



Atmospheric chemistry of trans-CF₃CH = CHF: products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation

Javadi, Meshkat Sadat; Søndergaard, Roar; Nielsen, Ole John; Hurley, M. D.; Wallington, T. J.

Published in:
Atmospheric Chemistry and Physics

Publication date:
2008

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Javadi, M. S., Søndergaard, R., Nielsen, O. J., Hurley, M. D., & Wallington, T. J. (2008). Atmospheric chemistry of trans-CF₃CH = CHF: products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation. *Atmospheric Chemistry and Physics*, 8(12), 3141-3147.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Atmospheric chemistry of trans-CF₃CH=CHF: products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation

M. S. Javadi¹, R. Søndergaard¹, O. J. Nielsen¹, M. D. Hurley², and T. J. Wallington²

¹Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark

²System Analytics and Environmental Sciences Department, Ford Motor Company, Mail Drop RIC-2122, Dearborn, Michigan 48121-2053, USA

Received: 4 December 2007 – Published in Atmos. Chem. Phys. Discuss.: 23 January 2008

Revised: 6 June 2008 – Accepted: 6 June 2008 – Published: 24 June 2008

Abstract. Smog chamber/FTIR techniques were used to study the products and mechanisms of OH radical and Cl atom initiated oxidation of trans-CF₃CH=CHF in 700 Torr of N₂/O₂ diluent at 295±1 K. Hydroxyl radical initiated oxidation leads to the formation of CF₃CHO and HC(O)F in yields which were indistinguishable from 100% and were not dependent on the O₂ partial pressure. Chlorine atom initiated oxidation gives HC(O)F, CF₃CHO, CF₃C(O)Cl, and CF₃C(O)CHFCl. The yields of CF₃C(O)Cl and CF₃C(O)CHFCl increased at the expense of HC(O)F and CF₃CHO as the O₂ 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-CF₃CH=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-CF₃CH=CHF. Specifically, smog chamber/FTIR techniques were used to determine the products of the OH radical and Cl atom initiated oxidation of trans-CF₃CH=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, CF₃CFH₂ (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-CF₃CH=CHF were investigated by irradiating trans-CF₃CH=CHF/CH₃ONO/O₂/N₂



Correspondence to: T. J. Wallington
(twalling@ford.com)

