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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

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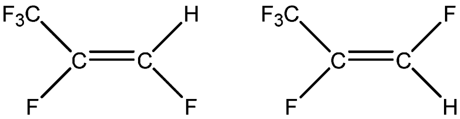
Smog chamber/FTIR techniques were used to study the atmospheric chemistry of the Z and E isomers of $CF_3CF{=}CHF$, which we refer to as $CF_3CF{=}CHF(Z)$ and $CF_3CF{=}CHF(E)$. The rate constants $k(Cl + CF_3CF{=}CHF(Z)) = (4.36 \pm 0.48) \times 10^{-11}$, $k(OH + CF_3CF{=}CHF(Z)) = (1.22 \pm 0.14) \times 10^{-12}$, and $k(O_3 + CF_3CF{=}CHF(Z)) = (1.45 \pm 0.15) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} were determined for the Z isomer of $CF_3CF{=}CHF$ in 700 Torr air diluent at 296 ± 2 K. The rate constants $k(Cl + CF_3CF{=}CHF(E)) = (5.00 \pm 0.56) \times 10^{-11}$, $k(OH + CF_3CF{=}CHF(E)) = (2.15 \pm 0.23) \times 10^{-12}$, and $k(O_3 + CF_3CF{=}CHF(E)) = (1.98 \pm 0.15) \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} were determined for the E isomer of $CF_3CF{=}CHF$ in 700 Torr air diluent at 296 ± 2 K. Both the Cl-atom and OH-radical-initiated atmospheric oxidation of $CF_3CF{=}CHF$ give $CF_3C(O)F$ and HC(O)F in molar yields indistinguishable from 100% for both the Z and E isomer. $CF_3CF{=}CHF(Z)$ has an atmospheric lifetime of approximately 18 days and a global warming potential (100 year time horizon) of approximately 6. $CF_3CF{=}CHF(E)$ has an atmospheric lifetime of approximately 10 days and a global warming potential (100 year time horizon) of approximately 3. $CF_3CF{=}CHF$ has a negligible global warming potential and will not make any significant contribution to radiative forcing of climate change.

Introduction

Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere[1,2] has led to an international effort to replace these compounds with environmentally acceptable alternatives. Unsaturated fluorinated hydrocarbons are a class of compounds which have been developed to replace CFCs and saturated hydrofluorocarbons as refrigerants in air-conditioning units. Prior to their large-scale industrial use, an assessment of the atmospheric chemistry and environmental impact of these compounds is needed. To address this need, the atmospheric chemistry of $CF_3CF{=}CHF$ was investigated. $CF_3CF{=}CHF$ exists in two isomeric forms: Z and E.



Z isomer E isomer

Smog chamber/FTIR techniques were used to determine the following properties for the Z and E isomers of $CF_3CF{=}CHF$: (i) kinetics of reaction with chlorine atoms, (ii) kinetics of reaction with hydroxyl radicals, (iii) kinetics of reaction with ozone, (iv) products formed during the Cl-atom-initiated oxidation, (v) products formed during the OH-radical-initiated oxidation, and (vi) atmospheric implications. The Z isomer will be referred to as $CF_3CF{=}CHF(Z)$ while the E isomer will be referred to as $CF_3CF{=}CHF(E)$.

Experimental Section

Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer.[3] The reactor was surrounded by 22 fluorescent blacklamps (GE F40T12BLB) which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.

$$Cl_2 + h\nu \rightarrow Cl + Cl \tag{1}$$

OH radicals were produced by photolysis of CH_3ONO in the presence of NO in air.

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{2}$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \tag{3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{4}$$

Relative rate techniques were used to measure the rate constant of interest relative to a reference reaction whose rate constant has been established previously. The relative rate method is a well-established technique for measuring the reactivity of Cl atoms and OH radicals with organic compounds.[4] Kinetic data are derived by monitoring the loss of $CF_3CF{=}CHF$ relative to one or more reference compounds. The decays of $CF_3CF{=}CHF$ and the reference are then plotted using the following expression:

$$\ln\left(\frac{[\text{Reactant}]_0}{[\text{Reactant}]_t}\right) = \frac{k_{\text{Reactant}}}{k_{\text{Reference}}} \ln\left(\frac{[\text{Reference}]_0}{[\text{Reference}]_t}\right) \tag{I}$$

where $[\text{Reactant}]_0$, $[\text{Reactant}]_t$, $[\text{Reference}]_0$, and $[\text{Reference}]_t$ are the concentrations of $CF_3CF{=}CHF$ and the reference compound at times “0” and “t”, and k_{Reactant} and $k_{\text{Reference}}$ are

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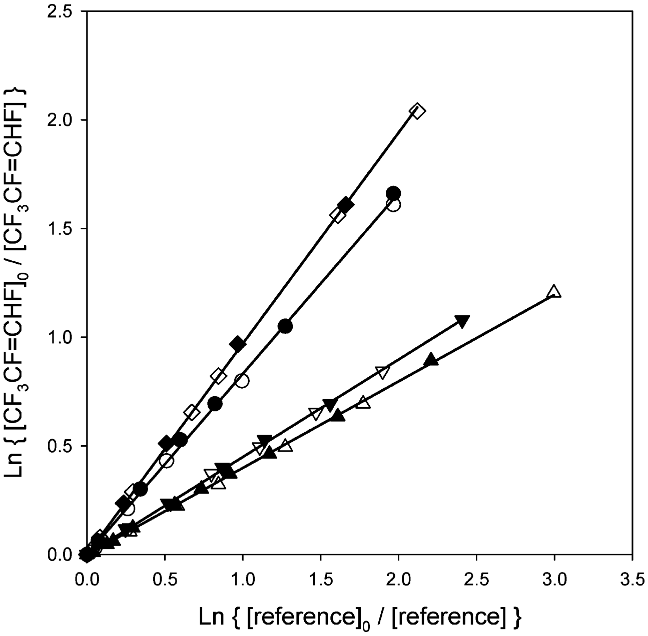

Figure 1. Loss of $CF_3CF{=}CHF(Z)$ vs C_2H_4 (triangles up) and C_2H_2 (circles) and the loss of $CF_3CF{=}CHF(E)$ vs C_2H_4 (triangles down) and C_2H_2 (diamonds) in the presence of Cl atoms in 700 Torr air at 296 ± 2 K. Open and closed symbols represent different experiments.

