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Product distribution and mechanism of the OH[•] initiated tropospheric degradation of three CFC replacement candidates: CH₃CF=CH₂, (CF₃)₂C=CH₂ and (E/Z)-CF₃CF=CHF[†]

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The OH radical initiated photodegradation of 2-fluoropropene (CH₃CF=CH₂), 3,3,3-trifluoro-2-(trifluoromethyl)propene ((CF₃)₂C=CH₂) and (E/Z)-1,2,3,3,3-pentafluoropropene ((E/Z)-CF₃CF=CHF) has been investigated for the first time using a 1080 L quartz-glass environmental chamber at 298 ± 2 K and atmospheric pressure of synthetic air coupled with *in situ* FTIR spectroscopy to monitor reactants and products. The major products observed in the OH reaction were CH₃C(O)F (98 ± 5)% together with HC(O)H (89 ± 7)% as a co-product, CF₃C(O)F (103 ± 8)% together with HC(O)F (96 ± 7)% as a co-product and CF₃C(O)CF₃ (91 ± 8)% together with HC(O)H (98 ± 12)% as a co-product from the C₁–C₂ bond cleavage channel of the intermediate hydroxyalkoxy radical, formed by addition of OH to the terminal carbon of the double bond which is designated C₁ of 2-fluoropropene, (E/Z)-1,2,3,3,3-pentafluoropropene and 3,3,3-trifluoro-2-(trifluoromethyl)propene, respectively. The present results are compared with previous studies for the reaction of OH with the separate isomers (E) and (Z) of 1,2,3,3,3-pentafluoropropene. In addition, atmospheric implications of the reactions studied are discussed.

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1. Introduction

Fluorinated compounds are environmentally persistent and have been demonstrated to bioaccumulate and contribute to climate change.^{1,2}

As it is known, the Montreal and Kyoto Protocols represent global initiatives that have worked to decrease climate change.^{2,3} However, other actions have also led to a reduction in climate impact from halocarbons. Many halocarbons, such as hydrofluoroethers (HFEs), are used in refrigeration and air conditioning as replacements for ozone-depleting chemicals. One of the simplest means of decreasing atmospheric concentrations of these chemicals is through improved leakage rates that was implemented also by the United States Environmental Protection Agency.⁴ As a result, alternatives are being proposed

that have lower Radiative Efficiency (REs) and Global Warming Potential (GWP), which include hydrofluorinated alkenes.⁵ Hydrofluorinated alkenes have IR absorption bands in the spectral regions where radiative forcing is most efficient, but they react relatively fast with OH radicals.^{6–9}

Within hydrofluoroalkenes, 2-fluoropropene (2-FP), (E/Z)-isomeric mixture of 1,2,3,3,3-pentafluoropropene (PFP) and 3,3,3-trifluoro-2-(trifluoromethyl)propene (HXFP) are widely used as water repellents, inert fluids, coatings and as building blocks in the production of perfluorinated polymers.^{10,11}

Emissions of these fluorinated alkenes to the atmosphere can occur during their production, processing and disposal and once in the atmosphere they will be subject to photo-degradation mainly by OH radicals and to a lesser extent NO₃ radicals and ozone and in certain environments also Cl atoms.^{6–9}

In order to assess the contribution of the atmospheric photooxidation of hydrofluorinated alkenes to the oxidizing capacity of the atmosphere, to the global warming potential and to the possible formation of perfluoroacetic acids, detailed kinetic and mechanistic information on their tropospheric gas-phase degradation pathways are required. There have been reported in literature few kinetic studies of 1,2,3,3,3-pentafluoropropene with OH radical^{12–14} and the Cl-initiated oxidation of 3,3,3-trifluoro-2-(trifluoromethyl)propene.^{13,15}

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[†] Electronic supplementary information (ESI) available: IR spectra plots used in the identification of the products formed in the reaction of OH with: HXFP (Fig. S3) and PFP (Fig. S6). Concentration–time profiles for the reaction of OH with 2-FP, HXFP and PFP, Fig. S1, S4 and S7, respectively. Yield plots for the reaction of OH radicals with 2-FP (S2) and HXFP (S5) in the absence of NO_x. See DOI: 10.1039/c8ra09627a

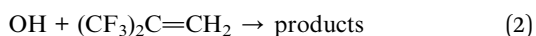
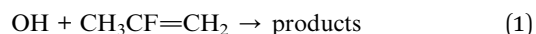


In contrast to the kinetic studies, only one product study concerning the OH- and Cl-initiated oxidation of (*Z*) and (*E*) individual isomers of 1,2,3,3,3-pentafluoropropene have been reported.¹² This product distribution study¹² was performed using a Pyrex reactor and FTIR technique as detection system. These authors have reported for both, Cl-atom and OH-radical-initiated atmospheric oxidations of CF₃CF=CHF, the presence of CF₃C(O)F and HC(O)F in molar yields indistinguishable from 100% for both the (*Z*) and (*E*) isomer.

