

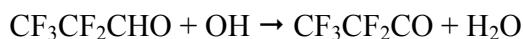
Kinetics with OH Radicals and Photochemistry of CF₃CF₂CHO

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Ozone-friendly species hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) were reported to contribute in a great extent to the Earth's global warming.¹ Other non-depleting ozone substances, such as fluorinated alcohols (FA), have recently been proposed as substitutes. HCFCs, HFCs and FA are degraded in the troposphere yielding perfluorinated aldehydes, C_xF_{2x+1}CHO.^{2,3} Perfluorinated aldehydes are thought to be precursors of perfluoroalkyl carboxylic acids (PFCAs, C_nF_{2n+1}COOH)⁴. Atmospheric removal of perfluorinated aldehydes is mainly initiated by reaction with OH radicals and sunlight. The aim of this work is to determine the **OH-reaction rate coefficient**, k_{OH} , for CF₃CF₂CHO as a function of temperature for the first time ($T = 263 - 358$ K) at different pressures ($P = 50 - 205$ Torr):



CF₃CF₂CHO was obtained from dehydration of CF₃CF₂CH(OH)₂ in the presence of P₂O₅ at 338 K and then stored in a stainless steel cylinder. OH radicals were generated by *pulsed laser photolysis* (PLP) of HNO₃(g) at 248 nm and subsequently probed to the first excited state by a frequency-doubled dye laser pumped by a Nd:YAG laser. *Laser induced fluorescence* (LIF) from OH radicals was detected by a filtered photomultiplier tube. Sulbaek Andersen et al.⁴ previously determined the relative k_{OH} only at room temperature. At 275 K, the global temperature of the troposphere, k_{OH} was measured to be 4.8×10^{-13} cm³ molecule⁻¹ s⁻¹, *i. e.*, its overall lifetime due to the OH-reaction is *ca.* 24 days. Additionally, the **absorption cross sections** ($\sigma_{\lambda=230-370 \text{ nm}}$) of CF₃CF₂CHO were determined as a function of temperature (269-323 K). The PLP technique was also used coupled to a Fourier transform infrared (FTIR) spectrometer to determine the **photodissociation quantum yields** of CF₃CF₂CHO ($\Phi_{\lambda=308 \text{ nm}}$) as a function of total pressure (75-760 Torr in air). The overall loss of CF₃CF₂CHO and the formation of photooxidation end-products were monitored by FTIR spectroscopy. From our results, the main removal process for CF₃CF₂CHO in the atmosphere seems to be UV photolysis rather than reaction with OH.

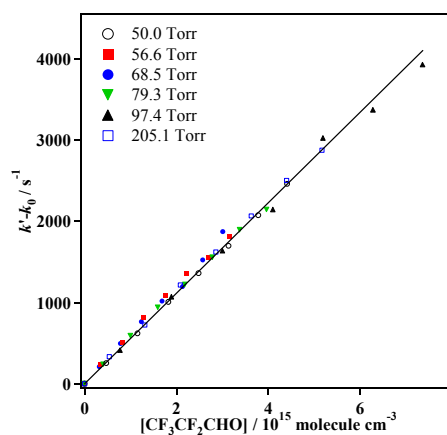


Fig. 1. Pseudo-first order plot at 298 K.

References

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- (2) Hurley, M.D.; Wallington, T.J.; Sulbaek Andersen, M.P.; Ellis, D.A.; Martin, J.W.; Mabury, S.A.. *J. Phys. Chem. A* **2004**, 108, 1973-1979.
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