

**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

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

H. Li<sup>1</sup>, Z. M. Chen<sup>1</sup>, L. B. Huang<sup>1</sup>, and D. Huang<sup>1,a</sup>

<sup>1</sup>State Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China  
<sup>a</sup>now at: School of Earth Sciences, Zhejiang University, Hangzhou, Zhejiang Province 310027, China

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Correspondence to: Z. M. Chen (zmchen@pku.edu.cn)

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Abstract

Organic peroxides, important species in the atmosphere, will promote secondary organic aerosols (SOA) aging, affect HO<sub>x</sub> 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 investigate 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<sub>2</sub>O<sub>2</sub>), hydroxymethyl hydroperoxide (HMHP), peroxyformic acid (PFA), peroxyacetic acid (PAA) and total peroxides (TPO, including unknown peroxides) and the fraction of peroxides in SOA. Comparing the gas-phase and particle-phase peroxides, we find that gas-particle partitioning coefficients of PFA and PAA are 10<sup>4</sup> times higher than 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 as  $(2-3) \times 10^{-4} \text{ m}^3 \mu\text{g}^{-1}$ . Even so, more than 80 % of the peroxides formed in the reaction remain in the gas phase. Water does not affect the total amount of peroxides in either the gas or 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<sub>2</sub>O<sub>2</sub>. This process can partially interpret the unexpected high H<sub>2</sub>O<sub>2</sub> yield under wet conditions. Transformation of organic peroxides to H<sub>2</sub>O<sub>2</sub> also saves OH in the atmosphere, helping to improve the understanding of OH cycling.

## Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 1 Introduction

Organic peroxides are important trace components in the atmosphere, serving as reservoirs of HO<sub>x</sub> and RO<sub>x</sub> 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<sub>2</sub>) and the hydroperoxy radical (HO<sub>2</sub>) and self-reactions of HO<sub>2</sub> are thought to be major sources of organic peroxides and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), respectively, in the atmosphere. Ozonolysis of biogenic volatile organic compounds (VOC) also produces H<sub>2</sub>O<sub>2</sub> in high yields

### Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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  $\text{H}_2\text{O}_2$ , 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  $\text{H}_2\text{O}_2$  as compared with field records in the airborne GABRIEL 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  $\text{H}_2\text{O}_2$ . Field observations and laboratory experiments showed that particulate components, possibly particle-bound organic peroxides, could be transformed to  $\text{H}_2\text{O}_2$ . Arellanes et al. (2006) found that  $\text{H}_2\text{O}_2$  in ambient SOA solution was 200–1000 times greater than expected levels based on the gas-liquid partitioning, implying that almost all  $\text{H}_2\text{O}_2$  is generated from SOA solution. Wang et al. (2011) investigated several kinds of SOA derived from the oxidation of  $\alpha$ -pinene,  $\beta$ -pinene, and toluene, and came to the similar conclusion that more than 97.5 %  $\text{H}_2\text{O}_2$  arose from SOA formation rather than from gas-liquid partitioning. However, this process happens in SOA solution and the amount of  $\text{H}_2\text{O}_2$  produced by such a pathway is too small to account for the large discrepancy between observations and simulations for the gas-phase  $\text{H}_2\text{O}_2$ .

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  $\text{H}_2\text{O}_2$  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 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 Crigee Intermediates (SCIs) and generate hydroxyalkyl hydroperoxides (HAHPs). It has been proposed that not only isolated wa-

**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ter 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<sub>2</sub>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  $\alpha$ -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

