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# Atmospheric Chemistry of $CF_3CH{=}CH_2$ and $C_4F_9CH{=}CH_2$: Products of the Gas-Phase Reactions with Cl Atoms and OH Radicals

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FTIR−smog chamber techniques were used to study the products of the Cl atom and OH radical initiated oxidation of $CF_3CH{=}CH_2$ in 700 Torr of $N_2/O_2$, diluent at 296 K. The Cl atom initiated oxidation of $CF_3CH{=}CH_2$ in 700 Torr of air in the absence of $NO_x$ gives $CF_3C(O)CH_2Cl$ and $CF_3CHO$ in yields of 70 ± 5% and 6.2 ± 0.5%, respectively. Reaction with Cl atoms proceeds via addition to the $>C{=}C<$ double bond (74 ± 4% to the terminal and 26 ± 4% to the central carbon atom) and leads to the formation of $CF_3CH(O)CH_2Cl$ and $CF_3CHClCH_2O$ radicals. Reaction with $O_2$ and decomposition via C−C bond scission are competing loss mechanisms for $CF_3CH(O)CH_2Cl$ radicals, $k_{O_2}/k_{diss} = (3.8 \pm 1.8) \times 10^{-18}$ cm$^3$ molecule$^{-1}$. The atmospheric fate of $CF_3CHClCH_2O$ radicals is reaction with $O_2$ to give $CF_3CHClCHO$. The OH radical initiated oxidation of $C_xF_{2x+1}CH{=}CH_2$ ($x$ = 1 and 4) in 700 Torr of air in the presence of $NO_x$ gives $C_xF_{2x+1}CHO$ in a yield of 88 ± 9%. Reaction with OH radicals proceeds via addition to the $>C{=}C<$ double bond leading to the formation of $C_xF_{2x+1}C(O)HCH_2OH$ and $C_xF_{2x+1}CHOHCH_2O$ radicals. Decomposition via C−C bond scission is the sole fate of $C_xF_{2x+1}CH(O)CH_2OH$ and $C_xF_{2x+1}CH(OH)CH_2O$ radicals. As part of this work a rate constant of $k(Cl+CF_3C(O)CH_2Cl) = (5.63 \pm 0.66) \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was determined. The results are discussed with respect to previous literature data and the possibility that the atmospheric oxidation of $C_xF_{2x+1}CH{=}CH_2$ contributes to the observed burden of perfluorocarboxylic acids, $C_xF_{2x+1}COOH$, in remote locations.

## 1. Introduction

Perfluorinated carboxylic acids (PFCAs, $C_xF_{2x+1}COOH$, where $x = 6-12$) have been observed in fish[1,2] and mammals[3] around the world. The sources, fate, and transport of PFCAs have been reviewed recently.[4] Although there are no known natural sources of long-chain PFCAs, these compounds have been directly emitted to the environment primarily via industrial processes. Such processes include use of PFCAs and their salts as processing aids in the polymerization of fluoropolymers, their largest use, and historically as an ingredient in fire-fighting foams.[1,4,5,6]

The observation of PFCAs in remote regions far from industrial sources and large population centers is puzzling since PFCAs are not expected to be particularly mobile in the atmosphere.[7] Among the direct emission pathways that might partially account for observed PFCA loadings in the Arctic are the potential transport of PFCAs by ocean surface waters,[4] marine aerosols,[8] and the local use of PFCA containing materials (e.g., the historic use of fire-fighting foams in military installations in the Arctic).[9,10] In addition, a portion of the observed PFCAs may originate from precursor substances which are transformed by environmental oxidation processes. Potential PFCA precursors include perfluoroalkyl sulfonamides and sulfonamido alcohols,[11,12] fluorotelomer alcohol, and fluorotelomer olefins.[4,13,14]

Fluorotelomer acrylate monomer is a principal raw material used to make fluorotelomer-based polymeric products.[15] When manufactured, the acrylate monomer contains fluorotelomer alcohols and/or fluorotelomer olefins as a residual raw material impurity at levels up to a few thousand parts per million by weight depending on the process of manufacture.[16] During industrial use, these residual alcohols and olefins are expected to be released to the air. Fluorotelomer alcohols, $C_xF_{2x+1}CH_2CH_2OH$ ($x$ = 6, 8, 10, and 12), have been observed in air samples and suggested as a potential source of PFCAs present in remote locations.[17] Fluorotelomer olefins, $C_xF_{2x+1}CH{=}CH_2$, have an atmospheric lifetime of approximately 8 days which is sufficient for their transport to remote locations.[18] Although fluorotelomer olefins have yet to be detected in the atmosphere and their flux into the atmosphere is unclear, the atmospheric oxidation of $C_xF_{2x+1}CH{=}CH_2$ may contribute to the PFCA burden in remote locations. To assess this possibility, we have conducted a study of the atmospheric chemistry of $CF_3CH{=}CH_2$ and $C_4F_9CH{=}CH_2$. The products of the Cl atom and OH radical initiated oxidation of $CF_3CH{=}CH_2$ and the products of the OH radical initiated oxidation of $C_4F_9CH{=}CH_2$ were determined.

## 2. Experimental Section

The experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer. The

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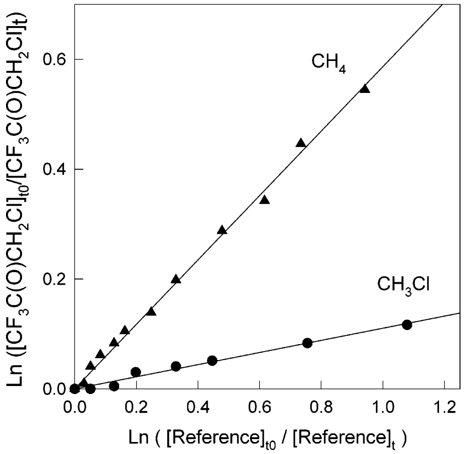

**Figure 1.** Loss of $CF_3C(O)CH_2Cl$ versus $CH_4$ and $CH_3Cl$ following exposure to Cl atoms in 700 Torr of $N_2$ at 296 K.

