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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Tropospheric photooxidation of CF_3CH_2CHO and $CF_3(CH_2)_2CHO$ initiated by Cl atoms and OH radicals" *by* M. Antiñolo et al.

Anonymous Referee #1

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Antinolo *et al.* report the results of a study of the kinetics of the reactions of OH radicals and chlorine atoms with CF_3CH_2CHO and $CF_3(CH_2)_2CHO$ using absolute rate techniques. I have one major comment and two minor comments:

Major comment

(1) As noted by Antinolo *et al.*, the time scale for loss and regeneration of chlorine atoms was not fully separated and as a result biexponential decays of chlorine atoms were observed following the flash photolysis of Cl_2/fluoroaldehyde/He mixtures. To reduce complications associated with chlorine atom regeneration via the $CF_3(CH_2)_xC(O)$ + Cl_2 reaction, 1 x 10^{16} molecule cm^{-3} O_2 was added to scavenge the $CF_3CH_2C(O)$

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radicals. At 100 Torr and 295 K the rate constant ratio CH_3CO+O_2/CH_3CO+Cl_2 = 3E-12/2.4E-11 = 0.125 (Tyndall et al., Int. J. Chem. Kinet., 29, 655 (1997)). For the conditions used by Antinolo *et al.* with $[O_2]/[Cl_2]$ = 50 and assuming that $CF_3(CH_2)_xC(O)$ radicals behave like CH_3CO radicals with k_{O2}/k_{Cl2} = 0.125 then one would expect approximately 15% regeneration of chlorine atoms. Hence, at room temperature the rate coefficient might be underestimated by about 15% and this might explain why the rate coefficient at 298 K for the Cl + CF_3CH_2CHO reaction is lower than reported in other studies. At higher temperatures the rate coefficient ratio k_{O2}/k_{Cl2} will decrease and regeneration of chlorine atoms will be $>$15%.

Antinolo *et al.* state that "a few experiments were performed with $[O_2]$ = 2×10^{16} molecule cm^{-3} for a limited range of aldehyde concentrations, and the obtained rate coefficients were similar to those obtained with $[O_2]$ =1×10^{16} molecule cm^{-3}". How similar were the results? Perhaps the authors should estimate the maximum difference that could exist between the two sets of O_2 experiments and then double this to provide an estimate of the maximum underestimation of the room temperature rate coefficient in experiments using $[O_2]$ =1×10^{16} molecule cm^{-3}. What is the likely magnitude of the underestimation of the rate coefficients at elevated temperature? A typical decay trace should be shown so readers can get a feel for the quality of the raw data and potential magnitude of chlorine regeneration.

From the information given in the manuscript it appears that regeneration of chlorine atoms is likely to be a serious problem and the k(Cl) values reported are lower limits.

Minor comments

(1) The claim in the Introduction that HFCs are "very strong greenhouse gases with high Global Warming Potentials (GWP) due to the long tropospheric lifetimes and strong absorption in the IR region" is too broad. HFCs are a class of compounds with a wide range of properties (including atmospheric lifetime). HFCs with short atmospheric lifetimes have low GWPs.

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(2) The statement in section 3.3 "the products of their reactions with OH radicals and UV photolysis may exert a great influence on the air quality" needs to be justified or deleted. Given the low abundance and low mechanistic reactivity of fluorinated aldehydes, I would not expect them to have any significant impact on air quality.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 24783, 2009.