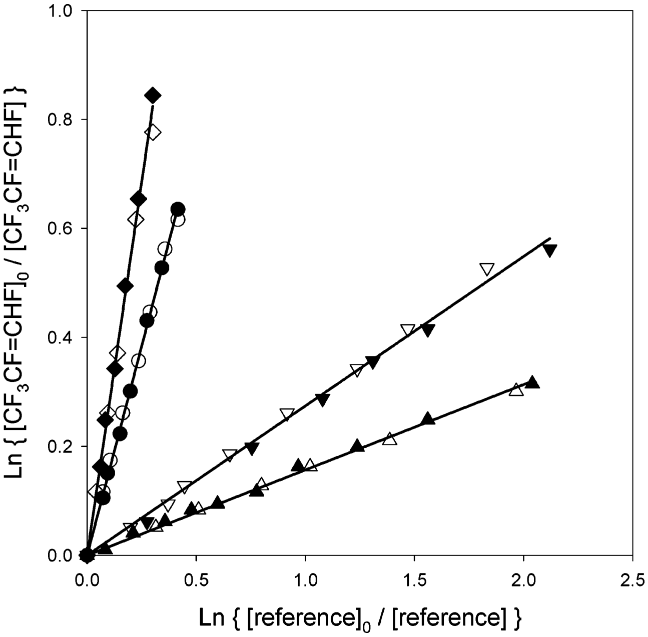

Figure 2. Loss of $CF_3CF{=}CHF(Z)$ vs C_2H_4 (triangles up) and C_2H_2 (circles) and the loss of $CF_3CF{=}CHF(E)$ vs C_2H_4 (triangles down) and C_2H_2 (diamonds) in the presence of OH radicals in 700 Torr air at 296 ± 2 K. Open and closed symbols represent different experiments.

the rate constants for reactions of Cl atoms or OH radicals with the $CF_3CF{=}CHF$ and the reference compound. Plots of Ln([Reactant]$_0$/[Reactant]$_t$) versus Ln([Reference]$_0$/[Reference]$_t$) should be linear, pass through the origin and have a slope of $k_{Reactant}/k_{Reference}$. The kinetics of the O_3 reaction were studied using an absolute rate method in which the pseudo first-order loss of $CF_3CF{=}CHF$ was measured in the presence of excess O_3.

O_3 was produced from O_2 via silent electrical discharge using a commercial O_3 ozonizer. CH_3ONO was synthesized by the dropwise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$ in methanol. $CF_3CF{=}CHF(Z)$ and $CF_3CF{=}CHF(E)$ were provided by INEOS Fluor at a purities of 99.38% and 99.96%, respectively. Other reagents were obtained from commercial sources. Experiments were conducted in 700 Torr total pressure of O_2/N_2 diluent at 296 ± 2 K. Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 co-added interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 m. To check for unwanted loss of reactants and reference compounds via heterogeneous reactions, reaction mixtures were left to stand in the chamber for 60 min. There was no observable (<2%) loss of any of the reactants or products in the present work. Unless stated otherwise, quoted uncertainties are 2 standard deviations from least-squares regressions.

Results and Discussion

Kinetics of the Cl + $CF_3CF{=}CHF$ Reaction. The rate of reaction 5 was measured relative to reactions 6 and 7 for the Z and E isomers:

$$Cl + CF_3CF{=}CHF \rightarrow products \quad (5)$$

$$Cl + C_2H_4 \rightarrow products \quad (6)$$

$$Cl + C_2H_2 \rightarrow products \quad (7)$$

For the Z isomer, reaction mixtures consisted of 6.8−9.7 mTorr $CF_3CF{=}CHF(Z)$, 100 mTorr Cl_2, and either 4.4−7.1 mTorr C_2H_4 or 2.2−2.9 mTorr C_2H_2 in 700 Torr of air diluent. For the E isomer, reaction mixtures consisted of 9.3−13.2 mTorr $CF_3CF{=}CHF(E)$, 100 mTorr Cl_2, and either 4.4−4.6 mTorr C_2H_4 or 1.6−3.1 mTorr C_2H_2 in 700 Torr air diluent. Figure 1 shows the loss of $CF_3CF{=}CHF$ plotted versus the loss of the reference compounds. Linear least-squares analysis of the data in Figure 1 gives the results shown in Table 1. For each isomer, the values of k_5 obtained using the two different references are indistinguishable within the experimental uncertainties. The final value is the average of the individual determinations together with error limits which encompass the extremes of the individual determinations; $k(Cl + CF_3CF{=}CHF(Z)) = (4.36 \pm 0.48) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $k(Cl + CF_3CF{=}CHF(E)) = (5.00 \pm 0.56) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Kinetic data for the reactions of chlorine atoms with propene and fluorinated propenes are presented in Table 3. The reaction of chlorine atoms with propene proceeds primarily via electrophilic addition to the $>C{=}C<$ double bond. Fluorine is an electron-withdrawing substituent and would be expected to lower the reactivity of chlorine atoms toward substituted propenes. Consistent with this expectation, inspection of Table 3 reveals a trend of generally decreasing reactivity with increasing number of electron-withdrawing fluorine substituents. Also presented in Table 3 are kinetic data for the reactions of chlorine atoms with the Z and E isomers of 2-butene. For both $CF_3CF{=}CHF$ and 2-butene, the reactivity toward chlorine atoms is comparable for the Z and E isomers.

