The authors thank the referees for their comments and have made the following changes in the manuscript.

Referee 1

The manuscript discusses results and implications of studies of the formation of alphahydroxy hydroperoxides (α-HHPs). Although previous results on this class of compounds exist they are quite limited. The work is very thorough and clearly presented and the authors make a strong case for the role of this compound class in tropospheric chemistry, primarily with respect to condensed phase (aerosol and cloud) processes but also the gas-phase, and they also point out the potential role of these compounds for human health. The topic is well suited to ACP. Although the atmospheric implication section is a little speculative, this section is important as I hope it will stimulate future work into this class of compounds, which, as this paper clearly demonstrates, is of high importance. I recommend the manuscript for publication after addressing the fairly minor comments below.

Comment 1: p. 5511 line 1: To my knowledge only hydroxy methyl hydroperoxide has been measured in the gas-phase. If this is the case I recommend stating it as such, in order to not give the impression that a whole range of alpha-HHPs have been observed in the gas-phase. (It is possible that the methyl case is unusual).

Response:

Several studies have detected 1-hydroxyethyl hydroperoxde (1-HEHP) (Hewitt and Kok 1991, Lee et al. 1998, He et al. 2010)and bis-hydroxymethyl hydroxide (BHMP) (He et al, 2010) in the gas phase. 1-hydroxy propyl hydroproxide (1-HPHP) has also being reported in rain water (Bachmann et al. 1992). That being said, we agree that hydroxy methyl hydroperoxide (HMP) is by far the most frequently detected α-HHP species from the ambient, and a wrong impression should be avoided.

The following section:

"α-Hydroxyhydroperoxides (α-HHPs) constitute a class of organic peroxide that has been observed in ambient air (He et al., 2010), rain water (Hellpointner and Gab, 1989; Sauer et al., 1996), and cloud water (Sauer et al., 1996; Valverde-Canossa et al., 2005), as reviewed by Hewitt and Kok (1991) and Lee et al. (2000)."

has been modified to:

"α-Hydroxyhydroperoxides (α-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 α-HHP in the ambient gas-phase (He et al, 2010), rain water (Hellpointner and Gab,1989; Sauer et al., 1996), and cloud water (Sauer et al., 1996; Valverde-Canossa et al.,2005), as reviewed by Hewitt and Kok (1991) and Lee et al. (2000). Other α-HHPs such as 1-hydroxyethyl hydroproxide, 1-hydroxypropyl hydroperoxide and bis-hydoxymethyl hydroperoxidehave 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 Kok, 1991)."

Comment 2: p. 5512 line 24-26: Could you clarify a little what exactly is meant with processing, what are the products and are they different than “regular” processing? This is a general comment also for the summary: A very interesting aspect of this work is in how far the alpha-HHPs present different reaction pathways and products. I am not sure how much more can be said at this point, but it clearly is an important future research direction.

Response:

The "regular" processing under the current context refers to relatively well studied processes such as photochemical processing by OH radical. This type of processing generally leads to irreversible formation of organic acids and oligomers, as studied in detail by Turpin and coworkers. The formation of α-HHP studied in the current work did not involve OH radicals, and the reaction is largely reversible. We propose in this work that α-HHP formation may lead to similar physico-chemical changes of SOA components (e.g. increased oxidation state and enhanced hygroscopicity). The formation of α-HHP may thus exhibits an alternative aqueous-phase processing mechanism.

The following section in the original manuscript:

"The formation of α-HHP via the Carbonyl Pathway may provide an additional mechanism of processing of such carbonyls in the atmospheric aqueous phase."

has been modified to:

"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 known mechanisms such as OH radical oxidation, thus exhibit an additional mechanism of aqueous-phase processing."

In terms of how the formation of α-HHP would affect reaction pathways and products, it is certainly an important research topic for the future. At the moment, we only noticed that the α-HHPs from glyoxal and methylglyoxal seem to lead to formation of formic acid and acetic acid, respectively (original manuscript, page 5531, line20).

Comment 3: p. 5513 line 3: If I understood correctly the solvent was H_2O and D_2O was only added for locking etc. Did you consider conducting the experiments in D_2O to reduce the problem of the water peak in the NMR. This could have helped with a number of assignments.

Response:

Yes, the referee's understanding is correct. Unfortunately, we did not perform any experiments with D_2O as the solvent. Using D_2O will certainly solve most of the water peak related problems shown in the current work and should be considered in future studies.

Comment 4: 5515 line 20: Is the problem with salt common to all NMR instruments or is it specific to the one used here? Such experiments would be very interesting.

Response:

The salt tolerance depends very much on the specific NMR probe and its design. Small micro-coil NMR probes are particularly salt tolerant and can withstand saturated salt solutions. Large diameter probes and cryogenically cooled probes tend to be generally less salt tolerant. Studies at very high salt levels could be performed in the future using a micro-coil probe.

