Interactive comment on “Photo-oxidation of pinonaldehyde at low NO$_X$: from chemistry to organic aerosol formation” by

H. J. Chacon-Madrid et al.

Anonymous Referee #2

The paper deals with SOA formation from pinonaldehyde, a stable product of the α-pinene oxidation, which can be achieved by a single attack of oxidant, but also as product of stable intermediate products. The SOA yields of pinonaldehyde at low NOX were compared to high NOX results, and to SOA yields of an aliphatic aldehyde and an aliphatic hydrocarbon, both with similar vapour pressure as pinonaldehyde. The higher yield of pinonaldehyde at high NOX compared to low NOX conditions was attributed to photolysis instability of products formed at low NOX. Aspects of NOX dependent chemistry of aldehydes are discussed. It is a neat little study, the findings are interesting and the paper is well written. Actually, there is not much to criticize, but at certain point felt left alone as I expected more results. As a consequence the generalizations are based on a very limited data set. So I consider the presented study more as an interesting start than as ripe and comprehensive findings. If we could label the manuscript as “rapid communication” or “research letter”, it could be published in ACP under such heading without major changes.

In any case, I would like the authors to comment on the following issues:

p. 7734, line 7: What is the reason for that assumption of “no-interference”? Did you perform tests for interferences with your PTR-MS signal? How much could uncertainties in the chemical turnover of the reactant contribute to the total error of your SOA yields?

p. 7736, line 3ff and Figure 3: The systems pinonaldehyde/low NOX and tridecanal/high NOX level off with still several ug of COA present. Does this imply that the yield is constant for small COA = small turnovers? In the same direction: why does the yield of tridecanal at low NOX tends to increase with decreasing COA? What is the reason for the difficulties (“high degree of uncertainty and noise”) to determine yields at COA < 20 ug?

p. 7733, line 5ff: How important is the wall loss correction for the different chemical systems, e.g. if in one case vapours preferably condense onto the Teflon walls instead of deposited ammonium sulphate?

Author's Response:

Atmospheric Chemistry and Physics does not have a separate category for a rapid communication or letter. This manuscript is relatively short, but the only relevant categories are Research Articles and Technical Notes. This is not a technical note; our conclusions are scientific and do not address largely technical issues associated with SOA formation experiments. We believe that this manuscript constitutes a significant, albeit succinct contribution for the following reasons.

First, the topic of SOA aging is very current and may play a central role in the lifecycle of organic aerosol in the atmosphere. While this has been addressed by several publications over the past few years, including publications involving our group, the focus has for the most part been on "bulk" experiments covering the aging of first-generation SOA produced via some process (i.e. ozonolysis, OH oxidation, photo-oxidation, etc.). The objective here is to complement the bulk experiments by starting with important first-generation products in order to constrain the SOA formation potential and volatility distribution of those species, whose oxidation products presumably constitute a subset of the more complex set of second-generation oxidation products from the parent precursor (i.e. α-pinene).

Second, the subject becomes very complex very quickly, and there is thus a role for contributions with a focused message. The story here is still fairly complicated. Pinonaldehyde is a "good" SOA precursor, but its yields are much lower than α-pinene even though it is several orders of magnitude less volatile than α-pinene. This helps to explain why aging of α-pinene SOA does increase SOA mass significantly but why it does not produce an overwhelming surge of SOA, as simple-minded models would suggest (models in which pinonaldehyde is as efficient or even more efficient than α-pinene as an SOA precursor). On top of that, however, the SOA mass yields from pinonaldehyde depend strongly on background conditions, including NO_x levels and UV illumination. This corroborates similar sensitivity observed for α-pinene SOA, especially after aging.

Third, the sensitivities just described suggest that organic aerosol may be highly sensitive to background conditions of atmospheric chemistry. A huge puzzle at present is that organic aerosol levels appear to be strongly associated with human activity, even though a majority of the carbon atoms are modern, suggesting a non-fossil source. Specifically, global OA appears to be strongly associated with CO, which is a good tracer for human influence (Spracklen et al., 2011), but ^{14}C measurements, even in the northeastern U.S., show high modern carbon (Wozniak et al., 2011). Chamber experiments such as ours showing a high sensitivity to conditions such as NO_x levels and UV for successive generations of SOA formation and aging thus present a possible explanation – to first order, if the average "generation number" of OA is g, and the sensitivity of SOA to conditions for one generation of oxidation is S, the overall sensitivity to conditions is something like S^g. This can become very significant very quickly.