Kinetics of the OH + $CF_3CF{=}CHF$ Reaction. The rate of reaction 8 was measured relative to reactions 9 and 10 for the Z and E isomers:

$$OH + CF_3CF{=}CHF \rightarrow products \quad (8)$$

$$OH + C_2H_4 \rightarrow products \quad (9)$$

$$OH + C_2H_2 \rightarrow products \quad (10)$$

TABLE 1: Results of the Relative Rate Constant Experiments To Determine $k(C + CF_3CF=CHF)$[a]

sample	reference	$k_{sample}/k_{reference}$	$k_{reference}$	$k(Cl + CF_3CF=CHF)$	$k_{avg}(Cl + CF_3CF=CH\ F)$
$CF_3CF=CHF(Z)$	C_2H_4	0.40 ± 0.04	1.1×10^{-10} [18]	$(4.40 \pm 0.44) \times 10^{-11}$	$(4.36 \pm 0.48) \times 10^{-11}$
$CF_3CF=CHF(Z)$	C_2H_2	0.83 ± 0.08	5.2×10^{-11} [18]	$(4.32 \pm 0.41) \times 10^{-11}$	
$CF_3CF=CHF(E)$	C_2H_4	0.45 ± 0.04	1.1×10^{-10} [18]	$(4.95 \pm 0.45) \times 10^{-11}$	$(5.00 \pm 0.56) \times 10^{-11}$
$CF_3CF=CHF(E)$	C_2H_2	0.97 ± 0.10	5.2×10^{-11} [18]	$(5.04 \pm 0.52) \times 10^{-11}$	

[a] Rate constant units are cm^3 molecule^{-1} s^{-1}.

TABLE 2: Results of the Relative Rate Constant Experiments To Determine $k(OH + CF_3CF=CHF)$[a]

sample	reference	$k_{sample}/k_{reference}$	$k_{reference}$	$k(OH + CF_3CF=CHF)$	$k_{avg}(OH + CF_3CF=CHF)$
$CF_3CF=CHF(Z)$	C_2H_4	0.16 ± 0.01	7.9×10^{-12} [18]	$(1.24 \pm 0.08) \times 10^{-12}$	$(1.22 \pm 0.14) \times 10^{-12}$
$CF_3CF=CHF(Z)$	C_2H_2	1.54 ± 0.15	7.8×10^{-13} [18]	$(1.20 \pm 0.12) \times 10^{-12}$	
$CF_3CF=CHF(E)$	C_2H_4	0.27 ± 0.03	7.9×10^{-12} [18]	$(2.16 \pm 0.22) \times 10^{-12}$	$(2.15 \pm 0.23) \times 10^{-12}$
$CF_3CF=CHF(E)$	C_2H_2	2.74 ± 0.27	7.8×10^{-13} [18]	$(2.14 \pm 0.21) \times 10^{-12}$	

[a] Rate constant units are cm^3 molecule^{-1} s^{-1}.

TABLE 3: Rate Constants (cm^3 molecule^{-1} s^{-1}) for Reactions of Cl, OH, and O_3 with $CF_3CF=CHF$, Analogous Fluorinated Propenes, and 2-Butene Measured at 296 ± 2 K[a]

compound	k_{Cl}	k_{OH}	k_{O_3}
$CH_3CH=CH_2$	2.44×10^{-10} [19]	2.6×10^{-11} [19]	1.0×10^{-17} [19]
$CF_3CH=CH_2$	9.07×10^{-11} [20]	1.45×10^{-12} [7,20]	3.5×10^{-19} [20]
$CF_3CF=CH_2$	6.9×10^{-11} [21]	1.06×10^{-12} [21]	2.8×10^{-20} [21]
$CF_3CH=CHF$	4.64×10^{-11} [5]	9.25×10^{-13} [5]	2.81×10^{-21} [5]
$CF_3CF=CHF(Z)$	4.36×10^{-11}	1.22×10^{-12}	1.45×10^{-21}
$CF_3CF=CHF(E)$	5.00×10^{-11}	2.15×10^{-12}	1.98×10^{-20}
$CF_3CF=CF_2$	2.7×10^{-11} [22]	2.4×10^{-12} [7,22–24]	6.2×10^{-22} [25]
$CH_3CH=CHCH_3$(Z) (cis)	3.7×10^{-10} [26,27]	5.5×10^{-11} [28–31]	1.4×10^{-16} [32–35]
$CH_3CH=CHCH_3$(E) (trans)	3.4×10^{-10} [26,27]	6.5×10^{-11} [28–31]	2.3×10^{-16} [32–35]

[a] Where multiple determinations exist, the value given is the average of the determinations.

For the Z isomer, reaction mixtures consisted of 6−8.2 mTorr $CF_3CF=CHF(Z)$, 100−200 mTorr CH_3ONO, and either 3.8−7.8 mTorr C_2H_4 or 1.8−3.5 mTorr C_2H_2 in 700 Torr total pressure air diluent. For the E isomer, reaction mixtures consisted of 7.3−9.7 mTorr $CF_3CF=CHF(E)$, 100−105 mTorr CH_3ONO, and either 2.94−5.15 mTorr C_2H_4 or 2.1−3.8 mTorr C_2H_2 in 700 Torr total pressure air diluent. Figure 2 shows the loss of $CF_3CF=CHF$ plotted versus loss of the reference compounds. Linear least-squares analysis of the data in Figure 2 gives the results shown in Table 2. For each isomer, the values of k_8 obtained using the two different references are indistinguishable within the experimental uncertainties. The final value is the average of the individual determinations together with error limits which encompass the extremes of the individual determinations: $k(OH + CF_3CF=CHF(Z)) = (1.22 \pm 0.14) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k(OH + CF_3CF=CHF(E)) = (2.15 \pm 0.23) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Kinetic data for the reactions of hydroxyl radicals with propene and fluorinated propenes are presented in Table 3. The reaction of hydroxyl radicals with propene proceeds mainly via electrophilic addition to the $>C=C<$ double bond. The presence of electron-withdrawing substituents such as fluorine would be expected to lower the reactivity of the molecule toward OH. Inspection of Table 3 reveals that the reactivity of propene is greater than that of the fluorinated propenes and there is a trend toward lower reactivity with increasing fluorine substitution; however, the most highly fluorinated compounds of the series are significantly more reactive than the less fluorinated propenes. It has been suggested[5] that hydrogen bonding between OH and fluorine leads to the observed enhancement of the reactivity of OH radicals with highly fluorinated propenes. Computational work would be of interest to confirm or refute this suggestion. Also presented in Table 3 are kinetic data for the reaction of OH radicals with the Z and E isomers of 2-butene. For 2-butene, the reactivity of the E isomer is 18% greater than that of the Z isomer. For $CF_3CF=CHF$, the reactivity of the E isomer is 80% greater than that of the Z isomer. The presence of fluorine substituents appears to exaggerate the difference in the reactivity of the two isomers toward OH radicals.

