Atmospheric Environment 43 (2009) 3717–3724

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Atmospheric chemistry of perfluorobutenes ($CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$): Kinetics and mechanisms of reactions with OH radicals and chlorine atoms, IR spectra, global warming potentials, and oxidation to perfluorocarboxylic acids

Cora J. Young [a], Michael D. Hurley [b], Timothy J. Wallington [b,*], Scott A. Mabury [a,*]

[a] Department of Chemistry, University of Toronto, 80 St George Street, Toronto, ON, Canada M5S 3H6
[b] Ford Motor Company, Mail Drop SRL-3083, Dearborn, MI 48121, USA

ARTICLE INFO

Article history:
Received 10 February 2009
Received in revised form
6 April 2009
Accepted 7 April 2009

Keywords:
Fluorinated alkene
Atmospheric oxidation
Radiative efficiency
Perfluorocarboxylic acid

ABSTRACT

Relative rate techniques were used to determine $k(Cl + CF_3CF{=}CFCF_3) = (7.27 \pm 0.88) \times 10^{-12}$, $k(Cl + CF_3CF_2CF{=}CF_2) = (1.79 \pm 0.41) \times 10^{-11}$, $k(OH + CF_3CF{=}CFCF_3) = (4.82 \pm 1.15) \times 10^{-13}$, and $k(OH + CF_3CF_2CF{=}CF_2) = (1.94 \pm 0.27) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} in 700 Torr of air or N_2 diluent at 296 K. The chlorine atom- and OH radical-initiated oxidation of $CF_3CF{=}CFCF_3$ in 700 Torr of air gives $CF_3C(O)F$ in molar yields of 196 ± 11 and 218 ± 20%, respectively. Chlorine atom-initiated oxidation of $CF_3CF_2CF{=}CF_2$ gives molar yields of 97 ± 9% $CF_3CF_2C(O)F$ and 97 ± 9% COF_2. OH radical-initiated oxidation of $CF_3CF_2CF{=}CF_2$ gives molar yields of 110 ± 15% $CF_3CF_2C(O)F$ and 99 ± 8% COF_2. The atmospheric fate of $CF_3CF_2C(O)F$ and $CF_3C(O)F$ is hydrolysis to give $CF_3CF_2C(O)OH$ and $CF_3C(O)OH$. The atmospheric lifetimes of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ are determined by reaction with OH radicals and are approximately 24 and 6 days, respectively. The contribution of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ to radiative forcing of climate change will be negligible.

1. Introduction

Following ratification of the Montreal Protocol and related agreements, there has been an international effort to replace ozone-depleting chemicals with more environmentally friendly alternatives. Hydrofluorocarbons are attractive alternatives because the strength of the C–F and H–F bonds precludes catalytic destruction of stratospheric ozone (Wallington et al., 1995). However, C–F bonds absorb in the optically thin spectral region of the atmosphere known as the atmospheric window, leading to a high radiative efficiency of fluorinated compounds. Saturated perfluorocarbons and some hydrofluorocarbons (HFCs) have high radiative efficiencies and are long-lived in the atmosphere, causing them to be classified as long-lived greenhouse gases.

Atmospheric lifetimes of HFCs are typically determined by their reaction with hydroxyl radicals. The presence of >C=C< double bond in an HFC leads to an increase in rate of reaction with hydroxyl radicals and reaction with ozone. Fluorinated alkenes have been proposed as potential replacements, because of their greatly reduced atmospheric lifetimes relative to saturated HFCs. The atmospheric chemistry of several fluorinated alkenes has already been studied. They have been shown to have lifetimes (determined mainly by reaction with OH and to a lesser extent by reaction with ozone) on the order of days or weeks (Acerboni et al., 2001; Hurley et al., 2007; Mashino et al., 2000; Nielsen et al., 2007; Orkin et al., 1997; Papadimitriou et al., 2008; Søndergaard et al., 2007) and consequently negligible global warming potentials (Acerboni et al., 2001; Hurley et al., 2007; Nielsen et al., 2007; Papadimitriou et al., 2008; Søndergaard et al., 2007). The perfluorobutenes ($CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$) are being considered for industrial applications. Prior to the use of these compounds information on their atmospheric chemistry and environmental impact is needed. Such information is not currently available.

The objective of this study was to examine the atmospheric chemistry of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$. Experiments were performed to provide the following information: (i) chlorine atom reaction rates; (ii) hydroxyl radical reaction rates; (iii) products of chlorine atom and hydroxyl radical-initiated oxidation; and (iv) infrared spectra.

2. Methods

2.1. Chemicals

A commercial sample of $CF_3CF{=}CFCF_3$ (97%) was obtained from ABCR Chemicals (Karlsruhe, Germany) and consisted of

* Corresponding authors.
E-mail addresses: [redacted]@ford.com (T.J. Wallington), [redacted]@chem.utoronto.ca (S.A. Mabury).

1352-2310/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2009.04.025

approximately 70% *trans* and 30% *cis* isomers. A sample of $CF_3CF_2CF{=}CF_2$ was custom synthesized by ABCR Chemicals (Karlsruhe, Germany). CH_3ONO was synthesized by the drop-wise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$ in methanol. All other reagents were obtained from commercial sources. Chemicals were subjected to repeated freeze–pump–thaw cycling to remove volatile impurities before use.

2.2. Kinetics

Experiments were performed in a 140 L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine:

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

Hydroxyl radicals were produced by photolysis of CH_3ONO in air:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO$$

$$HO_2 + NO \rightarrow OH + NO_2$$

In relative rate experiments the following reactions take place:

$$OH/Cl + \text{Reactant} \rightarrow \text{products}$$

$$OH/Cl + \text{Reference} \rightarrow \text{products}$$

It can be shown that:

$$\ln\left(\frac{[X]_t}{[X]_{t_0}}\right) = \left(\frac{k_X}{k_{ref}}\right)\ln\left(\frac{[ref]_t}{[ref]_{t_0}}\right)$$

where $[X]_{t_0}$, $[X]_t$, $[ref]_{t_0}$, and $[ref]_t$ are the concentrations of the compound of interest and reference at times t_0 and t, and k_X and k_{ref} are the rate constants for the reactant and the reference. Mixtures used to determine $k(Cl + CF_3CF{=}CFCF_3)$ were composed of 4.1–11.5 mTorr $CF_3CF{=}CFCF_3$, 100 mTorr Cl_2, and either 4.8 mTorr C_2H_2 or 25.2 mTorr CH_3CH_2Cl. Reaction mixtures used to determine $k(Cl + CF_3CF_2CF{=}CF_2)$ consisted of 2.8–13.2 mTorr $CF_3CF_2CF{=}CF_2$, 100 mTorr Cl_2, and either 2.2–2.9 mTorr C_2H_2 or 26.4 mTorr C_2H_5Cl. To test for potential complications caused by the formation of CF_3O radicals, rate constant ratios for $CF_3CF_2CF{=}CF_2$ were measured in the absence and in the presence (1.4–1.6 mTorr) of NO. NO provides an effective scavenging mechanism for CF_3O radicals (Wallington et al., 1994). There was no discernable impact of the presence of NO on the rate constant ratios measured suggesting that complications caused by the presence of CF_3O radicals are not significant. Mixtures used to determine $k(OH + CF_3CF{=}CFCF_3)$ were made up of 3.7–26.0 mTorr $CF_3CF{=}CFCF_3$, 100 mTorr CH_3ONO and either 4.3–4.7 mTorr C_2H_2 or 6.9 mTorr C_2H_4. Reaction mixtures used to determine $k(OH + CF_3CF_2CF{=}CF_2)$ consisted of 7.9–14.8 mTorr $CF_3CF_2CF{=}CF_2$, 100 mTorr CH_3ONO and either 2.5–4.7 mTorr C_2H_2 or 3.4–4.1 mTorr C_2H_4. All experiments were performed at 296 ± 1 K in 700 Torr total pressure of air or N_2 diluent. Concentrations of reactants and products were monitored by FTIR spectroscopy. Infrared spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.7 m. Quoted uncertainties include two standard deviations from the linear least-squares regression analysis. Quoted error limits do not include uncertainties associated with absolute calibration of the COF_2 and $CF_3C(O)F$ reference spectra (which we estimate add an additional 5% uncertainty to the molar product yields) or uncertainties associated with the reference rate constants (which we estimate add an additional 10% uncertainty to the rate constants reported herein).

