

# Atmospheric chemistry of trans-CF<sub>3</sub>CH=CHF: products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation

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**Abstract.** Smog chamber/FTIR techniques were used to study the products and mechanisms of OH radical and Cl atom initiated oxidation of trans-CF<sub>3</sub>CH=CHF in 700 Torr of N<sub>2</sub>/O<sub>2</sub> diluent at 295±1 K. Hydroxyl radical initiated oxidation leads to the formation of CF<sub>3</sub>CHO and HC(O)F in yields which were indistinguishable from 100% and were not dependent on the O<sub>2</sub> partial pressure. Chlorine atom initiated oxidation gives HC(O)F, CF<sub>3</sub>CHO, CF<sub>3</sub>C(O)Cl, and CF<sub>3</sub>C(O)CHFCl. The yields of CF<sub>3</sub>C(O)Cl and CF<sub>3</sub>C(O)CHFCl increased at the expense of HC(O)F and CF<sub>3</sub>CHO as the O<sub>2</sub> partial pressure was increased over the range 5–700 Torr. The results are discussed with respect to the atmospheric chemistry and environmental impact of trans-CF<sub>3</sub>CH=CHF.

radicals. HFC-134a has a direct global warming potential of 1430 over a 100 year time horizon; a factor of 8 lower than the CFC-12 that it replaced (World Meteorological Organization, 2007).

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 hence environmental impact, of these compounds is needed. The present paper provides information concerning the atmospheric oxidation products of trans-CF<sub>3</sub>CH=CHF. Specifically, smog chamber/FTIR techniques were used to determine the products of the OH radical and Cl atom initiated oxidation of trans-CF<sub>3</sub>CH=CHF. The present work builds upon a recent kinetic study in which values of  $k(\text{Cl}+\text{trans-CF}_3\text{CH=CHF})=(4.64\pm 0.59)\times 10^{-11}$  and  $k(\text{OH}+\text{trans-CF}_3\text{CH=CHF})=(9.25\pm 1.72)\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  in 700 Torr total pressure at 296 K were determined (Søndergaard et al., 2007).

## 1 Introduction

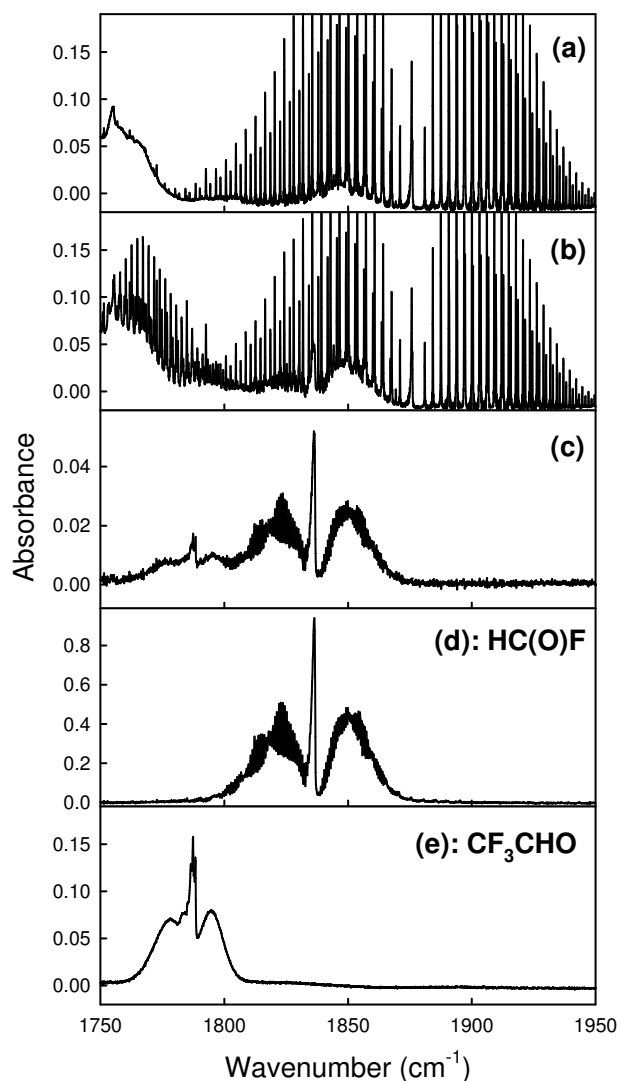
Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere (Molina et al., 1974; Farman et al., 1985) has led to an international effort to replace these compounds with environmentally acceptable alternatives. Saturated hydrofluorocarbons (HFCs) have become widely used CFC replacements. For example, CF<sub>3</sub>CFH<sub>2</sub> (HFC-134a) is used as the working fluid in all modern vehicle air conditioning systems. Hydrofluorocarbons do not contain chlorine and hence do not contribute to the well established chlorine based catalytic ozone destruction cycles (Wallington et al., 1994). The atmospheric lifetime of HFCs is determined by their reactivity towards OH