In addition, regarding to 3,3,3-trifluoro-2-(trifluoromethyl)propene, one product identification study of the OH and Cl initiated oxidation has been reported.¹⁵ This product distribution study was performed using an atmospheric simulation chamber and FTIR technique as detection system. HC(O)H and (CF₃)₂C(O) were identified as final oxidation products in both OH- and Cl-initiated oxidation of (CF₃)₂C=CH₂, while HC(O)Cl was additionally observed in the Cl-initiated oxidation.

No qualitative and quantitative products studies are currently available for OH-radical initiated degradation of 2-fluoropropene and 3,3,3-trifluoro-2-(trifluoromethyl)propene. In addition, there are not previous studies of the products distribution for the of OH with (*E/Z*)-isomeric mixture of 1,2,3,3,3-pentafluoropropene. Consequently, the present results are the first determination of the products distributions for the studied reactions.

Since, as stated above, fluorinated alkenes are widely used in the industry as chlorofluorocarbons (CFCs) direct replacements and are released to the atmosphere in substantial amounts¹⁶ this motivated us to investigate qualitatively and quantitatively the products formed in the OH-radical degradation of these fluoroalkenes according to:



It is known that the main reaction pathway for OH radicals with unsaturated compounds is the addition to the double bond of the alkene unit. The major aim of the work was, to assess the relative importance of the different subsequent reaction pathways that are available to the hydroxyalkoxy radicals formed in the reactions studied. The results will contribute to an improved representation of the degradation of fluorinated alkenes in the atmospheric chemical models used to assess the environmental impact of chemicals and their contribution to the oxidizing capacity of the atmosphere.

2. Experimental

All the experiments were performed in a 1080 L quartz-glass reaction chamber at (298 ± 2) K and a total pressure of (760 ± 10) torr of synthetic air. A detailed description of the reactor can be found elsewhere^{17,18} and only a brief description is given here. The photolysis system consists of 32 superactinic lamps (Philips TL05 40W: 320–480 nm, λ_{max} = 360 nm) and 32 low-

pressure mercury vapor lamps (Philips TUV 40W; λ_{max} = 254 nm). These lamps are wired in parallel and can be switched individually, which allows a variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber. 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 infrared absorption monitoring of reactants and products in the spectral range 4000–700 cm^{−1}. The White system was operated at 82 traverses, giving a total optical path length of (484.7 ± 0.8) m. The IR spectra were recorded with a spectral resolution of 1 cm^{−1} using a Nicolet Nexus FT-IR spectrometer, equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector.

A pumping system consisting of a turbo-molecular pump backed by a double stage rotary fore pump was used to evacuate the reactor to 10^{−3} torr. Three magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants.

Hydroxyl radicals were generated by the photolysis of H₂O₂ with the mercury lamps:



where possible, quantification of reactants and products was performed by comparison with calibrated reference spectra contained in the IR spectral data bases of the laboratories in Wuppertal and Ford Motor Company, Michigan.

The initial concentrations used in the experiments for the hydrofluoroalkenes in ppm (1 ppm = 2.46 × 10¹³ molecule cm^{−3} at 298 K and 760 torr of total pressure) were: 0.7 for 2-fluoropropene, 0.1 for 3,3,3-trifluoro-2-(trifluoromethyl)propene and 0.7 for 1,2,3,3,3-pentafluoropropene, (*E/Z*) mixture. The initial concentration for the precursor of the oxidant was typically around 5 ppm for H₂O₂. The infrared absorption frequency at 1259.8, 1407.8 and 1197.1 cm^{−1} was used to monitor the concentration–time behavior of 2-fluoropropene, 3,3,3-trifluoro-2-(trifluoromethyl)propene and 1,2,3,3,3-pentafluoropropene, (*E/Z*) mixture, respectively. Readily identifiable products were monitored at the following absorption frequencies (in cm^{−1}): HC(O)H at 2766; HC(O)F at 850; CF₃C(O)F at 1897.8; CH₃C(O)F at 1871.3 and CF₃C(O)CF₃ at 970.

