

Atmospheric Impact of HFO-1234yf ($\text{CF}_3\text{CF}=\text{CH}_2$)

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Outline

- Background
- Smog chamber experiments
- Impact on climate change
- Impact on stratospheric ozone
- Impact on tropospheric ozone
- Conclusions



Background

- CFC-12 (CF_2Cl_2) replaced by HFC-134a (CH_2FCF_3) in 90s.
- HFC-134a has GWP_{100} of 1430
- Regulations developed by the European Union require refrigerants with $\text{GWPs} < 150$ for all new vehicles by 2017.
- HFO-1234yf ($\text{CF}_3\text{CF}=\text{CH}_2$) under consideration as replacement for R-134a.

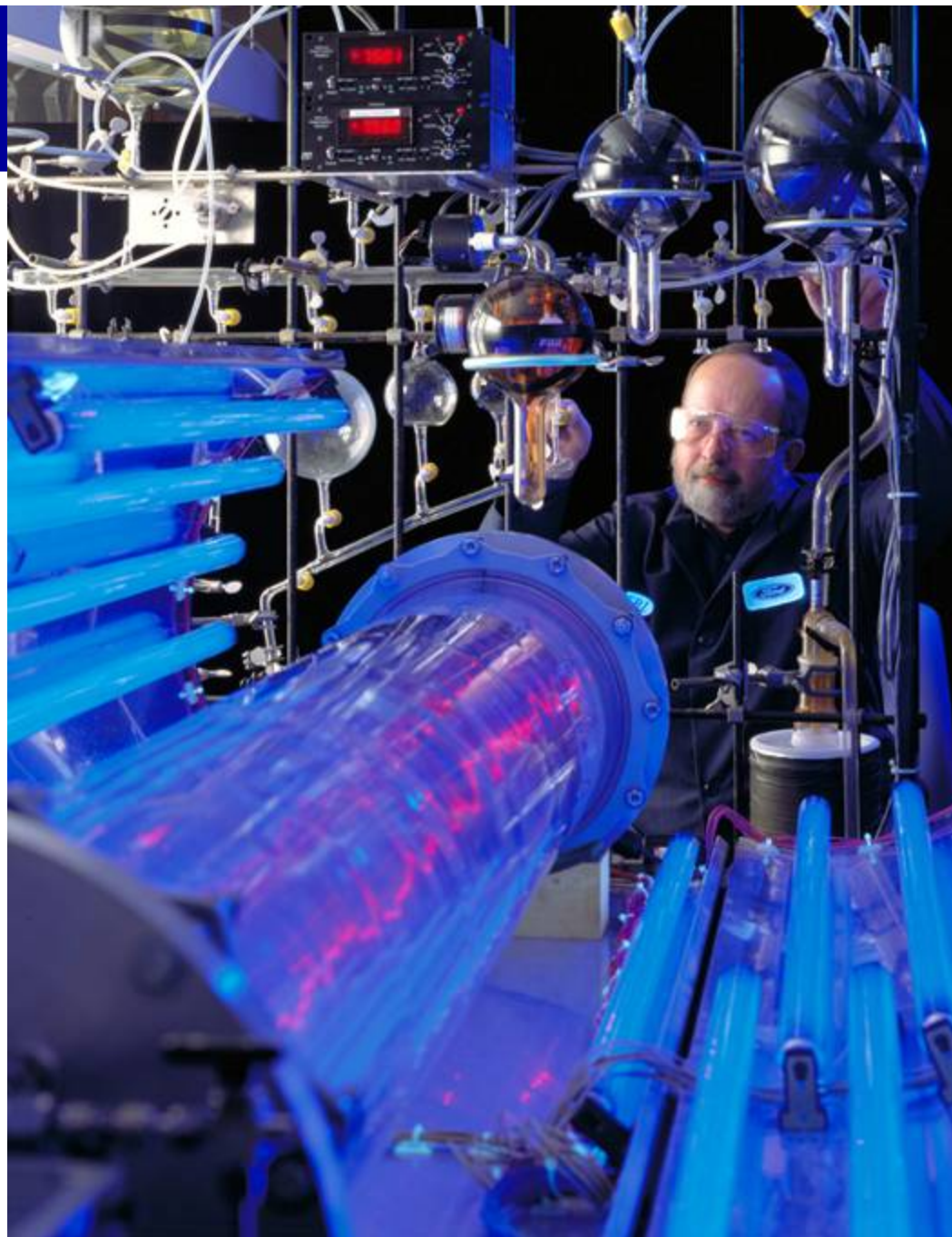


Ford Smog Chamber

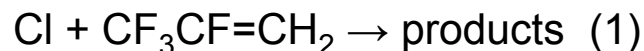
Experimental study of kinetics of reactions with OH radicals, Cl atoms, O₃.

Measurement of products of OH radical and Cl atom initiated oxidation.

IR spectrum, radiative efficiency, and global warming potential.