## 2 Experimental

Experiments were performed in a 1401 Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer (Wallington and Japar, 1989). 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 trans-CF<sub>3</sub>CH=CHF were investigated by irradiating trans-CF<sub>3</sub>CH=CHF/CH<sub>3</sub>ONO/O<sub>2</sub>/N<sub>2</sub>



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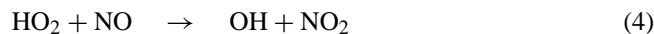
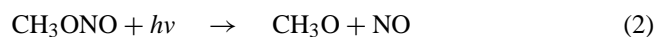
**Fig. 1.** Infrared spectra acquired before (a) and after (b) UV irradiation of a mixture of 34.9 mTorr trans-CF<sub>3</sub>CH=CHF, 82.3 mTorr CH<sub>3</sub>ONO, 19.6 mTorr NO and 126 Torr O<sub>2</sub> in 700 Torr total pressure of N<sub>2</sub> diluent. Panel (c) show the residual IR features after subtraction of features attributable to trans-CF<sub>3</sub>CH=CHF, H<sub>2</sub>O, NO, and HCHO from panel (b). Panels (d) and (e) show reference spectra of HC(O)F and CF<sub>3</sub>CHO, respectively.

and trans-CF<sub>3</sub>CH=CHF/Cl<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures. All samples of trans-CF<sub>3</sub>CH=CHF used in this work were supplied by Honeywell International Inc. at a purity >99.9% and were used without further purification.

Chlorine atoms were produced by photolysis of molecular chlorine,



OH radicals were produced by photolysis of CH<sub>3</sub>ONO in the presence of NO in air,



CH<sub>3</sub>ONO was synthesized by the drop wise addition of concentrated sulfuric acid to a saturated solution of NaNO<sub>2</sub> in methanol. Other reagents were obtained from commercial sources at purities >99%. Experiments were conducted in 700 Torr total pressure of N<sub>2</sub>/O<sub>2</sub>, or air diluent at 295±1 K.

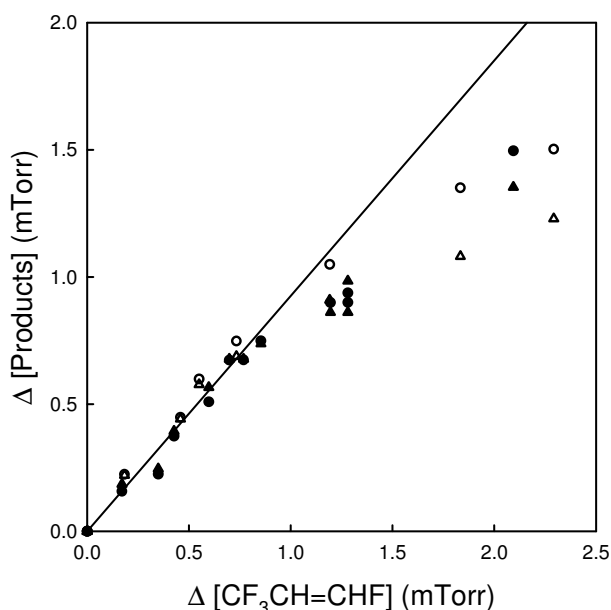
Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm<sup>-1</sup> and an analytical path length of 27.1 m. Unless stated otherwise, quoted uncertainties are two standard deviations from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

### 3 Results

#### 3.1 Products of OH radical initiated oxidation of trans-CF<sub>3</sub>CH=CHF

To investigate the products and mechanism of the reaction of OH radicals with trans-CF<sub>3</sub>CH=CHF, reaction mixtures consisting of 8.3–34.9 mTorr trans-CF<sub>3</sub>CH=CHF, 82.3–117.3 mTorr CH<sub>3</sub>ONO, 0–19.6 mTorr NO, and 126–700 Torr O<sub>2</sub> in 700 Torr total pressure of N<sub>2</sub> diluent were introduced into the chamber and subjected to UV irradiation. Figure 1 shows IR spectra at 1750–1950 cm<sup>-1</sup> obtained before (a) and after (b) subjecting a mixture containing 34.9 mTorr trans-CF<sub>3</sub>CH=CHF, 82.3 mTorr CH<sub>3</sub>ONO, 19.6 mTorr NO, and 126 Torr O<sub>2</sub> in 700 Torr of N<sub>2</sub> diluent to 6 min of UV irradiation. The consumption of trans-CF<sub>3</sub>CH=CHF was 6%. Subtraction of IR features attributable to CF<sub>3</sub>CH=CHF, H<sub>2</sub>O, NO, and HCHO (product of CH<sub>3</sub>ONO photolysis) from panel (b) gives the product spectrum shown in panel (c). Comparison of the IR features in panel (c) with the reference spectra of HC(O)F and CF<sub>3</sub>CHO in panels (d) and (e) shows the formation of these products. The banded structure in panel (a) reflects absorption by NO.

