We would like to thank the reviewers for their constructive feedback on the manuscript. Our answers to the different remarks are detailed below with comments from the reviewers in black, our answers in blue and suggested changes to the manuscript in italics.

Reply to anonymous referee #1

1. In general, synthetic standards should be isolated and characterized as pure compounds. While the mass spectrometric analysis presented in this manuscript is convincing that the structures proposed for the synthetic targets are correct, additional physicochemical data, for example, 1H NMR, is desirable for definitive proof.

To confirm the identity of the synthesized compounds, we collected the monoperacid and diperacid fraction of the chromatographic separation and subsequently performed NMR analysis. The compounds proved to be not sufficiently stable in the selected solvent to obtain pure NMR spectra of the different compounds. We do however feel confident that the measured 1-NMR and HSQC data of the collected fractions nevertheless strongly support the assigned structures. A detailed discussion of the NMR results can now be found in the supplement (Fig.S7-S17).

The authors report that the monoperoxy acids could not be well resolved, but effort directed towards achieving resolution is not clear. For example, a promising possibility would be the use of a HILIC column, such as recently reported for separation of carboxylic acids in SOA (J. Chromatogr. A 2011, 1218, 4417– 4425). The column used in this citation was also a 3 mm column, which would be adequate for collection of sufficient sample for NMR analysis. If the authors did investigate the separation more thoroughly, this information should be included.

We thank the reviewer for this interesting suggestion. Unfortunately, we have no HILIC column available for the current study but will consider this alternative separation technique in future studies. We decided to use the same solvents (acetonitrile and 0.1% formic acid in water) as in our previous study for easier comparison of the fragmentation patterns. We did however try different gradients with these two solvents, without any notable improvement in the separation of the two isomers.

2. Why was the LC/ESI-MS analysis not performed using a UPLC column? A UPLC version of the same column would likely provide significant improvement in resolution. It would be surprising if the authors did not have access to UPLC. Mass spectrometric data on better-resolved peaks could have acquired even though resolution on the semipreparative scale column was difficult to achieve.

We do not have access to UPLC instrumentation.

3. The observation of different MS2 spectra for isomers I and II indicates that 1-electron reduction in the ESI source did not make an important contribution to the mass spectra of the monoperoxy acids and that the anions of the more acidic carboxylic acids were the parent species. The fragmentation patterns provide sufficient information to distinguish between the two proposed structures, and the authors should be able to tentatively assign structures to isomers I and II. Although the literature on ESI-MS of carboxylic acids is sparse, there is sufficient precedent to propose plausible pathways to the observed product ions which are unique to each structure.

We have added an overview of potential fragmentation pathways to the Supplement. The proposed fragmentation schemes enable us to tentatively assign structures to isomer I and II. The following section has therefore been *added to the text (p.7, line 31):*

"Based on the available literature (Szmigielski et al., 2006; Yasmeen et al., 2010, 2011)*, we suggest potential fragmentation pathways for the two isomers (Fig. S20). This allows the tentative assignment of isomer I and II as the monoperoxy pinic acid isomer with a methyl peroxycarboxyl substituent and a peroxycarboxyl substituent, respectively.*

4. Graphic presentation of the actual MS and the MS2 data would be helpful to the readers. The mass spectra could be presented as supporting information.
A supplement is now available which contains the requested MS and MS/MS spectra *(Fig. S18 & S19)*. Appropriate cross references were added to the text of section 3.2.

5. The investigation of the effects of RH rules out the formation of the peroxyacids via a hydrolytic pathway, but does not preclude an oxidative pathway in the condensed phase. In the gas phase, peroxyacids can form via HO_2 chemistry (e.g., Atmos. Chem. Phys. 2012, 12, 6489–6504) without the participation of H_2O. Therefore insensitivity of yield to RH is not surprising, and the discussion might be amended to reflect this. The order of magnitude discrepancy between the observed and predicted relative yields of monoperoxypinic acids is probably not explicable entirely by peroxyacid degradation during work-up, and illustrates the importance of quantitation using authentic standards to improve models.
We agree that peroxy acids can form in the gas phase via HO_2 chemistry, without water vapour as a reactant, and have emphasised this in the revised manuscript. While a lack of RH dependence is therefore intuitively not surprising, the detailed MCM modelling confirms this quantitatively. Furthermore, the model results allow us to conclude that potential indirect effects of water vapour (e.g. changing the fate of precursor species such as Criegee intermediates) are also unimportant in determining the final yield of peroxypinic acid. We have modified the manuscript as follows (p.8):

"It is known that the gas-phase formation of peroxy acids can proceed via HO_2 chemistry, without direct involvement of H_2O (Docherty et al., 2005; Eddingsaas et al., 2012). The calculated yield of monoperoxypinic acid per O_3 molecule was ~6×10^{-5} (~ 1.2 ppb) under dry conditions and was insensitive to RH (0-100%) and initial precursor concentrations (1-300 ppm). This confirms the unimportant role for water vapour in the gas-phase formation of monoperoxypinic acid not only as a reactant, but also in terms of indirect effects on e.g. the concentrations of precursor species such as Criegee intermediates."