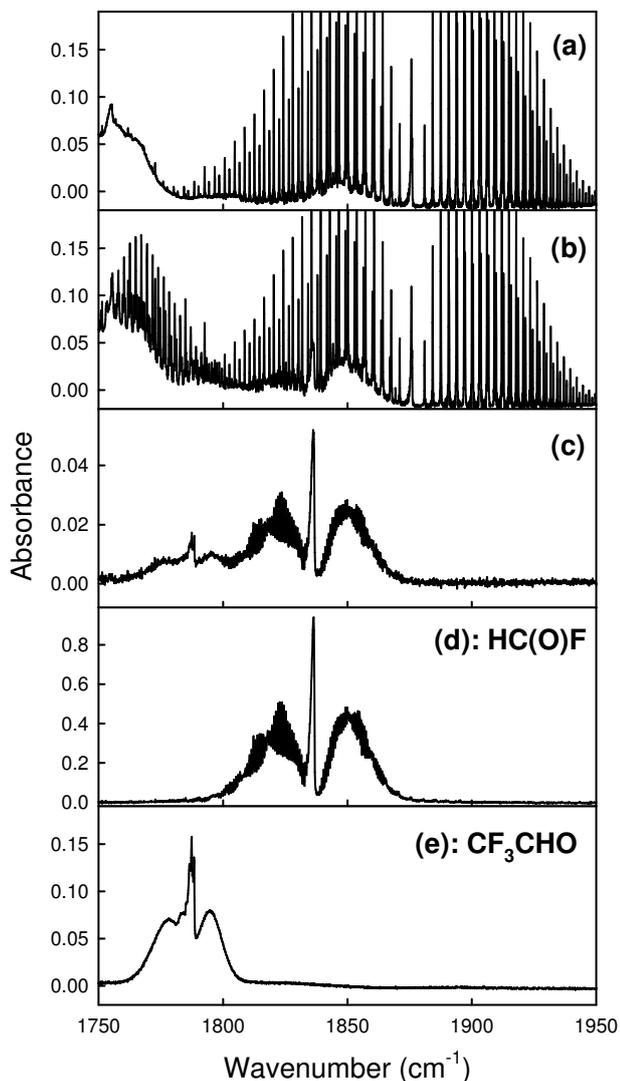


Fig. 1. Infrared spectra acquired before (a) and after (b) UV irradiation of a mixture of 34.9 mTorr trans-CF₃CH=CHF, 82.3 mTorr CH₃ONO, 19.6 mTorr NO and 126 Torr O₂ in 700 Torr total pressure of N₂ diluent. Panel (c) show the residual IR features after subtraction of features attributable to trans-CF₃CH=CHF, H₂O, NO, and HCHO from panel (b). Panels (d) and (e) show reference spectra of HC(O)F and CF₃CHO, respectively.

and trans-CF₃CH=CHF/Cl₂/O₂/N₂ mixtures. All samples of trans-CF₃CH=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 CH₃ONO in the presence of NO in air,



CH₃ONO was synthesized by the drop wise addition of concentrated sulfuric acid to a saturated solution of NaNO₂ in methanol. Other reagents were obtained from commercial sources at purities >99%. Experiments were conducted in 700 Torr total pressure of N₂/O₂, 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⁻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

3.1 Products of OH radical initiated oxidation of trans-CF₃CH=CHF

To investigate the products and mechanism of the reaction of OH radicals with trans-CF₃CH=CHF, reaction mixtures consisting of 8.3–34.9 mTorr trans-CF₃CH=CHF, 82.3–117.3 mTorr CH₃ONO, 0–19.6 mTorr NO, and 126–700 Torr O₂ in 700 Torr total pressure of N₂ diluent were introduced into the chamber and subjected to UV irradiation. Figure 1 shows IR spectra at 1750–1950 cm⁻¹ obtained before (a) and after (b) subjecting a mixture containing 34.9 mTorr trans-CF₃CH=CHF, 82.3 mTorr CH₃ONO, 19.6 mTorr NO, and 126 Torr O₂ in 700 Torr of N₂ diluent to 6 min of UV irradiation. The consumption of trans-CF₃CH=CHF was 6%. Subtraction of IR features attributable to CF₃CH=CHF, H₂O, NO, and HCHO (product of CH₃ONO 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 CF₃CHO 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 CF₃CHO were the only identified carbon containing products of the OH radical initiated oxidation of trans-CF₃CH=CHF. Figure 2 shows a plot of the observed formation of HC(O)F and CF₃CHO versus loss of trans-CF₃CH=CHF. The yields of HC(O)F and CF₃CHO were indistinguishable. There was no discernable effect on the HC(O)F and CF₃CHO yields of varying the O₂ 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-CF₃CH=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%.

