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

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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.

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, CF₃CH₂F (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 radicals. HFC-134a has a direct global warming potential of 1440 over a 100 y 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 hy-

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

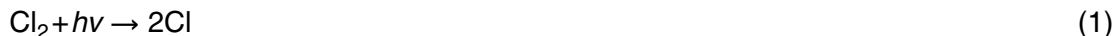
Interactive Discussion

drofluorocarbons. 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).

2 Experimental

Experiments were performed in a 140-liter 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 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,



Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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.

5 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

10 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, 15.1–19.6 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) 15
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) 20
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.

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 25
formation of HC(O)F and CF₃CHO versus loss of trans-CF₃CH=CHF. The yields of HC(O)F and CF₃CHO were indistinguishable. For low consumptions (<1 mTorr) the

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Atmospheric
chemistry of
trans-CF₃CH=CHF**

M. S. Javadi et al.

linear least squares fit to the combined data sets has a slope = 0.93 ± 0.08 indistinguishable from 100%. 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. For the 2–14% conversions of trans-CF₃CH=CHF in the data shown in Fig. 2, loss of HC(O)F and CF₃CHO via secondary reactions with OH radicals should be of minor importance as their reactivity with OH is 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 $k(\text{OH} + \text{CF}_3\text{CHO}) = (6 \pm 1.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2007). 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 possible explanation of this effect is the reaction of NO₂ (which 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. In the atmosphere such reactions 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 as 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.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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. Figures 4 and 5 show IR spectra 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. 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 and 109 mTorr Cl₂ in 700 Torr of air diluent. As seen from Fig. 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.,

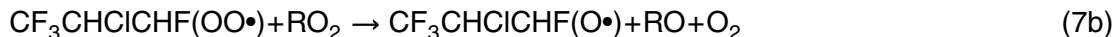
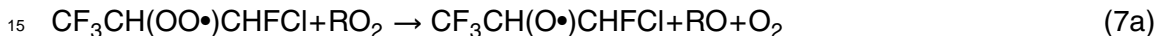
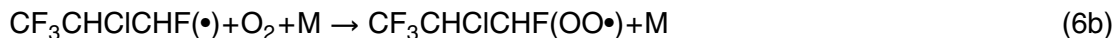
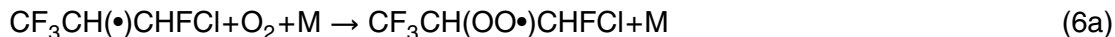
[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

2004). Previous work has shown that $\text{CF}_3\text{C}(\text{O})\text{Cl}$ is not lost by heterogeneous processes, photolysis, or reaction with Cl atoms in the chamber (Møgelberg et al., 1995).

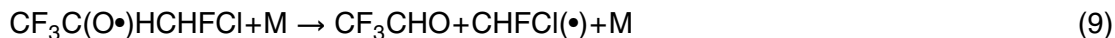
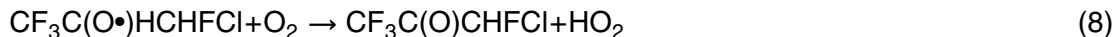
As shown in Fig. 7, the yields of $\text{HC}(\text{O})\text{F}$, CF_3CHO , $\text{CF}_3\text{C}(\text{O})\text{Cl}$ and $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ varied with $[\text{O}_2]$. In experiments with high $[\text{O}_2]$ the yields of $\text{CF}_3\text{C}(\text{O})\text{Cl}$ and $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ increased at the expense of $\text{HC}(\text{O})\text{F}$ and CF_3CHO . As in the case of the OH radical attack, the reaction of Cl atoms with $\text{trans-CF}_3\text{CH}=\text{CHF}$ is expected to proceed via electrophilic addition to the terminal and central carbon atoms:



The radicals produced in Reaction (5) will react with O_2 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_2 are likely fates of the alkoxy radicals. The observed formation of the ketone $\text{CF}_3\text{C}(\text{O})\text{CHFCl}$ in a yield which varies with $[\text{O}_2]$ shows that $\text{CF}_3\text{C}(\text{O}\bullet)\text{HCHFCl}$ radicals undergo reaction with O_2 and decomposition via C-C bond scission:



Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

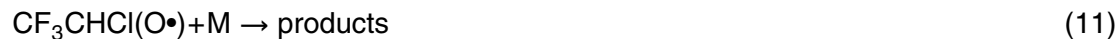
The CHFCl(•) radicals formed in Reaction (9) will add O₂, undergo reaction with other peroxy radicals in the system to give CHFCl(O•) radicals, and decompose via Cl atom elimination to give HC(O)F (Tuazon et al., 1993). The data in Fig. 7 contain information concerning the rate constant ratio k_8/k_9 . The yield of CF₃C(O)CHFCl, $Y_{CF_3C(O)CHFCl}$, can be described by the expression $Y_{CF_3C(O)CHFCl} = Y_{CF_3CH(O•)CHFCl} (k_8[O_2]/(k_8[O_2]+k_9)) + C$, where $Y_{CF_3CH(O•)CHFCl}$ 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 $k_{O_2}/k_{diss} = (3.8 \pm 1.8) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$ measured for CF₃CH(O•)CH₂Cl radicals (Nakayama et al., 2007). The increased importance of decomposition as an atmospheric fate of CF₃CH(O•)CHFCl 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)CHFCl yield reached at high [O₂] provides a measure of $k_{5a}/(k_{5a}+k_{5b}) = 47 \pm 7\%$.

Figure 8 shows the mechanism of Cl atom initiated oxidation of trans-CF₃CH=CHF which is consistent with our experimental observations. From $k_8/k_9 = (8.0 \pm 2.6) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ it can be calculated that in 700 Torr of O₂ the reaction with O₂ accounts for 92% of the CF₃CH(O•)CH₂Cl radicals with decomposition accounting for the remaining 8%. Given the estimate of $k_{5a}/(k_{5a}+k_{5b}) = 47 \pm 7\%$ 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 CF₃CHClCHF(O•) radicals. Decomposition via C-C bond scission is the dominant fate of CF₃CHClCHF(O•) radicals. Finally, the increase in the yield of CF₃C(O)Cl

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

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_{CF₃C(O)Cl}, can be described by the expression $Y_{CF_3C(O)Cl} = Y_{CF_3CHCl(O\bullet)} (k_{10}[O_2]/(k_{10}[O_2]+k_{11})) + C$, where Y_{CF₃CHCl(O•)} is the yield of CF₃CHCl(O•) radicals in the system, k₁₀ and k₁₁ 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 CF₃CHClCHF(O•) radicals. Increased loss of CF₃CHClCHF(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 k₁₀/k₁₁. 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 CF₃CHClCHF(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

**Atmospheric
chemistry of
trans-CF₃CH=CHF**

M. S. Javadi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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 lesser extents, 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 (Hurley et al., 2006) via reaction with HO₂ radicals. The hydrate, CF₃CH(OH)₂ is lost via reaction with OH radicals to give CF₃C(O)OH (Sulbaek Andersen et al., 2006). 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.

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**Atmospheric
chemistry of
trans-CF₃CH=CHF**

M. S. Javadi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- 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, 12443–12447, 2006.
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**Atmospheric
chemistry of
trans-CF₃CH=CHF**M. S. Javadi et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Atmospheric
chemistry of
 $\text{trans-CF}_3\text{CH=CHF}$