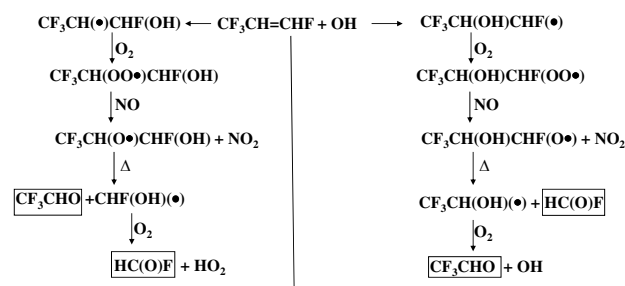
HC(O)F and CF<sub>3</sub>CHO were the only identified carbon containing products of the OH radical initiated oxidation of trans-CF<sub>3</sub>CH=CHF. Figure 2 shows a plot of the observed formation of HC(O)F and CF<sub>3</sub>CHO versus loss of trans-CF<sub>3</sub>CH=CHF. The yields of HC(O)F and CF<sub>3</sub>CHO were indistinguishable. There was no discernable effect on the HC(O)F and CF<sub>3</sub>CHO yields of varying the O<sub>2</sub> partial pressure over the range 126–700 Torr, or having NO present, or absent, in the initial reaction mixtures. As seen from Fig. 2, for consumptions of trans-CF<sub>3</sub>CH=CHF of <1 mTorr, (<10% of initial concentration) the linear least squares fit to the combined data set has a slope =0.93±0.08 which is indistinguishable from 100%.



**Fig. 2.** Formation of HC(O)F (triangles) and CF<sub>3</sub>CHO (circles) versus loss of trans-CF<sub>3</sub>CH=CHF observed following the UV irradiation of mixtures of 8.32–9.18 mTorr trans-CF<sub>3</sub>CH=CHF and 109.1–113.8 mTorr CH<sub>3</sub>ONO in 700 Torr total pressure of air diluent at 296±1 K. Open symbols were obtained in experiments in which NO was not present in the initial reaction mixture. Filled symbols were obtained in experiments in which up to 19.6 mTorr of NO was present initially.

For consumptions of CF<sub>3</sub>CH=CHF greater than 1 mTorr the observed yields of HC(O)F and CF<sub>3</sub>CHO are less than 100% indicating that either the efficiency of conversion of trans-CF<sub>3</sub>CH=CHF into HC(O)F and CF<sub>3</sub>CHO is lower, or there are significant losses of these products at higher trans-CF<sub>3</sub>CH=CHF conversions, or both. To test for heterogeneous loss of HC(O)F and CF<sub>3</sub>CHO, reaction mixtures were allowed to stand in the dark for 15 min; there was no discernable loss (<2%) of either compound. The largest conversion of CF<sub>3</sub>CH=CHF was 25%. However, even at 25% conversion of CF<sub>3</sub>CH=CHF the loss of HC(O)F and CF<sub>3</sub>CHO via secondary reactions with OH radicals will be of relatively minor importance as their reactivity with OH are less than that of trans-CF<sub>3</sub>CH=CHF;  $k(\text{OH} + \text{trans-CF}_3\text{CH=CHF}) = (9.25 \pm 1.72) \times 10^{-13}$  (Søndergaard et al., 2007),  $k(\text{OH} + \text{HC(O)F}) < 4 \times 10^{-15}$  (Wallington et al., 1993), and  $k(\text{OH} + \text{CF}_3\text{CHO}) = 5.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, 2007). Using the method outlined by Meagher et al. (1997) it can be calculated that secondary loss via reaction with OH consumes <0.06% and 9% of HC(O)F and CF<sub>3</sub>CHO, respectively, for a 25% consumption of CF<sub>3</sub>CH=CHF.

It seems likely that the curvature in Fig. 2 reflects a lower yield of both HC(O)F and CF<sub>3</sub>CHO with increased consumption of CF<sub>3</sub>CH=CHF. A plausible explanation of this effect is the reaction of NO<sub>2</sub> (which