2.3. Products

Products of the chlorine atom- and OH radical-initiated oxidation of $CF_3CF_2CF{=}CF_2$ and $CF_3CF{=}CFCF_3$ were monitored using FTIR spectroscopy. Mixtures to study the reaction of chlorine with $CF_3CF{=}CFCF_3$ consisted of 4.9 mTorr $CF_3CF{=}CFCF_3$ and 101 mTorr Cl_2. To study the reaction of chlorine with $CF_3CF_2CF{=}CF_2$, mixtures of 3.5–8.4 mTorr $CF_3CF_2CF{=}CF_2$ and 100 mTorr Cl_2 were employed. The reaction of $CF_3CF_2CF{=}CF_2$ with hydroxyl radicals was studied using mixtures of 9.7–9.9 mTorr $CF_3CF_2CF{=}CF_2$, 100 mTorr CH_3ONO, and 50 mTorr NO. Reaction mixtures to study the reaction of $CF_3CF{=}CFCF_3$ with hydroxyl radicals were composed of 4.7 mTorr $CF_3CF{=}CFCF_3$ and 100 mTorr CH_3ONO. All product experiments were performed in 700 Torr total pressure of air.

3. Results and discussion

3.1. Kinetics of reactions with Cl atoms

The kinetics of reaction (1) were measured relative to reactions (2) and (3)

$$Cl + CF_3CF{=}CFCF_3 \rightarrow \text{products} \quad (1)$$

$$Cl + C_2H_2 \rightarrow \text{products} \quad (2)$$

$$Cl + C_2H_5Cl \rightarrow \text{products} \quad (3)$$

Fig. 1a shows the loss of $CF_3CF{=}CFCF_3$ versus C_2H_2 and C_2H_5Cl following UV irradiation. The lines through the data in Fig. 1a are linear least-squares fits, which give $k_1/k_2 = 0.136 \pm 0.010$ and $k_1/k_3 = 0.952 \pm 0.058$. Using the effective second-order rate constant measured in air at 700 Torr $k_2 = 5.07 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (Wallington et al., 1990) and $k_3 = 8.04 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Wine and Semmes, 1983), we derive values of k_1 of $(6.89 \pm 0.50) \times 10^{-12}$ and $(7.65 \pm 0.47) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. Our final value of k_1 is the average of the two determinations, with errors that encompass the extremes of the individual measurements: $k_1 = (7.27 \pm 0.88) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The sample of $CF_3CF{=}CFCF_3$ used in our experiments was a mixture of 70% *trans* and 30% *cis* isomer. There was no discernable difference in the rates of decay of IR features of the $CF_3CF{=}CFCF_3$ sample and we conclude that there is no substantial difference in the reactivity of the two isomers towards chlorine atoms. This conclusion is similar to that reached for reaction of chlorine atoms with the *cis* and *trans* isomers of 2-butene (Kaiser et al., 2007) and the E and Z isomers of $CF_3CF{=}CHF$ (Hurley et al., 2007).

The kinetics of reaction (4) were measured relative to reactions (2) and (3):

$$Cl + CF_3CF_2CF{=}CF_2 \rightarrow \text{products} \quad (4)$$

Fig. 1b shows the loss of $CF_3CF_2CF{=}CF_2$ versus C_2H_2 and C_2H_5Cl following UV irradiation. The lines through the data in Fig. 1b are linear least-squares fits, which give $k_4/k_2 = 0.322 \pm 0.048$ and $k_4/k_3 = 2.42 \pm 0.31$. Using $k_2 = 5.07 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (Wallington et al., 1990) and $k_3 = 8.04 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Wine and Semmes, 1983), we derive values of k_4 of

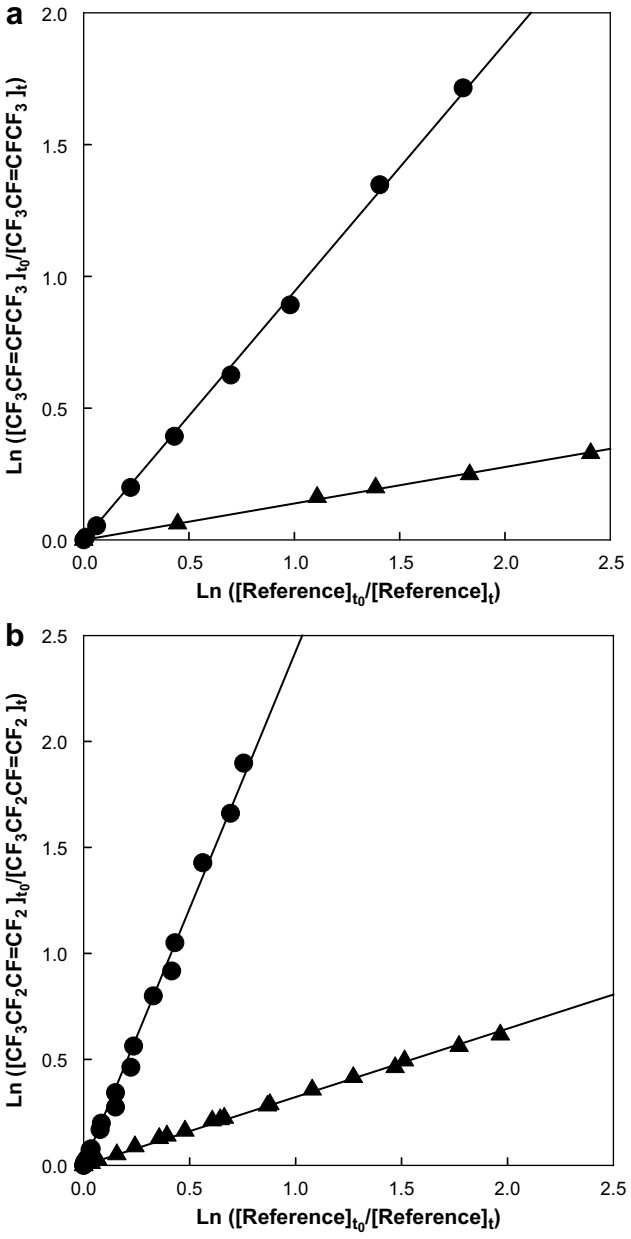

Fig. 1. Loss of (a) $CF_3CF{=}CFCF_3$ and (b) $CF_3CF_2CF{=}CF_2$ versus C_2H_2 (▲) and C_2H_5Cl (●) following exposure to Cl atoms.

