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

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Efficiency of peroxide measurements

Extraction efficiency is important to analyse an accurate proportion of peroxide in SOA. In order to evaluate the extraction efficiency, the loaded filter was immersed in H_3PO_4 solution and the SOA was extracted from the filter by shaking; this process was repeated twice. The concentration of total peroxides in the SOA solution was measured using the iodometric method. Experimental results showed that the extraction efficiency was reproducible and sufficient (Figure S1).

The iodometric method had different sensitivity with respect to different peroxides due to the different reaction rates of iodide ion with various peroxides. For example, the triiodide concentration (represented by UV/VIS absorbance) reached its maximum for H_2O_2 within 40 min, for lauroyl peroxide within 60 min, while for *tert*-butyl hydroperoxides the reaction does not go to completion even after 5 h when the reaction temperature was kept at 313 K (Mertes et al., 2012). To optimize the method, we determined the best conversion time from the evolution curves for the conversion of iodide ions to triiodide via molecular iodine. Figure S2 shows that triiodide concentration reached its maximum within 4 h for H_2O_2 and within 8 h for α -pinene SOA extract at 298 K and the triiodide concentration remained unchanged until 24 h. Therefore, we chose 12–24 h as the practical conversion time since the reaction of peroxides with iodide ions reached completion within this time and the formed triiodide was still stable.

Mutzel et al. (2013) investigated the influence of pH and found that the hydroperoxide concentration was significantly underestimated at pH 5 and the maximum was not observed at pH 7 in the UV/VIS spectrum compared to that at pH 3. This result may be attributed to the pH-dependence of the oxidation potential of H_2O_2 (Ovenston and Rees, 1950). Peroxides tend to react with KI slowly under neutral and weakly acidic conditions. In addition to the pH-dependence of the oxidation potential of peroxides, the stability of peroxides was influenced by pH as well. Peroxide levels measured at pH 7 were lower than those at pH 3.5 (Figure S3). The influence of extraction efficiency

can be excluded because the re-extraction of the same filter showed that most SOA were extracted at pH 7.

Influence of long-time collection on SOA

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%.

Influence of high mixing ratios of reactants

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 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 (Crouse 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%. 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.

Figure caption

Table S1. Total peroxide content in SOA produced from the ozonolysis of unsaturated hydrocarbons.

Table S2. Gas-phase H₂O₂ yield in the ozonolysis of α -pinene.

Figure S1. Extraction efficiency of total peroxides in loaded filters. One filter was extracted three times with H₃PO₄ solution. Efficiency of first extraction is labelled in the figure.

Figure S2. Time evolution curves for the conversion of iodide ions to triiodide via molecular iodine in α -pinene SOA solution and 22.8 μ M H₂O₂ solution at 298 K. The absorbance of triiodide was measured at 420 nm. Background levels were subtracted. Each data point represents the mean \pm s.d. of 3 observations.

Figure S3. Influence of the extract pH on the measured total peroxides in α -pinene SOA formed under dry and wet conditions. Data are expressed as the mean \pm s.d. of 3 observations.

Figure S4. The stability of peroxides in SOA stored on-filter at 255K and 298K in dark. Filters collected SOA for 4 h were used here. All the concentration of total peroxides (TPO) and hydrogen peroxides (H₂O₂) are normalized to those got when filters did not sit. Data are expressed as the mean \pm s.d. of 3 observations, while some data have no error bar.

Figure S5. The effect of collection time on collected SOA mass and particulate total peroxides amount. The SOA mass (g) and particulate total peroxides amount (mol) were normalized to those collected for 4 h respectively. Solid line and dash line are linear fittings for dependence of normalized mass and normalized total peroxides amount on collection time, respectively. \sim 275 ppbv α -Pinene and \sim 42 ppmv O₃ were used in these experiments. The data represent the mean \pm SD of 3 observations.

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Table S1. Total peroxide content in SOA produced from the ozonolysis of unsaturated hydrocarbons.

