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## ***Interactive comment on “ $\alpha$ -pinene photooxidation under controlled chemical conditions – Part 2: SOA yield and composition in low- and high-NO<sub>x</sub> environments” by N. C. Eddingsaas et al.***

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Received and published: 25 May 2012

We thank you for your careful review of our manuscript; your comments and suggestions are appreciated and have made the paper stronger. Please find below responses to your comments and the changes made to the manuscript.

This paper presents the aerosol-phase observations and analysis from a series of experiments on the photooxidation of  $\alpha$ -pinene, for which the gas-phase results are presented in another paper (Part 1). The use of ESI mass spectrometry on collected aerosol filter samples enables elucidation of aerosol-phase composition, which combined with gas-phase chemical ionization MS allows the authors to speculate on as-

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pects of the oxidation mechanism under high and low NO<sub>x</sub>, with neutral and acidic seed particles. Because this gas- and aerosol-phase analysis is so interconnected, this reviewer wonders why Parts 1 and 2 were not combined and published as a single paper? The paper presents several interesting observations and analyses elucidating the oxidation products of  $\alpha$ -pinene, some of which get a bit lost in the text. A bit of reorganization is recommended to make these major points come across more clearly (see discussion below).

Reply: We have decided not to put the part 1, gas-phase, and part 2, SOA, together because there are a number of interesting and important results from the gas-phase and particle-phase that have no bearing on the other and we believe that these results could get lost in a single paper that would be around 30 pages.

Specific comments 1. p. 8581, line 24: If you do not combine the papers into one, I suggest a few sentence summary of the major findings of Part 1 here, to help readers understand what information they would find there (and understand why it is not in this paper)

Reply: That is a good point; we have included the following sentences in the introduction outlining the major findings of the gas-phase experiments.

“It was determined that pinonaldehyde is an important oxidation product under both low- and high-NO<sub>x</sub> conditions. The formation of pinonaldehyde from low-NO<sub>x</sub> OH oxidation implies that the reaction of  $\alpha$ -pinene hydroxy hydroperoxy radical and HO<sub>2</sub> has a channel that produces an alkoxy radical and recycles OH. This type of reaction channel has been shown to be important only for acyl peroxy radicals and possibly toluene. In addition, it was demonstrated that number of organic acids formed from low-NO<sub>x</sub> OH oxidation, including pinonic acid and pinonic peracid, are not formed from high-NO<sub>x</sub> OH oxidation.”

2. p. 8582, lines 11-14: Last 2 sentences of introduction should be combined: “We compare SOA and gas-phase composition . . .” and omit last sentence. As written this

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implies that you tuned over a range of acidity.

Reply: Fixed

3. p. 8583 around line 6, further discussion lines 17-20: Even though you cannot exactly determine NO and NO<sub>2</sub> concentrations because of interferences, it would be nice to give the reader a sense of how different high-NO and high-NO<sub>2</sub> conditions are. Could you estimate the ratios for those 2 cases? Or provide some sort of bounding on how different they might be?

Reply: The value that determines what acyl peroxy radicals react with (NO or NO<sub>2</sub>) will be the ratio of NO to NO<sub>2</sub>. We have done some simulations of the NO<sub>x</sub> chemistry to get a better understand the concentrations of NO and NO<sub>2</sub> and more importantly the ratio of the two. In a typical HONO experiment, the ratio of NO to NO<sub>2</sub> increases with time while using methyl nitrite the ratio decreases with time. Within a short time the ratio of NO to NO<sub>2</sub> using HONO becomes greater than one and in our simulations typically reached a steady state at a ratio of 1.3-2.2. Using methyl nitrite we find the ratio of NO to NO<sub>2</sub> decreased to less than one between 0.3 – 1.2 hours and reached a steady state of about 0.3. What can be stated is that in all simulations, and in all experiments, nitric acid production was greater when methyl nitrite was the OH source (by a factor of 1.4 – 2). Also, in all experiments the gas phase PAN production was greater when methyl nitrite was the OH source while the gas phase concentration of organonitrates was insensitive to OH source. This indicates that there was greater NO<sub>2</sub> + OH reaction and that the overall ratio of NO<sub>2</sub> to NO was higher when methyl nitrite is the OH source. The following sentences were added to the experimental section to clarify; “While the exact NO and NO<sub>2</sub> concentration could not be determined, it was confirmed that greater NO<sub>2</sub> concentration and the ratio of NO<sub>2</sub> to NO is greater in the methyl nitrite experiments due to the increased gas-phase concentration of nitric acid and peroxyacyl nitrates (PANs). The gas-phase concentration of nitric acid and PANs in the methyl nitrite experiments was 1.4 – 2 times that in similar HONO experiments.”