$(1.63 \pm 0.24) \times 10^{-11}$ and $(1.95 \pm 0.25) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. Our final value of k_4 is the average of the two determinations, with errors that encompass the extremes of the individual measurements: $k_4 = (1.79 \pm 0.41) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

Chlorine atoms react approximately 2.5 times faster with $CF_3CF_2CF{=}CF_2$ than with $CF_3CF{=}CFCF_3$. The reaction of chlorine atoms with perfluorobutenes proceeds via electrophilic addition to the >C=C< double bond. The lower reactivity of $CF_3CF{=}CFCF_3$ presumably reflects the closer proximity of the electron withdrawing fluorine atom substituents to the >C=C< double bond. To our knowledge, there are no literature data for k_1 and k_4 to compare with our measurements. Kinetic data are available for the reaction of chlorine atoms with perfluoropropene; $k(Cl + CF_3CF{=}CF_2) = (2.7 \pm 0.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (Mashino et al., 2000). Consistent with its smaller number of electron withdrawing fluorine substituents, perfluoropropene is more reactive than the perfluorobutenes.

3.2. Kinetics of reactions with OH radicals

The kinetics of reaction (5) were measured relative to reactions (6) and (7):

$$OH + CF_3CF{=}CFCF_3 \rightarrow \text{products} \quad (5)$$

$$OH + C_2H_2 \rightarrow \text{products} \quad (6)$$

$$OH + C_2H_4 \rightarrow \text{products} \quad (7)$$

Fig. 2a shows the loss of $CF_3CF{=}CFCF_3$ versus C_2H_2 and C_2H_4 following UV irradiation. The lines through the data in Fig. 2a are linear least-squares fits that give values of $k_5/k_6 = 0.525 \pm 0.080$ and $k_5/k_7 = 0.061 \pm 0.009$. Using $k_6 = 8.45 \times 10^{-13}$ (Sørensen et al., 2003) and $k_7 = 8.52 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Calvert et al., 2000) we derive $k_5 = (4.44 \pm 0.68) \times 10^{-13}$ and $(5.20 \pm 0.77) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. We cite a final value of k_5 that is the average with error limits that include the extremes of the individual determinations: $k_5 = (4.82 \pm 1.15) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. The sample of $CF_3CF{=}CFCF_3$ used was a mixture of 70% *trans* and 30% *cis* isomer. As a result of spectral congestion caused by the presence of CH_3ONO and its oxidation products, we were only able to monitor the loss of $CF_3CF{=}CFCF_3$ via its absorption band at 687 cm^{-1}. We are unable to provide information on the relative reactivity of the two isomers.

The kinetics of reaction (8) were measured relative to reactions (6) and (7):

$$OH + CF_3CF_2CF{=}CF_2 \rightarrow \text{products} \quad (8)$$

$$OH + C_2H_2 \rightarrow \text{products} \quad (6)$$

$$OH + C_2H_4 \rightarrow \text{products} \quad (7)$$

Fig. 2b shows the loss of $CF_3CF_2CF{=}CF_2$ versus C_2H_2 and C_2H_4 following UV irradiation. The lines through the data in Fig. 2b are linear least-squares fits that give values of $k_8/k_6 = 2.18 \pm 0.18$ and $k_8/k_7 = 0.24 \pm 0.02$. Using the effective second-order rate constants in air at 700 Torr, $k_6 = 8.45 \times 10^{-13}$ (Sørensen et al., 2003) and $k_7 = 8.52 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Calvert et al., 2000) we derive $k_8 = (1.84 \pm 0.15) \times 10^{-12}$ and $(2.04 \pm 0.17) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. We choose to cite a final value of k_5 that is the average of the two values together with error limits that encompass the extremes of the individual determinations: $k_8 = (1.94 \pm 0.27) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

Hydroxyl radicals react approximately four times faster with $CF_3CF_2CF{=}CF_2$ than $CF_3CF{=}CFCF_3$. As with the chlorine atoms, OH radicals react with perfluorobutenes via electrophilic addition to the >C=C< double bond. The closer proximity of the electron withdrawing fluorine atoms to the double bond in $CF_3CF{=}CFCF_3$ and steric hinderance associated with the $-CF_3$ groups presumably contributes to its lower reactivity. While the kinetics of reactions (5) and (8) have not been studied previously, we can compare our results to the measurement of $k(OH + CF_3CF{=}CF_2) = (2.4 \pm 0.3) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Mashino et al., 2000). Consistent with its smaller number of electron withdrawing fluorine substituents, perfluoropropene is more reactive than the perfluorobutenes.

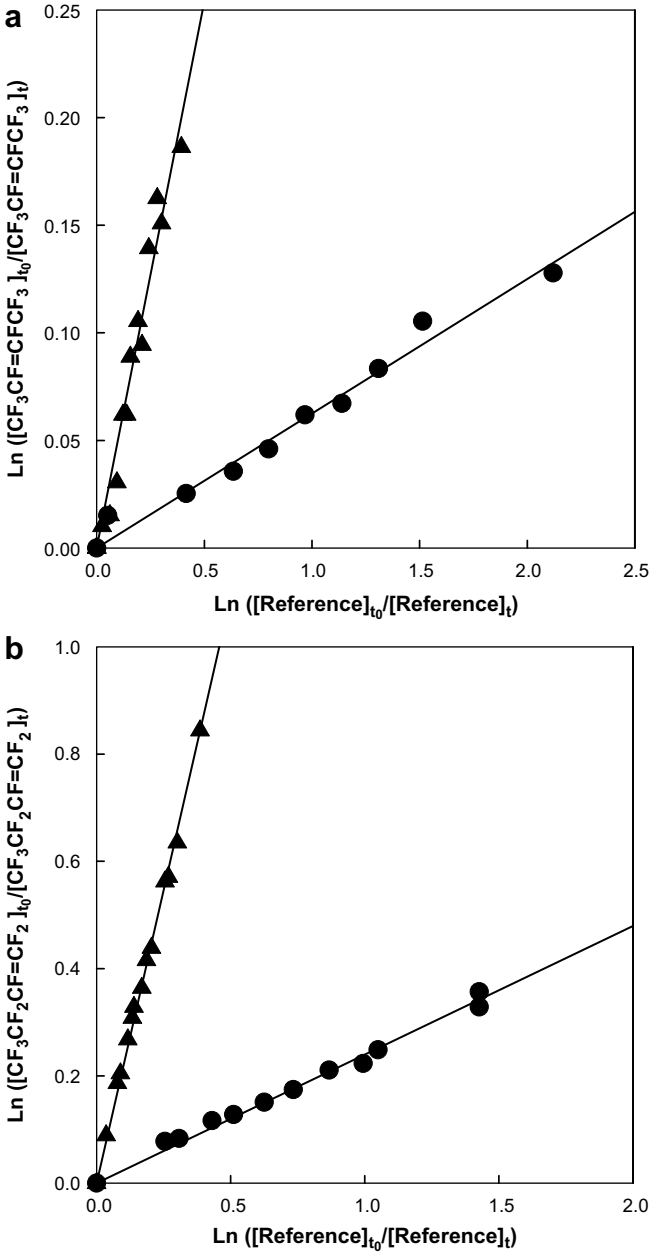

Fig. 2. Loss of (a) $CF_3CF{=}CFCF_3$ and (b) $CF_3CF_2CF{=}CF_2$ versus C_2H_2 (▲) and C_2H_4 (●) following exposure to hydroxyl radicals.

