



**Organic peroxide and OH formation in aerosol and cloud water**

Y. B. Lim and B. J. Turpin

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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<sub>2</sub>-C<sub>3</sub>) 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

Secondary organic aerosol (SOA) is a major component of atmospheric fine particulate matter [PM<sub>2.5</sub>] (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

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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 ( $\text{SOA}_{\text{aq}}$ ; Blando and Turpin, 2000), and could be comparable in magnitude to “traditional” SOA, formed via partitioning of semivolatile organic products of gas-phase oxidation ( $\text{SOA}_{\text{gas}}$ ) 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  $\text{SOA}_{\text{aq}}$  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  $\text{SOA}_{\text{gas}}$  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., 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.

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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; Taraborrelli et al., 2012).

Organic peroxides are known to be moderately water soluble (Henry’s law constant  $\sim 100$ – $1000 \text{ M atm}^{-1}$ ). They are present in rainwater with concentrations of 0.1–10  $\mu\text{M}$  (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 methylglyoxal) by ultra-high resolution mass spectrometry. We simulate organic peroxide and





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 =  $4 \times 10^3 \text{ M atm}^{-1}$ ; this is  $\sim 100$  times higher than that of OH radicals).

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 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 peroxyhemiacetals 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

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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 peroxyhemiacetals. 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 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.

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## 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 peroxy-hemiacetals 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 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  $\text{RO}_2$  and  $\text{HO}_2$  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  $[\text{HO}_2 + \text{HO}_2] \sim 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , (2) the concentration of OH in 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  $\text{HO}_2$  in the aqueous phase was estimated to be  $\sim 10^{-8} \text{ M}$  maintained by the Henry's law equilibrium; therefore, the excess  $\text{HO}_2$  produced by photooxidation in the aqueous phase was transported to the gas phase (Fig. S1b). All the reactions included in the model are listed in Table S1. For wet aerosol simulations, 1 M (the initial concentration) of methylglyoxal was used in the aqueous 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 ( $[\text{methylglyoxal}]_{\text{initial}} = 1 \text{ M}$ ,  $[\text{H}_2\text{O}_2]_{\text{initial}} = 0 \text{ M}$ ,  $[\text{OH}] \sim 10^{-14} \text{ M}$ , and  $[\text{HO}_2] \sim 10^{-8} \text{ M}$ ),  $\sim 400 \mu\text{M}$  of organic peroxides during the 12 h daytime were formed through aqueous OH radical reactions (Fig. 10a).

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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 1000 Matm<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 μM, [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), ~ 0.4 μM 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 μM) and similar to the concentration expected by Henry's law equilibrium from gas-phase organic peroxides (0.1–1 ppb).

### 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 peroxide (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). 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 μM of peroxyhemiacetal formation during the 12 h daytime and the minor increase during the nighttime (Fig. 10b). Under cloud conditions, peroxyhemiacetal for-



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

Organic Peroxide		Peroxyhemiacetal			
t-butyl hydroperoxide		PHA <sub>add</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
$[M + Na - O_2]^+ = 81.06803$	$m/z^+ 81.06971$	$[M + Na - O_2]^+ = 153.08916$	$m/z^+ 153.07158$	$[M + Na - MeOH]^+ = 153.05277$	$m/z^+ 153.05228$
R <sub>1</sub> OOH		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
$[M - H - O_2]^- = 59.01331$	$m/z^- 59.01377$	$[M - H - O_2]^- = 131.03444$	$m/z^- 131.01589$	$[M - H - MeOH]^- = 130.99805$	$m/z^- 131.01339$
R <sub>2</sub> OOH		PHA <sub>2</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
$[M - H - O_2]^- = 87.00822$	$m/z^- 87.00832$	$[M - H - O_2]^- = 159.02935^e$	$m/z^- 159.02946$	$[M - H - MeOH]^- = 159.00079$	$m/z^-$ (Not Detected)

