Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition on secondary organic aerosol" *by* H. Li et al.

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We gratefully thank you for your constructive comments and suggestions to improve the manuscript. Here are our responses to your comments.

(Q=Question, and A=Answer)

Q1. One, the mixing ratios of both α-pinene and ozone are very high, hundreds of ppbv for the terpene and tens of ppm for ozone. I understand why these conditions were chosen, i.e. high ozone to react all the α-pinene away, and high α-pinene to get sufficient signal (I assume). However, the conditions do bring up the questions of how

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representative are the results of behavior in the atmosphere. Indeed, for this reason, I would weaken the relationships as stated in the paper to the GABRIEL field measurements, given that the field conditions are quite different from those in the lab. It would have been nice to see similar experiments performed at longer times and lower mixing ratios in a chamber (although, chambers themselves have their own experimental issues, I admit). For example, does the very high ozone affect the SOA when passing through the filter upon which the SOA is collecting for many hours?

A: It is a very good and important question. The high mixing ratios of both α-pinene and ozone would have influence on the gas-phase and SOA chemistry and challenge the representativeness of experimental results. Our additional experiments verify that the high ozone does not affect SOA significantly when passing through the filter upon which the SOA is collecting for 4 h. Below is the detailed information.

Stabilized Criegee intermediates (SCI)-related peroxides formation chemistry in experiments with high mixing ratios of reactants may be similar to those in experiments with low mixing ratios. The fate of SCI is considered in two aspects. (I) SCI+RO_2 reaction. When the mixing ratios of both α-pinene and ozone are high, the mixing ratios of SCI and peroxy (RO_2) radicals are also high. As proposed by by Sadezky et al. (2008), sequential addition of SCI to RO_2 radicals is possible. Zhao et al. (2015) found that the SCI+RO_2 reactions play a key role in initial particle formation in the *trans*-3-hexene ozonolysis when the mixing ratios of *trans*-3-hexene and ozone are high. However, they also suggested that such oligomerization reactions may not play a major role in particle formation from large alkenes such as terpenes and sesquiterpenes based on the results of the α-cedrene ozonolysis experiments. It may be that the recently proposed extremely low volatile organic compounds (ELVOC) formation involving a series of intramolecular H abstractions/O_2 addition via RO_2 radicals (Crounse et al., 2013; Ehn et al., 2014; Rissanen et al., 2015) from ozonolysis is the major particle formation pathway. Hence, in our experiments, SCI+RO_2 reactions may be not important even though the mixing ratios of SCI and RO_2 are high due to the high mixing ratios of α-

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pinene and ozone. (II) SCI+ H_2O reaction. Jenkin (2004) suggested that the reaction of SCI with H_2O probably dominates in both dry (ca. 60 ppmv H_2O) and wet (60% relative humidity) chamber experiments where both α-pinene and ozone are low, because of no significant difference in the rate of accumulation of aerosol mass. We find that SOA yields and peroxides (major products of SCI+H_2O reactions) yields also show no significant difference in dry (<0.5% relative humidity) and wet (60% relative humidity) flow-tube experiments, indicating that SCI+H_2O reactions probably also dominates in experiments where reactants mixing ratios are high.

Another important formation pathway of organic peroxides is the reaction of RO_2 with HO_2. The HO_2/RO_2 decreases with the increasing mixing ratios of α-pinene and ozone, therefore, the peroxides yields in our experiments is not exactly same as that in nature. However, the species of formed organic peroxides are similar in high- and low-reactants experiments.

In summary, the species of formed peroxides are similar in high- and low-reactants ozonolysis, while the amount and distribution of peroxides would be different. However, the rapid transformation of organic peroxides on SOA surface in the presence of water found in our experiments is supposed to happen in nature, although the amount of peroxides which can undergo such transformation may be different in nature and our experiments.

When it comes to the gas-particle partitioning, mixing ratios of reactants would have influence. The SOA yields increase with increasing reacted reactants concentrations. The amount of SOA condensed onto the wall also increases with increasing SOA concentration, leading to a loss of collected SOA mass. However, the loss of peroxides to the wall is smaller when the oxidation rate is faster and at larger precursor VOC concentration (Zhang et al., 2014), leading to a higher fraction of peroxides in SOA. The amount of particle-phase peroxides is calculated based on the SOA mass and fraction of peroxides in SOA, hence, it is hard to predict whether the gas-particle partitioning coefficients of peroxides increase or decrease in high-reactants ozonolysis.

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To evaluate the effect of the very high ozone on the SOA when passing through the filter upon which the SOA is collecting for many hours, we let 2 standard L min^{-1} synthetic air or ozone (as high as ozone used in reactions) pass through a loaded filter for 2 h immediately after 4 h SOA collection. Loaded filters placed without gas passing through in dark and 298K for 2 h were used as the blank group. Results show that the total peroxides in SOA reduced about 25% in both air and ozone experiments, and no significant difference was observed between the two set experiments, indicating that the high ozone does not affect peroxides in SOA significantly when passing through the filter upon which the SOA is collecting for 4 h, although the gas flow does affect peroxides in SOA. Another evidence for little influence of ozone on SOA is the results of experiments aging SOA with ozone. Denjean et al. (2015) found that α-pinene-O_3 SOA is quite insensitive to ozone-induced aging based on the test of mass concentration, optical properties and hygroscopicity of SOA, most likely due to the molecular structure of α-pinene which limit the gas-phase oxidation by ozone of reaction products of α-pinene. In summary, high ozone does not affect SOA significantly. However, considering that gas flow can decrease total peroxides in SOA during collecting SOA, gas-particle partitioning coefficients of peroxides we got are underestimated by about 21% (see the answer to Q2). Advances in instrumentation and methods for quantify trace organic peroxides are needed to get explicit gas-particle partitioning coefficients of organic peroxides in the future. Large gas-particle partitioning coefficients of peroxides we got provide an insight into the possible heterogeneous reactions of organic peroxides in condensed phase.