3.3. Products of Cl atom- and OH radical-initiated oxidation of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$

Fig. 3 shows IR spectra acquired before (A) and after (B) a 10 s UV irradiation of a mixture of 4.85 mTorr $CF_3CF{=}CFCF_3$ and 100 mTorr Cl_2 in 700 Torr of air diluent. Subtraction of IR features attributable to $CF_3CF{=}CFCF_3$ gives the residual spectrum shown in panel (C). Comparison of panel (C) with a reference spectrum of $CF_3C(O)F$ in panel (D) shows the formation of $CF_3C(O)F$ as a major product.

Fig. 4 shows a plot of the observed formation of $CF_3C(O)F$ versus the loss of $CF_3CF{=}CFCF_3$ following irradiation of $CF_3CF{=}CFCF_3/Cl_2$ and $CF_3CF{=}CFCF_3/CH_3ONO/NO$ mixtures in 700 Torr of air diluent. Linear least-squares fits to the data give slopes of 196 ± 11% for the $CF_3CF{=}CFCF_3/Cl_2$ experiments and 218 ± 20% for the $CF_3CF{=}CFCF_3/CH_3ONO/NO$ experiments. The molar yield of

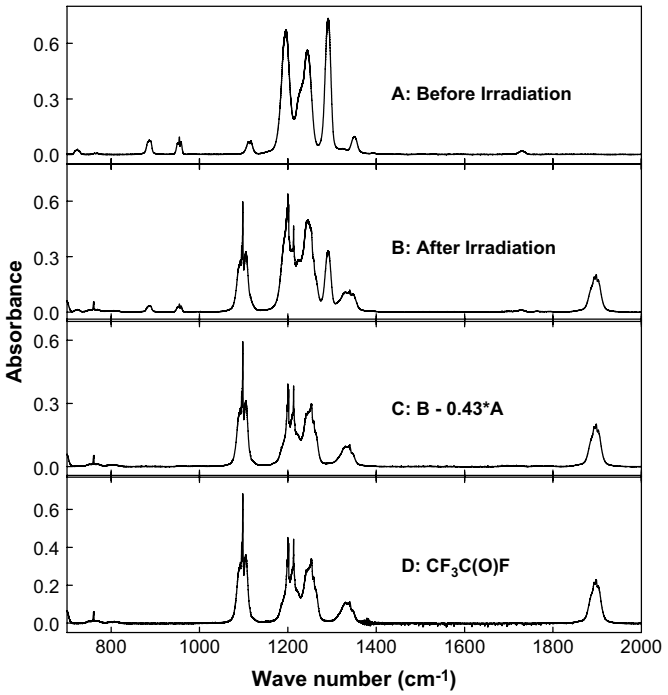

Fig. 3. IR spectra acquired before (A) and after (B) UV irradiation of a mixture of 4.85 mTorr $CF_3CF{=}CFCF_3$ and 100 mTorr Cl_2 in 700 Torr of air diluent. Panel (C) shows the product spectrum obtained after subtracting features attributable to $CF_3CF{=}CFCF_3$ from panel (B). Panel (D) is a reference spectrum of $CF_3C(O)F$.

$CF_3C(O)F$ following chlorine atom or OH radical-initiated oxidation of $CF_3CF{=}CFCF_3$ is indistinguishable from 200%. The line through the data in Fig. 4 has a slope of 2 and is provided to illustrate the data trend. We conclude that the atmospheric oxidation of $CF_3CF{=}CFCF_3$ proceeds via quantitative conversion into $CF_3C(O)F$.

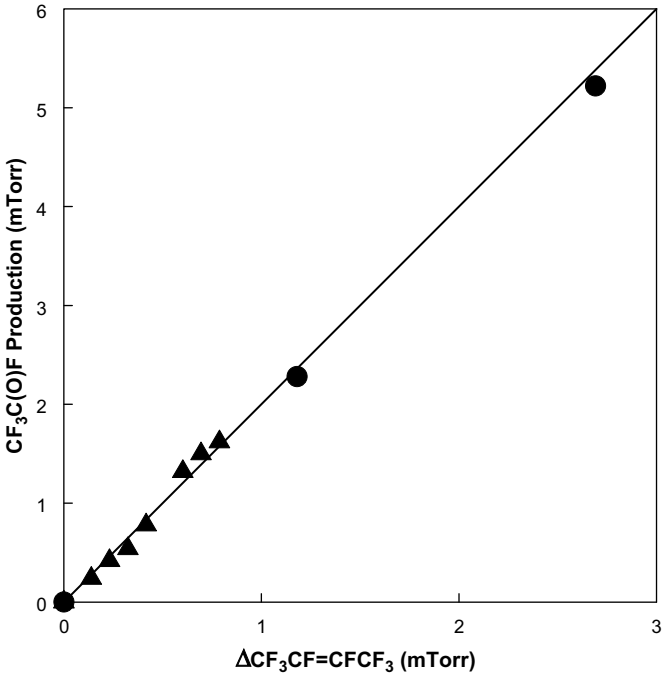

Fig. 4. Yield of $CF_3C(O)F$ following chlorine atom- (●) and hydroxyl radical- (▲) initiated oxidation of $CF_3CF{=}CFCF_3$. The line has a slope of two.

Fig. 5 shows IR spectra acquired before (A) and after (B) a 10 s UV irradiation of a mixture of 7.64 mTorr $CF_3CF_2CF{=}CF_2$ and 100 mTorr Cl_2 in 700 Torr of air diluent. Subtraction of IR features attributable to $CF_3CF_2CF{=}CF_2$ from panel (B) gives the spectrum shown in panel (C). Comparison of panel (C) with the reference spectrum in panel (D) shows the formation of COF_2 as a major product. Subtraction of IR features attributable to COF_2 from panel (C) gives the residual spectrum shown in panel (E). As illustrated by comparison with the reference spectrum for CF_3COF in panel (F), the feature centered at approximately 1890 cm^{-1} in panel (E) is consistent with the carbonyl absorption band expected for the formation of an acyl fluoride product. The product responsible for the carbonyl absorption band shown in panel (E) increased linearly with $CF_3CF_2CF{=}CF_2$ consumption.

Fig. 6a shows a plot of the formation of COF_2 versus the loss of $CF_3CF_2CF{=}CF_2$ observed following the UV irradiation of $CF_3CF_2CF{=}CF_2/Cl_2$ and $CF_3CF_2CF{=}CF_2/CH_3ONO/NO$ mixtures in 700 Torr of air diluent. Linear least-squares fits give molar COF_2 yields of 97 ± 9% and 99 ± 8% for the chlorine atom and hydroxyl radical-initiated oxidation, respectively. Thus, COF_2 is formed with a molar yield which is indistinguishable from 100%. It is expected that $CF_3CF_2C(O)F$ is formed as a co-product of COF_2. We do not have a reference spectrum for $CF_3CF_2C(O)F$ to compare with the residual spectrum in panel E of Fig. 5. However, as discussed above, the frequency of the absorption band of the unknown product is consistent with that expected for $CF_3CF_2C(O)F$. If we assume that the unknown product responsible for the absorption feature at 1890 cm^{-1} shown in Fig. 5e is formed in a molar yield of unity then from the integrated absorption in Fig. 5e over the range 1850–1930 cm^{-1} and the loss of $CF_3CF_2CF{=}CF_2$ (6.69 mTorr) we can calculate an integrated absorption cross-section of 2.62×10^{-17} cm $molecule^{-1}$ for this absorption band. This result is indistinguishable from the integrated absorption cross-section of 2.56×10^{-17} cm $molecule^{-1}$ for the analogous band (1850–1930 cm^{-1}) in our CF_3COF reference spectrum shown in Fig. 5f. The frequency and magnitude of the absorption in Fig. 5e is consistent with the formation of $CF_3CF_2C(O)F$. Assuming that the absorption in Fig. 5e is