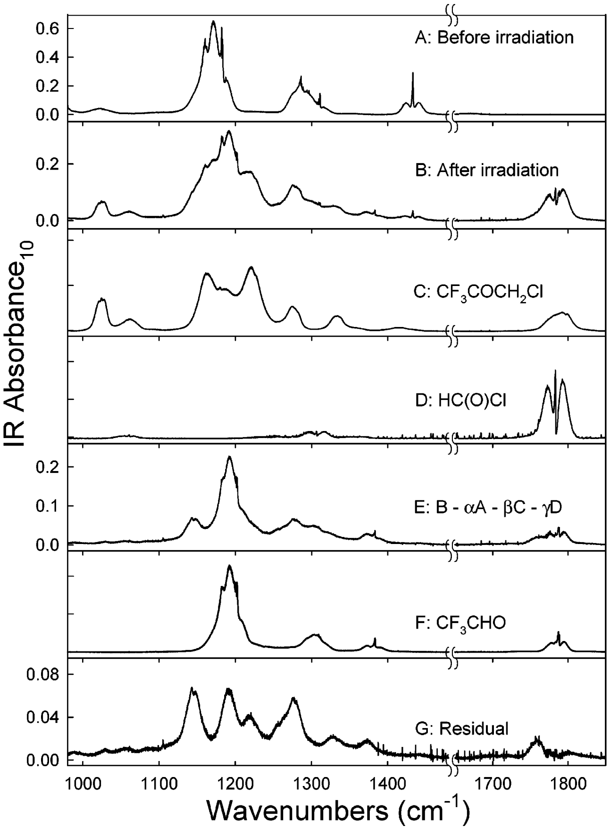

**Figure 2.** IR spectra of a mixture of 7.8 mTorr of $CF_3CH{=}CH_2$, 88.2 mTorr of $Cl_2$, and 10 Torr of $O_2$ in 700 Torr of $N_2$ before (A) and after (B) 40 s UV irradiation. Panels C, D, and F show reference spectra of $CF_3C(O)CH_2Cl$, HC(O)Cl, and $CF_3CHO$. Subtracting $CF_3CH{=}CH_2$, $CF_3C(O)CH_2Cl$, and HC(O)Cl features from panel B gives panel E. Panel G shows residual IR features (which we attribute to $CF_3CHClCHO$) present after subtraction of $CF_3CHO$ features from panel E.

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

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (1)$$

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

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \qquad (2)$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \qquad (3)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (4)$$

$CH_3ONO$ was synthesized by the dropwise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$ in methanol. Other reagents were obtained from commercial sources at purities >99%. Experiments were conducted in 700 Torr total pressure of $N_2$, or $N_2/O_2$, 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.

## 3 Results and Discussion

**3.1. Measurement of $k(Cl+CF_3C(O)CH_2Cl)$.** Prior to the study of the Cl atom initiated oxidation of $CF_3CH{=}CH_2$, experiments were performed to assess the reactivity of $CF_3C(O)CH_2Cl$ toward Cl atoms. Relative rate experiments were performed using mixtures of either (i) 7.35 mTorr $CH_3Cl$, 13.5 mTorr $CF_3C(O)CH_2Cl$, and 85.2 mTorr of $Cl_2$, or (ii) 7.35 mTorr $CH_4$, 14.4 mTorr $CF_3C(O)CH_2Cl$, and 88.3 mTorr of $Cl_2$ in 700 Torr of $N_2$ diluent. Figure 1 shows the loss of $CF_3C(O)CH_2Cl$ versus $CH_3Cl$ and $CH_4$ when such mixtures were irradiated using the UV fluorescent blacklamps. The lines through the data are linear least-squares fits which give $k_5/k_6 = 0.110 \pm 0.008$ and $k_5/k_7 = 0.586 \pm 0.043$

$$Cl + CF_3C(O)CH_2Cl \rightarrow \text{products} \qquad (5)$$

$$Cl + CH_3Cl \rightarrow \text{products} \qquad (6)$$

$$Cl + CH_4 \rightarrow \text{products} \qquad (7)$$

Using $k_6 = 4.9 \times 10^{-13}$ and $k_7 = 1.0 \times 10^{-13}$ [19] gives $k_5 = (5.39 \pm 0.39) \times 10^{-14}$ and $(5.86 \pm 0.43) \times 10^{-14}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, respectively. Indistinguishable values of $k_5$ were obtained using the two different references. We choose to cite a final value which is the average together with error limits which encompass the extremes of the individual determinations: $k_5 = (5.63 \pm 0.66) \times 10^{-14}$ $cm^3$ $molecule^{-1}$ $s^{-1}$.

**3.2. Cl Atom Initiated Oxidation of $CF_3CH{=}CH_2$ in the Absence of $NO_x$.** To investigate the products of the Cl atom initiated oxidation of $CF_3CH{=}CH_2$ in the absence of $NO_x$, mixtures consisting of 6.8−14.1 mTorr $CF_3CH{=}CH_2$, 85−88 mTorr $Cl_2$, and 10−700 Torr of $O_2$ in 700 Torr total pressure of $N_2$ diluent were introduced into the reaction chamber and subjected to UV irradiation. Figure 2 shows typical spectra acquired before (A) and after (B) a 40 s irradiation of a mixture containing 7.8 mTorr $CF_3CH{=}CH_2$, 88.2 mTorr $Cl_2$, and 10 Torr $O_2$ in total pressure of 700 Torr of $N_2$ diluent. The consumption of $CF_3CH{=}CH_2$ was 89.5%.

