The manuscript entitled “Synthesis and characterization of peroxypinic acids as proxies for highly oxygenated molecules (HOMs) in secondary organic aerosol” investigates the effect of RH on the formation of peroxycarboxylic acids. For this study important peracids were synthesized. In particular, the degradation of peroxides on filter samples is described that should be considered for all future work. The content is very good and the manuscript well written but lacks of many important points (e.g. literature comparison, chromatograms and spectra as evidence for the described findings etc.). As the described findings highly affect the aerosol community I recommend publication, but only after the following points were carefully addressed. I would also recommend to change the title. The reasons for this are explained in detail within the review.

General comments:

Introduction: To my opinion the introduction is too much concentrated on highly oxidized molecules (HOMs). Even that this group of compounds is a so-called “hot topic” the compounds that are described in the manuscript do not belong to HOMs. In the literature it is stated that HOMs contain hydroperoxide functions. The compounds described in the present manuscript are traditional peracids. Furthermore, HOMs are highly oxidized (O:C ≥ 1) and contain usually carbonyl groups. They are formed by autoxidation in the gas phase. The formation of peracids might proceed mainly via the reaction of an acylperoxy radical with HO_2 (Niki et al., 1985) and their O:C ratio is too small. Thus a basic discussion of formation pathways yielding peracids is largely missing in the present manuscript. Therefore it is questionable to me why peroxypinic acid is a proxy for HOMs. Thus the title is very misleading. Maybe the title should be reconsidered and also the relation between HOMs and peracids should not be highlighted or at least it should be discussed in a better and more logical way.

In the work by Ehn et al., or Riissanen et al., it is not stated the HOMs contain peracid structures. A discussion of the possible formation mechanism would be also helpful to understand the effect of RH that is one major focus of this manuscript.

Besides this discrepancy the introduction lacks of several references and thus, gives a very superficial impression. Several methods exist quantifying at least organic peroxides as a sum parameter (e.g., Docherty et al., 2005, Mutzel et al., 2013). Also studies are published characterising organic peroxides in SOA by LC/MS analysis (Krapf et al., 2016, Zhao et al., 2018, Ziemann et al., 2003). In particular the work by Zhao et al., should be recognized within the present manuscript as they also synthesised peroxy compounds and characterised them with LC/MS.

Page 3, line 10: Pinic acid was only characterised by 1H-NMR. Please provide the NMR spectrum in the manuscript and calculate the purity of pinic acid. According to the NMR characterisation given in the manuscript an assignment of the signals to the H-atoms in the molecule is complicated. Please number the carbon atoms in Figure 1 and use these numbers to clearly assign the H-atoms to the signal recorded in the NMR. Furthermore, I assume that "complex adsorption" means multiplett? Please use the exact NMR wording for the interpretation.

The NMR characterisation of the peroxy compounds is completely missing. Please add this to the manuscript together with the corresponding NMR spectra. Please indicate the level of purity. How can the authors ensure the identity and purity of the synthesized compounds without NMR characterisation? In particular, this is very important for the peroxy compounds as they are synthesised for the first time. And also the purity will highly effect the quantification results.

Is there a reason that the characterisation is only done with 1H-NMR? The amount of material is enough to prepare 13C, NOESY or COSY spectra to provide a complete characterisation of all synthesised compounds. Also the corresponding MS spectra of all synthesised compound should be shown.

Page 3, line 20: The experimental conditions seem to be very high. What is the reason the run the experiments under those high conditions? How was the concentration of a-pinene measured? This chosen concentration contradict also the relation to HOMs. HOMs formation and in particular, the contribution of HOMs to the early particle growth becomes more important under low mass loadings. Under higher mass loadings the contribution of HOMs decrease as the contribution of subsequent chemistry of first-generation oxidation products (semi-volatile oxidation products such as pinonaldehyde etc.) starts to increase.

Page 4, line1: I´m wondering that the samples very dried at 30°C,. Why not at room temperature? Can the authors ensure that none of the peroxides decompose under this temperature? Was the influence of the temperature investigated? How was the volume of 300 uL measured?

Page 5, line 18: It is not mentioned which efforts were made to separate the two overlapping peaks. Please show chromatogram and describe which parameters were tested to improve the separation. In addition, it is very questionable to use unseparated peaks for quantification. Even that it is stated that the second peak seems to be small Page 7, line 14), a reliable quantification should be done with well-separated peaks. Additionally an important picture is missing illustrating the BPC of the standard, the BPC from the flow tube experiment under humid conditions and the BPC under dry conditions.

Page 7, line 19: It is somehow not logical to describe the synthesised peracids as HOMs and to predict their formation with a model that does not contain any HOMs formation. As it is stated above. HOMs are formed via autoxidation during the initial phase of oxidation. Therefore MCM to predict and understand their formation is not suitable. The formation of peracids in MCM follows the traditional radical chemistry. This can be applied to the present peracids but it is not applicable to HOMs. Therefore a clear separation of both topics should be done! Furthermore, if the present peracids would be HOMs a discussion about their formation in the condensed phase would not make any sense (Page 7, line 26) as HOMs supposed to be formed solely in the gas phase. I also miss the corresponding pictures illustrating the simulation with AtChem vs. the experiment data.

Page 7, line 22: The yield should be also given as fraction in SOA. This is very common in studies investigating the contribution of peroxides to SOA formation. This would also enable a comparison to other literature studies which is also missing in the manuscript. Based on these values a better discussion of the effect of RH can be done.

Page 7, line 31: A comparison to literature studies is largely missing, e.g. Huang et al., 2013 investigated the influence of RH on hydroperoxides. The authors should also include other potential mechanism/precursor that can be affected by RH, like the Criegee intermediate.

Page 8, line 15: It is stated that peroxopinic acid degrades over time. Which other products were observed? I would expect the formation of decomposition products like pinic acid.
How were the samples treated between the repetitive analysis? Were they stored in a fridge or at room temperature? Were they always protected against UV light?

Minor comments

Page 1, Line 21: change particle phase to particle-phase
Page 2, Line 26: According to IUPAC nomenclature “Sulphuric acid” should be changed to “sulfuric acid”. This is also the case in Page 3, line 17.