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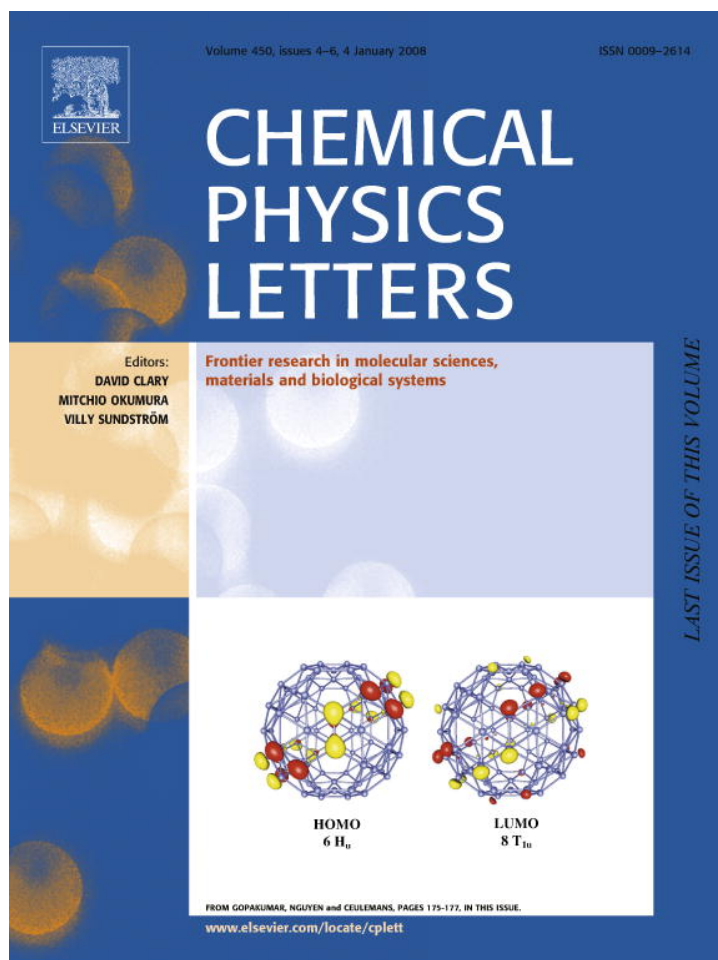**13** PUBLICATIONS   **180** CITATIONS

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Atmospheric chemistry of CF$_3$CF=CH$_2$: Products and mechanisms of Cl atom and OH radical initiated oxidation

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Abstract

The products of Cl atom and OH radical initiated oxidation of CF$_3$CF=CH$_2$ were studied in 700 Torr of N$_2$/O$_2$ diluent at 296 $\pm$ 1 K. The reactions of Cl atoms and OH radicals with CF$_3$CF=CH$_2$ proceed via electrophilic addition to the double bond. The reaction with chlorine atoms proceeds 56 $\pm$ 5% via addition to the central carbon. The chlorine atom initiated oxidation of CF$_3$CF=CH$_2$ gives CF$_3$C(O)F in a molar yield which is indistinguishable from 100% and independent of [O$_2$], and HC(O)Cl in a molar yield which increased from 30% to 59% as [O$_2$] was increased from 3 to 700 Torr. The OH radical initiated oxidation of CF$_3$CF=CH$_2$ gives CF$_3$C(O)F as major product in a yield of 91 $\pm$ 6%. The results are discussed with respect to the atmospheric chemistry and environmental impact of CF$_3$CF=CH$_2$.
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1. 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. Saturated hydrofluorocarbons (HFCs) have become widely used CFC replacements. HFCs do not contain chlorine and hence do not contribute to the well established chlorine based catalytic ozone destruction cycles [3]. The atmospheric lifetime of HFCs is determined by their reactivity towards OH radicals. CF$_3$CFH$_2$ (HFC-134a) is used as the working fluid in all modern vehicle air conditioning systems. Saturated HFCs such as HFC-134a display modest reactivity towards OH radicals and hence have modest global warming potentials. HFC-134a has a global warming potential of 1430 (100 year time horizon) which is approximately a factor of 8 lower than that of CFC-12 (10890) which it replaced [4].