$\alpha$ -Pinene (Aldrich, 99%), cyclohexane (Sigma-Aldrich,  $\geq 99.7\%$ ), potassium iodide (Alfa Aesar, 99.9%), hydrogen peroxide (Alfa Aesar, 35 wt%), *ortho*-phosphoric acid (Fluka, 85–90%), hemin (Sigma,  $\geq 98.0\%$ ), 4-hydroxyphenylacetic acid (Alfa Aesar, 99%), ammonia solution (NH<sub>3</sub>·H<sub>2</sub>O, Beijing Tongguang Fine Chemicals Company, 25.0–28.0%), ammonium chloride (NH<sub>4</sub>Cl, Beijing Chemical Works,  $\geq 99.5\%$ ), ultra-pure water (18 M $\Omega$ , Millipore), N<sub>2</sub> ( $\geq 99.999\%$ , Beijing Haikeyuanchang Practical Gas Company Limited, Beijing, China), O<sub>2</sub> ( $\geq 99.999\%$ , 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  $\alpha$ -pinene. All the experiments were conducted at  $298 \pm 0.5$  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).  $O_3$  ( $\sim 25$  ppmv) was used in the experiments.  $\alpha$ -Pinene gas was generated by passing a flow of  $N_2$  over liquid  $\alpha$ -pinene in a diffusion tube at the selected controlled temperature. The initial concentration of  $\alpha$ -pinene, determined by gas-chromatography-flame ionization detector (GC-FID, Agilent 7890A, USA), was  $\sim 273$  ppbv in the experiments. Water vapor was generated by passing  $N_2$  through a water bubbler. The mixing gases, including  $\alpha$ -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<sup>-1</sup> (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<sup>-1</sup>) was directed into a coil collector and scrubbed by  $H_3PO_4$  stripping solution ( $5 \times 10^{-3}$  M, pH 3.5) for hydroperoxides analysis. SOA produced from the ozonolysis of  $\alpha$ -pinene were collected onto a PTFE filter for 4 h at a flow rate of 4 standard L min<sup>-1</sup>, 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  $H_3PO_4$  solution ( $5 \times 10^{-3}$  M, pH 3.5) using a shaker (Shanghai Zhicheng ZWY 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<sup>-1</sup>) with  $\alpha$ -pinene ( $\sim 275$  ppbv) and  $O_3$  ( $\sim 42$  ppmv)

### Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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<sup>-1</sup>). The residence time was 68 s in the first reactor and 34 s in the second reactor. The concentration of  $\alpha$ -pinene at the outlet of the first reactor was found to be below the GC-FID detection limit (< 5 ppbv), meaning that  $\alpha$ -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 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 H<sub>2</sub>O<sub>2</sub>), with the exception of tertiary dialkyl peroxides, in the aqueous phase without distinction (Banerjee and Budke, 1964). Excess potassium iodide reacts with peroxides producing I<sub>3</sub><sup>-</sup> ion Reaction (R1), which can be quantified by UV/VIS spectrophotometry.



**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



$\alpha$ -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  $\text{H}_2\text{O}_2$ , hydroxymethyl 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 in the iodometric spectrophotometric method. 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 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  $\alpha$ -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  $\mu\text{g m}^{-3}$ . A comparison of the aerosol mass yields ( $Y_{\text{SOA}}$ ), defined as the ratio of the formed aerosol mass to the consumed  $\alpha$ -pinene mass, (Table 1) indicated that while the SOA yields were independent on the presence of water vapor, they were affected by the OH scav-



enger. The estimates of  $Y_{\text{SOA}}$  showed that the presence of the OH scavenger cyclohexane decreased  $Y_{\text{SOA}}$  to 28 % (Table 1).

Organic peroxides are considered to be one of the major constituents in SOA (Docherty et al., 2005; Ziemann, 2005; Surratt et al., 2006; Nguyen et al., 2010; Mertes et al., 2012; Kidd et al., 2014; Badali et al., 2015) (Table S1 in the Supplement). 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. 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:

$$F_{\text{peroxides}} = \frac{m_{\text{peroxides}}}{m_{\text{SOA}}} \quad (1)$$

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  $\sim 0.21$  (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 peroxyformic 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  $0.35 \pm 0.06$  and  $0.11 \pm 0.04 \text{ ng } \mu\text{g}^{-1}$ , respectively, without the OH scavenger and  $0.14 \pm 0.00$  and  $0.09 \pm 0.01 \text{ ng } \mu\text{g}^{-1}$ , respectively, with cyclohexane. After adding water vapor,  $F_{\text{PFA}}$  did not significantly change, but  $F_{\text{PAA}}$  approached 0.

## Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



### 3.1.2 Gas-phase peroxides

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

$$Y_{\text{peroxides}} = \frac{\Delta_{\text{peroxides}}}{\Delta_{\alpha\text{-pinene}}} \quad (2)$$

where  $\Delta$  peroxides are moles of formed gaseous peroxides, such as HMHP, PFA, PAA and TPO, and  $\Delta_{\alpha\text{-pinene}}$  are moles of consumed  $\alpha$ -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 scavenger (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 scavenger, 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  $\alpha$ -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 ( $\text{TPO(p)} / \text{TPO(g + p)}$ ) were essentially the same (Table 1) under both wet and dry conditions. To the best of our knowledge, for the ozonolysis of  $\alpha$ -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):

$$K_p = \frac{C_a}{C_g C_{om}} \quad (3)$$

where  $C_a$  is the concentration of this species in the aerosol phase,  $\mu\text{g m}^{-3}$ ;  $C_g$  is the concentration of this species in the gas phase,  $\mu\text{g m}^{-3}$ ; and  $C_{om}$  is the total concentration of condensed organic matter,  $\mu\text{g m}^{-3}$ . 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:

$$K_p = \frac{7.501 \times 10^{-9} RT}{MW_{om} \zeta \rho_L^\circ} \quad (4)$$

where  $R$  is the ideal gas constant,  $\text{J K}^{-1} \text{mol}^{-1}$ ;  $T$  is the temperature, K;  $MW_{om}$  is the mean molecular weight of the condensed organic material,  $\text{g mol}^{-1}$ . In the present study,  $MW_{om}$  is estimated to be  $130 \text{ g mol}^{-1}$ ;  $\zeta$  is the activity coefficient of the given species in the condensed organic phase, and here, is assumed to be unity;  $\rho_L^\circ$  is the liquid vapour pressure of this species, Torr. The theoretical  $\rho_L^\circ$  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  $(3-9) \times 10^{-5}$ ,  $(2-4) \times 10^{-5}$  and  $(2-3) \times 10^{-4} \text{ m}^3 \mu\text{g}^{-1}$ , respectively (Table 2), which, to the best of our knowledge, are reported here for the first time. Compared with the observed  $K_p$  values, theoretical  $K_p$  values of PFA and PAA,  $2 \times 10^{-9}$  and  $4 \times 10^{-9} \text{ m}^3 \mu\text{g}^{-1}$ ,

## Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion







conditions of high RH increased to  $0.16 \pm 0.01$  in control studies and to  $0.14 \pm 0.02$  in the presence of cyclohexane. Thus, the presence of water vapor elevated the  $\text{H}_2\text{O}_2$  yield, while the presence of a radical scavenger had no effect.

Our results for gas-phase  $\text{H}_2\text{O}_2$  yields may be viewed in the context of previous studies of the ozonolysis of  $\alpha$ -pinene (Table S2 in the Supplement). Becker et al. (1990) firstly reported that the presence of water vapor will significantly promote the  $\text{H}_2\text{O}_2$  yield, and our work confirmed this observation. However, our measured values of  $\text{H}_2\text{O}_2$  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  $\alpha$ -pinene and ozone used in other studies can produce a high level of SCI, and thus, the reaction of SCI with  $\text{RO}_2$  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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  observed in our study is the largest one compared to previous studies. The source of gas-phase  $\text{H}_2\text{O}_2$  remains unclearly. For collecting the gas-phase peroxides, the gas coming from the reactor stayed in the aqueous phase for  $\sim 8$  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  $\text{H}_2\text{O}_2$ . In this study, the online GC-FID test showed that  $\alpha$ -pinene was completely consumed in the gas phase. Hence, the contribution of aqueous-phase  $\alpha$ -pinene ozonolysis to the measured  $\text{H}_2\text{O}_2$  in the coil collector should be negligible. The main gas-phase non-peroxy organic products of  $\alpha$ -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  $\text{O}_3$ . The ozonolysis of  $\alpha$ -pinene produces the OH radical in high yield (0.68–0.91) (Berndt et al., 2003), which potentially oxidizes carbonyls and organ-

## Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ics. However, we observed no difference of  $Y_{\text{H}_2\text{O}_2}$  in the absence and presence of a OH scavenger, indicating that OH oxidation in the aqueous phase may not be a source of  $\text{H}_2\text{O}_2$ .