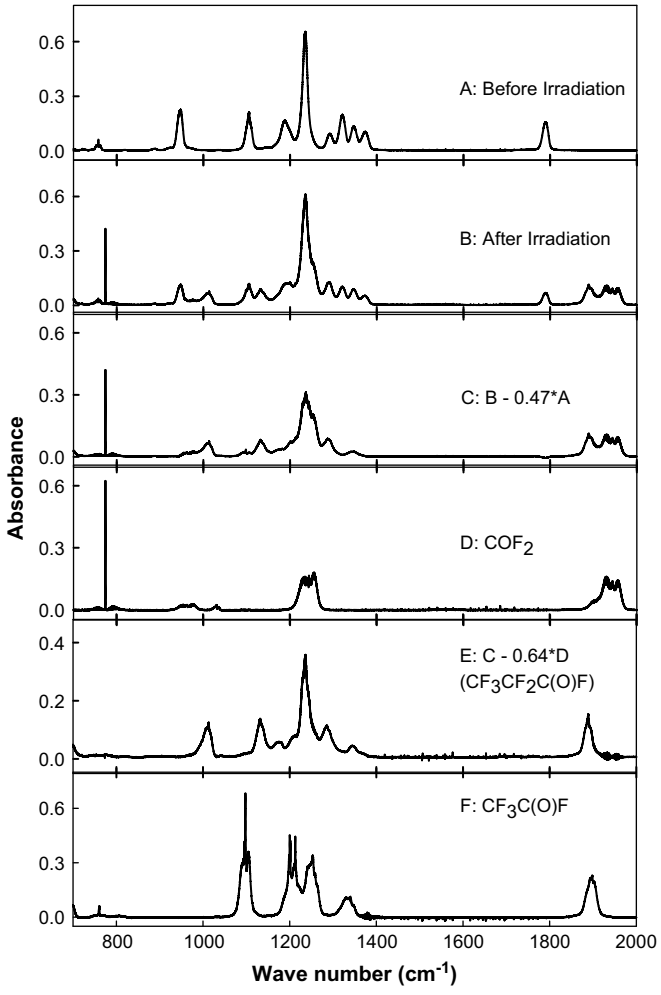

Fig. 5. IR spectra acquired before (A) and after (B) UV irradiation of a mixture of 7.64 mTorr $CF_3CF_2CF{=}CF_2$ and 100 mTorr Cl_2 in 700 Torr of air diluent. Panel (C) shows the product spectrum obtained after subtracting features attributable to $CF_3CF_2CF{=}CF_2$ from panel (B). Panels (D) and (F) are reference spectra of COF_2 and $CF_3C(O)F$. Panel E is the residual spectrum obtained after subtracting features attributable to COF_2 from the product spectrum (C).

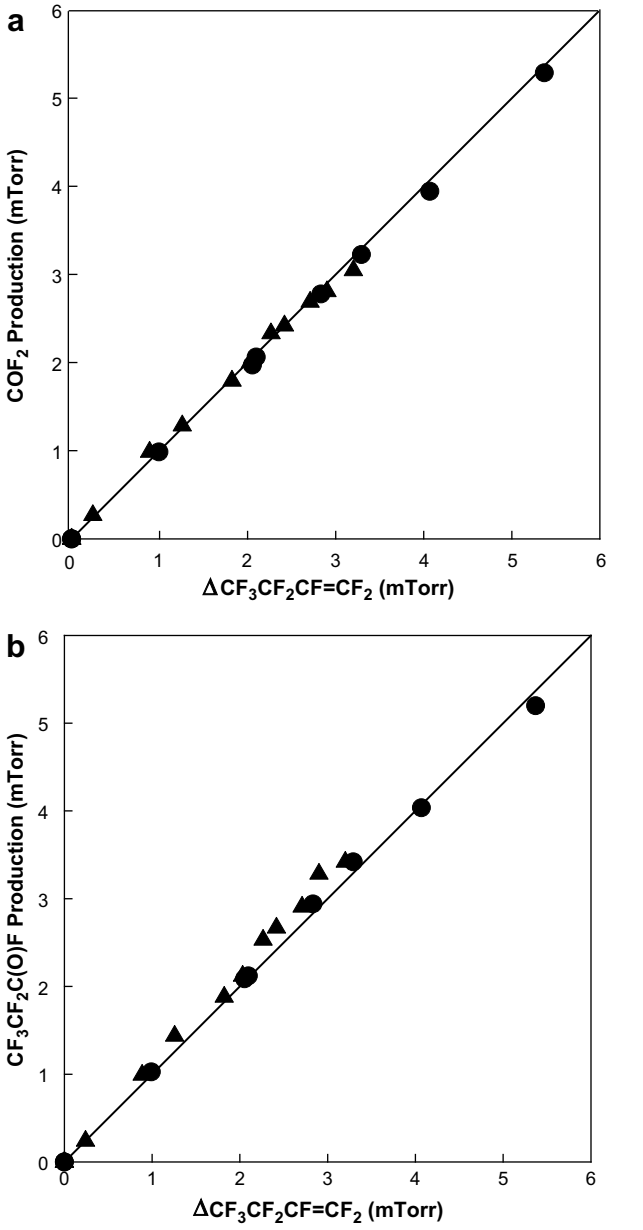

Fig. 6. Yields of COF_2 (a) and $CF_3CF_2C(O)F$ (b) following chlorine atom-initiated (●) and hydroxyl radical-initiated (▲) oxidation of $CF_3CF_2CF{=}CF_2$. The lines have slopes of unity.

attributable to $CF_3CF_2C(O)F$, and the carbonyl absorption band centered at 1890 cm^{-1} has the same integrated absorption cross-section as the analogous feature in CF_3COF, then we can calibrate the yields of $CF_3CF_2C(O)F$. This approach was used to derive the $CF_3CF_2C(O)F$ data shown in Fig. 6. Product yields for $CF_3CF_2C(O)F$ of 97 ± 9% and 110 ± 15% were observed from chlorine atom and hydroxyl radical addition, respectively. The atmospheric oxidation of $CF_3CF_2CF{=}CF_2$ leads to the formation of both COF_2 and $CF_3CF_2C(O)F$ in molar yields indistinguishable from 100%.

3.4. Proposed oxidation mechanisms

The reaction of chlorine atoms and hydroxyl radicals with $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ is expected to proceed via addition to the >C=C< double bond leading to a radical which will add O_2 to give a peroxy radical. The peroxy radical will react with NO or with another peroxy radical to give an alkoxy radical. The symmetry of $CF_3CF{=}CFCF_3$ leads to a single alkoxy radical (see Fig. 7). In principle this alkoxy radical could decompose via scission of one of two different C–C bonds giving two sets of products. In practice we observed only one product, $CF_3C(O)F$, showing that decomposition occurs essentially exclusively via scission of the central C–C bond. This preference presumably reflects thermochemical factors. The observed formation of COF_2 and $CF_3CF_2C(O)F$ from $CF_3CF_2CF{=}CF_2$ in molar yields indistinguishable from 100% shows that irrespective of the attacking radical (Cl or OH) or the carbon atom to which it adds (terminal or interior) the fate of the resulting alkoxy radical is decomposition via scission of the terminal C–C bond. This mechanism is illustrated in Fig. 7b for the radicals generated following addition of OH to the terminal carbon atom.