An experiment that would be informative with regard to whether the peroxyacids form in the gas or condensed phases would be to monitor the gas phase species by CIMS if the authors have access to such instrumentation. Although interesting, this experiment would not be a prerequisite to publication since access to CIMS instrumentation is required.
We do not have access to a CIMS.

Reply to anonymous referee #2

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 HO2 (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.

We would like to note that, although some structures proposed and summarised in the recent literature as HOMs have hydroperoxy groups only, there is a significant number of proposed structures that contain both hydroperoxy ***and*** peroxy acid groups or peroxy acid groups only (e.g. Mentel et al., 2015; Rissanen et al., 2015). The text has been amended to clarify that either functional group can be present in HOMs (p.2).
"Many studies state that HOMs have O:C ratios of ≥ 0.7 (Mentel et al., 2015; Mutzel et al., 2015). *There is no generally accepted definition of HOMs, but they typically contain multiple hydroperoxy and/or peroxy acid groups* (Mentel et al., 2015; Rissanen et al., 2015)*."*

There is no unified definition of O:C in HOMs in the literature but many papers argue that O:C ≥ 0.7 should be used (Mentel et al., 2015; Mutzel et al., 2015) rather than 1 as suggested by the reviewer. The structures we investigate here are have O:C of 0.55 and 0.66 and thus have O:C very close to the definition of HOMs. This is now explicitly mentioned, see comment above.

We like to emphasise that a main aspect of this study was to provide the atmospheric community with a simple procedure to synthesise and characterise a realistic HOMs ***proxy*** for quantitative studies on HOMs as stated in the abstract. Therefore, we like to keep the current title. This is now more clearly clarified (p.2, line 29).
"The structural similarity of these peroxy acids with HOMs (present in a wide range of SOA particles) makes them ideal and unique proxies and surrogate standards for future studies aiming to quantify the role of HOMs in organic aerosols."

We are aware that peroxypinic acids are not formed via autoxidation and have stated this more clearly in the manuscript (p.2, line 26).

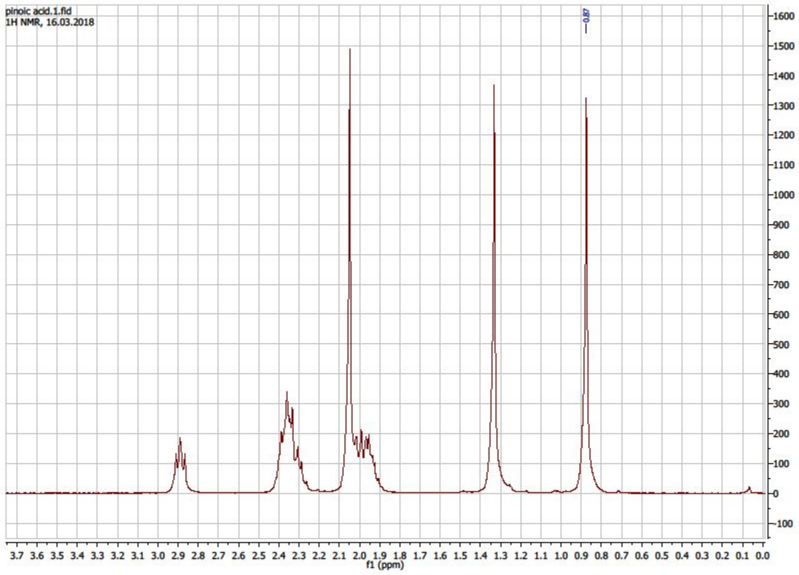
Besides this discrepancy the introduction lacks of several references and thus, gives a very superficial impression. Several methods exist quantifying at least organic peroxides as a sum parameter (e.g., Docherty et al., 2005, Mutzel et al., 2013). Also studies are published characterising organic peroxides 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.

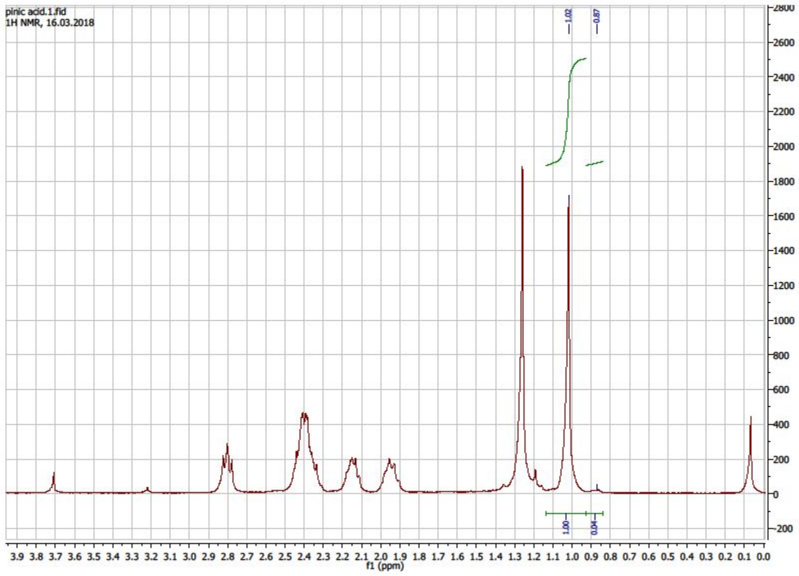
We would like to focus the introduction on peroxy acids and not widen it to a general review of analytical technique to characterise peroxides. We have therefore added only a few references describing MS studies in which other potentially atmospherically relevant peroxy compounds were synthesized and studied. The study by Krapf et al. 2016 was not included here, as they did not synthesize any specific peroxy compounds.
We added Zhou et al. as additional reference for the tentative identification of monoperoxypinic acid in α-pinene aerosol.

