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Interactive comment on “Aging of secondary organic aerosol generated from the ozonolysis of α -pinene: effects of ozone, light and temperature” by C. Denjean et al.

Anonymous Referee #3

Received and published: 7 October 2014

In this chamber study (Denjean et al., Aging of secondary organic aerosol generated via the ozonolysis of alpha-pinene: effects of ozone, light and temperature), a series of experiments was conducted to study physical properties (e.g. optical properties, hygroscopicity, particle size) and chemical composition of secondary organic aerosol (SOA) at different aging conditions: 1) at elevated ozone concentrations, 2) under light (controlled temperature), and 3) under light and heat (6 °C temperature increase). SOA was generated via ozonolysis of alpha-pinene at dry conditions (i.e., RH < ~1 %) and after 14 h of the start of SOA formation, the particles were exposed to forcing for 6 h. The aim of study was to investigate properties and aging of SOA particles

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over timescales of 20 h. The results showed that no change in SOA size, properties or chemical composition was observed during ozone and light exposure at constant temperature whereas the increase in temperature led to changes on SOA properties (particle size, optical properties, composition and hygroscopicity). The authors concluded that "SOA properties may be governed more by local temperature fluctuations than by oxidative processing and photochemistry".

The study presents novel and important results on aging of SOA particle produced by ozonolysis of alpha-pinene. In general, SOA have a significant impact on Earth's atmosphere and climate, and thus this study is an important increasing our knowledge of SOA. The methods have been described in detail in the manuscript (MS) as well as experiments have been well designed and conducted. Furthermore, the results were quite well reported and analyzed. The MS is well organized, written and in the scope of this journal, and thus MS is certainly suitable for publication in this journal. However, there are some comments, suggestions and technical corrections that should be considered before publication:

General comments:

The experiments have been conducted at very dry conditions ($RH < 1\%$). It is known that humidity has an important effect on SOA formation, chemistry, reactions, properties of particles, etc. Please discuss in more detail the effect of RH on the results and conclusions in the MS.

The increase in temperature influences both evaporation of semi-/low volatile compounds and kinetics of chemical reactions. In current version of MS, the interpretation of results has mainly been done based on an influence of temperature on volatility of compounds, not kinetics of chemical reactions. What is the effect of temperature increase on the chemistry and chemical reactions of SOA formation?

The increase in temperature has the most notable effect on SOA particles during aging mostly due to evaporation of low/semi volatile compounds. Was there any gas-phase

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component analysis during temperature aging (e.g. with FTIR or PTR-MS)? It would be very nice to know concentration of volatile compounds in gas-phase during experiments. The composition of gas-phase compounds may differ significantly particle-phase compounds which might explain, e.g., why O:C and f44/f43 ratios changed with increasing temperature (Fig. 6a, 6b).

The aging at ozone of 700 ppb did not show any significant effect on SOA properties. SOA has been produced via ozonolysis of α -pinene. In generally, α -pinene easily reacts with ozone but reaction products of α -pinene do not (no more C-C double bonds, see e.g. Kroll and Seinfeld, 2008). Is this the main reason why no effect has been observed during ozone aging? What will the situation be if OH radicals have been used as oxidant instead of ozone, or α -pinene has been replaced with other terpene with more double bonds (e.g. myrcene)? Please discuss in more detail about ozone-terpene chemistry during particle formation and aging.

SOA mass concentrations at the start time of forcing (Table 1, 14 h after the initiation of SOA formation) varied significantly from measurement to measurement (30 - 117 $\mu\text{g}/\text{m}^3$). It seems, however, that the initial VOC and ozone concentrations were practically identical in different experiments (ca. 250 ppb and 200 ppb, respectively). What is the reason for this mass concentration variation? Is a same amount of VOC injected to chamber in all experiments? How does this variation of SOA mass concentration affect aging and properties of SOA particles?