The chemicals used in the experiments had the following purities as given by the manufacturer and were used as supplied: synthetic air (Air Liquide, 99.999%), 2-fluoropropene (Apollo Scientific) purity around 95%, 3,3,3-trifluoro-2-(trifluoromethyl)propene (Apollo Scientific) purity around 95%, 1,2,3,3,3-pentafluoropropene (Apollo Scientific, mixture (*E/Z*) isomers 97%; no manufacture details on isomer ratio) and H₂O₂ (Peroxide Chemie, 85%).

3. Results and discussion

To investigate the mechanisms of the OH-radical initiated oxidation of the title compounds, mixtures of H₂O₂/fluoroalkene/air were irradiated for periods of around 20 minutes during which infrared spectra were recorded with the



FTIR spectrometer. Typically, 64 interferograms were co-added per spectrum over a period of approximately 1 min and 15–20 such spectra were collected during the course of the experiment.

Dark reactions, photolysis of the fluoroalkenes studied in the absence of radical precursor reactions, and wall losses were negligible compared to the loss that occurred on OH radical photo-induced degradation.¹⁹

To facilitate the discussion of the results exemplary reaction schemes are shown for the reactions of OH with 2-fluoropropene, 3,3,3-trifluoro-2-(trifluoromethyl)propene and (*E/Z*)-isomeric mixture of 1,2,3,3,3-pentafluoropropene in Fig. 1, 2 and 3, respectively.

For the OH radical reactions, the major reaction pathway involves initial addition of the OH to the carbon atom of the C=C bond, forming the hydroxyalkyl radicals.^{20,21}

Under the conditions of the present study the hydroxyalkyl radicals will react with O₂ to form the corresponding hydroxyalkyl peroxy radicals. In this work, under NO_x-free experimental conditions peroxy self reactions will occur. These will result in the formation of the corresponding alkoxy radicals.

2-Fluoropropene + OH reaction

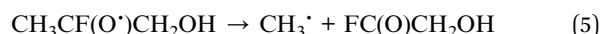
The OH radical could be added to the C₁ or C₂ of the double bond (see Fig. 1). And after the subsequent reactions with O₂ and RO₂ radicals, the hydroxyalkoxy radicals formed could decompose to give acetyl fluoride (CH₃C(O)F) and formaldehyde (HC(O)H) if the addition of OH occur in C₁ and/or C₂.

Fig. 4 shows IR spectra acquired after (panel A) UV irradiation of a mixture of 2-fluoropropene and H₂O₂ in air, in the

absence of NO_x where the 2-fluoropropene spectrum was subtracted. Panel B and C in Fig. 4 shows a reference spectra of CH₃C(O)F, and HC(O)H, respectively. In Panel D is shown the residual product spectrum obtained after subtraction of reactants and identified products from the spectrum in panel A. CH₃C(O)F and HC(O)H were readily identifiable as reaction products. The concentration–time profiles of CH₃C(O)F and HC(O)H (Fig. S1 of ESI†) show that they are both primary products.

Least-squares analyses of plots of the concentrations of CH₃C(O)F and HC(O)H, as a function of the amount of reacted 2-FP (Fig. S2†) give molar yields of (98 ± 5)% and (83 ± 6)%, respectively, for these compounds. Formaldehyde will be subject to secondary oxidation with OH whereas CH₃C(O)F reacts only very slowly with OH and loss *via* secondary react with OH should be negligible. Correction of the HC(O)H yield for secondary reaction with OH using the method outlined in Tuazon *et al.* yields a final value of (89 ± 7)% for the formaldehyde yield corrected. The mechanism presented in Fig. 1 (addition to C₁ and/or C₂) predicts equal yields of HCHO and CH₃C(O)F within the experimental error limits.