This part of the introduction now reads (p.2, line 14): *"Mass spectrometry, in particular coupled with chromatography, provides a method to characterize and identify specific compounds. Recently, several studies have utilised mass spectrometry to analyse different types of organic peroxy compounds with potential atmospheric relevance (Witkowski and Gierczak, 2013; Zhao et al., 2018; Zhou et al., 2018; Ziemann, 2003). However, to our best knowledge no such studies exist for peroxy acids."*

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.

We have measured additional C-NMR and 2-D NMR data and added the NMR spectra to the supplement. The description of the NMR spectra is now improved (p.3, line 18) and assignments of the carbon atoms and the hydrogen atoms are now given (some uncertainty remains for chemically different hydrogen atoms attached to the same carbon atom); the atom numbering has been added to figure 1. The purity in regards to the educt (*cis*-pinonic acid) is 96%, which has been added to the text (p.3, line 17). It was determined by integrating the peak of the methyl group of *cis*-pinonic acid at 0.87 ppm and the equivalent methyl group of *cis*-pinic acid at 1.02 ppm in the 1H-NMR and calculating the ratio of the two integrals. Spectra of both product and educt (in $CDCl_3$) that were used for this calculation are shown below.





The NMR section now reads as follows (p. 3):" *After subsequent filtration followed by evaporation, the yield of cis-pinic acid was estimated to be 2.5 g (88%) with a purity of 96% relative to the educt. To confirm the identity of the synthesised compound* ^{1}H, ^{13}C, *DEPT, COSY, HSQC and HMBC NMR spectra were collected using residual* CHD_2CN *as the internal standard. cis-Pinic acid:* ^{1}H *NMR (*CD_3CN*, 500 MHz)* δ_H *0.94 (s, 3H, H5), 1.20 (s, 3H, H6), 1.82 (m, 1H,* $H2_\alpha$*), 2.03 (m, 1H,* $H2_\beta$*), 2.3 (m, 3H, H1,H8), 2.74 (dd, J = 10.3 Hz, J' = 7.9 Hz, 1H, H3).* ^{13}C *NMR (*CD_3CN*, 500 MHz)* δ_C *17.8 (C5 or C6), 25.2 (C2), 30.0 (C5 or C6), 35.2 (C8), 38.9 (C1), 42.9 (C4), 46.4 (C3), 174.2 (C7), 174.4 (C9). A full overview of all NMR spectra used for the assignment is given in the supplement (Fig. S1-S6)."*

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.

We would like to note that the synthesized compounds are present as a mixture and we did not further purify the compounds, which is why no attempts at absolute quantification are made in this study.

As discussed above, to confirm the identity of the synthesized compounds, we have now collected the monoperacid and diperacid fraction of the chromatographic separation and subsequently performed NMR analysis. The compounds proved to be not sufficiently stable in the selected solvent to obtain pure NMR spectra of the different compounds. We do however feel confident that the measured 1-NMR and HSQC data of the collected fractions nevertheless strongly support the assigned structures. A discussion of those NMR results can now be found in the text (p.4, line 2) and the supplement (Fig. S7-S17).

Also the corresponding MS spectra of all synthesised compound should be shown.

Mass spectra of the educt and all synthesized compounds have been added to the supplement (Fig. S18).

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 α-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 pinonaldehydeetc.) starts to increase.

The reason to use high SOA precursor concentrations in this proof-of-concept study is the relatively low yield of monoperoxypinic acid; using concentrations closer to atmospheric conditions would have resulted in monoperoxypinic acid concentrations below the detection limit of our method.

α-Pinene was measured by PTR-MS according to the procedure described in Giorio et al. (2017); this is now shortly described on p.4, line 16.

We would like to emphasize again that we are aware that the formation of the synthesized peroxypinic acids does not proceed via autoxidation and their choice as a proxies for HOMs is purely due to chemical similarities, not similar formation processes. We emphasise this in the title and various part of the paper. The investigation of the peroxypinic acid formation process is independent from their suitability as HOMs proxies. We hope that this point is more clearly communicated in the current version of the manuscript.

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?
The samples were dried at 30 °C to speed up the time between collection and analysis. This is now mentioned in the text on p.4, line 32 where we also acknowledge that we cannot rule out some decomposition of peroxides, although we believe that this should be a minor effect as we are heating the SOA extract only slightly above room temperature. The 300 µL were determined volumetrically.

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.
A chromatogram is shown in Fig. 3 of the original manuscript. We decided to use the same solvents (acetonitrile and 0.1% formic acid in water) as in our previous study for easier comparison of the fragmentation patterns. To improve the separation, we tested multiple different gradients with these two solvents, varying total run time, starting concentration of the organic phase and the steepness of the gradient without any notable improvement in the separation of the two isomers.

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.

