Interactive comment on “Photo-oxidation of pinonaldehyde at low NOx: from chemistry to organic aerosol formation” by H. J. Chacon-Madrid et al.

Anonymous Referee #1

The study presents SOA yields of a sequence of molecules reacting with the OH radical at low NOx. Each molecule of the sequence (n-pentadecane, n-tridecanal, pinonaldehyde) has a similar vapor pressure but functionalities are different. This is a follow up study of an earlier paper presenting the same set of compounds reacting at high NOx. Similar to that study they find again a lower yield of the aldehyde compounds compared to the alkane. This can be understood from the high reactivity of the aldehydic H-atom which is attacked first by OH atoms and finally leads to a fragmentation of the molecule. Contrary to this alkanes are functionalized and therefore compounds of lower volatility are produced. Thereafter, the authors discuss the observed difference of SOA yield from pinonaldehyde photo-oxidation and attribute the lower yield at low NOx to UV photolysis of peroxides. The approach taken by the authors in order to investigate the influence of chemical structures and mechanisms on SOA yield and ageing is interesting. However, the experimental realization is inadequate. Each experiment has been performed only once! To my understanding this is not good laboratory practice. Smog chamber experiments are quite complex and variation from experiment to experiment can be substantial. The constant SOA yield in case of the dark experiment is quite unusual and makes me skeptical whether something went wrong with the experiment or if there are issues with the data analysis (e.g. changing collection efficiency in the AMS with increasing OM, could an impurity in pinonaldehyde produce SOA by ozonolysis in the dark experiment?). In Figure 4 SOA yields become similar at higher mass concentrations questioning the UV light effect. I do not consider the presented results to be convincing and recommend that the authors perform a decent set of experiments.
Author’s Response:

It is true that some of the data reported here come from single experiments for a given set of conditions. However, these experiments are part of a systematic exploration of how both precursor composition and background conditions (i.e. NOx levels, UV illumination) influence SOA formation. In this context it is not unusual for data to be reported in the literature from single experiments, so long as sufficient evidence exists to tie those data into a coherent and evidently precise set of measurements. Conducting an extensive series of SOA formation experiments places a significant demand on our experimental facilities, and there are times when we decide that the evidence is strong enough with a single experiment. We argue that this applies here.

Both n-tridecanal and pinonaldehyde are extremely similar molecules with regard to OH-radical reactivity. The aldehydic hydrogen is the center of reactivity, leading to the systematic fragmentation presented in Fig. 2, and both molecules have similar vapor pressures. In a previous paper (Chacon-Madrid et al., 2010) we established that SOA mass yields from n-tridecanal were repeatable under high-NOx conditions and that SOA mass yields from pinonaldehyde under the same conditions were very similar (Chacon-Madrid and Donahue, 2011), agreeing to within experimental error over the range 20 µg/m³ < COA < 100 µg/m³ (a second, higher COA experiment for n-tridecanal SOA formation was left off of Fig. 3 in the current manuscript but is shown in Fig. 3 of Chacon-Madrid and Donahue, (2011) and Fig. 4 of Chacon-Madrid et al. (2010) – this omission will be rectified in the revised manuscript, and the new figure is at the end of this document). Consequently, n-tridecanal and pinonaldehyde SOA mass-yield data presented here for low-NOx conditions effectively represent a replicate experiment. This is discussed in section 4.1, page 7737 of our present manuscript.

It can be seen in Fig. 3 how n-tridecanal and pinonaldehyde low-NOx experiments (open symbols) merge into one SOA mass yield curve very consistent with the previous explanation – the overlap is similar in precision to the overlap in Fig. 3 of Chacon-Madrid and Donahue, (2011) and Fig. 4 of Chacon-Madrid et al. (2010) – this omission will be rectified in the revised manuscript, and the new figure is at the end of this document). Consequently, n-tridecanal and pinonaldehyde SOA mass-yield data presented here for low-NOx conditions effectively represent a replicate experiment. This is discussed in section 4.1, page 7737 of our present manuscript.

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It is not unusual to have single experiments for a given precursor and condition in a relatively wide-ranging study, for example Ng et al. (2007a) presented only one experiment for each experimental condition. Another example is Lim and Ziemann, (2009) where only one data point is presented for SOA
mass yields of different alkanes. In fact, the duplication of chemical structure and volatility presented here is more repetition than can be found in numerous published studies.

**Constant SOA mass yield (Fig. 4).**

Flat SOA mass yield curves such as the one seen in Fig. 4 – dark experiment – are not the norm but they are neither rare nor inconsistent with thermodynamic interpretation. They can be seen throughout multiple experiments in the literature. For example Ng et al. (2007b) SOA mass yields of toluene and m-xylene at high-NO\textsubscript{x} conditions show a relatively constant yield at the higher end of C\textsubscript{OA} (Fig. 8 in Ng et al. 2007b).