If the OH addition is produced in the less substituted carbon (C₁) of 2-fluoropropene, the hydroxialkoxy radical (CH₃CF(O[•])CH₂OH) formed could also eliminate a –CH₃ group according to:



Unfortunately, this compound (FC(O)CH₂OH) is not commercially available for comparative and quantification

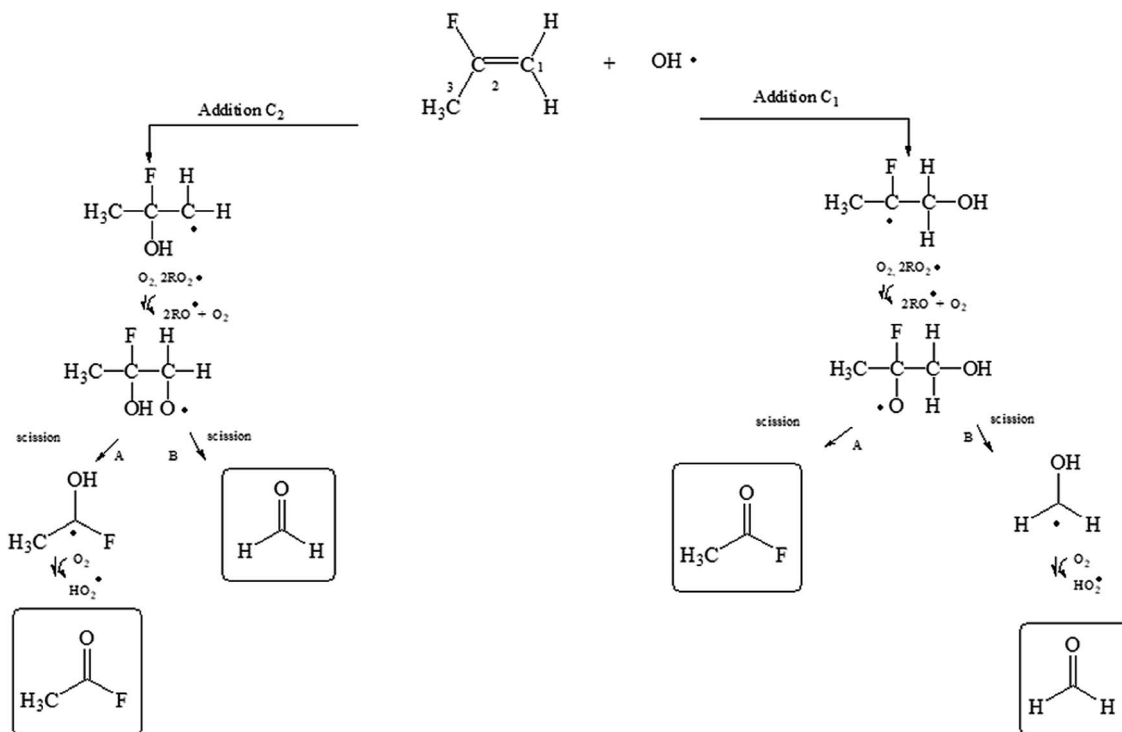
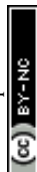


Fig. 1 Mechanism for the reaction of 2-fluoropropene with OH radicals *via* addition of OH to the double bond.