As stated above, we were not able to obtain a better separation of the two monoperoxy acid peaks. Due to the small peak areas seen in the SOA samples, the peaks are reasonably separated, although some uncertainty remains.
We assume that BPC stands for base peak chromatogram. The base peak chromatogram of the synthesized standard mixture is shown in Fig.3 of the original manuscript. We have stated this now more clearly in the respective figure caption. We do not feel that the base peak chromatograms of the flow tube experiments would add any value to the manuscript since the peroxypinic acid only gives a comparatively small signal and is therefore not directly visible in the base peak chromatograms of the SOA. As stated in the data analysis section, quantification was done using the extracted ion chromatogram of the MS/MS measurement.

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.
As stated previously, we are not suggesting that the investigated peracids are formed via a HOM formation mechanism and are aware that their formation pathway is different. We hope that the separation in the text where we describe (1) the potential usefulness of peracids as HOMs ***proxies*** for analytical purposes due to structural similarities and (2) the investigation of peracids as relevant compounds for atmospheric chemistry is clearer now (p.2).

A comparison between experiments and MCM is given in the text at the beginning of 3.3.1. As this is a minor aspect of the paper, we do not show a respective figure.

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.
As stated several times above we do *not* give absolute quantitative values for the concentrations of the peroxy acid standards in this paper. Therefore, we do not provide yields for these compounds.

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.
We have added a brief discussion of other investigations of the effect of humidity on peroxy compounds in the atmosphere (p.9, line 12).
"The fact that the peroxypinic acid yield per SOA mass does not depend on humidity agrees with observations made by Docherty et al. (2005), who found no dependence of the organic peroxide yield per SOA mass on humidity. Previous studies of the humidity dependence of individual peroxy compounds were focused on small molecules predominantly residing in the gas phase (e.g. Hasson et al., 2001; Huang et al., 2013) and are therefore not directly comparable with our results. However, the fact that different correlations with humidity were found for different peroxy compounds demonstrates the need for investigation of individual compounds."

We now also refer to Criegee as potential aspect where humidity could affect the experiments described here (p.8, line 28)
"This confirms the unimportant role for water vapour in the gas-phase formation of peroxypinic acid not only as a reactant, but also in terms of indirect effects on e.g. the concentrations of precursor species such as Criegee intermediates."

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?
We agree that formation of pinic acid upon peracid degradation is to be expected and we do observe its occurrence for the synthesized standard (see discussion of NMR results). However, the monoperoxy acid signal is very small in the SOA samples compared to the signal of pinic acid, so that even at full conversion from peracid to acid, the change to the acid signal would be too low to be detected. In general, the relatively minor contribution of monoperoxypinic acid to the total aerosol mass means that assignment of decomposition products was not feasible in this study and is of minor importance.
Filter samples were stored at room temperature between repeat measurements (as stated in line 11, page 4 of the original manuscript) and protected from UV radiation during storage (now mentioned on p.5, line 10):
"The three additional composite samples were extracted after being stored in their filter boxes at room temperature and under protection from UV radiation for up to 70 h to simulate typical field sampling conditions"

Minor comments
Page 1, Line 21: change particle phase to particle-phase
Fixed.

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.
Fixed.

Reply to anonymous referee #3

1. Page 3, lines 23–25: The concentrations of a-pinene and ozone used in these experiments were extremely high. Is it possible that a-pinene partitions to particles, walls, or the filter and that some of the reaction occurs there? Some discussion of the differences between reactions conducted under these conditions and at more typical atmospheric concentrations seems warranted.
Alpha-pinene has a vapour pressure of 633 Pa (US EPA) which corresponds to a vapour saturation concentration (C_{aP}) of 3.5 × 10^7 µg/m^3. Although the aerosol mass loading in the flow tube is high (C_{OA} ~5 × 10^4 µg/m^3), equilibrium partitioning theory (e.g. Kroll and Seinfeld, 2008) predicts only a small fraction (<1%) of alpha-pinene should partition into the particle phase under these conditions. However, we agree that condensed material on the flow tube walls and filter may allow even very volatile species to partition due to the large volume of material present (Matsunaga and Ziemann, 2010). Wall reactions of alpha-pinene are unlikely to directly modify the observed aerosol composition since lower volatility products should not repartition from the walls. Condensed phase reactions on the filter may be important, although the charcoal denuder should at that point have removed the majority of O_3. The text was amended as follows (p.4, line 23):

"The average particle mass concentration in the flow tube was about 5 × 10^4 µg·m^3, assuming a density of 1 g·cm^3, with a mode of 200 nm for the number concentration. Under these conditions, α-pinene partitioning to the particles is still negligible (<1%) and while wall partitioning could be significant, it is unlikely to directly modify the observed aerosol composition due to the lower volatility of the products. The produced α-pinene SOA was collected on Durapore® membrane filters (0.1 µm pore size, 47 mm diameter, Merck) for a sampling period of 45 min. Partitioning of α-pinene followed by condensed-phase reactions on the filter might occur and could change the aerosol composition compared to lower mass loadings, although the charcoal denuder should have removed the majority of organic gases and O_3, making this less likely."