Unsaturated hydrofluorocarbons are a class of compounds, which are potential replacements for CFCs and saturated HFCs in air conditioning units. In general, unsaturated hydrofluorocarbons react more rapidly with OH radicals, have shorter atmospheric lifetimes, and have lower global warming potentials than saturated hydrofluorocarbons. 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$_3$CF=CH$_2$ was investigated. Rate constants of k(Cl + CF$_3$CF=CH$_2$) = (7.03 $\pm$ 0.59) $\times$ 10^{-11}, k(OH + CF$_3$CF=CH$_2$) = (1.05 $\pm$ 0.17) $\times$ 10^{-12}, and k(O$_3$ + CF$_3$CF=CH$_2$) = (2.77 $\pm$ 0.21) $\times$ 10^{-21} cm^3 molecule^{-1} s^{-1} in 700 Torr of N$_2$/O$_2$ diluent at 296 K have been reported [5]. In the present work smog chamber/FTIR techniques were used to determine products of the chlorine atom and OH radical initiated oxidation of CF$_3$CF=CH$_2$.

2. Experimental

Experiments were performed in a 140-l Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer [6].

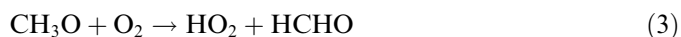* Corresponding author.
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The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to photochemically initiate the experiments. The products of the atmospheric oxidation of $CF_3CF=CH_2$ were investigated by irradiating $CF_3CF=CH_2/Cl_2/O_2/N_2$, $CF_3CF=CH_2/CH_3ONO/O_2/N_2$, and $CF_3CF=CH_2/CH_3ONO/NO/O_2/N_2$ mixtures. All samples of $CF_3CF=CH_2$ used in this work were supplied by the Honeywell International Inc. at a purity >99.9% and were used without further purification. Chlorine atoms were produced by photolysis of molecular chlorine

$$Cl_2 + hv \rightarrow 2Cl \tag{1}$$

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

$$CH_3ONO + hv \rightarrow CH_3O + NO \tag{2}$$

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

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

CH_3ONO was synthesized by the drop wise addition of concentrated sulfuric acid to a saturated solution of $NaNO_2$ in methanol. Other reagents were obtained from commercial sources at purities >99%. All experiments were conducted in 700 Torr of N_2/O_2 diluent at 296 ± 1 K.

Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 m. Unless stated otherwise, quoted uncertainties are two standard deviations from least squares regressions.

3. Results and discussion

3.1. Cl atom initiated oxidation of $Cl + CF_3CF=CH_2$

To investigate the products and mechanism of the Cl atom initiated oxidation of $CF_3CF=CH_2$, mixtures consisting of 9.6–40.6 mTorr $CF_3CF=CH_2$, 92.0–124.2 mTorr Cl_2, and 3.1–700 Torr O_2 in 700 Torr total pressure of N_2/O_2 diluent were introduced into the chamber and subjected to UV irradiation. Comparison of the IR features formed in low and high O_2 partial pressure experiments revealed that three distinct products, or sets of products, were formed in the chamber. Fig. 1 shows IR spectra obtained before (A) and after (B) a 30 s irradiation of a mixture containing 9.6 mTorr $CF_3CF=CH_2$ and 101.4 mTorr Cl_2 in 700 Torr total pressure of air diluent. Subtraction of IR features attributed to $CF_3CF=CH_2$ from panel B gives the product spectrum shown in panel C. By comparing panel C with the reference spectra in panels D, E, and F, it is clear that $CF_3C(O)F$, $HC(O)Cl$, and CO are formed as products in the system.