Compound	Relative humidity	OH scavenger	Reactor type	Extraction method	SOA mass measurement	SOA density (g cm ⁻³)	MW of peroxides (g mol ⁻¹)	Peroxides in SOA ^a (μg μg ⁻¹)	References
Oleic acid	Dry	1-propanol	Chamber	Sonication	SMPS	1.12	330	0.68	Ziemann, 2005
α-pinene	Dry/~50%	Cyclohexane/1-propanol/formaldehyde	Chamber	Sonication	SMPS	1	300	0.47	Docherty et al., 2005
β-pinene	Dry/~50%	Cyclohexane/1-propanol/formaldehyde	Chamber	Sonication	SMPS	1	300	0.85	Docherty et al., 2005
Δ ³ carane	Dry	Cyclohexane/1-propanol	Chamber	Sonication	SMPS	1	300	0.34	Docherty et al., 2005
Sabinene	Dry	Cyclohexane/1-propanol	Chamber	Sonication	SMPS	1	300	0.98	Docherty et al., 2005
Isoprene	Dry	Cyclohexane	Chamber	Sonication	Balance	–	300	0.31	Nguyen et al., 2010
Limonene	Dry	None	Chamber	PILS	SMPS	1.2	–	0.02 ^b	Bateman et al., 2011
α-pinene	50%	<i>n</i> -butanol	Chamber	–	SMPS	1.3	300	0.34	Mertes et al., 2012
α-pinene	Dry	None	Chamber	–	Balance	–	300	0.22	Epstein et al., 2014
α-pinene	Dry	None	Flow reactor	Shaker	Balance	–	300	0.23	This study
α-pinene	60%	None	Flow reactor	Shaker	Balance	–	300	0.25	This study
α-pinene	Dry	Cyclohexane	Flow reactor	Shaker	Balance	–	300	0.16	This study
α-pinene	60%	Cyclohexane	Flow reactor	Shaker	Balance	–	300	0.20	This study

^a All the experiments used the iodometric spectrophotometric method.^b One peroxide group per 50 SOA molecules

Table S2. Gas-phase H₂O₂ yield in the ozonolysis of α -pinene.

Initial conc. of α -pinene	Initial conc. of O ₃	OH scavenger	Reactor type	Measuring method	RH	Gas-phase H ₂ O ₂ yield	Reference
5–35 ppmv	2–60 ppmv	none	130 L glass cylinder reactor	TDLAS/White cell system	<0.5% ~45%	0.0010 0.005	Becker et al., 1990
~446 ppmv	~893 ppmv	none	12 L pyrex vessel	HPLC-Fluorescence	Super-saturated	~0.01	Hewitt and Kok, 1991
40–900 ppbv	58–406 ppbv	none	31 m ³ FEP teflon chamber	Dual-channel fluoremetric method	~15–40%	0.09	Simonaitis et al., 1991
2–8 ppmv	Slight excess	none	1080 L quartz reactor	HPLC-fluorescence	<0.5%	0.003±0.001	G äb et al., 1995
~273 ppbv	~25 ppmv	none	8 L quartz flow-tube reactor	HPLC-fluorescence	<0.5% 60%	0.048±0.012 0.16±0.01	This study
~273 ppbv	~25 ppmv	cyclohexane	8 L quartz flow-tube reactor	HPLC-fluorescence	<0.5% 60%	0.048±0.010 0.14±0.02	This study

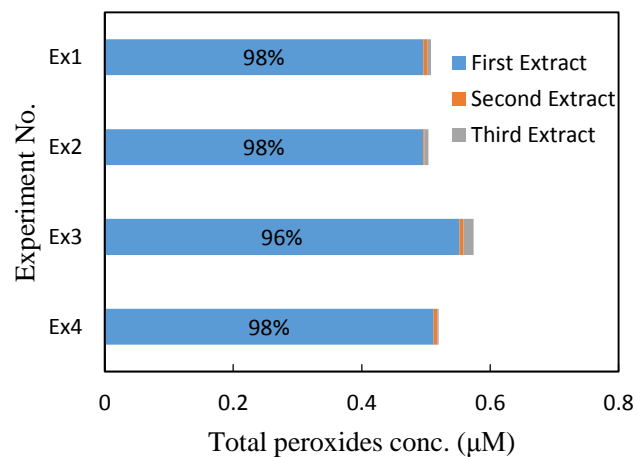


Figure S1. Extraction efficiency of total peroxides in loaded filters. One filter was extracted three times with H_3PO_4 solution. Efficiency of first extraction is labelled in the figure.

