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# Organic peroxide and OH formation in aerosol and cloud water: laboratory evidence for this aqueous chemistry

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## Abstract

Aqueous chemistry in atmospheric waters (e.g., cloud droplets or wet aerosols) is well accepted as an atmospheric pathway to produce secondary organic aerosol (SOA<sub>aq</sub>). Water-soluble organic compounds with small carbon numbers ( $C_2$ - $C_3$ ) are precursors

for SOA<sub>aq</sub> and products include organic acids, organic sulfates, and high molecular weight compounds/oligomers. Fenton reactions and the uptake of gas-phase OH radicals are considered to be the major oxidant sources for aqueous organic chemistry. However, the sources and availability of oxidants in atmospheric waters are not well understood. The degree to which OH is produced in the aqueous phase affects the balance of radical and non-radical aqueous chemistry, the properties of the resulting aerosol, and likely its atmospheric behavior.

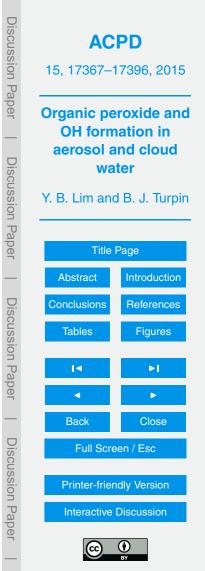
This paper demonstrates organic peroxide formation during aqueous photooxidation of methylglyoxal using ultra high resolution Fourier Transform Ion Cyclotron Resonance electrospray ionization mass spectrometry (FTICR-MS). Organic peroxides are known

to form through *gas-phase* oxidation of volatile organic compounds. They contribute secondary organic aerosol (SOA) formation directly by forming peroxyhemiacetals, and epoxides, and indirectly by enhancing gas-phase oxidation through OH recycling. We provide simulation results of organic peroxide/peroxyhemiacetal formation in clouds and wet aerosols and discuss organic peroxides as a source of condensed-phase OH
 radicals and as a contributor to aqueous SOA.

#### 1 Introduction

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Secondary organic aerosol (SOA) is a major component of atmospheric fine particulate matter  $[PM_{2.5}]$  (Zhang et al., 2007), contributes to adverse health, and affects climate by scattering (Seinfeld and Pandis, 1998) and sometimes by absorbing solar radiation (e.g., "brown carbon") (Andreae and Gelencser, 2006; Bones et al., 2010; Zhang et al., 2011). Although the chemical and physical properties of aerosols are needed to predict

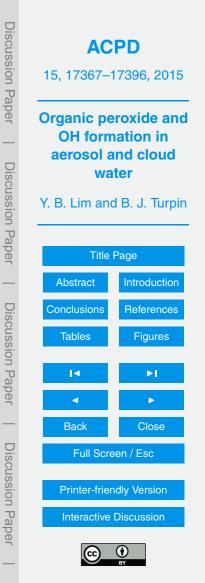


effects, the properties of SOA are poorly understood because SOA formation itself is poorly understood. Aqueous chemistry in atmospheric waters (e.g., cloud droplets or wet aerosols) is a potentially important pathway to produce SOA (SOA<sub>aq</sub>; Blando and Turpin, 2000), and could be comparable in magnitude to "traditional" SOA, formed via partitioning of semivolatile organic products of gas-phase oxidation (SOA<sub>gas</sub>) globally (Liu et al., 2012; Lin et al., 2012; Henze et al., 2008) and in locations where relative

humidity and aerosol hygroscopicity are high (Carlton and Turpin, 2013; Carlton et al., 2008; Fu et al., 2008; Chen et al., 2007). Because SOA<sub>aq</sub> is formed from small water-soluble precursors with high O/C ratios, it forms SOA (e.g., oligomers, organic salts)
with high O/C ratios and helps to explain the highly oxygenated nature of atmospheric organic aerosols, while SOA<sub>gas</sub> is less oxygenated (Aiken et al., 2008; Lim et al., 2010, 2013).

OH radicals are important oxidants in clouds. In the high solute concentrations present in wet aerosols a more complex system of organic radical and non-radical reactions occurs (Lim et al., 2010; McNeill et al., 2012; Ervens et al., 2014). Thus, an understanding of the availability of OH radicals is important to assessing the relative importance of radical and non-radical chemistry in aerosols. The uptake of gas-phase OH radicals into atmospheric waters (Faust and Allen, 1993) and Fenton reactions in the condensed/aqueous media (Arakaki and Faust, 1998) are considered the major oxidant sources for aqueous organic chemistry. Oxidant sources in organic-containing cloud, fog and aerosol waters and oxidant reactions with dissolved organic compounds

- have been documented (Arakaki et al., 2013; Weller et al., 2014; Long et al., 2013). Depending on sources of OH radicals, aqueous oxidation reactions could exhibit a surface area dependence (e.g., controlled by OH uptake), or a volume dependence (e.g.,
- <sup>25</sup> controlled by OH production through aqueous chemistry; Ervens et al., 2014). Herein, we explore the hypothesis that organic peroxides produce OH radicals within the atmospheric aqueous phase; we also demonstrate the formation of organic peroxides in the aqueous phase and their contribution to *condensed* phase chemistry.