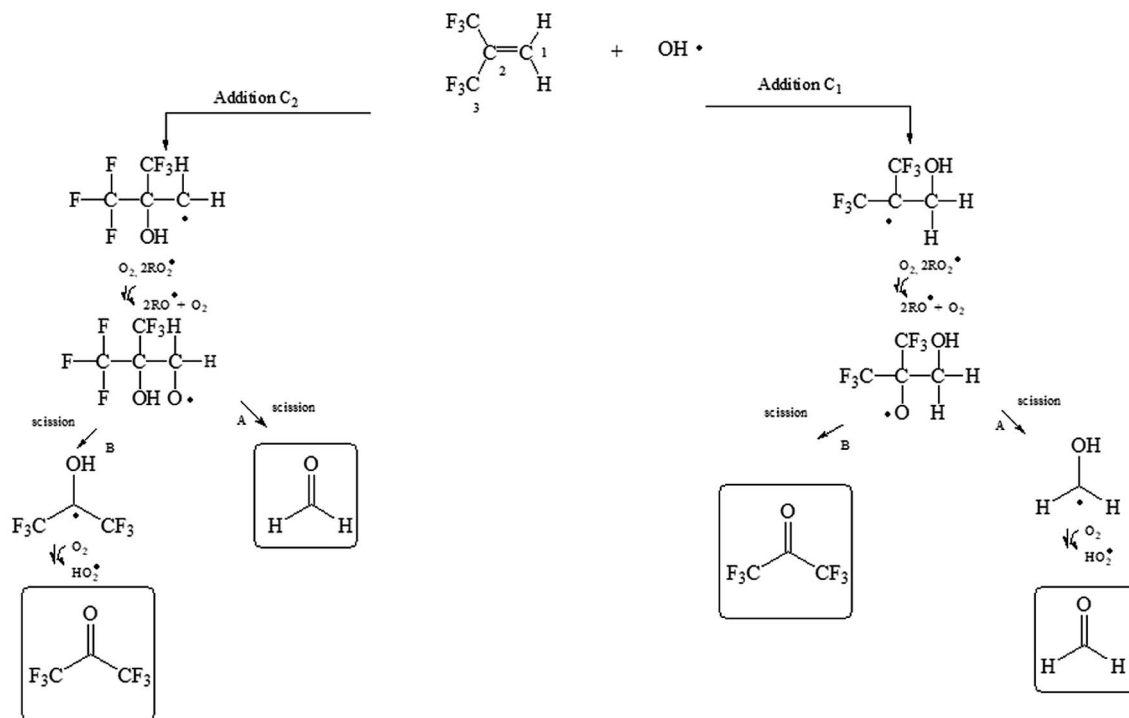


Fig. 2 Mechanism for the reaction of 3,3,3-trifluoro-2-(trifluoromethyl)propene with OH radicals *via* addition of OH to the double bond.

purposes. However, an infrared spectrum has been simulated for FC(O)CH₂OH using density functional methods (DFT) and composite quantum chemistry models of the Gaussian 09 chemistry package. In particular, the M06 hybrid meta

exchange–correlation DFT method was used. The spectrum was calculated using the M06/6-31G(d,p) level of theory. The simulated spectrum is presented in Fig. S8 of the ESI.†

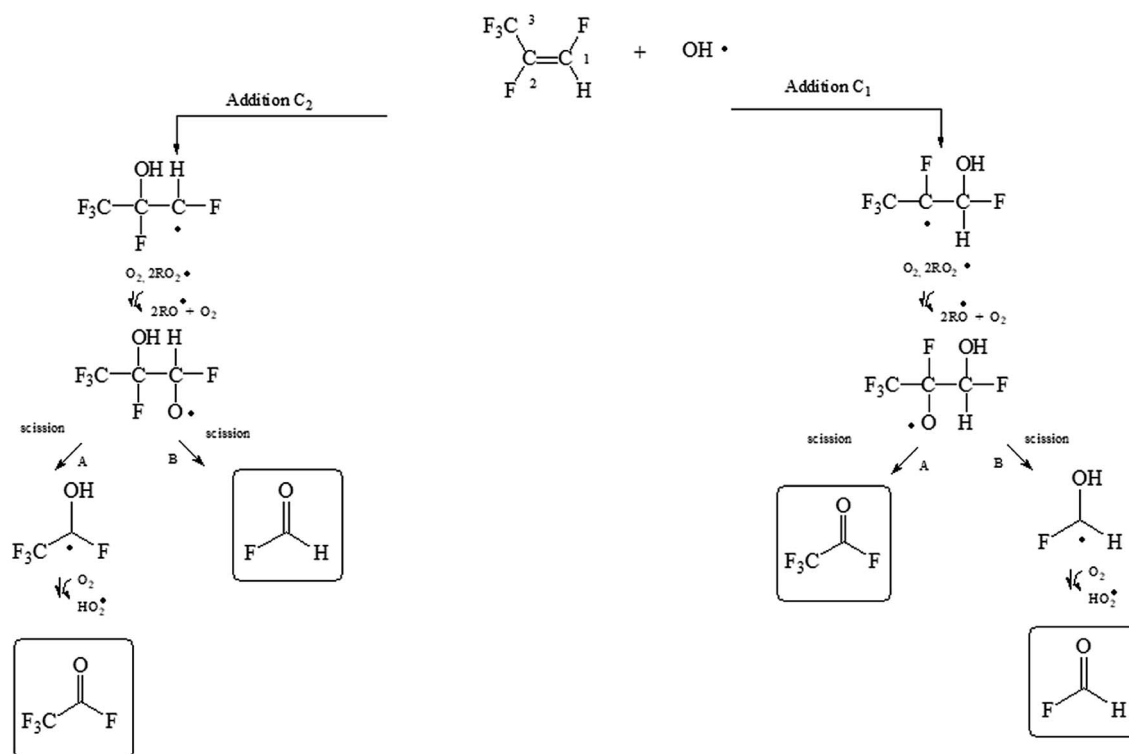


Fig. 3 Mechanism for the reaction of 1,2,3,3,3-pentafluoropropene (mixture E/Z) with OH radicals *via* addition of OH to the double bond.



