FTIR product study of the Cl-initiated oxidation products of CFC replacements: \((E/Z)-1,2,3,3,3\)-pentafluoropropene and hexafluoroisobutylene

Cynthia B. Rivela,a Rodrigo G. Gibilisco,b Carmen M. Tovar,b Ian Barnes,†b Peter Wiesen,b Maria B. Blanco b,a and Mariano A. Teruelc,d

A product study of the reactions of \((E/Z)-1,2,3,3,3\)-pentafluoropropene (\((E/Z)-\text{CF}_3\text{CF}==\text{CHF}\)) and hexafluoroisobutylenen (HFOs) initiated by Cl atoms were developed at 298 ± 2 K and atmospheric pressure. The experiments were carried out in a 1080 L quartz-glass environmental chamber coupled via in situ FTIR spectroscopy to monitor the reactants and products. The main products observed and their yields were as follows: \(\text{CF}_3\text{C(O)}\text{F}\) (106 ± 9)% with HC(O)F (100 ± 8)% as a co-product for \((E/Z)-\text{CF}_3\text{CF}==\text{CHF}\), and \(\text{CF}_2\text{C(O)}\text{CF}_3\) (94 ± 5)% with HC(O)Cl (90 ± 7)% as a co-product for \((\text{CF}_3)_2\text{C}==\text{CH}_2\). Atmospheric implications of the end-product degradation are assessed in terms of their impact on ecosystems to help environmental policymakers consider HFOs as acceptable replacements.

## 1 Introduction

The adverse effects of chlorofluorocarbons (CFCs) on the stratospheric ozone layer are known and have been extensively studied.1,2 Several viable CFC replacements have been proposed in the last decade, such as hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), and hydrofluoroalcohols (HFAs). Moreover, recently, hydrofluoroolefins (HFOs) have been proposed as the fourth-generation replacements for CFCs.3 Hydrofluoroolefins (HFOs) have been proposed as replacements mainly of refrigerants.4,5 In addition, HFOs have numerous other industrial applications as foaming agents, aerosol propellants, mobile air conditioning systems, precision solvent cleaners, MDIs (metered dose inhalers), medical propellants, coatings, and as basic components in the production of fluoropolymers, etc.4,6,7 HFOs are known to be highly reactive due to the presence of a C–C double bond, resulting in short atmospheric lifetimes and therefore zero ozone depletion potentials (ODP) and minimized global warming potentials (GWP).

Several experiments determined that the reactions of fluorinated alkenes in the troposphere are mainly controlled by OH radicals,8,9 while oxidation via Cl atoms can also be an important homogeneous loss process at dawn in coastal or marine regions and has also been observed in the central and urban areas.10,11

This present work aims to perform a detailed study on the atmospheric degradation mechanism of the reaction of \((E/Z)\)-isomeric mixture of \(1,2,3,3,3\)-pentafluoropropene (PFP) and hexafluoroisobutylene (HFIB) initiated by Cl atoms.

Only one product study related to OH and Cl-initiated oxidation of individual \((Z)\) and \((E)\) isomers of \(1,2,3,3,3\)-pentafluoropropene has been reported in the literature using a Pyrex reactor and the FTIR technique as a detection system.12 The authors have reported for both Cl and OH radical-initiated oxidations of \(\text{CF}_3\text{CF}==\text{CHF}\), and the presence of \(\text{CF}_3\text{C(O)}\text{F}\) and HC(O)F in 100% indistinguishable molar yields for both \((Z)\) and \((E)\) isomers.

Only a product identifications study of the reactions of hexafluoroisobutylene with OH radicals and Cl atoms was previously reported.13 This study was performed at 296 ± 1 K and atmospheric pressure using a Pyrex reactor and FTIR spectroscopy to monitor the reactants and products. HC(O)H and \(\text{CF}_3\text{C(O)}\text{CF}_3\) were identified as final oxidation products in both OH- and Cl-initiated oxidation reactions, while HC(O)Cl, HCl, and CO were observed in the Cl-initiated oxidation reaction. In addition, a theoretical study of the reaction of hexafluoroisobutylene (HFIB) with OH radicals has been performed, where two different reaction channels of HFIB with OH radicals were postulated: addition to the >C==C< bond and one H-abstraction reaction channel. These authors reported three possible reaction pathways for this reaction: two addition channels associated with the addition of OH radicals to the >C==C< bond and the abstraction of the H atom from the –CH₂ group. They further observed that while the
addition channels dominate the kinetics of this reaction, the contribution of the H abstraction channel cannot be completely neglected. This observation was particularly shown at the high temperature range of 250–1000 K used this study.9

To the best of our knowledge, previous product quantification studies of the reactions of Cl atoms with the isomeric mixture (E/Z) of 1,2,3,3,3-pentafluoropropane, or for hexafluoroisobutylene, are not available in literature. Consequently, the current work is the first determination of the product distribution for the title reactions.