Comparison with reference spectra of $CF_3C(O)CH_2Cl$ and HC(O)Cl shown in panels C and D indicate the formation of these species. Subtraction of IR features attributable to $CF_3CH{=}CH_2$, $CF_3C(O)CH_2Cl$, and HC(O)Cl gives the spectrum shown in panel E. The formation of the $CF_3CHO$ is evident by

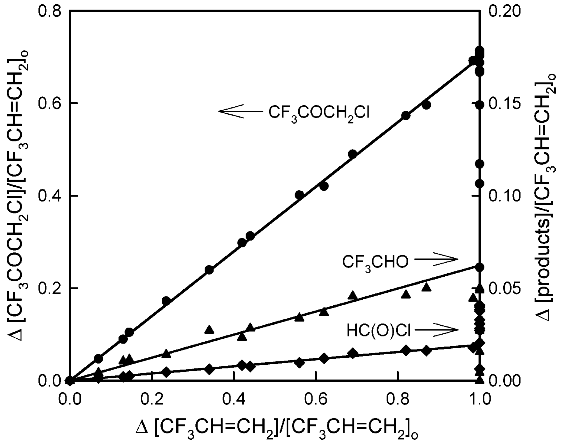

**Figure 3.** Yields of $CF_3C(O)CH_2Cl$ (circles), $CF_3CHO$ (triangles), and HC(O)Cl (diamonds) versus loss of $CF_3CH{=}CH_2$, normalized to the initial compounds, following the Cl atom initiated oxidation of $CF_3CH{=}CH_2$ in 700 Torr of air diluent.

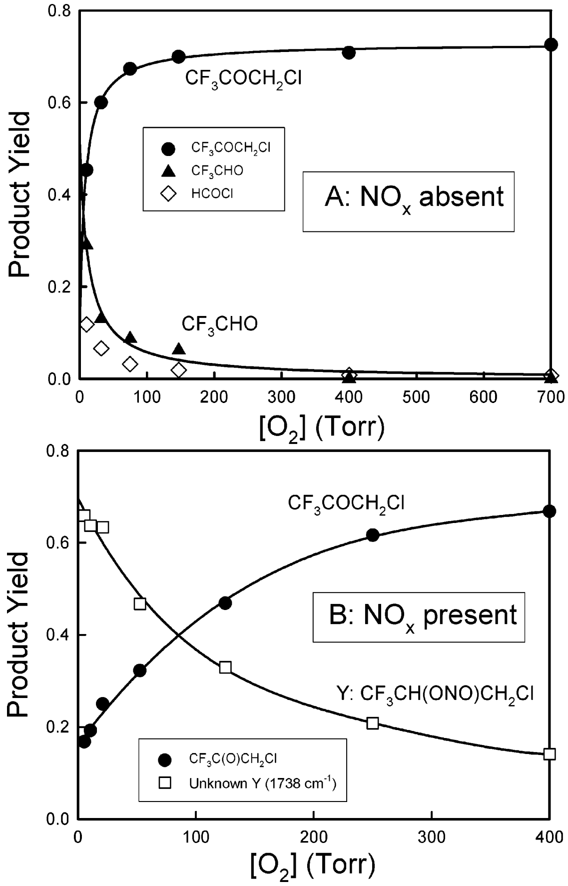

**Figure 4.** Molar yields of $CF_3C(O)CH_2Cl$ (circles), $CF_3CHO$ (triangles), HC(O)Cl (diamonds), and RONO (squares) versus the $O_2$ partial pressure for experiments conducted in 700 Torr total pressure at 296 K in the absence (A) or presence (B) of $NO_x$. The lines through the data in panel A are fits using the expressions described in the text. The lines through the data in panel B are third-order polynomial fits to aid visual inspection of the data trend.

comparison of the product features at 1383 and 1787 cm$^{-1}$ in panel E with those in the reference spectrum in panel F. Subtraction of IR features attributable to $CF_3CHO$ from spectrum E gives the residual spectrum shown in panel G. The IR features at 1145, 1191, 1276, and 1758 cm$^{-1}$ in panel G scale proportionately in all experiments (suggesting that they are attributable to one product) and increase linearly with $CF_3CH{=}CH_2$ loss. The feature at 1758 cm$^{-1}$ is consistent with that expected from the C=O stretch band in a carbonyl containing compound.

Figure 3 shows the formation of $CF_3C(O)CH_2Cl$ (circles), $CF_3CHO$ (triangles), and HC(O)Cl (diamonds) versus loss of $CF_3CH{=}CH_2$ following UV irradiation of gas mixtures containing $CF_3CH{=}CH_2$ and $Cl_2$ in 700 Torr of air diluent. Product formation and $CF_3CH{=}CH_2$ loss have been normalized to the initial $CF_3CH{=}CH_2$ concentration. Consistent with the fact that Cl atoms are $9.1 \times 10^{-11}/5.6 \times 10^{-14} = 1600$, $9.1 \times 10^{-11}/2.1 \times 10^{-12} = 43$ [20], and $9.1 \times 10^{-11}/7.8 \times 10^{-13} = 120$ [21] times less reactive toward $CF_3C(O)CH_2Cl$, $CF_3CHO$, and HC(O)Cl than toward $CF_3CH{=}CH_2$, there is no discernible evidence for loss of these products via secondary reactions until at least 90% of the $CF_3CH{=}CH_2$ had been consumed. The lines through the data in Figure 3 are least-squares fits for $CF_3CH{=}CH_2$ consumptions of less than 70% (i.e., $\Delta[CF_3CH{=}CH_2]_t/[CF_3CH{=}CH_2]_0 < 0.7$) and give molar yields of: $CF_3C(O)CH_2Cl$, 70 ± 5%; $CF_3CHO$, 6.2 ± 0.5%; and HC(O)Cl, 1.9 ± 0.2%, respectively.

Figure 4A shows a plot of the molar yields of $CF_3C(O)CH_2Cl$, $CF_3CHO$, and HC(O)Cl versus the $O_2$ partial pressure. The $CF_3C(O)CH_2Cl$ yield increases (at the expense of $CF_3CHO$) with increased $O_2$ partial pressure over the range 10−150 Torr, further increase in $[O_2]$ had no discernible effect on the product yields.