Chlorine atom kinetics



Linear least squares analysis gives

$$k_1/k_2 = 0.76 \pm 0.04 \text{ and } k_1/k_3 = 1.38 \pm 0.06.$$

Using $k_2 = (9.29 \pm 0.51) \times 10^{-11}$ and $k_3 = (5.07 \pm 0.34) \times 10^{-11}$

gives $k_1 = (7.06 \pm 0.54) \times 10^{-11}$ and $(7.00 \pm 0.56) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Hence $k_1 = (7.03 \pm 0.59) \times 10^{-11}$

$$k(\text{Cl} + \text{CH}_3\text{CH}=\text{CH}_2) = 2.4 \times 10^{-10}$$

$$k(\text{Cl} + \text{CF}_3\text{CH}=\text{CH}_2) = (9.07 \pm 1.08) \times 10^{-11}$$

$$k(\text{Cl} + \text{CF}_3\text{CF}=\text{CF}_2) = (2.7 \pm 0.3) \times 10^{-11}$$

Reaction with Cl atoms not major atmospheric loss of $\text{CF}_3\text{CF}=\text{CH}_2$.

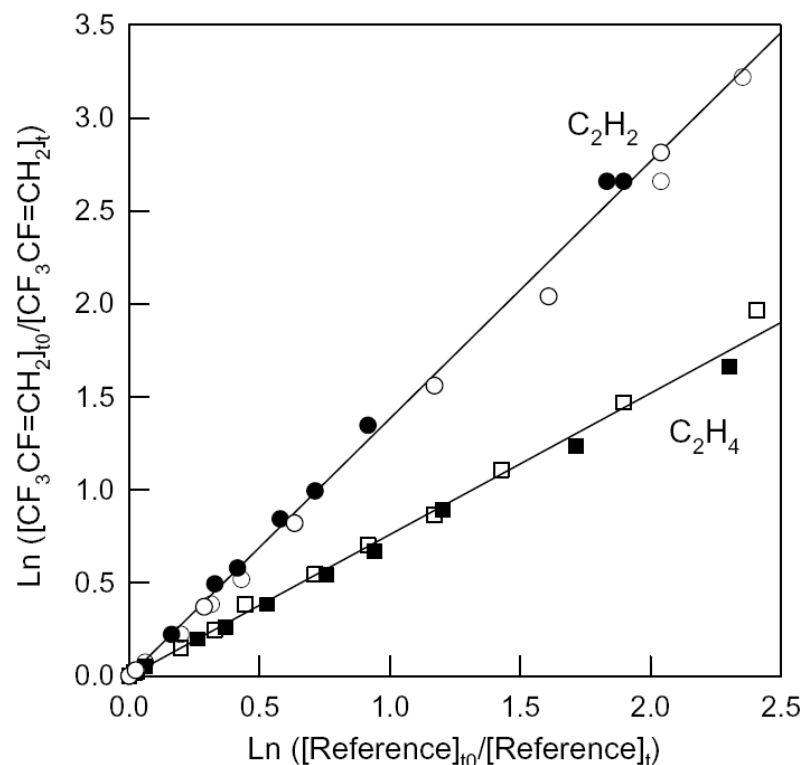
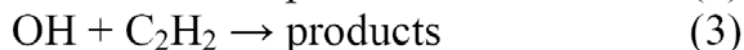
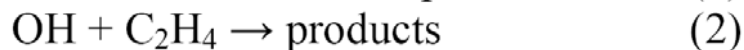
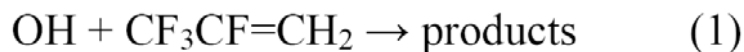


