



TNA User Report

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Project title	Atmospheric Chemistry of CHF ₂ CH=CF ₂ : OH and NO ₃ radicals, Cl-atoms and O ₃ kinetics and Intermediate and end-oxidation products investigation
Name of the accessed chamber	HELIOS
Number of users in the project	2 users (PI and 1 user)
Project objectives (max 100 words)	The project aimed to determine CHF ₂ CH=CF ₂ atmospheric lifetime (reaction rate coefficients with OH, Cl and O ₃), end-products and IR spectrum that will further our understanding on its atmospheric impact and can be utilized to determine critical metrics and diagnostics, RE, direct- and indirect-GWP, POCP, for its full-lifecycle assessment. CNRS/ICARE laboratory constitutes a very powerful facility equipped with chambers, that use both solar and artificial radiation and state-of-the-art equipment for real-time and on-line analysis. Further, the host co-workers experience and expertise in Atmospheric Chemistry and kinetics was critical for the project successful designation and implementation that lead to results of extremely high quality.
Description of work (max 100 words):	Rate coefficients for the reactions of OH radicals, Cl atoms and O ₃ with CHF ₂ CH=CF ₂ were determined at 296 K, 1 Atm (Syn. Air) in HELIOS. A white-cell FTIR spectrophotometer and a PTR/ToF-MS were used to in-situ monitoring reactants and stable products concentrations and to identify and quantify end-products on-line. H ₂ O ₂ and Cl ₂ and C ₂ O ₂ Cl ₂ were used as OH radicals and Cl atoms precursors, while O ₃ was produced via O ₂ discharge in an O ₃ -generator. IR spectrum of CHF ₂ CH=CF ₂ was also measured and along with the kinetic data, CHF ₂ CH=CF ₂ lifetime, RE and direct and indirect GWP and POCP were estimated.

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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 EXP= Engineer; ACA= Academic; TEC= Technician.

⁴ Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

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Name of the PI: Vasileios Papadimitriou

Chamber name and location: HELIOS, CNRS/ICARE Orleans

Campaign name and period: EUROCHAMP 2020, Atmospheric Chemistry of $\text{CHF}_2\text{CH}=\text{CF}_2$: OH and NO_3 radicals, Cl-atoms and O_3 kinetics and Intermediate and end-oxidation products investigation, June 11th – July 11th, 2019

Introduction and Motivation

Unsaturated fluorinated hydrocarbons (HdroFluoroOlefins, HFO) are the most recently proposed CFCs substitutes and there is an urgent need to further improve our understanding on their atmospheric reactivity and processing. In addition, in the light of their extensive industrial usage, their impact on Climate, Air-quality and humans' health, needs to be thoroughly evaluated. Particularly, $\text{CHF}_2\text{CH}=\text{CF}_2$ (HFO-1234zc) has been proposed to be used as foam-blowing agent (US patent, Patent Nr. US 20070100010), but it can be also used in several commercial and industrial applications, in a single component form or in a multi-component mixture, with applications as refrigerant, fire-suppressing and cleaning, etching and propellant agent. Therefore, the thorough kinetic and end-product study will assist first to understand how both degree and positioning of fluorination affects HFOs atmospheric reactivity, as well as, to evaluate the full-lifecycle of those compounds in the atmosphere. There are several OH, Cl and O_3 kinetic studies for fluorinated propylenes, such as $\text{CF}_3\text{CF}=\text{CH}_2$, $\text{CF}_3\text{CF}=\text{CHF}$ and $\text{CF}_3\text{CF}=\text{CF}_2$, (Orkin *et al.* 1997, Nielsen *et al.*, 2007, Papadimitriou *et al.*, 2008, Papadimitriou *et al.* 2010)¹⁻⁴. However, to the best of our knowledge there are no available data for $\text{CHF}_2\text{CH}=\text{CF}_2$ atmospheric reactivity that is a key compound for understanding the effect of fluorine positioning both in reactivity, as well as in the end-products formation.

