -furanone, 2,2-Dimethyl-3 (2H) -furanone, 5-propyl-dihydro-2 (3H) -furanone, 5-Ethyl-dihydro-2 (3H) -furanone.

Specific objectives met

-Kinetic studies of the reaction of 3 (2H) -furanone, 2-methyl-3 (2H) -furanone, 2,2-Dimethyl-3 (2H) -furanone with Cl atoms and OH radicals at 298 K.

- Mechanistic study of products formed in the OH radicals and Cl atoms reactions of 3 (2H) -furanone, 2-methyl-3 (2H) -furanone, 2,2-Dimethyl-3 (2H) -furanone.

-Kinetic studies of the reaction of ethyl-dihydro-2 (3H) -furanone and 5-propyl-dihydro-2 (3H) -furanone initiated by Cl atoms and OH radicals at 298 K.

-Mechanistic study of products formed in the OH radicals and Cl atoms reactions, ethyl-dihydro-2 (3H) -furanone and 5-propyl-dihydro-2 (3H) -furanone.

- Analysis of the reactivity trends for the compounds listed above and estimations of their atmospheric lifetimes.

Reason for choosing the simulation chamber/ calibration facility.

The Quarec Chamber was chosen because of the facility of working at low concentrations of the compounds, this since the chamber has multi-reflection mirrors, also allows simulating conditions of pressure and temperature very close to the real atmosphere, the procedure to work and manipulate the chamber is quite understandable.

Method and experimental set-up

Before starting with each kinetic study, the conditions for all the compounds were optimized, and experiments studies were carried out such as: Test the wall and/or photolysis of the compounds.

the conditions the experiments were as follows:

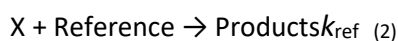
-The chamber is equipped with a White type multiple-reflection mirror system with a base length of (5.91 ± 0.01) m for sensitive in situ long path absorption monitoring of reactants and products in the IR spectral range $4000-700$ cm^{-1} . The IR spectra were regulated with a spectral resolution of 1 cm^{-1} using a Nicolet Nexus FTIR spectrometer, equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT).

-The Concentrations used for furanones were 2-4 ppm, for the references 3-5 ppm and 10-20 ppm for CH_3ONO y Cl, which were used as oxidizing agent. Where 1 ppmV is equal to 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure.

-The OH radicals were generated by the photolysis of $\text{CH}_3\text{ONO}/\text{NO}/\text{air}$ mixtures at 360 nm. Cl atoms were generated by the photolysis of Cl_2 with the fluorescent lamps at 360 nm.

-Rate coefficients were determined using the relative method. Product analyses were performed using in situ FTIR spectroscopy.

The following reactions were studied experimentally:



Where X= OH and Cl

The references used for the different reactions studied were: Isobutene, propene, isobutane, etene.

The decrease in the concentration of all compounds against chlorine atoms and OH during the experiment, two runs were made for each reference. Product studies with chlorine and OH atoms were performed for all compounds, using CH₃ONO/NO/and Cl₂ as the OH precursors and chlorine atoms respectively.

Preliminary results and conclusions

Preliminary results for 2-methyl-3 (2H) -furanone, 2,2-Dimethyl-3 (2H) -furanone with chlorine atoms.

The rate coefficients of 2-methyl-3 (2H) -furanone (2-MTHF), 2,2-Dimethyl-3 (2H) -furanone (2,2-DMTHF) with chlorine atoms at 298 K and 760 Torr were determined, using isobutene and propene as reference.

Preliminary studies showed that there are no significant side reactions. Preliminary results for the constants are presented in Table 1 and Figure (1). From the preliminary results we can observe a tendency of reactivity in which the reactivity of the compounds are related to the structure, which is 2,2-DMTHF > 2-MTHF, this can be attributed to the presence of methyl groups in 2,2-DMTHF and the presence of the double bond in the molecule, the reactivity of this furanone against chlorine atoms. This can be attributed to the presence of the methyl groups in 2,2-DMTHF and the presence of the double bond in the molecule, the reactivity of this furanone toward chlorine atoms.

