

Interactive comment on “Tropospheric photooxidation of $\text{CF}_3\text{CH}_2\text{CHO}$ and $\text{CF}_3(\text{CH}_2)_2\text{CHO}$ initiated by Cl atoms and OH radicals” by M. Antiñolo et al.

Anonymous Referee #2

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In this manuscript, the authors provide what appears to be a solid and useful dataset regarding the reactions of OH and Cl-atoms with two partially-fluorinated aldehydes. In particular, no previous studies of the 4,4,4-trifluorobutanal species have been reported. I believe the paper to be publishable in ACP subject to minor revision, as outlined below:

I think a few more experimental details are needed regarding the Cl-atom and OH kinetics methodology (Section 2.1 and 2.2) – for example, the excimer pulse rate in both sets of experiments, the total flow rate (and, hence, residence time) in the OH experiments, and the initial Cl-atom concentration should be given. More specifically, was the excimer pulse rate varied in order to quantitatively assess the statement made

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at the bottom of page 24787 (that accumulation of photolysis or reaction products was not an issue)?

I am confused by the paragraph on p.24798 discussing the aqueous phase removal. Did the authors mean (line 7) that the species remain predominantly in the gas phase? Also, for Henry's law coefficients of 100 M atm⁻¹ or so, the lifetime is much shorter than the 300 year value quoted, is it not?

I would suggest that the last paragraph prior to the conclusions, (p.24798-24799) be removed or greatly abbreviated. First, I do not think that these particular compounds are going to contribute in any significant way to air quality / smog formation, given that their abundances are likely quite low. The interest would seem to fall more in determining their lifetime and the nature of their breakdown products – for example, whether or not they are sources of fluorinated acids. Further, I did not see the relevance of the discussion regarding the impacts of chlorine chemistry and the 'weekend effect' – I think this can be deleted.

Suggested grammatical / typographical corrections:

Page 24784, line 12 – should be 'positive temperature dependence', rather than negative.

Page 24785, line 2 – change 'family' to 'families'.

Page 24788, line 20 – title would read better as "Optical measurement of ..."

Page 24789, line 13 – may read better as "In some experiments, CF₃(CH₂)_xCHO. . ."

Page 24790, line 21 – may read better as ". . .in large excess with respect to. . ."

Page 24795, line 10 – would be more precise as follows, ". . .is only 20-50% larger than. . .".

Page 24795, line 16 – change 'has' to 'have'

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Page 24797, line 5 – should be “Singh et al., 1996”

Page 24797, line 8 – might read better as follows, “is reported here, while. . .”

Page 24797, line 14 - might read better as follows, “. . .Cl atoms can contribute to the removal of. . .”

Page 24798, line 1 – maybe “throughout” instead of “along”?

Page 24799, line 27 - might read better as follows, “. . .that they are rapidly degraded in the troposphere. . .”

In Figure 2S, it might be useful to provide concentration / pathlength information in the figure caption so that interested readers are able to estimate peak absorption cross sections for these species.

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

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