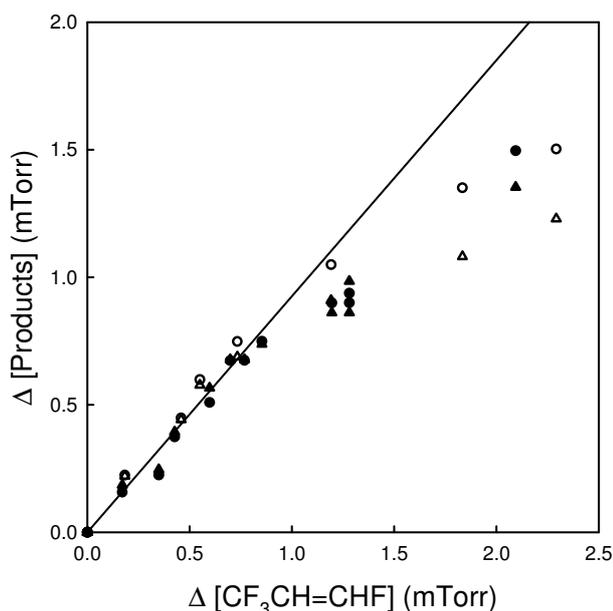


Fig. 2. Formation of HC(O)F (triangles) and CF₃CHO (circles) versus loss of trans-CF₃CH=CHF observed following the UV irradiation of mixtures of 8.32–9.18 mTorr trans-CF₃CH=CHF and 109.1–113.8 mTorr CH₃ONO in 700 Torr total pressure of air diluent at 296±1 K. Open symbols were obtained in experiments 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 CF₃CH=CHF greater than 1 mTorr the observed yields of HC(O)F and CF₃CHO are less than 100% indicating that either the efficiency of conversion of trans-CF₃CH=CHF into HC(O)F and CF₃CHO is lower, or there are significant losses of these products at higher trans-CF₃CH=CHF conversions, or both. To test for heterogeneous loss of HC(O)F and CF₃CHO, 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 CF₃CH=CHF was 25%. However, even at 25% conversion of CF₃CH=CHF the loss of HC(O)F and CF₃CHO via secondary reactions with OH radicals will be of relatively minor importance as their reactivity with OH are less than that of trans-CF₃CH=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 CF₃CHO, respectively, for a 25% consumption of CF₃CH=CHF.

It seems likely that the curvature in Fig. 2 reflects a lower yield of both HC(O)F and CF₃CHO with increased consumption of CF₃CH=CHF. A plausible explanation of this effect is the reaction of NO₂ (which

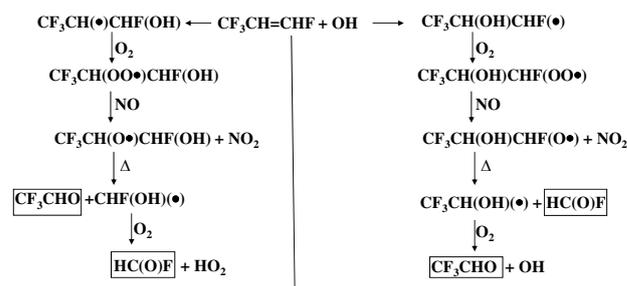


Fig. 3. Mechanism of OH radical initiated oxidation of trans-CF₃CH=CHF, boxes indicate observed products.

increases in concentration with consumption of trans-CF₃CH=CHF) with the alkoxy radicals formed in the system leading to the formation of small amounts of nitrates (CF₃CH(ONO₂)CHF(OH) and CF₃CH(OH)CHF(ONO₂)). Spectral congestion and the absence of authentic samples of CF₃CH(ONO₂)CHF(OH) and CF₃CH(OH)CHFONO₂ precluded the detection of small amounts (approx. 1 mTorr) of these nitrates. The concentration of NO₂ towards the end of the experiment was approximately 10 mTorr. Rate constants for reactions of NO₂ with alkoxy radicals are typically 1×10^{-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 NO₂ are expected to be approximately 10^4 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 NO₂ is a plausible explanation of the curvature seen in Fig. 2. In the atmosphere the reactions of the alkoxy radicals with NO₂ 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-CF₃CH=CHF is expected to proceed via addition to the >C=C< double bond. The mechanism of the OH radical initiated oxidation of trans-CF₃CH=CHF which explains the observed formation of HC(O)F and CF₃CHO 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 CF₃CHO.

3.2 Products of Cl atom initiated oxidation of trans-CF₃CH=CHF

The products of the Cl atom initiated oxidation of trans-CF₃CH=CHF were studied using the UV irradiation of trans-CF₃CH=CHF/Cl₂/O₂/N₂ mixtures. Mixtures consisting of 6.6–8.4 mTorr trans-CF₃CH=CHF, 102.9–134 mTorr Cl₂ and 5–700 Torr of O₂ in 700 Torr total pressure of N₂ diluent were introduced into the reaction chamber and subjected to UV irradiation. Figure 4 and 5 show IR spectra