Figure 5 shows a mechanism for the Cl initiated oxidation of $CF_3CH{=}CH_2$ in the absence of $NO_x$ that explains the experimental results. The initial step is electrophilic addition of Cl to the double bond. Addition occurs at the terminal and central carbon atoms to give $CF_3CHCH_2Cl$ and $CF_3CHClCH_2$ radicals. Secondary radicals are generally more stable than primary radicals, and hence from a thermodynamic perspective, it is expected that addition will occur predominately at the terminal carbon atom. In the reactions below, M represents a third body species which removes the energy associated with C−Cl bond formation:

$$CF_3CH{=}CH_2 + Cl + M \rightarrow CF_3CHCH_2Cl + M \quad (8a)$$

$$\rightarrow CF_3CHClCH_2 + M \quad (8b)$$

Reactions 9−12 and 13−16 describe the fate of the radicals produced in reactions 8a and 8b, respectively:

$$CF_3CHCH_2Cl + O_2 \rightarrow CF_3C(OO)HCH_2Cl \quad (9)$$

$$CF_3C(OO)HCH_2Cl + RO_2 \rightarrow CF_3C(O)HCH_2Cl + RO + O_2 \quad (10)$$

$$CF_3C(O)HCH_2Cl + O_2 \rightarrow CF_3C(O)CH_2Cl + HO_2 \quad (11)$$

$$CF_3C(O)HCH_2Cl + M \rightarrow CF_3CHO + CH_2Cl + M \quad (12)$$

$$CF_3CHClCH_2 + O_2 \rightarrow CF_3CHClCH_2O_2 \quad (13)$$

$$CF_3CHClCH_2(OO) + RO_2 \rightarrow CF_3CHClCH_2O + RO + O_2 \quad (14)$$

$$CF_3CHClCH_2O + O_2 \rightarrow CF_3CHClCHO + HO_2 \quad (15)$$

$$CF_3CHClCH_2O + M \rightarrow CF_3CHCl + HCHO + M \quad (16)$$

Reaction with $O_2$ and decomposition via C−C bond scission are competing loss mechanisms for $CF_3C(O)HCH_2Cl$ radicals. Reaction with $O_2$ gives $CF_3C(O)CH_2Cl$. Decomposition produces $CH_2Cl$ radicals and $CF_3CHO$. $CH_2Cl$ radicals add $O_2$ to give $CH_2ClO_2$ radicals which undergo self- and cross-reactions

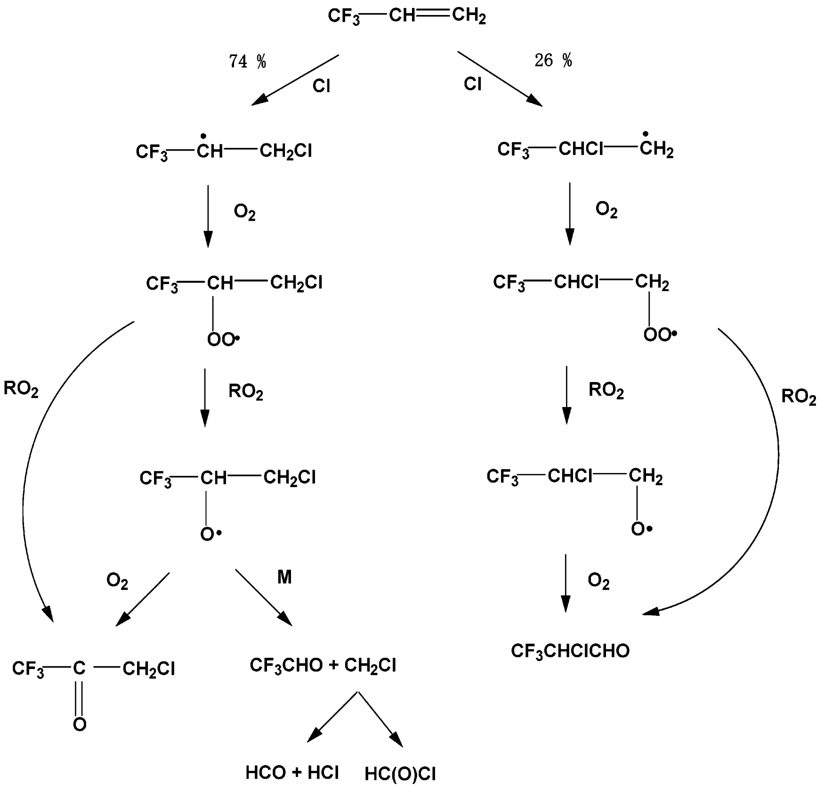

**Figure 5.** Mechanism for Cl atom initiated oxidation of $CF_3CH{=}CH_2$ in the absence of $NO_x$. The curved arrows represent channels of the self- and cross- reactions of $RO_2$ radicals giving carbonyl products directly.

with other peroxy radicals to give chloromethoxy radicals, $CH_2ClO$

$$CH_2Cl + O_2 \rightarrow CH_2ClO_2 \tag{17}$$

$$CH_2ClO_2 + RO_2 \rightarrow CH_2ClO + RO + O_2 \tag{18}$$

Reaction with $O_2$ to give HC(O)Cl and decomposition via intramolecular elimination of HCl are competing loss processes for $CH_2ClO$ radicals.[22]

$$CH_2ClO + O_2 \rightarrow HC(O)Cl + HO_2 \tag{19}$$

$$CH_2ClO + M \rightarrow HCO + HCl + M \tag{20}$$

The observed $O_2$ dependence of the molar yields of $CF_3C(O)CH_2Cl$ and $CF_3CHO$ contains information on the rate constant ratio $k_{11}/k_{12}$. From the mechanism described above, the molar yields of $CF_3C(O)CH_2Cl$ and $CF_3CHO$, $Y_{CF_3COCH_2Cl}$ and $Y_{CF_3CHO}$, can be related to the yield of $CF_3C(O)HCH_2Cl$ radicals, $Y_{RO}$, by the expressions $Y_{CF_3COCH_2Cl} = Y_{RO} \times (k_{11}/k_{12})[O_2]/((k_{11}/k_{12})[O_2]+1) + C$ and $Y_{CF_3CHO} = Y_{RO} \times 1/((k_{11}/k_{12})[O_2]+1)$ where $C$ accounts for the formation of $CF_3C(O)CH_2Cl$ via reaction of $CF_3CH(OO)CH_2Cl$ radicals with other peroxy radicals. The lines through the data in Figure 4A are fits of these expressions to the data. From the fit to the $CF_3C(O)CH_2Cl$ data, we obtain $Y_{RO} = 0.61 \pm 0.16$, $k_{11}/k_{12} = (3.8 \pm 1.8) \times 10^{-18}$ cm$^3$ molecule$^{-1}$, and $C = 0.12 \pm 0.12$, whereas from the $CF_3CHO$ data, we obtain $Y_{RO} = 0.51 \pm 0.20$ and $k_{11}/k_{12} = (2.4 \pm 1.8) \times 10^{-18}$ cm$^3$ molecule$^{-1}$. Within the admittedly large uncertainties, indistinguishable values of $k_{11}/k_{12}$ were obtained in the two independent analyses, we choose to quote a final value based upon the more precise $CF_3C(O)CH_2Cl$ data; $k_{11}/k_{12} = (3.8 \pm 1.8) \times 10^{-18}$ cm$^3$ molecule$^{-1}$.