M. S. Javadi et al.

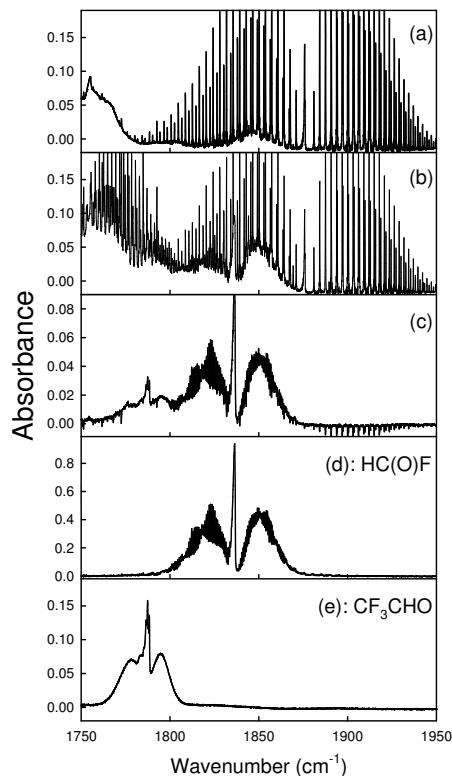


Fig. 1. Infrared spectra acquired before **(a)** and after **(b)** UV irradiation of mixtures 34.9 mTorr $\text{trans-CF}_3\text{CH=CHF}$, 82.3 mTorr CH_3ONO , 19.6 mTorr NO and 126 Torr O_2 in 700 Torr total pressure of N_2 diluent. Panel **(c)** show the residual IR features after subtraction of features attributable to $\text{trans-CF}_3\text{CH=CHF}$, H_2O , NO , and HCHO from panel (b). Panels **(d)** and **(e)** show reference spectra of HC(O)F and CF_3CHO , respectively.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Atmospheric
chemistry of
 $\text{trans-CF}_3\text{CH=CHF}$

M. S. Javadi et al.

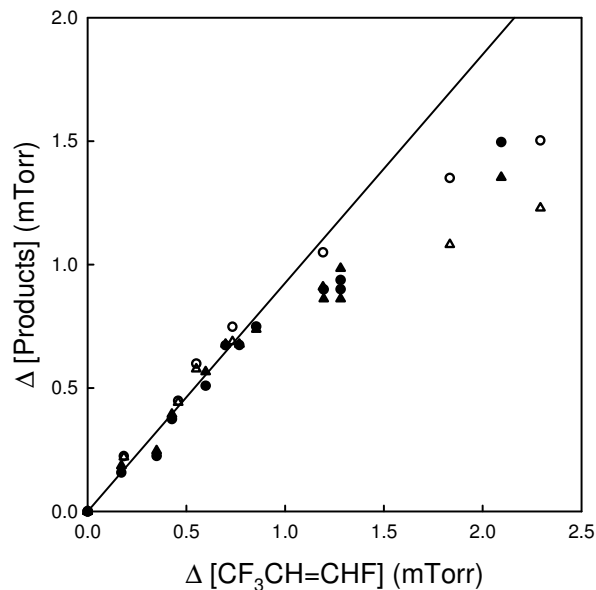


Fig. 2. Formation of HC(O)F (triangles) and CF_3CHO (circles) versus loss of $\text{trans-CF}_3\text{CH=CHF}$ observed following the UV irradiation of mixtures of 8.32–9.18 mTorr $\text{trans-CF}_3\text{CH=CHF}$ and 109.1–113.8 mTorr CH_3ONO in 700 Torr total pressure of air diluent at 296 ± 1 K. The open symbols are results obtained in the absence of NO .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Atmospheric chemistry of *trans*-CF₃CH=CHF

M. S. Javadi et al.

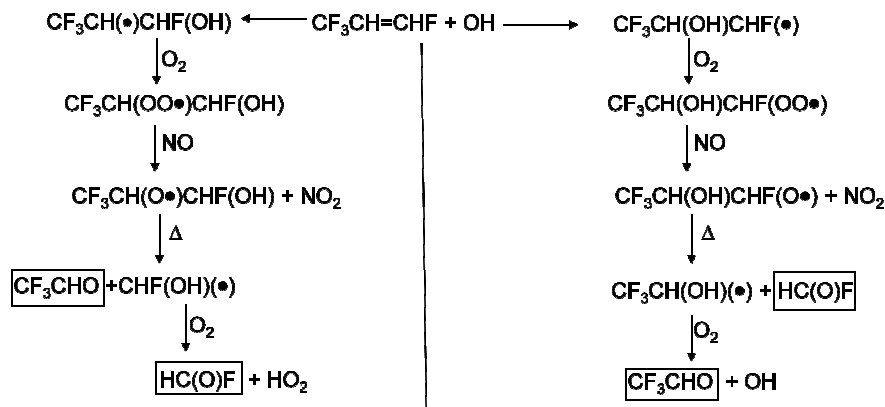


Fig. 3. Mechanism of OH radical initiated oxidation of *trans*-CF₃CH=CHF, boxes indicate observed products.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Atmospheric
chemistry of
 $\text{trans-CF}_3\text{CH=CHF}$