Fig. 1. Decay of $\text{CF}_3\text{CF}=\text{CH}_2$ vs. C_2H_4 and C_2H_2 in the presence of Cl atoms in 700 Torr of either air (open symbols) or N_2 (filled symbols) at $296 \pm 2 \text{ K}$.

OH radical kinetics



$$k_1/k_2 = 0.125 \pm 0.007 \text{ and } k_1/k_3 = 1.21 \pm 0.09$$

$$\text{Using } k_2 = (8.52 \pm 1.28) \times 10^{-12} \\ \text{and } k_3 = (8.45 \pm 0.85) \times 10^{-13}$$

$$\text{gives } k_1 = (1.07 \pm 0.17) \times 10^{-12} \\ \text{and } (1.02 \pm 0.13) \times 10^{-12}.$$

$$\text{hence } k_1 = (1.05 \pm 0.17) \times 10^{-12}.$$

assuming $[\text{OH}] = 10^6 \text{ cm}^{-3}$
gives lifetime = 11 days.

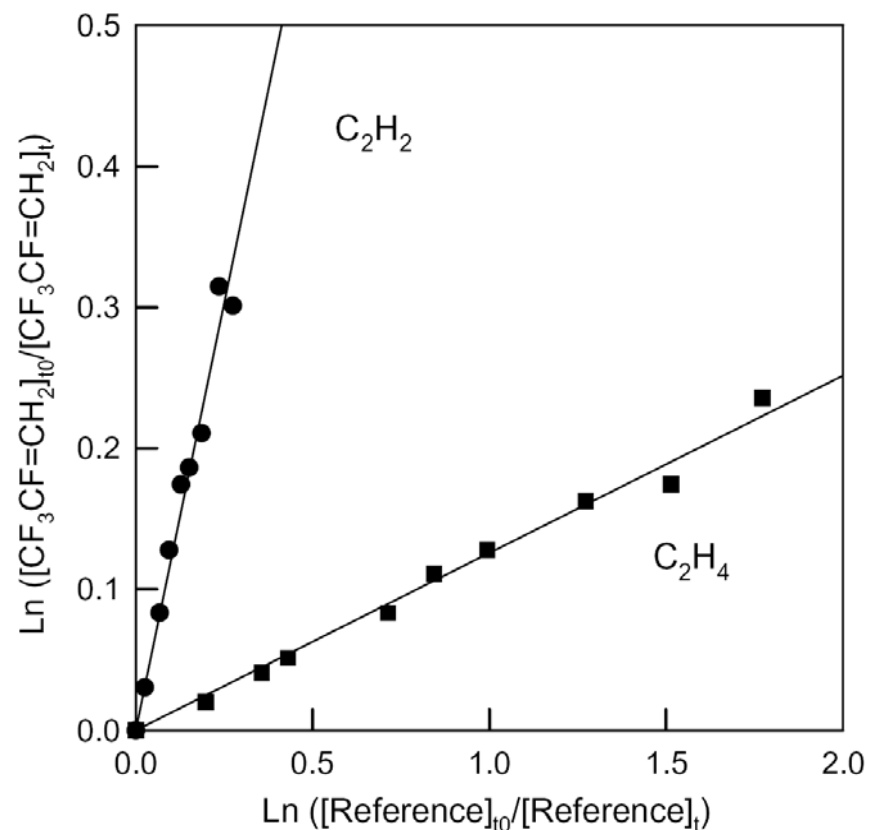


Fig. 2. Decay of $\text{CF}_3\text{CF}=\text{CH}_2$ vs. C_2H_4 and C_2H_2 in the presence of OH radicals in 700 Torr of air at $296 \pm 2 \text{ K}$.