Before the widespread use of these species, it is essential to investigate the potential environmental effects of its degradation products. For this purpose, the reaction products of the Cl atom-initiated gas phase degradation of the E/Z-isomeric mixture of 1,2,3,3,3-pentafluoropropane (PFP) and hexafluoroisobutylene (HFIB) have been studied:

\[
\begin{align*}
(E/Z)-\text{CF}_3\text{CF}═\text{CHF} + \text{Cl} & \rightarrow \text{products} \\
\text{(CF}_3)\text{C}═\text{CH}_2 + \text{Cl} & \rightarrow \text{products}
\end{align*}
\]

2 Experimental

The product studies were performed in a quartz chamber of 1080 L capacity in synthetic air at 298 ± 2 K and 760 Torr coupled with in situ FTIR spectroscopy. The reactor consists of two quartz glass container cylinders, each 3 m long and 45 cm internal diameter, joined in the middle with both open ends closed by aluminum flanges. The photolysis system consists of 32 super actinic black lamps (Philips TL05 40 W: 320–480 nm, \(\lambda_{\text{max}} = 360 \text{ nm}\)) and 32 low-pressure mercury vapor germicidal lamps (Philips TUV 40 W; \(\lambda_{\text{max}} = 254 \text{ nm}\)). The quartz chamber reactor has been used previously at the Wuppertal laboratory, and more relevant details are described by Barnes et al.14,15

Chlorine atoms were generated by the photolysis of molecular chlorine (Cl2) using the black lamps:

\[
\text{Cl}_2 + h\nu (\lambda \sim 360 \text{ nm}) \rightarrow 2\text{Cl}^\
\]

The initial mixing ratios used in the experiments for HFOs in ppm (1 ppm = \(2.46 \times 10^{13}\) molecule cm\(^{-3}\) at 298 K and 760 Torr total pressure) were 1.5 ppm for 1,2,3,3,3-pentafluoropropane, (E/Z) mixture and 1.5 ppm of hexafluoroisobutylene. The initial concentration for the precursor of the oxidant was typically around 6 ppm of Cl2. The infrared absorption frequencies at 1407.8 and 1383.7 cm\(^{-1}\) were used to monitor the concentration–time behavior of 1,2,3,3,3-pentafluoropropane, (E/Z) mixture and hexafluoroisobutylene, respectively. Readily identifiable products were monitored at the following absorption frequencies (in cm\(^{-1}\)): \(\text{CF}_3\text{C}═\text{O}\text{F} \) at 1897.7; \(\text{HC}═\text{O}\text{F} \) at 1837.7; \(\text{CF}_3\text{C}═\text{O}\text{F} + \text{C}═\text{F} \) at 974.7 and \(\text{HC}═\text{O}+\text{Cl} \) at 738.6.

The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: synthetic air (Air Liquide, 99.9999%); 1,2,3,3,3-pentafluoropropane (Apollo Scientific, mixture (E/Z) isomers 97%, no manufacture details on isomer ratio), hexafluorobutylene (Apollo Scientific, purity not specified), and Cl2 (Messer Griesheim, ≥99.8%). Wall deposition, reaction with the precursor of Cl, or photolysis was found to be negligible for both HFOs studied.

3 Results and discussion

To investigate the oxidation mechanism of HFOs initiated by Cl atoms, a mixture of HFO, Cl2, and air was irradiated for the time period of 10–30 minutes, during which infrared spectra were recorded on an FTIR spectrometer. Typically, up to 128 interferograms were co-added per spectrum for approximately 40 s, and 15–20 spectra were collected. Prior to the initiation of the reaction by Cl atoms, 5 spectra were collected in dark to check the homogeneity and the unexpected dark decay of the compounds (e.g., wall losses or dark reactions).