The sum of the molar yields of $CF_3C(O)CH_2Cl$ and $CF_3CHO$ provide a measure of the fraction of the reaction of Cl atoms with $CF_3CH{=}CH_2$ which proceeds via addition to the terminal carbon atom. The average sum of the molar yields of $CF_3C(O)CH_2Cl$ and $CF_3CHO$ for $O_2$ partial pressures between 10 and 700 Torr was 74 ± 4%. We conclude that Cl addition occurs 74% to the terminal and 26% to the central carbon atom; $k_{8a}/(k_{8a} + k_{8b}) = 0.74 \pm 0.04$, $k_{8b}/(k_{8a} + k_{8b}) = 0.26 \pm 0.04$.

Addition of Cl atoms to the central carbon atom (channel 8b) leads to either $CF_3CHCl$ radicals or $CF_3CHClCHO$ (reactions 13−16). Under the present experimental conditions, $CF_3CHCl$ radicals will be converted into $CF_3C(O)Cl$[23]

$$CF_3CHCl + O_2 + M \rightarrow CF_3CClHO_2 + M \tag{21}$$

$$CF_3CClHO_2 + RO_2 \rightarrow CF_3CClHO + RO + O_2 \tag{22}$$

$$CF_3CClHO + O_2 \rightarrow CF_3C(O)Cl + HO_2 \tag{23}$$

The absence of $CF_3C(O)Cl$ as a primary product (yield <2%) in the present work shows that reaction with $O_2$ is the dominant fate of $CF_3CHClCH_2O$ radicals. Therefore, we conclude that $CF_3CHClCHO$ is the dominant product formed following Cl atom addition to the central carbon atom. The IR feature in panel G at 1758 cm$^{-1}$ can be assigned to the carbonyl stretching mode and the features at 1145, 1191, and 1276 cm$^{-1}$ can be assigned to complex vibrations involving C−F and C−C stretching modes. We attribute most, possibly all, of the IR features in panel G to the aldehyde $CF_3CHClCHO$. In contrast to the behavior of $CF_3C(O)CH_2Cl$, there was no discernible change in the yield of $CF_3CHClCHO$ as $[O_2]$ was varied over the range of 10−700 Torr.

$HO_2$ radicals are formed in reactions 11 and 15. The fate of $HO_2$ radicals is self-reaction and reaction with $CF_3C(OO)HCH_2Cl$ and $CF_3CHClCH_2(OO)$ radicals. Based upon the database for reactions of $HO_2$ with fluoro- and chloro-substituted alkyl peroxy radicals (e.g., $CH_2FO_2$[24] and $CH_2ClO_2$[25]), it is expected

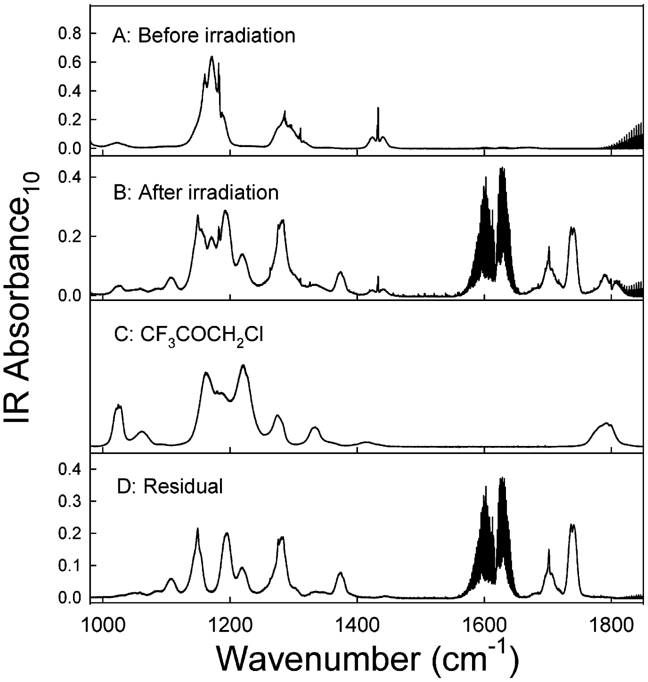

**Figure 6.** IR spectra of a mixture of 7.5 mTorr $CF_3CH{=}CH_2$, 15 mTorr NO, 93.0 mTorr $Cl_2$, and 10 Torr of $O_2$ in 700 Torr of $N_2$ before (A) and after (B) 45 s UV irradiation. Panel D shows the residual spectrum obtained by subtracting features of $CF_3CH{=}CH_2$, $CF_3C(O)CH_2Cl$, and ClNO from panel B.

that the reactions of $HO_2$ with $CF_3C(OO)HCH_2Cl$ and $CF_3CHClCH_2(OO)$ radicals will lead to the formation of the hydroperoxides $CF_3C(OOH)HCH_2Cl$ and $CF_3CHClCH_2OOH$ and the carbonyl compounds $CF_3C(O)HCH_2Cl$ and $CF_3CHClCHO$.

The present work is the first study of the Cl initiated oxidation of $CF_3CH{=}CH_2$. Vesine et al.[26] studied the Cl initiated oxidation of $C_4F_9CH{=}CH_2$ and $C_6F_{13}CH{=}CH_2$ in one atmosphere of air. In the absence of $NO_x$, Vésine et al. (2000) report the formation of $CF_2O$, CO, and a product with an absorption feature at 1788 cm$^{-1}$ which they ascribe to $C_xF_{2x+1}C(O)CH_2Cl$. The yields of these products were the same for experiments conducted in one atmosphere of air or $O_2$. Our finding that the ketone $CF_3C(O)CH_2Cl$ is the dominant product (~70%) for Cl initiated oxidation of $CF_3CH{=}CH_2$ in air is consistent with results of Vésine et al.[26] The lack of any observable dependence of the product yields on $[O_2]$ over the range 160−760 Torr by Vésine et al.[26] is consistent with the observations in the present work (see Figure 4).