Organic peroxides (herein particularly, organic hydroperoxides = ROOH) are known to play an important role in gas phase chemistry. They are commonly found in the atmosphere with mixing ratios of 0.1–1 ppb (Lee et al., 1993; De Serves et al., 1994; Sauer et al., 2001; Grossmann et al., 2003; Lee et al., 2000; Guo et al., 2014). They are known to form through gas-phase reactions of volatile organic compounds (VOCs) with OH radical, NO<sub>3</sub> radical and O<sub>3</sub> (Atkinson and Arey, 2003). While their chemistry is not fully understood, these atmospheric organic species are "key" to peroxy radical/NO<sub>x</sub> chemistry (Dibble, 2007; Glowacki et al., 2012), lead to photochemical smog formation, important to the HO<sub>x</sub>-NO<sub>x</sub>-O<sub>3</sub> balance (Wennberg et al., 1998; Singh et al., 1995), contribute to O<sub>3</sub> formation or depletion in the upper troposphere, and form SOA (Tobias and Ziemann, 2000). Organic peroxides (formed from gas-phase ozonolysis of monoterpenes, e.g.,  $\alpha$ - and  $\beta$ -pinenes) are major constituents of SOA (Docherty et al., 2005). Monoterpenes have a global flux second only to isoprene and maybe the

most efficient SOA<sub>gas</sub> precursor class (Kanakidou et al., 2005). Organic peroxides contribute to organic aerosol by forming peroxyhemiacetal oligomers with atmospherically

abundant organic carbonyls (e.g., aldehydes and ketones) via acid catalysis in aerosols

(Tobias and Ziemann, 2000, 2002). Due to the characteristically weak O-O bonds of organic peroxides, the gas-phase decomposition of organic peroxides through photolysis

or intermolecular radical reactions recycles OH radicals and can enhance gas-phase photooxidation of atmospheric organic compounds. Recent field studies demonstrate

that gas-phase OH recycling enhances isoprene photooxidation (Paulot et al., 2009;

Organic peroxides are known to be moderately water soluble (Henry's law constant

~ 100–1000 M atm<sup>-1</sup>). They are present in rainwater with concentrations of  $0.1-10 \,\mu M$ 

(Lind et al., 1986; Hellpointer and Gab, 1989; Liang et al., 2013), presumably by uptake

from the gas phase. In this work, we show that organic peroxides are also produced

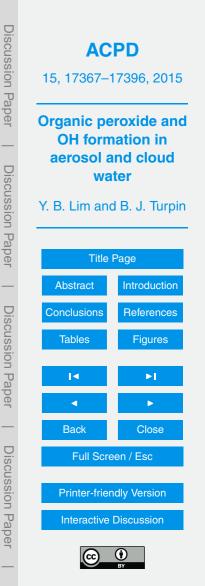
from aqueous-phase OH oxidation. We identify organic peroxide products from methylglyoxal and acid catalyzed oligomers (i.e., peroxyhemiacetals formed with methylgly-

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Taraborrelli et al., 2012).



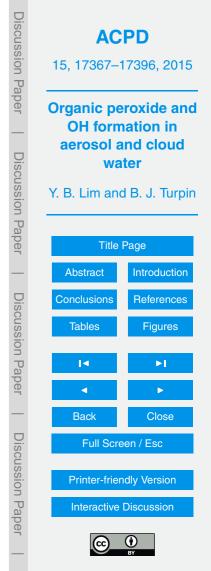
oxal) by ultra-high resolution mass spectrometry. We simulate organic peroxide and

peroxyhemiacetal formation under atmospheric conditions and explore organic peroxide contributions to aqueous-phase OH production and to SOA<sub>aq</sub> formation.

## 2 Experimental section

# 2.1 Cuvette chamber reactions

Reactions of methylglyoxal with OH radicals in the aqueous phase were conducted in a cuvette chamber, which holds 10 cuvettes (3 mL each; Spectrocell) equidistant from a 254 nm Hg UV lamp (Strahler). Cuvettes were immersed in a water bath to maintain the temperature at 25 °C. In each cuvette, 10 mM of methylglyoxal (Sigma-Aldrich) was dissolved in 18 M $\Omega$  Mili-Q water. OH radicals (10<sup>-13</sup>-10<sup>-12</sup> M) were generated in each cuvette by photolysis of 20 mM of H<sub>2</sub>O<sub>2</sub> (Sigma-Aldrich) with the rate constant of 10  $5.58 \times 10^{-5} \text{ M s}^{-1}$ . The H<sub>2</sub>O<sub>2</sub> photolysis rate constant was determined from H<sub>2</sub>O<sub>2</sub> + UV control experiments conducted in the same cuvette chamber as described previously (Tan et al., 2010) and corrected for light absorption by  $H_2O_2$  (Lim et al., 2013). The OH radical concentrations were estimated via modeling (Lim et al., 2013). It should be noted that using 20 mM of  $H_2O_2$  and the 254 nm UV lamp was not intended to 15 simulate tropospheric photolysis, rather to provide a source of OH radicals. According to our previous control experiments (i.e., methylglyoxal + UV; methylglyoxal +  $H_2O_2$ ), small amounts of pyruvic, acetic and formic acids form slowly in control experiments. However, dicarboxylic acids, the major products, did not form in the absence of OH radicals (i.e., in control experiments; Tan et al., 2010). Photooxidation of methylglyoxal 20 was allowed to proceed for 1 h. After being removed from the chamber, the cuvettes were kept frozen until analysis. No catalase was added in order to preserve organic peroxide products.



## 2.2 Organic peroxide and peroxyhemiacetal analysis

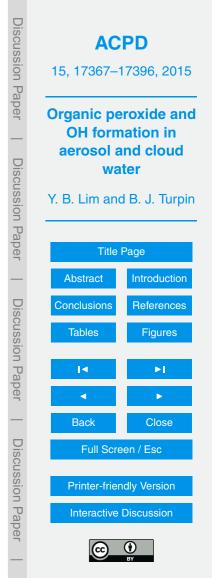
Ultra high resolution Fourier Transform Ion Cyclotron Resonance Electrospray Ionization Mass Spectrometer (FTICR-MS; Thermo-Finnigan LTQ-XL, Woods Hole Oceanographic Mass Spectrometer Facility) was used to determine the elemental composition

- of organic products as described previously (Altieri et al., 2008; Tan et al., 2012). The capillary voltage and a capillary temperature were -30.00 V and 300 °C, respectively for negative mode analyses. Positive mode analyses were conducted with a capillary voltage of 20.00 V and a capillary temperature of 260 °C. Both FTICR-MS and FTICR-MS/MS were used to analyze organic peroxide products from aqueous photooxidation
- of methylglyoxal and a standard solution, which was prepared by adding 10 mM of tert-butyl hydroperoxide (Sigma-Aldrich) and 10 mM of methylglyoxal (Sigma-Aldrich). These samples were diluted 100 fold with water (by volume), and diluted again with methanol (MeOH) by 2 fold (by volume). Thus, the mobile phase consisted of 50 % water and 50 % MeOH; 0.1 % of formic acid (by volume) was also added. These diluted
- samples were immediately introduced into the electrospray ionization source by direct infusion at 5 μL min<sup>-1</sup>. Photooxidation products of methylglyoxal were expected in both negative and positive modes due to a carboxylic group (negative mode) and a hydroxyl group (positive mode) in their structure (Table 1), whereas tert-butyl hydroperoxide is found only in the positive mode.

