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# Tropospheric photooxidation of $CF_3CH_2CHO$ and $CF_3(CH_2)_2CHO$ initiated by Cl atoms and OH radicals

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Abstract. The absolute rate coefficients for the tropospheric reactions of chlorine (Cl) atoms and hydroxyl (OH) radicals with $CF_3CH_2CHO$ and $CF_3(CH_2)_2CHO$ were measured as a function of temperature (263–371 K) and pressure (50–215 Torr of He) by pulsed UV laser photolysis techniques. Vacuum UV resonance fluorescence was employed to detect and monitor the time evolution of Cl atoms. Laser induced fluorescence was used in this work for the detection of OH radicals as a function of reaction time. No pressure dependence of the bimolecular rate coefficients, $k_{Cl}$ and $k_{OH}$, was found at all temperatures. At room temperature $k_{Cl}$ and $k_{OH}$ were (in $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$): $k_{Cl}(CF_3CH_2CHO)$ = (1.55±0.53); $k_{Cl}(CF_3(CH_2)_2CHO)$ = (3.39±1.38); $k_{Cl}(CF_3CH_2CHO)$ = (0.259±0.050); $k_{Cl}(CF_3(CH_2)_2CHO)$ = (1.28±0.24). A slightly positive temperature dependence of $k_{Cl}$ was observed for $CF_3CH_2CHO$ and $CF_3(CH_2)_2CHO$, and $k_{OH}(CF_3CH_2CHO)$. In contrast, $k_{OH}(CF_3(CH_2)_2CHO)$ did not exhibit a temperature dependence over the range investigated. Arrhenius expressions for these reactions were:

$k_{Cl}(CF_3CH_2CHO) = (4.4\pm1.0)\times10^{-11}\exp\{-(316\pm68)/T\}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

$k_{Cl}(CF_3(CH_2)_2CHO) = (2.9\pm0.7)\times10^{-10}\exp\{-(625\pm80)/T\}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

$k_{OH}(CF_3CH_2CHO) = (7.8\pm2.2)\times10^{-12}\exp\{-(314\pm90)/T\}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

The atmospheric impact of the homogeneous removal by OH radicals and Cl atoms of these fluorinated aldehydes is discussed in terms of the global atmospheric lifetimes, taking into account different degradation pathways. The calculated lifetimes show that atmospheric oxidation of $CF_3(CH_2)_x$ CHO are globally dominated by OH radicals, however reactions initiated by Cl atoms can act as a source of free radicals at dawn in the troposphere.

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