\((E/Z)\)-isomeric mixture of 1,2,3,3,3-pentafluoropropane + Cl reaction

In Fig. 1, a schematic representation of the expected reaction mechanism of PFP with Cl atoms and the obtained products, trifluoroacetyl fluoride (\(\text{CF}_3\text{C}═\text{O}\text{F}\)) and formyl fluoride (\(\text{HC}═\text{O}\text{F}\)), is presented. The proposed mechanism suggests that the Cl atom could be added to the carbon atom C1 or C2 of the double bond, followed by the subsequent reactions with O2 to form RO2 with further 1,2-chloroalkoxy radical production. This radical formed could decompose to give \(\text{CF}_3\text{O}\text{F}\) and \(\text{HC}═\text{O}\text{F}\).

Fig. 2 trace A shows the infrared spectrum of a PFP/Cl2/air reaction mixture after irradiation and subtraction of residual PFP. The spectra of the identified products are presented in Fig. 2, where trace B shows a reference spectrum of trifluoroacetyl fluoride and trace C shows a formyl fluoride spectrum. Trace D shows the residual spectrum obtained after the subtraction of the spectra in traces A, B, and C. The presence of unidentified absorption bands was negligible in the residual product spectrum. Therefore, it is assumed that trifluoroacetyl fluoride and formyl fluoride are the main reaction products of PFP with Cl atoms. This result is in agreement with results obtained in previous studies on the atmospheric degradation of PFP.16-17

The concentration–time profiles of PFP and its identified products are shown in Fig. 3. This graph supports the results that trifluoroacetyl fluoride and formyl fluoride are both primary products.

In Fig. 4, the concentrations of the products formed versus the consumed PFP in the reaction with Cl atoms show reasonable linearity. The average product yields obtained from the two experiments are \(\text{CF}_3\text{C}═\text{O}\text{F} \) (106 ± 9%) and \(\text{HC}═\text{O}\text{F} \) (100 ± 8%) (Table 1). These results indicate that the products formed are the result of the decomposition of the \(\text{CF}_3\text{C}═\text{Cl} \) radicals formed via the C1 and C2 bond scission.

The same results are expected for both (E) and (Z) isomers in the mixture of 1,2,3,3,3-pentafluoropropane.

Previous studies for the reactions of the (Z) and (E) isomers of \(\text{CF}_3\text{CF}═\text{CHF}\) initiated by OH radicals, Cl atoms, and O3
molecules by Hurley et al.\textsuperscript{18} using a 140 L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer reported yields of \((98 \pm 4)\%\) for CF\textsubscript{3}C(O)F and \((100 \pm 5)\%\) for HC(O)F for the Cl reactions with both CF\textsubscript{3}CF=CHF isomers. These results are in agreement with those obtained in the present study. Furthermore, Papadimitriou et al.\textsuperscript{16} reported rate coefficients and product yields for the gas-phase reactions of Cl atoms and NO\textsubscript{3} radicals with \((Z)\text{-CF}_3\text{CF}=\text{CHF}\) using a temperature-regulated Pyrex reactor with a pulsed excimer laser photolysis source to produce Cl atoms and FTIR to monitor the reactant and product concentrations. The experiments were carried out in the

![Reaction mechanism of (E/Z)-1,2,3,3,3-pentafluoropropene with Cl atoms via the addition to the double bond.](image1)

![Trace A shows the infrared spectrum obtained from a PFP/Cl\textsubscript{2}/air reaction mixture after UV irradiation. Traces B and C show the reference spectra of trifluoroacetyl fluoride and formyl fluoride, respectively. Trace D shows the residual product spectrum obtained after the subtraction of features due to the reference spectra from the spectrum in trace A.](image2)

![Concentration–time profiles of PFP and the reaction products, trifluoroacetyl fluoride and formyl fluoride, obtained from the UV photolysis of the PFP/Cl\textsubscript{2}/air reaction mixture.](image3)
presence of O₃ over a range of temperatures (247–380) K and pressures ranging from (50–630) Torr. As a result, the authors observed that the reaction was independent of temperature and pressure. The product yields obtained were (108 ± 8)% for CF₃C(O)F and (112 ± 8)% for HC(O)F. The present study is in excellent agreement with all previous determinations for the reactions of similar HFOs from the literature.

**Hexafluoroisobutylene + Cl reaction**

In the same way as the reaction described above, the reaction of Cl atoms with HFIB follows the addition of the Cl atom to the C₁–C₂ double bond to form chloroalkyl radicals, which react rapidly under experimental conditions with O₂ to form the peroxy radicals, and after further reduction, chloroalkoxy radicals are formed. The proposed reaction mechanism is displayed in Fig. 5.