2. Page 3, line 26: For these reactant concentrations the ozone should be gone in a few seconds, so the statement that the reaction time is 6.25 min could be clarified. This may give the time for particle-phase reactions, but these will then continue after collection on the filter.
To clarify, the text has been changed as follows (p.4, line 14):
"Gaseous α-pinene was introduced into the flow tube by passing N_2 (200 mL/min) over 500 µL of liquid α-pinene (about 340 ppm initial concentration, measured by PTR-MS according to the procedure described in Giorio et al. (2017)), which results in a residence time of approximately 6.3 min. Under these conditions, the reaction is limited by O_3, which according to model calculations is consumed within ~20 s under both humid and dry conditions. The lifetime of O_3 and α-pinene in the flow tube was estimated using the AtChem (http://atchem.leeds.ac.uk) numerical box-model alongside the Master Chemical Mechanism (MCM) v3.3.1 (http://mcm.leeds.ac.uk) (Jenkin et al., 1997; Saunders et al., 2003)."

3. Because of the unstable nature of peroxides it seems that some of the conditions in the HPLC-MS/MS analysis could impact the analysis. For example, the use of 0.1% formic acid, and heater and capillary temperatures of 250 C and 275 C. Please comment on this.
Presence of formic acid should not negatively influence peroxy acid stability. Synthesis of the peroxy acids is carried out under strongly acidic conditions and they are generally more stable at low pH.

While the influence of source temperature was not explicitly tested for peroxypinic acid, we did test it for a wide range of other peroxy acids during a previous study (Steimer et al., 2017). While this is not explicitly mentioned in that paper, we found that peak area improved with increasing temperature, likely due to improved solvent evaporation outweighing any potential decomposition. We did not test the effects of the capillary temperature and can therefore not exclude thermal degradation in the mass spectrometer transfer line.

4. Did the authors consider measuring the total peroxide content of their SOA so that they could estimate the fraction of total peroxides that their molecular analysis detects?
This is a good idea but outside the scope of the present study.

5. Might it be possible to collect particles in a cooled filter apparatus in order to reduce the decomposition of peroxides?
This should be possible and would be a good idea for future experiments. However, in the present study we explicitly decided to perform the collection at room temperature to better simulate the conditions under which samples are usually collected in the field.

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Synthesis and characteri~~z~~sation of peroxypinic acids as proxies for highly oxygenated molecules (HOMs) in secondary organic aerosol

Sarah S. Steimer[1], Aurélie Delvaux[1], Steven J. Campbell[1], Peter J. Gallimore[1], Peter Grice[1], Duncan J. Howe[1], Dominik Pitton[2], Magda Claeys[3], Thorsten Hoffmann[2], Markus Kalberer[1]

[1]Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, UK
[2]Institute of Inorganic and Analytical Chemistry, University of Mainz, 55128 Mainz, Germany
[3]Department of Pharmaceutical Sciences, University of Antwerp, 2610 Antwerp, Belgium

Correspondence to: Sarah S. Steimer (ss2349@cam.ac.uk), Markus Kalberer (markus.kalberer@atm.ch.cam.ac.uk)

Abstract. Peroxy acids ~~might contribute significantly to particle toxicity and~~ were recently found to be involved in new particle formation in the atmosphere, and could also substantially contribute towards particle toxicity. However, a lack of suitable analytical methods for the detection and characteris~~z~~ation of peroxy acids in the particle phase is currently hindering the quantitative investigation of their contribution to these important atmospheric processes. Further development of appropriate techniques and relevant standards is therefore urgently needed. In this study, we synthesi~~z~~sed three peroxypinic acids, developed a liquid chromatography separation method and characterised them with tandem mass spectrometry. The observed fragmentation patterns clearly distinguish the different peroxypinic acids from both the acid and each other, showing several neutral losses previously already observed for other peroxy acids. Both monoperoxypinic acids were found to be present in secondary organic aerosol generated from ozonolysis of α-pinene in laboratory experiments. The yield of monoperoxypinic acid formation was not influenced by humidity. Monoperoxypinic acid quickly degrades on the filter, with about 60% lost within the first 5 hours. This fast degradation shows that time delays in traditional off-line analysis will likely lead to severe underestimates of peroxy compound concentrations in ambient particles.

1 Introduction

In recent years, organic peroxy compounds have emerged as important particle-~~-~~phase constituents of secondary organic aerosol (SOA). They are discussed as components of a family of compounds ~~summarised~~ denoted as highly oxygenated molecules (HOMs), important in new particle formation (Ehn et al., 2014; Rissanen et al., 2015), and they could be involved in particle toxicity due to their oxidising properties, contributing to overall particle-bound reactive oxygen species (ROS) concentrations (Arashiro et al., 2017; Jiang et al., 2017). Multiple studies have shown that exposure to atmospheric aerosols is correlated with a wide variety of negative health outcomes (Brunekreef and Holgate, 2002; Dockery et al., 1993; Hoek et al., 2013; Nel, 2005). While it is not yet known which particle constituents are the main cause of particle toxicity, ROS, which summarises various oxygen-containing species with strong oxidative capacities, are implicated as a potential main contributor (Dellinger et al., 2001; Li et al., 2003; Tao et al., 2003).

