January 18, 2016
ACP Editor

Dear Prof. Frank Keutsch,

Enclosed please find our revised manuscript entitled “Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition on secondary organic aerosol”, revised supplement and three responses to the anonymous referees #1, #3, and #4 respectively. We gratefully thank for the three referees’ constructive comments and suggestions to improve the manuscript. Detailed, point-by-point responses to the comments and corresponding revisions to the manuscript and supplement have been submitted. We believe that the revised manuscript is significantly improved.

The major revisions are specified as follows:

I. We have evaluated the influence of high mixing ratios of reactants on results in the supplement.

II. We have evaluated the influence of long-time collection on SOA in the supplement.

III. We have tested the stability of peroxides in SOA stored on-filter and stated it in the supplement.

IV. We have shortened and clarified the sections 3.3 and 3.4. Section 3.4 is named as “Rapid heterogeneous decomposition of gaseous organic peroxides” instead of “water effect”.

V. We have carefully checked the English and corrected the language and grammar errors of the manuscript.

Thanks for your time.

Sincerely yours,
Zhongming Chen and co-authors
Response to the Anonymous Referee #1

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. Abstract: will promote -> promote.
A: We have revised it.

A: Thank you for your suggestion. “Preserves” instead of “saves” is used in the revised manuscript.

Q3. Experimental section (p. 28138) and elsewhere: the authors should make it very clear (and probably add a disclaimer of some sort in the abstract) that they realize that the concentrations they use in their experiments are very high, and therefore, yields of peroxides may not represent actual yields of peroxides in oxidation of alpha-pinene in nature.
A: Thank you for your suggestion. We have added this in the results and discussion section. The detailed analysis of the effects of high concentration on these results and conclusions has been added in the supplement.

Q4. Future studies: It would be really great if the authors analyzed a field sample from an alpha-pinene-dominated region, such as boreal forests, and determined the same peroxides they observe in their lab experiments in field samples by the same methods they use. No action is needed in response to this comment.
A: Thank you for your suggestion. We would like to do this work if possible.

Q5. p28136: I presume “GABRIEL” stands for something? (Guyanas Atmosphere- Biosphere exchange and Radicals Intensive Experiment with a Learjet)
A: Yes, we have added the full name of this campaign in the revised manuscript.

Q6. p28148: please verify the $1.5 \times 10^{30}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ value; it seems to be too low to me.
A: We checked again, and confirmed that $1.5 \times 10^{30}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was given by Aplincourt and Anglada (2003).

References
Response to the Anonymous Referee #3

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 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-pinene and ozone. (II) SCI+
H$_2$O reaction. Jenkin (2004) suggested that the reaction of SCI with H$_2$O probably dominates in both dry (ca. 60 ppmv H$_2$O) 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$_2$O 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$_2$O 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.

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.

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$_2$O$_2$ yields are significantly higher in the presence of water vapor. Several possible sources of H$_2$O$_2$ 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$_2$O$_2$ do not cause such high H$_2$O$_2$ yields, and analyses of (c) and (d) show that current formation mechanisms of H$_2$O$_2$ in ozonolysis cannot explain such high H$_2$O$_2$ yields. Based on the conclusions in section 3.3, we focus on the role of water vapor in H$_2$O$_2$ 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$_2$O$_2$.

Finding the unexpectedly high yields of H$_2$O$_2$ 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.

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.

References


Response to the Anonymous Referee #4

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+RO₂ reaction. When the mixing ratios of both α-pinene and ozone are high, the mixing ratios of SCI and peroxy (RO₂) radicals are also high. As proposed by by Sadezky et al. (2008), sequential addition of SCI to RO₂ radicals is possible. Zhao et al. (2015) found that the SCI+RO₂ 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/O₂ addition via RO₂ 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+RO₂ reactions may be not important even though the mixing ratios of SCI and RO₂ are high due to the high mixing ratios of α-pinene and ozone. (II) SCI+H₂O reaction. Jenkin (2004) suggested that the reaction of SCI with H₂O probably dominates in both dry (ca. 60 ppmv H₂O) 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+H₂O reactions) yields also show no significant difference in dry (<0.5% relative humidity) and wet (60% relative humidity) flow-tube experiments, indicating that SCI+H₂O reactions probably also dominates in experiments where reactants mixing ratios are high.

Another important formation pathway of organic peroxides is the reaction of RO₂ with HO₂. The HO₂/RO₂ 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-O₃ 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 Supplement). 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 HO₂/RO₂ 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 H₂O₂ 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 RWALL 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. RWALL for α-pinene photolysis is rather low, only 1.6±0.3 and 1.3±0.1 under low- and high-NOₓ conditions respectively where reacted α-pinene is about 47 ppbv. In addition, Zhang et al. (2014) suggested that “the calculated RWALL varies with oxidant and VOC concentration (actually, VOC loss rate), with smaller RWALL 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 RWALL. 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 H₂O₂ 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 H₂O₂? While the experiments with the two separate flow reactors have nicely allowed to differentiate effects of humidity and the particle phase on the H₂O₂ 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. H₂O₂ 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 H₂O₂ 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 H₂O₂ 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.
References


Rissanen, M. P., Kurtén, T., Sipilä, M., Thornton, J. A., Kausiala, O., Garmash, O., Kjaergaard,


Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition on secondary organic aerosol

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Abstract

Organic peroxides, important species in the atmosphere, promote secondary organic aerosols (SOA) aging, affect HO\textsubscript{x} radicals cycling, and cause adverse health effects. However, the formation, gas-particle partitioning, and evolution of organic peroxides are extremely complicated and still unclear. In this study, we investigated in the laboratory the production and gas-particle partitioning of peroxides from the ozonolysis of \(\alpha\)-pinene, which is one of the major biogenic volatile organic compounds in the atmosphere and is an important precursor for SOA at a global scale. We have determined the molar yields of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), hydromethyl hydroperoxide (HMHP), peroxyformic acid (PFA), peroxyacetic acid (PAA) and total peroxides (TPO, including unknown peroxides) and the fraction of peroxides in SOA.\(\alpha\)-pinene/O\textsubscript{3}, SOA. Comparing the gas-phase with the particle-phase peroxides, we find that gas-particle partitioning coefficients of PFA and PAA are 10\textsuperscript{4} times higher than values from theoretical prediction, indicating that organic peroxides play a more important role in the SOA formation than expected previously. Here, we give the partitioning coefficients of TPO were determined as high as (2–3)\times10\textsuperscript{-4} m\textsuperscript{3} μg\textsuperscript{-1}. Even so, more than 80% of the peroxides formed in the reaction remain in the gas phase. Water does change the distribution of gaseous
peroxides, while it does not affect the total amount of peroxides in either the gas or the particle phase, but can change the distribution of gaseous peroxides. About 18% gaseous peroxides undergo rapid heterogeneous decomposition on SOA particles in the presence of water vapor, resulting in the additional production of H$_2$O$_2$. This process can partially interpret explain the unexpected unexpectedly high H$_2$O$_2$ yields under wet conditions. Transformation of organic peroxides to H$_2$O$_2$ also preserves OH in the atmosphere, helping to improve the understanding of OH cycling.

