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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric chemistry of trans-CF_3CH=CHF: products and mechanisms of hydroxyl radical and chlorine atom initiated oxidation" *by* M. S. Javadi et al.

M. S. Javadi et al.

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Reviewer 1

The authors present an FTIR product study of the oxidation of trans-CF3CH=CHF, a potential replacement compound for CFC/HFCs. The studies are conducted using either OH or Cl atoms to initiate the oxidation. The methods used are certainly wellestablished, and the senior authors are certainly expert in this type of study. The work conducted using Cl-atoms seems thorough and complete. Effects of oxygen partial pressure on product yields are examined, and a quantitative explanation of the results (in terms of competing alkoxy radical reactions) is clearly presented. However, it is my opinion that more work on the OH system is required before publication in ACP can be

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recommended, for reasons described below.

The OH data presented indicate 100

Due to spectral congestion and the absence of authentic samples of the nitrates (CF3CH(ONO2)CHF(OH) and CF3CH(OH)CHFONO2) we are not able to discern whether small amounts (approx. 1 mTorr) of these nitrates are formed. The concentration of NO2 towards the end of the experiment is typically of the order of 10 mTorr. Rate constants for reaction of NO2 with alkoxy radicals are typically (1-5) x 10-11 cm-3 molecule-1 s-1 and hence the pseudo first order loss rate of RO radicals with respect to reaction with NO2 is of the order of 104 s-1 which is comparable to the rates of decomposition reported for fluorinated alkoxy radicals comparable to CF3CHOCHF(OH) and CF3CH(OH)CHFO (e.g., Maricq and Szente, J. Phys. Chem. 96, 10862, 1992) report kdiss(CF3CFHO) = (2 ś 1) 61620; 104 s-1 at 297 K).

Were any experiments conducted with small amounts of added NO2 to test the hypothesis?

No. We believe that the 100

How much NO2 was present at the onset of the curvature, and what does this say about the reactivity of the alkoxy radicals?

See response to first question.

With respect to this last question, the decomposition of hydroxy-alkoxy radicals is usually quite rapid, and is at least sufficiently rapid in this case to render reaction with O2 negligible. I would suspect that only a few mTorr of NO2 are present at the onset of curvature? If this is sufficient NO2 to compete with alkoxy decomposition, this would be a significant finding. In summary, it seems to me that more experiments and analysis can and should be done to answer these and related questions.

As discussed above, reaction with NO2 provides a plausible explanation of the curvature. An extensive discussion of the likely secondary reactions involved with the

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curvature seems out of place. The observed initial slope of 100

There are also a couple of minor points that require clarification: 1) The text refers to 2-14

The section has been rewritten for clarity.

2) The caption to Figure 2 refers to data "obtained in the absence of NO". Does this refer to experiments conducted without any NO added initially? These experiments are not talked about in the text, I don8217;t think.

The section has been rewritten for clarity.

Reviewer 2

This manuscript reports on a kinetic and product study of the reactions of OH radicals and Cl atoms with trans- CF3CH=CHF, a potential replacement compounds for hydrofluorocarbons such as HFC-134a. This experimental study is thorough and the conclusions well supported by the data. Comments which would, in my view, improve the presentation are as follows:

Page 1072, line 12. A comma after CF3CH=CHF seems appropriate.

Yes, comma is added in the text

Page 1072, line 26. The authors could note the

Yes, text added.

Page 1073, lines 11-13. The authors should state the maximum fraction of CF3CHO removed by secondary reactions with OH radicals.

Now stated.

Page 1073, lines 15-19. Do the authors mean the formation of CF3CH(ONO2)CHFOH and CF3CH(OH)CHFONO2 formed from the reactions of the corresponding alkoxy radicals with NO2? Some additional discussion and specificity is needed here. Clearly,

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the same effect is not observed in the Cl atom reaction system, suggesting that the decrease in CF3CHO and HC(O)F yields at larger extents of reaction does involve NO2 (and not NO).

The section describing the OH product yields has been rewritten for clarity. The chlorine initiated oxidation experiments were performed in the absence of NO.

Page 1074, line 12. Maybe add "(see below)" after "we attribute to the ketone CF3C(O)CHFCl."

Yes, added in the text

Page 1075, line 2. I assume that the lack of loss of CF3C(O)Cl was in the same chamber as used here. If so, say so.

Yes, added in the text

Page 1075, line 17, Maybe replace "the alkoxy" by "these alkoxy", since this statement is specific to the alkoxy radicals formed in reactions (7a) and (7b).

Text modified to explicitly state the alkoxy radicals.

Page 1076, line 23. The CF3CH(O)CH2Cl radical should be CF3CH(O)CHFCl.

Yes, corrected in the text

Page 1076, lines 28-29. I suggest adding "therefore" after "bond scission is". The present product data presumably suggest that approximately 70

Yes, added in the text

Page 1077, lines 9-21. I would have thought it possible to include formation of the not observed product CF3C(O)CHFCl and use the previously measured rate constant ratio k10/k11 in a more comprehensive modeling of the data.

A more comprehensive modeling of the data is beyond the scope of the present work.

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Figure 1. I assume that the banded structure in traces (a) and (b) is due to NO? This could be noted in the figure caption or labeled on the trace,

Yes, added in the text

Figure 8. The inclusion of reactions involving NO in Figure 8 (converting RO2 to RO) means that Figure 8 is more applicable to the atmosphere than the chamber experiments discussion in this article. This should be noted.

Yes, added in the text

Furthermore, it would be useful for the reader to indicate the percentages associated with the various reaction steps for 700 Torr of air conditions. Alternatively, the reaction numbers cited in the text could be added to aid the reader.

Yes, the reaction numbers are added in the figure

What is the measured carbon balance at 700 Torr of air?

Yes, added in the text

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 1069, 2008.