

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 #1

The study presents SOA yields of a sequence of molecules reacting with the OH radical at low NO_x. 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 NO_x. 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 NO_x 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. NO_x 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-NO_x 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 < C_{OA} < 100 μg/m³ (a second, higher C_{OA} 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-NO_x 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-NO_x 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 et al. (2011). In the revised manuscript we will be more clear in Section 1.3 that *n*-tridecanal SOA mass yields, both at high and low-NO_x conditions, constitute an effective repetition of experiments involving pinonaldehyde since they have almost identical OH-radical chemistry and vapor pressures.

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_x conditions show a relatively constant yield at the higher end of C_{OA} (Fig. 8 in Ng et al. 2007b).

Flat mass yields plotted vs C_{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_{OA} range of an experiment. This is especially likely at low C_{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/m³; consequently, the observed SOA formation for C_{OA} < 300 μg/m³ 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_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_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.

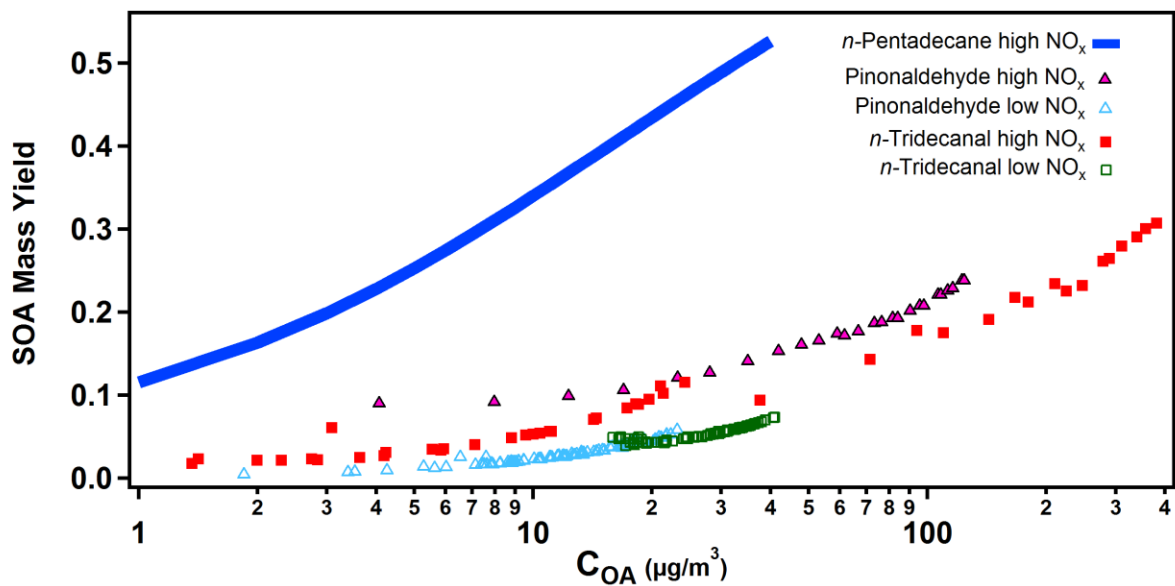


Fig. 3. Pinonaldehyde and n -tridecanal SOA mass yields at high and low NO_x . The potential to form organic aerosol from pinonaldehyde + OH – and n -tridecanal – is less than that from n -pentadecane + OH under high and low NO_x . n -Pentadecane yields come from Presto et al. (2010). Pinonaldehyde (triangles) 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

Bateman, A. P., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Photolytic processing of secondary organic aerosols dissolved in cloud droplets, *Phys. Chem. Chem. Phys.*, **13**, 12199-12212, 2011.

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.

Chacon-Madrid, H. J., and Donahue, N. M.: Fragmentation vs. functionalization: chemical aging and organic aerosol formation, *Atmos. Chem. Phys.*, **11**, 10553–10563, 10.5194/acp-11-10553-2011, 2011.

Glasius, M., Calogirou, A., Jensen, N. R., Hjorth, J., and Nielsen, C. J.: Kinetic Study of Gas-Phase Reactions of Pinonaldehyde and Structurally Related Compounds, *Int. J. Chem. Kinet.*, **29**, 527-533, 1997.

Hatakeyama, S., Izumi, K., Fukuyama, T., and Akimoto, H. j.: Reactions of Ozone with α -Pinene and β -Pinene in Air: Yields of Gaseous and Particulate Products, *J. Geophys. Res.*, **94**, 13013-13024, 1989.

Henry, K. M., and Donahue, N. M.: Photochemical Aging of α -Pinene Secondary Organic Aerosol: Effects of OH Radical Sources and Photolysis, *J. Phys. Chem. A*, **Published online**, 2012.

Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A. S. H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., and Baltensperger, U.: Identification of Polymers as Major Components of Atmospheric Organic Aerosols, *Science*, **303**, 1659 - 1166, 2004.

Kalberer, M., Sax, M., and Samburova, V.: Molecular Size Evolution of Oligomers in Organic Aerosols Collected in Urban Atmospheres and Generated in a Smog Chamber, *Environ. Sci. Technol.*, **40**, 5917-5922, 2006.

Kroll, J. H., and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmos. Environ.*, **42**, 3593-3624, 2008.

Lim, Y. B., and Ziemann, P. J.: Effects of Molecular Structure on Aerosol Yields from OH Radical-Initiated Reactions of Linear, Branched, and Cyclic Alkanes in the Presence of NO_x, *Environ. Sci. Technol.*, **43**, 2328-2334, 2009.

McMurry, J. E., and Bosch, G. K.: Synthesis of macrocyclic terpenoid hydrocarbons by intramolecular carbonyl coupling: bicyclogermacrene, lepidozene, and casbene, *J. Org. Chem.*, **52**, 4885-4893, 1987.

Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D. C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C., and Seinfeld, J. H.: Effect of NO_x level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, *Atmos. Chem. Phys.*, **7**, 5159-5174, 2007a.

Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, *Atmos. Chem. Phys.*, 7, 3909–3922, 2007b.

Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H.: Gas/Particle Partitioning and Secondary Organic Aerosol Yields, *Environ. Sci. Technol.*, 30, 2580-2585, 1996.

Pankow, J. F., and Asher, W. E.: SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds, *Atmos. Chem. Phys.*, 8, 2773-2796, 2008.

Presto, A. A., Huff Hartz, K. E., and Donahue, N. M.: Secondary Organic Aerosol Production from Terpene Ozonolysis. 1. Effect of UV Radiation, *Environ. Sci. Technol.*, 39, 7036-7045, 2005.