

Interactive comment on “Tropospheric photooxidation of CF₃CH₂CHO and CF₃(CH₂)₂CHO initiated by Cl atoms and OH radicals” by M. Antiñolo et al.

Anonymous Referee #1

Received and published: 15 December 2009

Antinolo *et al.* report the results of a study of the kinetics of the reactions of OH radicals and chlorine atoms with CF₃CH₂CHO and CF₃(CH₂)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 Cl₂/fluoroaldehyde/He mixtures. To reduce complications associated with chlorine atom regeneration via the CF₃(CH₂)_xC(O) + Cl₂ reaction, 1 × 10¹⁶ molecule cm⁻³ O₂ was added to scavenge the CF₃CH₂C(O)

C8427

radicals. At 100 Torr and 295 K the rate constant ratio CH₃CO+O₂/CH₃CO+Cl₂ = 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 [O₂]/[Cl₂] = 50 and assuming that CF₃(CH₂)_xC(O) radicals behave like CH₃CO radicals with $k_{O_2}/k_{Cl_2} = 0.125$ 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 + CF₃CH₂CHO reaction is lower than reported in other studies. At higher temperatures the rate coefficient ratio k_{O_2}/k_{Cl_2} will decrease and regeneration of chlorine atoms will be >15%.

Antinolo *et al.* state that "a few experiments were performed with [O₂] = 2 × 10¹⁶ molecule cm⁻³ for a limited range of aldehyde concentrations, and the obtained rate coefficients were similar to those obtained with [O₂] = 1 × 10¹⁶ molecule cm⁻³". How similar were the results? Perhaps the authors should estimate the maximum difference that could exist between the two sets of O₂ experiments and then double this to provide an estimate of the maximum underestimation of the room temperature rate coefficient in experiments using [O₂] = 1 × 10¹⁶ 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 $k(\text{Cl})$ 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.

C8428

(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.

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