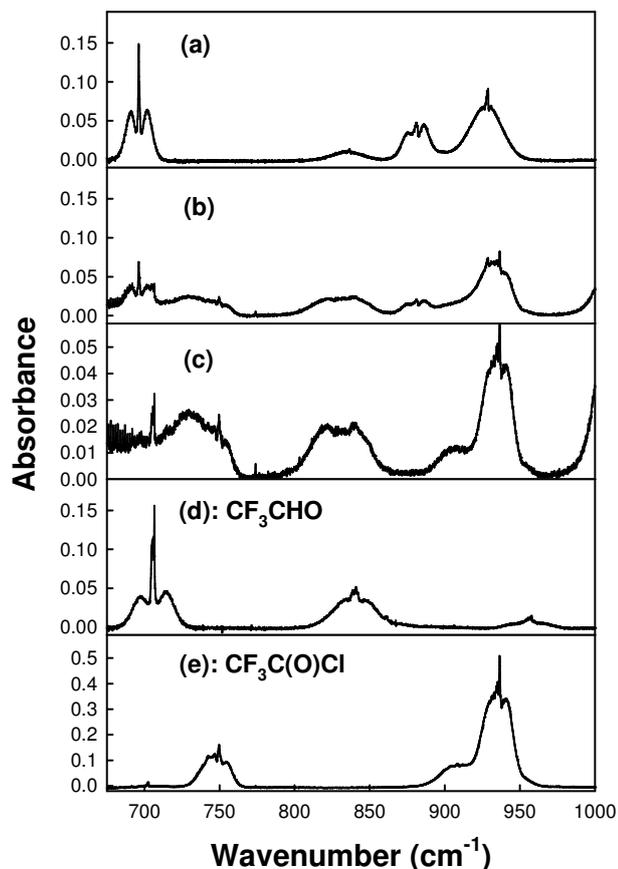


Fig. 4. Infrared spectra acquired before (a) and after (b) UV irradiation of 6.6 mTorr trans-CF₃CH=CHF and 109 mTorr Cl₂ in 700 Torr of air diluent. Panel (c) show the residual IR features after subtraction of trans-CF₃CH=CHF from panel (b). Panels (d) and (e) show reference spectra of CF₃CHO and CF₃C(O)Cl, respectively.

at 675–1000 cm⁻¹ and 1650–2000 cm⁻¹, respectively, obtained before (a) and after (b) subjecting a mixture containing 6.6 mTorr trans-CF₃CH=CHF and 109 mTorr Cl₂ in 700 Torr air diluent to 20 s of UV irradiation. Comparison of the IR features formed in low and high [O₂] experiments revealed that four products were formed in the chamber; HC(O)F, CF₃CHO, CF₃C(O)Cl, and a product with a broad absorption feature in the carbonyl stretching region centered at 1801 cm⁻¹ which we attribute to the ketone CF₃C(O)CHFCl (see below). We do not have a calibrated reference spectrum for CF₃C(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⁻¹ is the same as that in CF₃C(O)CH₂Cl (1.06×10^{-17} cm molecule⁻¹ (Nakayama et al., 2007)).

Figure 6 shows a plot of the concentrations of HC(O)F, CF₃CHO, CF₃C(O)Cl, and CF₃C(O)CHFCl versus the loss of trans-CF₃CH=CHF observed following the UV irradiation of a mixture of 6.61 mTorr trans-CF₃CH=CHF