1 Introduction

Organic peroxides are important trace components in the atmosphere, serving as reservoirs of HO$_x$ and RO$_x$ radicals, participating in the formation of secondary organic aerosols (SOA), and causing adverse health effects as reactive oxygen species (ROS). Recently, peroxides have been found to play a key role in the aging of SOA. The particle-bound organic peroxides undergo atmospheric photolysis with a lifetime of about 6 days (Epstein et al., 2014), and decline significantly within the mean SOA age of 4–7 days (Rudich et al., 2007). A laboratory experiment on the photolysis of SOA shows a high yield of hydroxyl radicals (OH), which are considered to form from the decomposition of peroxides (Badali et al., 2015). This OH may cause the in-particle oxidation of SOA.

Model studies have tried to simulate the SOA formation in chamber experiments, but great discrepancies still exist between predicted and observed results (Camredon et al., 2010; Hoffmann et al., 1997; Griffin et al., 1999; Cocker III et al., 2001; Saathoff et al., 2009; Presto et al., 2005; Pye and Seinfeld, 2010; Farina et al., 2010). Jenkin (2004) added the formation of dimers and improved the simulation, especially at the beginning of SOA formation. Organic peroxides were found to be highly abundant in SOA (Ziemann, 2005; Docherty et al., 2005; Surratt et al., 2006; Nguyen et al., 2010; Bateman et al., 2011; Mertes et al., 2012; Epstein et al., 2014), possibly in the form of oligomers, which are even more important than carboxylic acids (Bonn et al., 2004). In order to improve the simulation of the production of the SOA mass within the chamber, explicit parameters about gas-particle partitioning of organic peroxides are urgently needed.

The reactions and processes that generate or remove peroxides have been studied for many years. Cross-reactions of organic peroxy radicals (RO$_2$) and the hydroperoxy radical (HO$_2$) and
self-reactions of HO₂ are thought to be major sources of organic peroxides and hydrogen peroxide (H₂O₂), respectively, in the atmosphere. Ozonolysis of biogenic volatile organic compounds (VOC) also produces H₂O₂ in high yields although its mechanism is unknown (Zhang et al., 2009; Huang et al., 2013). Hydrolysis and reaction with OH are the main removal pathways for both organic peroxides and H₂O₂, and dry/wet deposition removes only a small portion of peroxides (Khan et al., 2015). However, existing theories about sources of and removal of peroxides cannot account for the field observation results. Model simulations showed an overestimation on total peroxides (TPO) and a underestimation on H₂O₂ as compared with field records in the airborne GABRIEL field campaign (Guyana Atmosphere-Biosphere exchange and Radicals Intensive Experiment with the Learjet) field campaign (Kubistin et al., 2010), indicating the existence of possible underestimated or new removal paths for organic peroxides and overestimated or new formation paths for H₂O₂. Field observations and laboratory experiments showed that particulate components, possibly particle-bound organic peroxides, could be transformed to H₂O₂. Arellanes et al. (2006) found that H₂O₂ in ambient SOA solution was 200–1000 times greater than expected levels based on the gas-liquid partitioning, implying that almost all H₂O₂ is generated from SOA solution. Wang et al. (2011) investigated several kinds of SOA derived from the oxidation of α-pinene, β-pinene, and toluene, and came to the similar conclusion that more than 97.5% H₂O₂ arose from SOA formation rather than from gas-liquid partitioning. However, this process happens in SOA solution and the amount of H₂O₂ produced by such a pathway is too small to account for the large discrepancy between observations and simulations for the gas-phase H₂O₂.

The effect of water on peroxides is complex. Laboratory experiments suggested that yields of particle-phase total peroxides in the ozonolysis of alkenes are not influenced by water vapor (Docherty et al., 2005). Unlike the total peroxides, yields of individual peroxides depend on relative humidity (RH). Yield of H₂O₂ increases under wet conditions (Becker et al., 1990; Hewit and Kok, 1991; Simonaitis et al., 1991; Gab et al., 1995; Huang et al., 2013), while the yields of bis-hydroxymethyl hydroperoxide and three unknown organic peroxides decrease under wet conditions (Huang et al., 2013). Theoretical studies suggest that water helps both the formation and decomposition of organic peroxides. Water can react with stabilized Criegee intermediates (SCIs) and generate hydroxyalkyl hydroperoxides (HAHPS). It has been proposed that not only isolated water molecules, but also water dimers react with SCI,
and the latter path could even be more important (Ryzhkov and Ariya, 2004). Numerous laboratory experiments support this proposal (Chao et al., 2015; Lewis et al., 2015; Berndt et al., 2014). As a result, the reaction with water dimers will be the largest sink for CH$_2$OO. However, the quantum-chemical calculations predict that the larger SCIs react more slowly with water, both the water monomer and dimer (Vereecken et al., 2014). Water also helps gas-phase decomposition of HAHPs, although the decomposition rate constant is small according to the theoretical calculations (Crehuet et al., 2001; Aplincourt and Anglada, 2003).

This study investigates the ozonolysis of α-pinene, which is considered as one of the largest contributors to SOA and a dominant source of organic peroxides on a global scale (Khan et al., 2015), focusing on the formation of peroxides in both the gas and the particle phase. Gas-particle partitioning and water effect are examined carefully.

2 Material and methods

2.1 Chemicals

α-Pinene (Aldrich, 99%), cyclohexane (Sigma-Aldrich, ≥ 99.7%), potassium iodide (Alfa Aesar, 99.9%), hydrogen peroxide (Alfa Aesar, 35 wt %), ortho-phosphoric acid (Fluka, 85–90%), hemin (Sigma, ≥ 98.0%), 4-hydroxyphenylacetic acid (Alfa Aesar, 99%), ammonia solution (NH$_3$•H$_2$O, Beijing Tongguang Fine Chemicals Company, 25.0–28.0%), ammonium chloride (NH$_4$Cl, Beijing Chemical Works, ≥ 99.5%), ultrapure water (18 MΩ, Millipore), N$_2$ (≥ 99.999%, Beijing Haikeyuanchang Practical Gas Company Limited, Beijing, China), O$_2$ (≥ 99.999%, Beijing Haikeyuanchang Practical Gas Company Limited, Beijing, China), and polytetrafluoroethylene (PTFE) filter membrane (Whatman Inc., 47 mm in diameter) were used in this study.