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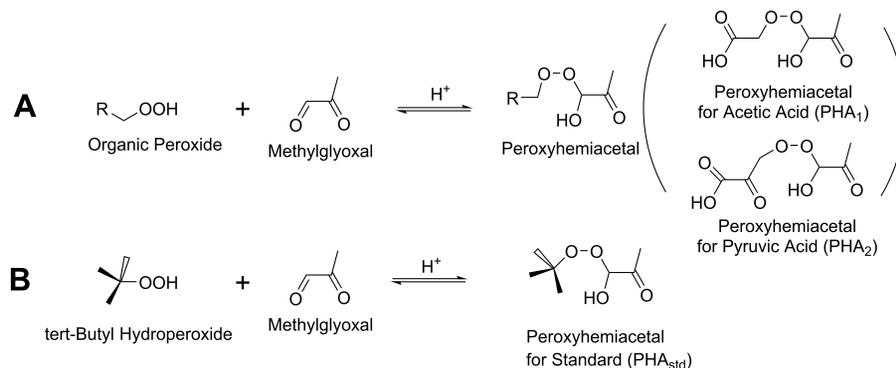
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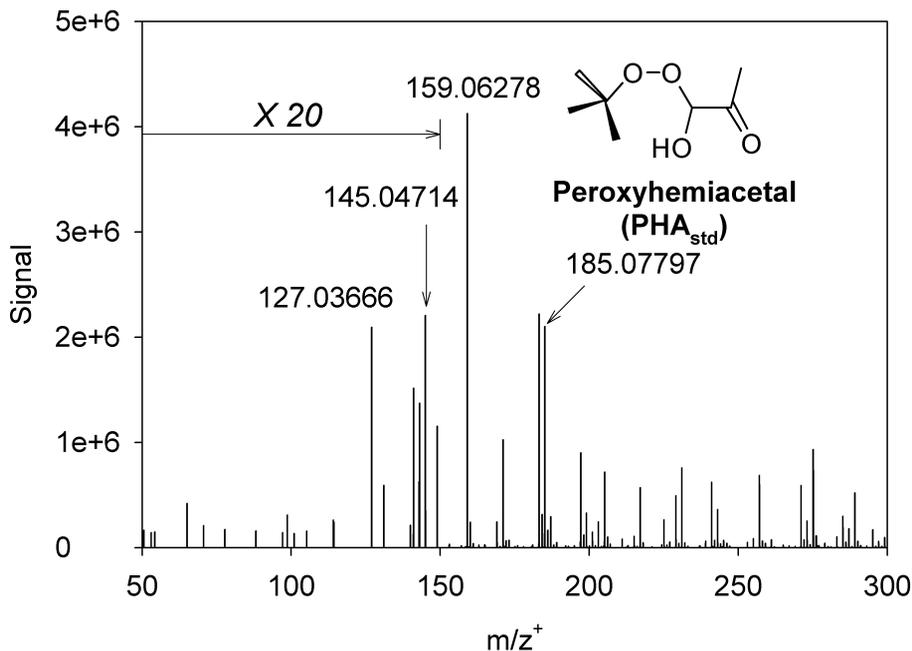


**Figure 2.** Acid-catalyzed peroxyhemiacetal formation from a precursor, methylglyoxal with organic peroxide products of aqueous photooxidation **(a)** and from methylglyoxal with tert-butyl hydroperoxide in standard solutions **(b)**.

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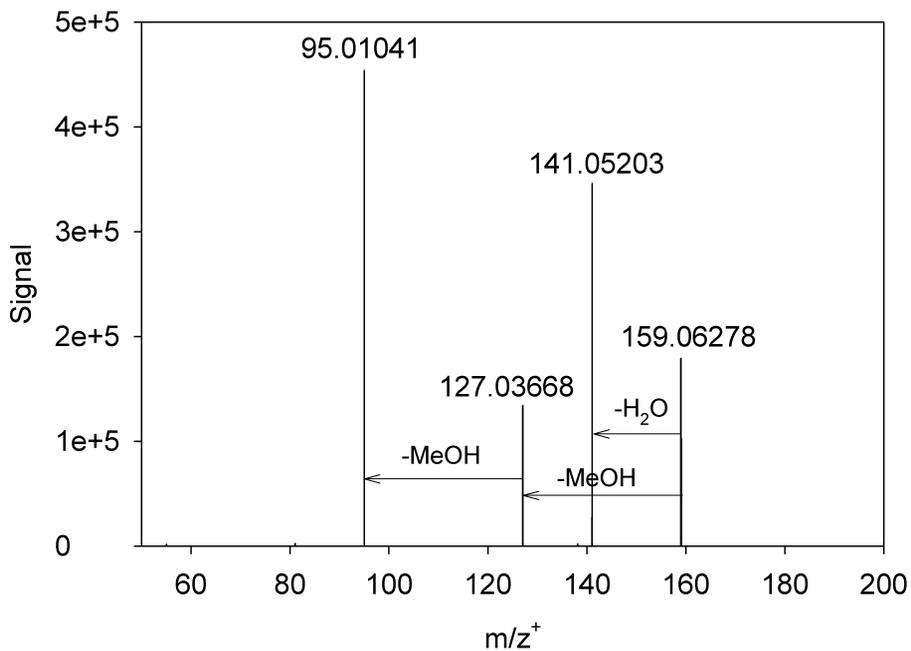
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**Figure 3.** A full FTICR-MS spectrum for the standard solution of methylglyoxal (10 mM) and tert-butyl hydroperoxide (10 mM) in the positive mode.

