**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.

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We thank the referee for the helpful and constructive comments. We carefully considered all of them.

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

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(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

Comment: 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.

Reply: This is an important comment. Our work focuses on water dependent reaction paths in the ozonolysis of α-pinene. Indeed Pinonaldehyde is not only being produced via the suggested reaction presented in scheme 1. As shown in table 1a and in Fig. 5 Pinonaldehyde was also detected under dry conditions. The only water dependent path for the formation of Pinonaldehyde suggested so far is via the reaction presented in scheme 1. We clarified the text and the figure caption of scheme 1 accordingly stating:

"The mechanism forming pinonaldehyde from the ozonolysis of α-pinene is still under discussion (Johnson and Marston, 2008). Pinonaldehyde has been detected under

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dry and humid reaction conditions. The reaction of the stabilized Criegee Intermediate (SCI) with water (reaction scheme 1) has been suggested to yield pinonaldehyde under humid conditions (Alvarado et al., 1998)."

Comment: 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).

Reply: Table 3 now provides an overview of the molar yields of PA determined for the ozonolysis of α pinene in the literature. Experimental conditions are described. We included the following discussion of the comparison of the literature data to our findings at the end of chapter 3.3:

"The molar yields of PA determined at ambient temperature were compared to the literature data (see table 3). As can be seen in Table 3 there are plenty of experiments at a wide range of different experimental conditions with RH often not specified. Taking the literature data obtained from humid experiments (RH > 4%) in the presence of an OH scavenger provides a molar yield of PA in the range of 0.06 − 0.34. Our value under humid conditions of 0.30 ± 0.06 is in support of the higher end of the given range. Experiments carried out in absence of an OH scavenger (Hatakeyama et al., 1989; Warscheid and Hoffmann, 2001) have higher molar yields of PA (0.23 − 0.53) arising from the reaction of α-pinene with OH radicals being produced during the ozonolysis (Atkinson and Arey, 2003). Literature data for dry conditions are inconclusive. Warscheid and Hoffmann (2001) found a lower value while Berndt et al. (2003) observed a higher value at dry compared to humid conditions. The trend with humidity observed by Warscheid and Hoffmann (2001) is in agreement with our observation however their values are larger because of the absence of a scavenger. Our value determined under dry conditions (0.07) is at the lower end of the molar yield range obtained of all studies, conducted under dry and humid conditions, in the presence of

an OH scavenger. We suggest that a humidity independent reaction path exists for the ozonolysis of α-pinene with a molar PA yield of 0.07 and a humidity dependent path beside, which adds up to a molar PA yield of ∼0.3 at RH = 40 - 50%.."

Comment: 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.

Reply: The link between the two papers and other papers derived from the campaigns is now stated at the end of the introduction:

"A summary of all measurements and the temperature dependence of the SOA yields from the ozonolysis of α-pinene and limonene are described by Saathoff et al. (2009). That paper also provides parameters specifically useful for aerosol yield calculations in atmospheric models. The temperature dependence on the kinetics of α-pinene with ozone and the volatility of produced SOA are presented in Tillmann et al. (2009) and Jonsson et al. (2007), respectively. The focus of this paper is on the interplay of humidity and temperature in the formation and partitioning of pinonaldehyde..."

Comment: Page 3136, lines 19-21: Is "accuracy" the most appropriate term here? Should it simply be uncertainty?

Reply: As uncertainty is the more general term and we state the 1s uncertainty of the calibration (page 3136, line 19) we changed "accuracy" to "uncertainty"

Comment: 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.

Reply: The sentence has been changed to:

"For SOA mass loads > 30 μg m-3 it is evident from the data presented in Fig. 4 that particulate water is detectable in the humid cases, while it is zero under dry conditions."

Comment: 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?