Scientific Objectives

In the frame of Eurochamp 2020, kinetic measurements for OH radicals, Cl atoms and O_3 gas phase reactions with HFO-1234zc were conducted in HELIOS at 296 K and 1 Atm of air-pressure, as well end-products were identified via both FTIR spectroscopy and PTR/ToF-MS spectrometry. IR spectrum of HFO-1234zc was also determined as a part of this project and along with the kinetic data, lifetimes, and critical evaluation metrics that are used to evaluate the atmospheric impact of those compounds, on climate, air-quality and humans' health, such as lifetime, radiative efficiency (RE), direct and indirect Global Warming Potential (GWP) and photochemical ozone creation potential (POCP) were estimated.

Reason for choosing the simulation chamber/ calibration facility

Helios is a chamber with low surface to volume ratio 1.2 m^{-1} and a high transparency to solar radiation, >90 %, that not only allows to monitor in real-time the product formation, but also to quantify the end-products with on-line the state-of-the-art detections equipment that are assorted to the chamber. FTIR spectrophotometer equipped with a white-cell of 200 m optical path and a PTR/ToF-MS (Ionicon 8000) can be utilized complementarily to fully evaluate the end-products and to cross-calibrate the PTR/ToF-MS, if needed. CIMS/MS, a Horiba (APOA-370) ultra-violet ozone analyser and various other analyzers, such as HCHO analysers are always available and easily attached to the chamber. Moreover, artificial light can also be used and intercomparison between the two different radiation sources can be evaluated. Last but not least, the expertise and the experience of the host co-workers on Atmospheric

Chemistry, processing and chemical kinetics plays a key-role for the most efficient designing of the experiments and their best implementation within the timeframe of the project.

Method and experimental setup

The majority of the measurements were carried out in the hemispheric HELIOS atmospheric simulation chamber with a total volume of 90 m³ and a surface to volume ratio of 1.2 m⁻¹. Helios is protected from intense weather phenomena via a specially designed movable dark-housing and it is made of a 250 μm Teflon FEP film that allows >90 % of the solar radiation to penetrate into the chamber. A variety of instrumentation are available to be assorted to HELIOS such as 200 m of optical path on-line FTIR, PTR-ToF-MS (Ionicon 8000), Aerodyne ToF-CIMS, ATD-GC-MS, UHPLC, IC, SMPS, LOPAP HONO analyser, Aerolaser 4021 HCHO analyser, Spectroradiometer and monitors of O₃, NO_x (NO + NO₂) and SO₂, as well as CRDS for NO₃ and N₂O₅ detection. In the present study, FTIR and PTR/ToF-MS were primarily used along with O₃ monitor wherever needed. All kinetics measurements were conducted at 296 ± 2 K and at ambient pressure, i. e., 1 Atm, employing relative rate methods with the O₃ kinetics to be the only exception, at which the absolute rate coefficient was measured at controlled Pseudo-First-Order (PFO) conditions. Several kinetic determinations were also conducted using a smaller available atmospheric chamber of 7.3 m³ and surface to volume ratio of 3.2 m⁻¹, equipped with artificial light source with peak light intensity either at 254 nm (UV-C, OH radicals reactions) or at 365 nm (UV-A). Gas reactants were admitted into the photoreactor via calibrated buffer volumes, while liquids were directly injected via titrated syringes or for compounds of lower volatility by using bubblers that they were compounds vapors were flushed into the chamber via synthetic air flow. SF₆ was used as non-reactive marker in all determinations in order to measure dilution and other first-order losses of the reactants, e. g., wall-loss.