In addition, it was recently shown that ~~molecules with multiple hydroperoxy and peroxy acid groups,~~ HOMs, which are suggested to form~~ed~~ through autoxidation in the gas phase, are highly relevant for the initial stages of SOA formation (Ehn et al., 2014; Rissanen et al., 2014). Many studies state that HOMs have O:C ratios of ≥ 0.7 (Mentel et al., 2015; Mutzel et al., 2015). There is no generally accepted definition of HOMs, but they typically contain multiple hydroperoxy and/or peroxy acid groups (Mentel et al., 2015; Rissanen et al., 2015).

Therefore, the characteri~~z~~sation and quantification of peroxy compounds in the particle phase has become an important issue. However, there is currently a lack of suitable analytical methods, which is exacerbated by the lack of appropriate standards for method development and validation. One subgroup of peroxy compounds are peroxy acids, which, apart from their relevance for atmospheric chemistry, are widely used as chemical reagents, disinfectants and bleaching agents (Holah et al., 1990; Luukkonen and Pehkonen, 2017; Milne, 1998; Ramirez, 2008; Reinhardt and Borchers, 2009). Due to their widespread practical applications, several methods have been developed both for the quantification of the overall peracid content (Davies and Deary, 1988; Greenspan and MacKellar, 1948), as well as separation and detection of specific peracids (Cairns et al., 1975; Effkemann et al., 1998; Kirk et al., 1992). These methods use relatively unspecific detectors such as flame ioni~~z~~sation, electrochemical and UV/VIS detectors. This poses a problem for the analysis of ambient particles, as they can contain several thousands of organic species, ~~especially given the lack of available~~ demonstrating the need for authentic standards. Mass spectrometry, in particular coupled with chromatography, provides a method to characteri~~z~~se and identify specific~~ peroxyacids~~ compounds. Recently, several studies have utilised mass spectrometry to analyse different types of organic peroxy compounds with potential atmospheric relevance (Witkowski and Gierczak, 2013; Zhao et al., 2018; Zhou et al., 2018; Ziemann, 2003). However, to our best knowledge no such studies exist for peroxy acids. In a previous paper, we synthesis~~z~~ed one cyclic and several linear aliphatic peroxy acids and showed their separation and detection with liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) (Steimer et al., 2017). This study revealed that all investigated peroxy acids show common and specific mass spectrometry fragmentation patterns, which could be used as diagnostics to identify unknown peroxy acids in complex organic mixtures. However, as all structures synthesised in Steimer et al. (2017) are likely not prominent in secondary organic aerosol, we expand in this study the characterisation of peroxy acids towards structures that are likely present in atmospheric SOA particles. Monoperoxypinic acids have~~s~~ been suggested as ~~a~~ potential products of α-pinene and β-pinene ozonolysis (Docherty et al., 2005) and have~~s~~ been tentatively identified in α-pinene and β-pinene SOA using online MS/MS (Reinnig et al., 2009; Zhou et al., 2018). They are suggested to form in the gas phase via HO_2 chemistry (Docherty et al., 2005). In this study, we have synthesis~~z~~ed three peroxypinic acids, ~~characterised~~ identified their structure via their MS/MS and NMR spectra and investigated their presence and stability in α-pinene SOA generated in laboratory experiments under varying conditions. The structural similarity of these peroxy acids with HOMs (present in a wide range of SOA particles) makes them ideal and unique proxies and surrogate standards for future studies aiming to quantify the role of HOMs in organic aerosols.

2 Experimental section

2.1 Chemicals and Synthesis

Sulf~~ph~~uric acid (H_2SO_4, 95-98%), hydrogen peroxide (H_2O_2, 50%, stabili~~z~~sed), α-pinene ($C_{10}H_{16}$, ≥ 98%), *cis-*pinonic acid, bromine, dioxane, diethyl ether and hydrochloric acid were bought from Sigma-Aldrich. D(+)-Camphoric acid ($C_{10}H_{16}O_4$, ≥ 99%) was purchased from Acros Organics. Dichloromethane was bought from Carl-Roth, sodium sulfate was supplied by Acros, sodium hydroxide was purchased from Merck and charcoal pellets were provided by Fluka. Water, formic acid (0.1% in water) and acetonitrile, all in OPTIMA® LC/MS grade, were purchased from Fisher Scientific.