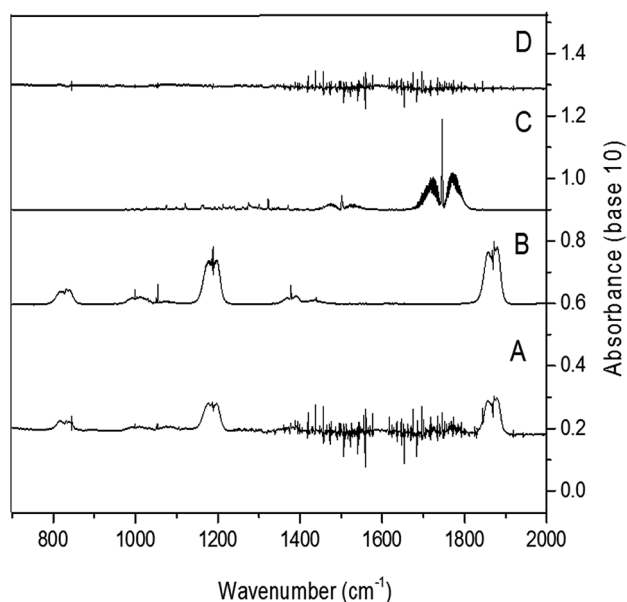


Fig. 4 Panel A shows the infrared product spectrum obtained from a 2-fluoropropene/H₂O₂/air reaction mixture after UV irradiation after subtraction of 2-fluoropropene bands. Panels B and C show reference spectra of acetyl fluoride and formaldehyde, respectively. Panel D shows the residual product spectrum obtained after subtraction of features due to the reference spectra from the spectrum in panel A.

Absorption bands corresponding to FC(O)CH₂OH were not observed in the residual product spectra concluding that the pathway of -CH₃ elimination (reaction (5)) was not observed under our experimental conditions.

3,3,3-Trifluoro-2-(trifluoromethyl)propene + OH reaction

Fig. S3, panel A† shows a spectrum of a HXFP/H₂O₂/air reaction mixture after irradiation and subtraction of spectral features due to HXFP, while panels B and C show the reference spectra of hexafluoroacetone and formaldehyde, respectively.

In the residual product spectrum (Fig. S3, panel D†) absorption bands can be seen in the regions (1065–1143) cm⁻¹.

Concentration–time profiles of 3,3,3-trifluoro-2-(trifluoromethyl)propene, hexafluoroacetone and formaldehyde are shown in Fig. S4.† The concentration–time profiles of HXFP, CF₃C(O)CF₃ and HC(O)H show that are all primary in origin. The amounts of hexafluoroacetone and formaldehyde formed, plotted as a function of the amount of reacted HXFP, are shown in Fig. S5.† The plots are linear and give molar yields for hexafluoroacetone and formaldehyde of (91 ± 8)% and (94 ± 12)%, respectively. The corrected yield of formaldehyde using Tuazon²² method was (98 ± 12)%.

The formation of hexafluoroacetone and formaldehyde with yields near to 100% indicates that OH could be added indistinctly to C₁ and/or C₂ (see Fig. 2). However, according to the chemical structure of 3,3,3-trifluoro-2-(trifluoromethyl)propene, it is expected that the OH addition to carbon 2 could be less probable than to the OH addition to C₁ due to

a possible steric hindrance on carbon 2 in the (CF₃)₂C=CH₂. Consequently, it can be proposed that the addition reaction with the OH radical, takes place on carbon 1, which has less nucleophilic character, due to the presence of the H atoms as substituent.