## 20 3 Organic peroxide chemistry

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We hypothesize that aqueous-phase OH radical reactions of methylglyoxal lead to organic peroxide formation as shown in Fig. 1. OH radical reactions are initiated by Hatom abstraction. Subsequent  $O_2$  addition and  $HO_2$  decomposition mainly lead to the formation of pyruvic acid and acetic acid (Lim et al., 2013). Both pyruvic and acetic acid react further with OH radicals and  $O_2$ , forming peroxy radicals ( $RO_2$ ), which undergo bimolecular  $RO_2$ - $RO_2$  reactions (Lim et al., 2013). However, substantial amounts of



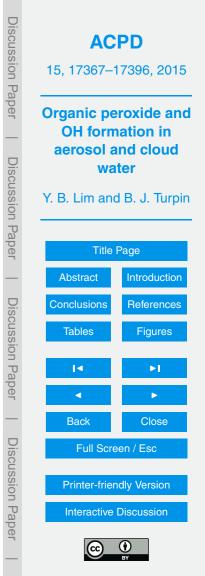
peroxy radicals could also react with HO<sub>2</sub> forming organic peroxides (as indicated by a bold arrow) since HO<sub>2</sub> is a common byproduct of aqueous photooxidation (Lim et al., 2010 and 2013) and is also water soluble (Henry's law constant =  $4 \times 10^3$  M atm<sup>-1</sup>; this is ~ 100 times higher than that of OH radicals).

- <sup>5</sup> We further expect organic peroxides to form peroxyhemiacetals with aldehydes via acid catalysis in the aqueous phase (Fig. 2a), as they do in dry aerosols (Tobias and Ziemann, 2000; Docherty et al., 2005). Below we document the formation of peroxyhemiacetals from a commercially available organic peroxide, tert-butyl hydroperoxide and methylglyoxal in aqueous solution (Fig. 2b). Then we argue that organic peroxide
- <sup>10</sup> products (R<sub>1</sub>OOH and R<sub>2</sub>OOH in Fig. 1) from the aqueous OH oxidation of methylglyoxal react further with methylglyoxal in water to produce peroxyhemiacetals. Briefly, a carbonyl group (aldehyde) in methylglyoxal is protonated by H<sup>+</sup>, then a hydroperoxyl group (-OOH) attacks a protonated carbonyl group forming peroxyhemiacetal. This peroxyhemiacetal chemistry is a well established oligomerization mechanism for
- SOA from gas-phase ozone reactions of alkenes in smog chamber studies (Tobias and Ziemann, 2000). In Tobias and Ziemann study, organic peroxides are first formed in the gas phase and become particles through gas-particle partitioning. Then organic peroxides form peroxyhemiacetals with by-product aldehydes through acid-catalyzed heterogeneous reactions on the particle surface. In current study, the detection of per-
- <sup>20</sup> oxyhemiacetals in our aqueous chemistry experiments (see below) provides evidence for organic peroxide formation through aqueous photochemistry.

#### 4 Results and discussion

## 4.1 Standard solution (mixture of methylglyoxal and t-butyl hydroperoxide)

FTICR-MS and FTICR-MS/MS analyses of the aqueous mixture of methylglyoxal and t-butyl hydroperoxide show methylglyoxal ( $m/z^+$  127.03666, 145.04714 and 159.06278) and a peroxyhemiacetal (PHA<sub>std</sub>;  $m/z^+$  185.07797) in the positive

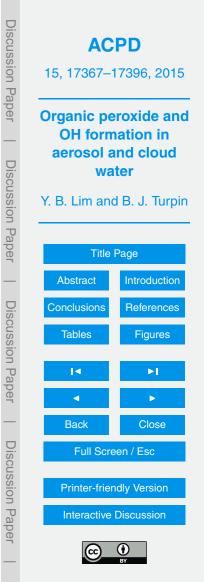


mode (Fig. 3). In a mobile phase of 50% MeOH and 50% water, methylglyoxal undergoes solvation both with water (hydration) and with MeOH, and is detected as a sodium adduct (i.e.,  $m/z^+$  127.03666 = [methylglyoxal + MeOH + Na]<sup>+</sup>,  $145.04714 = [methylglyoxal + H_2O + MeOH + Na]^+,$  $m/z^+$ and  $m/z^+$  $159.06278 = [methylglyoxal + 2MeOH + Na]^{+})$ . Methylglyoxal solvation with MeOH was verified by FTICR-MS/MS (Fig. 4). The fragments of  $m/z^+$  159.06278 are  $m/z^+$  141.05203 (H<sub>2</sub>O loss),  $m/z^+$  127.03668 (MeOH loss), and  $m/z^+$  95.01041 (another MeOH loss). The ion  $m/z^+$  95.01041 is the sodium adduct to methylglyoxal (a theoretical reading for [methylglyoxal + Na]<sup>+</sup> is  $m/z^+$  95.01090). A sodium adduct is also expected for a peroxyhemiacetals, and seen in Fig. 3 as  $m/z^+$  185.07797 10 (= [PHA<sub>std</sub> + Na]<sup>+</sup>). Details of FTICR-MS readings and theoretical readings based on actual molecular/atomic masses are shown in Table 1.