**3.3. Cl Atom Initiated Oxidation of $CF_3CH{=}CH_2$ in the Presence of $NO_x$.** To investigate the products of the Cl atom initiated oxidation in the presence of $NO_x$, mixtures consisting of 6.8−8.2 mTorr $CF_3CH{=}CH_2$, 83.6−93.0 mTorr $Cl_2$, 14.4−17.8 mTorr NO, and 5.3−400 Torr $O_2$ in 700 Torr total pressure of $N_2$ diluent were introduced into the reaction chamber and subjected to UV irradiation. Figure 6 shows typical spectra acquired before (A) and after (B) a 45 s irradiation of a mixture containing 7.4 mTorr $CF_3CH{=}CH_2$, 93.0 mTorr $Cl_2$, 16.5 mTorr NO, and 10 Torr of $O_2$ in 700 Torr of $N_2$ diluent. The consumption of $CF_3CH{=}CH_2$ was 78%. $CF_3C(O)CH_2Cl$, ClNO, HONO, and $HNO_3$ were detected as products. Small amounts (yields 1−2%) of $CF_3CHO$ and HC(O)Cl were also detected. There was no detectable $CF_3C(O)Cl$ (<2% yield). Subtraction of features attributable to $CF_3CH{=}CH_2$, $CF_3C(O)CH_2Cl$, and ClNO, from panel B in Figure 6 gives the residual shown in panel D.

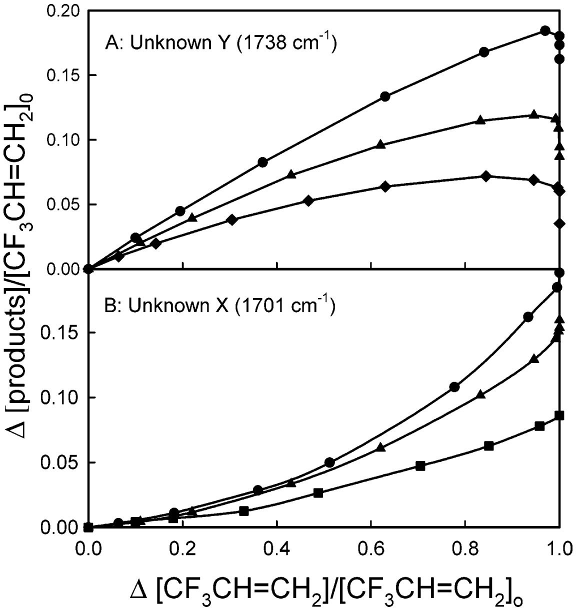

**Figure 7.** Yield plots (in arbitrary units) for unknowns X and Y with absorption features at 1701 and 1738 cm$^{-1}$, respectively, following the UV irradiation of mixtures initially containing 7.5 mTorr $CF_3CH{=}CH_2$, 15 mTorr NO, 88 mTorr $Cl_2$, and either 15.3 (circles), 52.5 (triangles), 125 (diamonds), or 400 (squares) Torr $O_2$ in 700 Torr of $N_2$ diluent.

When panel D in Figure 6 is compared with panel B in Figure 2, it is clear that the presence of 15 mTorr of $NO_x$ has a pronounced impact on the products following the Cl atom initiated oxidation of $CF_3CH{=}CH_2$ in the presence of 10 Torr of $O_2$. The product features at 1701 and 1738 cm$^{-1}$ in Figure 6D are particularly striking. These features do not match any in our reference library. The features lie in a region of the spectrum which is characteristic of N−O stretching modes. We will refer to the compound(s) responsible for absorption at 1701 cm$^{-1}$ as unknown "X" and the compound(s) responsible for absorption at 1738 cm$^{-1}$ as unknown "Y". The product features centered at approximately 1615 cm$^{-1}$ are attributable to $NO_2$.

To provide insight into the likely identity of X and Y, their yields were studied as a function of $[O_2]$ (5 − 400 Torr) and $CF_3CH{=}CH_2$ consumption. Figure 7 shows the yields of X and Y (in arbitrary units) versus loss of $CF_3CH{=}CH_2$ following UV irradiation of gas mixture containing 7.5 mTorr of $CF_3CH{=}CH_2$, 88 mTorr of $Cl_2$, and 15 mTorr of NO in 700 Torr of $N_2/O_2$ diluent. The yield of the unknowns and loss of $CF_3CH{=}CH_2$ have been normalized to the initial $CF_3CH{=}CH_2$ concentration. There are three interesting trends in the data shown in Figure 7. First, the yields of X and Y increase with decreasing $[O_2]$. Second, although the yield of X increases with $CF_3CH{=}CH_2$ consumption (data in bottom panel curve upward), the yield of Y decreases with increasing $CF_3CH{=}CH_2$ consumption (data in top panel curve downward). Third, irrespective of $[O_2]$, the yields of X tend to zero at low $CF_3CH{=}CH_2$ consumptions.

Figure 4B shows a plot of the yields of $CF_3C(O)CH_2Cl$ and Y (evaluated from the initial slope of plots such as those shown in Figure 7A). The $CF_3C(O)CH_2Cl$ yield in Figure 4B is in absolute units, the yield of Y is in arbitrary units. In contrast to the $NO_x$-free experiments (Figure 4A), the $CF_3C(O)CH_2Cl$ yield decreases continuously as $[O_2]$ is decreased with no apparent sign of a threshold. The decrease in $CF_3C(O)CH_2Cl$ yield in Figure 4B is not caused by the competition between reactions 11 and 12. We conclude that in the presence of $NO_x$ there is an additional loss mechanism for $CF_3C(O)HCH_2Cl$ radicals; reaction with $NO_x$ to give the nitrite and nitrate

$$CF_3C(O)HCH_2Cl + NO + M \rightarrow CF_3C(ONO)HCH_2Cl + M \quad (24)$$

$$CF_3C(O)HCH_2Cl + NO_2 + M \rightarrow CF_3C(ONO_2)HCH_2Cl + M \quad (25)$$

Reaction with NO will be most important at low consumptions of $CF_3CH{=}CH_2$ when [NO] is near its initial value of 15 mTorr. Reaction with $NO_2$ will be least important at low consumptions of $CF_3CH{=}CH_2$ when there is little $NO_2$ in the system and will increase in importance with increasing consumption of $CF_3CH{=}CH_2$ and increasing $[NO_2]$.