3.5. Infrared spectra and radiative efficiency of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$

IR spectra were recorded at 296 K using 2.2–7.5 mTorr of $CF_3CF{=}CFCF_3$ and 1.79–9.05 mTorr of $CF_3CF_2CF{=}CF_2$ (separately) in 700 Torr of air diluent. The IR features scaled linearly with the perfluorobutene concentration. The absolute absorption spectra are shown in Fig. 8. The integrated cross-sections (650–1500 cm^{-1}) of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ are 2.88 and 2.14 × 10^{-16} cm $molecule^{-1}$, respectively. Uncertainties in the cross-section measurement arise from following sources: sample concentration (2%), sample purity (2%), path length (1.5%), spectrum noise (±10^{-20} cm^2 $molecule^{-1}$), and residual baseline offset after subtraction of background (1.5%). From these individual uncertainties, the total (random) uncertainty in the integrated absorption cross-section is ±4%. We prefer to quote a conservative uncertainty of ±5%. Hence, the integrated cross-sections of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ are (2.88 ± 0.14) and (2.14 ± 0.11) × 10^{-16} cm $molecule^{-1}$, respectively.

Pinnock et al. (1995) have presented a simple method that can be used to estimate radiative efficiency from IR absorption spectra. In this method, the region between 0 and 2500 cm^{-1} is divided up into 250 bands 10 cm^{-1} wide. The radiative efficiency for a 0 → 1 ppbv change in atmospheric concentration of the compound can then be calculated using the expression:

$$\text{Radiative efficiency} = \sum_{i=1}^{250} 10\left(\text{cm}^{-1}\right)\sigma_{av}^{i}F_{\sigma}^{i}$$

where $\sigma_{av}{}^{i}$ is the average absorption cross-section in band i in units of cm^2 $molecule^{-1}$, and $F_{\sigma}{}^{i}$ is the radiative forcing per unit cross-section per wavenumber per part-per-billion in band i in units of W m^{-2} $(cm^{-1})^{-1}$ $(cm^2$ $molecule^{-1})^{-1}$. Using this method, the IR spectra of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ shown in Fig. 8, and the IR spectrum of CFC-11 reported elsewhere (Ninomiya et al., 2000), we calculate radiative efficiencies for $CF_3CF{=}CFCF_3$, $CF_3CF_2CF{=}CF_2$, and CFC-11 of 0.32, 0.29, and 0.26 W m^{-2} ppb^{-1}, respectively. Although $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ are isomers, the radiative efficiency of $CF_3CF{=}CFCF_3$ is about 10% greater reflecting the fact that chemical structure impacts the radiative efficiency of fluorinated compounds (Young et al., 2008).

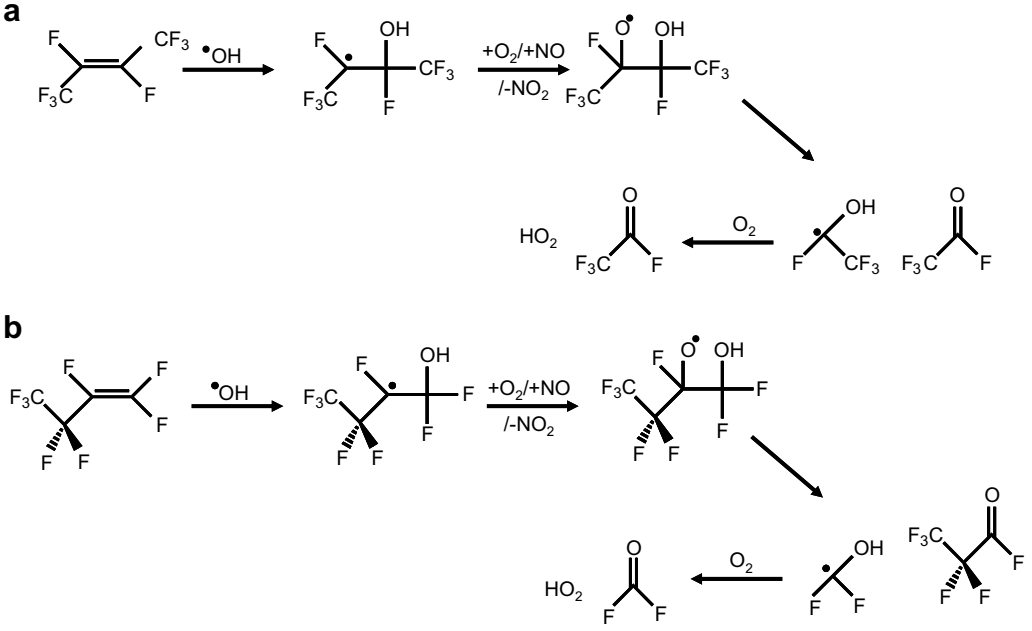

Fig. 7. Proposed mechanism for the atmospheric oxidation of (a) $CF_3CF{=}CFCF_3$ and (b) $CF_3CF_2CF{=}CF_2$ initiated by hydroxyl radicals. Stable products are given in boxes. In part (b), only addition to the terminal carbon is depicted for simplicity.

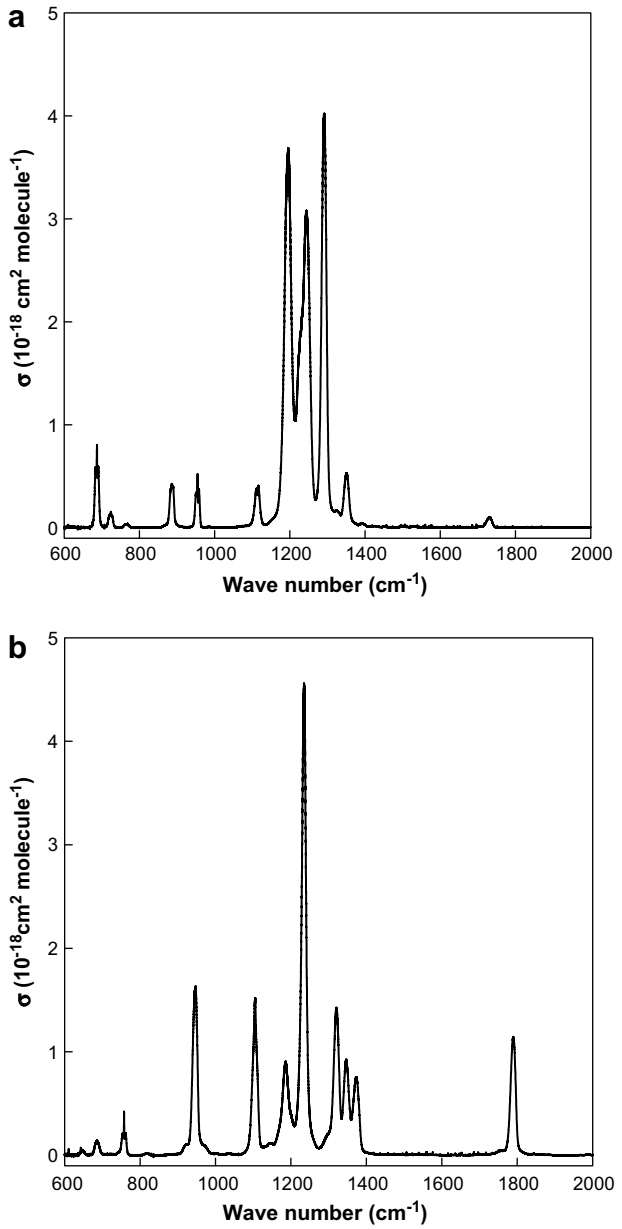

Fig. 8. Infrared spectra of (a) $CF_3CF{=}CFCF_3$ and (b) $CF_3CF_2CF{=}CF_2$.