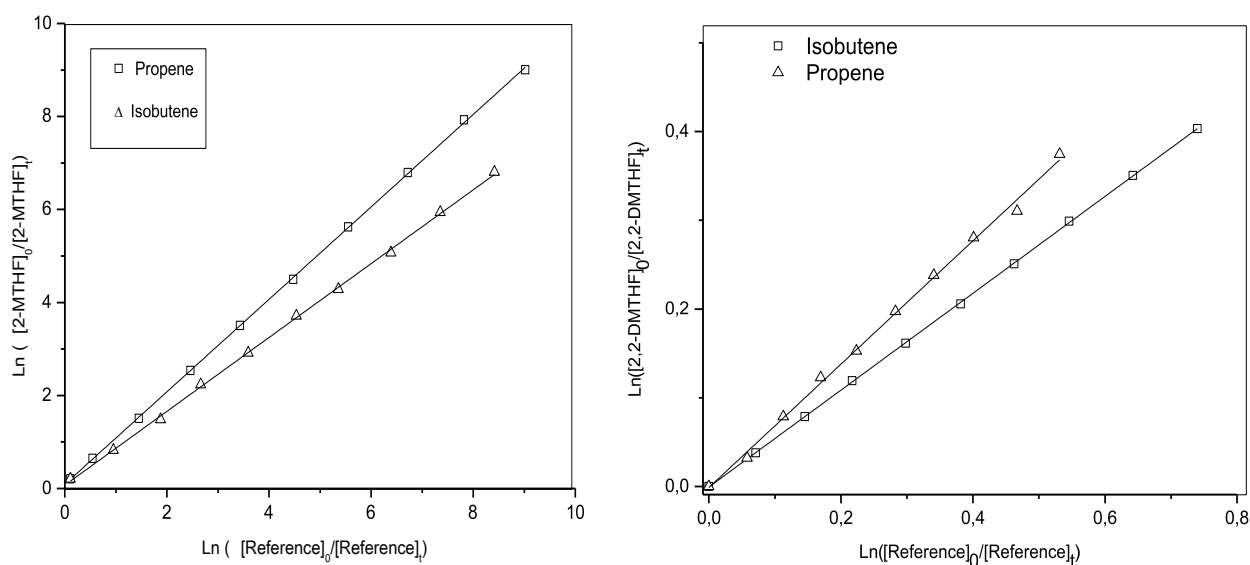
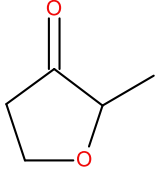
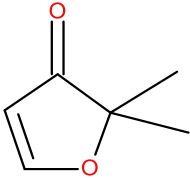


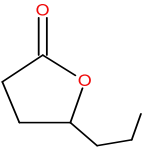
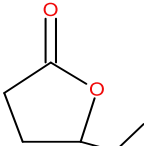
Fig. 1. Relative kinetics graph for 2-methyl-3 (2H) -furanone (2MTHF), 2,2-Dimethyl-3 (2H)-Furanone (2,2-DMTHF), ethyl-dihydro-2 (3H) -furanone with Cl atoms using as reference: Isobutene and Propene at 298 K and 760 Torr.

Table 1. Results obtained for rate coefficients, references and $k_{\text{furanone}}/k_{\text{reference}}$ ratios for the reaction of furanones with Cl atoms measured at 298 K and 760 Torr.

Compound	Reference	$k_{\text{furanone}}/k_{\text{reference}}$	$k_{\text{furanone}} \times 10^{-10}$ (cm ³ molecule ⁻¹ s ⁻¹)
2-MTHF 	Isobutene	(0.4013±0.003)	(1.36±0.12)
	Propene	(0.5025±0.002)	(1.33±0.10)
	Average (1.35± 0.11)		
2,2-DMTHF 	Isobutene	(0.5458±0.002)	(1.86±0.15)
	Propene	(0.6951±0.002)	(1.87±0.18)
	Average (1.87±0.17)		

The preliminary results obtained for the reaction of chlorine atoms with ethyl-dihydro-2 (3H) - furanone and 5-propyl-dihydro-2 (3H) – furanone are presented in Table 2 and Figure 2. The difference in the rate coefficients obtained for ethyl-dihydro-2 (3H) -furanone and 5-propyl-dihydro-2 (3H) –, can be attributed to the inductive and stabilizing effect of the alkyl groups, an increase in the number of carbons and hydrogen of the alkyl chain linked to the ring increases the reactivity of the compound toward chlorine atoms. These results are consistent with those obtained by Barnes [3], when comparing the rate coefficient reaction with chlorine of a series with lactones. Barnes [3] showed in his work that the reactivity of lactones with chlorine atoms is influenced by the carbon site adjoining to heterocyclic oxygen.

Table 2. Rate coefficients and references and $k_{\text{furanone}}/k_{\text{reference}}$ ratios for the reaction of furanones with Cl atoms measured at 298 K and 760 Torr

Compound	Reference	$k_{\text{furanone}}/k_{\text{reference}}$	$k_{\text{furanone}} \times 10^{-10}$ (cm ³ molecule ⁻¹ s ⁻¹)
PDHF 	Isobutene	(0.402±0.003)	(1.36 ±0.12)
	Propene	(0.503±0.004)	(1.36±0.11)
	Average (1.36±0.12)		
EDHF 	Isobutene	(0.295±0.001)	(1.00±0.10)
	Propene	(0.3823±0.014)	(1.03±0.11)
	Average (1.02 ±0.11)		