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

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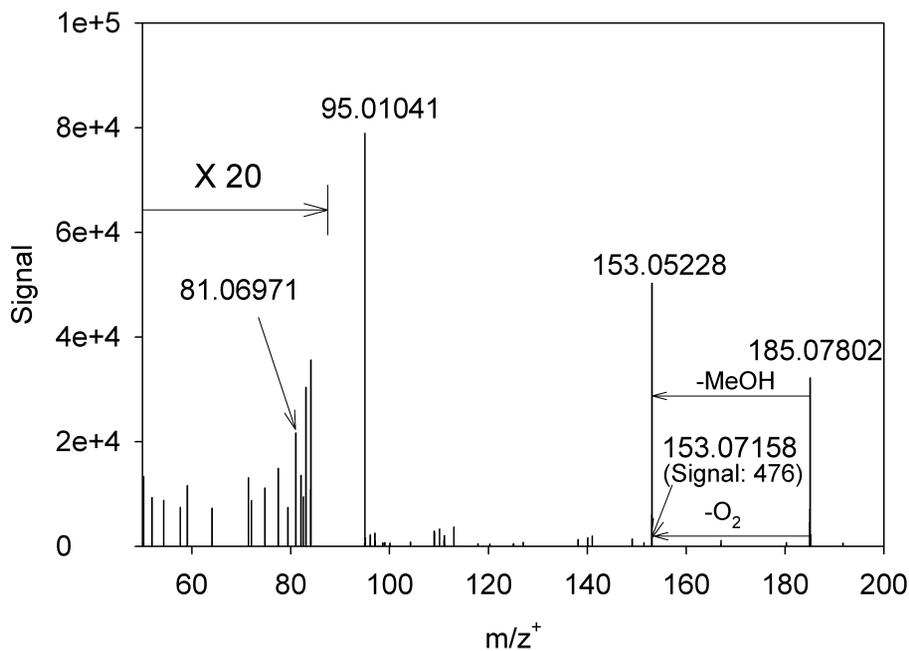
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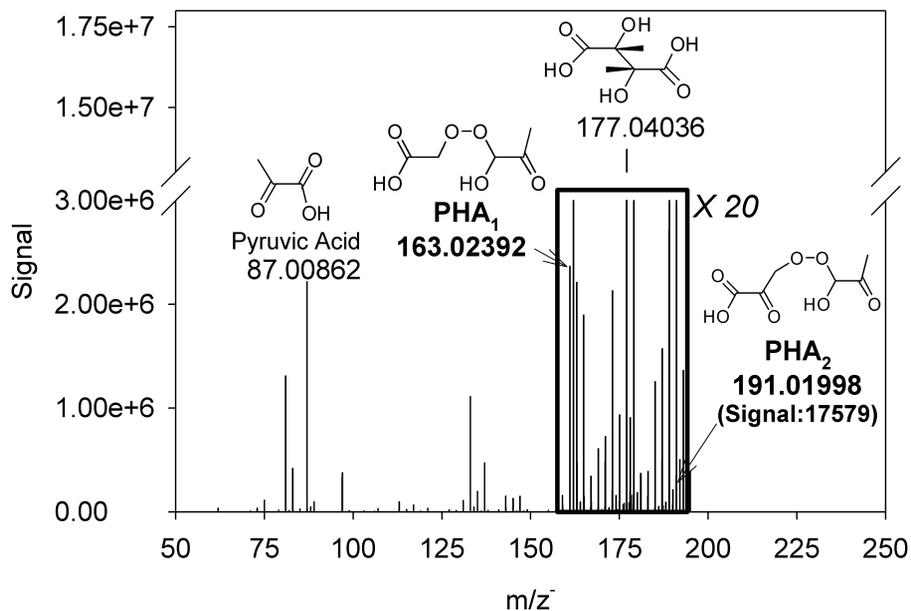
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**Figure 5.** FTICR-MS/MS for  $m/z^+$  185 (PHA<sub>std</sub>).[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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