(E/Z)-isomeric mixture of 1,2,3,3,3-pentafluoropropene + OH reaction

The OH radical could be added to the C₁ or C₂ of the double bond (see Fig. 3) followed by the subsequent reactions with O₂ and RO₂ radicals. The hydroxyalkoxy radicals formed could decompose to give acetyl fluoride (CF₃C(O)F) and formyl fluoride (HC(O)F) if the addition of OH occurs to C₁ and/or C₂.

Fig. S6† shows an IR spectrum acquired after UV irradiation of a mixture of (E/Z)-isomeric 1,2,3,3,3-pentafluoropropene and H₂O₂ in air in the absence of NO_x where the bands of HFP were subtracted (panel A). Panel B and C in Fig. S6† show reference spectra of CF₃C(O)F and HC(O)F, respectively. Panel D represents the residual product spectrum obtained after subtraction of reactants and identified products from the spectrum in panel A. CF₃C(O)F and HC(O)F were readily identifiable as reaction products. The presence of unidentified absorption bands was negligible in the residual product spectrum. The concentration–time profiles of CF₃C(O)F and HC(O)F shows that they are both primary products (Fig. S7†).

Least-squares analyses of plots of the concentrations of CF₃C(O)F and HC(O)F as a function of the amount of reacted PFP (Fig. 5) give molar yields of (103 ± 8)% and (96 ± 7)%, respectively, for these compounds. The mechanism presented in Fig. 3 (addition to C₁ and/or C₂) predicts equal yields of HC(O)F and CF₃C(O)F within the experimental error limits this is the case.

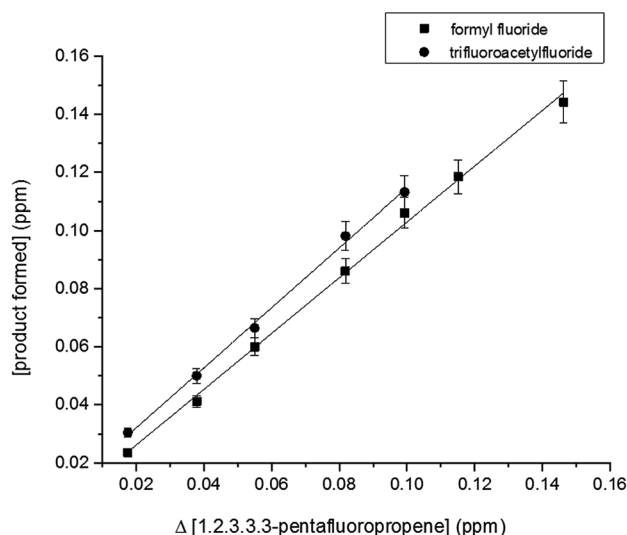
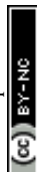


Fig. 5 Plots of the concentrations of the reaction products formyl fluoride and trifluoroacetyl fluoride as a function of reacted 1,2,3,3,3-pentafluoropropene (mixture *cis/trans*) obtained from UV photolysis of 1,2,3,3,3-pentafluoropropene (mixture *E/Z*)/H₂O₂/air reaction mixtures.



Hurley *et al.*,¹² have studied the atmospheric chemistry of the *Z* and *E* isomers of $\text{CF}_3\text{CF}=\text{CHF}$ initiated by OH radicals, Cl atoms and O_3 molecules using a 140-L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer. They have reported yields of $(94 \pm 8)\%$ for $\text{CF}_3\text{C}(\text{O})\text{F}$ and $(104 \pm 9)\%$ for $\text{HC}(\text{O})\text{F}$ in the OH initiated degradation of both isomers. Additionally, these authors determined molar yields of $(98 \pm 4)\%$ for $\text{CF}_3\text{C}(\text{O})\text{F}$ and $(100 \pm 5)\%$ for $\text{HC}(\text{O})\text{F}$ for the Cl reactions with both $\text{CF}_3\text{CF}=\text{CHF}$ isomers. Our results are in excellent agreement with the values reported by Hurley *et al.*,¹² indicating that the fate of $\text{CF}_3\text{CF}(\text{OH})\text{CO}^*\text{HF}$ and $\text{CF}_3\text{CO}^*\text{FCHF}(\text{OH})$ radicals formed is decomposition *via* C–C bond scission for both separate isomers and for the (*E/Z*) mixture of 1,2,3,3,3-pentafluoropropene.