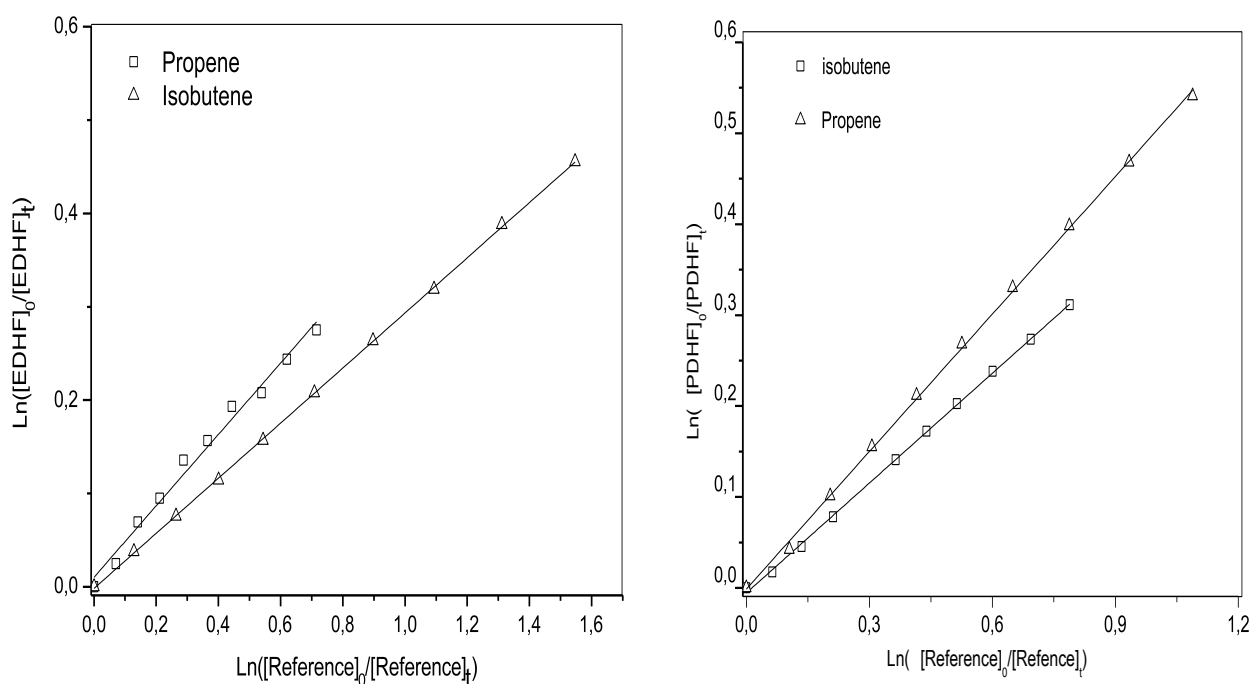


Fig. 2. Relative kinetics graph for ethyl-dihydro-2 (3H) -furanone (EDHF) and 5-propyl-dihydro-2 (3H)-furanone (PDHF) with Cl atoms using as reference: Isobutene and Propene at 298 K and 760 Torr.

Preliminary conclusions

Rate coefficients with chlorine atoms were determined experimentally for a series of cyclic furanones, establishing an order of reactivity trend, controlled by the number of carbons or alkyl groups linked to the ring, of furanones derived from 2 (3H) -Furanone. The reactivity trend observed experimentally is 2-MTHF < 2,2-DMTHF. While for the furanones derived from 3 (2H) -furanone we observe an order of reactivity EDHF < PDHF.

Future studies

During the stay in the Quarec chamber not only experiments were carried out for the furanones presented, the kinetic study with chlorine atoms of the 3 (2H) -furanone was also carried out, in addition to the products with chlorine atoms, in addition, the kinetic study and products with the OH radical with the furanones: 3 (2H) -furanone, 2-methyl-3 (2H) -furanone, 2,2-Dimethyl-3 (2H) -furanone, 5-propyl-dihydro-2 (3H) – furanone. Once all the experimentally obtained data has been processed, it will start with the publication in atmospheric chemistry scientific journals, in addition to its dissemination in meetings related to the area

Reference

- [1] Lourenço, A., Neiva, D. M., Gominho, J., Curt, M. D., Fernández, J., Marques, A. V., & Pereira, H. (2015). Biomass production of four *Cynara cardunculus* clones and lignin composition analysis. *Biomass and Bioenergy*, 76, 86-95.
- [2] Tapia, A., Villanueva, F., Salgado, M.S., Cabanas, B., Martinez, E., Martin, P., 2011. Atmospheric degradation of 3-methylfuran: Kinetic and products study. *Atmos. Chem. Phys.* 11, 3227-32413.
- [3] Barnes, I., Kirschbaum, S., & Simmie, J. M. (2014). Combined Experimental and Theoretical Study of the Reactivity of γ -Butyro-and Related Lactones, with the OH radical at Room Temperature. *The Journal of Physical Chemistry A*, 118(27), 5013-5019.