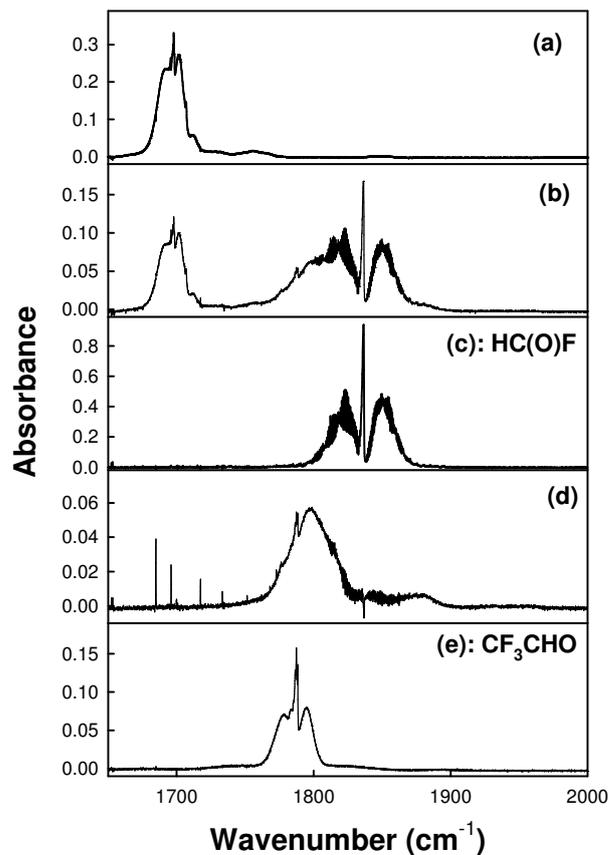


Fig. 5. Infrared spectra acquired before (a) and after (b) UV irradiation of 6.6 mTorr trans-CF₃CH=CHF and 109 mTorr Cl₂ in 700 Torr of air diluent. Panel (c) show a reference spectrum of HC(O)F. Panel (d) show the residual IR features after subtraction of trans-CF₃CH=CHF and HC(O)F from panel (b). Panel (e) shows a reference spectrum of CF₃CHO.

and 109 mTorr Cl₂ in 700 Torr of air diluent. As seen from Figure 6 the formation of HC(O)F, CF₃C(O)H, CF₃C(O)Cl and CF₃C(O)CHFCl scaled linearly with the loss of trans-CF₃CH=CHF over the range of trans-CF₃CH=CHF consumption of 10–95%. The linearity of the formation of HC(O)F, CF₃CHO, CF₃C(O)Cl and CF₃C(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-CF₃CH=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 $k(\text{Cl} + \text{CF}_3\text{CHO}) = (1.85 \pm 0.26) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ (Sulbaek Andersen et al., 2004). Previous work has shown that CF₃C(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).

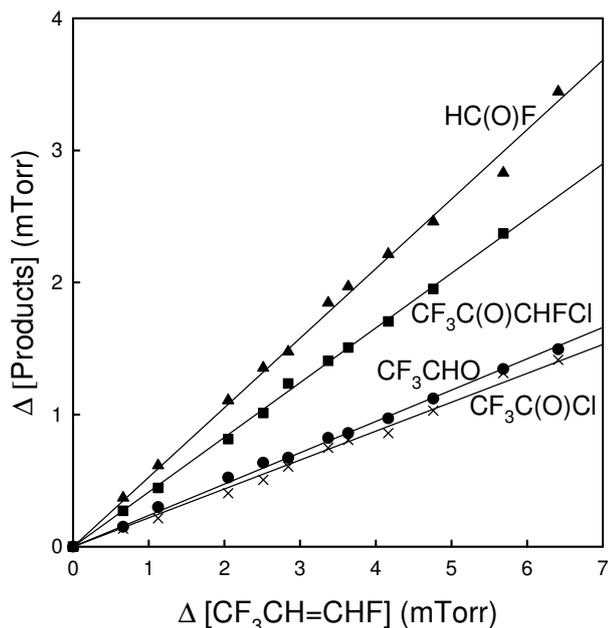


Fig. 6. Formation of HC(O)F (triangles), CF₃C(O)CHFCl (squares), CF₃CHO (circles) and CF₃C(O)Cl (crosses) versus loss of trans-CF₃CH=CHF observed following the UV irradiation of a mixture of 6.6 mTorr trans-CF₃CH=CHF and 109 mTorr Cl₂ in 700 Torr of air diluent.

As shown in Fig. 7, the yields of HC(O)F, CF₃CHO, CF₃C(O)Cl and CF₃C(O)CHFCl varied with [O₂]. In experiments with high [O₂] the yields of CF₃C(O)Cl and CF₃C(O)CHFCl increased at the expense of HC(O)F and CF₃CHO. As in the case of the OH radical attack, the reaction of Cl atoms with trans-CF₃CH=CHF is expected to proceed via electrophilic addition to the terminal and central carbon atoms:



The radicals produced in Reaction (5) will react with O₂ 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 O₂ are likely fates of the CF₃CH(O•)CHFCl and CF₃CHClCHF(O•) alkoxy radicals. The observed formation

