

Authors' Response to Anonymous Referee #2 Interactive comment on "Atmospheric lifetimes and ozone depletion potentials of trans-1-chloro-3,3,3-trifluoropropylene and trans-1,2-dichloroethylene in a three-dimensional model"

K. O. Patten and D. J. Wuebbles

Department of Atmospheric Sciences, University of Illinois, Urbana, Illinois USA

We thank Referee #2 for consideration of our manuscript. In answer to the questions (shown in italics):

1) The lifetimes of the two species are about three times different, yet their OH rate coefficients differ by about a factor of 5 or more. Can the authors provide a reason for this non-linearity?

The OH reaction rate constant expression is an important factor in the atmospheric lifetime, but the ratio of atmospheric lifetimes between two VSLSs only equals that of rate constants between two VSLSs when other factors remain equal. In the case of tDCE and tCFP, the faster OH reaction of tDCE means that nearly none of that VSLS reaches the tropical middle troposphere, and that nearly all tDCE is concentrated in Northern middle and polar latitudes (Fig. 1b) which have limited OH concentrations to react with tDCE. While tCFP also concentrates in Northern latitudes, a larger fraction reaches latitudes south of 30 °N in the middle troposphere (Fig. 1a) where tropospheric OH concentrations are highest. The effective OH concentration encountered by tCFP is thus somewhat greater than that for tDCE, countering the effect of the large rate constant ratio and resulting in a smaller ratio for tCFP atmospheric lifetime to tDCE atmospheric lifetime.

2) The authors assume that the intermediate product, HC(O)Cl, is rapidly destroyed, leading to immediate Cl release. I agree that some of the HC(O)Cl might be lost via heterogeneous processes, thus limiting the amount of overall Cl-release from the parent alkenes. However, I think HC(O)Cl is fairly resistant to gas-phase destruction in the troposphere. Could it thus act as an additional agent for the transport of Cl to the stratosphere, and could this process have any impact on the ODPs determined?

HC(O)Cl, a possible initial product of OH-initiated tCFP oxidation (though we are unaware of measurements of the actual products of tCFP oxidation under atmospheric conditions) and a likely product of OH-initiated tDCE oxidation (Zhang et al., 1991), could transport chlorine to the stratosphere, as could inorganic Cl_y species ultimately produced from tCFP or tDCE oxidation. Further gas-phase oxidation of HC(O)Cl would possibly be quite slow in the troposphere: the OH rate constant recommendation is $< 5.0 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2008) based on a single study near 300 K, and a Cl reaction has been recommended with rate constant expression $\mathbf{k} = 8.1 \times 10^{-12} \exp(-710/\mathbf{T})$ (Atkinson et al., 2008) for \mathbf{k} in $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and \mathbf{T} in K. Photolysis could be significant: absorption cross sections at tropospheric relevant wavelengths are

structured with maxima of about $2 \times 10^{-21} \text{ cm}^2$ around 300 nm, decreasing to less than $1 \times 10^{-22} \text{ cm}^2$ around 315 nm (Atkinson et al., 2008). Both solvation and heterogeneous reactions on cloud water or ice could be expected to contribute to HC(O)Cl removal, but we are unaware of measurements of such potential HC(O)Cl processes that are usable in atmospheric chemistry modeling at this time. Because of the current uncertainty in HC(O)Cl atmospheric processing and even in its product yield from tCFP + OH, we did not incorporate it into this study.

If HC(O)Cl is highly soluble in cloud water, its removal by rainout could reduce the ODP of tDCE. However, if HC(O)Cl is slightly soluble and its heterogeneous reactions are slow, its production in the atmosphere could increase the ODP for tDCE somewhat. Many feasible routes for atmospheric tCFP oxidation can produce HC(O)Cl, particularly if the first step is predominantly OH addition at the 1-carbon, so that the effects on tCFP ODP appropriate to the tropospheric processing of HC(O)Cl would apply to the extent that tCFP oxidation produces HC(O)Cl.

Our existing text on degradation products (p. 16640 line 22 to p. 16641 line 3) is replaced by a paragraph in the revised manuscript, and we have added a brief paragraph on possible CHClO (as we represented HC(O)Cl in the manuscript) formation to the second-to-last paragraph of the Results section plus a sentence and additional clause in the Summary paragraph. We thank Referee #2 again for pointing out this issue.

With regard to the minor suggestions given:

Page 16640, line 5/6: Should read “This is the first study. . .”

Agreed; "is" will be added to the beginning of that sentence in our revised manuscript.

Page 16646, line 20, should be a period after the word “substances”, not a comma.

Agreed; that comma will be corrected to a period in our revised manuscript.

Page 16647, line 6/7: I think the sentence beginning “Notably, Table 4. . .” should be re-worded, replacing the words “much” and “most” with more quantitative language.

Our revised manuscript will express this more quantitatively.

References

Atkinson, R., D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, and T. J. Wallington, Evaluated kinetic and photochemical data for atmospheric chemistry: Volume IV - gas phase reactions of organic halogen species, *Atmos. Chem. Phys.*, 8, 4141-4496, 2008.

Zhang, Z., R. Liu, R. E. Huie, and M. J. Kurylo, A Gas-Phase Reactivity Study of OH Radicals with 1,1-Dichloroethene and *cis*- and *trans*-1,2-Dichloroethene over the Temperature Range 240-400 K, *J. Phys. Chem.*, 95, 194-196, 1991.