*cis-*Pinic acid was synthesi~~z~~sed using a similar procedure as described by Moglioni et al. (2000). 2.8~~4~~ g *cis-*pinonic acid was dissolved in 50 mL dioxane. 8.2 g sodium hydroxide was dissolved in 196 mL water and loaded with 7.5~~49~~ g bromine (0 °C). The prepared sodium hydrobromite solution was added dropwise to the pinonic acid solution (30 min, −~~-~~15 °C). After 2 h of stirring at 0 °C and over~~-~~night (approx. 16 h) at room temperature, the resulting solution ~~has been~~was extracted three times each with 20 mL dichloromethane. 60 mL of a 40% sodium hydrogensulfate solution, prepared by dissolving sodium sulfate in water, was added to the water~~y~~ phase. The pH was set to 1 using hydrochloric acid. This solution was extracted 5 times using 5 x 40 mL diethyl ether. The collected ethereal~~ic~~ phases were dried using 1 g sodium sulfate. After filtration and evaporation, the slightly yellow powder was purified~~cleaned~~ by dissolving it in 2 mL diethyl ether and addition of 5 pellets of charcoal. After subsequent filtration followed by evaporation, the yield of *cis*-pinic acid was estimated to be 2.5~~4~~ g (88%) with a purity of 96% regarding the educt. ~~^{1}H NMR (CDCl$_3$) 1.01 (s, 3H), 1.25 (s, 3H), 1.95 (complex absorption, 1H), 2.14 (complex absorption, 1H), 2.39 (complex absorption, 3H), 2.79 (dd, J = 10.2 Hz, J' = 7.55 Hz, 1H).~~ To confirm the identity of the synthesised compound ^{1}H, ^{13}C, DEPT, COSY, HSQC and HMBC NMR spectra were collected using residual CHD_2CN as the internal standard. *cis*-Pinic acid: ^{1}H NMR (CD_3CN, 500 MHz) δ_H 0.94 (s, 3H, H5), 1.20 (s, 3H, H6), 1.82 (m, 1H, H2$_\alpha$), 2.03 (m, 1H, H2$_\beta$), 2.3 (m, 3H, H1,H8), 2.74 (dd, J = 10.3 Hz, J' = 7.9 Hz, 1H, H3). ^{13}C NMR (CD_3CN, 500 MHz) δ_C 17.8 (C5), 25.2 (C2), 30.0 (C6), 35.2 (C8), 38.9 (C1), 42.9 (C4), 46.4 (C3), 174.2 (C7), 174.4 (C9). A full overview of all NMR spectra used for the assignment is given in the supplement (Fig. S1-S6)

A mixture of diperoxypinic acid ($C_9H_{14}O_6$) and two different monoperoxypinic acids ($C_9H_{14}O_5$) was synthesi~~z~~sed from pinic acid ($C_9H_{14}O_4$) using a procedure adapted from Parker et al. (1957), who describe~~s~~ the synthesis of various aliphatic diperoxy acids. The structures of the synthesi~~z~~sed compounds are shown in Fig. 1. For the synthesis, 10 mg of pinic acid was dissolved in 22 µL of concentrated sulf~~ph~~uric acid and the resulting solution was cooled to 10-15 °C in an ice water bath. Under constant stirring, 13 µL of 50% H_2O_2 was slowly added dropwise to the solution. After 180 min reaction time, 100 µL of ammonium sulf~~ph~~ate solution (350 mg·ml^{-}~~-~~^{1}, 4 °C) was added to the product solution. Since no precipitate was formed, the solution was mixed with 0.5 ml 20:80 water:acetonitrile and stored in a freezer (−~~-~~22 °C) until further analysis. The product solution consists of two phases, of which the upper one (acetonitrile phase) was used for analysis. To confirm the identity of the synthesised products, the monoperoxypinic acid and diperoxypinic acid fraction of the chromatographic separation were collected four times each and the two resulting solutions were dried at 30 °C under a steady flow of nitrogen and then dissolved in deuterated acetonitrile for subsequent NMR measurements. The NMR spectra of the monoperoxypinic acid fraction confirm that both monoperoxypinic acid isomers are present. However, they are not stable under the present conditions and have largely already reacted back to pinic acid by the time of the first measurement. Additional spectra taken several hours after the first one show a continuing decay into pinic acid. The NMR spectra of the diperoxypinic acid fraction are initially dominated by diperoxypinic acid, although both monoperoxypinic acid isomers and pinic acid are also present. Spectra taken several hours after the initial measurement show a marked increase in pinic acid and both monoperoxypinic acid isomers as diperoxypinic acid decays further. A more detailed discussion of the NMR results and corresponding figures (Fig. S7-S17) can be found in the supplement.

2.2 Flow tube experiments

An aerosol flow tube (2.5 L) was used to produce α-pinene SOA. An overview of the setup for sampling under humid conditions is shown in Fig. 2. Ozone (O_3) was produced by irradiating a flow of synthetic air (200 mL/min) with a UV-lamp (185/254 nm, Appleton Woods®). The resulting average O_3 concentrations were 21-22 ppm under dry conditions and 16-19 ppm under humid conditions as some of the ~~ozone~~ O_3 was removed in the Gore-Tex tube of the humidifier (~~see~~ Fig. 2). Gaseous α-pinene was introduced into the flow tube by passing N_2 (200 mL/min) over 500 µL of liquid α-pinene (about ~~300~~ 340 ppm initial concentration, measured by PTR-MS according to the procedure described in Giorio et al. (2017)), ~~resulting~~ which results in a ~~reaction~~ residence time of approximately 6.3~~25~~ min. Under these conditions, the reaction is limited by O_3, which according to model calculations is consumed within ~20 s under both humid and dry conditions. The lifetime of O_3 and α-pinene in the flow tube was estimated using the AtChem (http://atchem.leeds.ac.uk) numerical box-model alongside the Master Chemical Mechanism (MCM) v3.3.1 (http://mcm.leeds.ac.uk) (Jenkin et al., 1997; Saunders et al., 2003). For the experiments at higher humidity (~85%), a humidifier was added to the setup. A scanning mobility particle sizer (SMPS) was used to monitor the concentration of produced SOA before and after sample collection. The SMPS consists of a TSI 3080 differential mobility analyser (DMA) connected to a TSI 3775 condensation particle counter (CPC). The average particle mass concentration in the flow tube was about $5 \times$ ~~·~~10^4 µg·m^3, assuming a density of 1 g·cm^3, with a mode of 200 nm for the number concentration. Under these conditions, α-pinene partitioning to the particles is still negligible (<1%) and while wall partitioning could be significant, it is unlikely to directly modify the observed aerosol composition due to the lower volatility of the products. The produced α-pinene SOA was collected on Durapore® membrane filters (0.1 µm pore size, 47 mm diameter, Merck) for a sampling period of 45 ~~-~~min~~utes~~. Partitioning of α-pinene followed by condensed-phase reactions on the filter might occur and could change the aerosol composition compared to lower mass loadings, although the charcoal denuder should have removed the majority of organic gases and O_3, making this less likely. After sample collection, 100 µL of a 0.60 mg/L camphoric acid solution (20:80 H_2O:ACN) was added to each filter as an internal standard. The filters were extracted by vortexing in 1.5 mL ACN for 5 min. The extracts were then evaporated down to a volume of 300 µL ~~at 30°C~~ under a steady flow of nitrogen at 30°C to minimize the time between collection and analysis. While the increased temperature might lead to thermal decomposition, this effect should be small and is likely outweighed by the reduction of the total analysis time. As a final step, 1.2 mL of 0.1% formic acid in water was added to better match initial mobile phase conditions of the HPLC analysis.