It should be noted that the model of radiative efficiency utilized here (Pinnock et al., 1995) assumes a uniform distribution of the chemical in question. For short-lived compounds such as $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$, greater concentrations will be found in the boundary layer, where radiative effects are lower. Radiative efficiencies based on distributions calculated using chemical transport models can be substantially lower for fluoroalkenes (by factors of 23 for C_2F_4 and 8 for C_3F_6) than those based on uniform distributions (Acerboni et al., 2001). Thus, our values should be considered upper limits for the radiative efficiencies of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$.

4. Atmospheric implications

Assuming an average global concentration of hydroxyl radicals of 1×10^6 molecules cm^{-3} (Prinn et al., 2001) gives lifetimes for $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ with respect to reaction with OH of about twenty-four and six days, respectively. The approximate nature of these lifetimes must be stressed. The concentration of hydroxyl radicals, and hence atmospheric lifetime, varies substantially with season and latitude.

Tropospheric concentrations of chlorine atoms are highly variable and uncertain, levels in the marine boundary layer of up to 1×10^5 molecules cm^{-3} have been reported (Spicer et al., 1998), with a tropospheric average of <5–10×10^2 molecules cm^{-3} (Singh et al., 1996). Thus, typical lifetimes for $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ with respect to reaction with chlorine atoms will be on the order of a few years in the free troposphere, and a few weeks under marine boundary layer conditions. Reaction with chlorine atoms is not expected to be a significant fate of $CF_3CF{=}CFCF_3$ or $CF_3CF_2CF{=}CF_2$. Reactions of alkenes with ozone can contribute to degradation of these compounds in the atmosphere. The reaction of ozone with perfluoropropene proceeds with a rate constant of 6.2×10^{-22} cm^3 $molecule^{-1}$ s^{-1} (Acerboni et al., 2001). As discussed for chlorine atom and OH radical reactions we would expect the reactivity of the perfluorobutenes to be lower than perfluoropropene. Hence, the lifetime of the perfluorobutenes with respect to reaction with O_3 will probably be greater than 8 years and not significant. We conclude that the atmospheric lifetimes of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ are determined by reaction with hydroxyl radicals and are approximately twenty-four and six days, respectively.

The halocarbon global warming potential for $CF_3CF_2CF{=}CF_2$ (relative to CFC-11) can be estimated using the expression:

$$\mathrm{HGWP_X} = \left(\frac{\mathrm{RE_X}}{\mathrm{RE_{CFC\text{-}11}}}\right)\left(\frac{\tau_X M_{\mathrm{CFC\text{-}11}}}{\tau_{\mathrm{CFC\text{-}11}} M_X}\right)\left(\frac{1-\exp(-t/\tau_X)}{1-\exp(-t/\tau_{\mathrm{CFC\text{-}11}})}\right)$$

where RE_X, $RE_{CFC\text{-}11}$, M_X, $M_{CFC\text{-}11}$, τ_X, and $\tau_{CFC\text{-}11}$ are the radiative efficiencies, molecular weights, and atmospheric lifetimes of the molecule of interest and CFC-11, and t is the time horizon over which the forcing is integrated. Assuming $\tau(CF_3CF{=}CFCF_3) = 24$ days, $\tau(CF_3CF_2CF{=}CF_2) = 6$ days, and $\tau(\text{CFC-11}) = 45$ years (Forster et al., 2007), we estimate the HGWPs of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ (relative to CFC-11) are 1.3×10^{-3} and 2.5×10^{-4} for a 100 year horizon, respectively. Relative to CO_2, the GWP of CFC-11 on a 100 year time horizon is 4750 (Forster et al., 2007). Thus, we estimate that relative to CO_2, the GWPs of $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ are approximately 6 and 1, respectively, for a 100 year time horizon. It should be noted that these GWP values are upper limits, due to the likelihood that the radiative efficiency values are over-estimated (see Section 3.5). It is clear that neither $CF_3CF{=}CFCF_3$ nor $CF_3CF_2CF{=}CF_2$ will contribute to radiative forcing of climate change. $CF_3CF{=}CFCF_3$ and $CF_3CF_2CF{=}CF_2$ do not contain chlorine, bromine, or iodine and hence they will not have any significant impact on stratospheric ozone.

Atmospheric oxidation of $CF_3CF{=}CFCF_3$ gives $CF_3C(O)F$, while oxidation of $CF_3CF_2CF{=}CF_2$ gives COF_2 and $CF_3CF_2C(O)F$. COF_2 is a common product of the atmospheric oxidation of fluorinated compounds and is the dominant product of the degradation of numerous hydrofluorocarbons (Taketani et al., 2005; Tuazon and Atkinson, 1993), hydrochlorofluorocarbons (Tuazon and Atkinson, 1993) and hydrofluoroethers (Sulbaek Andersen et al., 2005; Tuazon, 1997). The atmospheric fate of COF_2 is hydrolysis to yield CO_2 and HF. At the levels expected from atmospheric oxidation of perfluorobutenes (and HFCs in general) the formation of HF is not of any environmental significance. The fate of $CF_3C(O)F$ and $CF_3CF_2C(O)F$ is hydrolysis to form $CF_3C(O)OH$ (trifluoroacetic acid, TFA) and $CF_3CF_2C(O)OH$ (perfluoropropionic acid, PFPrA), respectively. TFA and PFPrA are members of the class of compounds called perfluorocarboxylic acids (PFCAs) which have attracted attention because they are persistent and accumulate in biota. However,

PFCAs with less than eight carbons such as TFA and PFPrA do not appear to be bioaccumulative (Martin et al., 2003a,b).

TFA is widespread in the environment (Scott et al., 2005, 2006) and is produced during the atmospheric degradation of several anthropogenic pollutants (World Meteorological Organization, 2007). TFA has been detected in deep ocean water and appears to be a natural trace component of the oceanic environment (Frank et al., 2002). It is generally accepted that any additional environmental burden of TFA resulting from the atmospheric degradation of HCFCs and HFCs will not have any significant environmental impact (World Meteorological Organization, 2007). PFPrA is present in the environment and has been detected in rainwater (Scott et al., 2006), although its source is unclear. Further work is needed to clarify the sources, fate, and environmental impact of PFPrA. As illustrated in the present work, the yields and identity of PFCAs formed in the atmosphere are dictated by the molecular structure of the parent fluorinated organic compounds.

Acknowledgments

The authors thank Craig Butt for experimental assistance. CJY is grateful to the Natural Science and Engineering Research Council of Canada for a CGS Fellowship.

References

Acerboni, G., Beukes, J.A., Jensen, N.R., Hjorth, J., Myhre, G., Nielsen, C.J., Sundet, J.K., 2001. Atmospheric degradation and global warming potentials of three perfluoroalkenes. Atmospheric Environment 35, 4113–4123.

Calvert, J.G., Atkinson, R., Kerr, J.A., Madronich, S., Moortgat, G.K., Wallington, T.J., Yarwood, G., 2000. The Mechanisms of Atmospheric Oxidation of the Alkenes. Oxford University Press, Oxford.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., Van Dorland, R., 2007. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), Climate Change 2007: The Physical Science Basis. Cambridge University Press, Cambridge, United Kingdom.

Frank, H., Christoph, E.H., Holm-Hansen, O., Bullister, J.L., 2002. Trifluoroacetate in ocean waters. Environmental Science and Technology 36, 12–15.