a. OH kinetics and product studies

The kinetics for the reactions of OH radicals with HFO-1234zc were carried out employing relative rate methods using as reference the well documented reactions of OH with C₃H₈,⁵ $k_{\text{ref},1}(298 \text{ K}, 1 \text{ Atm}) = (1.10 \pm 0.06) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and with C₂H₄,⁵ $k_{\text{ref},2}(298 \text{ K}, 1 \text{ Atm}) = (8.15 \pm 1.22) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. H₂O₂ was used as OH radicals precursor and either solar light radiation or UV-C lamps in the case of the smaller chamber. Reactants and products were recorded both with PTR/ToF-MS (1 s averaging time) and FTIR spectroscopy, R = 1 cm⁻¹, with the co-added scans to be adjusted so as to observe measurable changes in both HFO-1234zc and reference compound. End-products were identified and quantified in the absence of references using PTR/ToF-MS (1 s averaging time, full mass-scan) and FTIR spectroscopy.

b. Cl kinetics and product studies

For Cl kinetics oxalyl chloride was used as Cl atoms precursor in HELIOS, and Cl₂ in the case of the smaller chamber. As the Cl reference reactions are concerned three different compounds with very well established reactivity towards Cl atoms were used: C₃H₈,⁵ $k_{\text{ref},3}(296 \text{ K}, 1 \text{ Atm}) = (1.40 \pm 0.14) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, C₂H₄,⁵ $k_{\text{ref},4}(298 \text{ K}, 1 \text{ Atm}) = (1.06 \pm 0.50) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and C₂H₆,⁵ $k_{\text{ref},5}(298 \text{ K}, 1 \text{ Atm}) = (5.70 \pm 0.40) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In small chamber's measurements UV-A lamps with a peak-emission at 365 nm. Similarly to OH kinetics, PTR/ToF-MS (1 s averaging time) and FTIR spectroscopy, R = 1 cm⁻¹ were used for monitoring reactants concentrations and with the co-added scans were adjusted accordingly. End-products were identified and quantified in the absence of references using both PTR/ToF-MS (1 s averaging time, full mass-scan) and FTIR spectroscopy.

c. O_3 kinetics

O_3 was introduced in the chamber using a Trailigaz O_3 generator and was continuously monitored using a Horiba (APOA-370) or Horiba (APOA-360) ultra-violet ozone analyzer and Infrared spectroscopy. Absolute rate for the reaction of O_3 with HFO-1234zc was measured under PFO in HFO-1234zc, i. e., $[O_3] \gg [HFO-1234zc]$, in the presence of excess of 2-butanol to scavenge Criegee intermediates and OH radicals. Concentrations were adjusted so as to have measurable decays of HFO-1234z taking into account dilution and other first order loss-processes.

d. IR Spectra measurements

IR cross-section spectrum was measured as part of this project, first to quantify compound concentration in product yields measurements and secondly to estimate RE and GWP of HFO-1234zc. A white cell of 10 m optical path was used during the measurements and peak cross sections and integrated band strengths (IBS) were determined using Beer-Lambert and ideal gas laws. Two mixtures of different mixing ratios of HFO in He were manometrically prepared in 10 L bulbs. Then, absorbance and IBS were determined at least 10 different pressures at 1 and 0.5 cm^{-1} resolution with 128 co-added scans, for both mixtures, using different range of pressures and after flushing (fill-pump cycles), thoroughly the white cell, with the prepared mixtures, several times. Finally, a high quality IR spectrum was recorded at 0.5 and 1 cm^{-1} resolution with 1024 co-added scans. Not that separate backgrounds were recorded just before the measurements, filling the white cell with He, at the exact pressure with the actual measurement.

Data description

Relative rate coefficients were determined by applying rate laws and assuming that both HFO-1234zc and the reference compound are solely consumed via their reaction with the oxidant of interest. In that case, it can be derived:

$$\ln \frac{[HFO - 1234zc]_0}{[HFO - 1234zc]_t} = \frac{k_1}{k_{Ref}} \ln \frac{[Ref]_0}{[Ref]_t}$$