Ozone kinetics

Pseudo first order decays of $\text{CF}_3\text{CF}=\text{CH}_2$ observed in all experiments.

Second order plot gives

$$k = (2.77 \pm 0.21) \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Combining with $[\text{O}_3] = 35 \text{ ppb}$ gives lifetime of 13 years with respect to reaction with O_3 .

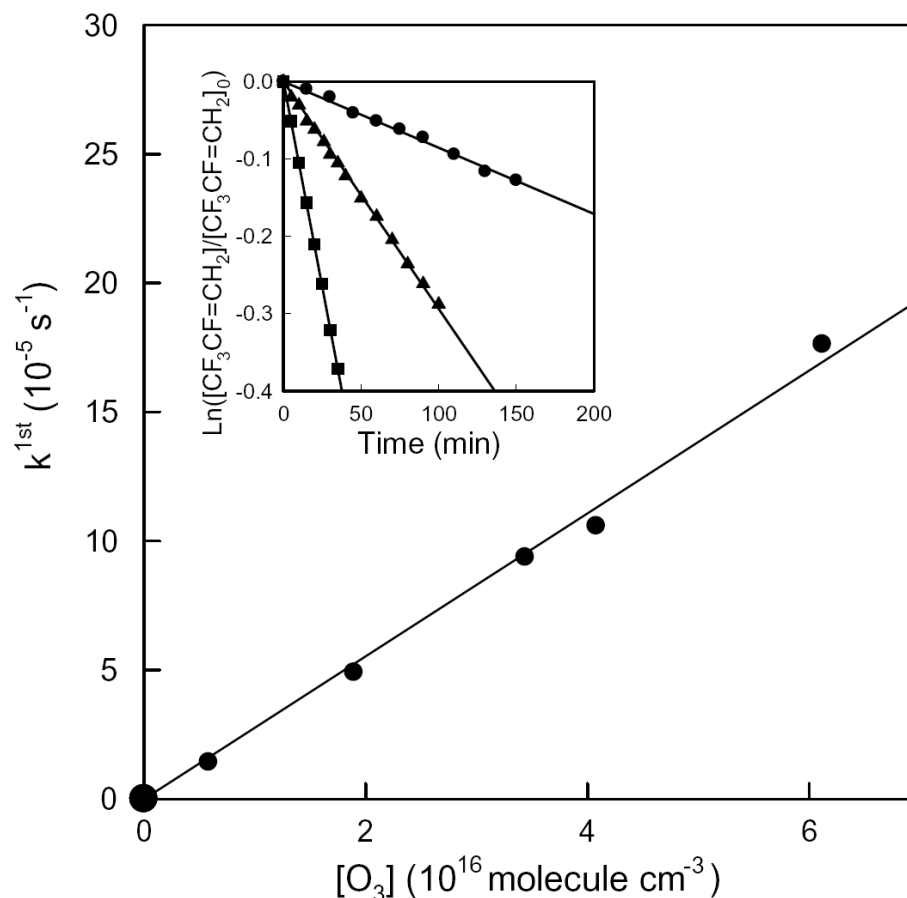


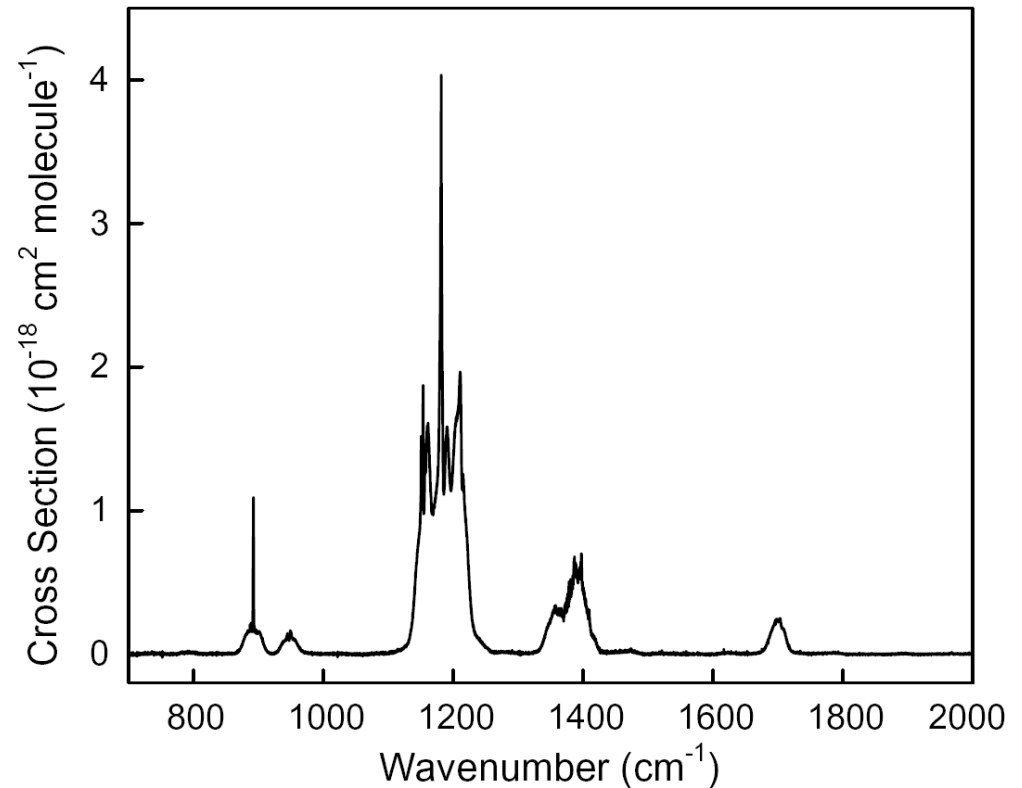
Fig. 3. Pseudo first-order loss of $\text{CF}_3\text{CF}=\text{CH}_2$ versus O_3 concentration. The insert shows typical decay plots for $\text{CF}_3\text{CF}=\text{CH}_2$ when exposed to 180 mTorr (circles), 585 mTorr (triangles), or 1890 mTorr (squares) of O_3 .

IR spectrum, radiative efficiency, and GWP

Integrated IR absorption cross section (800–2000 cm^{-1}) =
 $(1.63 \pm 0.09) \times 10^{-16} \text{ cm molecule}^{-1}$.

Instantaneous cloudy-sky radiative efficiency estimated using method of Pinnock et al. to be $0.22 \text{ W m}^{-2} \text{ ppb}^{-1}$.

Global warming potential (100 year time horizon) = 4.