2.2 Apparatus and procedures

A flow tube reactor (2 m length, 70 mm inner diameter, quartz wall) equipped with a water jacket for controlling temperature was used to investigate the ozonolysis of α-pinene. All the
experiments were conducted at 298±0.5 K and in dark. O$_3$ was generated by the photolysis of O$_2$ in a 2 L quartz tube with low-pressure Hg lamp, and the detailed quantification method of O$_3$ was described in our previous study (Chen et al., 2008). O$_3$ (~25 ppmv) was used in the experiments. α-Pinene gas was generated by passing a flow of N$_2$ over liquid α-pinene in a diffusion tube at the selected controlled temperature. The initial concentration of α-pinene, determined by gas-chromatography-flame ionization detector (GC-FID, Agilent 7890A, USA), was ~273 ppbv in the experiments. Water vapor was generated by passing N$_2$ through a water bubbler. The mixing gases, including α-pinene, O$_3$, and dry or wet synthetic air (80% N$_2$ and 20% O$_2$), were continuously introduced into the reactor with a total flow rate of 4 standard L min$^{-1}$ (standard liters per minute) and a residence time of 120 s. The relative humidity (RH) was controlled at two levels: <0.5% RH (dry conditions) and 60% RH (wet conditions). Gas from the reactor (2 standard L min$^{-1}$) was directed into a coil collector and scrubbed by H$_2$PO$_4$ stripping solution (5×10$^{-3}$ M, pH 3.5) for hydroperoxides analysis. SOA produced from the ozonolysis of α-pinene were collected onto a PTFE filter for 4 h at a flow rate of 4 standard L min$^{-1}$, and the mass of SOA on the filter was immediately measured by a semi-micro balance (Sartorius, Germany). After that, each loaded filter was extracted with 20 mL H$_2$PO$_4$ solution (5×10$^{-3}$ M, pH 3.5) using a shaker (Shanghai Zhicheng ZYW 103D, China) at 180 rpm and 4 °C for 15 min, and then the SOA solution was immediately analyzed to determine the particle-phase peroxides. Each SOA solution was analyzed 7 times at different times to investigate the evolution of SOA solution.

To explore the effect of water vapor on the formation of peroxides in the ozonolysis, two-stage reaction experiments were designed and carried out. In the first stage, dry synthetic air (2 standard L min$^{-1}$) with α-pinene (~275 ppbv) and O$_3$ (~42 ppmv) entered the first 2 L flow-tube reactor; in the second stage, the gas passed through the second 2 L flow-tube reactor but with the addition of dry or wet synthetic air (2 standard L min$^{-1}$). The residence time was 68 s in the first reactor and 34 s in the second reactor. The concentration of α-pinene at the outlet of the first reactor was found to be below the GC-FID detection limit (< 5 ppbv), meaning that α-pinene was almost completely consumed before the gas entered the second reactor. Thus, water vapor appearing in the second reactor only affected the products from the first reactor. A filter was placed at the outlet of the first reactor or second reactor to collect SOA when necessary.
2.3 Peroxides analysis

The low-weight molecular peroxides were measured using high-performance liquid chromatography (HPLC, Agilent 1100, USA) coupled with a post-column derivatization module and fluorescence detection, and the concentration of total peroxides was determined by an iodometric spectrophotometer method. Details about the HPLC-fluorescence method have been reported in our previous study (Hua et al., 2008). Briefly, this method is based on the reaction of \( p \)-hydroxyphenylacetic acid (POPHA) with organic hydroperoxides or hydrogen peroxide in the catalysis of the hemin forming POPHA dimer (2,2'-bisphenol-5,5'-diacetic acid), which is a fluorescent substance, and then is quantified by fluorescence detector. The separation of peroxides was implemented by column chromatography before the peroxides were reacted with POPHA. The synthetic method for organic peroxides standards is described in our previous study (Huang et al., 2013).

An iodometric spectrophotometric method has been developed to quantify all classes of peroxides (ROOR', ROOH and \( \text{H}_2\text{O}_2 \)), with the exception of tertiary dialkyl peroxides, in the aqueous phase without distinction (Banerjee and Budke, 1964). Peroxyhemiacetals formed in \( \alpha \)-pinene ozonolysis can be measured with this method. Excess potassium iodide reacts with peroxides producing \( \text{I}_3^- \) ion (R1), which can be quantified by UV/VIS spectrophotometry.

\[ 3\text{I}^- + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{I}_3^- + 2\text{H}_2\text{O} \quad \text{(R1)} \]

\( \alpha \)-Pinene SOA is freely soluble in polar solvents, e.g., water, acetonitrile and methanol, but it is poorly soluble in nonpolar solvents, e.g., chloroform and toluene (Nguyen et al., 2010). Hence, a \( \text{H}_3\text{PO}_4 \) solution, as a kind of polar solvent, could entirely extract SOA from filters. The HPLC fluorescence method uses \( \text{H}_3\text{PO}_4 \) solution as a solvent for peroxides such as \( \text{H}_2\text{O}_2 \), hydromethyl hydroperoxide (HMHP), performic acid (PFA), and peracetic acid (PAA) which are more stable in acidic solution than in pure water (Zhou and Lee, 1992). In order to be comparable with the HPLC fluorescence method, SOA loaded filters were also extracted by \( \text{H}_3\text{PO}_4 \) solution. The influence of pH on extraction efficiency is discussed in the Supplement. In this study, SOA solution (2.5 mL) was added into a 10 mL airtight micro reaction vessel (Supelco, USA). Each solution was then purged of oxygen by bubbling with \( \text{N}_2 \) for 5 min. After purging, an aqueous solution of KI (250 \( \mu \text{L}, 0.75 \text{ M} \) ) was added into the vessel. The vessel was then capped tightly, covered with aluminium foil, and allowed to stand in the dark for 12–24 h.
The solution absorbance was then measured at 420 nm by an UV/VIS spectrophotometer (SHIMADZU UV-1800, Japan). The efficiency of peroxide measurements was discussed in the supplement.

3 Results and discussion

3.1 Gas-particle partitioning of peroxides

3.1.1 Particle-phase peroxides

We measured the different mass values of SOA produced from the ozonolysis of α-pinene at different RHs in the presence or absence of the OH scavenger cyclohexane, and found that the typical in-reactor SOA concentration was 450–650 μg m\(^{-3}\). A comparison of the aerosol mass yields (\(Y_{\text{SOA}}\)), defined as the ratio of the formed aerosol mass to the consumed α-pinene mass, (Table 1) indicated that while the SOA yields were independent on the presence of water vapor, they were affected by the OH scavenger. The estimates of \(Y_{\text{SOA}}\) showed that the presence of the OH scavenger cyclohexane decreased \(Y_{\text{SOA}}\) to 28% (Table 1) decreased in the presence of OH scavenger.