Fig. 6 trace A shows the infrared spectrum of an HFIB/Cl₂/air mixture recorded after UV irradiation and subtraction of residual absorptions of HFIB. The presence of the CO vibration band centered at 2140 cm⁻¹ can also be observed. Fig. 6 trace B shows a reference spectrum of hydrochloric acid (HCl), trace C is the reference formyl chloride (HC(O)Cl) spectrum, trace D is the hexafluorooctone reference spectrum, and trace E is the residual product spectrum after the subtraction of all four identified products from trace A. In the residual spectrum, the unidentified absorption bands were negligible. No other reaction products were expected, and again, these results are consistent with the previous study of the reaction of HFIB initiated by Cl atoms rather than atmosphere.¹²

The CO and HCl infrared absorptions observed could be due to the rapid thermal decomposition of HC(O)Cl via a reaction in the walls. This has been previously observed by Libuda et al.¹⁹ and Papadimitriou et al.¹³ This decomposition can also be observed in the concentration–time profiles shown in Fig. 7. In Fig. 8, the concentrations of carboxylic and formic acids in the consumed HFIB in the reaction with Cl atoms show reasonable linearity. The average product yields obtained from the two experiments are CF₃C(O)CF₃ (94 ± 5)% and HC(O)Cl (90 ± 7)% (Table 1).

In a previous product identification study performed by Papadimitriou et al., the experiments were carried out under atmospheric conditions in two different collapsible Teflon FEP reaction chambers of 7300 L and 140 L, respectively. Chlorine atoms were generated by the photolysis of molecular chlorine using fluorescent lamps, which provided radiation sources centered at 365 nm. The reagents and oxidation products were detected using a multiple reflection target-type mirror system (path length 143 m), which is mounted inside the reactor and connected to an FT-IR spectrometer ( Nicolet Magna 5700).¹³ CF₃C(O)CF₃, HC(O)Cl, HCl, and CO were identified as HFIB degradation products in the reaction with Cl atoms, although no product yields were reported. The experiments were carried out at room temperature and atmospheric pressure using two atmospheric simulation chambers and a static photochemical reactor. The identified products are in accordance with the identified and quantified products reported in this study. To the best of our knowledge, no other study has been conducted on the atmospheric degradation mechanism of HFIB with Cl atoms. Consequently, this is the first product quantification study of the reaction of HFIB with Cl atoms.

The end-products found in both HFO reactions with Cl atoms suggest that all reactions proceed mainly via a reaction in the walls. This behavior is consistent with a previous study that reported the degradation reactions of similar HFOs with the atmospheric oxidants.²¹–²⁷

**Atmospheric implications**

Atmospheric lifetimes of 1,2,3,3,3-pentafluoropropene (PFP) and hexafluoroisobutylene (HFIB) with OH radicals and Cl atoms have been previously reported by our research group,²⁶,²⁹ and they were also measured by Papadimitriou et al. and Tokuhashi et al.¹³,²⁹ Considering these results, it was possible to

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*Fig. 4 Plots of the concentrations of the reaction products, trifluoroacetyl fluoride and formyl fluoride, as a function of reacted PFP obtained from the UV photolysis of PFP/Cl₂/air reaction mixtures.*
observe that the reaction with OH radicals is the main atmospheric sink of these species (few days). Besides, other sinks could also be relevant, such as reactions with Cl (days) mainly in areas with significant concentrations of Cl. It is also known that ozonolysis reactions generally represent a minor or insignificant atmospheric loss for halo-olefins. The atmospheric lifetimes of both compounds were calculated in previous studies, and the values obtained were $\tau_{\text{OH}} = 4$ and $\tau_{\text{Cl}} = 51$ days for PFP and $\tau_{\text{OH}} = 18$ and $\tau_{\text{Cl}} = 66$ days for HFIB by Tovar et al. Moreover, the values obtained by Rivela et al. were $\tau_{\text{OH}} = 2$ and $\tau_{\text{Cl}} = 18$ days for PFP, and $\tau_{\text{OH}} = 9$ and $\tau_{\text{Cl}} = 33$ days for HFIB. Therefore, it is expected that HFOs will react close to their emission sources and have a local impact due to their short lifetimes. OH-initiated degradation will be the main atmospheric sink of these species, although in industrial areas or marine troposphere where Cl atoms could reach a peak, the Cl-initiated oxidation could be a significant sink of HFO studied.