Oxidation products

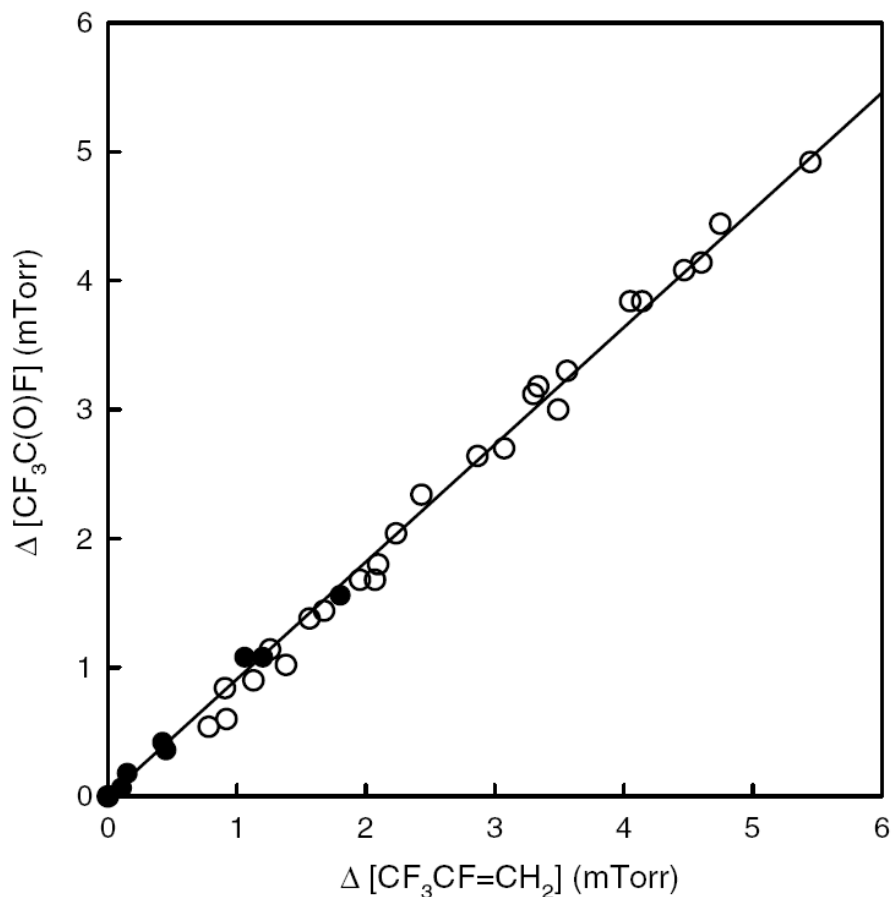


Fig. 4. Formation of $\text{CF}_3\text{C}(\text{O})\text{F}$ versus loss of $\text{CF}_3\text{CF}=\text{CH}_2$ observed following the UV irradiation of mixtures of 8.7–14 mTorr $\text{CF}_3\text{CF}=\text{CH}_2$ and 106–203 mTorr CH_3ONO (open symbols) or 10.6–16 mTorr $\text{CF}_3\text{CF}=\text{CH}_2$, 105–108 mTorr CH_3ONO and 17–25 mTorr NO (filled symbols) in 700 Torr air diluent.

OH radical initiated oxidation gives $\text{CF}_3\text{C}(\text{O})\text{F}$ in a molar yield of $91 \pm 6\%$.

Atmospheric fate of $\text{CF}_3\text{C}(\text{O})\text{F}$ is hydrolysis to give $\text{CF}_3\text{C}(\text{O})\text{OH}$ (trifluoroacetic acid).

Oxidation of $\text{CF}_3\text{CF}=\text{CH}_2$ gives trifluoroacetic acid in yield close to 100%.

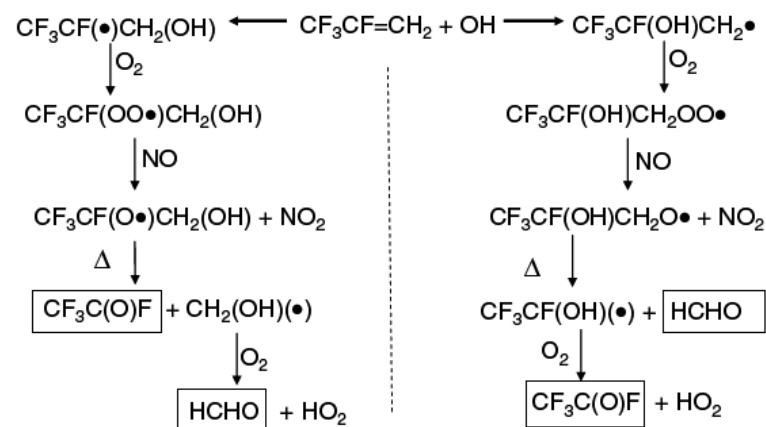


Fig. 5. Mechanism of the OH radical initiated oxidation of $\text{CF}_3\text{CF}=\text{CH}_2$.