Organic peroxides are considered to be one of the major constituents in SOA (Docherty et al., 2005; Ziemann, 2005; Suratt et al., 2006; Nguyen et al., 2010; Mertes et al., 2012; Kidd et al., 2014; Badali et al., 2015) (Table S1). The sensitivity of the iodometric method to ROOR is critical to obtain an accurate concentration of total peroxides since peroxyhemiacetals are a significant component (Docherty et al., 2005). In the present study, we determined the total molar concentration of peroxides in SOA using the iodometric method. Stability of peroxides in SOA stored on-filter was also tested, and the results show that peroxides concentration decrease with increasing sitting time (Figure S4). Hence, the peroxides in SOA were determined immediately after collection. Here, the mass fraction of peroxides in SOA (\(F_{\text{peroxides}}\)) is defined as the ratio of mass of particle-bound peroxides to SOA mass, which is defined as follows:

\[
F_{\text{peroxides}} = \frac{m_{\text{peroxides}}}{m_{\text{SOA}}}
\]
where $m_{\text{peroxides}}$ is the mass of particle-bound peroxides, such as PFA, PAA and TPO, and $m_{\text{SOA}}$ is the mass of SOA. Assuming that the average molecular weight of peroxides is 300, we obtained the mass fraction of total peroxides in SOA ($F_{\text{TPO}}$) as ~0.21 (Table 1), which is consistent with 0.22 reported by Epstein et al. (2014), but less than 0.47 reported by Docherty et al. (2005) and 0.34 reported by Mertes et al. (2012). Several factors, such as the presence of OH scavengers, reactor type, extraction method, SOA mass measurements, and SOA density assumptions, may cause these discrepancies. In addition to the concentration of total peroxides, we measured the concentration of two small organic peroxides per oxyformic acid (PFA) and peroxyacetic acid (PAA) in SOA and calculated the contribution of PFA ($F_{\text{PFA}}$) and PAA ($F_{\text{PAA}}$) to SOA mass (Table 1). Under dry conditions, the $F_{\text{PFA}}$ and $F_{\text{PAA}}$ were 0.35±0.06 and 0.11±0.04 ng μg$^{-1}$, respectively, without the OH scavengers and 0.14±0.00 and 0.09±0.01 ng μg$^{-1}$, respectively, with cyclohexane. After adding water vapor, $F_{\text{PFA}}$ did not significantly change, but $F_{\text{PAA}}$ approached 0.

### 3.1.2 Gas-phase peroxides

In addition to the particle phase peroxides, we measured the gas-phase peroxides generated in the ozonolysis of α-pinene. Here, the molar yield of gaseous peroxides ($Y_{\text{peroxides}}$) is defined in eq (2):

$$Y_{\text{peroxides}} = \frac{\Delta \text{peroxides}}{\Delta \alpha\text{-pinene}}$$  \hspace{1cm} (2)

where $\Delta \text{peroxides}$ are moles of formed gaseous peroxides, such as HMHP, PFA, PAA and TPO, and $\Delta \alpha\text{-pinene}$ are moles of consumed α-pinene. The molar yield of total peroxides ($Y_{\text{TPO}}$) were estimated to be nearly the same under both dry conditions and wet conditions in the absence of OH scavengers (Table 1), indicating that total yield of peroxides was unaffected by water vapor. Moreover, when we employed the MCM v3.1 mechanism to simulate the present reaction system, the modelled yield of total peroxides was about 0.25, consistent with our experimental result. The model results also suggested that hydroperoxides account for more than 99% of total peroxides. The yields of HMHP ($Y_{\text{HMHP}}$), PFA ($Y_{\text{PFA}}$) and PAA ($Y_{\text{PAA}}$) are shown in Table 1. Compared with dry conditions, $Y_{\text{HMHP}}$ and $Y_{\text{PFA}}$ doubled under wet conditions, while $Y_{\text{PAA}}$ increased only slightly. However, yields of these three organic peroxides were all
lower in the presence of the OH scavengers, indicating the importance of OH in the formation of small organic peroxides.

Considering that all the peroxides originally existed in the gas phase at the beginning of the ozonolysis of α-pinene, we estimated the fraction of peroxides that entered the particulate phase from the gas phase through gas-particle partition based on measured peroxides in the particle and gas phases. The fraction of particulate TPO in gaseous and particulate TPO (TPO(p)/TPO(g+p)) were essentially the same (Table 1) under both wet and dry conditions. To the best of our knowledge, for the ozonolysis of α-pinene, this is the first report of the yield of gas-phase total peroxides (including hydrogen peroxide and organic peroxides) and the gas-particle partitioning fraction.

The gas-particle partitioning coefficient ($K_p$) describes the partitioning ability of a given species, calculated as follows (Odum et al., 1996):

$$K_p = \frac{C_a}{C_g C_{om}}$$

(3)

where $C_a$ is the concentration of this species in the aerosol phase, $\mu$g m$^{-3}$; $C_g$ is the concentration of this species in the gas phase, $\mu$g m$^{-3}$; and $C_{om}$ is the total concentration of condensed organic matter, $\mu$g m$^{-3}$. Based on the gas-phase peroxides concentration, particle-phase peroxides concentration, and the aerosol yields summarized in Table 1, we can obtain the observed $K_p$ (Table 2).

The Pankow absorption model (Pankow, 1994) is the most widely accepted mechanism to explain the gas-particle partitioning, and has been used to predict aerosol yields in chamber experiments (Cocker III et al., 2001; Jenkin, 2004; Yu et al., 1999). Theoretical $K_p$ can be calculated by the following equation:

$$K_p = \frac{7.501 \times 10^{-3} RT}{MW_{om} \zeta P_i}$$

(4)

where $R$ is the ideal gas constant, J K$^{-1}$ mol$^{-1}$; $T$ is the temperature, K; $MW_{om}$ is the mean molecular weight of the condensed organic material, g mol$^{-1}$. In the present study, $MW_{om}$ is estimated to be 130 g mol$^{-1}$; $\zeta$ is the activity coefficient of the given species in the condensed
organic phase, and here, is assumed to be unity; \( \rho \) is the liquid vapour pressure of this species, Torr. The theoretical \( \rho \) can be calculated by an expended, semi-empirical form of Clausius-Clapeyron equation (Baum, 1997). Theoretical gas-particle partitioning coefficients of PFA and PAA are shown in Table 2.

The observed gas-particle partitioning coefficients of PFA, PAA and TPO were \((3–9)\times10^{-5}, (2–4)\times10^{-5}\) and \((2–3)\times10^{-4}\) \(\text{m}^3\text{μg}^{-1}\), respectively (Table 2), which, to the best of our knowledge, are reported here for the first time. However, the long time collection for SOA do 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 slightly with increasing collection time, and peroxides amount decreases faster than SOA mass (Supplement). Hence, the gas-particle partitioning coefficients of peroxides given here are underestimated by about 21%. Compared with the observed \( K_p \) values, theoretical \( K_p \) values of PFA and PAA, \(2\times10^{-8} \text{ m}^{-1} \text{ μg}^{-1}\) and \(4\times10^{-9} \text{ m}^{-1} \text{ μg}^{-1}\), respectively, were lower by a factor of \(10^4\). This large difference between observed and theoretical \( K_p \) values has also been reported previously (Cocker III et al., 2001; Jenkin, 2004; Kamens and Jaoui, 2001). Jenkin (2004) considered the existence of a significant systematic error, which is independent of key parameters involved in prediction of \( K_p \) values, or the inability to interpret the Pankow absorption model. After inducing a species-independent scaling factor of ca. 120 for all partitioning species, Jenkin obtained a reasonable simulation of the final experimental aerosol concentration, but was still unable to interpret the early stages of aerosol accumulation. In addition to the absorptive partitioning mechanism, the participation of bi- and multifunctional acid dimers in the aerosol formation process was also considered, resulting in the presentation of simulated results. Organic peroxides are also an important species compounds in dimer formation, for instance, hydroperoxides can react with aldehydes subsequently producing peroxyhemiacetals (Tobias and Ziemann, 2000, 2001; Ziemann, 2005). The vapor pressures of hydroperoxides decreased in the formation of peroxyhemiacetal by an additional factor of \(\sim10^2–10^5\) (Tobias and Ziemann, 2000), which could partially explain the large discrepancy between the observed and theoretical gas-particle partitioning coefficient. However, related thermodynamic and kinetic parameters need further study to resolve the problem.
3.2 Evolution of SOA in the aqueous phase