Kinetics of the $O_3 + CF_3CF=CHF$ Reaction. The kinetics of reaction 11 were studied by observing the decay of $CF_3CF=CHF(Z)$ when exposed to ozone in the reaction chamber.

$$CF_3CF=CHF(Z) + O_3 \rightarrow \text{products} \qquad (11)$$

Reaction mixtures consisted of 15.0−18.5 mTorr $CF_3CF=CHF(Z)$, 14−25 mTorr cyclohexane, and 463−1759 mTorr O_3 in 700 Torr air diluent. Cyclohexane was added to avoid potential problems associated with the loss of $CF_3CF=CHF(Z)$ via reaction with any OH radicals formed in reaction 11. Variation of the [cyclohexane]/[$CF_3CF=CHF(Z)$] ratio had no discernible effect on the observed decay of $CF_3CF=CHF(Z)$, suggesting that loss via reaction with OH radicals is not a significant complication. The loss of $CF_3CF=CHF(Z)$ followed pseudo first-order kinetics in all experiments (see insert in Figure 3). Figure 3 shows a plot of the pseudo first-order loss of $CF_3CF=CHF(Z)$ versus O_3 concentration. The line through the data gives $k_{11} = (1.45 \pm 0.15) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}.

The kinetics of reaction 12 were studied by observing the decay of $CF_3CF=CHF(E)$ when exposed to ozone in the reaction chamber.

$$CF_3CF=CHF(E) + O_3 \rightarrow \text{products} \qquad (12)$$

Reaction mixtures consisted of 14.7−18.6 mTorr $CF_3CF=CHF(E)$, 15−27 mTorr cyclohexane, and 436−2049 mTorr O_3 in 700 Torr air diluent. Variation of the [cyclohexane]/[$CF_3CF=CHF(E)$] ratio had no discernible effect on the observed decay of $CF_3CF=CHF(E)$, suggesting that loss via reaction with OH radicals is not a significant complication. The loss of $CF_3CF=CHF(E)$ followed pseudo first-order kinetics in all experiments (see insert in Figure 4). Figure 4 shows a plot of the

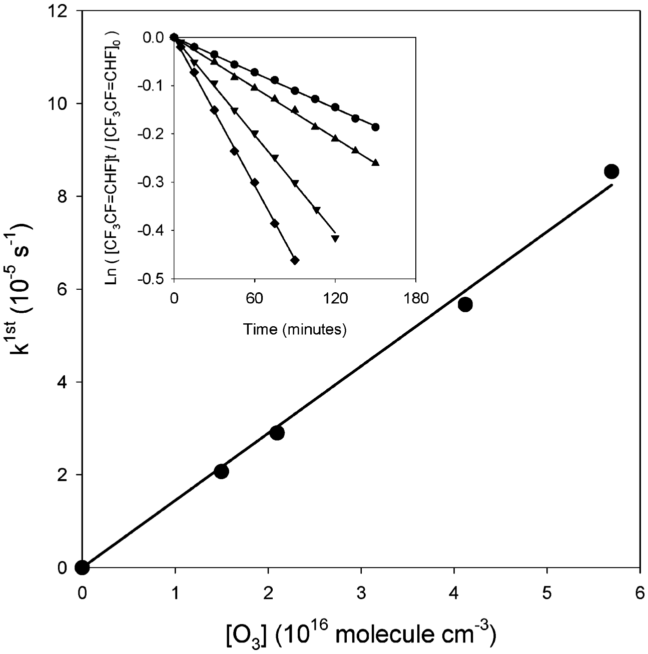

Figure 3. Pseudo first-order loss of $CF_3CF{=}CHF(Z)$ versus O_3 concentration. The insert shows typical decay plots for $CF_3CF{=}CHF$-(Z) when exposed to 465 mTorr (circle), 648 mTorr (triangle up), 1273 mTorr (triangles down) or 1759 mTorr (diamonds) O_3.

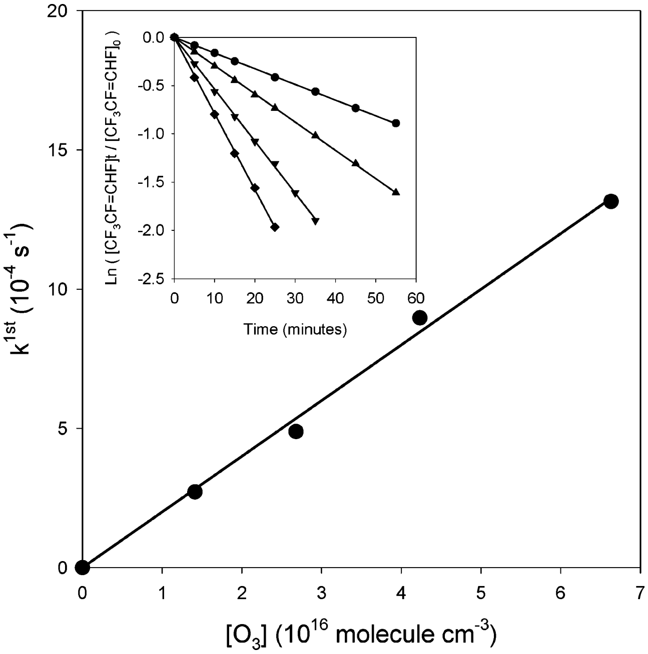

Figure 4. Pseudo first-order loss of $CF_3CF{=}CHF(E)$ versus O_3 concentration. The insert shows typical decay plots for $CF_3CF{=}CHF$-(E) when exposed to 436 mTorr (circle), 828 mTorr (triangle up), 1308 mTorr (triangles down) or 2047 mTorr (diamond) O_3.

pseudo first-order loss of $CF_3CF{=}CHF(E)$ versus O_3 concentration. The line through the data gives $k_{12} = (1.98 \pm 0.15) \times 10^{-20}$ cm^3 molecule^{-1} s^{-1}.