HAHPs and PCAs, two kinds of organic peroxides, are the probable candidate for generating  $\text{H}_2\text{O}_2$ . HAHPs are the main products of the reaction of SCI with water molecules and dimers (Ryzhkov and Ariya, 2004), and they can decompose to  $\text{H}_2\text{O}_2$  plus the corresponding aldehyde or  $\text{H}_2\text{O}$  plus the corresponding organic acid (Hellpointner and Gäb, 1989). The hydrolysis of PCAs, which are generated from the reaction of  $\text{RC(O)OO}$  with  $\text{HO}_2$ , is another possible source of  $\text{H}_2\text{O}_2$ . Several kinds of PCAs have been qualitatively observed in the ozonolysis of  $\alpha$ -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  $\text{H}_2\text{O}_2$  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  $0.64 \text{ h}^{-1}$ , respectively (Fig. 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  $\text{H}_2\text{O}_2$  plus aldehydes is the only decomposition pathway of HAHPs, the upper limit of  $\text{H}_2\text{O}_2$  formed in

## Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the aqueous phase within 8 min may be estimated to be 1.2 % of TPO. However, the observed ratio of gas-phase  $\text{H}_2\text{O}_2$  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,  $\text{H}_2\text{O}_2$  formed in aqueous phase within 8 min is estimated to be 13.2 % of TPO, which can partially explain the observed  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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 gas-phase formation of  $\text{H}_2\text{O}_2$  possible? The self-reaction of  $\text{HO}_2$  is considered to be the main source of ambient  $\text{H}_2\text{O}_2$  (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  $\text{H}_2\text{O}_2$  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  $1.5 \times 10^{-30} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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  $\text{H}_2\text{O}_2$  observed in our experiments.

Taken together, our findings suggest that gaseous organic peroxides and SOA dissolved in the aqueous phase alone do not cause a high yield of  $\text{H}_2\text{O}_2$ , and the gas-phase decomposition of organic peroxides make a negligible contribution to the in-



terpretation of the formation of  $\text{H}_2\text{O}_2$ . There could be an unknown or underestimated pathway producing  $\text{H}_2\text{O}_2$ . In this study, our data indicate that gaseous products formed under dry conditions will undergo rapid heterogeneous decomposition in the presence of water vapor or condensed water.

### 3.4 Water effect

Our results demonstrate that water vapor has no 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  $\text{H}_2\text{O}_2$ , PFA and PAA in the gas phase and particle phase in an opposite manner (Table 1). In the presence of water vapor,  $\text{H}_2\text{O}_2$  yield increased dramatically by  $\sim 300\%$  (from 0.048 to 0.16), and gas-phase  $\text{H}_2\text{O}_2/\text{TPO}$  increased from 0.26 to 0.78, while  $F_{\text{H}_2\text{O}_2}$  decreased dramatically from  $5.09 \pm 0.99$  to  $2.67 \pm 0.17 \text{ ng } \mu\text{g}^{-1}$  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 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  $\alpha$ -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  $\text{H}_2\text{O}_2$  by aerosol water content can be roughly estimated according to Henry's Law:

$$[\text{H}_2\text{O}_2(\text{aq})] = H_a \times [\text{H}_2\text{O}_2(\text{g})] \quad (5)$$

where [H<sub>2</sub>O<sub>2</sub> (aq)] is the aqueous-phase H<sub>2</sub>O<sub>2</sub> concentration, M; [H<sub>2</sub>O<sub>2</sub> (g)] is gas-phase H<sub>2</sub>O<sub>2</sub> concentration, atm; H<sub>a</sub> is the Henry's Law constant for H<sub>2</sub>O<sub>2</sub>, which is 1.0 × 10<sup>5</sup> Matm<sup>-1</sup> at 298 K (Lind and Kok, 1986). The mass fraction of the uptake of H<sub>2</sub>O<sub>2</sub> into the SOA mass (F<sub>H<sub>2</sub>O<sub>2</sub>(aq)</sub>) can be calculated as follows:

$$F_{\text{H}_2\text{O}_2(\text{aq})} = m_{\text{SOA}}/d_{\text{SOA}} \times G_f^3 \times [\text{H}_2\text{O}_2(\text{aq})] \times \text{MW}_{\text{H}_2\text{O}_2}/m_{\text{SOA}} \quad (6)$$

where m<sub>SOA</sub> is the mass of SOA collected by filter; d<sub>SOA</sub>, density of SOA, assumed to be 1.0 g cm<sup>-3</sup>; and MW<sub>H<sub>2</sub>O<sub>2</sub></sub> is the relative molecular weight of H<sub>2</sub>O<sub>2</sub>. Assuming the growth factor to be 1.05 at 60 % RH, the F<sub>H<sub>2</sub>O<sub>2</sub>(aq)</sub> is calculated as 0.17 and 0.14 ng μg<sup>-1</sup> 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 × 10<sup>-4</sup> and 1.66 × 10<sup>-4</sup> ng μg<sup>-1</sup> in the absence and presence of cyclohexane, respectively, with a Henry's Law constant of 8.47 × 10<sup>2</sup> Matm<sup>-1</sup> 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<sub>2</sub>O<sub>2</sub> under dry conditions with one reactor. The concentration of H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub>. 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> at 50 % RH (Huang