The chamber illumination system provides a good reproduction of the solar energy distribution at the Earth's surface. What kind of atmospheric chemistry can this illumination produce? Are there any OH-radicals (i.e. OH chemistry) in the chamber during illumination experiments (especially when humidity is very low)?

Optical properties (CRI) changed when chamber temperature increased. At the same time particle size decreased due to evaporation of volatile compounds. How much does the decrease of particle size affect optical properties? Is this size-change-effect

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as significant as the change of particle composition?

Heating of the chamber can increase evaporation of semi/low volatile VOC from walls. Can this have some effect on the gas-particle partitioning and thus composition of SOA particles?

Specific comments:

Abstract:

Please indicate already in abstract that the experiments have been conducted at very dry conditions.

Please also point out that the results and conclusions are probably valid only for α -pinene ozonolysis (see the final statement "SOA properties may be governed more by local temperature fluctuations than by oxidative processing and photochemistry"). Please discuss in more detail whether the conclusions are also valid for other terpenes/VOC or for different chemistry (e.g. OH radicals)? I am not very sure that the results of this study can be generalized to other terpenes or oxidants.

Please also discuss in the abstract why the increase in temperature affects SOA properties (what are reasons). For instance, you have already stated at the end of chapter 3.4 (p. 22453) "These results suggest that the changes in SOA physical and chemical properties observed in these experiments resulted from the heating-induced evaporation of semi-volatile and less oxidized SOA species, which in turn modified the optical and hygroscopic properties of the condensed phase". Is this the main conclusion of this study?

Introduction:

Page 22441, line 12: Check brackets (before Lambe not needed).

Methods:

Page 22443, line 10: I think that the reference to the supplementary figure (Fig. S1) is

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not needed at all. Just refer to the original paper Wang et al., Atmos. Meas. Tech., 4, 2465–2494, 2011.

2.4 Modeling SOA formation and aging (p. 22448, l. 10-12): The models "simulate gas/particle partitioning in terms of equilibria between the gas phase and an ideal liquid homogeneous condensed phase". As mentioned in the paper, recent studies have shown that SOA particles are like solid/semisolid, not liquid. How does the solidity of SOA particles affect model results?

Results:

3.1 Changes in SOA size distribution during simulated atmospheric processing: Please plot also an average particles size (GMD) as a function of time for different experiments (as 3rd panel in Fig 2). This would help to compare different experiments.

3.3 Changes in SOA chemical composition during simulated atmospheric processing: Page 22451, l. 5-7: Text "m/z 43 is associated to lower oxygenated groups, such as aldehydes and alcohols" is written two times.

Fig. 6a and 6b show an increase in O:C and f44/f43 ratios with increasing temperature. Does this only mean that particles with lower O:C and f44/f43 ratios evaporates easier?

3.4 Effect of phase partitioning on SOA properties (p. 22451-22453): Recent studies have been shown that in the chamber experiments, the wall losses of very low volatile compounds might have significant implications on their partitioning between the gas and particle phase (see, e.g., Kokkola et al. Atmos. Chem. Phys., 14, 1689–1700, 2014). How do wall losses of low volatile VOC affect your result interpretation? Is the difference between measured and simulated SOA mass concentration caused (partially) by the wall losses of semi/low volatile compounds.

Conclusions:

Page 22456, line 8-10: "a-pinene-O3 SOA is quite insensitive to light- and ozone-induced aging under our experimental conditions, most likely as a result of kinetic limi-

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tations imposed by its physical state (semi-solid/glassy)." Please discuss also the effect of a-pinene - ozone chemistry on SOA properties. I suppose that the kinetic limitations due to SOA physical state is not main reason for observed insensitivity of light- and ozone-induced aging, rather the chemistry of a-pinene derived SOA.

Supplement:

The supplementary figure (Fig. S1) is not needed. The figure is same as previously published: Wang et al., Atmos. Meas. Tech., 4, 2465–2494, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 22437, 2014.

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