We investigated the evolution of SOA in the aqueous phase, focusing on the change of H$_2$O$_2$ in SOA. The initial concentration of H$_2$O$_2$ was low, but it increased rapidly in the first 3.5 h, approaching the peak at ~7.5 h, and then decreased slowly. We observed the existence of a sustained release of H$_2$O$_2$ into the SOA solution at room temperature (298 K) (Figure 1). The molar fraction of peak-H$_2$O$_2$ to total peroxides in SOA (H$_2$O$_2$(p)/TPO(p)) under dry conditions was twice as high as that observed under wet conditions in the absence of scavengers (Table 1). The contribution of H$_2$O$_2$ to the SOA mass ($F_{H2O2}$) was 1.9 times higher under dry conditions (5.09±0.99 ng μg$^{-1}$) than under wet conditions (2.67±0.17 ng μg$^{-1}$) (Table 1). In the presence of cyclohexane, H$_2$O$_2$(p)/TPO(p) was slightly higher under dry conditions than wet conditions (0.09±0.00 and 0.06±0.00, respectively) while $F_{H2O2}$ values were not significantly affected by RH (Table 1). Our observations are consistent with those of Wang et al. (2011) who studied α-pinene-derived SOA, and measured the $F_{H2O2}$ as 2.01±0.76 ng μg$^{-1}$, which was unchanged by a variety of oxidants (NO/light, O$_3$ and O$_3$/cyclohexane) over the range of 14–43% RH.

The sustained release of H$_2$O$_2$ coupled with the attenuation of total peroxides provided experimental evidence for the hypothesis that the decomposition/hydrolysis of organic peroxides generates H$_2$O$_2$ (see Section 3.4). The decay of H$_2$O$_2$ in SOA solution after 18 h is a comprehensive phenomenon including formation and decomposition, and the rate was estimated to be 0.06 μM h$^{-1}$ and 0.03 μM h$^{-1}$ for SOA produced under dry and wet conditions, respectively. To assess the formation, we determined the decomposition rates of pure H$_2$O$_2$ at different concentrations. At a H$_2$O$_2$ concentration of ~5 μM, (~2.5 μM), the rate of decomposition was 0.11 μM h$^{-1}$ and (~0.05 μM h$^{-1}$ at a H$_2$O$_2$ concentration of ~2.5 μM). The H$_2$O$_2$ concentrations were equivalent to those of H$_2$O$_2$ in SOA solution. Thus, we can estimate H$_2$O$_2$ formation in the SOA solution after 18 h to have a rate of 0.05 μM h$^{-1}$ under dry conditions and 0.02 μM h$^{-1}$ under wet conditions. As shown in Figure 2, the peroxycarboxylic acids (PCAs) (PFA and PAA), decayed quickly while the HAHP (HMHP) decayed slowly. Hence, the formation of H$_2$O$_2$ after 18 h could be attributed to the decomposition of HAHPs. However, in the first 7.5 h period, H$_2$O$_2$ increased rapidly which is more consistent with the decay of PCAs rather than HAHPs. Not all the organic peroxides decayed during the
observation time, since the attenuation of TPO almost stopped after 40 h. The residual peroxides were more stable, possibly due to the formation of ROOR by oligomerization.

### 3.3 Unexpectedly high levels of H$_2$O$_2$ in the gas phase

Table 1 shows the molar yields of gas-phase H$_2$O$_2$. The H$_2$O$_2$ yield in the absence and presence of cyclohexane was essentially the same in dry conditions, but under conditions of high RH increased to 0.16±0.01 in control studies and to 0.14±0.02 in the presence of cyclohexane. Thus, the presence of water vapor elevated the H$_2$O$_2$ yield, while the presence of a radical scavenger had no effect.

Our results for previous studies on gas-phase H$_2$O$_2$ yields may be viewed in the context of previous studies of the ozonolysis of α-pinene are reviewed (Table S2). Becker et al. (1990) firstly reported that the presence of water vapor will significantly promote the H$_2$O$_2$ yield, and our work confirmed this observation. However, our measured values of H$_2$O$_2$ were ten times higher than those reported by others under both dry and wet conditions, except that by Simonaitis et al. (1991). Differences in reactant concentration, reactor type and measuring methods account for these discrepancies. The higher concentrations of α-pinene and ozone used in other studies can produce a high level of SCI, and thus, the reaction of SCI with RO$_2$ should be considered (Zhao et al., 2015). This reaction will produce oligomers and compete with the reaction of SCI with water vapor, resulting in a decrease of H$_2$O$_2$ yield. Variations in reaction time can have an impact on the distribution of products, especially for the unstable components such as peroxides. In the online measurements used in our experiments, the ozonolysis reaction time, 2 min, is far shorter than that of other studies, which may explain that the yield of H$_2$O$_2$ observed in our study is the largest one compared to previous studies. The source of gas-phase H$_2$O$_2$ remains unclearly. For collecting the gas-phase peroxides, the gas coming from the reactor stayed in the aqueous phase for ~8 min. Even so, we suggest that further ozonolysis and OH oxidation of gaseous products in the aqueous phase were not likely to be the main source of the gas-phase H$_2$O$_2$. In this study, the online GC-FID test showed that α-pinene was completely consumed in the gas phase. Worth noting, the reactants concentrations used in these previous and our experiments are very high, therefore, yields of peroxides may not represent actual yields of peroxides in oxidation of α-pinene in nature (Supplement).
The source of gas-phase H₂O₂ remains unclear. We suggest that further ozonolysis and OH oxidation of gaseous products and reactants in the aqueous phase during and after gas collection are not likely to be the main sources of H₂O₂. In this study, the online GC-FID test showed that α-pinene was completely consumed in the gas phase. Hence, the contribution of aqueous-phase α-pinene ozonolysis to the measured H₂O₂ in the coil collector should be negligible. The main gas-phase non-peroxy organic products of α-pinene ozonolysis are carbonyls and organic acids, e.g., pinonaldehyde, formaldehyde, acetone and pinic acid; these compounds without carbon-carbon double bonds cannot be oxidized by O₃. The ozonolysis of α-pinene produces the OH radical in high yield (0.68–0.91) (Berndt et al., 2003), which potentially oxidizes carbonyls and organics. However, we observed no difference of Y_H₂O₂ in the absence and presence of α-OH scavengers, indicating that OH oxidation in the aqueous phase may not be a source of H₂O₂.