The simplest explanation of the experimental observations is that Y is the nitrite $CF_3C(ONO)HCH_2Cl$ (and, probably, $CF_3CHClCH_2ONO$) and X is the nitrate $CF_3C(ONO_2)HCH_2Cl$ (and, probably, $CF_3CHClCH_2ONO_2$). Interestingly, extrapolation of the $CF_3C(O)CH_2Cl$ data in Figure 4B gives a nonzero yield at very low $[O_2]$. Such a nonzero yield suggests that a fraction of the reaction of $CF_3C(O)HCH_2Cl$ radicals with NO gives $CF_3C(O)CH_2Cl$ (and HNO) as product. The data in Figure 4B suggests that at approximately 100 Torr of $O_2$ the loss of $CF_3C(O)HCH_2Cl$ radicals via reactions 11 and 24 are of approximately equal importance. Reactions of alkoxy radicals with NO proceed with rate constants of the order of $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ in one atmosphere pressure at room temperature.[27] Hence, from $k_{24}[NO] \approx k_{11}[O_2]$ and assuming $k_{24} = 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, we derive an order of magnitude estimate of $k_{11} \approx 1.5 \times 10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. Combining this result with $k_{11}/k_{12} = (3.8 \pm 1.8) \times 10^{-18}$ $cm^3$ $molecule^{-1}$ provides an estimate of $k_{12} = 400$ $s^{-1}$. The data base concerning the kinetics of reactions of haloalkoxy radicals with $O_2$ is very limited with direct studies having been reported only for $CH_2ClO$,[28] $CF_2ClCH_2O$,[29] and $CFCl_2CH_2O$.[29,30] The reactivity of haloalkoxy radicals is generally lower than that of unsubstituted alkoxy radicals toward $O_2$.[28,29,30] Large ($C_3-C_4$) alkoxy radicals react with $O_2$ with rate constants of approximately $1 \times 10^{-14}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at ambient temperature.[27] Hence, the estimate of $k_{11} \approx 1.5 \times 10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ is consistent with expectations based upon the existing (limited) kinetic data base for reactions of alkoxy radicals.

It is clear that the chemistry occurring in the Cl atom initiated oxidation in the presence of $NO_x$ in the smog chamber is complex. It should be noted that in the real atmosphere the typical concentrations of $NO_x$ are several orders of magnitude lower than those employed in our smog chamber experiments. As such, reactions 24 and 25 will not be significant in the atmosphere.

Vésine et al.[26] studied the products of Cl initiated oxidation of $C_4F_9CH{=}CH_2$ and $C_6F_{13}CH{=}CH_2$ in the presence of $NO_x$ in air. They used initial mixtures of 15−30 mTorr $C_4F_9CH{=}CH_2$, 60−80 mTorr $Cl_2$, and 40−80 mTorr of NO in one atmosphere of air. After irradiation for 60 min they observed product features at 1163, 1304, 1741, and 1841 $cm^{-1}$ typical of peroxyacyl nitrates (PAN). The experimental apparatus and the initial reaction mixtures employed by Vésine et al. are similar to those employed here and we would expect the formation of the nitrites and nitrates described above. However, the irradiation time (60 min) is approximately 100 times longer than typical irradiation times used in our experiments. Use of such long irradiation times probably results in the photolysis of the nitrites and nitrates leading to the formation of $C_xF_{2x+1}CHO$ which would then undergo further reactions leading to the PAN type products observed by Vésine et al.[26]

### 3.4. Products of the OH Radical Initiated Oxidation of $C_xF_{2x+1}CH{=}CH_2$ ($x = 1$ and 4).

To investigate the products and mechanism of the reaction of OH radicals with $CF_3CH{=}CH_2$ and $C_4F_9CH{=}CH_2$, reaction mixtures consisting of 15.5−16.7 mTorr $C_xF_{2x+1}CH{=}CH_2$, 45.8 − 86.5 mTorr $CH_3ONO$, 14.7−19.1 mTorr of NO and 10−400 Torr $O_2$ in $N_2$ or air were introduced into the reaction chamber and subjected to UV irradiation. Consumptions of $C_xF_{2x+1}CH{=}CH_2$ were in the range 1−22%. $C_xF_{2x+1}CHO$ was observed as the major product in these experiments. Figure 8 shows a plot of the formation of $C_xF_{2x+1}CHO$ (normalized to the initial $C_xF_{2x+1}CH{=}CH_2$ concentration) versus the fractional loss of $C_xF_{2x+1}CH{=}CH_2$. Small corrections (<7%) for loss of $C_xF_{2x+1}CHO$ via reaction with OH radicals have been applied to the data in Figure 8 using the procedure described elsewhere[31] with $k(OH{+}C_xF_{2x+1}CHO)/k(OH{+}C_xF_{2x+1}CH{=}CH) = 6.5 \times 10^{-13}/1.36 \times 10^{-12} = 0.48$.[18,20] As seen from Figure 8, there was no discernible effect of $[O_2]$ or size of the $C_xF_{2x+1}-$ group on the $C_xF_{2x+1}CHO$ yield. The line through the data is a linear least-squares analysis which gives a $C_xF_{2x+1}CHO$ yield of 88 ± 9%. A trace amount of $COF_2$ was observed consistent with a small loss of $C_xF_{2x+1}CHO$ via reaction with OH noted above. No other $C_xF_{2x+1}CH{=}CH_2$ oxidation products were detected. The mechanism which explains the observed formation of $C_xF_{2x+1}CHO$ in a yield approaching unity is illustrated for $CF_3CH{=}CH_2$ in Figure 9. By analogy to the corresponding reactions in the oxidation of $C_3H_6$,[32] it is expected that small amounts (probably 1−2%) of the nitrates $C_xF_{2x+1}CH(OH)CH_2ONO_2$ and $C_xF_{2x+1}CH(ONO_2)CH_2OH$ will be formed in the reaction of the peroxy radicals