Impact on climate change

Degradation is initiated by reaction with OH radicals (Orkin et al., 1997; Nielsen et al. 2007, Papadimitriou et al.2008)

We estimate an atmospheric lifetime of approximately 11 days and a GWP of approximately 4.

Papadimitriou et al. (2008) estimated an atmospheric lifetime of approximately 12 days and a GWP of < 4.4.

Atmospheric lifetime and GWP of HFO-1234yf are well established. No significant contribution to radiative forcing of climate change.

References

O.J. Nielsen, M.S. Javadi, M.P. Sulbaek Andersen, M.D. Hurley, T.J. Wallington, R. Singh, Chem. Phys. Lett., 439, 18 (2007); V. L. Orkin, R. E. Huie and M. J. Kurylo, J. Phys. Chem. A, 1997, 101, 9118–9124; V.C. Papadimitriou, R.K. Talukdar, R.W. Portman, A.R. Ravishankara, J.B. Burkholder, Phys. Chem. Chem. Phys., 10, 808 (2008).



Impact on Stratospheric Ozone

HFO-1234yf does not contain chlorine or bromine and hence will not contribute to the well established Cl- and Br-based catalytic ozone destruction cycles.

Papadimitriou et al. (2008) concluded that ozone-depletion potential for HFO-1234yf is “nearly zero”.

References

V.C. Papadimitriou, R.K. Talukdar, R.W. Portman, A.R. Ravishankara, J.B. Burkholder, Phys. Chem. Chem. Phys., 10, 808 (2008).



Impact on Tropospheric Ozone

$\text{CF}_3\text{CF}=\text{CH}_2$ reacts with OH radicals with rate constant of approximately $1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The peroxy radicals formed will oxidize NO to NO_2 which will photolyze and contribute to ozone formation. Using method of Jenkin (1998) the photochemical ozone creation potential (POCP) for $\text{CF}_3\text{CF}=\text{CH}_2$ is estimated to be 7. POCP for $\text{CF}_3\text{CF}=\text{CH}_2$ lies between those for methane and ethane. $\text{CF}_3\text{CF}=\text{CH}_2$ is not expected to make a significant contribution to tropospheric ozone formation.

POCPs for selected hydrofluoroolefins and related alkanes, alkenes, and hydrofluorocarbons.

Compound	POCP	Compound	POCP	Compound	POCP
$\text{CH}_2=\text{CH}_2$	100 ^{a,b}	CH_2F_2	0.2 ^c	$\text{CH}_2=\text{CF}_2$	17.5 ^d
$\text{CH}_3\text{CH}=\text{CH}_2$	112.3 ^b	CH_3CF_3	0.0 ^c	$\text{CF}_2=\text{CF}_2$	12.5 ^d
$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	107.9 ^b	CH_2FCF_3	0.1 ^c	$\text{CH}_2=\text{CHCF}_3$	10.5 ^d
CH_4	0.6	CH_3CHF_2	1.0 ^c	$\text{CH}_2=\text{CFCF}_3$	7.0 ^d
C_2H_6	12.3 ^b	CF_3CHF_2	0.0 ^c	$\text{CF}_2=\text{CFCF}_3$	5.4 ^d
C_3H_8	17.6 ^b	$\text{CH}_2\text{FCH}_2\text{CF}_3$	0.2 ^d	Z- $\text{CHF}=\text{CFCF}_3$	7.6 ^d
<i>n</i> - C_4H_{10}	35.2 ^b	CHF_2CHF_2	0.0 ^d	$\text{CH}_2=\text{CHCF}_2\text{CF}_3$	6.6 ^d

a: by definition; b: Derwent et al., 1998; c: Hayman and Derwent (1997); d: Estimated using method described by Jenkin (1998)