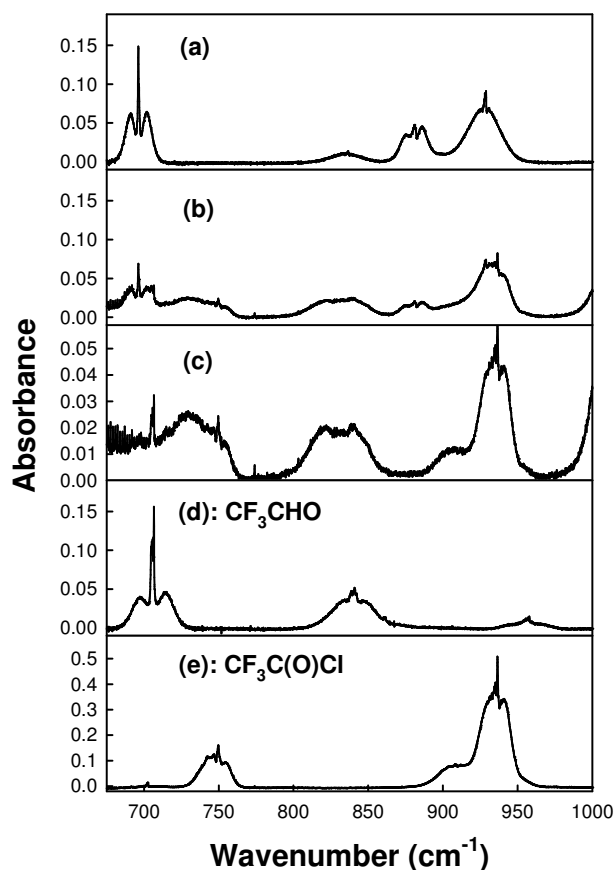
**Fig. 3.** Mechanism of OH radical initiated oxidation of trans-CF<sub>3</sub>CH=CHF, boxes indicate observed products.

increases in concentration with consumption of trans-CF<sub>3</sub>CH=CHF) with the alkoxy radicals formed in the system leading to the formation of small amounts of nitrates (CF<sub>3</sub>CH(ONO<sub>2</sub>)CHF(OH) and CF<sub>3</sub>CH(OH)CHF(ONO<sub>2</sub>)). Spectral congestion and the absence of authentic samples of CF<sub>3</sub>CH(ONO<sub>2</sub>)CHF(OH) and CF<sub>3</sub>CH(OH)CHFONO<sub>2</sub> precluded the detection of small amounts (approx. 1 mTorr) of these nitrates. The concentration of NO<sub>2</sub> towards the end of the experiment was approximately 10 mTorr. Rate constants for reactions of NO<sub>2</sub> with alkoxy radicals are typically  $1 \times 10^{-11}$  to  $5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and hence the pseudo first order loss rate of RO radicals with respect to reaction with NO<sub>2</sub> are expected to be approximately  $10^4 \text{ s}^{-1}$ . This is comparable to the rates of decomposition reported for fluorinated alkoxy radicals, for example  $k_{\text{diss}}(\text{CF}_3\text{CFHO}) = (2 \pm 1) \times 10^4 \text{ s}^{-1}$  at 297 K (Maricq and Szente, 1992). Formation of nitrates via reaction of alkoxy radicals with NO<sub>2</sub> is a plausible explanation of the curvature seen in Fig. 2. In the atmosphere the reactions of the alkoxy radicals with NO<sub>2</sub> will not be of any significance and we did not pursue the origin of the curvature further.

By analogy to the well established oxidation mechanism of propene (IUPAC, 2007), the reaction of OH radicals with trans-CF<sub>3</sub>CH=CHF is expected to proceed via addition to the >C=C< double bond. The mechanism of the OH radical initiated oxidation of trans-CF<sub>3</sub>CH=CHF which explains the observed formation of HC(O)F and CF<sub>3</sub>CHO is shown in Fig. 3. The results from the present work indicate that irrespective of whether the OH radicals add to the terminal, or central carbon atom, the subsequent reactions lead to the formation of one molecule of both HC(O)F and CF<sub>3</sub>CHO.

### 3.2 Products of Cl atom initiated oxidation of trans-CF<sub>3</sub>CH=CHF

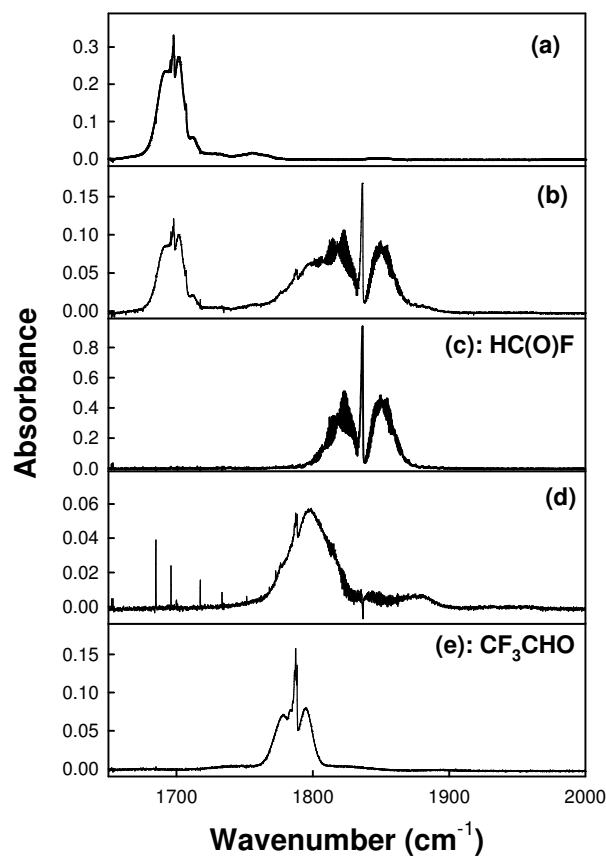
The products of the Cl atom initiated oxidation of trans-CF<sub>3</sub>CH=CHF were studied using the UV irradiation of trans-CF<sub>3</sub>CH=CHF/Cl<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> mixtures. Mixtures consisting of 6.6–8.4 mTorr trans-CF<sub>3</sub>CH=CHF, 102.9–134 mTorr Cl<sub>2</sub> and 5–700 Torr of O<sub>2</sub> in 700 Torr total pressure of N<sub>2</sub> diluent were introduced into the reaction chamber and subjected to UV irradiation. Figure 4 and 5 show IR spectra