The peak.  $m/z^+$ 185.07802 (theoretical reading PHA<sub>std</sub> of [PHA<sub>std</sub> + Na]<sup>+</sup> = 185.07899) was fragmented by infrared multiphoton dissociation (IRMPD). Major fragments (Fig. 5) are  $m/z^+$  153.05228 (MeOH loss) and  $m/z^+$ 15 95.01041 ([methylglyoxal + Na]<sup>+</sup>). In electron impact (hard ionization), fragmentation of organic peroxides results in the loss of HO<sub>2</sub> (Tobias and Ziemann, 2000; Docherty et al., 2005). However, O<sub>2</sub> loss is expected for soft ionization, IRMPD fragmentation in FTICR-MS/MS (M. Soule and E. Kujawinski, personal communication, 2013). In Fig. 5, the ion  $m/z^+$  81.06971 indicates the loss of O<sub>2</sub> from t-butyl hydroperoxide. We also 20 observed the O<sub>2</sub> loss ( $m/z^+$  153.07158) from PHA<sub>std</sub>. FTICR-MS/MS and theoretical

readings are provided in Table 2.

Note that no organic peroxide peak was observed in the standard solution (nor in methylglyoxal + OH samples). This is not surprising because (1) high temperature of the capillary in an electrospray chamber (~ 250 °C) is likely to decompose organic peroxides (M. Soule, personal communication, 2013), (2) it is difficult to ionize organic peroxides (Witkowski and Gierczak, 2013) and organic peroxides react with methylglyoxal to form peroxyhemiacetals. These peroxyhemiacetals are much more stable (lesser volatile) than organic peroxides (Tobias and Ziemann, 2000). These peroxy-



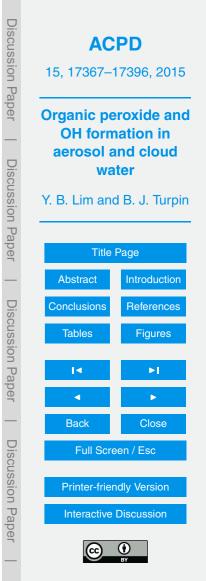
hemiacetal peaks (and fragments) appear in FTICR-MS (and FTICR-MS/MS) analysis of standard solutions and samples (see below), providing evidence for the presence (and formation) of organic peroxides from methylglyoxal + OH. FTICR-MS/MS of peroxyhemiacetal peaks show corresponding organic peroxide fragments, methylglyoxal and other fragments as expected (Tobias and Ziemann, 2000; Docherty et al., 2005).

## 4.2 Aqueous photooxidation products of methylglyoxal

A FTICR mass spectrum of an aqueous methylglyoxal solution exposed to OH radicals for 60 min is shown in Fig. 6 (negative mode). Main photooxidation products (Tan et al., 2012; Lim et al., 2013) are seen at  $m/z^-$  87.00862 (pyruvic acid) and  $m/z^-$ 177.04036 (2, 3-dimethyltartaric acid; structure shown in Fig. 6). This spectrum also provides evidence for peroxyhemiacetal formation at  $m/z^-$  163.02392 (= [PHA<sub>1</sub>-H]<sup>-</sup>) and  $m/z^-$  191.01998 (= [PHA<sub>2</sub>-H]<sup>-</sup>) since these readings are very close to the theoretical readings,  $m/z^-$  163.02405 for PHA<sub>1</sub> and  $m/z^-$  191.01918 for PHA<sub>2</sub> (Table 1). Fragmentation of these peaks by FTICR-MS/MS supports their identification as perox-

- <sup>15</sup> yhemiacetals. In Fig. 7a,  $m/z^-$  131.01339 and  $m/z^-$  131.01585 result from the losses of MeOH and O<sub>2</sub>, respectively, from PHA<sub>1</sub>, and  $m/z^-$  59.01377 results from the loss of O<sub>2</sub> from R<sub>1</sub>OOH, which is the organic peroxide constituent of PHA<sub>1</sub>. Similarly, in Fig. 7b,  $m/z^-$  159.02946 results from the loss of O<sub>2</sub> from PHA<sub>2</sub>, and  $m/z^-$  59.01377 results from the loss of O<sub>2</sub> from R<sub>2</sub>OOH, which is the organic peroxide constituent of
- <sup>20</sup> PHA<sub>2</sub>. Note, as was the case with the mixed peroxide-aldehyde standard, the organic peroxides themselves were not observed (see previous section). Detected and theoretical readings are provided in Table 2.

The FTICR-MS/MS was also conducted in the positive mode (Fig. 8) for PHA<sub>1</sub> ( $m/z^+$  187.02069 in Fig. 8a) and PHA<sub>2</sub> ( $m/z^+$  215.01565 in Fig. 8b). The theoretical readings are 187.02186 for PHA<sub>1</sub> and 215.01678 for PHA<sub>2</sub> (Table 1). The methylglyoxal fragments ( $m/z^+$  95.1041 in Fig. 8a and  $m/z^+$  95.0140 in Fig. 8b) appear. This confirms that both PHA<sub>1</sub> and PHA<sub>2</sub> are indeed acid-catalyzed products of methylglyoxal.

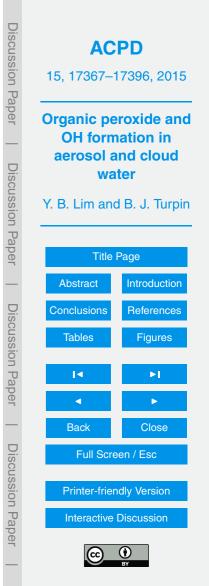


## 5 Atmospheric implications

Using ultra-high resolution FTICR-MS and FTICR-MS/MS, we observed the presence of peroxyhemiacetals, after aqueous photooxidation of methylglyoxal and in aqueous methylglyoxal-organic peroxide standard solutions. The presence of stable peroxyhemiacetals is an indicator of the existence of the less stable organic peroxides. Thus, this work provides evidence for the formation of organic peroxides through aqueous phase OH radical oxidation of methylglyoxal.

