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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Multi-generation Chemical Aging of α-Pinene Ozonolysis Products by Reactions with OH" *by* Ningxin Wang et al.

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(1) *This study investigated the OH-oxidation of a-pinene ozonolysis products by reporting the mass yields and elemental composition of SOA produced. The main finding of this study is that OH-oxidation of a-pinene ozonolysis products that is equivalent of 2-4 days of atmospheric OH exposure leads to 20-40 percent net increase in the SOA yields and an increase in the aerosol O:C ratio by up to 0.04. While highlighting the importance of multi-generation aging in the atmospheric evolution of SOA, a topic that has been extensively studied previously, this finding alone, however, does not warranty the scientific significance and publication of this manuscript on ACP. Substantial revisions are needed, as described in the individual points below.*

We address the various comments of the reviewer below. Our responses and corresponding changes in the paper follow each comment.

General:

(2) *To what extent the experimental observations that 20-40 percent increase in SOA yields by further OH-oxidation could be applied to the actual atmospheric conditions? The authors used HONO as the OH precursor, which means that hundreds of ppbv levels of NO were present in the experiments conducted. Such an experimental condition is quite different from what is in the atmosphere, where most monoterpene emissions are from remote regions that encounter low NO air masses (e.g., a few ppb or less). As we know, NO significantly alters the VOCs oxidation mechanisms primarily by reacting with RO_2 radicals, leading to vastly different product distributions from those observed in the absence of NO, a chemical regime where RO_2+HO_2 and RO_2+RO_2 reactions dominate the fate of RO_2 radicals. That said, the experimental results presented in this study only represent a barely-seen scenario in the atmosphere and does not have any atmospheric relevance. The authors are suggested to conduct 'low-NO_x' experiments as well where H_2O_2, for example, can be used as the OH precursor. The observed increase in SOA yields, together with the high-NO experiments, can be used as upper and lower limits for the a-pinene SOA aging in the atmosphere.*

Fundamentally, the issue of "atmospheric relevance" is one of whether the elementary chemical reactions occurring in the experimental system are the same as in the atmosphere. In this case, the question is the fate of peroxy radicals (RO_2). The chemical meaning of "high-NO_x" is "high-NO" in the sense that the dominant fate of RO_2 radicals is to react with NO. Therefore, by working at relatively high NO concentrations, we isolate the high-NO_x pathway for the aging reactions. This is the same as experiments using H_2O_2 photolysis, which typically have extremely high H_2O_2 concentrations and thus a large flux through the reaction OH + H_2O_2 → H_2O + HO_2. Those experiments tend to isolate the RO_2 + HO_2 pathway. In general, it is an error to conflate "atmospherically relevant" with "atmospheric concentrations," though it is important to establish that the rate-limiting chemistry is relevant to the atmosphere. We have added the above important point in the revised paper.

(3) *The methodology of this study, including the chamber experimental approach, SOA yield measurements corrected by particle wall loss, O:C ratio calculations by AMS measurements, has been widely used in the community for decades. The main result of this study, i.e., SOA yields increase by 20-40 percent upon OH-oxidation aging, is insufficient to warranty publication of this manuscript. The authors should endeavor to explore more detailed mechanisms involved in the a-pinene SOA aging by thoroughly analyzing the AMS data, e.g., What functionalities/products have changed and contributed to SOA production during aging? Any indication of PMF analysis, for example, on the key processes involved in the chemical aging?*

PMF analysis works by separating the AMS-measured mass spectra into individual factors, and comparing those factors to existing libraries of mass spectra for the purpose of identifying potential sources for the SOA components. It is mostly used on ambient measurements where the sources for the OA are uncertain, while in these chamber experiments, we know that the SOA is formed via monoterpene oxidation. Application of this technique usually results in two or three factors with the fresh, aged and may be an intermediate product. While there could be useful information in this analysis it rarely provides the necessary chemical insights in cases where the changes in the spectra are relatively small like here.