**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

et al., 2013). When we maintained the water vapor and moved the filter to the outlet of the second reactor (scenario 1w), the  $\text{H}_2\text{O}_2$  concentration increased to  $165 \pm 6\%$  of baseline. In scenario 3w, with water vapor added to the second reactor and without a filter in the gas flow, the  $\text{H}_2\text{O}_2$  concentration was  $172 \pm 5\%$ , almost the same as that in scenario 1w. In scenario 3d, no water vapour and no filter were used, but a high  $\text{H}_2\text{O}_2$  concentration,  $164 \pm 9\%$ , was also observed. For scenarios 1w, 3w, and 3d, where  $\text{H}_2\text{O}_2$  increased by  $\sim 67\%$ , 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 Sect. 3.3) did not result in a high yield of  $\text{H}_2\text{O}_2$ . We therefore concluded that the presence of three components together, the gaseous products, SOA, and water, was necessary for a high yield of  $\text{H}_2\text{O}_2$ . Once the gaseous products and SOA had been in contact with water vapor in the second reactor, the levels of  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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.,  $\text{HNO}_3$ ,  $\text{NO}_2$  and  $\text{N}_2\text{O}_5$ ),  $\text{SO}_2$ ,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  and oxygenated VOCs

**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

(Liggio et al., 2005; Kroll et al., 2005; Prince et al., 2007; Zhao et al., 2010, 2011, 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  $\alpha$ -pinene, organic peroxides account for  $\sim 21\%$  of the SOA mass and this fraction is not affected by RH and the presence of a OH scavenger. 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. 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  $\sim 0.22$ , which was independent of RH and the OH scavenger. The MCM v3.1 mechanism predicted this yield but failed to interpret the yields of individual peroxides, i.e.,  $\text{H}_2\text{O}_2$ , HMHP, PFA and PAA, indicating that our previous understanding of  $\alpha$ -pinene ozonolysis was insufficient. For  $\text{H}_2\text{O}_2$  with a yield of 0.048 under dry conditions and

## Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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  $\text{H}_2\text{O}_2$ . The presence of both water and SOA leads to the rapid transformation of gaseous organic peroxides into  $\text{H}_2\text{O}_2$ . This heterogeneous process increases the  $\text{H}_2\text{O}_2$  yield by  $\sim 67\%$ . Our results also show that water vapor will affect the distribution of gaseous peroxides, it cannot change the yield of total peroxides.

The rapid heterogeneous transformation of organic peroxides to  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  was underestimated and (2) OH and  $\text{HO}_2$  were also underestimated, especially when concentrations of VOCs were high. These investigators suggested the occurrence of additional recycling from  $\text{HO}_2$  to OH or the contributions of additional direct OH sources. Our finding that organic peroxides can transform to  $\text{H}_2\text{O}_2$  by rapid heterogeneous reactions can address the first discrepancy directly and the second indirectly. Peroxides influence OH through the removal pathways:



Predominant removal paths for organic peroxides in the atmosphere are reaction with OH (95%) and photolysis (4.4%) (Khan et al., 2015), while for  $\text{H}_2\text{O}_2$ , these two paths are almost equally important. The OH oxidation process consumes OH while photolysis process produces OH. Obviously,  $\text{H}_2\text{O}_2$  plays a different role in the OH cycling compared with organic peroxides. One molecule of organic peroxides transformed into  $\text{H}_2\text{O}_2$  yields  $\sim 1.4$  molecules of OH. Thus, the rapid transformation of organic perox-

ides to H<sub>2</sub>O<sub>2</sub> by the heterogeneous process would increase OH levels. However, not all the organic peroxides could be transformed to H<sub>2</sub>O<sub>2</sub> 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.