**Fig. 4.** Infrared spectra acquired before (a) and after (b) UV irradiation of 6.6 mTorr trans-CF<sub>3</sub>CH=CHF and 109 mTorr Cl<sub>2</sub> in 700 Torr of air diluent. Panel (c) show the residual IR features after subtraction of trans-CF<sub>3</sub>CH=CHF from panel (b). Panels (d) and (e) show reference spectra of CF<sub>3</sub>CHO and CF<sub>3</sub>C(O)Cl, respectively.

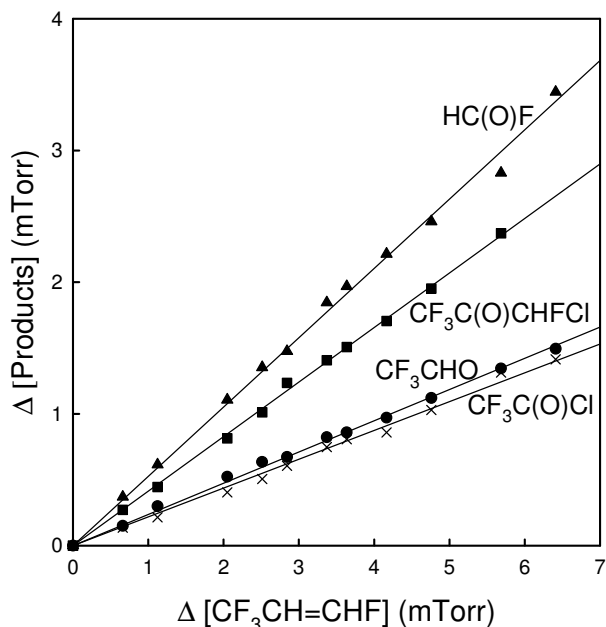
at 675–1000 cm<sup>-1</sup> and 1650–2000 cm<sup>-1</sup>, respectively, obtained before (a) and after (b) subjecting a mixture containing 6.6 mTorr trans-CF<sub>3</sub>CH=CHF and 109 mTorr Cl<sub>2</sub> in 700 Torr air diluent to 20 s of UV irradiation. Comparison of the IR features formed in low and high [O<sub>2</sub>] experiments revealed that four products were formed in the chamber; HC(O)F, CF<sub>3</sub>CHO, CF<sub>3</sub>C(O)Cl, and a product with a broad absorption feature in the carbonyl stretching region centered at 1801 cm<sup>-1</sup> which we attribute to the ketone CF<sub>3</sub>C(O)CHFCl (see below). We do not have a calibrated reference spectrum for CF<sub>3</sub>C(O)CHFCl. The concentration of this compound in the chamber was estimated by assuming that the carbonyl stretching band integrated absorption cross section at 1780–1820 cm<sup>-1</sup> is the same as that in CF<sub>3</sub>C(O)CH<sub>2</sub>Cl ( $1.06 \times 10^{-17}$  cm molecule<sup>-1</sup> (Nakayama et al., 2007)).

Figure 6 shows a plot of the concentrations of HC(O)F, CF<sub>3</sub>CHO, CF<sub>3</sub>C(O)Cl, and CF<sub>3</sub>C(O)CHFCl versus the loss of trans-CF<sub>3</sub>CH=CHF observed following the UV irradiation of a mixture of 6.61 mTorr trans-CF<sub>3</sub>CH=CHF



**Fig. 5.** Infrared spectra acquired before (a) and after (b) UV irradiation of 6.6 mTorr trans-CF<sub>3</sub>CH=CHF and 109 mTorr Cl<sub>2</sub> in 700 Torr of air diluent. Panel (c) show a reference spectrum of HC(O)F. Panel (d) show the residual IR features after subtraction of trans-CF<sub>3</sub>CH=CHF and HC(O)F from panel (b). Panel (e) shows a reference spectrum of CF<sub>3</sub>CHO.

