HCFC-133a (CF₃CH₂Cl): OH Rate Coefficient, UV Absorption Spectrum and Atmospheric Implications

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Introduction:

HCFC-133a has recently been detected in the atmosphere, with mixing ratios steadily increasing over the last 20 years [Laube et al., 2014]. It is an ozone-depleting substance and a potent greenhouse gas that is removed primarily via reaction with OH and stratospheric UV photolysis. Discrepancies exist in literature UV absorption cross section temperature dependence $\sigma(\lambda,T)$ and the OH reaction rate coefficient temperature dependence, *k*(T). It is a primary aim of this work to reduce this uncertainty and in doing so, provide an



UV absorption experiments: UV light sources which were directed through an absorption cell containing a known concentration of HCFC-133a and detected with either a monochromator equipped with a PMT, or else a photodiode with a 185 nm narrow band pass filter (see Figure 2)

•184.95–240 nm wavelength range •213–323 K temperature range •90.4 ±0.3 cm path length •Deuterium and mercury light sources •[HCFC-133a] = $3 \times 10^{15} - 2 \times 10^{19}$ molecule cm⁻³ Temperature-dependent cross sections $\sigma(\lambda,T)$, were determined from a Beer-Lambert law linear least-squares fit, i.e., A = *σL*[HCFC-133a]







accurate dataset for use in model calculations.

Uncertainties in k(T) and $\sigma(\lambda,T)$ are significant contributing factors to the overall uncertainty in its global lifetime and, thus, model calculations of stratospheric ozone recovery and climate change. In this work, k(T) was measured over 233–379 K and $\sigma(\lambda,T)$ was measured over a range of wavelength (184.95–240 nm) and temperature (213–323 K).

Experimental methods:

OH rate coefficient measurements:

- Rate coefficients determined using pulsed laser photolysis-laser induced fluorescence (PLP-LIF) (see Figure 1)
- Experiments conducted under *pseudo*first-order conditions in OH i.e. [HCFC-133a] >> [OH] such that:

 $-(k[HCFC - 133a] + k_d)t = -k't$

Figure 1: Reaction between OH and HCFC-133a occurs throughout the volume of the excimer beam. OH concentrations are probed by a pulsed YAG laser which intercepts the excimer beam in the center of the reactor. Changing the delay time between these lasers alters the reaction time

IR absorption experiments: Measurements made at room temperature using an FTIR spectrometer, a single-pass absorption cell with KBr windows •500–4000 cm⁻¹ range •[HCFC-133a] = $7 \times 10^{15} - 8 \times 10^{16}$ 15 cm path length Infrared cross section determined using the **Beer-Lambert law**

IR measurements:





Figure 3: HCFC-133a + OH Arrhenius diagram. Upper panel: rate coefficient measurements. Lower panel: % difference from JPL recommendation

OH rate coefficient:

- •Extended temperature range at low temperature
- •The Arrhenius expression:

Figure 4: HCFC-133a UV absorption spectrum. Upper panel: this study (filled symbols), literature (open symbols) and parameterized spectra (lines). Lower panel: ratio of measured values to parameterization

UV measurements:

•Precision, accurate data acquired (2σ uncertainty estimated to be 4%) •Systematic spectrum temperature dependence is measured for the first time •Spectrum parameterization reproduces data to within experimental precision

- [HCFC-133a] was monitored on-line using FTIR
- 233–379 K temperature range
- Independent of pressure between 50-200 Torr
- H_2O_2 and $(CH_3)_3COOH OH precursors$ use
- 248 nm photolysis wavelength
- Initial [OH] varied from $10^{9}-10^{11}$ molecule cm⁻³
- [HCFC-133a] varied from $10^{15} - 10^{17}$ molecule cm⁻³



DAQ

Photodiode

Hg lamp

Figure 2: Schematic of the UV absorption apparatus. The graph shows a typical Beer-Lambert plot obtained from this approach

Figure 5: HCFC-133a IR absorption spectrum. Inset: Beer-Lambert plot of integrated absorbance vs [HCFC-133a]

