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Supplement of

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.

Figure caption.

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

Table S2. Gas-phase H_2O_2 yield in the ozonolysis of α-pinene.

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 ± 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 ± s.d. of 3 observations.

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

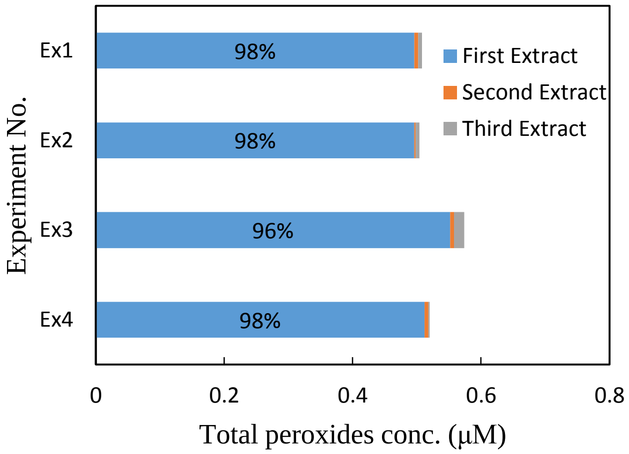
Compound	Relative humidity	OH scavenger	Reactor type	Extraction method	SOA mass measurement	SOA density (g cm^{-3})	MW of peroxides (g mol^{-1})	Peroxides in SOA[a] (μg μg^{-1})	References
Oleic acid	Dry	1-propanol	Chamber	Sonication	SMPS	1.12	330	0.68	Ziemann, 2005
α-pinene	Dry/~50%	Cyclohexane/1-propanol/formaldehyde	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^3carane	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%	*n*-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 H_2O_2 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_2O_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	Hewit 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	Gab 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



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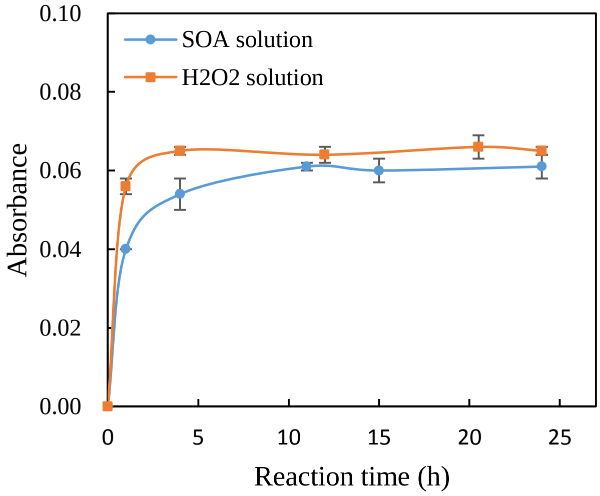
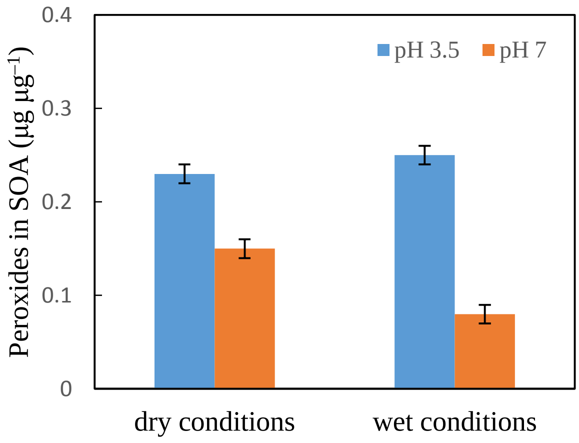


Figure S2. Time evolution curves for the conversion of iodide ions to triiodide via molecular iodine in α-pinene SOA solution and 22.8 μM H_2O_2 solution at 298 K. The absorbance of triiodide was measured at 420 nm. Background levels were subtracted. Each data point represents the mean ± s.d. of 3 observations.



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