Reaction of Cl atoms with $CF_3CF=CH_2$ occurs via electrophilic addition to the double bond. Addition can occur to the central or terminal carbon atom to give $CF_3CFClCH_2$ or CF_3CFCH_2Cl radicals:
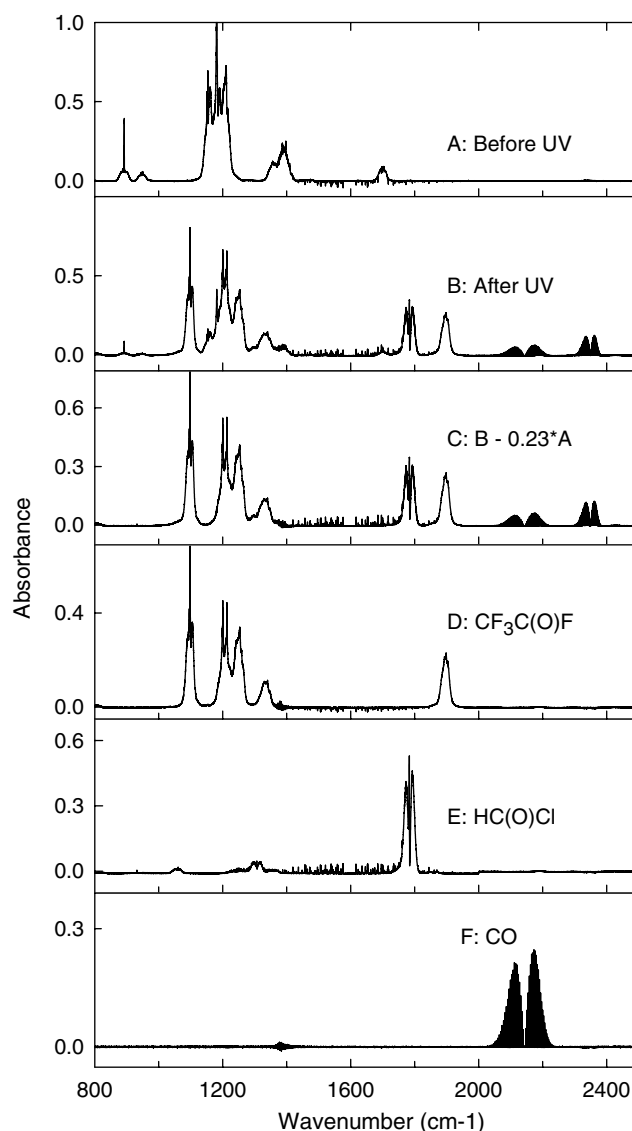
Fig. 1. IR spectra of a mixture of 9.6 mTorr $CF_3CF=CH_2$ and 101.4 mTorr Cl_2 in 700 Torr of air before (A) and after (B) 30 s UV irradiation. Panel C shows the residual IR features after subtraction of features attributable to $CF_3CF=CH_2$ from panel B. Reference spectra of $CF_3C(O)F$, $HC(O)Cl$, and CO are given in panels D, E, and F.

$$CF_3CF=CH_2 + Cl \rightarrow CF_3CFClCH_2 \tag{5a}$$
$$\rightarrow CF_3CFCH_2Cl \tag{5b}$$

The reaction mechanism for the Cl atom initiated oxidation of $CF_3CF=CH_2$ is shown in Fig. 2. The radicals produced in reaction (5) react with O_2 to give peroxy radicals

$$CF_3CFClCH_2 + O_2 \rightarrow CF_3CFClCH_2OO \tag{6a}$$
$$CF_3CFCH_2Cl + O_2 \rightarrow CF_3CF(OO)CH_2Cl \tag{6b}$$

In the atmosphere the peroxy radicals will react with NO to produce the corresponding alkoxy radicals

$$CF_3CFClCH_2OO + NO \rightarrow CF_3CFClCH_2O + NO_2 \tag{7a}$$
$$CF_3CF(OO)CH_2Cl + NO \rightarrow CF_3CF(O)CH_2Cl + NO_2 \tag{7b}$$

Fig. 2. Mechanism of the Cl atom initiated oxidation of $CF_3CF=CH_2$.

In the chamber the conversion of the peroxy into alkoxy radicals is accomplished by peroxy radical self- and cross-reactions. As shown in Fig. 2, the alkoxy radical $CF_3CF(O)CH_2Cl$ is expected to decompose via C–C bond scission leading to the formation of $CF_3C(O)F$, $HC(O)Cl$, and CO products. The alkoxy radical $CF_3CFClCH_2O$ is expected to undergo both decomposition via C–C bond scission leading to the formation of $CF_3C(O)F$ and HCHO, and reaction with O_2 giving the aldehyde $CF_3CFClCHO$. As indicated in Fig. 2, the aldehyde is expected to be reactive towards Cl atoms and be oxidized to give $CF_3C(O)F$, CO, and CO_2.

Fig. 3 shows a plot of the formation of $CF_3C(O)F$, $HC(O)Cl$, CO, and HCHO versus the loss of $CF_3CF=CH_2$ following UV irradiation of a mixture of 33.8 mTorr $CF_3CF=CH_2$ and 111.7 mTorr Cl_2 in 700 Torr of air diluent. CF_3CHO yield data for experiments conducted with 3.1–700 Torr partial pressure of O_2 (at total pressure of 700 Torr, made up with N_2) are also included in Fig. 3. As seen from Fig. 3, the yield of $CF_3C(O)F$ is independent of $[O_2]$. The line through the data is a linear least squares fit which gives a molar $CF_3C(O)F$ yield of $92 \pm 5\%$. The line through the $HC(O)Cl$ data gives a yield of $54 \pm 6\%$. The curves through the CO and HCHO are second order polynomial fits to aid visual inspection of the data trends. The curvature in the CO data indicates it is formed as a secondary product, the curvature in the HCHO data indicate that it is lost via secondary reactions (probably with Cl atoms).