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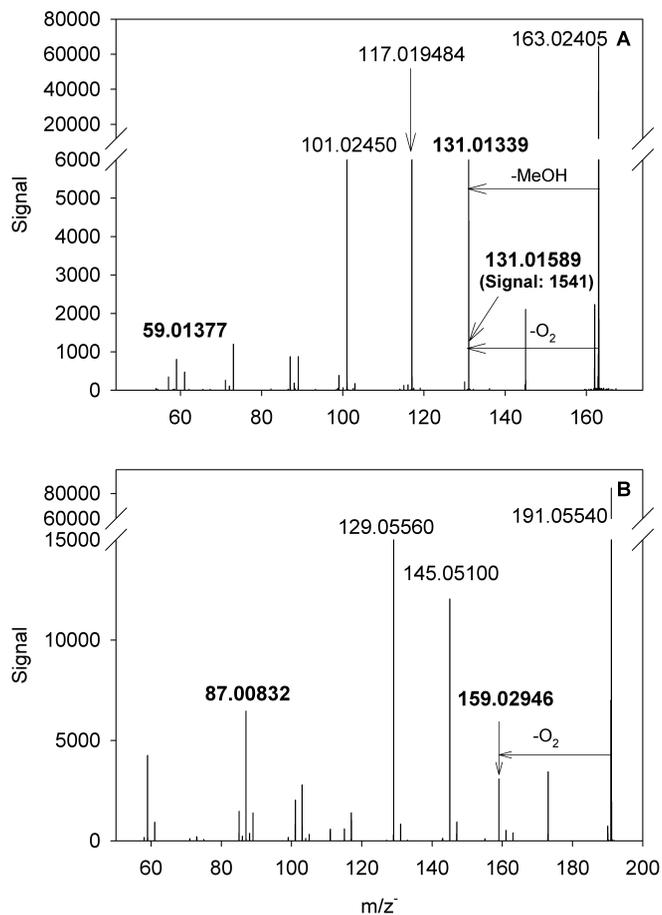
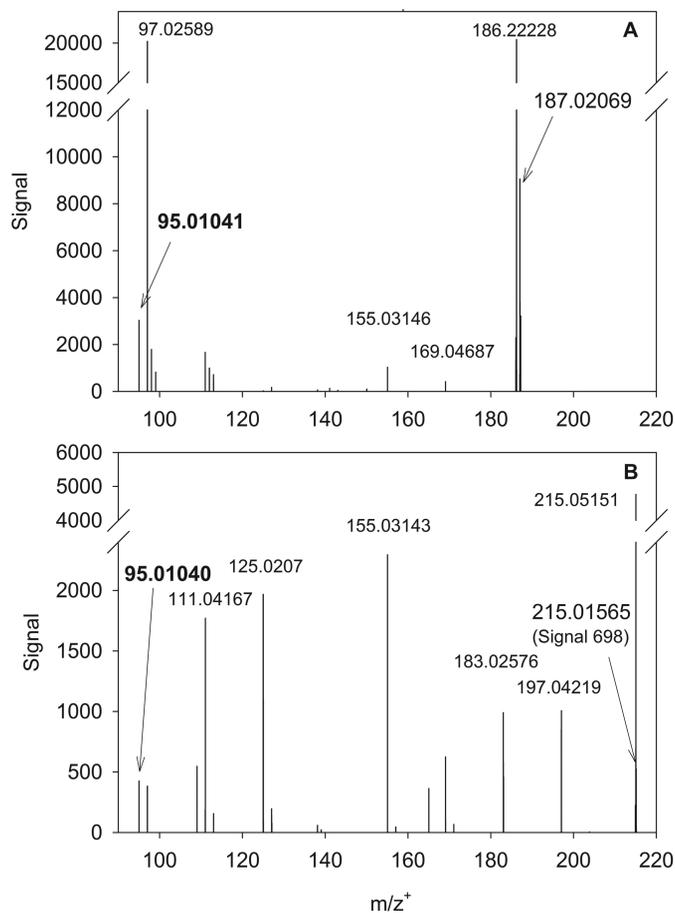


Figure 7. FTICR-MS/MS for  $m/z^-$  163 for PHA<sub>1</sub> (a) and  $m/z^-$  191 PHA<sub>2</sub> (b).