#### 5.1 Organic peroxide production in clouds and wet aerosols

Below we demonstrate through chemical modeling that organic peroxides photochemically form from organics present both in clouds and wet aerosols. We used the full 10 kinetic model for glyoxal and methylglyoxal (Lim et al., 2013) to simulate the formation of organic peroxides and peroxyhemiacetals. The following updates were made to the model: (1) the rate constant for the bimolecular reactions of RO<sub>2</sub> and HO<sub>2</sub> was given as  $3 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$  (Reactions R213–R219 in Table S1 in the Supplement) based on the rate constant for  $[HO_2 + HO_2] \sim 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , (2) the concentration of OH in 15 the aqueous phase was set to  $\sim 10^{-14}$  (previously  $\sim 10^{-12})$  according to recent estimations (Arakaki et al., 2013) (Fig. S1a in the Supplement), (3) the concentration of  $HO_2$  in the aqueous phase was estimated to be ~  $10^{-8}$  M maintained by the Henry's law equilibrium; therefore, the excess HO<sub>2</sub> produced by photooxidation in the aqueous phase was transported to the gas phase (Fig. S1b). All the reactions included in 20 the model are listed in Table S1. For wet aerosol simulations, 1 M (the initial concentration) of methylglyoxal was used in the agueous phase. Note that we do not expect that methylglyoxal is present at 1 M in aerosols. However, water-soluble organic matter is present at 1–10 M. So this analysis treats all water-soluble organic matter as if it behaves like methylglyoxal. Under wet aerosol conditions ([methylglyoxal]<sub>initial</sub> = 1 M, 25  $[H_2O_2]_{initial} = 0 M$ ,  $[OH] \sim 10^{-14} M$ , and  $[HO_2] \sim 10^{-8} M$ ),  $\sim 400 \mu M$  of organic peroxides



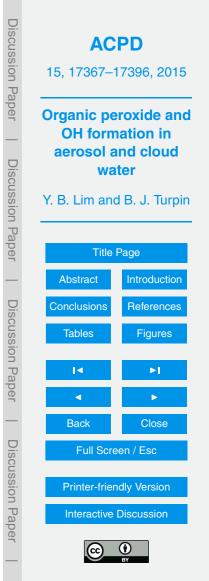
The model also includes the sinks of aqueous-phase organic peroxides: OH radical reactions (Reactions R220–R225), photolysis (Reaction R230), and the evaporation to the gas phase (Reaction R234) in Table S1. Note that organic peroxide (ROOH) formation in Fig. 10a and b does not change within the Henry's law constant, 100 to

- <sup>5</sup> 1000 M atm<sup>-1</sup>, and the evaporation rate is assumed to be a diffusion-controlled transfer coefficient (Lelieveld and Crutzen, 1991; Lim et al., 2005), which is the upper limit based on the equation provided by Lelieveld and Crutzen (1991). Here, the gas-phase [ROOH] is assumed to be 1 ppb (R234 in Table S1). In atmospheric cloud conditions ([methylglyoxal]<sub>initial</sub> = 10  $\mu$ M, [H<sub>2</sub>O<sub>2</sub>]<sub>initial</sub> = 0 M, [OH] ~ 10<sup>-14</sup> M, and [HO<sub>2</sub>] ~ 10<sup>-8</sup> M),
- $\sim 0.4 \,\mu$ M of organic peroxide formation during the 12 h daytime is expected (Fig. 10b) while all the sinks of organic peroxides listed above are included. This concentration of aqueous-phase photochemically produced organic peroxides is within the range of measured rainwater concentrations (0.1–10  $\mu$ M) and similar to the concentration expected by Henry's law equilibrium from gas-phase organic peroxides (0.1–1 ppb).

#### 15 5.2 Peroxyhemiacetal formation in wet aerosol

The formation of peroxyhemiacetals competes with (1) hydration of methylglyoxal and (2) photolysis and OH reactions of organic peroxides (Fig. 9). Competing with methylglyoxal hydration means that only a dehydrated methylglyoxal (DeMGLY), not hydrated methylglyoxal (MGLY), forms a peroxyhemiacetal (PHA) with an organic perox-

- ide (ROOH), since the aldehyde reacts with peroxides. The dehydration equilibrium for methylglyoxal is included in the model (R226 in Table S1). In wet aerosols, ~ 0.4 mM of DeMGLY out of 1 M MGLY will undergo peroxyhemiacetal formation and react with OH radicals (Reactions R227 and R228 in Table S1) at the same time (Fig. S2a). The main sink for peroxyhemiacetals is expected to be OH reaction (no evaporation is expected).
- <sup>25</sup> The peroxyhemiacetal formation equilibrium (Reaction R229) and the OH reaction of peroxyhemiacetals (Reaction R231) are listed in Table S1. The modified model simulates ~ 0.4  $\mu$ M of peroxyhemiacetal formation during the 12 h daytime and the minor increase during the nighttime (Fig. 10b). Under cloud conditions, peroxyhemiacetal for-



mation is negligible (Note that the model simulates  $\sim 4 \times 10^{-15}$  M peroxyhemiacetal formation during the daytime from 10  $\mu$ M of methylglyoxal photooxidation in Fig. 10b).

## 5.3 OH recycling due to the photolysis of organic peroxides in atmospheric waters

In both cloud and wet aerosol conditions, 7.5 × 10<sup>-15</sup> M of aqueous-phase OH production is expected from the photolysis of organic peroxides ([ROOH]<sub>initial</sub> ~ 400 μM in wet aerosols and [ROOH]<sub>initial</sub> ~ 0.4 μM in cloud droplets) formed by aqueous photooxidation during the 12 h daytime (Fig. S3) while the sink of ROOH is OH reaction. Note that ~ 10<sup>-14</sup> M of OH was recently estimated in atmospheric waters (Arakaki et al., 2013) and ~ 10<sup>-14</sup>–10<sup>-15</sup> M of OH was previously estimated in the core of the bulk phase (Jacob, 1986). Thus, the aqueous production of organic peroxides in atmospheric waters could be an important source of aqueous OH through organic peroxide photolysis.