Degradation products found in the studied reactions (1) and (2): HC(O)Cl and HC(O)F have relatively small reaction rate coefficients towards OH radicals ($3.2 \times 10^{-13}$ and $<5 \times 10^{-15}$...
reaction mixtures. In the case of HC(O)Cl, it could be hydrolyzed and removed by wet deposition in the environment. HC(O)OH, which is a ubiquitous component of the troposphere, is expected to occur primarily by photolysis where they are removed from the atmosphere in the order of days. This phenomenon occurs in marine and coastal regions and in urban areas as well, where the oxidation through Cl atoms could be a significant loss. For the aforementioned, HFCs are not expected to enter aquatic environments, including aquifers, which would prevent their pollution.

The short-chain HFCs studied in this work have short atmospheric lifetimes, in the order of days, when reacting with the main atmospheric oxidants (OH/Cl). Their ability to contribute to the ozone photochemical potentials (POCP) is negligible as well as the ozone depletion potential (ODP), the global warming potentials (GWP), and the contribution to rain acidification. As for the primary oxidation products, they are benign, and they would have an unimportant impact on ecosystems.

This study aims to provide more information about the degradation mechanism of the HFCs mentioned above and the possible environmental impact of their final degradation products. This is necessary since HFCs have been proposed for several industrial uses, such as eco-friendly refrigerants, aerosol propellants, and the production of fluoropolymers.

Further experiments to study the product distribution of PFP and HFIB in the presence of NO₂ would be desirable to compare degradation mechanisms and performance of the reaction pathways with the chemistry of polluted areas and with large amounts of NO₂.

4 Conclusions

For the first time, in this study, the degradation products of the reaction with hydrofluorolefinic (HFCs), isomeric mixture (E/Z)-1,2,3,3,3-pentafluoropropene and hexafluorosobutylene, in atmospheric conditions have been studied. The end-products observed and their yields were: CF₃/C(O)F (106 ± 9)% with HC(O)F (100 ± 8)% as a co-product for (E/Z)-1,2,3,3,3-pentafluoropropene, and CF₃/C(O)CF₃ (94 ± 5)% with HC(O)Cl (90 ± 7)% as a co-product for hexafluorosobutylene. The proposed mechanism for both compounds suggest that the Cl atom could be added to the C₁ or C₂ carbon atom of the double bond, followed by subsequent reactions with O₂ to give RO₂ with additional production of 1,2-chloroalkoxy radicals. The radicals formed could be decomposed to give the corresponding products. However, for the HFIB + Cl reaction, the formation of CO + HC(O)Cl gives values of approximately 100%, indicating that chlorine atoms attacked the C₁ of the C≡C bond preferentially.

probably, this fluorinated VOC will be removed via heterogeneous wet and dry deposition processes. On the other hand, its photolysis generates CF₃ and CO. CF₃ radicals further will be oxidized to produce CF₂O and subsequently be hydrolyzed to HF and CO₂. Probably, this fluorinated VOC will be removed via heterogeneous wet and dry deposition processes. On the other hand, its photolysis generates CF₃ and CO. CF₃ radicals further will be oxidized to produce CF₂O and subsequently be hydrolyzed to HF and CO₂. Probably, this fluorinated VOC will be removed via heterogeneous wet and dry deposition processes. On the other hand, its photolysis generates CF₃ and CO. CF₃ radicals further will be oxidized to produce CF₂O and subsequently be hydrolyzed to HF and CO₂.

These compounds have high vapor pressures, and most of them are gases at 25 °C. Consequently, these materials will not accumulate in water and will partition rapidly into air. Furthermore, it is known that the reactions of HFCs in the atmosphere occur primarily with OH radicals where they are removed from the atmosphere in the order of days. This phenomenon occurs in marine and coastal regions and in urban areas as well, where the oxidation through Cl atoms could be a significant loss.
It is known that short-chain halo-olefins have a short atmospheric life in the order of days when they react with OH radicals or Cl atoms. Therefore, their ability to contribute towards photochemical ozone potentials, global warming potentials, and acidification contribution from rain are negligible. With respect to the final oxidation products, as discussed above, short-chain halo-olefins would not have a significant impact on ecosystems.

Conflicts of interest

There are no conflicts to declare.

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