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4. p. 8588 lines 19-20: I don't understand the sentence about "independent of NO<sub>2</sub> concentration" – clarify. Just that high-NO was equivalent to high-NO<sub>2</sub>? or high-NO<sub>x</sub> equiv. to "low-NO<sub>x</sub>"? Why specifically call out NO<sub>2</sub> here?

Reply: The sentence has been reworded to say, "In the presence of AS+SA seed, the SOA yield was the same under high-NO and high-NO<sub>2</sub> conditions."

5. GENERAL COMMENT ON SECTION 3.2: Some of your interesting interpretation could easily get lost here. I suggest breaking this up to into subsections with more descriptive titles to guide the reader through your discussion better. One option would be to separate out your straight observations (e.g. which products observed in which experiments) from you interpretation (e.g. likely that certain compounds previously observed were from ozonolysis not OH, there must be other pathways to 3-MBTCA). Granted this is a matter of style, so this is simply a suggestion.

Reply: To clarify and focus the attention to the important results, we have split up section 3.2 into three sections; 3.2.1 Comparison of SOA composition between low-NO<sub>x</sub>, high-NO, and high-NO<sub>2</sub> OH oxidation in the presence of ammonium sulfate seed, 3.2.2 Change in SOA composition in the presence of highly acidic aerosol seed, and 3.2.3 Bulk SOA functionality determined by AMS.

6. p. 8590 line 3: please write out the chemical name of 3-MBTCA at first instance

Reply: 3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA) is first mentioned in the introduction and the name is provided as well as in tables 2 and 3.

7. GENERAL COMMENT ABOUT STRUCTURES: It might be helpful to readers to include a figure of the important chemical structures that feature in your discussion. In particular, maybe a figure showing the structures in your mechanism discussion on p. 8591, lines 1-4

Reply: We are not speculating on a mechanism for the formation of either terpenylic acid or diaterpenylic acid acetate, we are just stating what the data implies (i.e. that

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they appear to come from different sources). We have included a figure to go along with tables 2 and 3 showing the structures of the identified compounds from the tables.

8. p. 8593, lines 1-5: (for your “interpretation” subsection . . .): Do you think this is because there is in fact another precursor? Or could acidity control partitioning of one but not the other?

Reply: Thank you for bringing our attention to this section. Previously it has been proposed that 2-hydroxy terpenylic acid comes from aerosol processing of terpenylic acid, not diaterpenylic acid acetate. In addition, that is not the point we are trying to make and therefore the last part (“the presumed precursor”) has been removed. The point being made is that 2-hydroxy terpenylic acid behaves the same under high-NO and high-NO<sub>2</sub> conditions, however, diaterpenylic acid acetate behaves differently (is less important to SOA composition with AS+SA seed under high-NO conditions but does not change under high-NO<sub>2</sub> conditions). Removing the small part of the sentence makes the point more clear.

9. p. 8594 line 3: for completeness, what does van Krevelen say about high-NO? Anything interesting?

Reply: Unfortunately the AMS was not running during any of the HONO experiments so we cannot comment on this.

10. p 8595, line 5-7: is SA or SA/volume the relevant parameter here?

Reply: We do not believe it matters in this instance. What the result indicates is that there is no gas phase loss with the addition of aerosol seed that does not include sulfuric acid, i.e. anything that simply condense onto a surface already has.

11. p. 8595 line 20-23: does this mean some species partition more readily to inorganic seeds only? Or is this just a consequence of an overall increase in SA?

Reply: The increased partitioning only occurs in the presence of AS+SA seed, not in the presence of AS seed alone. This indicates that partitioning is not due to ammonium

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sulfate itself but rather due to the incorporation of SA into the seed. To be more accurate, the use of acidic seed has been replaced by AS+SA seed throughout the paper. In addition, the sentence that started at line 21 on page 8595 has been amended to read "... of isoprene are not lost from the gas phase due to the addition of either AS or AS+SA seed particles."

12. line 26: Does uptake of 1st-generation products compete with later-generation gas-phase chemistry?

Reply: If a species partitions to the aerosol it will not be available for gas phase oxidation. Line 26 starts a sentence that states we saw twice as much gas-phase loss as growth of SOA when AS+SA seed was added after gas phase oxidation of  $\alpha$ -pinene. If you are asking if fresh AS+SA seed was available throughout the experiment would the gas phase composition change due to uptake of first generation species, we believe it would as a number of first generation species are shown to be lost from the gas phase when fresh AS+SA seed was added. This cannot be conclusively determined from the results presented, but would be an interesting set of experiments to explore.

13. p. 8596 line 20-21: is the supposed m/z 316 product from  $\alpha$ -pinene or norpinonaldehyde PAN the same molecule or different with same mass? Is the structure known or is this just a mass observed in both cases without knowing what it is?

Reply: A first generation oxidation product observed in the gas phase by the CIMS at m/z 316 that has been assigned to  $\alpha$ -pinene dihydroxynitrate based on previous analysis by Aschmann (2002). A later generation product is assigned to norpinonaldehyde PAN. This has been clarified here as well as in section 3.2 where the UPLC/ESI-TOFMS m/z 310 is discussed.