Decomposition/hydrolysis of organic peroxides in the aqueous phase during and after gas collection are also found to be a minor source of gas-phase H₂O₂. HAHPs and PCAs, two kinds of organic peroxides, are the probable candidate for generating H₂O₂. HAHPs are the main products of the reaction of SCI with water molecules and dimers (Ryzhkov and Ariya, 2004), and they can decompose to H₂O₂ plus the corresponding aldehyde or H₂O plus the corresponding organic acid (Hellpointner and Gäb, 1989). The hydrolysis of PCAs, which are generated from the reaction of RC(O)OO with HO₂, is another possible source of H₂O₂. Several kinds of PCAs have been qualitatively observed in the ozonolysis of α-pinene: 2-(3-formyl-2,2-dimethylcyclobutyl) ethaneperoxoic acid, 3-(2-hydroperoxy-2-oxoethyl)-2,2-dimethylcyclobutanecarboxylic acid and 2-(3-(2-hydroperoxy-2-oxoethyl))-2,2-dimethylcyclobutyl) acetic acid (Venkatachari and Hopke, 2008). In this study, we quantitatively observed PFA and PAA in the gas phase (Table 1), and simulated the formation of PCAs using MCM v3.1 mechanism. Model results showed that the yield of total PCAs was extremely low, 0.0005, and PAA contributed more than half of the yield while the formation pathway of PFA was not included. The large discrepancy between modelled and experimental results indicates that PCAs play a more important role than was expected previously.

We estimate the H₂O₂ generated from organic peroxides in the aqueous phase by measuring the decomposition/hydrolysis rate of organic peroxides. Considering the effects of
concentration, coexisting components, and ionic strength, we conducted the measurements with coil collection solutions rather than with synthesized samples. The decomposition/hydrolysis of organic peroxides is a pseudo-first order reaction due to the excess of the other reactant, i.e., water. The decay rate constants of HMHP, PFA and PAA were determined to be 0.09, 1.06 and 0.64 h\(^{-1}\), respectively (Figure 2). Larger HAHPs were less active compared with HMHP and should have lower decay rate constants. If all the TPO are composed of HAHPs and the production of H\(_2\)O\(_2\) plus aldehydes is the only decomposition pathway of HAHPs, the upper limit of H\(_2\)O\(_2\) formed in the aqueous phase within 8 min may be estimated to be 1.2% of TPO. However, the observed ratio of gas-phase H\(_2\)O\(_2\) to TPO was 28%–78%, indicating that the aqueous-phase decomposition of HAHPs is insignificant. Compared with HMHP, the decay rates of PFA and PAA were quite high. Assuming that all the TPO, except for PFA, are PCAs and their decay rates were the same as PAA’s, H\(_2\)O\(_2\) formed in aqueous phase within 8 min is estimated to be 13.2% of TPO, which can partially explain the observed H\(_2\)O\(_2\) level. However, the yield of PCAs in the ozonolysis of \(\alpha\)-pinene should be low in the MCM v3.1 model. The experimental results mentioned above concluded that the aqueous-phase formation of H\(_2\)O\(_2\) is not as important as we expected, for the decay rate of HAHPs was too slow, and the amount of PCAs was too low, although their decay rate was higher.

Is the self-reaction of HO\(_2\) and decomposition of HAHP in the gas-phase formation the main sources of H\(_2\)O\(_2\)? The self-reaction of HO\(_2\) is considered to be the main source of ambient H\(_2\)O\(_2\) (Lee et al., 2000; Reeves and Penkett, 2003) and occurs in the ozonolysis of \(\alpha\)-pinene. When we estimated the contribution of this pathway to the observed H\(_2\)O\(_2\) from \(\alpha\)-pinene ozonolysis using MCM v3.1 mechanisms, the yield was less than 0.001 under both dry and wet conditions, meaning that this pathway is negligible.

Chamber experiments showed that SCI mainly reacts with water vapor even under dry conditions (Jenkin, 2004), and the major product is HAHP. Aplincourt and Anglada (2003) considered that the unimolecular decomposition of gaseous HAHPs was unlikely to occur, and only the water-assisted decomposition was efficient in the gas phase. They estimated the water-assisted decomposition rate constant of 2-propenyl \(\alpha\)-hydroxy hydroperoxide to be \(1.5 \times 10^{-30}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) by quantum chemical calculation. Based on their work, the gas-phase
decomposition fraction of HAHP in 2 min can be calculated to be less than 0.01%, which is too small to account for the H$_2$O$_2$ observed in our experiments.

Taken together, our findings suggest that gaseous organic peroxides and SOA dissolved in water in the aqueous gas phase alone do not cause a high yield of H$_2$O$_2$, and the gas-phase decomposition of organic peroxides make a negligible contribution to cannot be explained by the interpretation of bias caused by measuring method and the current formation mechanism of H$_2$O$_2$. There could be an unknown or underestimated pathway producing H$_2$O$_2$. In this study, our data indicate section 3.4, we propose that gaseous products formed under dry conditions will organic peroxides can undergo rapid heterogeneous decomposition in the presence of water vapor or condensed water and producing H$_2$O$_2$.

3.4 Water effect

3.4 Rapid heterogeneous decomposition of gaseous organic peroxides

Our results demonstrate that water vapor has no significant effect on either the yield of total peroxides (combining gaseous and particulate peroxides) or the contribution of peroxides to SOA mass. However, water vapor does change the concentrations of H$_2$O$_2$, PFA and PAA in the gas phase and particle phase in an opposite manner (Table 1). In the presence of water vapor, H$_2$O$_2$ yield increased dramatically by ~300% (from 0.048 to 0.161%) and gas-phase H$_2$O$_2$/TPO increased from 0.26 to 0.78, while F$_{H2O2}$ decreased dramatically from 5.00 ± 0.99 ng μg$^{-1}$ to 2.67 ± 0.17 ng μg$^{-1}$ in the absence of OH scavenger and decreased slightly in the presence of cyclohexane as OH scavenger (Table 1). Yields of HMHP, PFA and PAA also increased with the presence of water vapor, and the contribution of PFA and PAA to SOA mass decreased. PAA was not detectable in the particle phase under wet conditions. These results clearly indicate that water vapor can change the formation and distribution of peroxides.

With respect to Physical uptake of peroxides by aerosol water, hygroscopic growth of SOA is a typical behavior in humid air, and the growth factor ($G_f$), a term used to quantify this behavior, is largely influenced by the composition of SOA. Typically, water uptake by inorganic components is considered to be more efficient than that by organic components. The growth factor of SOA derived from α-pinene is rather low due to high organic fraction of the aerosol.
with values of 1.04 at 50% RH and 1.09 at 85% RH (Cocker III et al., 2001). The uptake of
H$_2$O$_2$ by aerosol water content can be roughly estimated according to Henry’s Law:

\[
[H_2O_2(g)] - H_2O_2(aq) = \frac{\text{Henry's Law constant}}{\text{Relative molecular weight}}
\]

where $[H_2O_2(g)]$ is the aqueous-phase $H_2O_2$ concentration, $M$ is the relative molecular weight of $H_2O_2$. Assuming the growth factor to be 1.05 at 60% RH, the uptake of $H_2O_2$ is calculated as $0.17 \mu g \cdot m^{-3}$ and $0.14 \mu g \cdot m^{-3}$ in the absence and presence of cyclohexane, respectively. This result shows that the physical uptake is negligible under humid air, which is consistent with previous studies (Arellanes et al., 2006; Wang et al., 2011). Similarly, the physical uptake values of PAA were estimated to be $5.48 \times 10^{-4} \mu g \cdot m^{-3}$ and $1.66 \times 10^{-5} \mu g \cdot m^{-3}$ in the absence and presence of cyclohexane, respectively, with a Henry’s Law constant of $8.47 \times 10^2 M \cdot atm^{-1} \cdot mol^{-1}$ for PAA at 298 K (O’Sullivan et al., 1996).