# The Supplement related to this article is available online at doi:10.5194/acpd-15-17367-2015-supplement.

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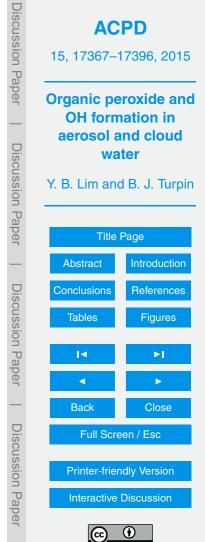
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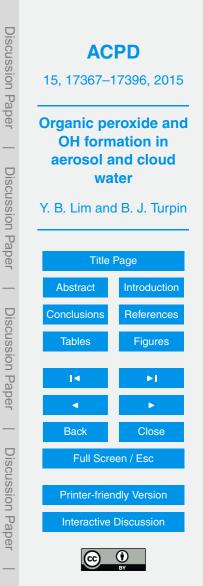
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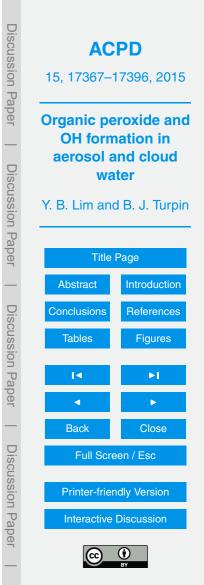
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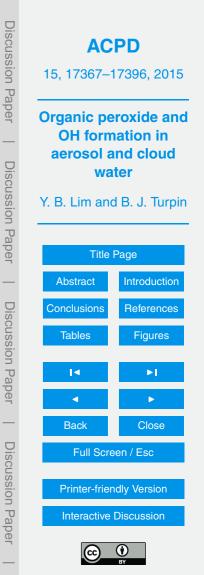
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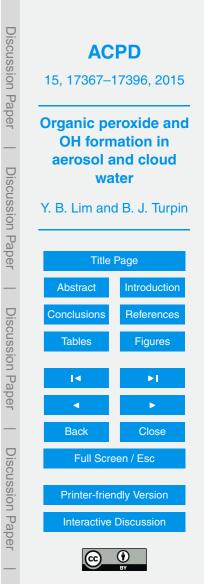
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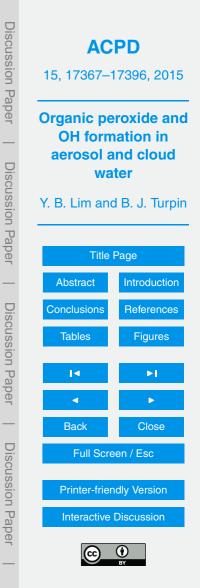
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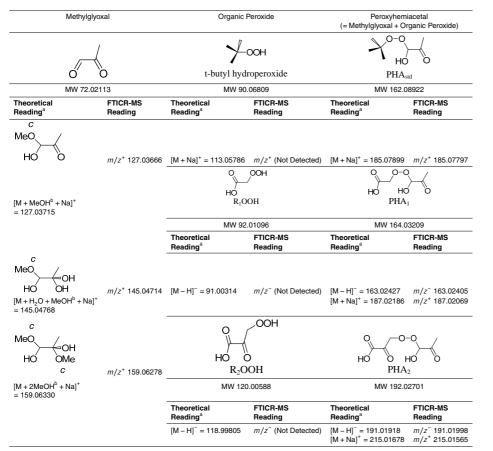


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**Table 1.** FTICR-MS and theoretical readings for methylglyoxal, organic peroxides and peroxy hemicetals.

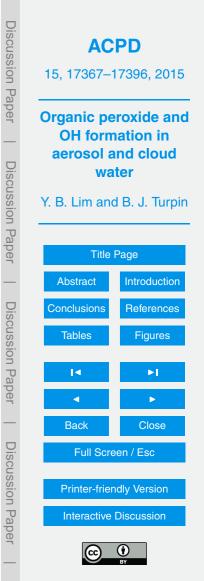
<sup>a</sup> Theoretical reading is based on actual atomic/molecular weights obtained by online software, "Molecular Isotopic Distribution Analysis (MIDAs)" (http://www.pobi.plm.nib.acu/CPBroscoped/////midos/index.htm)

(http://www.ncbi.nlm.nih.gov/CBBresearch/Yu/midas/index.html)

<sup>b</sup> MeOH = Methanol. Note that the mobile phase contains 50 % water (with 0.05 % formic acid) and 50 % MeOH.

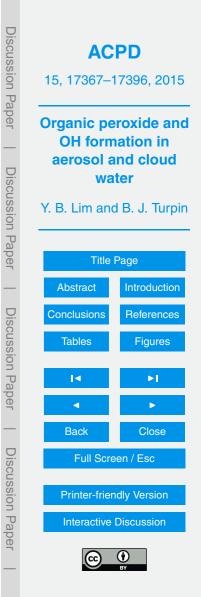
<sup>c</sup> MeO is a deprotonated MeOH.

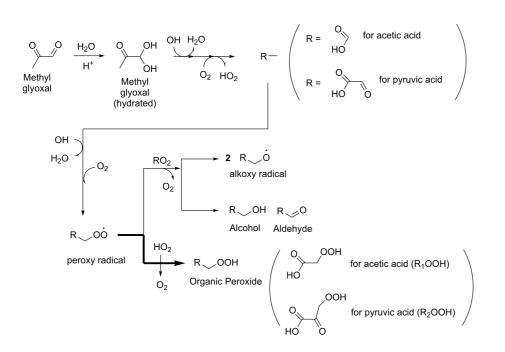
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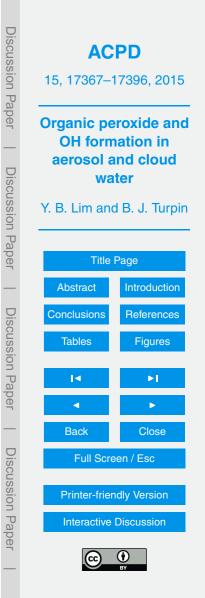
#### **Table 2.** FTICR-MS/MS and theoretical readings for fragments of peroxyhemiacetals and organic peroxides.