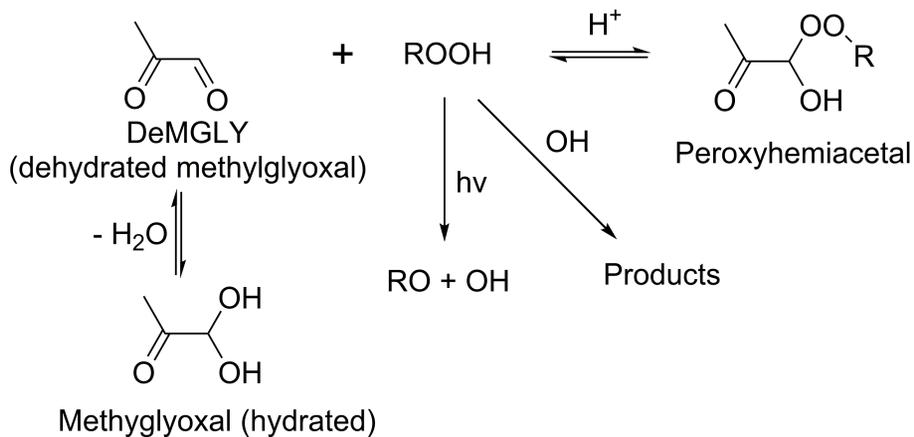
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**Figure 8.** FTICR-MS/MS for  $m/z^+$  187 for PHA<sub>1</sub> (a) and  $m/z^+$  215 for PHA<sub>2</sub> (b).



**Figure 9.** Peroxyhemiacetal formation.

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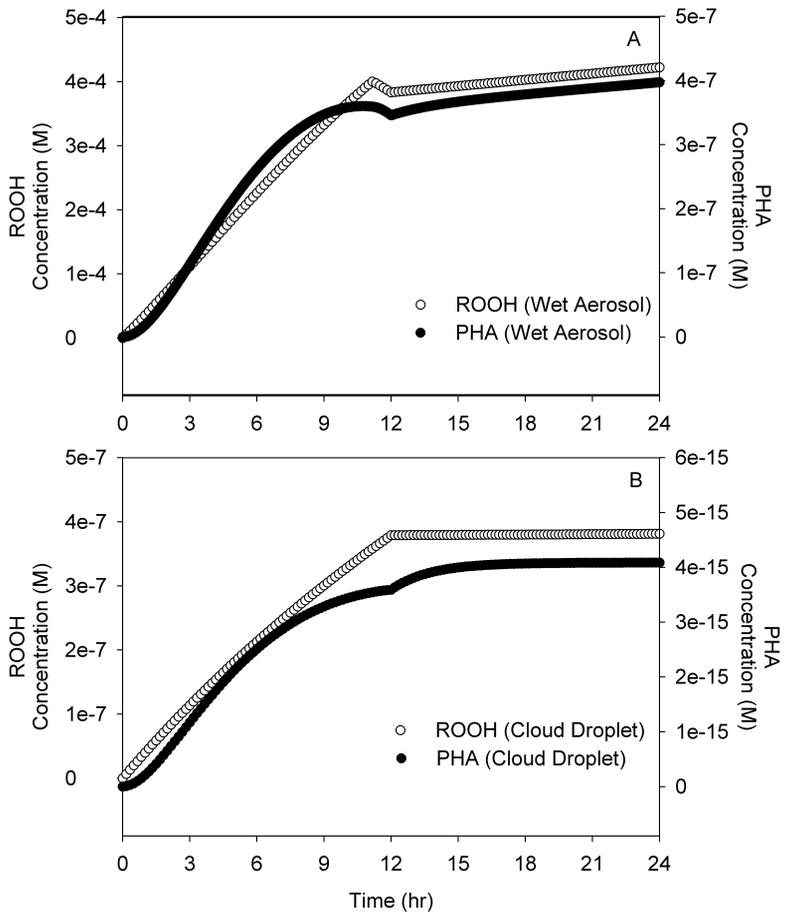
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**Figure 10.** The atmospheric simulated concentrations of ROOH (organic peroxides) and PHA (peroxyhemiacetals) in wet aerosols (a) and cloud droplets (b) during 24 h. The first 12 h are daytime.