We carried out a series of two-stage experiments using two reactors under various scenarios to further study the effect of water vapor on peroxides (Table 3). In scenario 1d, no water vapor was added and a filter was used to intercept SOA entering the coil collector, which is similar to measuring $H_2O_2$ under dry conditions with one reactor. The concentration of $H_2O_2$ observed in the coil collection solution under this condition was considered to be the baseline value, 100%.

When the filter was placed at the outlet of the first reactor (scenario 2d) instead of at the second reactor, the concentration of $H_2O_2$ was 103±6%, almost the same as the baseline, indicating that the coexistence of gaseous products and SOA will not lead to the formation of $H_2O_2$. In scenario 2w, a filter was placed at the outlet of the first reactor and water vapor was added to the second reactor, resulting in the coexistence of gaseous products and water vapor (50% RH) in the second reactor. The concentration of $H_2O_2$ observed in this scenario was 87%, slightly lower than the baseline, possibly due to losses on the wall of the reactor under wet conditions, which has been reported to be 5% for $H_2O_2$ at 50% RH (Huang et al., 2013). When we maintained the
water vapor and moved the filter to the outlet of the second reactor (scenario 1w), the H$_2$O$_2$ concentration increased to 165±6% of baseline. In scenario 3w, with water vapor added to the second reactor and without a filter in the gas flow, the H$_2$O$_2$ concentration was 172±5%, almost the same as that in scenario 1w. In scenario 3d, no water vapor and no filter were used, but a high H$_2$O$_2$ concentration, 164±9%, was also observed. For scenarios 1w, 3w, and 3d, where H$_2$O$_2$ increased by ~67%, gaseous products, SOA, and water were all present in the second reactor or coil collector. The coexistence of gaseous products and water vapor (see scenario 2d and 2w), the coexistence of gaseous products and SOA (see scenario 1d and 2d), and the coexistence of SOA and water (see section 3.3) did not result in a high yield of H$_2$O$_2$. We therefore concluded that the presence of three components together, the gaseous products, SOA, and water, was necessary for a high yield of H$_2$O$_2$. Once the gaseous products and SOA had been in contact with water vapor in the second reactor, the levels of H$_2$O$_2$ were increased to the same extent, whether or not these compounds were mixed with condensed water (see scenario 1w and 3w), indicating that the process producing H$_2$O$_2$ in the gas phase is quite rapid.

When we measured the total peroxides formed from gaseous products and SOA in scenarios 1d and 1w, the results showed that for these two scenarios, the levels of the total peroxides in both gaseous products and SOA were not significantly different, indicating that SOA does not change in the presence of water vapor and no new peroxides formed in the gas phase. This outcome supports the idea that the increment of H$_2$O$_2$ comes from the redistribution of gaseous peroxides, which is induced by the heterogeneous decomposition of gaseous products in the presence of both SOA and water. Based on the measured increment of H$_2$O$_2$ and concentration of gaseous total peroxides, we concluded that 18% of the gaseous total peroxides undergo rapid heterogeneous decomposition.

Heterogeneous reactions of trace gases on the surface of particles relevant to the atmosphere have been studied for many years. The investigated trace gases, including nitrogen oxides (e.g., HNO$_3$, NO$_2$ and N$_2$O$_5$), SO$_2$, O$_3$, H$_2$O$_2$ and oxygenated VOCs (Liggio et al., 2005; Kroll et al., 2005; Prince et al., 2007; Zhao et al., 2010; Zhao et al., 2011; Zhao et al., 2014; Huang et al., 2015), could react with the active sites on the surfaces of mineral dust (Goodman et al., 2001; Fu et al., 2007). Unlike mineral dust, however, SOA has no such active sites. The elucidation
of the mechanism of the rapid heterogeneous decomposition of organic peroxides on SOA particles remains a great challenge and needs urgent study.

4 Conclusions and atmospheric implications

Our laboratory study has provided more evidence that organic peroxides are important components of SOA derived from the ozonolysis of alkenes. In the case of α-pinene, organic peroxides account for ~21% of the SOA mass and this fraction is not affected by RH and the presence of α-OH scavengers. More interestingly, the gas-particle partitioning coefficients of organic peroxides have been estimated for the first time based on the measurements of both gaseous and particulate peroxides. Due to the long-time collection for SOA, these coefficients reported here are lower bounds in this study. For PFA and PAA, the observed values were 10^4 times higher than that of the theoretical value calculated by the Pankow absorption model. This discrepancy indicates a more important role of peroxides in SOA formation than expected previously and the existence of yet undefined mechanisms in addition to the absorption. The reaction of organic hydroperoxides with carbonyls forming peroxyhemiacetals may explain part of the enhancement of the partitioning of peroxides. However, the kinetic parameters of peroxyhemiacetal formation are lacking. The explicit mechanisms of gas-particle partitioning and the determination of gas-particle partitioning coefficients of larger organic peroxides deserve further study to improve the simulation of SOA mass.

We also examined gas-phase peroxides. The yield of gaseous total peroxides was ~0.22, which was independent of RH and α-OH scavengers. The MCM v3.1 mechanism predicted this yield but failed to interpret the yields of individual peroxides, i.e., H₂O₂, HMHP, PFA and PAA, indicating that our previous understanding of α-pinene ozonolysis was insufficient. For H₂O₂ with a yield of 0.048 under dry conditions and 0.16 under wet conditions, the known pathways, including dissolution of SOA, aqueous oxidation of gaseous compounds, and decomposition/hydrolysis of organic peroxides in the aqueous phase, cannot explain such an unexpectedly high yield of H₂O₂. The presence of both water and SOA leads to the rapid transformation of gaseous organic peroxides into H₂O₂. This heterogeneous process increases the H₂O₂ yield by ~67%. Our results also show that water vapor affects the distribution of gaseous peroxides, although it cannot change the yield of total peroxides.
The rapid heterogeneous transformation of organic peroxides to H$_2$O$_2$ helps to explain the differences between modelled and observed levels of peroxides and OH in the forest area. In the airborne GABRIEL field campaign in equatorial South America (Surinam) in October 2005 (Kubistin et al., 2010), two issues arose: (1) organic peroxides were overestimated while H$_2$O$_2$ was underestimated and (2) OH and HO$_2$ were also underestimated, especially when concentrations of VOCs were high. These investigators suggested the occurrence of additional recycling from HO$_2$ to OH or the contributions of additional direct OH sources. Our finding that organic peroxides can transform to H$_2$O$_2$ by rapid heterogeneous reactions can address the first discrepancy directly and the second indirectly. Peroxides influence OH through the removal pathways:

\[
\text{ROOH} + \text{hv} \rightarrow \text{RO} + \text{OH} \quad \text{(R2)}
\]

\[
\text{ROOH} + \text{OH} \rightarrow \text{RO}_2 + \text{H}_2\text{O} \quad \text{(R3)}
\]

