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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. Due to the limited reaction time and the need to provide sufficient SOA and analyte masses within reasonable times, relatively large precursor concentrations and very large ozone excess had to be used. The authors should explicitly discuss the consequences for the SOA chemistry.

A: Thanks for your comments. 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.

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-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.

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.

Q2. While the impact of the addition of an OH scavenger on the peroxide properties was rather small overall, the large OH production may change the nature of the SOA matrix and the oxidation scheme.

A: The OH radical formed in the ozonolysis is an interference to study the ozonolysis itself, and the OH scavenger is usually employed to isolate ozonolysis. Theoretically, the large OH production may change the nature of the SOA matrix and the oxidation scheme. However, the SOA yields and SOA peroxides yields are found independent of OH scavenger in our experiments. This phenomenon consists with the results of Docherty et al. (2005). They found that average SOA yield and SOA peroxides yields for ozonolysis of α-pinene were 45±7% and 47±12% respectively, and both independent of OH scavenger and relative humidity. Jenkin (2004) employed a chemical model containing 200 compounds to investigate the effect of OH radical scavengers on SOA yields for α-pinene, and predicted no significant effect of OH scavengers on SOA yields. The effect of OH scavenger on SOA yields differs for monoterpenes. A mechanism based on changes in the HO$_2$/RO$_2$ ratio caused by OH scavengers can be used to

explain the SOA yields of β-pinene but not α-pinene. It is important to figure out how OH scavenger affect α-pinene ozonolysis in the future.

Q3. Several recent studies have addressed the issue of partitioning between SOA and chamber walls, which must be an even more relevant issue for a flow tube. The authors should comment on the way this may impact the results of the present study, apart from the comment on this made in the context of the H_2O_2 budget.

A: Losses of vapors to chamber walls can affect SOA formation and lead to underestimation of SOA yields (Zhang et al., 2014). The biases of SOA yields due to vapor wall losses are different for various VOCs. The ratio R_{WALL} is used by Zhang et al. (2014) to quantitatively assess this bias, which is defined as the ratio of simulated SOA concentration in chamber with no wall loss to that with best-fit wall loss. R_{WALL} for α-pinene photolysis is rather low, only 1.6±0.3 and 1.3±0.1 under low- and high-NO_x conditions respectively where reacted α-pinene is about 47 ppbv. In addition, Zhang et al. (2014) suggested that "the calculated R_{WALL} varies with oxidant and VOC concentration (actually, VOC loss rate), with smaller R_{WALL} when oxidation rate is faster and at larger precursor VOC concentration." Hence, the high mixing ratios of reactants used in our experiments can lead to a lower R_{WALL}. More importantly, the short residence time in flow-tube experiments, about 2 min in our study, reduces wall contact, thereby reducing wall losses. In summary, vapor losses to walls are considered to insignificantly affect the gas-particle partitioning in our experiments.

Q4. P28141: the impact of the formation of peroxyhemiacetals on the determination of peroxides by iodometry should be explained in an additional sentence for the less informed reader. This is important since hemiacetal formation is relevant for the discussion of the gas–particle partitioning.

A: Thank you for your suggestion. We have added this in the revised manuscript.

Q5. Discussion on p28143: Is it possible that apart from wall effects, gas-particle equilibrium is not established on the relatively short flow tube residence times due to

effects of high viscosity in the particle phase?

A: We cannot exclude the possibility that gas-particle equilibrium is not established on the relatively short flow tube residence times. Comparing with previous chamber studies (Table S1 in Supplement), the fraction of peroxides in SOA we got are as much as that of Epstein et al. (2014), but less than that of Mertes et al. (2012) and Doherty et al. (2005). Apart from gas-particle disequilibrium, long-time gas flow passing through filter is proved to lower the peroxides in SOA by 10% (Supplement). Hence, the gas-particle partitioning coefficients of peroxides are the lower bounds and we have put this evaluation in the revised manuscript.

Q6. P28144/18145: decomposition and H_2O_2 formation in SOA solution: can the authors also speculate on the corresponding rates and life time in the native aerosol phase, i.e., in absence of dilution? Have the authors tried to let the filters sit for different times under dry or humid conditions and measure the formation of H_2O_2? While the experiments with the two separate flow reactors have nicely allowed to differentiate effects of humidity and the particle phase on the H_2O_2 yields, longer times would be required to assess peroxide stability under aerosol conditions.

A: It is hard to speculate the corresponding rates and life time in the native aerosol phase. H_2O_2 formed in SOA solution per unit mass of SOA decreases with increasing SOA concentration according to our experiments, indicating that the decomposition of organic peroxides is depressed at high concentration. In the native aerosol phase, the state and the concentration of peroxides are different from that in SOA solution. Hence expend the law of decomposition and H_2O_2 formation in SOA solution to that in the native aerosol phase may be not reasonable.

We carried out additional experiments to test the peroxides stability under aerosol conditions at 255K and 298K in dark. Figure S4 (Supplement) shows that the total peroxides decrease more slowly than H_2O_2 with the increasing sitting time, and the peroxides are more stable at 255K than at 298K. The decreasing rates of peroxides are

little different from those reported by Badali et al. (2015), possibly due to the different measuring method and SOA concentration.

Q7. There are some small language and grammar errors throughout the manuscript (not listed in detail here), which require attention. Some of it can also be taken care of in the type setting process for ACP.

A: Thank you for your patience. We have carefully checked the English and corrected the language and grammar errors of the manuscript.

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