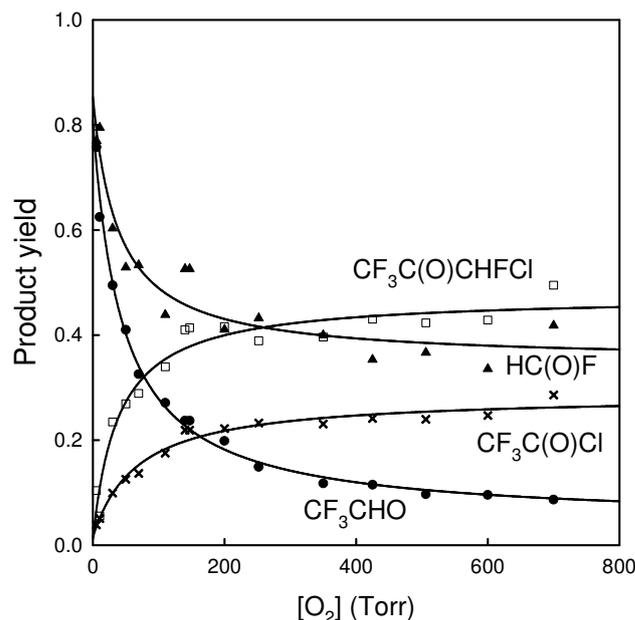
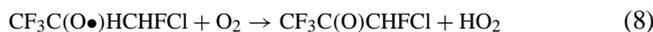


Fig. 7. Observed molar yields of HC(O)F (triangles), CF₃CHO (circles), CF₃C(O)Cl (crosses) and CF₃C(O)CHFCl (squares) versus the O₂ partial pressure following the UV irradiation of trans-CF₃CH=CHF/Cl₂/N₂/O₂ mixtures at 700 Torr total pressure. Curves through the CF₃C(O)CHFCl and CF₃C(O)Cl are fits to the data using the expressions described in the text. The curves through the HC(O)F and CF₃CHO data are polynomial fits to aid visual inspection of data trends.

of the ketone CF₃C(O)CHFCl in a yield which varies with [O₂] shows that CF₃C(O•)HCHFCl radicals undergo reaction with O₂ and decomposition via C-C bond scission:



The CHFCl(•) radicals formed in Reaction (9) will add O₂, 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 CF₃C(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 CF₃CH(O•)CHFCl radicals in the system, k_8 and k_9 are the rate constants for Reactions (8) and (9), and C is the [O₂] independent yield of CF₃C(O)CHFCl (e.g. from self-reaction of CF₃CH(OO•)CHFCl peroxy radicals).

The curve through the CF₃C(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

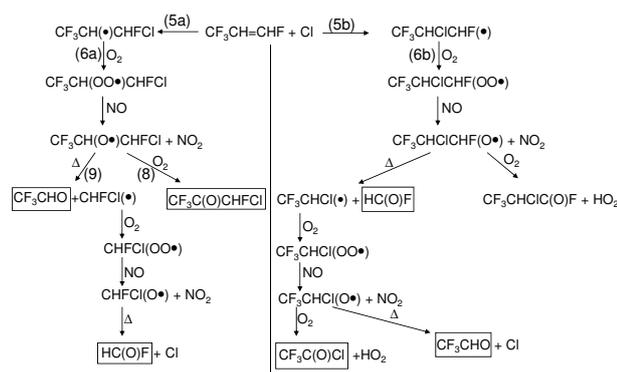


Fig. 8. Atmospheric mechanism of Cl atom initiated oxidation of trans-CF₃CH=CHF, boxes indicate observed products.

CF₃CH(O•)CH₂Cl radicals (Nakayama et al., 2007). The increased importance of decomposition as an atmospheric fate of CF₃CH(O•)CHFCI compared to CF₃CH(O•)CH₂Cl 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 CF₃C(O)CHFCI yield reached at high [O₂] 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-CF₃CH=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 O₂ the reaction with O₂ accounts for 92% of the CF₃CH(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 O₂ to the decomposition of CF₃CHCl(O•) radicals. Decomposition via C-C bond scission is therefore the dominant fate of CF₃CHCl(O•) radicals. Finally, the increase in the yield of CF₃C(O)Cl with [O₂] evident in Fig. 7 is consistent with the expected competition between reaction with O₂ and decomposition for the available CF₃CHCl(O•) radicals. The yield of CF₃C(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 CF₃CHCl(O•) radicals in the system, k_{10} and k_{11} are the rate constants for Reactions (10) and (11), and C is the [O₂] independent yield of CF₃C(O)Cl.