In an attempt to explore the functionalities/products that may have changed during aging, we used the AMS high-resolution family analysis. Each fitted ion is grouped into a "family" based on their chemical formula, and the families used are: CH, CHO, CHO_2, C_x, HO, and NO. These are the main components of the organics formed, with family HO calculated by subtracting the other families from the total organic signals, because sulfate can fragment into water and thus interfere with family HO. We used family NO

to represent the organonitrate compounds formed during the aging step.

Based on the results, for example, of Experiments 1 and 2, the less oxidized ion family CH decreased around 10 percent during the aging process (from 41.9 to 38.1 percent of the OA in Exp. 1 and from 40.5 to 35.3 percent in Exp. 2) while the more oxidized components CHO_2 increased 4 percent in Exp. 1 (from 12.8 to 13.3 percent) and 16 percent in Exp. 2 (from 14.9 to 17.3 percent). The changes in the family CHO were +4 percent in Exp. 1 and -6 percent in Exp. 2 suggesting that there is both production and destruction of the corresponding family members. The organonitrate compounds as expected were close to zero initially in these experiments. In the end of the aging process the NO family represent 3-3.5

CO_2^+ (*m/z* 44) from family CHO_2 and $C_2H_3O^+$ (*m/z* 43) from family CHO are usually identified in aged and relatively fresh aerosols, respectively. Their fractions of the total organics, f_{44} and f_{43}, have been used as chemical indicators in chamber experiments (Donahue et al., 2012). During the dark ozonolysis period of Exp. 1, the f_{43} increased initially and stayed practically constant after t=0.2 h while f_{44} decreased. This indicates the majority of the SOA formed initially was fresh. After the first introduction of OH, both f_{43} and f_{44} showed a stepwise increase, indicating formation of relatively fresh SOA and oxidation of the SOA. After the second introduction of OH, the f_{43} decreased while f_{44} increased over time until the end of the experiment, indicating the formed SOA was getting more oxidized with aging. During Exp. 2, the f_{43} increased sharply initially and then slowly decreased over the dark ozonolysis period. This is consistent with the "ripening" effect observed during the MUCHACHAS campaign (Donahue et al., 2012). Overall, f_{43} decreased while f_{44} increased over the course of Exp. 2, indicating formed SOA being oxidized during aging.

We added the above analysis to the revised paper and also added the corresponding figures to the Supplementary Information.

Specific:

(4) *Page 2, Line 35-36: There have been a number of studies investigating the SOA aging processes using both static chamber and flow tube reactors (e.g., Robinson et al., Science, 2007; Loza et al., ACP, 2012; Lambe et al., EST, 2012). The authors need to revise the statement 'Most laboratory studies of SOA formation so far have focused on the ...'*

We have revised the corresponding sentence noting that the early SOA studies focused on the first stage of reactions.

(5) *Page 3, Line 64: References need to be given here.*

We have the corresponding three references at this point.

(6) *Page 6, Line 154: What is the particle size range measured by SMPS?*

The SMPS was set to measure particles from 15-700 nm for the experiments in this work. This information has been added to the paper.

(7) *Page 6, Line 171: The OH radical molar yield from ozonolysis of a-pinene is roughly 0.7. So technically, the measured SOA yield at first stage is already a result of certain OH aging. Have the authors estimated the fraction of a-pinene that was oxidized by OH radical in the ozonolysis experiments? Have the authors considered adding any OH scavengers (e.g., H_2O_2, CO, methanol) in the first stage of the experiments?*

This is a good point. OH scavengers cannot be used in the first phase of these aging experiments, because they will react with the OH in the second phase and will not allow the chemical aging to take place. The exception is hydrogen peroxide, as described in Henry et al. (2011), which acts as an OH scavenger (producing HO_2) under dark conditions but as an OH source under UV illumination. However, a-pinene is much more reactive (by a factor of 3-10) than the first-generation products and so most of the OH radicals react directly with a-pinene precursor. Because we do not employ a scavenger, the first phase of the experiment includes reactions of the precursor and to a limited extent of the first-generation products with OH. We have used a kinetic box model of the system to estimate the extent of these reactions. Assuming a molar yield of 0.7 for a-pinene ozonolysis the model predicts that a little more than one third of the a-pinene reacted with OH in these experiments. Please note that these two reactions also take place together in the ambient atmosphere. This information has been added to the revised manuscript.