Comment 5: 5517 line 22 quantification: Where the NMR experiments conducted quantitatively by making sure that the delay between pulses was long enough for small molecules to fully relax? It should be ensured that the used pulse delay time was appropriate.

Response:

Thank you for pointing this out. We have now clarified in the experimental section that this was the case. The following text has been added:

*"*The recycle delay was set at 5 times the measured T1 to ensure full relaxation between scans.*"*

Comment 6: 5519 line 9-10: "Thus the use of K_{app} negates the need for unambiguous quantification of all the peaks." Could you clarify this. Do you need to be quantitative with respect to relative peak heights.

Response:

Yes, the original sentence is unclear: we do have to be quantitative in terms of the relative peak integrations for the determination of K_{app}. What K_{app} negates is unambiguous peak assignment for all the peaks.

"unambiguous quantification of all the peaks" has now been modified to *"unambiguous assignment of all the peak".*

Comment 7: 5519 line 21-26 just for completeness: Was pH affected by addition of H_2O_2 and could this affect the hydration / HHP equilibria or rates? Also was the pH of all solutions the same. A brief statement whether pH can affect the experiments or not would be helpful.

Response:

We did not monitor or adjust the pH of all the solutions. We did measure pH of several acetaldehyde and formaldehyde solutions before and after the addition of H_2O_2, and we did not see significant change in the solution pH. Based on the results from previous studies, we assume that pH would not affect the equilibrium of a-HHP formation, but may affect its kinetics.

The independence of the equilibria to solution pH is further clarified in the original manuscript P5525 line 23 - 26:
"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 α-HHP have been reported to be pH dependent (Zhou and Lee, 1992)."

Comment 8: 5521 line 15-16 I know it is labeled in the figure, but it would be clearer to use "methylene proton peaks of the hydrated formaldehyde"; as written hydrated formaldehyde protons could also refer to the OH group protons as they are on the molecule as well.

Response:

Thank you for the suggestion. We have made changes to the manuscript.

Comment 9: 5528 line 9-14. Although the following equations clarify this, it would be helpful to phrase more clearly whether effective K_H or K_H is discussed as K_H (not effective) of formaldehyde is much smaller than effective K_H.

Response:

Precisely, the K_H (not effective) values of formaldehyde and acetaldehyde referred in the current context are the effective Henry's law constants of these aldehydes over pure water. These values consider the hydration reaction of these aldehydes, and hence should be distinguished from their physical Henry's law constants. However, having two effective Henry's law constants (one for pure water, one for α-HHP formation) might be misleading. We would like to keep K_H (effective Henry's law constant on pure water) as it is, but add the following clarifications in the text and in the caption of Table 6.

Clarification in the text:
Note that the K_H values for aldehydes are, precisely, the effective Henry's law constant of these aldehydes over pure water (i.e. they consider the hydration reaction of these aldehyde undergoing in water). The K_{Heff} and K_H values used here should be considered as Henry's law constants with and without α-HHP formation, respectively.

Clarification in the caption of Table 6:
[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); H_2O_2 (Martin and Damschen, 1981).

Comment 10: A general comment with respect to the hydration equilibria: The Taft equation (linear free energy relationships J. Am. Chem. Soc. 74, 2729, (1952)), especially the polar substituent constant, have been used very successfully before for carbonyl hydration equilibria, e.g., R.P. Bell Advances in Physical Organic Chemistry 4, 1-29 (1966); Greenzaid et al. JACS 89, 749-756 (1967). It could be interesting to incorporate it into this work also as this aspect could be useful for modeling efforts and section 4.2 as it might provide a pathway to structure reactivity aspects of Kapp. However the Taft equation does not explain the effect of sulfate (Yu et al. Environ. Sci. Technol., 45, 6336–6342, 2011).

Response:

In fact, we did try to incorporate the Taft equation to the current work, but could not get very conclusive results.

Fig.1 below plots the K_{app} values of four aldehydes from the current work against $\Sigma\sigma^*$, Taft's polar substituent constant. The three aliphatic aldehydes (i.e. formaldehyde, acetaldehyde and propionaldehyde) lie on an apparently linear trend, as shown by the red line. However, glycolaldehyde does not obey this trend. In fact, when Betterton and Hoffmann 1988 investigated the relationship between $\log(K_H)$ with the $\Sigma\sigma^*$ parameters, they also found a deviation of glycolaldehyde from its expected trend. We suspect that the hydroxyl functional group on glycolaldehyde may be causing certain effects that cannot be captured by Taft's equation.

In conclusion, we reliably determined the K_{app} values of only four aldehydic compounds from the current work, and only three of them showed an apparently linear trend. For this reason we've decided not to incorporate this part into the manuscript.