The curve through the CF₃C(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 CF₃CHCl(O•) radicals are formed in the present system. As indicated in Fig. 8, decomposition and reaction with O₂ are possible competing fates for CF₃CHCl(O•) radicals. Increased loss of CF₃CHCl(O•) via reaction with O₂ at high [O₂] will lead to a decreased yield of CF₃CHCl(O•) radicals and hence CF₃C(O)Cl. The net effect will be to cause the CF₃C(O)Cl yield to plateau at a lower [O₂] which will lead to an overestimation of k_{10}/k_{11} . To investigate this effect further would require the use of [O₂] levels higher than 700 Torr where a decrease in the yield of CF₃C(O)Cl would be expected with increased loss of CF₃CHCl(O•) via reaction with O₂. Such experiments are beyond the scope of the present work.

4 Atmospheric chemistry and environmental impact of trans-CF₃CH=CHF

The present work improves our understanding of the atmospheric chemistry of trans-CF₃CH=CHF. The atmospheric lifetime of trans-CF₃CH=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-CF₃CH=CHF gives CF₃CHO and HC(O)F in yields of approximately 100%. CF₃CHO 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 CF₃ and HCO radicals (Chiappero et al., 2006) while reaction with OH gives CF₃CO radicals. CF₃ radicals will add O₂ to give CF₃O₂ radicals which are then converted into COF₂ (Wallington et al., 1994) which hydrolyzes to give CO₂ and HF. CF₃CO radicals will add O₂ to give CF₃C(O)O₂ radicals, the majority of which will be converted into COF₂, with a small fraction converted into CF₃C(O)OH via reaction with HO₂ radicals (Hurley et al., 2006). The hydrate, CF₃CF(OH)₂ is lost via reaction with OH radicals to give CF₃C(O)OH. The available data suggest that while CF₃C(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-CF₃CH=CHF oxidation will be of negligible environmental significance. We conclude that the products of the atmospheric oxidation of trans-CF₃CH=CHF will have negligible environmental impact.

Acknowledgements. MSJ, RS and OJN acknowledge financial support from the Danish Natural Science Research Council for the Copenhagen Center for Atmospheric Research (CCAR).