where, $[X]_0$ and $[X]_t$, (X: HFO-1234zc or Ref) represent the concentration of HFO or reference at time zero and after reaction time t, respectively, k_{Ref} is the second-order rate coefficient for the reference reaction and k_1 the reaction rate coefficient for the reaction of the oxidant with HFO-1234zc. IR spectra were recorded sequentially and the rate coefficients were obtained by subsequent subtractions of the recorded spectra from the initial – no reaction (No exposure to light) – using internally made procedures in Wavemetrics Igor. Since, the concentration ratios is needed in kinetics, cross-section are not required in the analysis. For product yields measurements though, where the yield is determined via plotting the HFO-1234zc loss with time, as a function of the corresponding formation of each product, IR cross sections are required. Mass-spectra were also used in product analysis to sensitively and rapidly (temporal profiles) detect and identify the products and cross-validated calibration using the complementary primary detection techniques can be employed where required. External calibration of PTR/ToF-MS for several observed products are also possible, either running commercial available standards or synthesize and prepare the standards, e. g., CHF_2CHO that is a potent product can be synthesized from the corresponding hemiacetal, i. e., $CHF_2CH(OH)-O-C_2H_5$.

Preliminary results and conclusions

OH and Cl Kinetics

The results for the kinetic measurements are summarized in figure 1. Various variations in concentrations of reactants or precursors did not affect the measurements and for all different reference reactions used in both Cl and OH reactions, the results always agreed better than 5%. Note that no dark, or photolysis loss for any of the reactants was observed, under all conditions tested, within the precision of the measurements.

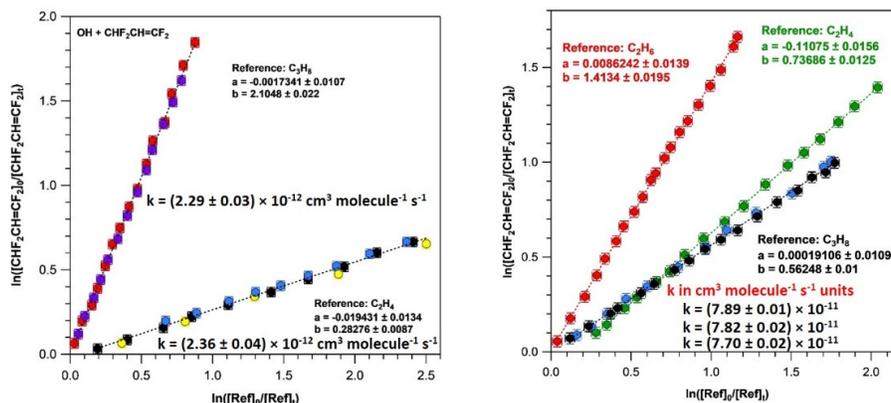


Figure 1. Relative rate coefficients determinations, $k(296\text{ K}, 1\text{ Atm})$, for both OH radicals and Cl atoms reactions with HFO-1234zc.

Cl and OH radicals initiated end-oxidation products and IR Spectra

In figure 2 and 3 a simplified proposed mechanism based on the PTR/ToF-MS and IR peaks detected, for both Cl and OH initiated atmospheric oxidation of HFO-1234zc, is shown.