•In agreement with Etminan et al. [2014] •Calculated spectra were also used to quantify lower energy modes which fall outside our measurement range •These were found to effect the GWP by <1% $k(T) = (9.32 \pm 0.8) \times 10^{-13} \exp(-(1296 \pm 28)/T)$

reproduces data to within experimental precision

Comparison with literature data:

•Excellent agreement with DeMore [2005] temperature dependent relative rate study and absolute room temperature measurement of Howard and Evenson [1976]

•Systematic differences with absolute measurements of Handwerk and Zellner [1978]; Clyne and Holt [1979]; Fang et al. [1999], although generally good agreement in terms of temperature dependence

Comparison with literature data:

•Large discrepancies (up to 300%) are observed with literature studies Green and Wayne [1976] and Hubrich and Stuhl [1980] •No direct comparisons of the temperature dependence can be made

Summary:

•Measurements of the OH rate coefficient and UV absorption spectrum of HCFC-133a as a function of temperature are reported together with the infrared cross section

Implications:

•HCFC-133a + OH measurements are in good agreement with JPL-2010 recommendation (but uncertainty is reduced) • UV cross section measurements indicate that photolysis lifetime is longer than previously thought (103 years), therefore reaction with OH represents the dominant sink for HCFC-133a

References:

Clyne, M.A.A., and P.M. Holt (1979), Reaction-kinetics involving ground $X^2\Pi$ and excited $A^2\Sigma^+$ hydroxyl radicals. 2. Rate constants for reactions of OH $X^2\Pi$ with halogenomethanes and halogenoethanes, J. Chem. Soc. Farad. Trans. 2, 75, 585–591.

Etminan, M., E.J. Highwood, J.C. Laube, R. McPheat, G. Marston, K.P. Shine and K.M. Smith (2014), Infrared Absorption Spectra, Radiative Efficiencies, and Global Warming Potentials of Newly-Detected Halogenated Compounds: CFC-113a, CFC-112 and HCFC-133a, Atmos., 5, 473-483.

•Significant reduction in the uncertainties of the HCFC-133a OH reaction and photolysis rates

•The impact of the new measurements on calculated atmospheric lifetime and ODP were quantified using the NASA Goddard Space Flight Center 2-D coupled chemistry-radiation-dynamics model •The total atmospheric lifetime is found to be 4.45 years •The ODP is determined to be 0.02

•Based on atmospheric lifetime and the infrared cross section of this work, the global-warming potential of HCFC-133a is estimated to be 374 on the 100 year time horizon

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Fang, T.D., P.H. Taylor, and R.J. Berry (1999), Kinetics of the reaction of OH radicals with CH2ClCF2Cl and CH2ClCF3 over an extended temperature range, J. Phys. Chem. A, 103, 2700–2704.

Green, R.G., and R.P. Wayne (1977), Vacuum ultra-violet spectra of halogenated methanes and ethanes, J. Photochem., 6, 375–377.

Handwerk, V., and R. Zellner (1978), Kinetics of reactions of OH radicals with some halocarbons (CHCIF2, CH2ClF, CH2ClCF3, CH3CClF2, CH3CHF2) in temperature-range 260 K–370 K, Ber. Bunsen Phys. Chem., 82, 1161–1166.

Howard, C.J., and K.M. Evenson (1976), Rate constants for reactions of OH with ethane and some halogen substituted ethanes at 296 K, J. Chem. Phys., 64, 4303–4306.

Hubrich, C., and F. Stuhl (1980), The ultraviolet absorption of some halogenated methanes and ethanes of atmospheric interest, J. Photochem., 12, 93–107.

Laube, J.C., M.J. Newland, C. Hogan, C.A.M. Brenninkmeijer, P.J. Fraser, P. Martinerie, D.E. Oram, C.E. Reeves, T Röckmann, J. Schwander, E. Witrant, and W.T. Sturges (2014), Newly detected ozone-depleting substances in the atmosphere, Nat. Geosci., 7, 266–269.