Finally, the issues outlined above are highly current. Thus there is indeed a compelling reason for "rapid" publication, even if the journal does not have a separate category for such submissions (indeed, given the public forum for *ACPD*, it is hard to get much more "rapid"). For these reasons, we feel that this submission stands on its own.

Specific comments.

p. 7734, line 7:

There is no reason to think that there are interferences with the PTR-MS signal of the parent molecule at the beginning of an experiment. The parent molecule is the only major organic species in the gas phase. As the experiment evolves and the parent molecule reacts with the OH radical, it is possible to find isobaric ions (at unit-mass resolution). There are very specific paths that would form isobaric ions such as the one presented in Fig. 5 of Chacon-Madrid et al. (2010). This was the case for *n*-tridecanal after approximately 1 hour of OH-radical photo-oxidation. This can be seen in Fig. A of the Supporting Information of Chacon-Madrid et al. (2010); however, in that same figure it can be seen how we corrected (blue line) for this interference. We were able to do this correction for *n*-tridecanal because we determined the OH-radical concentration by using methanol as a tracer and used an implied rate constant for OH + *n*-tridecanal from Kwok and Atkinson, (1995). In the case of pinonaldehyde, we did not see evidence for any interference after inferring its decay in a similar way done for *n*-tridecanal. Because of the careful check on the decay of the parent molecule, we believe that the decay itself does not add significantly to SOA mass yield uncertainties.

We will edit the sentence in page 7734, line 7 and 8 for improved clarity, from "A key assumption is that interferences from other species were minimal" to "There is no evidence for interference from isobaric ions for either the precursors or the OH tracer; they are the dominant gas-phase organics, and the observed precursor decay matches that expected based on the inferred OH concentration. This is discussed in detail in Chacon-Madrid et al. (2010) in Fig. 5 and Fig. A."

p. 7736, line 3 and Figure 3:

The data for SOA formation from pinonaldehyde at low NO_x and *n*-tridecanal at high NO_x in Fig. 3 show relatively constant SOA mass yields at low C_{OA} levels (less than 4 μg m^{-3}). There are two reasons for this. First, the yield variations are so small with respect to the range of the *y* axis (0 – 0.35) that they are not noticeable. Second, the plotted data points (dynamic yields) are approximately 5 minutes apart, so the precision of the earliest points (which are easy to identify because the x values are widely spaced) is limited for $C_{OA} < 4$ μg m^{-3}. However, as discussed in the reply to Reviewer #1, there is no *a priori* reason to exclude "flat" mass yield curves, so we have no reason to exclude these data.

p. 7733, line 5:

We do not see any evidence that vapors condense directly to Teflon walls; we do see evidence that they do not. We are adding a figure in the Supplementary Data, Figure E (new), covering a series of straight-chain aldehydes with up to thirteen carbons. The molecules are not exposed to UV light or any oxidant in these data. There is no evidence for long-term condensation to the chamber walls; the PTR-MS signals are constant for the duration of each experiment (about an hour). As the referee correctly pointed out, if vapors were lost to the Teflon walls, the calculated SOA mass yields would be biased low, but we do not see evidence for this. We discussed this in the ACPD draft in page 7735 lines 6 – 11.

References

Chacon-Madrid, H. J., Presto, A. A., and Donahue, N. M.: Functionalization *vs.* Fragmentation: *n*-Aldehyde Oxidation Mechanisms and Secondary Organic Aerosol Formation, Phys. Chem. Chem. Phys., 12, 13975-13982, 2010.

Kwok, E. S. C., and Atkinson, R.: Estimation of Hydroxyl Radical Reaction Rate Constants for Gas-Phase Organic Compounds Using a Structure-Reactivity Relationship: An Update, Atmos. Environ., 29, 1685-1695, 1995.

Spracklen, D. V., Jimenez, J. L., Carslaw, K. S., Worsnop, D. R., Evans, M. J., Mann, G. W., Zhang, Q., Canagaratna, M. R., Allan, J., Coe, H., McFiggans, G., Rap, A., and Forster, P.: Aerosol mass spectrometer constraint on the global secondary organic aerosol budget, Atmos. Chem. Phys., 11, 12109-12136, 2011.

Wozniak, A. S., Bauer, J. E., and Dickhut, R. M.: Fossil and contemporary aerosol particulate organic carbon in the eastern United States: Implications for deposition and inputs to watersheds Global Biochem. Cy., 25, 1-14, 2011.