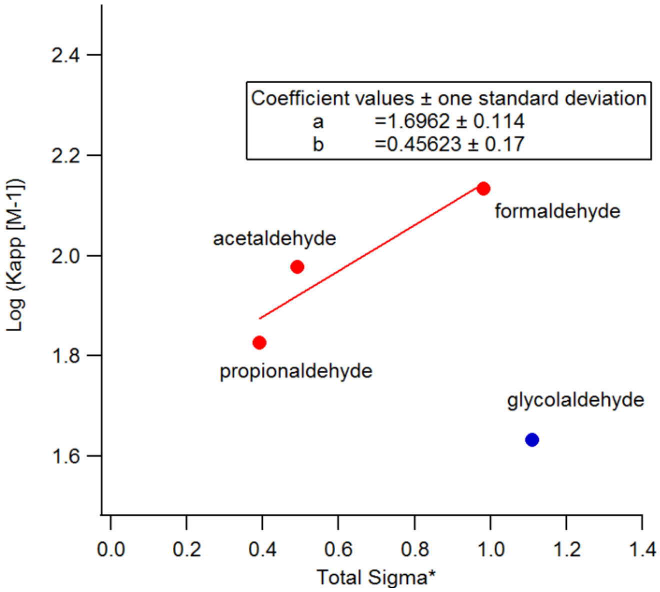

Fig.1 Plot of the apparent formation equilibrium constants (Kapp) against Taft's $\Sigma\sigma^*$ parameter. The linear fitting for formaldehyde, acetaldehyde and propionaldehyde is shown in the red line, and the fitting parameters are also displayed. References used for the $\Sigma\sigma^*$ values: Betterton and Hoffmann 1988 for formaldehyde, acetaldehyde and glycolaldehyde; Brandstrom 1999 for propionaldehyde.

Referee 2

This is a very interesting study on HHPs which could lay the groundwork to better treat these compound in atmospheric aqueous phase models. It is a very thorough and innovative study.
I think the manuscript could be accepted when a few points are treated in addition to the current version.

Comment 1: I wonder if the carbonyl pathway requires the hydration of the carbonyl into the diol at which then hydrogen peroxide performs as a nucleophlic attack. What is the state of knowledge for this in literature ? I t would be good to discuss this in the introduction and in the context of Figure 1 which might be a bit simplistic. I find this very important because the whole manuscript is about the quantifying Khydr and Kadd. This is also important in the course of the manuscript with regard to Figure 4, see the next comment.

Response:

The general understanding of this reaction is that H_2O_2 adds to the non-hydrated aldehydic functional group. As experimental evidence, Satterfield and Case found that the initial rate of H_2O_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_2O_2 addition. This observation leads to their conclusion that H_2O_2 addition has to occur on unhydrated aldehydic functional groups.

We also would like to note that the current work is focused on thermodynamic equilibria; therefore, the difference in reaction kinetics mentioned above is not expected to affect our conclusions. However, we agree that this reaction mechanism is the core of the entire manuscript and have made several modifications in the Introduction.

Comment 2: Page 5518, line 10ff: I would like to suggest to also give values of Keq wherever possible. It is stated that these values are calculated but values are not given. If such values exist (as stated), a comparison of the product Khydr * Kadd vs. Keq could be performed: Is the product of Khydr times Kadd different from Keq ?

Response:

Thank you very much for the interesting suggestion. We have added this approach to the manuscript as a confirmation of our determined K_{app} values. The K_{eq} values determined for four of the aldehydes are below in Table 1. Table 1 has been added to Supplementary Information.

	K_{eq} determined (M^{-1})	K_{hyd} determined	K_{eq} / K_{hyd} (M^{-1})	K_{app} determined (M^{-1})
Formaldehyde	1663405	2300*	723	164
Acetaldehyde	230	1.43	161	113.5**
propionaldehyde	116	1.256	92	67.5**
glycolaldehyde	727	16	45	43.3

Table 1. Comparison of K_{app} values experimentally determined and calculated as (K_{eq}/K_{app}).

*Was not determined from the current work, but taken from Betterton and Hoffmann 1988.

** Are the averaged values from the ^{1}H NMR and the PTR-MS measurements.

We found that for acetaldehyde, propionaldehyde and glycolaldehyde, the agreement between the experimentally determined K_{app} and Keq/Khyd was fairly good. For these three aldehydes, the discrepancy may be explained by the fact that they do not hydrate completely in the aqueous phase (see the mathematical explanation below).