In contrast to the behaviour observed for $CF_3C(O)F$, the yield of $HC(O)Cl$ varied with $[O_2]$. The insert in Fig. 3 shows the yield of $HC(O)Cl$ observed in experiments using $[O_2] = 3.1$–700 Torr. The variation of $HC(O)Cl$ with $[O_2]$ reflects a competition between reaction with O_2 and decomposition via HCl elimination as fates for $CH_2ClO^{\cdot}$ radicals in the system. This competition has been studied previously and a rate constant ratio of $k_8/k_9 = 5.0 \times 10^{-18}$ cm^3 molecule^{-1} has been reported [7].

Fig. 3. Formation of $CF_3C(O)F$ (triangles), $HC(O)Cl$ (circles), CO (squares), and HCHO (crosses) versus loss of $CF_3CF=CH_2$ observed following UV irradiation of a mixture of 33.8 mTorr $CF_3CF=CH_2$ and 111.7 mTorr Cl_2 in 700 Torr of air diluent. Additional CF_3COF data are shown for experiments conducted with different $[O_2]$: 3.1 Torr, (gray diamonds); 7.5 Torr, (gray inverted triangles); 10 Torr, (filled inverted triangles); 50 Torr (gray squares); 300 Torr, (gray stars); 400 Torr (filled stars); 550 Torr (gray circles), and 700 Torr, (gray triangles). The insert shows the $HC(O)Cl$ yield versus $[O_2]$, see text for details.

$$CH_2ClO + O_2 \rightarrow HC(O)Cl + HO_2 \qquad (8)$$

$$CH_2ClO + M \rightarrow HC(O) + HCl + M \qquad (9)$$

M represents a third body (mainly N_2 in this case). The $HC(O)Cl$ yield is described by the expression,

$$Y(HC(O)Cl) = Y(CH_2ClO)\left[\frac{\frac{k_8}{k_9}[O_2]}{\frac{k_8}{k_9}[O_2]+1}\right] + C \qquad (10)$$

where Y(CH$_2$ClO) is the yield of CH$_2$ClO radicals in the system, k_8/k_9 is the ratio of the rate constants for reactions (8) and (9) and C is the [O$_2$] independent HC(O)Cl yield in the system (e.g., via the CH$_2$ClO$_2$ + HO$_2$ reaction [8]). The curve through the data in the insert in Fig. 3 is a fit of expression (10) to the data with k_8/k_9 fixed at 5.0×10^{-18} cm^3 molecule^{-1} [7]. It can be seen from Fig. 3 that the variation of the HC(O)Cl yield with [O$_2$] is consistent with that expected from the literature value of k_8/k_9. At [O$_2$] > 100 Torr the HC(O)Cl yield reaches a limiting value. The experiments conducted using [O$_2$] > 100 Torr give a HC(O)Cl yield of 56 ± 5% which we equate to the fraction of Cl atom attack that proceeds via addition to the terminal carbon atom; $k_{5b}/(k_{5a} + k_{5b}) = 0.56 \pm 0.05$.

The observation of a small, but significant, yield of HCHO (see Fig. 3) is interesting as it implies that decomposition via C–C bond scission is a significant loss mechanism for CF$_3$CFClCH$_2$O radicals. This observation is unexpected as it is well established that the atmospheric loss mechanism of structurally similar molecules such as CCl$_3$CH$_2$O, CF$_3$CH$_2$O, CFCl$_2$CH$_2$O, and CF$_2$ClCH$_2$O is reaction with O$_2$ [9]. Further work, for example a computational study of the rate of decomposition of CF$_3$CF$_x$-Cl$_{2-x}$CH$_2$O radicals would be of interest, but is beyond the scope of the present work.