Flat mass yields plotted vs C\textsubscript{OA} in an “Odum” plot (Odum et al., 1996) indicate a product or products with very low volatility and few semi-volatiles over the C\textsubscript{OA} range of an experiment. This is especially likely at low C\textsubscript{OA} if some products are extremely low volatility; SOA mass yields stay relatively constant. That is our interpretation of the pinonaldehyde + OH SOA formation in the dark. As seen in Fig. 2 of this manuscript, in the absence of UV light, the main first-generation gas-phase product should be the peroxyacid (blue structure). By structure activity relationships (Pankow and Asher, 2008) this product should have a C* of roughly 300 µg/m\textsuperscript{3}; consequently, the observed SOA formation for C\textsubscript{OA} < 300 µg/m\textsuperscript{3} must arise from a minor product (consistent with the 0.05 µg/µg mass yield). Our interpretation is that a higher molecular weight association product (a.k.a. an oligomer, Kroll and Seinfeld, 2008) may be formed in the dark experiment (Fig. 4) and it is vulnerable to photolytic cleavage; the more photolytically stable semi-volatile monomer products thus dominate the Odum plot under illumination (albeit with very low mass yields), while the photo-sensitive product dominates in the dark. The formation of oligomers in organic aerosol has been observed in previous experiments in the literature (Kalberer et al., 2004; Kalberer et al., 2006). Though we do not have direct evidence of their presence, it is something worth investigating in future projects. However, it is out of the scope of the present manuscript. However, we will add the previous comments about our interpretation of flat SOA mass yields from pinonaldehyde in the dark (Fig. 4) in section 4.3.

The UV effect is not a solitary finding. Henry and Donahue (2012) have recently reported a strong sensitivity to UV illumination for SOA formed from α-pinene oxidation at low-NO\textsubscript{x}. The SOA is especially prone to photolytic loss when first-generation SOA has been aged with OH radicals to form second-generation SOA. This is consistent with the findings of Bateman et al. (2011). The SOA formed from pinonaldehyde here is expected to be an important subset of the SOA formed during α-pinene SOA
aging, as pinonaldehyde is a major first-generation product of α-pinene oxidation (Hatakeyama et al., 1989; Glasius et al., 1997). Presto et al. (2005) also reported an effect of UV radiation on SOA production from terpene ozonolysis, showing suppression of SOA formation with exposure to UV lights. Consequently, the higher SOA mass yields presented here under dark low-NO\textsubscript{x} conditions are part of a growing body of evidence that highly oxidized SOA is especially vulnerable to photolysis.

**Data Analysis, Contamination.**

The SOA mass yields presented throughout this manuscript come from SMPS measurements – mentioned in page 7732, lines 22-24 – consequently changes in collection efficiencies from an AMS are not an issue.

Impurities are something we take very seriously. Our synthesis procedure for pinonaldehyde is discussed in Chacon-Madrid and Donahue, (2011). The general agreement of SOA mass yields for pinonaldehyde and n-tridecanal and the consistency of PTR-MS mass spectra for the pinonaldehyde as well as the first-generation products such as nor-pinonaldehyde all support our assertion that any impurities in the pinonaldehyde do not bias our findings. That evidence concerns illuminated experiments with relatively low ozone; the higher yield results for a dark chamber could conceivably be different, but this is unlikely. In order to have an impurity that would react with ozone in the dark experiment (Fig. 4) (a concern expressed by Referee # 1), it would have to be a species with a double bond. However, the pinonaldehyde was synthesized by ozonolysis of α-pinene with a large excess of ozone to guarantee complete oxidation of the α-pinene (McMurry and Bosch, 1987). Residual unsaturation is thus extremely unlikely. Finally, we present a series of NMR spectra in the Supplementary Information, and no evidence of double bond species exists.
Fig. 3. Pinonaldehyde and \( n \)-tridecanal SOA mass yields at high and low NO\(_x\). The potential to form organic aerosol from pinonaldehyde + OH – and \( n \)-tridecanal – is less than that from \( n \)-pentadecane + OH under high and low NO\(_x\). \( n \)-Pentadecane yields come from Presto et al. (2010). Pinonaldehyde (triangles) and \( n \)-tridecanal (squares), independent from NO\(_x\) concentration, suffer fragmentation paths in its first-generation chemistry that limits its SOA formation potential. \( n \)-Alkanes such as \( n \)-pentadecane do not experience significant fragmentation in their first-generation chemistry (Lim and Ziemann, 2005).
References