For an alkyl aldehyde (A) that forms only one α-HHP spceies,

$$A \quad + \quad H_2O \quad \leftrightarrow \quad A_{hyd}$$

$$A \quad + \quad H_2O_2 \quad \leftrightarrow \quad \alpha HHP$$

$$K_{hyd} = \frac{[A_{hyd}]\mathrm{eq}}{[A]\mathrm{eq}}; \quad K_{eq} = \frac{[\alpha HHP]eq}{[A]eq \times [H_2O_2]eq}$$

$$\frac{K_{eq}}{K_{hyd}} = \frac{[\alpha HHP]eq \times [A]eq}{[A_{hyd}]eq \times [A]eq \times [H_2O_2]eq} = \frac{[\alpha HHP]eq}{[A_{hyd}]eq \times [H_2O_2]eq}$$

As defined in the manuscript,

$$K_{app} = \frac{[\alpha HHP]eq}{([A]eq + [A_{hyd}]eq) \times [H_2O_2]eq}$$

If A is almost entirely hydrated (i.e. $[A_{hyd}]$eq >> $[A]$eq),

$$K_{app} \approx \frac{[\alpha HHP]eq}{[A]eq \times [H_2O_2]eq} = \frac{K_{eq}}{K_{hyd}}$$

This indicates that if A's hydration equilibrium constant K_{hyd} is large, then its K_{app} is essentially equal to K_{eq}/K_{app}, as suggested by the reviewer.

The discrepancy between K_{eq}/K_{app} and K_{app} determined for acetaldehyde, propionaldehyde and glycolaldehyde can be explained by the fact that they do not hydrate completely in aqueous phase (i.e. $[A_{hyd}]$eq is not overwhelmingly larger than [A]eq). In fact, glycolaldehyde has the largest K_{hyd} among these three aldehydes, and its discrepancy is also the smallest.

However, the discrepancy of formaldehyde is very large, and we are not entirely sure about the reason. Considering the fact that our determined K_{app} value shows excellent agreement with available literature values, we do not consider that there is a large systematic error in our measurement. Please note also that we could not directly determine the K_{hyd} of formaldehyde, and it was instead referred from Betterton and Hoffmann 1988. Using a number that was not obtained from our own system may have contributed to part of the discrepancy. Another explanation is that, as described in the paper, formaldehyde forms bis-hydroxymethyl hydroperoxide (BHMP) besides hydroxymethyl hydroperoxide (HMP), which may have lead to a more complicated system than the one demonstrated by the mathematical explanation above.

For the dicarbonyl compounds (i.e. glyoxal and methylglyoxal), we did not test this relationship because they form multiple hydration and α-HHP equilibria.

Details about these comparisons are now included in the paper.

Comment 3: Page 5520, line 11: What is the reason for the large discrepancy in the hydration constant for formaldehyde ?

Response:

We are not entirely sure which discrepancy in K_{hyd} of formaldehyde the reviewer is referring to. We provide the answer below assuming that the reviewer is pointing at the discrepancy of K_{hyd} for formaldehyde determined using ^{1}H NMR in the current work and the literature (shown in Table 1).

The K_{hyd} value of formaldehyde in the current work (>18) is obtained from the detection limit of the ^{1}H NMR technique, as mentioned in the footnotes of Table 1. The detection limit was determined as 3 times the standard deviation of the baseline noise. Since the peak for non-hydrated formaldehyde was not detected by the ^{1}H NMR method, the detection limit of this peak was used to calculated the lower limit of K_{hyd} of formaldehyde (i.e. >18).

The detection limit is certainly a limitation in the methods employed in the current work. It makes comparison of K_{hyd} with literature values difficult. Please see our response to Comment 6 below.

Comment 4: Page 5522, line 21: Gäb or Gaeb, not Gab. This needs to be corrected throughout the manuscript.

Response:

We sincerely apologize for our carelessness. The name has been corrected throughout the manuscript.

Comment 5: Page 5532, Conclusions: I suggest to not just list bullet points but use regular flow text.

Response:

Thanks for the suggestion. We have changed the conclusion into regular flow text format.

Comment 6: Table 1: Reference 1 in Table 1 is not Betterton and Hermann, but Betterton and Hoffmann, please correct. Please check all referencing again for correct author names.
I feel it would be good to plot the values of the Table against each other and discuss this in the text.

Response:

We again sincerely apologize for the mistake in the authors' names. All the references have been checked again to avoid similar type of mistakes.

Plotting the K_{hyd} values determined in the current study against the literature values might illustrate potential bias in our measurement. However, the major limitation in applying such data presentation under the current work is the discrepancy between some of the K_{hyd} values as explained in our response to Comment 3 above. Due to the detection limit of the ^{1}H NMR technique, we could only report a lower limit of K_{hyd} for heavily hydrated carbonyls (i.e. formaldehyde, glyoxylic acid and methylglyoxal), while an upper limit for poorly hydrated carbonyls (i.e. methacrolein, acetone and methylethyl ketone). Plotting such lower/upper limits of K_{hyd} against the literature values would not be very informative. Moreover, the main purpose of Table 1 is to show the agreement between experimentally determined K_{hyd} values and their literature values. We think the current tabular format of data presentation is sufficient for this purpose.

References

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