Your assumption is right: high mixing ratios of reactants are needed to get enough signal and react all the α-pinene away in our flow-tube experiments. We would also like to see experiments performed at longer times and lower mixing ratios in a chamber as contrasts. Unfortunately, a chamber is currently unavailable in our laboratory. However, lower mixing ratios of reactants means lower mixing ratios of products, leading to high level of difficulty of quantifying peroxides.

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Q2. Two, I would like to see some discussion of how the gas and aerosol constituents are experimentally separated. In particular, how are the gases stripped (and analyzed) without affecting the SOA? Could re-partitioning of species between the two phases occur when the separation process is being performed?

A: This is also an important question. Hereinafter, how the gas and aerosol constituents were experimentally separated will be described. In our experiments, a polytetrafluoroethylene (PTFE) filter (Whatman Inc., 2 μm in pore size, 47 mm in diameter, USA) was placed in outlet of the flow tube to let all 4 standard L min^{-1} gas pass through the filter. An air extracting pump was used to keep the gas pressure in flow tube at standard atmospheric level. Aerosol Spectrometer (GRIMM Aerosol Technik GmbH & Co., mini-WRAS 1371, Germany) signal shows that more than 92% aerosol were collected onto the filter. Hence, constituents of gas after the filter were regarded as gas constituents, and constituents of SOA on the filter were regarded as aerosol constituents in this study.

To evaluate to what extent the long-time collection of SOA affects gas and aerosol phase, tests on SOA collected for different time were additionally conducted. Figure S5 (Supplement) shows that SOA mass and total peroxides amount both have good linear relationships with collection time, however, slopes of the two linear fitting lines are less than 0.25. If SOA mass and peroxides amount in SOA collected in unit time are independent of collection time, the two slopes should be at least 0.25. Therefore, the long collection time does have effects on gas- and particle-phase constituents possibly due to re-partitioning of species between the two phases. Collected SOA mass and peroxides amount per unit time decreases with increasing collection time. At least about 9% SOA mass and 18% peroxides are lost during long-time collection, hence, fraction of peroxides in SOA is underestimated by 10%, and the gas-particle partitioning coefficients of peroxides given in our manuscript are the lower bounds. It is noted that the gas-particle partitioning coefficients of peroxides in our manuscript are not corrected with these losses. Assuming all the molecules lost in SOA come into gas

phase again without structure-changes, the underestimation of gas-particle partitioning coefficients of peroxides is calculated to be about 21%.

Q3. Three, I found some sections of the paper really quite hard to read–especially those dealing with discussion of results (Sections 3.3 and 3.4). I recommend that these discussion sections be shortened and clarified, focusing on just the main points.

A: Thanks for your suggestion. Here we would like to present our logic in these two sections first. In Sections 3.3 and 3.4, we try to figure out that why H_2O_2 yields are significantly higher in the presence of water vapor. Several possible sources of H_2O_2 are evaluated in Section 3.3: (a) ozonolysis and OH oxidation in the aqueous phase during and after gas collection; (b) decomposition/hydrolysis of organic peroxides in the aqueous phase during and after gas collection; (c) self-reaction of HO_2 in the gas phase; (d) decomposition of hydroxyalkyl hydroperoxides in the gas phase. These analyses of (a) and (b) show that and measuring method for H_2O_2 do not cause such high H_2O_2 yields, and analyses of (c) and (d) show that current formation mechanisms of H_2O_2 in ozonolysis cannot explain such high H_2O_2 yields. Based on the conclusions in section 3.3, we focus on the role of water vapor in H_2O_2 formation in Section 3.4. Results of a series of two-stage experiments show that rapid decomposition of organic peroxides on SOA surface in the presence of water is an important source of H_2O_2.

Finding the unexpectedly high yields of H_2O_2 in the gas phase and uncovering the rapid heterogeneous transformation of organic peroxides are the main points of Sections 3.3 and 3.4. Furthermore, these two sections are connected tightly by the role of water vapor, and the conclusions in Section 3.3 are the foundation of discussion in Section 3.4. Therefore, we prefer to keep the contents of the two sections. However, the expression of these sections are weak and may cause the contents hard to read. We have shortened and clarified the two sections.

Q4. Line 11, page 28134 – mention the type of SOA

A: We have revised it.

Q5. Line 20, page 28134 – perhaps "explain" instead of "interpret"

A: We have revised it.

Q6. Line 22, page 28134 – perhaps "preserves" instead of saves

A: We have revised it.

Q7. Line 28, page 28136 – Criegee

A: We have revised it.

Q8. Line 19, page 28146 – unclear instead of unclearly

A: We have revised it.

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