To the best of our knowledge, this work represents the first product study of the reactions of OH radicals with 2-fluoropropene, (*E/Z*)-1,2,3,3,3-pentafluoropropene mixture and 3,3,3-trifluoro-2-(trifluoromethyl)propene. The reaction products obtained in this work, confirm that the reaction proceeds *via* an addition mechanism of the OH radical to the double bond similar to that proposed by Atkinson for the OH radical addition to alkenes.^{21,23}

The hydroxyalkoxy radical formed in the OH addition step, decomposes in the presence of O_2 and RO_2 radicals, leading mainly to the corresponding halocarbonyl compound and $\text{HC}(\text{O})\text{H}$ or $\text{HC}(\text{O})\text{F}$. Although the observed products do not indicate which is the main reaction pathway, we expected that the OH-addition to the less substituted carbon of the double bond (carbon 1) be the most likely.

The molar product yields obtained from linear least-squares analyses of the plots in Fig. 5, S2 and S5† are listed in Table 1. The errors given in Table 1 are the 2σ standard deviations from the analyses of the plots.

Atmospheric implications

The persistence of fluoroalkenes in the atmosphere is relatively short, in the order of few days (dominated by OH radical chemistry).⁹ These short lifetimes indicate that the fluoroalkenes will be degraded near to their emission sources. Other processes, as photolysis, wet deposition and heterogeneous reactions are not expected to contribute significantly to the atmospheric removal of these compounds.⁷

Table 1 Formation yields of the oxidation products identified from the OH radical oxidation of the fluoroalkenes studied in the absence of NO_x

Fluoroalkene	Product	Yield ^a (%)
$\text{CH}_3\text{CF}=\text{CH}_2$	$\text{HC}(\text{O})\text{H}$	$(89 \pm 7)^b$
	$\text{CH}_3\text{C}(\text{O})\text{F}$	(98 ± 5)
$\text{CF}_3(\text{CF}_3)\text{C}=\text{CH}_2$	$\text{HC}(\text{O})\text{H}$	$(98 \pm 12)^b$
	$\text{CF}_3\text{C}(\text{O})\text{CF}_3$	(91 ± 8)
$(\text{E/Z})\text{-CF}_3\text{CF}=\text{CHF}$	$\text{CF}_3\text{C}(\text{O})\text{F}$	(103 ± 8)
	$\text{HC}(\text{O})\text{F}$	(96 ± 7)

^a The errors quoted are 2σ statistical errors from the linear regression analysis. ^b Yield corrected for secondary reaction with OH radicals.

Among the products observed in the reactions studied, $\text{CF}_3\text{C}(\text{O})\text{F}$ could be incorporated into rain-cloud-seawater, followed by hydrolysis to give trifluoroacetic acid ($\text{CF}_3\text{C}(\text{O})\text{OH}$, TFA) and acetic acid, respectively. TFA has been detected in surface of oceans, rivers and lakes and also in fog, snow and rainwater samples around the globe^{24,25} and it to be a ubiquitous persistent accumulating component of the hydrosphere.

Formyl fluoride ($\text{HC}(\text{O})\text{F}$) and acetyl fluoride ($\text{CH}_3\text{C}(\text{O})\text{F}$) is believed to be removed of atmosphere by hydrolysis on contact with cloud-rain-seawater giving HF and $\text{HC}(\text{O})\text{OH}$. Acetic and formic acid can contribute significantly to the acidity of precipitation and cloud water, especially in remote regions.²⁶

On the other hand, hexafluoroacetone ($\text{CF}_3\text{C}(\text{O})\text{CF}_3$) could photolyze or interact with water surfaces. Photolysis of hexafluoroacetone will generate CF_3 radical and CO. The fate of CF_3 radicals is the formation of CF_2O , which is then hydrolyzed giving HF and CO_2 .²⁷ Moreover, formaldehyde plays important roles in atmospheric photochemistry and air quality. It is a large component of the total Volatile Organic Compound (VOC) reactivity of the atmosphere, providing sources of new radicals that drive ozone formation.²⁷ The major loss processes of $\text{HC}(\text{O})\text{H}$ are photolysis and reaction with the hydroxyl radical (OH). $\text{HC}(\text{O})\text{H}$ serves as an important primary source for the hydroperoxyl radical (HO_2).

Since the degradation products can contribute to ozone and photooxidants formation in the troposphere to different degrees it is important to know the product branching in atmospheric conditions.

Conflicts of interest

There are no conflicts to declare.

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