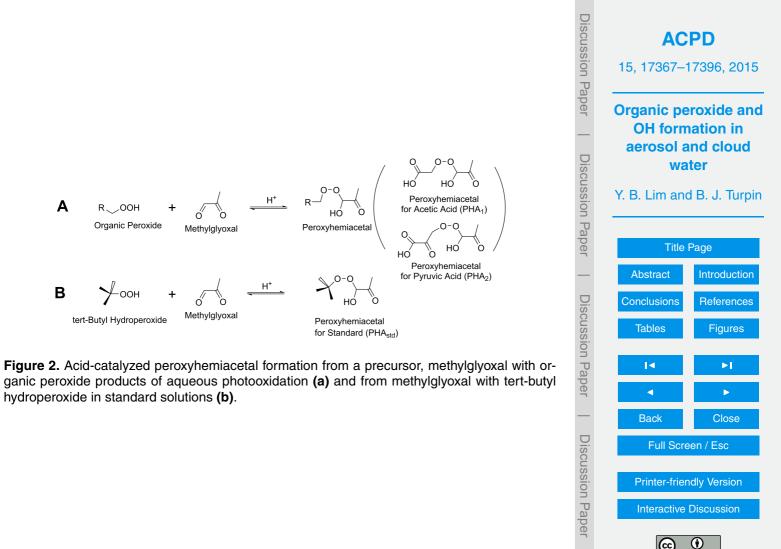
Organic Perox	kide	Peroxyhemiacetal				
Уюн		$\gamma^{\circ}$				
t-butyl hydropere	oxide	PHA <sub>std</sub>				
Fragment (loss of O <sub>2</sub> )		Fragment (loss of O <sub>2</sub> )		Fragment (loss of MeOH)		
Theoretical Reading	FTICR-MS/MS Reading	Theoretical Reading	FTICR-MS/MS Reading	Theoretical Reading	FTICR-MS/MS Reading	
$[M + Na - O_2]^+ = 81.06803$	<i>m/z</i> <sup>+</sup> 81.06971	$[M + Na - O_2]^+ = 153.08916$	<i>m/z</i> <sup>+</sup> 153.07158	[M + Na - MeOH] <sup>+</sup> = 153.05277	<i>m/z</i> <sup>+</sup> 153.05228	
	Н		O HO			
RIOOH			110	PHA <sub>1</sub>		
Fragment (loss of O <sub>2</sub> )		Fragment (loss of O <sub>2</sub> )		Fragment (loss of MeOH)		
Theoretical Reading	FTICR-MS/MS Reading	Theoretical Reading	FTICR-MS/MS Reading	Theoretical Reading	FTICR-MS/MS Reading	
[M – H – O <sub>2</sub> ] <sup>-</sup> = 59.01331	<i>m/z</i> <sup>-</sup> 59.01377	$[M - H - O_2]^- = 131.03444$	<i>m/z</i> <sup>-</sup> 131.01589	[M - H - MeOH] <sup>-</sup> = 130.99805	<i>m/z</i> <sup>-</sup> 131.01339	
$ \begin{array}{c}                                     $						
Fragment (loss of O <sub>2</sub> )		Fragment (loss of O <sub>2</sub> )		Fragment (loss of MeOH)		
Theoretical Reading	FTICR-MS/MS Reading	Theoretical Reading	FTICR-MS/MS Reading	Theoretical Reading	FTICR-MS/MS Reading	





**Figure 1.** Organic peroxide formation from aqueous-phase OH radical reactions of methylglyoxal.





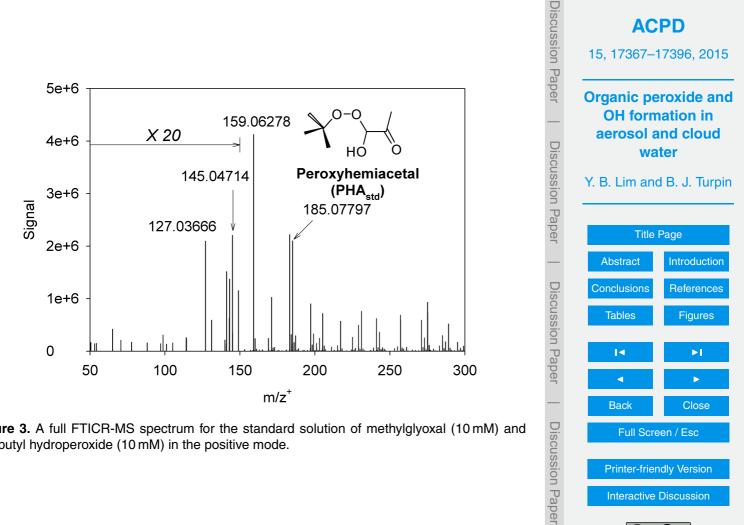


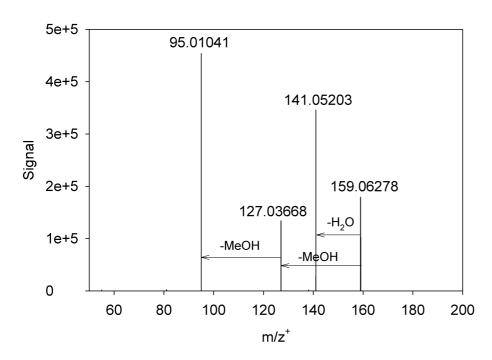
Figure 3. A full FTICR-MS spectrum for the standard solution of methylglyoxal (10 mM) and tert-butyl hydroperoxide (10 mM) in the positive mode.