and 109 mTorr Cl<sub>2</sub> in 700 Torr of air diluent. As seen from Figure 6 the formation of HC(O)F, CF<sub>3</sub>C(O)H, CF<sub>3</sub>C(O)Cl and CF<sub>3</sub>C(O)CHFCl scaled linearly with the loss of trans-CF<sub>3</sub>CH=CHF over the range of trans-CF<sub>3</sub>CH=CHF consumption of 10–95%. The linearity of the formation of HC(O)F, CF<sub>3</sub>CHO, CF<sub>3</sub>C(O)Cl and CF<sub>3</sub>C(O)CHFCl suggests that loss of these compounds via secondary reactions is not significant. This observation is consistent with the fact that Cl atoms react much more slowly with these products than with the parent trans-CF<sub>3</sub>CH=CHF compound;  $k(\text{Cl} + \text{trans-CF}_3\text{CH=CHF}) = (4.64 \pm 0.59) \times 10^{-11}$  (Søndergaard et al., 2007),  $k(\text{Cl} + \text{HC(O)F}) = (1.9 \pm 0.2) \times 10^{-15}$  (Meagher et al., 1997), and  $k(\text{Cl} + \text{CF}_3\text{CHO}) = (1.85 \pm 0.26) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Sulbaek Andersen et al., 2004). Previous work has shown that CF<sub>3</sub>C(O)Cl is not lost by heterogeneous processes, photolysis, or reaction with Cl atoms in the chamber used in the present work (Møgelberg et al., 1995).

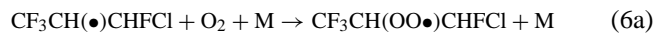


**Fig. 6.** Formation of HC(O)F (triangles), CF<sub>3</sub>C(O)CHFCl (squares), CF<sub>3</sub>CHO (circles) and CF<sub>3</sub>C(O)Cl (crosses) versus loss of trans-CF<sub>3</sub>CH=CHF observed following the UV irradiation of a mixture of 6.6 mTorr trans-CF<sub>3</sub>CH=CHF and 109 mTorr Cl<sub>2</sub> in 700 Torr of air diluent.

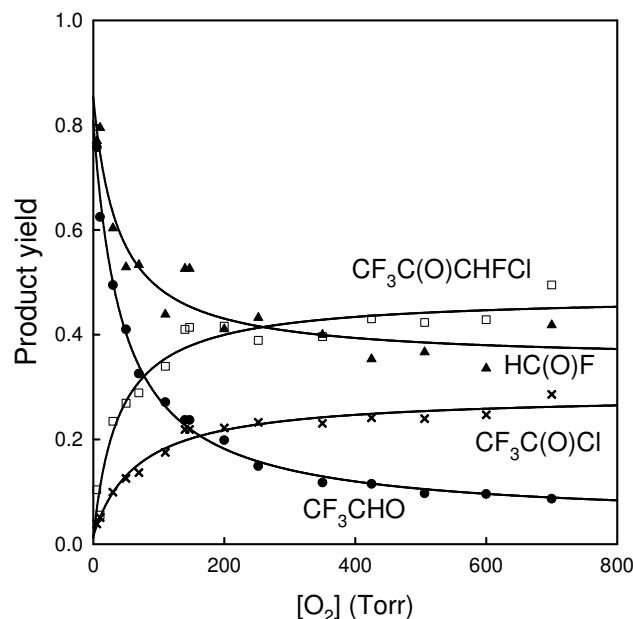
As shown in Fig. 7, the yields of HC(O)F, CF<sub>3</sub>CHO, CF<sub>3</sub>C(O)Cl and CF<sub>3</sub>C(O)CHFCl varied with [O<sub>2</sub>]. In experiments with high [O<sub>2</sub>] the yields of CF<sub>3</sub>C(O)Cl and CF<sub>3</sub>C(O)CHFCl increased at the expense of HC(O)F and CF<sub>3</sub>CHO. As in the case of the OH radical attack, the reaction of Cl atoms with trans-CF<sub>3</sub>CH=CHF is expected to proceed via electrophilic addition to the terminal and central carbon atoms:



The radicals produced in Reaction (5) will react with O<sub>2</sub> to give peroxy radicals which will undergo self- and cross-reaction to give the corresponding alkoxy radicals (in the equations below M represents a third body):

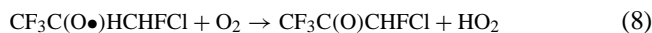


Decomposition via C-C bond scission or reaction with O<sub>2</sub> are likely fates of the CF<sub>3</sub>CH(O•)CHFCl and CF<sub>3</sub>CHClCHF(O•) alkoxy radicals. The observed formation