(8)*Page 7, Line 205: The assumption that the particle loss rate in the 300-600 nm range is the same potentially leads to underestimation of the corrected SOA yields, as bigger particles have higher wall loss rate due to gravity deposition.*

Gravitational settling predominantly affects particles bigger than 1 micrometer (Crump and Seinfeld, 1981; McMurry and Rader, 1985), while the majority of the particle mass in our experiments was in the range of 100-600 nm. We have regularly performed experiments with seed particles to characterize the k's for the aforementioned size range and the loss constant does not vary in our chamber from 300 to 600 nm. We evaluated the errors caused by using a constant fit value for particles of 300-600 nm by applying the same k's to the seed loss periods during Exp. 1. The variability for the final seed loss period (t=4.2-8.5h) was 4.2 percent, indicating the corrected seed particle volume stayed relatively constant (Fig. 3). We have assumed the same uncertainty of 4.2 percent for particles during the SOA formation. This explanation has been added to the paper.

(9) *Page 8, Line 236: The authors are suggested calculate the SOA density from the AMS measured O:C and H:C ratio of SOA (Kuwata et al., EST, 2012) and compare with the current value used.*

We used an SOA density of 1.4 g cm^{-3} in our calculations based on results from previous studies. We also used the approach described in Kostenidou et al. (2007), matching the AMS-mass/composition distribution with the SMPS measured volume distributions and estimated an average density of 1.3±0.15 g cm^{-3}. The Kuwata et al. (2012) parameterization also predicted 1.3 g cm^{-3}. This information has been added to the manuscript.

(10) *Page 9, Line 237-238: Adding the 'V(t)/Vmax' factor in the SOA yield correction procedure does not seem necessary. The authors stated that 'deviations of V(t) from Vmax are caused by the uncertainty associated in applying the size dependent wall loss corrections'. As we know, particle wall loss rate depends on a few parameters, including chamber size, eddy diffusion, static charges on the Teflon surface, and etc. For most experiments presented here that only lasted for a few hours, these parameters should be fairly constant so that the particle wall loss rate should be quite consistent before and after one experiment. Where are the deviations originating from? I wonder if the assumption that particle loss rate in the 300-600 nm range is the same has any impact on the SOA yield correction here.*

We defined the parameter, ϵ_V (Line 223), as an estimation for the uncertainties caused by our particle wall-loss correction. We calculated an ϵ_V of 4.2 percent for Exp. 1 based on how much the loss-corrected seed volume (t=4.2-8.5 h) deviated from its average value. The deviation of V(t) from Vmax is likely caused by the uncertainty of our particle wall-loss correction, which is 4.2 percent in this case, and may well include the effect of using a constant value for particles ranging in size of 300-600 nm. When calculating the corrected SOA volume, we have to subtract the seed from the corrected total volume concentration. With the goal in mind of minimizing the impact of the uncertainties caused by the particle loss correction on formed SOA, we introduced the 'V(t)/Vmax' factor to attribute part of this 4.2 percent error to the seed. If we subtract a constant seed volume, we are intrinsically attributing this 4.2 percent error all and only to the corrected SOA and we get the lower limit of the corrected SOA volume.

(11) *Page 27, Figure 5: Why the O:C ratio of SOA kept decreasing in the second dark*

period? What are the concentrations of NO_x and O_3 during this period? Is there any NO_3-initiated chemistry going on?

Similar evolution of the AMS spectra during periods without photochemistry has been observed in a number of similar studies. Donahue et al. (2012) called this evolution ripening to distinguish it from OH aging. The nature of this process is not well understood but it probably involves heterogeneous reactions. In our experiments the ozone concentration during this period was practically zero, so the production of NO_3 and the consecutive reactions were highly unlikely. We have added a short discussion and the corresponding reference to ripening in the paper.

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