Hurley, M.D., Ball, J.C., Wallington, T.J., 2007. Atmospheric chemistry of the Z and E isomers of $CF_3CF{=}CHF$; kinetics, mechanisms, and products of gas-phase reactions with Cl atoms, OH radicals, and O_3. Journal of Physical Chemistry A 111, 9789–9795.

Kaiser, E.W., Donahue, C.J., Pala, I.R., Wallington, T.J., Hurley, M.D., 2007. Kinetics, products and stereochemistry of the reaction of chlorine atoms with *cis*- and *trans*-2-butene in 10–700 Torr of N_2 or N_2/O_2 diluent at 297 K. Journal of Physical Chemistry A 111, 1286–1299.

Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003a. Dietary accumulations of perfluorinated acids in juvenile rainbow trout (*Oncorhynchus mykiss*). Environmental Toxicology and Chemistry 22, 189–195.

Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003b. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). Environmental Toxicology and Chemistry 22, 196–204.

Mashino, M., Ninomiya, Y., Kawasaki, M., Wallington, T.J., Hurley, M.D., 2000. Atmospheric chemistry of $CF_3CF{=}CF_2$: kinetics and mechanism of its reactions with OH radicals, Cl atoms, and ozone. Journal of Physical Chemistry A 104, 7255–7260.

Nielsen, O.J., Javadi, M.S., Sulbaek Andersen, M.P., Hurley, M.D., Wallington, T.J., Singh, R., 2007. Atmospheric chemistry of $CF_3CF{=}CH_2$: kinetics and mechanisms of gas-phase reactions with Cl atoms, OH radicals, and O_3. Chemical Physics Letters 439, 18–22.

Ninomiya, Y., Kawasaki, M., Gushin, A., Molina, L.T., Molina, M., Wallington, T.J., 2000. Atmospheric chemistry of n-$C_3F_7OCH_3$: reaction with OH radicals and Cl atoms and atmospheric fate of n-$C_3F_7OCH_2O$. Environmental Science and Technology 34, 2973–2978.

Orkin, V.L., Huie, R.E., Kurylo, M.J., 1997. Rate constants for the reactions of OH with HFC-245cb ($CH_3CF_2CF_3$) and some fluoroalkenes (CH_2CHCF_3, CH_2CFCF_3, and CF_2CF_2). Journal of Physical Chemistry A 101, 9118–9124.

Papadimitriou, V.C., Talukdar, R.K., Portmann, R.W., Ravishankara, A.R., Burkholder, J.B., 2008. $CF_3CF{=}CH_2$ and (*Z*)-$CF_3CF{=}CHF$: temperature dependent OH rate coefficients and global warming potentials. Physical Chemistry Chemical Physics 10, 808–820.

Pinnock, S., Hurley, M.D., Shine, K.P., Wallington, T.J., Smyth, T.J., 1995. Radiative forcing of climate by hydrochlorofluorocarbons and hydrofluorocarbons. Journal of Geophysical Research 100, 23227–23238.

Prinn, R.G., Huang, J., Weiss, R.F., Cunnold, D.M., Fraser, P.J., Simmonds, P.G., McCulloch, A., Salameh, P., O'Doherty, S., Wang, R.H.J., Porter, L., Miller, B.R., 2001. Evidence for substantial variation of atmospheric hydroxyl radicals in the past two decades. Science 292, 1882–1888.

Scott, B.F., Macdonald, R.W., Kannan, K., Fisk, A., Witter, A., Yamashita, N., Durham, L., Spencer, C., Muir, D.C.G., 2005. Trifluoroacetate profiles in the Arctic, Atlantic and Pacific Oceans. Environmental Science and Technology 39, 6555–6560.

Scott, B.F., Spencer, C., Mabury, S.A., Muir, D.C.G., 2006. Poly and perfluorinated carboxylates in North American precipitation. Environmental Science and Technology 40, 7167–7174.

Singh, H.B., Thakur, A.N., Chen, Y.E., Kanakidou, M., 1996. Tetrachloroethylene as an indicator of low Cl atom concentrations in the troposphere. Geophysical Research Letters 23, 1529–1532.

Spicer, C.W., Chapman, E.G., Finlayson-Pitts, B.J., Plastridge, R.A., Hubbe, J.M., Fast, J.D., Berkowitz, C.M., 1998. Unexpectedly high concentrations of molecular chlorine in coastal air. Nature 394, 353–356.

Sulbaek Andersen, M.P., Nielsen, O.J., Wallington, T.J., Hurley, M.D., DeMore, W.B., 2005. Atmospheric chemistry of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$: reaction with Cl atoms and OH radicals, degradation mechanism, global warming potentials, and empirical relationship between k(OH) and k(Cl) for organic compounds. Journal of Physical Chemistry A 109, 3926–3934.

Søndergaard, R., Nielsen, O.J., Hurley, M.D., Wallington, T.J., Singh, R., 2007. Atmospheric chemistry of *trans*-$CF_3CH{=}CHF$: kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O_3. Chemical Physics Letters 443, 199–204.

Sørensen, M., Kaiser, E.W., Hurley, M.D., Wallington, T.J., Nielsen, O.J., 2003. Kinetics of the reaction of OH radicals with acetylene in 25–8000 Torr of air at 296 K. International Journal of Chemical Kinetics 35, 191–197.

Taketani, F., Nakayama, T., Takahashi, K., Matsumi, Y., Hurley, M.D., Wallington, T.J., Toft, A., Sulbaek Andersen, M.P., 2005. Atmospheric chemistry of CH_3CHF_2 (HFC-152a): kinetics, mechanisms, and products of Cl atom- and OH radical-initiated oxidation in the presence and absence of NO_x. Journal of Physical Chemistry A 109, 9061–9069.

Tuazon, E.C., 1997. Tropospheric degradation products of novel hydrofluoropolyethers. Environmental Science and Technology 31, 1817–1821.

Tuazon, E.C., Atkinson, R., 1993. Tropospheric transformation products of a series of hydrofluorocarbons and hydrochlorofluorocarbons. Journal of Atmospheric Chemistry 17, 179–199.

Wallington, T.J., Andino, J.M., Lorkovic, I.M., Kaiser, E.W., Marston, G., 1990. Pressure dependence of the reaction of chlorine atoms with ethene and acetylene in air at 295 K. Journal of Physical Chemistry 94, 3644–3648.

Wallington, T.J., Schneider, W.F., Worsnop, D.R., Nielsen, O.J., Sehested, J., DeBruyn, W., Shorter, J.A., 1994. Environmental impact of CFC replacements: HFCs and HCFCs. Environmental Science and Technology 28, 320A.

Wallington, T.J., Schneider, W.F., Sehested, J., Nielsen, O.J., 1995. Hydrofluorocarbons and stratospheric ozone. Journal of Chemical Society, Faraday Discussions 100, 55.

Wine, P.H., Semmes, D.H., 1983. Kinetics of $Cl(^2P_j)$ reactions with the chloroethanes CH_3CH_2Cl, CH_3CHCl_2, CH_2ClCH_2Cl, and $CH_2ClCHCl_2$. Journal of Physical Chemistry 87, 3572–3578.

World Meteorological Organization. 2007. Scientific Assessment of ozone Depletion: 2006.

Young, C.J., Hurley, M.D., Wallington, T.J., Mabury, S.A., 2008. Molecular structure and radiative efficiency of fluorinated ethers: a structure–activity relationship. Journal of Geophysical Research 113. doi:10.1029/2008JD010178.