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{OH} \quad \text{(R4)}
\]

\[
\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2 \quad \text{(R5)}
\]

Predominant removal paths for organic peroxides in the atmosphere are reaction with OH (95%) and photolysis (4.4%) (Khan et al., 2015), while for H$_2$O$_2$, these two paths are almost equally important. The OH oxidation process consumes OH while photolysis process produces OH. Obviously, H$_2$O$_2$ plays a different role in the OH cycling compared with organic peroxides. One molecule of organic peroxides transformed into H$_2$O$_2$ yields ~1.4 molecules of OH. Thus, the rapid transformation of organic peroxides to H$_2$O$_2$ by the heterogeneous process would increase OH levels. However, not all the organic peroxides could be transformed to H$_2$O$_2$ by the heterogeneous process. Further studies are needed to clarify this process in the atmosphere and unveil the features of the peroxides undergoing heterogeneous transformation.

**Acknowledgements**

We gratefully acknowledge the National Natural Science Foundation of China (grants 41275125, 21190053, 21477002) and the State Key Laboratory of Environment Simulation and Pollution Control (special fund) for financial support.
References


Table 1. Peroxide content in the gas phase and particle phase of α-pinene ozonolysis as affected by the OH radical scavenger cyclohexane.

<table>
<thead>
<tr>
<th>OH scavenger</th>
<th>None</th>
<th>60%</th>
<th>Cyclohexane</th>
<th>60%</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH</td>
<td>&lt;0.5%</td>
<td></td>
<td>&lt;0.5%</td>
<td></td>
</tr>
<tr>
<td>H₂O₂(g)/TPO(g) (ppb / ppb)</td>
<td>0.26±0.02</td>
<td>0.78±0.04</td>
<td>0.18±0.02</td>
<td>0.50±0.04</td>
</tr>
<tr>
<td>H₂O₂(p)/TPO(p) (μM / μM)</td>
<td>0.20±0.03</td>
<td>0.10±0.01</td>
<td>0.09±0.01</td>
<td>0.06±0.01</td>
</tr>
<tr>
<td>TPO(p)/TPO(g+p) (%)</td>
<td>0.19±0.02</td>
<td>0.18±0.03</td>
<td>0.07±0.01</td>
<td>0.09±0.01</td>
</tr>
</tbody>
</table>

- 275 ppbv α-pinene, ~1300 ppmv cyclohexane and ~42 ppmv O₃ were used in these experiments. The data represent the mean ± s.d. of 3 observations.
- molar yield of peroxides
- mass yield of SOA
- contribution of peroxides to SOA mass
- fraction of particulate TPO in gaseous and particulate TPO
Table 2. Comparison of observed and theoretical gas-particle partitioning coefficients ($K_p$) of PFA, PAA and TPO at different scenarios (298K).

<table>
<thead>
<tr>
<th></th>
<th>$K_p$ (observed)</th>
<th>$K_p$ (theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m$^3$ μg$^{-1}$)</td>
<td>(m$^3$ μg$^{-1}$)</td>
</tr>
<tr>
<td>Sc1</td>
<td>8.06×10^{-5}</td>
<td>2.95×10^{-5}</td>
</tr>
<tr>
<td>Sc2</td>
<td>9.19×10^{-5}</td>
<td>4.20×10^{-5}</td>
</tr>
<tr>
<td>Sc3</td>
<td>4.20×10^{-5}</td>
<td>2.17×10^{-4}</td>
</tr>
<tr>
<td>Sc4</td>
<td>2×10^{-9}</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Sc1</th>
<th>Sc2</th>
<th>Sc3</th>
<th>Sc4</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFA</td>
<td>1.76×10^{-5}</td>
<td>0</td>
<td>4.38×10^{-5}</td>
<td>0</td>
</tr>
<tr>
<td>PAA</td>
<td>3.47×10^{-4}</td>
<td>3.39×10^{-4}</td>
<td>1.61×10^{-4}</td>
<td>2.17×10^{-4}</td>
</tr>
<tr>
<td>TPO</td>
<td>1.06×10^{-3}</td>
<td>9.19×10^{-3}</td>
<td>4.20×10^{-3}</td>
<td>2×10^{-9}</td>
</tr>
</tbody>
</table>

$^a$ The four scenarios represent four reaction conditions: Sc1 (<0.5% RH, no OH scavenger), Sc2 (60% RH, no OH scavenger), Sc3 (<0.5% RH, with cyclohexane) and Sc4 (60% RH, with cyclohexane). Cyclohexane used here was ~1300 ppmv.
Table 3. Hydrogen peroxide in the coil collector at different scenarios in the two-stage experiments.

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Filter positiona</th>
<th>Water vaporb</th>
<th>H2O2c</th>
<th>Species in second reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>Second reactor</td>
<td>No</td>
<td>100±1%</td>
<td>Gaseous products, SOA</td>
</tr>
<tr>
<td>1w</td>
<td>Second reactor</td>
<td>Yes</td>
<td>165±6%</td>
<td>Gaseous products, SOA, water vapor</td>
</tr>
<tr>
<td>2d</td>
<td>First reactor</td>
<td>No</td>
<td>103±6%</td>
<td>Gaseous products</td>
</tr>
<tr>
<td>2w</td>
<td>First reactor</td>
<td>Yes</td>
<td>87±7%</td>
<td>Gaseous products, water vapor</td>
</tr>
<tr>
<td>3d</td>
<td>No filter</td>
<td>No</td>
<td>164±9%</td>
<td>Gaseous products, SOA</td>
</tr>
<tr>
<td>3w</td>
<td>No filter</td>
<td>Yes</td>
<td>172±5%</td>
<td>Gaseous products, SOA, water vapor</td>
</tr>
</tbody>
</table>

- **a** The filters were placed at the outlet of the first reactor or second reactor.
- **b** Water vapor was induced into the second reactor.
- **c** Although gaseous products and SOA did not contact water vapor in the second reactor, they were in contact with the condensed water in the coil collector.
Figure 1. Evolution of total peroxides and H$_2$O$_2$ contents in SOA produced under dry (<0.5% RH) and wet (60% RH) conditions at 298K. Circles and diamonds represent total peroxides and H$_2$O$_2$ contents in SOA, respectively; and solid lines and dash lines represent that obtained under dry and wet conditions, respectively. The data represent the mean ± s.d. of 3 observations.
Figure 2. Decomposition/hydrolysis of organic peroxides in the aqueous phase. $C_t/C_0$ is the ratio of peroxides concentration at time $= t$ h to peroxides concentration at time $= 0$ h. Lines are exponential fits for HMHP, PFA and PAA. The decay rate constants of HMHP, PFA and PAA are 0.09, 1.06 and 0.64 h$^{-1}$, respectively. The data represent the mean ± s.d. of 3 observations.