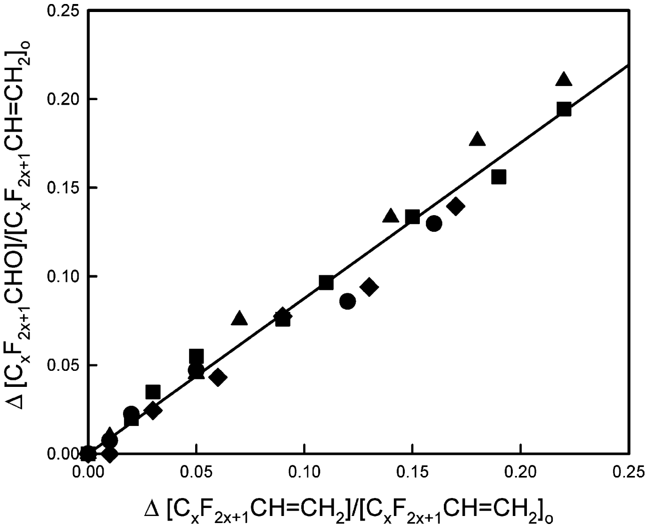

**Figure 8.** Yield of $C_xF_{2x+1}CHO$ following the OH radical initiated oxidation of $C_xF_{2x+1}CH{=}CH_2$ ($x = 1$ and 4) in the presence of NO in 700 Torr of $N_2/O_2$ diluent: squares, $CF_3CH{=}CH_2$ with $[O_2] = 10$ Torr; circles, $CF_3CH{=}CH_2$ with $[O_2] = 140$ Torr; triangles, $CF_3CH{=}CH_2$ with $[O_2] = 400$ Torr, diamonds, $C_4F_9CH{=}CH_2$ with $[O_2] = 140$ Torr.

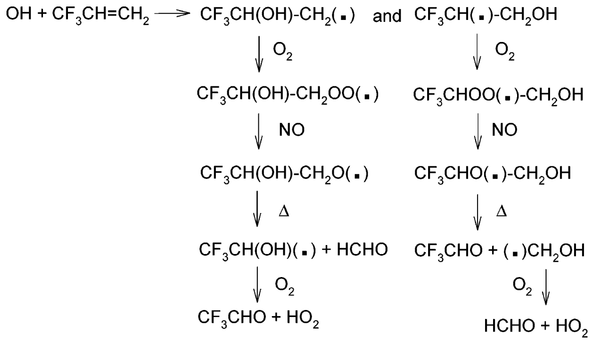

**Figure 9.** Mechanism of the OH radical initiated oxidation of $CF_3CH{=}CH_2$ in the presence of $NO_x$.

with NO. Our analysis method is not sufficiently sensitive to detect such products. Our observation of $C_xF_{2x+1}CHO$ formation in a yield close to 100% following the OH radical initiated oxidation of $CF_3CH{=}CH_2$ and $C_4F_9CH{=}CH_2$ is consistent with the finding by Vésine et al.[26] that $C_xF_{2x+1}CHO$ is the major product in the OH radical initiated oxidation of $C_4F_9CH{=}CH_2$ and $C_6F_{13}CH{=}CH_2$. On the basis of the present work and that by Vésine et al.,[26] it seems reasonable to conclude that the OH radical initiated atmospheric oxidation of all members of the $C_xF_{2x+1}CH{=}CH_2$ series gives $C_xF_{2x+1}CHO$ in a yield close to 100%.

It is interesting to contrast the behavior of the alkoxy radicals formed following OH radical and Cl atom addition to the $>C{=}C<$ double bond in $CF_3CH{=}CH_2$. As discussed in section 3.2, reaction with $O_2$ is an important loss mechanism for both $CF_3CHClCH_2O$ and $CF_3CH(O)CH_2Cl$ radicals. There is no evidence that reaction with $O_2$ is a significant loss for $CF_3CH(OH)CH_2O$ and $CF_3CH(O)CH_2OH$ radicals (even in the presence of 400 Torr of $O_2$). The fate of $CF_3CH(OH)CH_2O$ and $CF_3CH(O)CH_2OH$ radicals is decomposition via C−C bond scission. These observations are consistent with the behavior of alkoxy radicals formed following Cl atom or OH radical addition to alkenes as discussed by Orlando et al.[33]

## 4. Atmospheric Implications

The aim of the present study was to assess the possibility that the atmospheric oxidation of $C_xF_{2x+1}CH{=}CH_2$ contributes to the burden of perfluorocarboxylic acids ($C_xF_{2x+1}COOH$) in remote locations. As discussed in the Introduction, the atmospheric lifetime of $C_xF_{2x+1}CH{=}CH_2$ is determined by its reaction with OH radicals and is approximately 8 days. This is sufficient for $C_xF_{2x+1}CH{=}CH_2$ emitted in urban areas to be transported to remote locations. We show herein that the OH radical initiated oxidation of $C_xF_{2x+1}CH{=}CH_2$ leads to the formation of $C_xF_{2x+1}CHO$ in a yield which is close to 100%. This result confirms that the atmospheric degradation pathways for both fluorotelomer olefins and fluorotelomer alcohols lead to $C_xF_{2x+1}CHO$ as a common transformation product. Atmospheric degradation routes by which $C_xF_{2x+1}CHO$ can be transformed into $C_xF_{2x+1}COOH$ as a minor ($<10\%$) product have been documented.[17,34] We therefore conclude that it is possible that the atmospheric degradation of $C_xF_{2x+1}CH{=}CH_2$ contributes to the perfluorocarboxylic acids observed in remote locations. To quantify the importance of this contribution information concerning the rate of release of $C_xF_{2x+1}CH{=}CH_2$ into the atmosphere is needed. Further work is needed to provide such information but is beyond the scope of the present study.

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