Reply: We now point out that figure 7 was prepared from the sectional yield data recorded in table 1b. The mean molecular mass of the aerosol constituents were calculated as a weighted average of the aerosol components detected from the ozonolysis of α-pinene in the paper from Yu et al. (1999a). This information has been included:

"Figure 7 shows the relationship of 1/YPA,gas vs. Morg applying the sectional yield data recorded in Table 1b. Using this linear relationship one can extract further physical properties for PA and its partitioning. In order to derive a total molecular yield YPA.total from the intercept we have to know the average molecular weight MWom of the products. A value of 180 g mol-1 was calculated from the weighted average molecular masses of the aerosol components detected from the ozonolysis of α-pinene as presented by Yu et al., (1999a). Using 180 g mol-1 for MWom we derive a total molecular yield YPA.total of 0.30 $\pm$ 0.06. The error provides the standard deviation of the non error weighted linear regression parameters derived from figure 7. The product (γPA$\times$p0PA) is calculated to be (3.0 $\pm$ 1.5) $\times$ 10-3 Pa."

Comment: 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?

Reply: See comment #2. and #1. We clearly state our findings at the end of chapter 3.3.

Comment: 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).

Reply: A comparison to the IUPAC value of the OH yield has been introduced on page 3148, line 28 stating the following:

"….an absolute OH yield of 0.67 $\pm$ 0.17 under humid conditions (cf. Table 2). This value agrees exactly with the OH yield in the α-pinene ozonolysis also observed by Berndt et al. (2003), however is lower than the OH yield of 0.80 as recommended by IUPAC (IUPAC, 2005)."

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

Reply: We now include the results from experiment SOA05-1 into table 1. The data was omitted in the 1st version of table 1, because the results of the experiments SOA05-1 and SOA05-13 are comparable.

Comment: 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.

Reply: The description of the different OH yields in the footnote of table 2 has been extended accordingly. The uncertainty of the OH yields is given on page 3149, lines 1-4. This value is now included to the footnotes of table 2:

"The uncertainty of the OH yields is about 25 %."

Comment: 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?

Reply: The errors of 1/Y(PA) are calculated from the standard deviation of Y(PA) as provided in table 1b. Figure 7 has been updated to show these errors. The errors for the total molecular yield YPA.total of 0.30 $\pm$ 0.06 and for (γPA$\times$p0PA) = (3.0 $\pm$ 1.5) $\times$ 10-3 Pa given on page 3144, lines 5-6, provide the standard deviation of the non error weighted linear regression parameters derived from figure 7. This information has been included in the text:

"The error provides the standard deviation of the non error weighted linear regression parameters derived from figure 7."

Technical Corrections

Comment: Page 3135: change "Proton-Transfer-Reaction Mass Spectrometry" to "Proton Transfer Reaction-Mass Spectrometry". Twice on this page.

Reply: This has been changed accordingly.

Comment: Page 3135 and 3136: remove "-" from "AIDA-chamber" and "m/z-signal"

Reply: The "-" has been removed.

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

Reply: Changed

Comment: Page 3137: change "sulphate" to "sulfate". The latter is the recommended IUPAC spelling.

Reply: We now use the spelling recommended by IUPAC.

Comment: 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.

Reply: Throughout the text the mass concentration is now reported in μg m-3 In figures μg/m3 is used.

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

Reply: The correct RH is 68%. The value on Page 3141, line 25 and in table 2 were corrected.

Comment: Both vapour and vapor are used in the manuscript. Again, the authors

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should be consistent here.

Reply: The spelling vapour is now used throughout the manuscript.

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

Reply: Rounded values were used in the original manuscript. The exact values have been included on Page 3149, line 6

Comment: In the captions to Table 1b and Table 2, the "sigma" looks a little like a "delta". Has the correct symbol been used?

Reply: The symbol has been changed to a sigma.

Comment: Page 3162, figure 1: move "(FTIR)" so that it appears before "spectrometer"

Reply: This has been changed accordingly.

Comment: Page 3168, Figure 7: The use of "silently" is incorrect. This sentence should be rewritten.

Reply: We removed "silently" from the text.

Comment: Page 3171, Scheme 1: Only one "path" is represented in the scheme. Suggest rephrasing the caption.

Reply: The caption has been rephrased.

References

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