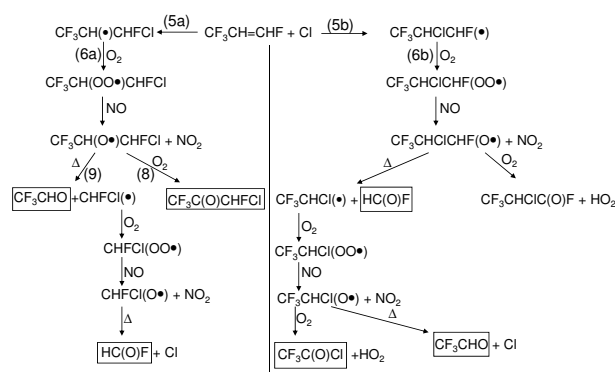
**Fig. 7.** Observed molar yields of HC(O)F (triangles), CF<sub>3</sub>CHO (circles), CF<sub>3</sub>C(O)Cl (crosses) and CF<sub>3</sub>C(O)CHFCl (squares) versus the O<sub>2</sub> partial pressure following the UV irradiation of trans-CF<sub>3</sub>CH=CHF/Cl<sub>2</sub>/N<sub>2</sub>/O<sub>2</sub> mixtures at 700 Torr total pressure. Curves through the CF<sub>3</sub>C(O)CHFCl and CF<sub>3</sub>C(O)Cl are fits to the data using the expressions described in the text. The curves through the HC(O)F and CF<sub>3</sub>CHO data are polynomial fits to aid visual inspection of data trends.

of the ketone CF<sub>3</sub>C(O)CHFCl in a yield which varies with [O<sub>2</sub>] shows that CF<sub>3</sub>C(O•)HCHFCl radicals undergo reaction with O<sub>2</sub> and decomposition via C-C bond scission:



The CHFCl(•) radicals formed in Reaction (9) will add O<sub>2</sub>, undergo reaction with other peroxy radicals in the system to give CHFCl(O•) radicals, and decompose via Cl atom elimination to give HC(O)F (Tua-zon et al., 1993). The data in Fig. 7 contain information concerning the rate constant ratio  $k_8/k_9$ . The yield of CF<sub>3</sub>C(O)CHFCl,  $Y_{\text{CF}_3\text{C}(\text{O})\text{CHFCl}}$ , can be described by the expression  $Y_{\text{CF}_3\text{C}(\text{O})\text{CHFCl}} = Y_{\text{CF}_3\text{CH}(\text{O}\bullet)\text{CHFCl}} (k_8[\text{O}_2]/(k_8[\text{O}_2]+k_9)) + C$ , where  $Y_{\text{CF}_3\text{CH}(\text{O}\bullet)\text{CHFCl}}$  is the yield of CF<sub>3</sub>CH(O•)CHFCl radicals in the system,  $k_8$  and  $k_9$  are the rate constants for Reactions (8) and (9), and C is the [O<sub>2</sub>] independent yield of CF<sub>3</sub>C(O)CHFCl (e.g. from self-reaction of CF<sub>3</sub>CH(OO•)CHFCl peroxy radicals).

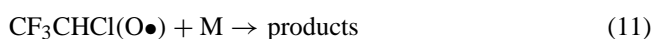
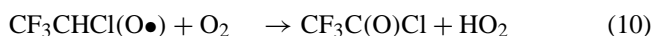
The curve through the CF<sub>3</sub>C(O)CHFCl data in Fig. 7 is a fit of the expression above to the data which gives  $k_8/k_9 = (8.0 \pm 2.6) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ . This value can be compared to the analogous rate constant ratio  $k_{\text{O}_2}/k_{\text{diss}} = (3.8 \pm 1.8) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$  measured for



**Fig. 8.** Atmospheric mechanism of Cl atom initiated oxidation of trans-CF<sub>3</sub>CH=CHF, boxes indicate observed products.

CF<sub>3</sub>CH(O•)CH<sub>2</sub>Cl radicals (Nakayama et al., 2007). The increased importance of decomposition as an atmospheric fate of CF<sub>3</sub>CH(O•)CHFCI compared to CF<sub>3</sub>CH(O•)CH<sub>2</sub>Cl radicals is consistent with theoretical work showing that the barrier to C-C bond scission decreases as the degree of fluorine substitution on the two carbon atoms becomes more even and the bond becomes less polar (Somnitz et al., 2001). The limiting value for the CF<sub>3</sub>C(O)CHFCI yield reached at high [O<sub>2</sub>] provides a measure of  $k_{5a}/(k_{5a}+k_{5b})=47\pm7\%$ . The measured total carbon yield at 700 Torr air is approximately 90%.