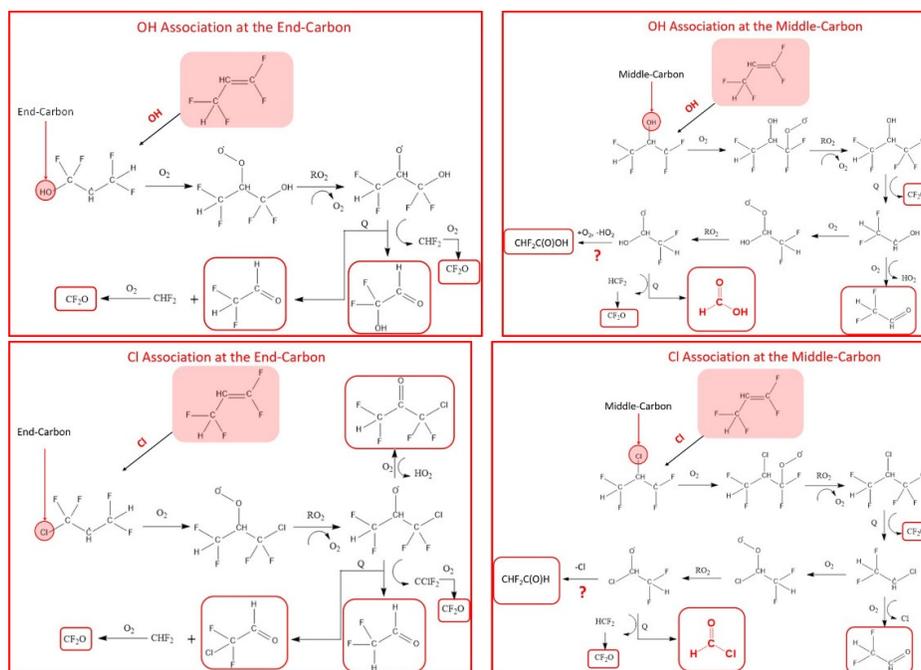


Figure 2. Simplified proposed atmospheric degradation of HFO-1234zc, initiated by OH and Cl atoms. Red frames refer to the products that were identified via either PTR/ToF-MS and/or FTIR.

Figure 3 shows the IR spectrum of HFO-1234zc measured as part of this work within the relevant to the atmosphere wavenumber range. No significant pressure (2 -760 Torr) or resolution dependence was observed.

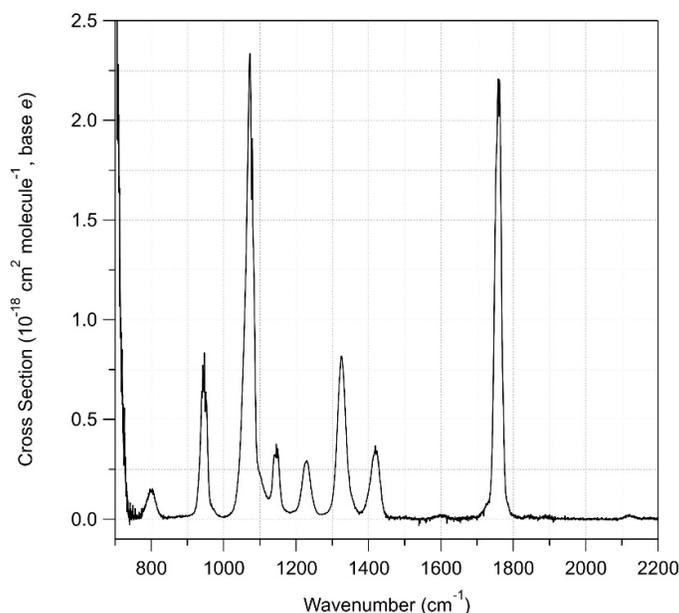


Figure 3. IR cross-section spectrum of HFO-1234zc in the relevant for the atmosphere wavenumber range. Spectrum was recorded at both 0.5 and 1 cm^{-1} resolution with 1024 co-added scans.

O₃ Kinetics and Discussion

HFO-1234zc reactivity towards O₃ was low with a measured second order rate coefficient of $\sim 2 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Therefore, O₃ atmospheric loss will not play a key role in determining the atmospheric lifetime of the compound, which is going to be dominated from its reactions with OH radicals and Cl atoms. HFO-1234zc is a very short lived compound (VSLC) and OH radicals are expected to be the determinative atmospheric oxidants. However, Cl chemistry cannot be neglected, especially since in the location where the higher emissions are expected, e. g., Cl atoms levels are elevated and can be of similar importance with the OH radicals.

Outcome and future studies

The work within this project is going to be published in a peer-reviewed journal and is also part of Maria Angelaki's PhD thesis. Future studies include full data compilation, NO₃ reactivity measurements of HFO-1234zc and calibration of the PTR/ToF-MS for the primary reactions end-products.

References

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