M. S. Javadi et al.

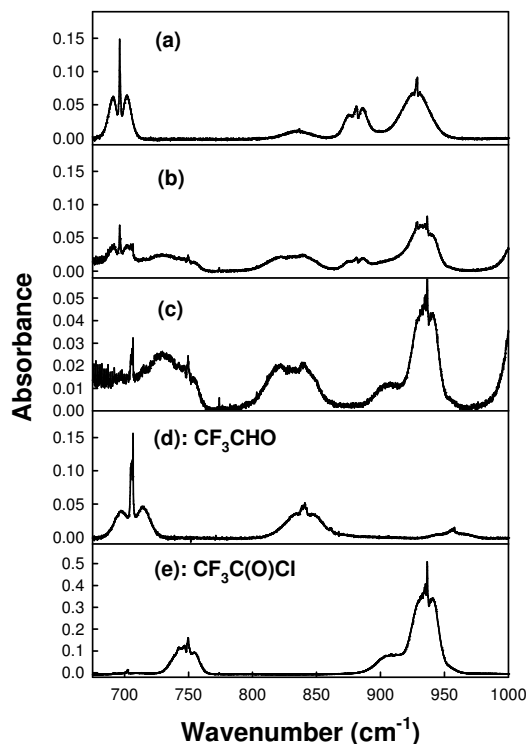


Fig. 4. Infrared spectra acquired before (a) and after (b) UV irradiation of 6.6 mTorr $\text{trans-CF}_3\text{CH=CHF}$ and 109 mTorr Cl_2 in 700 Torr of air diluent. Panel (c) show the residual IR features after subtraction of $\text{trans-CF}_3\text{CH=CHF}$ from panel (b). Panels (d) and (e) show reference spectra of CF_3CHO and $\text{CF}_3\text{C(O)Cl}$, respectively.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Atmospheric
chemistry of
trans-CF₃CH=CHF

M. S. Javadi et al.

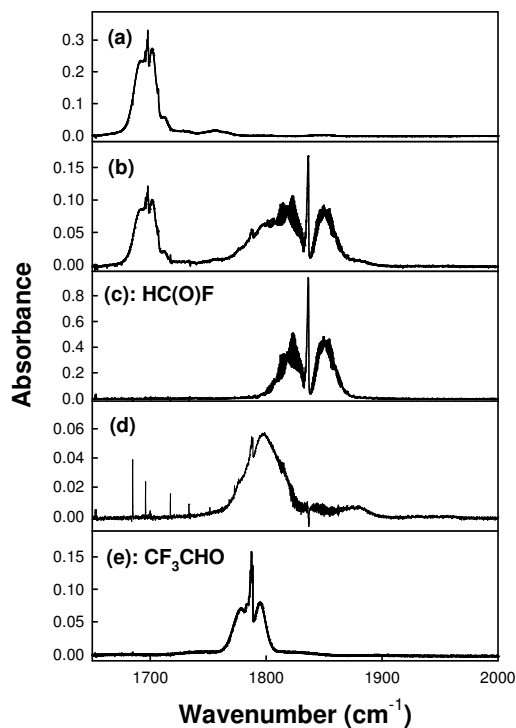


Fig. 5. Infrared spectra acquired before **(a)** and after **(b)** UV irradiation of 6.6 mTorr trans-CF₃CH=CHF and 109 mTorr Cl₂ in 700 Torr of air diluent. Panel **(c)** show a reference spectrum of HC(O)F. Panel **(d)** show the residual IR features after subtraction of trans-CF₃CH=CHF and HC(O)F from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

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Atmospheric
chemistry of
 $\text{trans-CF}_3\text{CH=CHF}$