Figure 8 shows the mechanism of Cl atom initiated oxidation of trans-CF<sub>3</sub>CH=CHF which is consistent with our experimental observations. From  $k_8/k_9=(8.00\pm 2.6)\times 10^{-19}\text{ cm}^3\text{ molecule}^{-1}$  it can be calculated that in 700 Torr of O<sub>2</sub> the reaction with O<sub>2</sub> accounts for 92% of the CF<sub>3</sub>CH(O•)CHFCI radicals with decomposition accounting for the remaining 8%. Given the estimate of  $k_{5a}/(k_{5a}+k_{5b})=47\pm7\%$  we then expect a 4% HC(O)F yield resulting from addition of Cl atoms to the terminal carbon atom (left hand side of Fig. 8). Hence, we can attribute the bulk of the approximately 40% HC(O)F yield in experiments in 700 Torr of O<sub>2</sub> to the decomposition of CF<sub>3</sub>CHClCHFO• radicals. Decomposition via C-C bond scission is therefore the dominant fate of CF<sub>3</sub>CHClCHFO• radicals. Finally, the increase in the yield of CF<sub>3</sub>C(O)Cl with [O<sub>2</sub>] evident in Fig. 7 is consistent with the expected competition between reaction with O<sub>2</sub> and decomposition for the available CF<sub>3</sub>CHCl(O•) radicals. The yield of CF<sub>3</sub>C(O)Cl,  $Y_{\text{CF}_3\text{C(O)Cl}}$ , can be described by the expression  $Y_{\text{CF}_3\text{C(O)Cl}}=Y_{\text{CF}_3\text{CHCl(O}\bullet)}\cdot(k_{10}[\text{O}_2]/(k_{10}[\text{O}_2]+k_{11}))+\text{C}$ , where  $Y_{\text{CF}_3\text{CHCl(O}\bullet)}$  is the yield of CF<sub>3</sub>CHCl(O•) radicals in the system,  $k_{10}$  and  $k_{11}$  are the rate constants for Reactions (10) and (11), and C is the [O<sub>2</sub>] independent yield of CF<sub>3</sub>C(O)Cl.



The curve through the CF<sub>3</sub>C(O)Cl data in Fig. 7 is a fit of the expression above to the data which gives  $k_{10}/k_{11}=(4.6\pm 1.9)\times 10^{-19}\text{ cm}^3\text{ molecule}^{-1}$ . This result is larger than the previous more direct determination of  $k_{10}/k_{11}=(2.1\pm 0.4)\times 10^{-19}\text{ cm}^3\text{ molecule}^{-1}$  (Møgelberg et al., 1995). A likely explanation for this discrepancy lies in the indirect and complex route by which CF<sub>3</sub>CHCl(O•) radicals are formed in the present system. As indicated in Fig. 8, decomposition and reaction with O<sub>2</sub> are possible competing fates for CF<sub>3</sub>CHClCHFO• radicals. Increased loss of CF<sub>3</sub>CHClCHFO• via reaction with O<sub>2</sub> at high [O<sub>2</sub>] will lead to a decreased yield of CF<sub>3</sub>CHCl(O•) radicals and hence CF<sub>3</sub>C(O)Cl. The net effect will be to cause the CF<sub>3</sub>C(O)Cl yield to plateau at a lower [O<sub>2</sub>] which will lead to an overestimation of  $k_{10}/k_{11}$ . To investigate this effect further would require the use of [O<sub>2</sub>] levels higher than 700 Torr where a decrease in the yield of CF<sub>3</sub>C(O)Cl would be expected with increased loss of CF<sub>3</sub>CHClCHFO• via reaction with O<sub>2</sub>. Such experiments are beyond the scope of the present work.

#### 4 Atmospheric chemistry and environmental impact of trans-CF<sub>3</sub>CH=CHF

The present work improves our understanding of the atmospheric chemistry of trans-CF<sub>3</sub>CH=CHF. The atmospheric lifetime of trans-CF<sub>3</sub>CH=CHF is dictated by its reaction with OH radicals (Søndergaard et al., 2007) and has been estimated at approximately 2 weeks. The OH initiated oxidation of trans-CF<sub>3</sub>CH=CHF gives CF<sub>3</sub>CHO and HC(O)F in yields of approximately 100%. CF<sub>3</sub>CHO is removed from the atmosphere via photolysis and, to a lesser extent, reaction with OH radicals (Chiappero et al., 2006) and addition of water to give the hydrate (Sulbaek Andersen et al., 2006). Photolysis gives CF<sub>3</sub> and HCO radicals (Chiappero et al., 2006) while reaction with OH gives CF<sub>3</sub>CO radicals. CF<sub>3</sub> radicals will add O<sub>2</sub> to give CF<sub>3</sub>O<sub>2</sub> radicals which are then converted into COF<sub>2</sub> (Wallington et al., 1994) which hydrolyzes to give CO<sub>2</sub> and HF. CF<sub>3</sub>CO radicals will add O<sub>2</sub> to give CF<sub>3</sub>C(O)O<sub>2</sub> radicals, the majority of which will be converted into COF<sub>2</sub>, with a small fraction converted into CF<sub>3</sub>C(O)OH via reaction with HO<sub>2</sub> radicals (Hurley et al., 2006). The hydrate, CF<sub>3</sub>CF(OH)<sub>2</sub> is lost via reaction with OH radicals to give CF<sub>3</sub>C(O)OH. The available data suggest that while CF<sub>3</sub>C(O)OH is not a natural component of the freshwater environment (Nielsen et al., 2001), it is a natural component of the background oceanic environment (Frank et al., 2002), and any additional burden associated with trans-CF<sub>3</sub>CH=CHF oxidation will be of negligible environmental significance. We conclude that the products of the atmospheric oxidation of trans-CF<sub>3</sub>CH=CHF will have negligible environmental impact.

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