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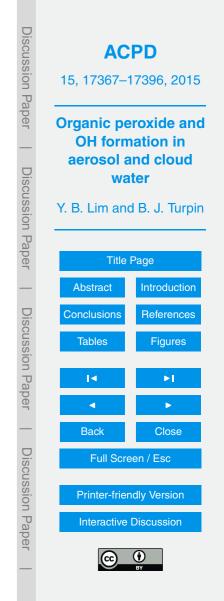
**ACPD** 

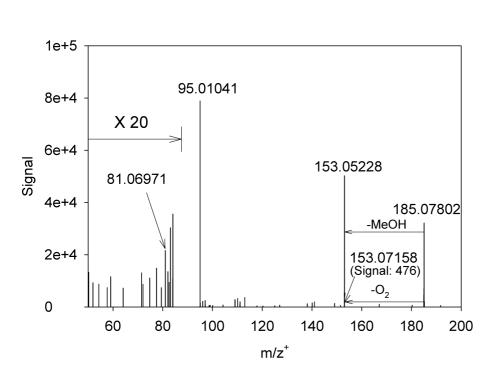
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**Printer-friendly Version** Interactive Discussion

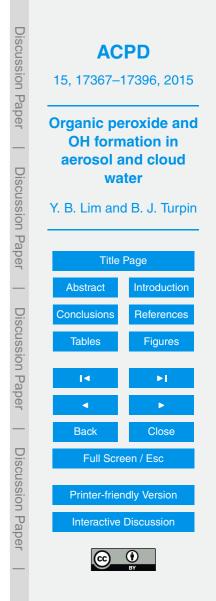


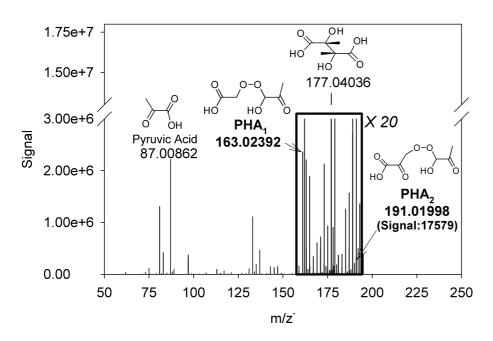
**Figure 4.** FTICR-MS/MS for  $m/z^+$  159 (methylglyoxal).



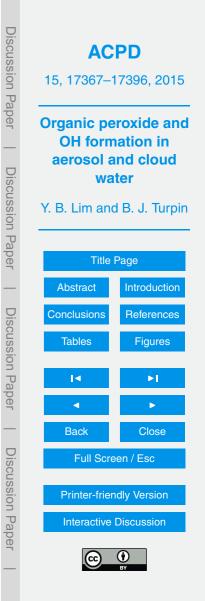


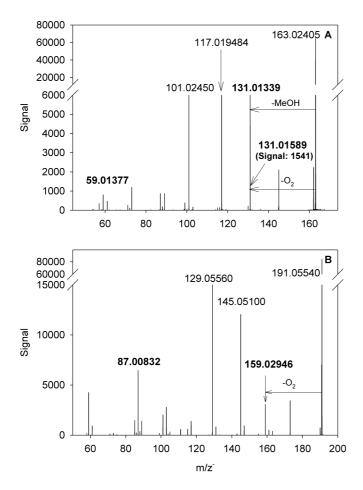
**Figure 5.** FTICR-MS/MS for  $m/z^+$  185 (PHA<sub>std</sub>).



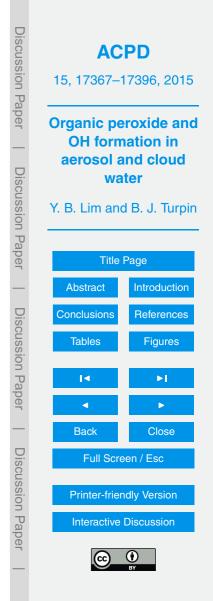


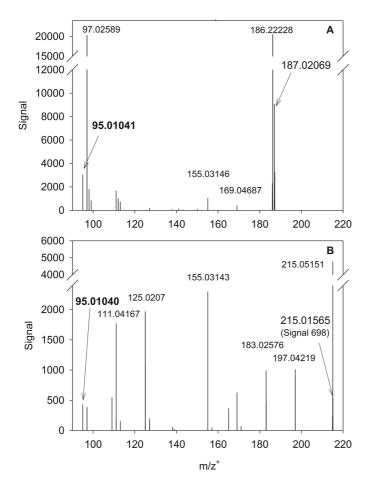
**Figure 6.** A full FTICR-MS spectrum for products of 1 h aqueous photooxidation of methylglyoxal in the negative mode.

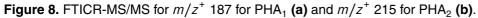


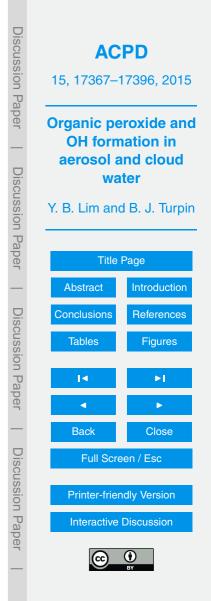


**Figure 7.** FTICR-MS/MS for  $m/z^-$  163 for PHA<sub>1</sub> (a) and  $m/z^-$  191 PHA<sub>2</sub> (b).









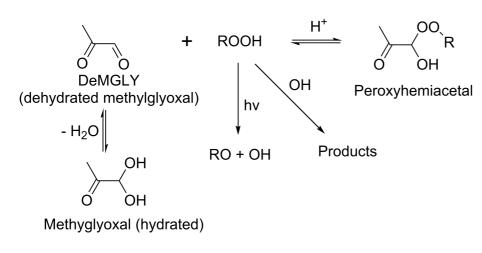


Figure 9. Peroxyhemiacetal formation.