14. p. 8597 line 14 remove "levels" and describe conditions / which experiments you're talking about in more details?

Reply: The sentence has been changed to the following; "In high-NO<sub>2</sub> experiments,

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1.4 to 2 times greater concentrations of PANs and nitric acid were observed in the gas phase compared to the high-NO experiments.”

15. around line 17: Can you make some estimate of how much HNO<sub>3</sub> deposition would make H<sub>2</sub>SO<sub>4</sub> irrelevant – is there enough here?

Reply: We are not implying that nitric acid uptake will make the aerosol as acidic as the AS+SA aerosol. We are implying that there may be enough nitric acid and/or PANs to lower the pH of the SOA enough to allow other species to partition.

16. line 25 – p. 8598 line 4: Maybe omit the discussion of coating earlier in the paper so it has more “punch” here? Again – stylistic suggestion to take or leave! Might this coating affect WHICH products partition?

Reply: We have left in the discussion about the coating in the results and discussion but have moved the discussion about the potential to underestimate SOA yield in the presence of highly acid aerosol to the implication section.

17. line 10-14: again, this is a repeat of earlier discussion of the 3-MBTCA hypothesis. Punchier if you only say this in one place (here is good!)

Reply: We remove the statement that there must be another mechanism to form 3-MBTCA from the results in discussion section so now it is only discussed in the implications. In the results and discussion section we left in the statement that 3-MBTCA is observed under both high-NO<sub>x</sub> (where no pinonic acid is observed) and low-NO<sub>x</sub> (where reactions with NO will not occur).

18. Fig. 3: Do I correctly understand that you observed greater SOA yield from the lower  $\alpha$ -pinene experiment at low-NO<sub>x</sub>? This is interesting and should be discussed in the text!

Reply: We do, but it is only one experiment and it is not known if it is reproducible. It is an interesting result and one that is worth investigating further. In paragraph four of section 3.1 we state that we do not know the origin of the increased SOA yield.

19. Fig. 6 caption text about greater  $\alpha$ -pin concentration at the beginning of some expts than others should be mentioned in the text, too.

Reply: The following sentence has been added to the third paragraph of section 3.3, “The difference in SOA volume growth from self-nucleation from both low- and high-NO<sub>x</sub> experiments was due to greater gas-phase  $\alpha$ -pinene concentration at the beginning of each AS seed experiments compared to the AS+SA experiments.”

20. Figs 7-8: this makes a lot of sense to me – you never see NO gas-phase loss for high mass species, only the very volatile one. Nice! I’m confused about the y-axes, though – I thought you said these experiments weren’t quantitative?

Reply: Figures 7 and 8 (now 8 and 9) are gas phase measurements made by chemical ionization mass spectrometry (CIMS). We can calculate CIMS sensitivity to analytes in the negative mode as described in the experimental section. What is not quantitative is the aerosol composition as measured by the UPLC/ESI-TOFMS.

Technical corrections 21. p. 8580, line 14: Since you have not yet addressed “high-NO” vs “high-NO<sub>2</sub>”, suggest changing both instances of “high-NO” in the abstract to “high-NO<sub>x</sub>” for consistency with “low-NO<sub>x</sub>”

Reply: It has been changed.

22. p. 8582, line 16: Remove “and pinonaldehyde” from 1st sentence of Experimental. You don’t describe any experiments starting with pinonaldehyde here.

Reply: Pinonaldehyde experiments were performed and are discussed in the aerosol composition section, specifically under low-NO<sub>x</sub> conditions. The following sentence has been added to the experimental section discussing the addition of hydrocarbon. “In photooxidation experiments where pinonaldehyde was the initial hydrocarbon, pinonaldehyde was introduced into the chamber by passing dry nitrogen over a liquid sample.”

The following have all been fixed, thank you for noticing them.



throughout: Shouldn't the abbreviation for liter be "L" not "l"?

p. 8583 line 5: insert comma between "chamber" and "resulting"

p. 8584 line 14: omit "the detection of"

p. 8585 line 15: change "a previous publication" to "previous publications" line 17: "or that are organosulfates . . ."

p. 8586 line 24: change "high-NO<sub>x</sub>" to "high-NO<sub>2</sub>"

p. 8588 line 26: remove "presence of"

p. 8589 line 7: "mass loading"

p. 8595 line 15: "noticeably"

p. 8596 line 4: "partitioning"

line 12: "photooxidation from pre-seeded laboratory. . ."

p. 8597 line 5: add high-NO<sub>2</sub> conditions as well?

line 13: change "between high" to "in high"

Fig. 2: mg should be  $\mu\text{g}$ ?

Fig. 8: caption text: photooxidation misspelled

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 8579, 2012.

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