M. S. Javadi et al.

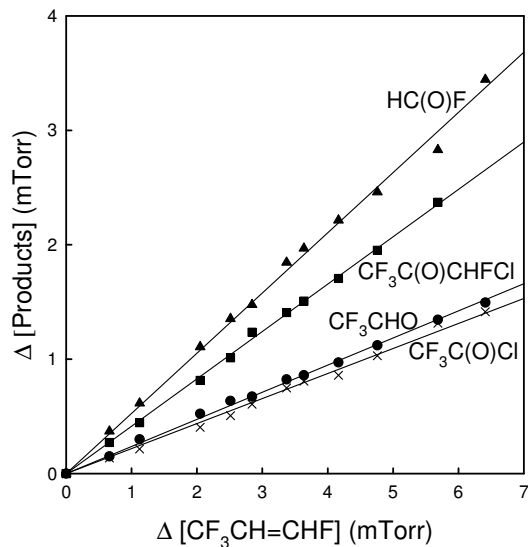


Fig. 6. Formation of HC(O)F (triangles), $\text{CF}_3\text{C(O)CHFCl}$ (squares), CF_3CHO (circles) and, $\text{CF}_3\text{C(O)Cl}$ (crosses) versus loss of $\text{trans-CF}_3\text{CH=CHF}$ observed following the UV irradiation of a mixture of 6.6 mTorr $\text{trans-CF}_3\text{CH=CHF}$ and 109 mTorr Cl_2 in 700 Torr of air diluent.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Atmospheric
chemistry of
 $\text{trans-CF}_3\text{CH=CHF}$

M. S. Javadi et al.

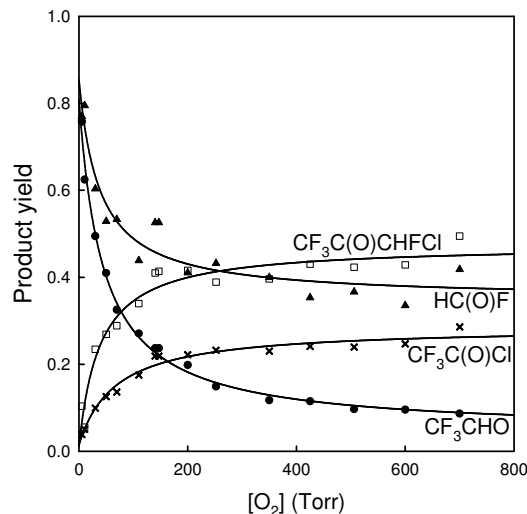


Fig. 7. Observed molar yields of HC(O)F (triangles), CF₃CHO (circles), CF₃C(O)Cl (crosses) and CF₃C(O)CHFCl (squares) versus the O₂ partial pressure following the UV irradiation of trans-CF₃CH=CHF/Cl₂/N₂/O₂ mixtures at 700 Torr total pressure. Curves through the CF₃C(O)CHFCl and CF₃C(O)Cl are fits to 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.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Atmospheric chemistry of trans-CF₃CH=CHF

M. S. Javadi et al.

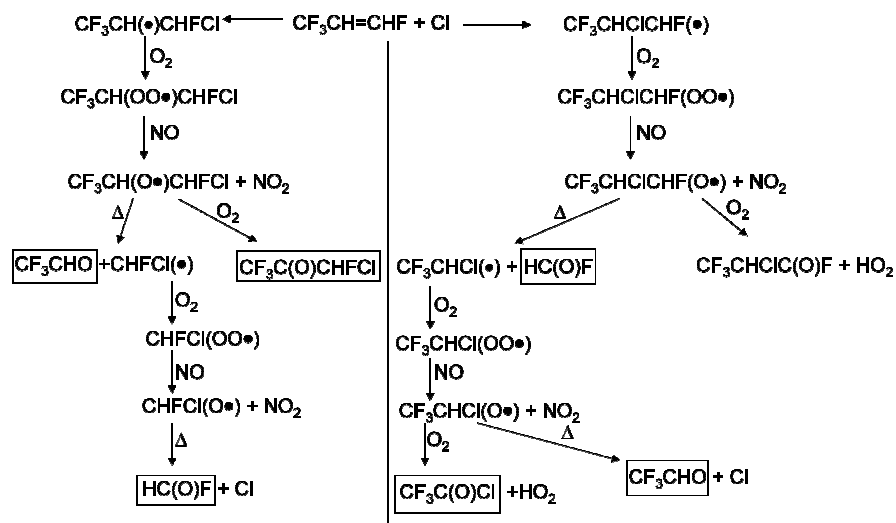


Fig. 8. Mechanism of Cl atom initiated oxidation of trans-CF₃CH=CHF, boxes indicate observed products.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion