Formation of aqueous-phase $\alpha$-hydroxyhydroperoxides ($\alpha$-HHP): potential atmospheric impacts

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Abstract. The focus of this work is on quantifying the degree of the aqueous-phase formation of $\alpha$-hydroxyhydroperoxides ($\alpha$-HHPs) via reversible nucleophilic addition of H$_2$O$_2$ to aldehydes. Formation of this class of highly oxygenated organic hydroperoxides represents a poorly characterized aqueous-phase processing pathway that may lead to enhanced SOA formation and aerosol toxicity. Specifically, the equilibrium constants of $\alpha$-HHP formation have been determined using proton nuclear-magnetic-resonance ($^1$H NMR) spectroscopy and proton-transfer-reaction mass spectrometry (PTR-MS). Significant $\alpha$-HHP formation was observed from formaldehyde, acetaldehyde, propionaldehyde, glycolaldehyde, glyoxylic acid, and methyglyoxal, but not from methacrolein and ketones. Low temperatures enhanced the formation of $\alpha$-HHPs but slowed their formation rates. High inorganic salt concentrations shifted the equilibria toward the hydrated form of the aldehydes and slightly suppressed $\alpha$-HHP formation. Using the experimental equilibrium constants, we predict the equilibrium concentration of $\alpha$-HHPs to be in the mM level in cloud water, but it may also be present in the mM level in aerosol liquid water (ALW), where the concentrations of H$_2$O$_2$ and aldehydes can be high. Formation of $\alpha$-HHPs in ALW may significantly affect the effective Henry’s law constants of H$_2$O$_2$ and aldehydes but may not affect their gas-phase levels. The photochemistry and reactivity of this class of atmospheric species have not been studied.

1 Introduction

Recent studies have shown that organic peroxides can be a significant portion of secondary organic aerosol (SOA) (Bonn et al., 2004; Docherty et al., 2005; Kroll and Seinfeld, 2008). Besides their contribution to SOA, organic peroxides also damage plant leaves (Polle and Junkermann, 1994), contribute to acid precipitation by oxidizing SO$_2$ to H$_2$SO$_4$ in the aqueous phase (Lind et al., 1987), and regenerate OH radicals (Matthews et al., 2005; Monod et al., 2007; Roehl et al., 2007; Kamboures et al., 2010). $\alpha$-Hydroxyhydroperoxides ($\alpha$-HHPs) constitute a class of organic peroxide that has been observed in the ambient environment. In particular, hydroxymethyl hydroperoxide (HMP) is the most frequently detected $\alpha$-HHP in the ambient gas phase (He et al., 2010), rain water (Hellpointner and Gäch, 1989; Sauer et al., 1996), and cloud water (Sauer et al., 1996; Valverde-Canossa et al., 2005), as reviewed by Hewitt and Kock (1991) and Lee et al. (2000). Other $\alpha$-HHPs such as 1-hydroxyethyl hydroprooxide, 1-hydroxypropyl hydroperoxide, and bis-hydroxymethyl hydroperoxide have also been detected in the air or in cloud water, but much less frequently (He et al., 2010; Lee et al., 1998; Bachmann et al., 1992; Hewitt and Kock, 1991).

Despite their observation in the atmosphere, our understanding of the formation mechanisms of $\alpha$-HHP is still incomplete. It has been suggested that the recombination reaction of peroxy radical (RO$_2$) and hydroperoxy radical (HO$_2$), which is the major formation of organic hydroperoxides in gas phase, may not be a major formation pathway for $\alpha$-HHPs (Carter et al., 1979; Atkinson, 1990; Gäch et al., 1995). Instead, other formation pathways, including aqueous-phase reactions have been proposed (Fig. 1). The first formation
pathway, herein referred to as the Criegee pathway, involves hydrolysis of the stabilized Criegee intermediate (SCI) generated during alkene ozonolysis (Lee et al., 2000; Hasson et al., 2003; Ziemann and Atkinson, 2012). The second pathway involves reversible addition of H$_2$O$_2$ to carbonyls and is herein referred to as the carbonyl pathway (Hellpointner and Gäß, 1989; Zhou and Lee, 1992). The Criegee pathway has gained the majority of attention because α-HHPs have been observed from laboratory ozonolysis of a variety of alkenes and monoterpenes (Hewitt and Kok, 1991; Neeb et al., 1997; Sauer et al., 1999; Hasson et al., 2001; Hasson and Paulson, 2003; Wang et al., 2012). This reaction pathway occurs in both the gas and aqueous phases, but a few studies (Gäß et al., 1995; Chen et al., 2008; Wang et al., 2012) have shown that aqueous-phase ozonolysis may lead to more efficient formation of α-HHPs compared to their gas-phase counterparts. In these studies, however, α-HHPs formed in the aqueous phase dominantly decomposed to H$_2$O$_2$ and aldehydes when analysed under dilute conditions. The observed rapid decomposition of α-HHPs in such laboratory experiments has lead to a general perception that α-HHPs are unstable, and are merely a class of intermediates in the formation of carbonyls and H$_2$O$_2$ during ozonolysis.

However, recent studies have observed significant α-HHP formation upon the addition of H$_2$O$_2$ to aqueous solutions of dicarboxyls (Lee et al., 2011; Zhao et al., 2012) and laboratory SOA extract (Liu et al., 2012) using advanced mass spectrometric techniques. Specifically, in our previous work (Zhao et al., 2012), α-HHP formation from glyoxal and methylglyoxal with H$_2$O$_2$ was monitored using an iodide ($I^-$) chemical ionization mass spectrometer coupled to a heated inlet line (Aerosol CIMS). This technique enabled the direct detection and characterization of α-HHPs using online mass spectrometry. In particular, the formation of α-HHPs from glyoxal and methylglyoxal was observed to be fast and reversible, with equilibrium constants between 40 and 200 M$^{-1}$ for both compounds. As described below, an equilibrium constant of this magnitude suggests that α-HHPs could be formed in significant concentrations in aerosol liquid water (ALW) if aldehyde and H$_2$O$_2$ concentrations are high (Arellanes et al., 2006; Volkamer et al., 2009; Lim et al., 2010). However, the quantification using Aerosol CIMS is potentially complicated by thermodecomposition of α-HHPs and unknown processes involving droplet evaporation in the heated inlet, giving rise to the need for a more quantitative study using alternative techniques.

We note that although the carbonyl pathway is rarely discussed in the atmospheric chemistry literature, it has been studied somewhat in the 1940s and 1950s by physical organic chemists using high precursor concentrations. For example, the formation of α-HHPs has been observed from several aldehydes (Satterfield and Case, 1954; Sander and Jencks, 1968) and ketones (Milaš and Golubovic, 1959a, b). These early works established the reaction mechanism of the carbonyl pathway: the reaction proceeds via a nucleophilic addition of H$_2$O$_2$ to a non-hydrated carbonyl because the carbonyl carbon acts as an efficient electrophile. In particular, Satterfield and Case (1954) found that the initial rate of H$_2$O$_2$ addition to aldehydes increases in the following order: formaldehyde < acetaldehyde < propionaldehyde. The explanation for this observed trend is the difference in the aldehydes’ degree of hydration, with the most hydrated aldehyde (i.e. formaldehyde) exhibiting the slowest rate of H$_2$O$_2$ addition. This observation leads to their conclusion that H$_2$O$_2$ addition has to occur on non-hydrated aldehyde functional groups. We also note that a closely related particle-phase reaction, peroxyhemiacetal formation (Fig. 1, pathway 3), which involves nucleophilic addition of an organic hydroperoxide to an aldehyde, has been previously proposed (Tobias and Ziemann, 2000). As of late, small carbonyls have been gaining attention as potential SOA precursors via aqueous-phase processing (Ervens et al., 2011). The formation of α-HHP via the carbonyl pathway may change the physico-chemical properties of carbonyl-containing SOA in a different way compared to other relatively well known mechanisms such as OH radical oxidation, thus representing an additional mechanism of aqueous-phase processing. Once formed in aqueous-phase, α-HHPs may also react with OH radicals (Zhao et al., 2012). How this class of compound may alter the reaction mechanisms proposed for aqueous-phase chemistry is still unclear at the moment.

![Fig. 1. Two aqueous-phase pathways of α-hydroxyhydroperoxide (α-HHP) formation: (1) The Criegee pathway, (2) the carbonyl pathway, and a related reaction (3) peroxyhemiacetal formation.](image-url)
Given that the potential of many carbonyls to form \( \alpha \)-HHPs is currently unknown, the specific goals of this work were to experimentally determine the equilibrium constants of \( \alpha \)-HHP formation via the carbonyl pathway from a range of atmospherically relevant carbonyl compounds using two separate analytical methods: proton nuclear-magnetic-resonance (\( ^1 \text{H} \) NMR) spectroscopy and proton-transfer-reaction mass spectrometry (PTR-MS). \( ^1 \text{H} \) NMR spectroscopy directly quantifies the chemical changes in the aqueous phase when a carbonyl is mixed with \( \text{H}_2\text{O} \), and is particularly well suited for the investigation of thermodynamic equilibria. On the other hand, online PTR-MS measurement of the gas-phase concentration of carbonyls after addition of \( \text{H}_2\text{O}_2 \) provides better insight into the kinetics of the reactions and can assess the impact of \( \alpha \)-HHP formation on the effective Henry’s law constants (\( K_{\text{Hefl}} \)) of the carbonyls. We note that thermodynamic information of the type derived in this paper is required to quantify the importance of different derivative organics in aerosol and cloud water, and yet it is frequently missing from the literature. The paper concludes with an assessment of the atmospheric importance of \( \alpha \)-HHP formation by the carbonyl pathway.

2 Experimental

2.1 \( ^1 \text{H} \) NMR measurements

The formation of \( \alpha \)-HHPs from a suite of atmospherically relevant carbonyl species has been studied: formaldehyde (Sigma Aldrich, 37 wt % in water with 10–15% methanol as stabilizer), acetaldehyde (Sigma Aldrich, > 99.5 %), propionaldehyde (Sigma Aldrich, < 97 %), glyceraldehyde (Sigma Aldrich, in solid dimer form), glyoxal (Sigma Aldrich, 40 wt % in \( \text{H}_2\text{O} \)), methylglyoxal (Sigma Aldrich, 40 wt % in \( \text{H}_2\text{O} \)), glyoxylic acid (Sigma Aldrich, 50 wt % in \( \text{H}_2\text{O} \)), methacrolein (Sigma Aldrich, 95 %), methylethyl ketone (ACP Chemicals Inc., 99 %), and acetone (EMD, 99.8 %). These compounds have low molecular weights and exist largely in the gas phase. However, several compounds (e.g. glyoxal, methylglyoxal, glyoxylic acid, and glycolaldehyde) are quite water soluble and can be important aqueous-phase SOA precursors (Carlton et al., 2007; Altieri et al., 2008; Perri et al., 2009; Ervens and Volkamer, 2010; Lim et al., 2010; Tan et al., 2010; Ervens et al., 2011; Lee et al., 2011; Ortiz-Montalvo et al., 2012; Zhao et al., 2012).

Aqueous solutions (10 mM) of a targeted carbonyl were prepared individually from the commercial standards mentioned above. A known concentration (0.5 mM) of dimethylsulfoxide (DMSO, Fisher Scientific, 99.9 %) was added as an internal standard to assist the quantification and chemical shift calibration. A portion of commercial \( \text{H}_2\text{O}_2 \) stock solution (Sigma Aldrich, 30 % in water) was also added to the carbonyl solutions shortly after they were prepared at concentrations usually between 8.9 and 20 mM, but up to 100 mM for ketones and methacrolein due to insignificant \( \alpha \)-HHP formation from these species. A 500 \( \mu \)L aliquot of the mixed solution was transferred into a 500 \( \mu \)L glass NMR tube along with 25 \( \mu \)L of \( \text{D}_2\text{O} \) (Cambridge Isotope Laboratories, Inc., 99.96 %) as a lock reagent for the \( ^1 \text{H} \) NMR measurement. Using an autosampler (Bruker B-ACS 120), \( ^1 \text{H} \) NMR spectra were acquired with a Bruker Avance 500 MHz spectrometer using a \( ^1 \text{H}, ^{19}\text{F}, ^{13}\text{C}, ^{15}\text{N} \) 5 mm quadruple resonance inverse (QXI) probe fitted with an actively shielded Z gradient. \( ^1 \text{H} \) NMR experiments were performed with presaturation using relaxation gradients and echoes (PURGE) (Simpson and Brown, 2005) water suppression and 128 scans, a recycle delay of 3 s, and 16 K time domain points. Spectra were apodized through multiplication with an exponential decay corresponding to 0.3 Hz line broadening in the transformed spectrum and a zero filling factor of 2, then manually phased and calibrated to the DMSO at 2.5 ppm. The recycle delay was set at 5 times the measured T1 to ensure full relaxation between scans. Spectral predictions were performed in Advanced Chemistry Development’s ACD/SpecManager using a neural network prediction algorithm (version 12.5).

All calculations were performed using water as the solvent with a spectral line shape 2 Hz chosen to match those of the real datasets as closely as possible.

For most of the samples, the \( ^1 \text{H} \) NMR spectra were taken within 24 h after the samples were prepared, and within 48 h for a small number of samples. The time scale of \( \alpha \)-HHP equilibration is 30 to 60 min (confirmed in the PTR-MS experiments), so the equilibria should be fully established when \( ^1 \text{H} \) NMR spectra are taken. The sample solutions were no longer protected from room light once loaded onto the autosampler. To examine potential evaporation of carbonyls and OH generation from \( \text{H}_2\text{O}_2 \) photolysis, some methacrolein samples were analysed a second time 10 h after the first measurement. Methacrolein was chosen because it is the most volatile aldehyde studied here (Allen et al., 1998) and is highly reactive to OH radicals (Herrmann et al., 2010). The concentration of methacrolein did not show observable change before and after 10 h of room light exposure, and so it is assumed that evaporative loss and room-light exposure induced negligible effects to other samples as well.

The temperature inside the NMR instrument was controlled at 25 °C. A NMR tube typically stayed inside the instrument for 20 min for the homogenization of its magnetic field before the spectra were acquired. Water blanks and control experiments were performed to ensure that the peaks in the spectra are not from \( \text{H}_2\text{O}_2 \) reacting with water impurities or DMSO. The effect of pH was not examined. Previous studies reported that acid can catalyse the rate of \( \alpha \)-HHP formation and decomposition, but does not affect the equilibria (Marklund, 1971; Zhou and Lee, 1992).
2.2 Effects of inorganic salts

Aerosol liquid water (ALW) can contain high concentrations of inorganic salts up to and beyond their saturation concentrations (Tang et al., 1997), making it important to investigate the effect of high concentrations of aqueous-phase inorganic salts on the equilibria. To do this, 1 M of either (NH₄)₂SO₄ (AS) or Na₂SO₄ (SS) was added to a number of acetaldehyde and glycolaldehyde samples. The NMR probe used in the current method is not compatible with any higher salt concentrations. The salts were added after the α-HHP equilibrium had been fully established.

2.3 PTR-MS measurements

To confirm the equilibrium constants determined by ¹H NMR spectroscopy and further investigate the effects of these condensed-phase equilibria to the $K_{H_{eff}}$ of the carboxyls, a setup involving a bubbler and a PTR-MS (Ionicon Analytik, quadruple mass spectrometer) was used, as shown in Fig. 2. This system was used to measure the effect on a carbonyl vapour pressure arising from the addition of H₂O₂.

Ultra-pure N₂ (BOC Linde, grade 4.8) was introduced to a temperature-controlled glass bubbler containing an aqueous solution (10 mM) of a carbonyl compound. The gas-phase carbonyl loading exiting the bubbler was measured by the PTR-MS after dilution (2 to 3 lpm) with ultra-pure N₂. The bubbler was placed in the dark during experiments to minimize light exposure. Teflon lines and connections were used downstream of the bubbler to minimize surface reactions and loss of carbonyls. N₂ was continuously introduced through the carbonyl solution until a stable PTR-MS signal was achieved at the mass-to-charge ratio ($m/z$) of the protonated carbonyl. A known concentration of H₂O₂ (typically 8.9 to 17.7 mM) was then added to the bubbler, and the N₂ flow was resumed until the PTR-MS signal reached a new equilibrium. Equilibrium constants were determined from the difference of the carbonyl signals detected before and after the H₂O₂ injection. With the detection limit set by the PTR-MS, this approach could be used only for sufficiently volatile carbonyls: acetaldehyde, propionaldehyde, methacrolein, methylethyl ketone, and acetone. The experiments were typically performed at 25 °C except for those with acetaldehyde reaction giving rise to the formation of 1-hydroxyethyl hydroperoxide (1-HEHP), which were conducted also at 15 and 5 °C.

2.4 Reversibility test: addition of catalase

In both the NMR and PTR-MS experiments, catalase from bovine liver was added to the reaction mixture to react away H₂O₂ to test the reversibility of the reaction. In our previous study (Zhao et al., 2012), quenching of H₂O₂ led to the decomposition of α-HHPs and regeneration of the original aldehydes. For the ¹H NMR experiments, 1 µL of the catalase solution (Sigma Aldrich, 34 mg protein mL⁻¹) was added to 1 mL of the carbonyl-H₂O₂ reaction mixtures after the equilibrium was fully established. Control experiments were performed to confirm that there was no contribution of catalase to the ¹H NMR spectra. For the PTR-MS experiments, one drop of catalase was added to the 25 mL reaction mixture after the equilibrium was fully established. The N₂ flow was resumed after the catalase addition, and the change of the carbonyl signals was monitored. Control experiments demonstrated that catalase did not cause any change in the PTR-MS signal at the $m/z$ of interest.

3 Results and discussion

3.1 ¹H NMR results

With the exclusion of methacrolein, significant changes in the ¹H NMR spectra were observed for all the aldehydes upon addition of H₂O₂ to the carbonyl solution, with the magnitude of the change increasing with the concentration of H₂O₂. The reactions were also observed to be largely reversible from the catalase addition experiments. As described below, the formation of α-HHP from acetone and methylethyl ketone was observed to be minor. Spectral assignment was based on manual interpretation and comparison to standards, followed by confirmation using spectral prediction.

The experiment involving acetaldehyde is shown in Fig. 3 as an example. Before the addition of H₂O₂, acetaldehyde and its hydrated gem-diol coexist in the solution (Fig. 3a). Based on their chemical shift and splitting patterns, the identities of the peaks are assigned and labelled. After addition of 17.7 mM of H₂O₂ (Fig. 3b), two new peaks appeared at chemical shifts 5.06 and 1.06 ppm, respectively, corresponding to the V and VI protons in 1-HEHP. It is not surprising that the two new peaks appeared very close to the peaks of hydrated acetaldehyde (i.e. the III and IV protons), given the similar structure between hydrated acetaldehyde and 1-HEHP. The reversibility of the reaction was confirmed upon addition of catalase (Fig. 3c), with the spectra then resembling those at the start of the experiment.

The water peak was very large in each spectrum even with the water suppression procedures, such that some...
overlapping analyte peaks complicated their peak assignment and quantification. For peaks partially overlapping with water (e.g. at 5.04 ppm in Fig. 3), baseline corrections were performed before quantification. Also, we note that the gain of each NMR spectrum was auto-adjusted by the instrument so that the quantification of compounds had to be conducted by comparing the analytes’ peak area and number of protons (#H), with signals arising from 0.5 mM of DMSO added as the internal standard. The calculation was performed in the following manner (Wallace, 1984):

\[
\text{Concentration of analyte (M)} = \frac{\text{Concentration of internal standard (M)}}{\frac{\text{Peak area of analyte}}{\text{Peak area of internal standard}} \times \frac{\#H_{\text{internal standard}}}{\#H_{\text{analyte}}}}.
\]

Based on the quantified concentrations, we calculated three equilibrium constants: the hydration equilibrium constant \( K_{\text{hyd}} \), equilibrium constant for \( \alpha \)-HHP formation \( K_{\text{eq}} \), and the apparent equilibrium constant for \( \alpha \)-HHP formation \( K_{\text{app}} \). The relationship between the three constants is illustrated in Fig. 4, and their definitions are below:

\[
K_{\text{hyd}} = \frac{[\text{Carbonyl}_{\text{hydr}}]_{\text{eq}}}{[\text{Carbonyl}_{\text{non-hyd}}]_{\text{eq}}},
\]

\[
K_{\text{eq}} = \frac{[\alpha - \text{HHP}]_{\text{eq}}}{[\text{H}_2\text{O}_2]_{\text{eq}} \times [\text{Carbonyl}_{\text{non-hyd}}]_{\text{eq}}},
\]

\[
K_{\text{app}} = \frac{[\text{Total } \alpha - \text{HHP}]_{\text{eq}}}{[\text{H}_2\text{O}_2]_{\text{eq}} \times [\text{Total Carbonyl}]_{\text{eq}}},
\]

where \([\text{Carbonyl}_{\text{hydr}}]_{\text{eq}}\) and \([\text{Carbonyl}_{\text{non-hyd}}]_{\text{eq}}\) represent the equilibrium concentrations of the hydrated form and the non-hydrated form of a carbonyl, respectively. The hydration equilibria of many atmospherically relevant carbonyls are well studied, and thus comparing our results to the literature values is a good way to verify our \(^1\)H NMR method. In Eq. (3), \([\alpha - \text{HHP}]_{\text{eq}}\) and \([\text{H}_2\text{O}_2]_{\text{eq}}\) represent the equilibrium concentrations of an \( \alpha \)-HHP and \( \text{H}_2\text{O}_2 \). The usefulness of the \( K_{\text{eq}} \) defined this way is, however, limited especially for dicarbonyls such as methylglyoxal that can form multiple \( \alpha \)-HHP equilibria. Unambiguous determination of all the \( K_{\text{eq}} \) values is also impossible because some of the peaks are missing due to overlap with the water peak. \( K_{\text{app}} \), on the other hand, is a better indicator for the overall potential of \( \alpha \)-HHP formation from each carbonyl compound. The \([\text{Total } \alpha - \text{HHP}]_{\text{eq}}\) and \([\text{Total Carbonyl}]_{\text{eq}}\) in Eq. (4) represent the summed equilibrium concentrations of \( \alpha \)-HHPs and carbonyls (i.e. hydrated and non-hydrated forms), respectively. Given that the \( K_{\text{hyd}} \) values did not change with the \( \text{H}_2\text{O}_2 \) addition, \([\text{Total Carbonyl}]_{\text{eq}}\) can be estimated from determination of the concentration of either the hydrated or non-hydrated form of the carbonyl. Thus the use of \( K_{\text{app}} \) negates the need for unambiguous assignment of all the peaks. We also note that Eqs. (2) to (4) indicate that \( K_{\text{app}} \) and \( K_{\text{eq}}/K_{\text{hyd}} \) should be essentially equal if the aldehydes exist mostly in the hydrated form. We have used this relationship as an independent confirmation of our measurement reliability (see Sect. 3.3). The measured \( K_{\text{hyd}} \) and \( K_{\text{app}} \) values of the carbonyls using \(^1\)H NMR are
Table 1. Summary of hydration equilibrium constants ($K_{\text{hyd}}$) measured by NMR. The constants are reported with their standard deviation arising from the number of replicates indicated in the table.

<table>
<thead>
<tr>
<th>NMR (this work)</th>
<th>Literature$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{hyd}}$</td>
<td>$K_{\text{hyd}}$</td>
</tr>
<tr>
<td># Replicates</td>
<td># Replicates</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>&gt;18$^b$</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>1.43 ± 0.04</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>1.26 ± 0.13</td>
</tr>
<tr>
<td>Methacrolein</td>
<td>5 x 10$^{-3}$$^b$</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>n.d.$^d$</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>&gt;57±155$^b$</td>
</tr>
<tr>
<td>Glyoxylic acid</td>
<td>&gt;18$^b$</td>
</tr>
<tr>
<td>Acetone</td>
<td>2 x 10$^{-2}$$^b$</td>
</tr>
<tr>
<td>Methylene ketone</td>
<td>5 x 10$^{-3}$$^b$</td>
</tr>
</tbody>
</table>


$^b$ Calculated using the limit of quantification of the current methods.

Table 2. Summary of the apparent equilibrium constants of $\alpha$-HHP formation ($K_{\text{app}}$) measured and reported in literature at 25°C. The constants are reported with their standard deviation acquired from the number of replicates shown on the table.

<table>
<thead>
<tr>
<th>NMR Measurement</th>
<th>PTR-MS Measurement</th>
<th>Literature$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{app}}$ (M$^{-1}$)</td>
<td># Replicates</td>
<td>Catalase recovery (%)</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>94.8 ± 12.5</td>
<td>11</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>51.1 ± 8.0</td>
<td>12</td>
</tr>
<tr>
<td>Glycolaldehyde</td>
<td>43.3 ± 3.9</td>
<td>12</td>
</tr>
<tr>
<td>Methacrolein</td>
<td>0.8 ± 0.7</td>
<td>12</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>p.o.</td>
<td>12</td>
</tr>
<tr>
<td>Acetone</td>
<td>8 x 10$^{-3}$$^h$</td>
<td>2</td>
</tr>
<tr>
<td>Methylene ketone</td>
<td>2 x 10$^{-2}$$^h$</td>
<td>6</td>
</tr>
</tbody>
</table>


$^b$ Including the formation of BHMP (see text).

$^c$ p.o.: Values could not be determined due to peaks overlapping with the H$_2$O peak.

$^d$ n.p.: Experiment not performed.

$^e$ n.d.: Not detected at the current detection limit of PTR-MS.

$^f$ A significant amount of formic acid was observed. The $K_{\text{app}}$ value is determined with the consideration of irreversible formic acid formation.

$^g$ A decreasing trend of the recovery with increasing concentration of H$_2$O$_2$ addition.

$^h$ Calculated using the limit of quantification of the current methods.

Table 1 and Table 2, respectively, along with values from the literature. The determined $K_{eq}$ values are reported in Table S1 in the Supplement.

3.2 PTR-MS results

Acetaldehyde, propionaldehyde, methacrolein, acetone, and methylethyl ketone were detected in their protonated form at $m/z$ 45, 59, 71, 59, and 73, respectively. Besides their protonated molecular ions, three other major fragment ions at $m/z$ 31, 39, and 49 were detected from propionaldehyde, and one major fragment ion at $m/z$ 55 was detected from methylethyl ketone. For these two carbonyls, the total signal intensity of the protonated molecular ion and the major fragments were used for quantification. No $\alpha$-HHP signal was detected using the current PTR-MS method.

Figure 5 illustrates data from a sample experiment for acetaldehyde at 25°C. Acetaldehyde signal normalized to the H$_3$O$^+$ reagent ion became stable 20 min after a 10 mM solution was placed in the bubbler at time (i). After 17.7 mM of
H$_2$O$_2$ was injected into the solution at time (ii), the acetaldehyde signal decreased and rapidly reached a new equilibrium due to the formation of 1-HEHP in the solution. Upon addition of catalase at time (iii), the acetaldehyde signal recovered close to its original level. A similar trend was observed for propionaldehyde, but methacrolein, acetone, and methylethyl ketone did not show any observable change upon H$_2$O$_2$ addition.

The equilibrium constants of $\alpha$-HHP formation from acetaldehyde and propionaldehyde were calculated from the difference in their signals before and after H$_2$O$_2$ addition (Table 2). The high recovery illustrates that the reaction is mostly reversible due to $\alpha$-HHP formation. The volatilization loss of acetaldehyde and propionaldehyde from pure solutions at 25°C over two hours of bubbling could be up to 11 and 14%, based on the flow rate of N$_2$ through the bubbler, the solution volume, concentration, and the Henry’s law constants ($K_H$) of the two aldehydes.

### 3.3 Comparison of equilibrium constants

In general, the $K_{\text{hyd}}$ values showed good agreement with values from the literature (Table 1), and the $K_{\text{app}}$ values determined from the two methods reasonably agreed with each other and with the literature (Table 2). The agreement between $K_{\text{app}}$ and $K_{\text{eq}}/K_{\text{hyd}}$ was good (Table S1) for acetaldehyde, propionaldehyde, and glycolaldehyde, but the values of formaldehyde showed a deviation of more than a factor of 4 (see discussion for formaldehyde below). The inability of methacrolein, acetone, and methylethyl ketone to form $\alpha$-HHP was confirmed from both methods. Formic acid formation was observed upon H$_2$O$_2$ addition to methylglyoxal and glyoxylic acid. Detailed discussion of results for each compound is provided below, and an example $^1$H NMR spectra for each compound is provided in the Supplement.

#### 3.3.1 Formaldehyde

The equilibrium concentration of formaldehyde was calculated by subtracting the amount of hydroxymethyl hydroperoxide (HMP) observed (Fig. 6, proton III) from the total concentration of 10 mM. In particular, the $K_{\text{hyd}}$ of formaldehyde is so large that the aldehydic proton peak (proton I) was below the $^1$H NMR detection limit, which is determined to be approximately 100 μM. This observation is supported by the large $K_{\text{hyd}}$ value in the literature: 2.3 × 10$^3$ (Betterton and Hoffmann, 1988). The methylene proton peak (II) was also not observed in the $^1$H NMR spectra likely due to overlap with the water peak.

We propose that the small peak that appeared at 4.94 ppm is due to formation of bis-hydroxymethyl hydroperoxide (BHMP, proton IV). This peroxymethacetal compound forms by HMP further reacting with non-hydrated formaldehyde. BHMP has been observed in a number of laboratory studies (Marklund, 1971; Zhou and Lee, 1992; Gäß et al., 1995) and in the atmosphere (He et al., 2010). The $K_{\text{app}}$ for BHMP formation ($K_{\text{app,BHMP}}$) is calculated by Eq. (5),

$$K_{\text{app,BHMP}} = \frac{[\text{BHMP}]_{\text{eq}}}{[\text{HMP}]_{\text{eq}} \times [\text{Total Carbonyl}]_{\text{eq}}} \times 10^4,$$

where the uncertainties are precisions derived from a number of replicates, showing excellent agreement with two reported values: 11.7 M$^{-1}$ from Zhou and Lee (1992) and 14.0 M$^{-1}$ from Marklund (1971). The overall $K_{\text{app}}$ value for formaldehyde is determined to be 164 ± 31 M$^{-1}$. This value is slightly larger than the three
literature values reported because those values are for only HMP formation, while the value in this work incorporates BHMP formation.

The deviation between $K_{\text{app}}$ and $K_{\text{eq}}/K_{\text{hyd}}$ was larger compared to acetaldehyde, propionaldehyde, and glycolaldehyde (Table S1). We are not entirely sure about the reason for this deviation, but it could be due to the fact that we used a $K_{\text{hyd}}$ value from the literature not measured in our own system, and/or that formaldehyde forms BHMP beside HMP and exhibits a more complicated reaction pathway.

### 3.3.2 Acetaldehyde

The $K_{\text{hyd}}$ value, $1.43 \pm 0.04$, agrees very well with the reported value (Greenzaid et al., 1967). Our measured value of $K_{\text{app}}$, $94.8 \pm 12.5 \text{ M}^{-1}$, is larger than the only literature value by a factor of 2 (Kooijman and Ghijsen 1947). The results from the PTR-MS, $132 \pm 15 \text{ M}^{-1}$, showed reasonable agreement with the $^1\text{H}$ NMR results.

### 3.3.3 Propionaldehyde

The experimental $K_{\text{hyd}}$ value, $1.26 \pm 0.13$, was slightly larger than the reported value 0.7 (Greenzaid et al., 1967). The agreement between the $^1\text{H}$ NMR and the PTR-MS measurements was fair, with the $K_{\text{app}}$ value determined to be $51.1 \pm 8.0$ and $84 \pm 12 \text{ M}^{-1}$, respectively. The catalase recovery was $83 \pm 3$ and $85 \%$, respectively.

### 3.3.4 Glycolaldehyde

Glycolaldehyde solutions were prepared by dissolving glycolaldehyde dimer (2,5-dihydroxy-1,4-dioxane) in water. The major peaks in the $^1\text{H}$ NMR spectra were from glycolaldehyde monomers, indicating that monomerization proceeds almost to completion in the solution at the current concentration used (Yaylayan et al., 1998; Glushonok et al., 2000). The observed $K_{\text{hyd}}$ value, $16.0 \pm 1.3$, fell into the same range as several other reported $K_{\text{hyd}}$ values (Sorensen, 1972; Yaylayan et al., 1998). There are no prior reports of the equilibrium constant of $\alpha$-HHP formation.

### 3.3.5 Methacrolein

Among the carbonyl compounds studied, methacrolein was the only aldehyde that did not show significant $\alpha$-HHP formation, as confirmed by both the $^1\text{H}$ NMR and PTR-MS studies. The $K_{\text{app}}$ was determined to be $0.8 \pm 0.7 \text{ M}^{-1}$ from the $^1\text{H}$ NMR, but no observable $\alpha$-HHP formation was observed using PTR-MS. We propose that the carbonyl group and the C=C double bond in methacrolein form $\pi$-electron conjugation which stabilizes the aldehyde from nucleophilic attacks. Although Claeys et al. (2004) proposed a mechanism of polyol formation from methacrolein and H$_2$O$_2$ in the particle phase (Claeys et al., 2004), no such products were observed in the current experiment.

### 3.3.6 Glyoxal

No quantitative data for glyoxal could be acquired from the current study. In particular, the PTR-MS is not highly sensitive to glyoxal, and most of the glyoxal peaks in the $^1\text{H}$ NMR spectra were hidden behind the water peak. The only literature value for $K_{\text{app}}$ of glyoxal is from our previous work (Zhao et al., 2012), where we estimated the lower limit of $K_{\text{app}}$ to be $40 \text{ M}^{-1}$ using an Aerosol CIMS.

### 3.3.7 Methylglyoxal

Hydration and $\alpha$-HHP formation occurring on one or both of the carbonyl groups in methylglyoxal would lead to a slightly different chemical environments for the protons, making the $^1\text{H}$ NMR spectra of methylglyoxal highly complicated. We performed peak assignment based on the predicted chemical shift of each proton by spectra prediction and on changes in the peak intensity upon H$_2$O$_2$/catalase additions, but the peak assignment for methylglyoxal is associated with a higher level of uncertainty than with the other molecules. A non-negligible amount of formic acid formation was also observed with H$_2$O$_2$ addition (8.2 ppm, Fig. S2). Formic acid likely forms irreversibly, as shown by a decreasing trend in catalase recovery, 91, 87, and 84 %, with increasing amount of H$_2$O$_2$ addition: 10, 15, and 20 mM. We assumed that formic acid formation was slow compared to the $\alpha$-HHP formation equilibrium, such that $K_{\text{app}}$ can still be
calculated from the amount of $\alpha$-HHP formed and methylglyoxal remaining. This way, the $K_{app}$ value is determined to be $25 \pm 4 \text{M}^{-1}$. This value falls below the range of our previous estimation: $40–200 \text{M}^{-1}$ (Zhao et al., 2012). The discrepancy between the two studies may be explained either by the uncertainties associated with the Aerosol CIMS method (see Introduction), or by the methylglyoxal peak assignment here.

### 3.3.8 Glyoxylic acid

The $^1$H NMR spectra of glyoxylic acid solutions indicates that it exists mostly in its hydrated form, qualitatively agreeing with its large reported $K_{hyd}$ value ($3 \times 10^3$, Sorensen et al., 1974). Upon $\text{H}_2\text{O}_2$ addition, a significant amount of formic acid formation (8.1 ppm, Fig. S5) – up to 50% of the total glyoxylic acid – was observed. Irreversible formic acid formation from glyoxylic acid and $\text{H}_2\text{O}_2$ in the aqueous phase is well documented (Tan et al., 2009; Lee et al., 2011; Ortiz-Montalvo et al., 2012). We propose that at least some of the glyoxylic acid exists in its $\alpha$-HHP form because the decay of glyoxylic acid was larger than the amount of formic acid formation, and some of glyoxylic acid was regenerated with catalase addition. However, a reliable quantification of the $K_{app}$ value is highly challenging, as reflected by the large uncertainties in the reported value ($440 \pm 270 \text{M}^{-1}$).

### 3.3.9 Acetone and methylethyl ketone

The two ketones studied did not exhibit significant $\alpha$-HHP formation in either the $^1$H NMR or the PTR-MS experiments. In general, ketones are known to be relatively stable against nucleophilic addition as compared to aldehydes. This is because the additional alkyl group stabilizes the carbonyl functional group via electron donation. Such a trend can be also seen from the small $K_{hyd}$ reported for ketones (e.g. 0.002 for acetone, Bruice, 2004). The unstable nature of $\alpha$-HHPs from ketones has also been reported previously (Sauer et al., 1999; Wang et al., 2012). However, we note that these simple ketones do not fully represent the diversity of ketones in SOA. In fact, the current work and past studies have implied ketones do not fully represent the diversity of ketones in SOA.

### 3.4 Temperature dependence of $K_{app}$

We observed enhanced 1-HEHP formation from acetaldehyde with decreasing temperature, but with slower reaction rates. Example data are shown in Fig. 7a. The ratio of acetaldehyde signal to its initial level at 5, 15, and 25 $^\circ\text{C}$ is plotted as a function of time. The injection of $\text{H}_2\text{O}_2$ (13.3 mM) was performed at time (i). The time required for equilibration was approximately 1, 2, and 5 h at the three temperatures. The signal level at equilibrium, determined by fitting an exponential function to the signal, decreases with decreasing temperature, as indicated by the horizontal dashed lines in Fig. 7a. The temperature dependence observed here implies more significant $\alpha$-HHP formation at colder temperatures. The $K_{app}$ values determined at the three temperatures are listed in Table 3. From a van ’t Hoff plot of these data (Fig. 7b), a positive slope was observed corresponding to a standard enthalpy change ($\Delta^{\text{f}}H$) of $-29.7 \pm 1.3 \text{kJ mol}^{-1}$.

Since the equilibrium is reached slowly in the 15 and 5 $^\circ\text{C}$ experiments, we can estimate the rate coefficient of 1-HEHP formation by fitting an exponential curve to the decaying acetaldehyde signal and obtaining its slope at early reaction times where there is no reverse reaction occurring and the initial concentrations of acetaldehyde and $\text{H}_2\text{O}_2$ are known. Using this method, the second-order rate constants of 1-HEHP formation were determined to be $0.012 \pm 0.002$ and $0.0045 \pm 0.0005 \text{M}^{-1} \text{s}^{-1}$, respectively. The kinetics at 25 $^\circ\text{C}$ were too fast to be estimated. We note that the pH of the solution is not controlled in our experiment. Even though the equilibrium is independent of the solution pH, both the formation and decomposition rates of $\alpha$-HHP have been reported to be pH dependent (Zhou and Lee, 1992).
3.5 Effects of inorganic salt addition

The results of the inorganic salt addition experiments are summarized in Table 4. We observed that the addition of AS and SS caused a small increase in $K_{\text{hyd}}$ and a small decrease in $K_{\text{app}}$ for both acetaldehyde and glycolaldehyde. To assess whether the differences are statistically significant, one-tail $t$ tests were performed to make comparisons between the average $K_{\text{hyd}}$ and $K_{\text{app}}$ values with and without salt addition, and the $p$ values from the $t$ tests are listed in Table 4. $p$ values that are statistically significant at the 95% confidence level (i.e. $p < 0.05$) are indicated with an * label in Table 4. All the equilibrium constants for glyoxaldehyde and the $K_{\text{hyd}}$ of acetaldehyde with AS addition have been determined to be statistically significant, whereas the other three values point in the same direction but with less statistical significance.

These observations qualitatively agree with Yu et al. (2011), who observed that addition of SS shifted the hydration equilibrium of glyoxal to the dihydrated form of the monomer. The enhancement of $K_{\text{hyd}}$ and the suppression of $K_{\text{app}}$ by SS and AS observed in the current study is likely arising from similar effects at the molecular level, especially those associated with $SO_2^-$. The current observation implies that the inorganic effects may affect aqueous-phase equilibria of aldehydes in general. Yu et al. (2011) suggested that this effect might be more pronounced for aldehydic functional groups adjacent to an electron-withdrawing group (e.g. glyoxal). Glycolaldehyde has an additional electron-withdrawing hydroxyl group compared to acetaldehyde, which may explain why the inorganic salt effect appears to be larger for glycolaldehyde.

4 Atmospheric implications

With the first thorough assessment of the equilibrium constants for $\alpha$-HHP formation, we can make initial assessments for the likely atmospheric significance for these compounds.

4.1 Equilibrium concentrations of $\alpha$-HHPs in cloud water and aerosol liquid water

The amount of $\alpha$-HHP formation via the carbonyl pathway in atmospheric aqueous phases is directly dependent on the abundance of the different reactants. Cloud/fog water and ALW are commonly considered as two qualitatively different reaction media (Volkamer et al., 2009; Ervens and Volkamer, 2010; Lim et al., 2010) due to orders of magnitude differences in their liquid water content (LWC), surface-to-volume ratio, and aqueous-phase reactant concentrations. The aldehyde species studied here span a wide range of water solubility. Specifically, the aqueous-phase concentrations of volatile species such as acetaldehyde, propionaldehyde, and methacrolein, whose $K_H$ values are typically below $20 \text{M atm}^{-1}$ (Zhou and Mopper, 1990; Allen et al., 1998), are expected to be low. However, aqueous-phase concentrations of highly water-soluble aldehydes, such as glycolaldehyde, methylglyoxal, and glyoxal can be substantial. In particular, the concentration of glyoxal can be up to hundreds of $\mu$M in polluted fog water (Carlton et al., 2007; Tan et al., 2009) and has been proposed to be present up to the molar level in ALW (Volkamer et al., 2009). Furthermore, there are also studies suggesting that $H_2O_2$ concentration in ALW can also be unexpectedly high. Based on filter extracts of ambient aerosol and model calculations, Arellanes et al. (2006) suspected that $H_2O_2$ concentration in ALW might be up to $100 \text{mM}$, although there is some possibility that the $H_2O_2$ that is detected has arisen from decomposition from other species or been formed post collection in such off-line analyses. The concentration of $H_2O_2$ in cloud water usually does not exceed $100 \mu$M (Sakugawa et al., 1990).

Assuming an average $K_{\text{app}}$ of $100 \text{M}^{-1}$, which is approximately the middle point of the measured $K_{\text{app}}$ values from the current study, we calculated the concentrations of $\alpha$-HHPs that would be present with various equilibrium concentrations of $H_2O_2$ and total aldehyde (Fig. 8). Note that the effect of inorganic salts is not considered in this calculation but our studies suggest that these effects are likely to be minor relative to the uncertainties in the assumed reactant concentrations. The simulation indicates that $\alpha$-HHP formation in cloud water is unlikely to be significant, with its concentration not exceeding $10 \mu$M even with the highest combination of reactant concentrations. In ALW, however, $\alpha$-HHP concentrations may be comparable to that of $H_2O_2$. When the equilibrium concentrations of $H_2O_2$ and aldehydes reach $10 \text{mM}$ and $100 \text{mM}$, their respective upper limits in ALW, $100 \text{mM}$ of $\alpha$-HHPs may be formed.

4.2 Impact of $\alpha$-HHP formation on the atmospheric partitioning of aldehydes and $H_2O_2$

The water solubility of $\alpha$-HHP can be very high. The $K_H$ has only been reported for one $\alpha$-HHP, i.e. that from formaldehyde (HMP): $5 \times 10^5 \text{M atm}^{-1}$ (Zhou and Lee, 1992) and $1.67 \times 10^6 \text{M atm}^{-1}$ (O’Sullivan et al., 1996). These values are two orders of magnitude larger than that of formaldehyde and one order of magnitude larger than that of $H_2O_2$. This implies that the formation of $\alpha$-HHP in the aqueous phase will enhance the $K_{\text{Heff}}$ of aldehydes and/or $H_2O_2$.
Table 4. Effects of inorganic salt addition on the hydration equilibrium constant ($K_{\text{hyd}}$) and the apparent $\alpha$-HHP formation equilibrium constant ($K_{\text{app}}$).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Acetaldehyde</th>
<th>Glycolaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{\text{hyd}}$ and $K_{\text{app}}$ (M$^{-1}$)</td>
<td># Replicates</td>
</tr>
<tr>
<td>No Salt</td>
<td>1.43 ± 0.04</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>94.8 ± 12.5</td>
<td>11</td>
</tr>
<tr>
<td>1 M (NH$_4$)$_2$SO$_4$</td>
<td>1.48 ± 0.07</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>81.3 ± 12.7</td>
<td>3</td>
</tr>
<tr>
<td>1 M Na$_2$SO$_4$</td>
<td>1.58 ± 0.04</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>82.3 ± 10.0</td>
<td>3</td>
</tr>
</tbody>
</table>

* Statistically significant at the 95% confidence level ($p$ value <0.05).

Fig. 8. Simulation of the equilibrium concentration of $\alpha$-hydroxyhydroperoxide ([H$_2$O$_2$,aq]) arising from various equilibrium concentrations of H$_2$O$_2$ ([H$_2$O$_2$,aq]) and total aldehyde ([Total Aldehyde],aq). The concentrations are all presented in log scale. Conditions relevant to cloud water and aerosol water are also indicated. This simulation considers $\alpha$-HHP formation via only the carbonyl pathway, with an average equilibrium constant of 100 M$^{-1}$.

$$K_{\text{eff,Ald}} = K_{H, Ald}(1 + K_{\text{app}}[\text{H}_2\text{O}_2,\text{aq}])$$ (6)

$$K_{\text{eff,H}_2\text{O}_2} = K_{H, H_2O_2}(1 + K_{\text{app}}[\text{Total Aldehyde}],\text{aq}).$$ (7)

Note that the $K_H$ values for aldehydes are the effective Henry’s law constant of these aldehydes over pure water (i.e. they incorporate the hydration reaction of these aldehydes in water). The $K_{\text{eff}}$ and $K_H$ values used here should be considered as Henry’s law constants with and without $\alpha$-HHP formation, respectively. As shown in Eqs. (6) and (7), the enhancement of $K_{\text{eff}}$ compared to $K_H$ depends on the value of $K_{\text{app}}$ and the amount of H$_2$O$_2$ or total aldehyde existing in the aqueous phase.

We simulated the partitioning of an initial mixing ratio of 1 ppb gas-phase aldehyde or H$_2$O$_2$ that is exposed to typical cloud water or ALW conditions, both with and without $\alpha$-HHP formation (see Table 5). In particular, in the case of the aldehydes, we assume a fixed concentration of H$_2$O$_2$ in solution (as specified in Table 5), and in the case of H$_2$O$_2$, we assume a fixed concentration of dissolved total aldehydic functional group. The LWC is orders of magnitude higher in the cloud water scenario than with ALW, i.e. 1 g m$^{-3}$ vs. 1 µg m$^{-3}$. By contrast, the equilibrium concentrations of total aldehyde and H$_2$O$_2$ are assumed to be much higher in the ALW case. The purpose of this simple simulation is to assess how the enhancement of $K_{\text{eff}}$ arising from $\alpha$-HHP formation leads to an associated alteration in the gas-aqueous phase partitioning of H$_2$O$_2$ and aldehydes based only on the thermodynamic equilibria of Henry’s law partitioning and $\alpha$-HHP formation. Kinetic issues, such as formation rate constants and mass transfer rates, are not addressed, and we assume the HHPs are involatile. We again

Table 5. Conditions assumed in the atmospheric partitioning simulation of 1 ppb of aldehydes or H$_2$O$_2$.

<table>
<thead>
<tr>
<th></th>
<th>Cloud water</th>
<th>Aerosol liquid water (ALW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>25°C</td>
<td>25°C</td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>1 atm</td>
<td>1 atm</td>
</tr>
<tr>
<td>Liquid water content</td>
<td>1 g m$^{-3}$</td>
<td>1 µg m$^{-3}$</td>
</tr>
<tr>
<td>Aqueous-phase H$_2$O$_2$</td>
<td>100 µM</td>
<td>10 mM</td>
</tr>
<tr>
<td>Aqueous-phase total aldehyde</td>
<td>100 µM</td>
<td>100 mM</td>
</tr>
</tbody>
</table>

Table 6. Results of the atmospheric partitioning simulation.

<table>
<thead>
<tr>
<th></th>
<th>Formaldehyde</th>
<th>Acetaldehyde</th>
<th>H2O2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cloud water</td>
<td>ALW</td>
<td></td>
</tr>
<tr>
<td>Without α-HHP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>formation</td>
<td>$K_H$ (M atm$^{-1}$)</td>
<td>$3.0 \times 10^3$</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Gas-phase mixing ratio (ppb)</td>
<td>0.932</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>Fraction in aqueous phase</td>
<td>$0.068$</td>
<td>$7.33 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$K_{app}$ (M$^{-1}$)</td>
<td>$164$</td>
<td>$113^b$</td>
</tr>
<tr>
<td>With α-HHP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>formation</td>
<td>$K_{Heff}$ (M atm$^{-1}$)</td>
<td>$3.05 \times 10^3$</td>
<td>$7.92 \times 10^3$</td>
</tr>
<tr>
<td></td>
<td>Gas-phase mixing ratio (ppb)</td>
<td>0.931</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>Fraction in aqueous phase</td>
<td>$6.93 \times 10^{-2}$</td>
<td>$1.94 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Aqueous-phase total α-HHP (M)</td>
<td>$4.27 \times 10^{-8}$</td>
<td>$4.92 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

$^a$ $K_H$ values for formaldehyde and acetaldehyde represent their effective Henry’s law constants in pure water, not having been affected by α-HHP formation. References: formaldehyde (Betterton and Hoffmann, 1988); acetaldehyde (Zhou and Mopper, 1990); H2O2 (Martin and Damschen, 1981).

$^b$ Value taken from the current work as the average of the NMR results and the PTR-MS results.

$^c$ Value assumed as the average $K_{app}$ for α-HHP from all the aldehyde species.

stress that the chemical concentrations in ALW are highly uncertain. The assumed concentrations here (i.e. 10 mM for H2O2 and 100 mM for total aldehyde) can be considered as their respective upper limits, and these calculations should be viewed as a simple modelling exercise to highlight potential atmospheric importance only. The simulation was performed for formaldehyde, acetaldehyde and H2O2, and the results are shown in Table 6.

Without α-HHP formation, the majority of formaldehyde and acetaldehyde exists in the gas phase under both scenarios, leaving their gas-phase mixing ratio essentially unaffected at 1 ppb. More than half of the H2O2 population will dissolve into the aqueous phase under the cloud water scenario due to its relatively high $K_H$, but the majority stays in the gas phase under the ALW scenario due to the small LWC. The measured $K_{app}$ values for formaldehyde and acetaldehyde from the current work are used for the simulation of α-HHP formation. For the case of H2O2 simulation, an average $K_{app}$ of 100 M$^{-1}$ was assumed.

The first conclusion from the simulation is that, in the ALW scenario, $K_{Heff}$ values of H2O2 are enhanced by up to an order of magnitude relative to the $K_H$ values when α-HHP formation occurs, while the enhancement in the cloud water scenario was minor. However, even with such large enhancement in the $K_{Heff}$ values, the gas-phase mixing ratio of aldehydes and H2O2 are essentially unchanged from the case without α-HHP formation because of the low LWC. The $K_{Heff}$ values for formaldehyde and acetaldehyde were also enhanced by over a factor of two in ALW when α-HHP formation occurs.

The second conclusion arises from the resulting α-HHP concentration in the aqueous phase. Particularly in the H2O2 simulation, by assuming a total aldehyde concentration of 100 mM at equilibrium in the ALW scenario, approximately 0.7 mM of α-HHP forms in ALW. We raise the possibility that this high concentration of α-HHP may partially explain the surprisingly high concentrations of H2O2 previously observed from ambient aerosol (Hasson et al., 2003; Arellanes et al., 2006). As suggested by these researchers, because of the dilution associated with ambient aerosol extraction, α-HHPs should completely decompose to H2O2 upon analysis, contributing to its high concentrations observed from the extract. Indeed, for this simulation, the concentration of the α-HHP present in solution is roughly an order of magnitude larger than the concentration of H2O2 in solution. The α-HHP concentrations in the formaldehyde and acetaldehyde simulations were all enhanced, but not nearly as much as the H2O2 simulation case.
Of course, these assumptions are highly dependent on the assumed concentration of aldehydic functional groups in ALW, and that they all participate in α-HHP formation with the assumed $K_{\text{app}}$. The degree to which such groups are present in ALW is poorly characterized; however it would be expected that fresh SOA, for example that formed by ozonolysis, will have these species present.

### 4.3 Other atmospheric implications

As mentioned previously, α-HHP can also form via the hydrolysis of SCI, i.e. the Criegee pathway. If this reaction occurs in cloud water, the resultant α-HHP would most likely decompose to H$_2$O$_2$ and a corresponding carbonyl compound. However, if a hydrolysis reaction of SCI occurs in ALW, which is generally more concentrated than cloud water, the resulting α-HHP may not fully decompose given the α-HHP equilibria studied in the current work. If the α-HHP does decompose, the H$_2$O$_2$ generated from the decomposition of α-HHP may meet another aldehydic species with higher concentration (e.g. glyoxal) to form a different α-HHP.

As α-HHP concentration builds up in ALW, α-HHP themselves can act as nucleophiles and form peroxyhemiacetals by reacting with aldehydic functional groups (see pathway 3 in Fig. 1), as in the case of BHMP formation from HMP and formaldehyde (Sect. 3.3.1). This reaction of α-HHP is a specific mechanism of peroxyhemiacetal formation initially proposed by Ziemann and co-workers (Tobias and Ziemann, 2000; Docherty et al., 2005) and later confirmed by several recent laboratory studies (Hall and Johnston, 2012; Yee et al., 2012). The current study is an indication that H$_2$O$_2$ can undergo the analogous reaction.

Formation of such hydroxyl and hydroperoxyl functional groups reduces the vapour pressure of an organic compound substantially (Kroll and Seinfeld, 2008) and increases its solubility. It is possible that peroxyhemiacetals and α-HHPs can stay in the particle phase even after water evaporation and can thus be a pathway by which relatively volatile aldehydes are involved in SOA formation. Recently, Liu et al. (2012) observed that addition of H$_2$O$_2$ to the water extract of isoprene SOA caused significant increases in its degree of oxygenation and enhancement of its hygroscopicity. It is likely that the α-HHP and peroxyhemiacetals contributed to such physico-chemical changes of the SOA water extract. In fact, decay of carbonyls and significant formation of 1-HEHP were observed in their study.

The α-HHPs may also be photolysed by actinic radiation, leading to the cleavage of the peroxide (O–O) bond and the regeneration of an OH radical (Monod et al., 2007; Roehl et al., 2007; Kamboures et al., 2010). It needs to be determined whether this process occurs more readily with α-HHPs or with their precursor, H$_2$O$_2$. As well, the reactivity of α-HHPs with the OH radical is likely to be high. Our previous study (Zhao et al., 2012) suggested that a major fraction of formic acid observed during glyoxal photooxidation proceeded via an α-HHP intermediate.

Finally, we note that α-HHPs will likely decompose if aerosol is exposed to the fluid lining the lung, providing a source of reactive oxygen species such as H$_2$O$_2$ to the body. In particular, Hasson and Paulson (2003) indicate that the minimum H$_2$O$_2$ concentration to cause damage to alveolar cell is likely to be at the order of 0.1 to 1 mM in ALW. Our simulations above suggest that the α-HHP concentration have the potential to be at or above this minimum level.

### 5 Conclusions

We have investigated the thermodynamics of aqueous-phase formation of α-hydroxyhydroperoxides (α-HHP) arising from H$_2$O$_2$ reacting with a suite of atmospherically relevant carbonyl compounds. We find that formation of α-HHP was significant from many small, atmospherically relevant aldehydes, but not from methacrolein and ketones. We have also performed preliminary simulations to demonstrate that α-HHP formation will likely be of minor importance in cloud water but is more likely to be of importance in aerosol liquid water (ALW) where the concentrations of H$_2$O$_2$ and aldehydes are higher. In ALW, α-HHP may significantly enhance the effective Henry’s Law constants of aldehydes and H$_2$O$_2$, leading to significant concentrations of α-HHP in solution but probably not affecting the gas-phase levels of these chemicals. The influence of α-HHP formation at lower temperatures, however, may be more significant due to the enhancement of their formation equilibrium constants. We have also found that α-HHPs can further act as nucleophiles to form peroxyhemiacetals. In general, this chemistry is likely to lead to higher concentrations of organic peroxides than expected in ALW. The fate of this class of compounds and their influence in aqueous-phase reaction mechanisms should be further investigated.

Supplementary material related to this article is available online at: [http://www.atmos-chem-phys.net/13/5857/2013/acp-13-5857-2013-supplement.pdf](http://www.atmos-chem-phys.net/13/5857/2013/acp-13-5857-2013-supplement.pdf).

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