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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Influence of relative humidity and temperature on the production of pinonaldehyde and OH radicals from the ozonolysis of $\vec{\alpha}$-pinene" *by* R. Tillmann et al.

Anonymous Referee #1

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General Comments

This paper reports measurements of the yields of pinonaldehyde and hydroxyl radicals produced from the ozonolysis of alpha-pinene as a function of temperature and relative humidity. A series of experiments has been performed in the AIDA simulation chamber, which is capable of operating at low temperatures. In particular, new information on the reactivity of the alpha-pinene/ozone system has been obtained at low temperatures (243 and 253 K). The authors use the results to assess the influence of water and temperature on the reaction mechanism.

The article is, in general, well written and the results are presented in a clear and

logical manner. The experimental data are of high quality and the interpretation and discussion of the results is appropriate, although there is insufficient comparison with previous studies. Overall, this is a good paper which highlights the uncertainties in our current understanding of the mechanisms for the ozone-initiated atmospheric oxidation of volatile organic compounds.

The article would be suitable for publication following revision of the manuscript in line with the following comments and suggestions.

Specific Comments

1. Page 3133, lines 7-9 and scheme 1: The authors imply that the reaction of the Stabilised Criegee Intermediate with water is the only source of pinonaldehyde. However, in the recent review by Johnson and Marston (2008), it is stated that a number of different reaction pathways have been proposed by various researchers and that there is "no consensus on the mechanism leading to formation of even the first generation of products" in the alpha-pinene/ozone system. Is more definitive information on the mechanism for pinonaldehyde formation now available? If the authors believe that this is the only formation route, then they should explain why.

2. Page 3133, lines 10-14: The authors highlight the discrepancies between several previous studies of the effect of relative humidity on pinonaldehyde formation yields and indicate that the results obtained in this work will help to explain them. However, this has not been done. In fact there is insufficient comparison with the existing literature in the results and discussion section (see comment below).

3. Page 3135, lines 5-14: The experiments and the effect of temperature on the aerosol yields have been reported in a previous paper (Saathoff et al., 2009). The present work involves determination of pinonaldehyde and OH yields in the same set of experiments. The link between the two papers should therefore be clearly stated at the end of the introduction and/or start of the experimental section.

ACPD
10, C892–C896, 2010

4. Page 3136, lines 19-21: Is “accuracy” the most appropriate term here? Should it simply be uncertainty?

5. Page 3141, line 6: The phrase “...where it is zero (253 K), respectively was set to zero (303 K).” does not make sense and should be changed.

6. Page 3144, lines 3-6: The authors should point out that they used the sectional yield data recorded in Table 1b to construct the plot in figure 7. Why is the mean molecular mass of the aerosol constituents taken to be 180 g mol-1?

7. Section 3.3: The authors should compare their pinonaldehyde yield values to those previously reported in the literature, maybe in the form of a Table. Do the results obtained in this work help to explain the reported discrepancies between the previous studies?

8. Section 3.4: The authors should compare their OH yields with those previously reported in the literature, maybe in the form of a Table. It is worth noting that the OH yields differ from the value of 0.80 recommended by IUPAC (Johnson and Marston, 2008).

9. Page 3160, Table 1b: Some data from experiment SOA05-1 is included here. However, this experiment is not listed in Table 1.

10. Page 3161, Table 2: The difference between the two types of OH yields should be clarified. The errors in the OH yields should also be listed.

11. Page 3168, Figure 7: Are the very large error bars on the third point real? Have these errors been incorporated into the vapour pressure and partitioning coefficient values that are derived from this plot?

Technical Corrections

1. Page 3135: change “Proton-Transfer-Reaction Mass Spectrometry” to “Proton Transfer Reaction-Mass Spectrometry”. Twice on this page.

ACPD

10, C892–C896, 2010

2. Page 3135 and 3136: remove “-“ from “AIDA-chamber” and “m/z-signal”

3. Page 3136: SLM should be in lower case.

4. Page 3137: change “sulphate” to “sulfate”. The latter is the recommended IUPAC spelling.

5. At numerous points throughout the manuscript, the units for mass concentration are reported as both microgram/m3 and microgram m-3. The authors should choose one of these and stick to it.

6. Page 3141, line 25: According to Table 1a the RH never reached 86% - is this an error?

7. Both vapour and vapor are used in the manuscript. Again, the authors should be consistent here.

8. Page 3149, line 6; Should the values be 0.71 and 0.57 (as indicated in Table 2)?

9. In the captions to Table 1b and Table 2, the “sigma” looks a little like a “delta”. Has the correct symbol been used?

10. Page 3162, figure 1: move “(FTIR)” so that it appears before “spectrometer”

11. Page 3168, Figure 7: The use of “silently” is incorrect. This sentence should be rewritten.

12. Page 3171, Scheme 1: Only one “path” is represented in the scheme. Suggest rephrasing the caption.

References

Johnson, D. and Marston, G.: The gas-phase ozonolysis of unsaturated volatile organic compounds in the troposphere, Chem. Soc. Rev., 37, 699–716, doi:10.1039/b704260b, 2008.

Saathoff, H., Naumann, K.-H., Mohler, O., Jonsson, A° . M., Hallquist, M., Kiendler-

ACPD

10, C892–C896, 2010

Interactive Comment

Scharr, A., Mentel, Th. F., Tillmann, R., and Schurath, U.: Temperature dependence of yields of secondary organic aerosols from the ozonolysis of alpha-pinene and limonene, Atmos. Chem. Phys., 9, 1551–1577, 2009, http://www.atmos-chem-phys.net/9/1551/2009/.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 3129, 2010.