5 **The Supplement related to this article is available online at doi:10.5194/acpd-15-28133-2015-supplement.**

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## Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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- 30

**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Table 1.** Peroxide content in the gas phase and particle phase of  $\alpha$ -pinene ozonolysis as affected by the OH radical scavenger cyclohexane<sup>a</sup>.

OH scavenger RH	None		Cyclohexane	
	< 0.5 %	60 %	< 0.5 %	60 %
Gas phase				
$Y_{\text{H}_2\text{O}_2}^b$	$0.048 \pm 0.012$	$0.16 \pm 0.01$	$0.048 \pm 0.010$	$0.14 \pm 0.02$
$Y_{\text{HMHP}}^b$	$0.0030 \pm 0.0003$	$0.0062 \pm 0.0005$	$0.0024 \pm 0.0005$	$0.0037 \pm 0.0006$
$Y_{\text{PFA}}^b$	$0.0057 \pm 0.0020$	$0.012 \pm 0.002$	$0.0020 \pm 0.0003$	$0.005 \pm 0.001$
$Y_{\text{PAA}}^b$	$0.0067 \pm 0.0006$	$0.009 \pm 0.001$	$0.0022 \pm 0.0002$	$0.0024 \pm 0.0001$
$Y_{\text{TPO}}^b$	$0.18 \pm 0.01$	$0.20 \pm 0.01$	$0.27 \pm 0.02$	$0.25 \pm 0.02$
$\text{H}_2\text{O}_2(\text{g}) / \text{TPO}(\text{g})$ (ppbv ppbv <sup>-1</sup> )	$0.26 \pm 0.02$	$0.78 \pm 0.04$	$0.18 \pm 0.02$	$0.50 \pm 0.04$
Particle phase				
$Y_{\text{SOA}}^c$	$0.41 \pm 0.01$	$0.39 \pm 0.02$	$0.28 \pm 0.02$	$0.27 \pm 0.01$
$F_{\text{H}_2\text{O}_2}^d$ (ng $\mu\text{g}^{-1}$ )	$5.09 \pm 0.99$	$2.67 \pm 0.17$	$1.61 \pm 0.11$	$1.41 \pm 0.21$
$F_{\text{PFA}}^d$ (ng $\mu\text{g}^{-1}$ )	$0.35 \pm 0.06$	$0.27 \pm 0.02$	$0.14 \pm 0.01$	$0.16 \pm 0.04$
$F_{\text{PAA}}^d$ (ng $\mu\text{g}^{-1}$ )	$0.11 \pm 0.04$	0	$0.09 \pm 0.01$	0
$F_{\text{TPO}}^d$ ( $\mu\text{g} \mu\text{g}^{-1}$ )	$0.23 \pm 0.01$	$0.25 \pm 0.01$	$0.16 \pm 0.01$	$0.20 \pm 0.01$
$\text{H}_2\text{O}_2(\text{p}) / \text{TPO}(\text{p})$ ( $\mu\text{M} \mu\text{M}^{-1}$ )	$0.20 \pm 0.03$	$0.10 \pm 0.01$	$0.09 \pm 0.01$	$0.06 \pm 0.01$
$\text{TPO}(\text{p}) / \text{TPO}(\text{g} + \text{p})^e$	$0.19 \pm 0.02$	$0.18 \pm 0.03$	$0.07 \pm 0.01$	$0.09 \pm 0.01$

<sup>a</sup> ~ 275 ppbv  $\alpha$ -pinene, ~ 1300 ppmv cyclohexane and ~ 42 ppmv  $\text{O}_3$  were used in these experiments. The data represent the mean  $\pm$  SD of 3 observations.

<sup>b</sup> Molar yield of peroxides.

<sup>c</sup> Mass yield of SOA.

<sup>d</sup> Contribution of peroxides to SOA mass.

<sup>e</sup> Fraction of particulate TPO in gaseous and particulate TPO.

## Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition

H. Li et al.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

**Table 2.** Comparison of observed and theoretical gas-particle partitioning coefficients ( $K_p$ ) of PFA, PAA and TPO at different scenarios (298 K).