Edited by: J. N. Crowley

References

- Chiappero, M. S., Malanca, F. E., Argüello, G. A., Wooldridge, S. T., Hurley, M. D., Ball, J. C., Wallington, T. J., Waterland, R. L., and Buck, R. C.: Atmospheric chemistry of perfluoroaldehydes (C_xF_{2x+1}CHO) and fluorotelomer aldehydes (C_xF_{2x+1}CH₂CHO): quantification of the important role of photolysis, *J. Phys. Chem. A*, 110, 11 944–11 953, 2006.
- Farman, J. D., Gardiner, B. G., and Shanklin, J. D.: Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction, *Nature*, 315, 207–210, 1985.
- Frank, H., Christoph, E. H., Holm-Hansen, O., and Bullister, J. L.: Trifluoroacetate in ocean waters, *Environ. Sci. Technol.*, 36, 12–15, 2002.
- Hurley, M. D., Ball, J. C., Wallington, T. J., Sulbaek Andersen, M. P., Nielsen, O. J., Ellis, D. A., Martin, J. W., and Mabury, S. A.: Atmospheric chemistry of *n*-C_xF_{2x+1}CHO (*x* = 1, 2, 3, 4): fate of *n*-C_xF_{2x+1}C(O) radicals, *J. Phys. Chem. A*, 110, 12 443–12 447, 2006.
- IUPAC, available at: <http://www.iupac-kinetic.ch.cam.ac.uk>, 2007, last access: January 2008.
- Maricq, M. M. and Szente, J. J.: Flash photolysis-time-resolved UV spectroscopy of the 1, 2, 2, 2-tetrafluoroethylperoxy radical self-reaction, *J. Phys. Chem.*, 96, 10 862–10 868, 1992.
- Meagher, R. J., McIntosh, M. E., Hurley, M. D., and Wallington, T. J.: A kinetic study of the reaction of chlorine and fluorine atoms with HC(O)F at 295±2 K, *Int. J. Chem. Kinet.*, 29, 619–625, 1997.
- Molina, M. J. and Rowland, F. S.: Stratospheric sink for chlorofluoromethanes: chlorine atom catalysed destruction of ozone, *Nature*, 249, 810–812, 1974.
- Møgelberg, T. E., Nielsen, O. J., Sehested, J., and Wallington, T. J.: Atmospheric chemistry of HCFC-133a: the UV absorption spectra of CF₃CClH and CF₃CClHO₂ radicals, reactions of CF₃CClHO₂ with NO and NO₂, and fate of CF₃CClHO radicals, *J. Phys. Chem.*, 99, 13 437–13 444, 1995.
- Nakayama, T., Takahashi, K., Matsumi, Y., Sulbaek Andersen, M. P., Nielsen, O. J., Waterland, R. L., Buck, R. C., Hurley, M. D., and Wallington, T. J.: Atmospheric chemistry of CF₃CH=CH₂ and C₄F₉CH=CH₂: products of the gas-phase reactions with Cl atoms and OH radicals, *J. Phys. Chem. A*, 111, 909–915, 2007.
- Nielsen, O. J., Scott, B. F., Spencer, C., Wallington, T. J., and Ball, J. C.: Trifluoroacetic acid in ancient freshwater, *Atmos. Environ.*, 35, 2799–2801, 2001.
- Somnitz, H. and Zellner, R.: Theoretical studies of the thermal and chemically activated decomposition of CF₃CY₂O (Y = F, H) radicals, *Phys. Chem. Chem. Phys.*, 3, 2352–2364, 2001.
- Sulbaek Andersen, M. P., Nielsen, O. J., Hurley, M. D., Wallington, T. J., Stevens, J. E., Marten, J. W., Ellis, D. A., and Mabury, S. A.: Atmospheric chemistry of *n*-C_xF_{2x+1}CHO (*x* = 1, 3, 4): reaction with Cl atoms, OH radicals and IR spectra of C_xF_{2x+1}C(O)O₂NO₂, *J. Phys. Chem. A*, 108, 5189–5196, 2004.
- Sulbaek Andersen, M. P., Toft, A., Nielsen, O. J., Hurley, M. D., Wallington, T. J., Chishima, H., Tonokura, K., Mabury, S. A., Martin, J. W., and Ellis, D. A.: Atmospheric chemistry of perfluorinated aldehyde hydrates (*n*-C_xF_{2x+1}CH(OH)₂, *x* = 1, 3, 4): hydration, dehydration, and kinetics and mechanism of Cl atom and OH radical initiated oxidation, *J. Phys. Chem. A*, 110, 9854–9860, 2006.
- Søndergaard, R., Nielsen, O. J., Hurley, M. D., Wallington, T. J., and Singh, R.: Atmospheric chemistry of trans-CF₃CH=CHF: kinetics of the gas-phase reactions with Cl atoms, OH radicals, and O₃, *Chem. Phys. Lett.*, 443, 199–204, 2007.
- Tuazon, E. C. and Atkinson, R.: Tropospheric transformation products of a series of hydrofluorocarbons and hydrochlorofluorocarbons, *J. Atmos. Chem.*, 17, 179–199, 1993.
- Wallington, T. J. and Hurley, M. D.: Atmospheric chemistry of formyl fluoride: reaction with hydroxyl radicals, *Environ. Sci. Technol.*, 27, 1448–1452, 1993.
- Wallington, T. J. and Japar, S. M.: Fourier transform infrared kinetic studies of the reaction of HONO with HNO₃, NO₃ and N₂O₅ at 295 K, *J. Atmos. Chem.*, 9, 399–409, 1989.
- Wallington, T. J., Schneider, W. F., Worsnop, D. R., Nielsen, O. J., Sehested, J., DeBruyn, W., and Shorter, J. A.: The environmental impact of CFC replacements-HFCs and HCFCs, *Environ. Sci. Technol.*, 28, 320A–326A, 1994.
- World Meteorological Organization, Scientific Assessment of Ozone Depletion: 2006, Geneva, 2007.