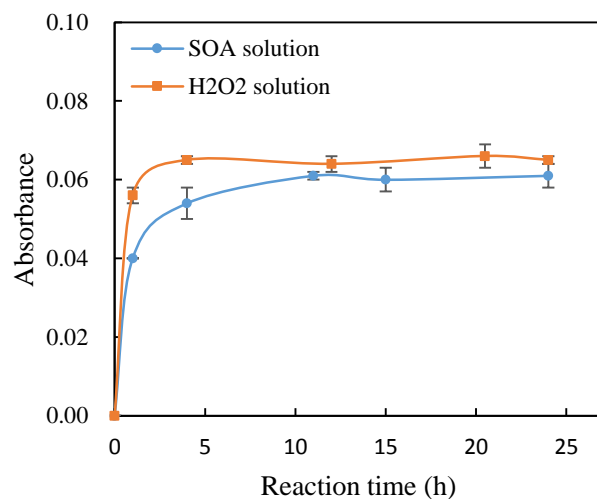


Figure S2. Time evolution curves for the conversion of iodide ions to triiodide via molecular iodine in α -pinene SOA solution and 22.8 μM H_2O_2 solution at 298 K. The absorbance of triiodide was measured at 420 nm. Background levels were subtracted. Each data point represents the mean \pm s.d. of 3 observations.

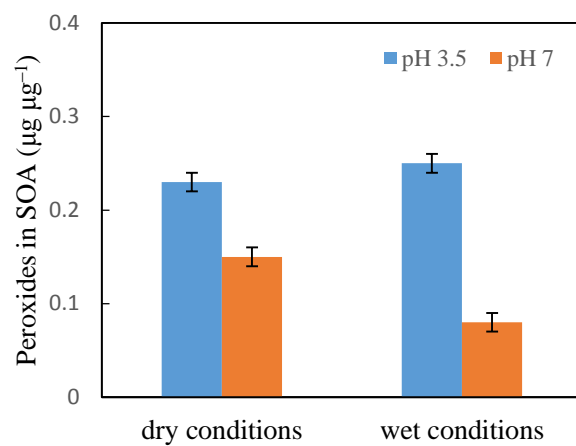


Figure S3. Influence of the extract pH on the measured total peroxides in α -pinene SOA formed under dry and wet conditions. Data are expressed as the mean \pm s.d. of 3 observations.

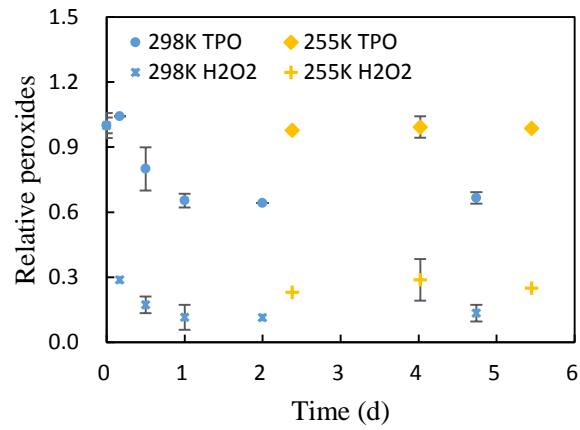


Figure S4. The stability of peroxides in SOA stored on-filter at 255K and 298K in dark. Filters collected SOA for 4 h were used here. All the concentrations of total peroxides (TPO) and hydrogen peroxide (H₂O₂) are normalized to those got when filters did not sit. Data are expressed as the mean \pm s.d. of 3 observations, while some data have no error bar.

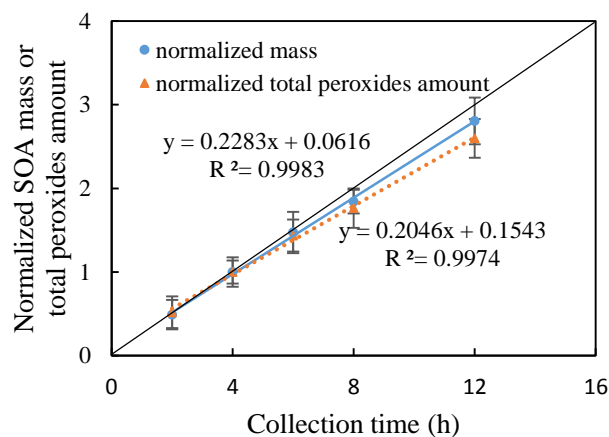


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