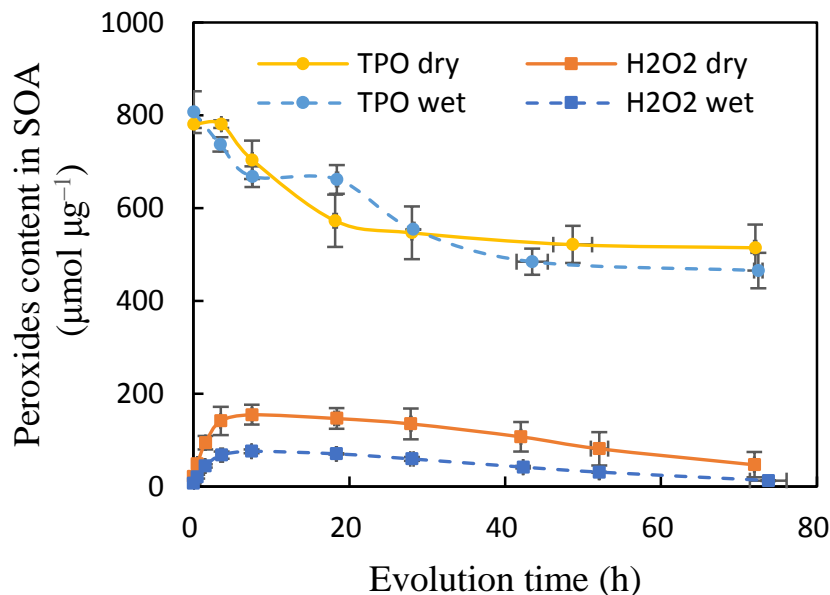
	$K_p$ (observed) ( $\text{m}^3 \mu\text{g}^{-1}$ )*				$K_p$ (theoretical) ( $\text{m}^3 \mu\text{g}^{-1}$ )
	Sc1	Sc2	Sc3	Sc4	
PFA	$8.06 \times 10^{-5}$	$2.95 \times 10^{-5}$	$9.19 \times 10^{-5}$	$4.20 \times 10^{-5}$	$2 \times 10^{-9}$
PAA	$1.76 \times 10^{-5}$	0	$4.38 \times 10^{-5}$	0	$4 \times 10^{-9}$
TPO	$3.47 \times 10^{-4}$	$3.39 \times 10^{-4}$	$1.61 \times 10^{-4}$	$2.17 \times 10^{-4}$	–

\* 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  $\sim 1300$  ppmv.



**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.

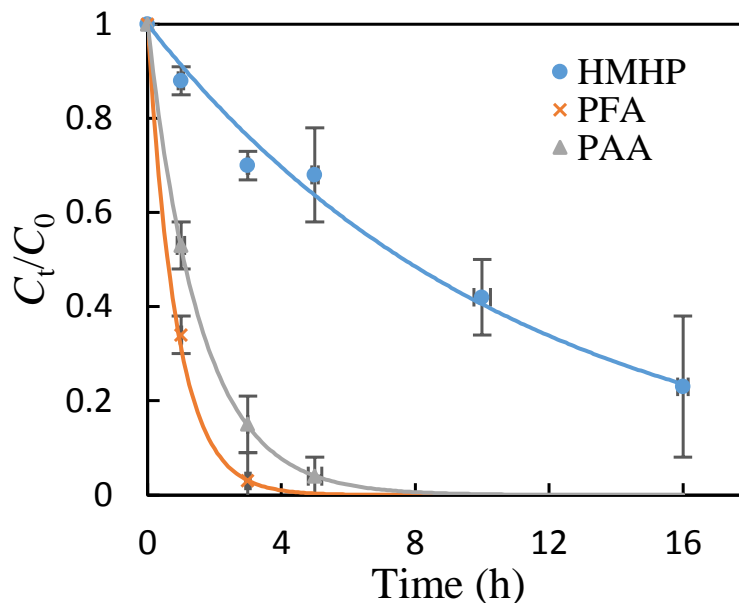


**Figure 1.** Evolution of total peroxides and  $\text{H}_2\text{O}_2$  contents in SOA produced under dry (< 0.5% RH) and wet (60% RH) conditions at 298 K. Circles and diamonds represent total peroxides and  $\text{H}_2\text{O}_2$  contents in SOA, respectively; and solid lines and dash lines represent that obtained under dry and wet conditions, respectively. The data represent the mean  $\pm$  SD of 3 observations.



**Organic peroxides  
gas-particle  
partitioning and rapid  
heterogeneous  
decomposition**

H. Li et al.



**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  $0.64 \text{ h}^{-1}$ , respectively. The data represent the mean  $\pm$  SD of 3 observations.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)