3.2. Study of the mechanism of the atmospheric oxidation of OH + CF$_3$CF=CH$_2$

To investigate the products and mechanism of the OH radical initiated oxidation of CF$_3$CF=CH$_2$, mixtures consisting of 8.7–16.0 mTorr CF$_3$CF=CH$_2$, 105–203 mTorr CH$_3$ONO, and 0–25 mTorr NO in air diluent were introduced into the chamber and subjected to UV irradiation. The consumption of CF$_3$CF=CH$_2$ was in the range 10–41%. CF$_3$C(O)F was observed as the major product in all experiments. As seen from Fig. 4, there was no discernable difference in the yield of CF$_3$C(O)F in experiments conducted with, and without, added NO. The line through the data is a linear least squares fit to the combined data set which gives a CF$_3$C(O)F yield of 0.91 ± 0.06. The observed CF$_3$C(O)F yield is less than 100%. This may reflect the formation of a small yield of the nitrates CF$_3$(ONO$_2$)CH$_2$OH and CF$_3$CF(OH)-CH$_2$ONO$_2$ in the reactions of the corresponding peroxy radicals with NO shown in Fig. 5, or it may reflect uncertainties in our calibration of the CF$_3$C(O)F reference spectrum, or both.

4. Atmospheric chemistry and environmental impact

The atmospheric lifetime of CF$_3$CF=CH$_2$ is dictated by its reaction with OH radicals and is approximately 11 days [5]. We show here that CF$_3$C(O)F is the major atmospheric oxidation product of CF$_3$CF=CH$_2$. The atmospheric fate of CF$_3$C(O)F is hydrolysis which occurs on a time scale of approximately 10 days to give CF$_3$C(O)OH [3]. The
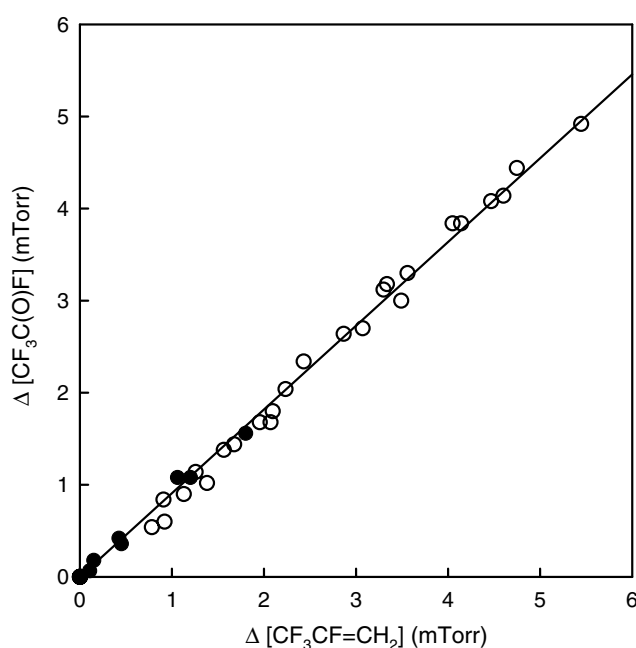
Fig. 4. Formation of CF$_3$C(O)F versus loss of CF$_3$CF=CH$_2$ observed following the UV irradiation of mixtures of 8.7–14 mTorr CF$_3$CF=CH$_2$ and 106–203 mTorr CH$_3$ONO (open symbols) or 10.6–16 mTorr CF$_3$CF=CH$_2$, 105–108 mTorr CH$_3$ONO and 17–25 mTorr NO (filled symbols) in 700 Torr air diluent.
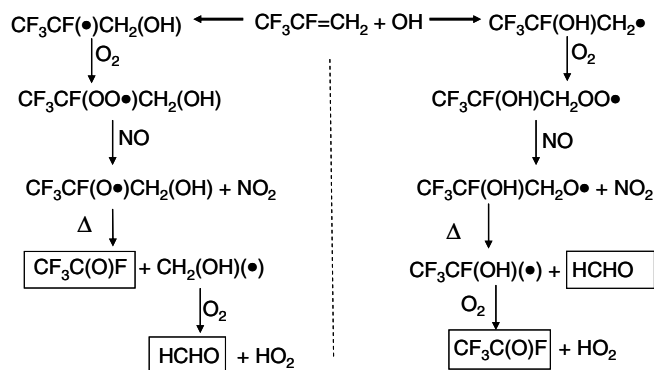
Fig. 5. Mechanism of the OH radical initiated oxidation of CF$_3$CF=CH$_2$.

available data suggest that while CF$_3$C(O)OH is not a natural component of the freshwater environment [10], it is a natural component of the background oceanic environment [11], and any additional burden associated with CF$_3$CF=CH$_2$ oxidation will be of negligible environmental significance. We conclude that the products of the atmospheric oxidation of CF$_3$CF=CH$_2$ have negligible environmental impact.

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