Derwent, R.G., M.E. Jenkin, S.M. Saunders, and M.J. Pilling, *Atmos. Environ.*, 32, 2429–2441, 1998. Hayman, G.D., and R.G. Derwent, *Environ. Sci. Technol.*, 31, 327–336, 1997; Jenkin, M.E., *Photochemical Ozone and PAN Creation Potentials: Rationalisation and Methods of Estimation*, AEA Technology plc, Report AEAT-4182/ 20150/003, 1998



Impact of trifluoroacetic acid

Atmospheric oxidation of $\text{CF}_3\text{CF}=\text{CH}_2$ gives $\text{CF}_3\text{C}(\text{O})\text{OH}$ (TFA).

Tang et al. conclude “no significant risk is anticipated from TFA produced by atmospheric degradation of the present and future production of HFCs and HCFCs as there is a 1000-fold difference between the PNEC (Predicted No Effect Concentration) and the PEC (Predicted Environmental Concentration)”. Based on risk assessment of $\text{CF}_3\text{C}(\text{O})\text{OH}$ by Tang et al. (1988) and analysis by WMO (2006), Hurley et al. conclude that “the products of the atmospheric oxidation of $\text{CF}_3\text{CF}=\text{CH}_2$ have negligible environmental impact”.

It has been shown that trifluoroacetic acid is ubiquitous in precipitation and ocean water even in remote areas (Berg et al., 2000; Frank et al., 2002; Scott et al, 2005, 2006; Von Sydow et al. 2000). Contribution of $\text{CF}_3\text{CF}=\text{CH}_2$ expected to be negligible.

References

Berg, M., S.R. Müller, J. Mühlemann, A. Wiedmer, and R.P. Scharzenbach, *Environ. Sci. Technol.* 34, 2675-2683, 2000; M.D. Hurley, T.J. Wallington, M.S. Javadi, O.J. Nielsen, *Chem. Phys. Lett.*, 450, 263 (2008); X. Tang, S. Madronich, T. J. Wallington, D. Calamari, , *J. Photochem. Photobiol.*, B 46, 83, (1998); WMO, Scientific Assessment of Stratospheric Ozone: 2006, World Meteorological Organization, Geneva (2007); Frank, H., E.H. Christoph, O. Holm-Hansen, J.L. Bullister, *Environ. Sci. Technol.* 36, 12-15, 2002. Scott, B.F., C. Spencer, S.A. Mabury, and D.C.G. Muir, *Environ. Sci. Technol.*, 40, 7167-7174, 2006; Scott, B.F., R.W. Macdonald, K. Kannan, A. Fisk, A. Witter, N. Yamashita, L. Durham, C. Spencer, D.C.G. Muir, *Environ. Sci. Technol.*, 39, 6555-6560, 2005; Von Sydow, L.M., A.B. Grimvall, H.B. Borén, K. Laniewski, and A.T. Nielsen, *Environ. Sci. Technol.*, 34, 3115-3118, 2000.



Conclusions

Atmospheric chemistry of $\text{CF}_3\text{CF}=\text{CH}_2$ is well defined.

Lifetime is approximately 11 days.

GWP is approximately 4.

No impact on stratospheric ozone.

POCP estimated to be 7. $\text{CF}_3\text{CF}=\text{CH}_2$ not expected to make a significant contribution to tropospheric ozone formation

Atmospheric oxidation of $\text{CF}_3\text{CF}=\text{CH}_2$ gives $\text{CF}_3\text{C}(\text{O})\text{F}$ which hydrolyzes to give $\text{CF}_3\text{C}(\text{O})\text{OH}$ (trifluoroacetic acid, TFA) in a molar yield of essentially 100%. No significant environmental impact is expected for additional environmental TFA burden associated with expected volumes of $\text{CF}_3\text{CF}=\text{CH}_2$ use.