This result is compared with the reported reactivity of ozone toward propene and other fluoropropenes in Table 3. As seen from Table 3, the results from the present work are consistent with the existing database showing a successive decrease in reactivity on increasing fluorination. In their reactions with O_3, $CF_3CF{=}CHF(Z)$ and $CF_3CF{=}CHF(E)$ are less reactive than their non-fluorinated counterpart by factors of 6900 and 505, respectively. Reaction occurs by electrophilic addition of O_3 across the $>C{=}C<$ double bond. When compared with Cl atoms and OH radicals, O_3 has the lowest reactivity and is therefore most sensitive to the presence of the electron-withdrawing fluorine substituents. Also presented in Table 3 are kinetic data for the reaction of ozone with the Z and E isomers of 2-butene. For 2-butene, the E isomer is 1.6 times more reactive toward ozone than the Z isomer. For $CF_3CF{=}CHF$, the E isomer is 13.6 times more reactive toward ozone than the Z isomer. The presence of fluorine substituents appears to exaggerate the difference in the reactivity of the two isomers toward ozone.

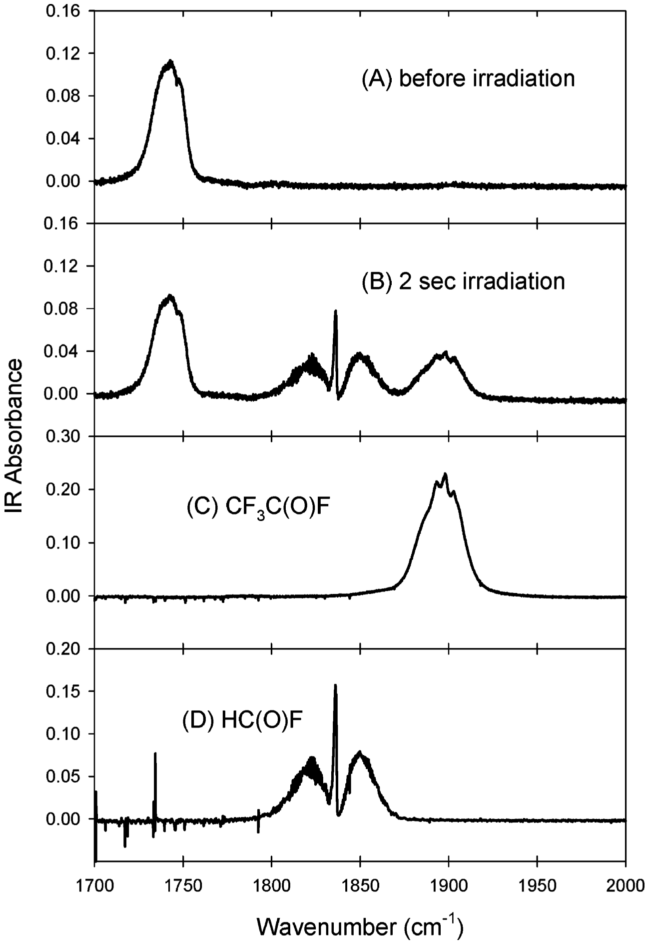

Figure 5. Infrared spectra acquired (A) before and (B) after a 2 s irradiation of a mixture of 6.8 mTorr $CF_3CF{=}CHF(Z)$ and 9.9 mTorr Cl_2 in 700 Torr air. Panels (C) and (D) are reference spectra of CF_3C-(O)F and HC(O)F.

Products and Mechanism of Cl-Atom-Initiated Oxidation of $CF_3CF{=}CHF$ in the Absence and Presence of NO. The mechanism of Cl-atom-initiated oxidation of $CF_3CF{=}CHF$ was investigated by irradiating mixtures consisting of 6.8−10.1 mTorr $CF_3CF{=}CHF(Z)$, 7.3−9.1 mTorr $CF_3CF{=}CHF(E)$, 99−101 mTorr Cl_2, and 0−38.1 mTorr NO in 10−700 Torr oxygen. Nitrogen was added as needed to provide 700 Torr total pressure. Figure 5, panels A and B, show spectra acquired before and after a 2 s irradiation of a mixture of 6.8 mTorr $CF_3CF{=}CHF$-(Z) and 9.9 mTorr Cl_2 in 700 Torr air. The consumption of $CF_3CF{=}CHF(Z)$ in this experiment was 17%. Comparison of the IR features in panel B with reference spectra of $CF_3C(O)F$ and HC(O)F in panels C and D shows the formation of these compounds. $CF_3C(O)F$ and HC(O)F were the only products observed from the Cl-initiated oxidation of either isomer. Figure 6 shows the formation of $CF_3C(O)F$ and HC(O)F versus the loss of $CF_3CF{=}CHF$ for experiments in 10 Torr O_2, 140 Torr

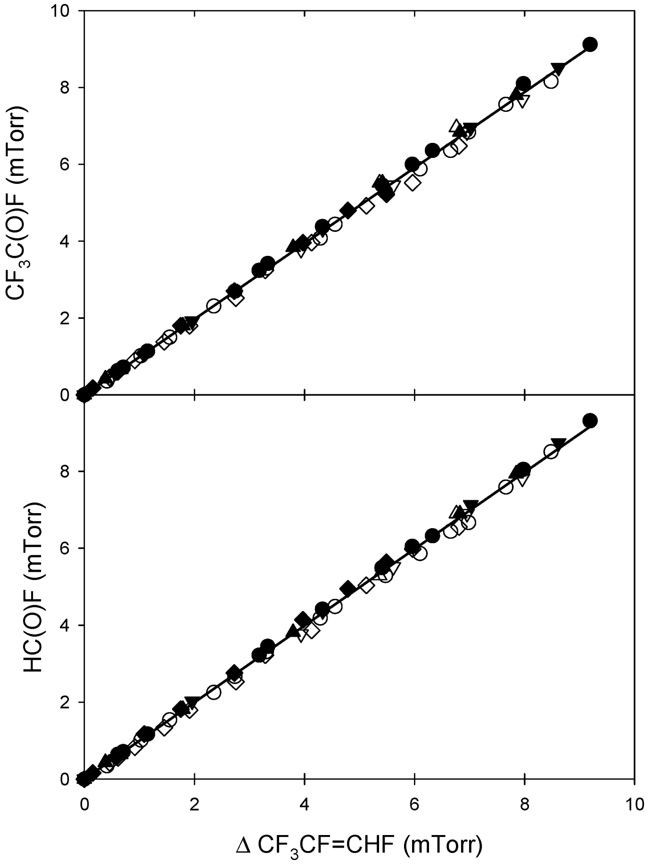

Figure 6. Formation of $CF_3C(O)F$ and HC(O)F vs loss of $CF_3CF{=}CHF$ following UV irradiation of $CF_3CF{=}CHF/Cl_2$ mixtures in 140 Torr O_2 (circles), 10 Torr O_2 (triangles up), 700 Torr O_2 (triangles down), and 140 Torr O_2 with NO (diamonds). Closed symbols are for the Z isomer of $CF_3CF{=}CHF$, and open symbols are for the E isomer of $CF_3CF{=}CHF$.

O_2 in the absence of NO, 140 Torr O_2 in the presence of NO, and 700 Torr O_2 for both isomers. As seen from Figure 6, there were no discernible differences in the yields of $CF_3C(O)F$ and HC(O)F in experiments performed with and without added NO. Linear least-squares analysis of the composite data sets gives molar yields of 98 ± 4% $CF_3C(O)F$ and 100 ± 5% HC(O)F. Quoted uncertainties are two standard deviations from the regression analyses.

The reaction of Cl atoms with both isomers of $CF_3CF{=}CHF$ proceeds via addition to give two different substituted alkyl radicals:

$$CF_3CF{=}CHF + Cl \rightarrow CF_3CFClC{\cdot}HF \tag{13a}$$

$$CF_3CF{=}CHF + Cl \rightarrow CF_3C{\cdot}FCHFCl \tag{13b}$$

which, in the presence of O_2, are expected to react to give the corresponding peroxy radicals:

$$CF_3CFClC{\cdot}HF + O_2 \rightarrow CF_3CFClCOO{\cdot}HF \tag{14}$$

$$CF_3C{\cdot}FCHFCl + O_2 \rightarrow CF_3COO{\cdot}FCHFCl \tag{15}$$

No information is available concerning the branching ratio k_{13a}/k_{13b}, and we will assume that both radicals are formed. Peroxy radicals react rapidly with NO,[6] and for those experiments where NO was present the sole fate of the peroxy radicals will be reaction with NO. Such reactions proceed via two channels, giving alkoxy radicals as major products and alkyl nitrates as minor products; however, in the present experiments there was no evidence of nitrate formation, which is consistent with previous work that showed low nitrate yields from the reaction of halogenated alkyl peroxy radicals with NO.[6] Whether by peroxy radical self-reactions, cross-reactions, or by peroxy radical and NO reactions, two alkoxy radicals are produced: $CF_3CFClCO{\cdot}HF$ and $CF_3CO{\cdot}FCHFCl$. From the fact that the observed $CF_3C(O)F$ and HC(O)F and products account for 100% of the loss of CF3CF═CHF and the absence of other products, we conclude that the fate of $CF_3CFClCO{\cdot}HF$ and $CF_3CO{\cdot}FCHFCl$ radicals is decomposition via C−C bond scission:

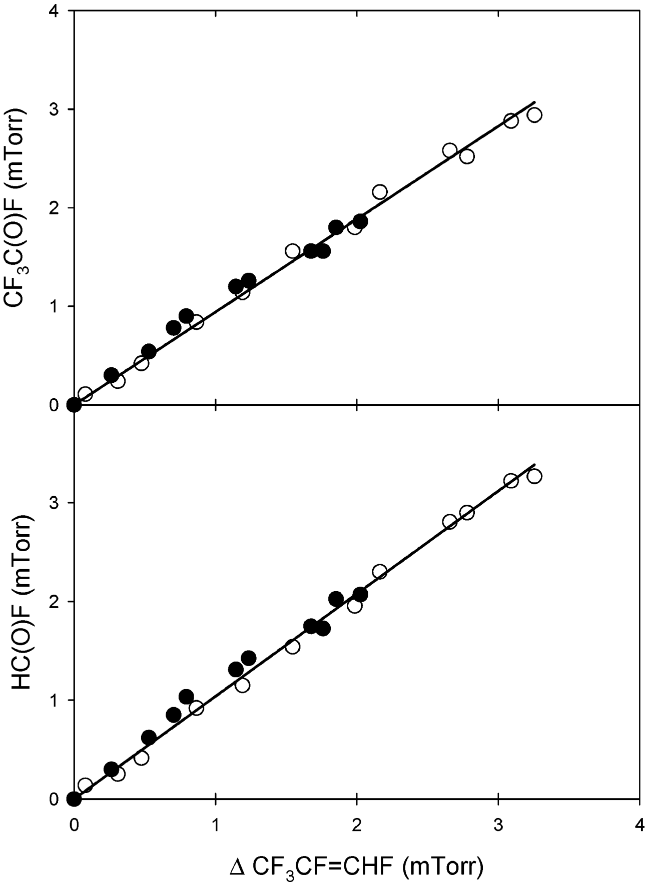

Figure 7. Formation of $CF_3C(O)F$ and HC(O)F vs loss of $CF_3CF{=}CHF$ following UV irradiation of $CF_3CF{=}CHF/CH_3ONO$ mixtures in 140 Torr O_2. Closed symbols are for the Z isomer of $CF_3CF{=}CHF$, and open symbols are for the E isomer of $CF_3CF{=}CHF$.

$$CF_3CFClCO{\cdot}HF \rightarrow CF_3C{\cdot}FCl + HC(O)F \tag{16}$$

$$CF_3CO{\cdot}FCHFCl \rightarrow CF_3C(O)F + C{\cdot}HFCl \tag{17}$$

The atmospheric fate of $CF_3C{\cdot}FCl$ and $C{\cdot}HFCl$ radicals is addition of O_2 to give a peroxy radical, reaction with RO_2 or NO to give an alkoxy radical, and elimination of a Cl atom to give either $CF_3C(O)F$ or HC(O)F.

Products and Mechanism of OH-Radical-Initiated Oxidation of $CF_3CF{=}CHF$. The mechanism of OH-radical-initiated oxidation of $CF_3CF{=}CHF$ was investigated by irradiating mixtures consisting of 7.6−8.8 mTorr of $CF_3CF{=}CHF(Z)$, 6.2−7.9 mTorr $CF_3CF{=}CHF(E)$, and 99−105 mTorr CH_3ONO in 140 Torr oxygen. Figure 8 shows the formation of $CF_3C(O)F$ and HC(O)F versus the loss of $CF_3CF{=}CHF$ for experiments in 140 Torr O_2 for both isomers. Linear least-squares analysis of the composite data sets gives molar yields of 94 ± 8% $CF_3C(O)F$ and 104 ± 9% HC(O)F. Quoted uncertainties are two standard deviations from the regression analyses.

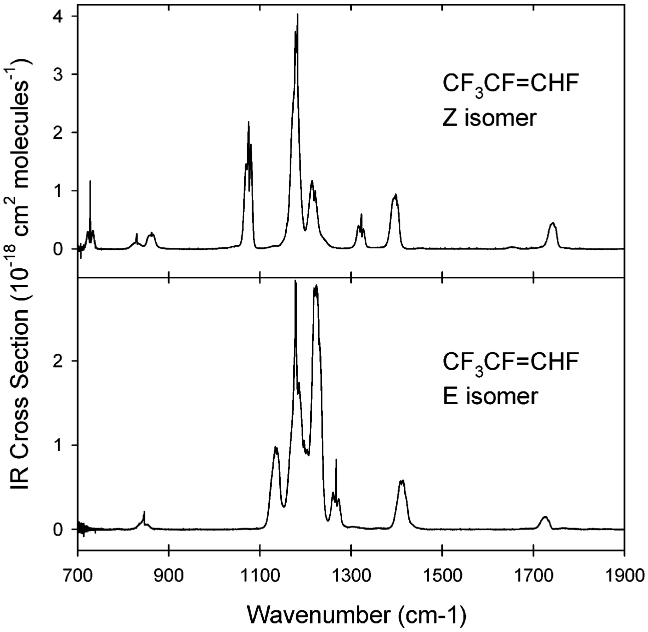

Figure 8. IR spectrum of the Z and E isomers of CF$_3$CF=CHF.

The reaction of OH radicals with both isomers of CF$_3$CF=CHF proceeds via addition to give two different substituted alkyl radicals:

$$\mathrm{CF_3CF{=}CHF + OH \rightarrow CF_3CFOHC{\cdot}HF} \qquad (18a)$$

$$\mathrm{CF_3CF{=}CHF + OH \rightarrow CF_3C{\cdot}FCHFOH} \qquad (18b)$$

which, in the presence of O$_2$, are expected to react to give the corresponding peroxy radicals.

$$\mathrm{CF_3CFOHC{\cdot}HF + O_2 \rightarrow CF_3CFOHCOO{\cdot}HF} \qquad (19)$$

$$\mathrm{CF_3C{\cdot}FCHFOH + O_2 \rightarrow CF_3COO{\cdot}FCHFOH} \qquad (20)$$

There is no available information concerning the branching ratio k_{18a}/k_{18b}, and we will assume that both radicals are formed. Since peroxy radicals react rapidly with NO[6] and in the present experiments there was no evidence of nitrate formation, two alkoxy radicals are produced CF$_3$CFOHCO·HF and CF$_3$CO·FCHFOH. From the fact that the observed CF$_3$C(O)F and HC(O)F and products account for 100% of the loss of CF$_3$CF=CHF and the absence of other products, we conclude that the fate of CF$_3$CFOHCO·HF and CF$_3$CO·FCHFOH radicals is decomposition via C−C bond scission:

$$\mathrm{CF_3CFOHCO{\cdot}HF \rightarrow CF_3C{\cdot}FOH + HC(O)F} \qquad (21)$$

$$\mathrm{CF_3CO{\cdot}FCHFOH \rightarrow CF_3C(O)F + C{\cdot}HFOH} \qquad (22)$$

The atmospheric fate of CF$_3$C·FOH and C·HFOH radicals is reaction with O$_2$ to give HO$_2$ and either CF$_3$C(O)F or HC(O)F:

$$\mathrm{CF_3C{\cdot}FOH + O_2 \rightarrow CF_3C(O)F + HO_2} \qquad (23)$$

$$\mathrm{C{\cdot}HFOH + O_2 \rightarrow HC(O)F + HO_2} \qquad (24)$$

Atmospheric Lifetime, Global Warming Potential, and Environmental Impacts. CF$_3$CF=CHF will not undergo photolysis[7] and is not expected to be removed effectively by either wet or dry deposition. Cl atoms are not present in the atmosphere in sufficient quantity to impact the lifetime of CF$_3$CF=CHF. Reaction with OH and O$_3$ are the expected loss mechanisms for CF$_3$CF=CHF.

The values of k(OH + CF$_3$CF=CHF) and k(O$_3$ + CF$_3$CF=CHF) measured in the present work can be used to provide an estimate of the atmospheric lifetime of CF$_3$CF=CHF. Scaling k(OH + CF$_3$CF=CHF(Z)) and k(OH + CF$_3$CF=CHF(E)) to k(OH + CH$_3$CCl$_3$) = 1.0×10^{-14} cm^3 molecule^{-1} s^{-1}[8] and assuming a lifetime of 6.1 years for CH$_3$CCl$_3$[9] provides an estimate for the lifetime of CF$_3$CF=CHF(Z) and CF$_3$CF=CHF(E) with respect to reaction with OH radicals in the atmosphere of approximately 18 days and 10 days, respectively. Ideally, such scaling would be conducted using OH rate constants at 272 K; however, such data are not available for CF$_3$CF=CHF. OH radicals react with CH$_3$CCl$_3$ and CF$_3$CF=CHF via different mechanisms. Reaction with CH$_3$CCl$_3$ proceeds via hydrogen atom abstraction and has a rate which decreases by approximately 40% as the temperature is decreased from 298 to 272 K.[8] In contrast, the reaction of OH radicals with CF$_3$CF=CHF proceeds via an addition mechanism, and the rate of this reaction is not expected to decrease with temperature. Therefore, the lifetimes with respect to OH radicals calculated above are probably somewhat over-estimated, but this does not make a material impact on the following conclusions. Our value of k(O$_3$ + CF$_3$CF=CHF(Z)) and k(O$_3$ + CF$_3$CF=CHF(E)) can be combined with the global background O$_3$ concentration of approximately 35 ppb[10] to provide an estimated lifetime with respect to reaction with ozone of 25 years and 1.9 years for CF$_3$CF=CHF(Z) and CF$_3$CF=CHF(E), respectively. We conclude that the atmospheric lifetime of CF$_3$CF=CHF is determined by its reaction with OH and will proceed with lifetimes of approximately 18 days and 10 days for CF$_3$CF=CHF(Z) and CF$_3$CF=CHF(E), respectively. Finally, the approximate nature of this lifetime estimate is emphasized; the average daily concentration of OH radicals varies significantly with both location and season.[11] The quoted lifetime is a global average; local lifetimes could be significantly shorter or longer.

The IR spectra of the Z and E isomers of CF$_3$CF=CHF measured in the present work are shown in Figure 8. CF$_3$CF=CHF(Z) has IR features at 728, 830, 862, 1075, 1182, 1214, 1323, 1398, and 1742 cm^{-1}. CF$_3$CF=CHF(E) has IR features at 846, 1136, 1178, 1223, 1267, 1412, and 1726. The integrated IR absorption cross sections of CF$_3$CF=CHF(Z) (700−1800 cm^{-1}) and CF$_3$CF=CHF(E) (800−1800 cm^{-1}) are indistinguishable: $(1.86 \pm 0.18) \times 10^{-16}$ cm molecule^{-1}. There are no literature IR data for CF$_3$CF=CHF to compare with our result. Using the method outlined by Pinnock et al.,[12] the IR spectra of CF$_3$CF=CHF(Z) and CF$_3$CF=CHF(E) shown in Figure 8 and the IR spectrum of CFC-11[13] we calculate instantaneous forcings for CF$_3$CF=CHF(Z), CF$_3$CF=CHF(E), and CFC-11 of 0.25, 0.24, and 0.26 W m^{-2} ppb^{-1}, respectively. Values of the halocarbon global warming potential, HGWP,[14] for CF$_3$CF=CHF (relative to CFC-11) can then be estimated using the following expression:

$$\mathrm{HGWP}_{\mathrm{CF_3CF{=}CHF}} = \left(\frac{\mathrm{IF}_{\mathrm{CF_3CF{=}CHF}}}{\mathrm{IF}_{\mathrm{CFC-11}}}\right)\left(\frac{\tau_{\mathrm{CF_3CF{=}CHF}}\mathrm{M}_{\mathrm{CFC-11}}}{\tau_{\mathrm{CFC-11}}\mathrm{M}_{\mathrm{CF_3CF{=}CHF}}}\right) \times \left(\frac{1-\exp(-t/\tau_{\mathrm{CF_3CF{=}CHF}})}{1-\exp(-t/\tau_{\mathrm{CFC-11}})}\right) \qquad \text{(II)}$$

where $\mathrm{IF}_{\mathrm{CF_3CF{=}CHF}}$, $\mathrm{IF}_{\mathrm{CFC-11}}$, $\mathrm{M}_{\mathrm{CF_3CF{=}CHF}}$, $\mathrm{M}_{\mathrm{CFC-11}}$, $\tau_{\mathrm{CF_3CF{=}CHF}}$, and $\tau_{\mathrm{CFC-11}}$ are the instantaneous forcings, molecular weights, and atmospheric lifetimes of CF$_3$CF=CHF and CFC-11, and t is the time horizon over which the forcing is integrated. Using

$\tau(CF_3CF{=}CHF(Z)) = 18$ days and $\tau_{CFC-11} = 45$ years,[15] we estimate that the HGWP of $CF_3CF{=}CHF(Z)$ relative to CFC-11 is 3.1×10^{-3} for a 20 year horizon and 1.2×10^{-3} for a 100 year time horizon, respectively. Using $\tau(CF_3CF{=}CHF(E)) = 10$ days and $\tau_{CFC-11} = 45$ years,[15] we estimate that the HGWP of $CF_3CF{=}CHF(E)$ relative to CFC-11 is 1.7×10^{-3} for a 20 year horizon and 6.8×10^{-4} for a 100 year time horizon, respectively. Relative to CO_2, the GWP of CFC-11 on 20 and 100 year time horizons are 6730 and 4750.[15] Therefore, relative to CO_2, the GWP of $CF_3CF{=}CHF(Z)$ is approximately 21 for a 20 year horizon and 6 for a 100 year time horizon. Relative to CO_2, the GWP of $CF_3CF{=}CHF(E)$ is approximately 11 for a 20 year horizon and 3 for a 100 year time horizon. $CF_3CF{=}CHF$ has a negligible global warming potential and will not make any significant contribution to radiative forcing of climate change.

The atmospheric oxidation of $CF_3CF{=}CHF$ gives $CF_3C(O)F$ and $HC(O)F$ in molar yields indistinguishable from 100%. $CF_3C(O)F$ and $HC(O)F$ will be removed from the atmosphere by hydrolysis giving $CF_3C(O)OH$ and $CO_2 + HF$.[16] $CF_3C(O)OH$ is a natural trace component of the oceanic environment,[17] and any additional burden from $CF_3CF{=}CHF$ oxidation will be negligible. Similarly, the additional burden of CO_2 and HF from $CF_3CF{=}CHF$ oxidation will not be environmentally significant.

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