To investigate the influence of humidity on the formation of monoperoxypinic acid, a total of 13 filter samples were collected: 7 under dry conditions (≤3% RH), and 6 for α-pinene oxidation at ~85% RH. The average filter mass loading was 0.87 mg for the dry and 0.55 mg for the humid oxidation. All filters were extracted immediately after sampling. Three LC-MS/MS runs were conducted for each filter extract.

The degradation of peroxypinic acid in α-pinene SOA was investigated by subsequently collecting SOA on four filters under dry conditions. After collection of the final filter sample, the filters were cut into quarters and divided into four identical composite samples, containing one quarter from each filter. The first composite sample was extracted immediately, following the procedure described in the introduction to section 2.3. The three additional composite samples were extracted after being stored in their filter boxes at room temperature and under protection from UV radiation for up to 70 h to simulate typical field sampling conditions. All extracts were analysed by HPLC-MS/MS multiple (2-5) times.

2.3 HPLC-MS/MS Analysis

All samples were analysed via HPLC-ESI-MS/MS. An Accela system (Thermo Scientific, San Jose, USA) equipped with a T3 Atlantis C18 column (3 µm; 3.0 × 150 mm; Waters, Milford, USA) was used for the chromatographic separation. The detector was a high-resolution LTQ Orbitrap Velos mass spectrometer (Thermo Scientific, Bremen, Germany) with a heated electrospray ioni~~z~~sation (HESI) source. All data were analysed with Thermo Xcalibur 2.2.

For analysis of the synthesi~~z~~sed standard, 10 µL of the product mixture were diluted with 1 mL of an 80:20 water:acetonitrile mixture. For the flow tube experiments, filters were extracted according to the procedure described in the previous section and measured without further sample processing.

Pinic acid and its synthesi~~z~~sed peroxy acids were separated using gradient elution at a flow rate of 200 µL/min. The mobile phase was composed of a mixture of 0.1% formic acid in water (solvent A) and acetonitrile (solvent B). The initial concentration of 20% B was kept constant for ~~two~~ 2 min~~utes~~ and then increased to 23% over the course of 20 min. ~~After this~~Thereafter, it was further increased to 90% within the next 6 min. Over the next 5 min, it was then decreased back to 20% and subsequently kept at this concentration for an additional 10 min, resulting in a ~~method~~ total analysis time of 43 min ~~total length~~.

The mass spectrometer was calibrated using Pierce$^{®}$ ESI Negative Ion Calibration Solution (Thermo Scientific, Rockford, USA). All samples were analysed in negative ionization mode, using the following source parameters: spray voltage −3.3 kV, source heater temperature 250 °C, capillary temperature 275 °C, sheath gas flow 40 arbitrary units, auxiliary gas flow 10 arbitrary units, no sweep gas flow and S-lens RF level 70%. Mass spectra were collected in full scan mode over a mass range of *m/z* 100−650, using the lock mass of the deprotonated dimer of formic acid at *m/z* 91.0037 and a resolution of

100 000 at *m/z* 400. For the majority of measurements, alternating MS/MS scans were performed using a global mass list including the masses of deprotonated pinic, monoperoxypinic and diperoxypinic acid as well as deprotonated camphoric acid, which was used as an internal standard in the flow tube experiments. The MS/MS scans were performed with a resolution of 60 000, an isolation width of 4 mass units and a mass range that was *m/z* 50−220 for pinic acid and its derivatives and 50−210 for camphoric acid. The collision energy level was 27% for pinic acid and its derivatives and 22% for camphoric acid. A few additional runs were performed with isolation width 1.5, leading to a strongly reduced signal of monoperoxypinic acid isomer I. For investigation of the monoperoxyacid dimeric adduct, alternating MS^3 scans were performed instead with the mass of the deprotonated monoperoxypinic acids selected for the second fragmentation. In this case, the collision energy level was 27% for both fragmentation steps, the resolution was 60 000, the mass range was *m/z* 55−410 and the isolation width was 4 mass units for the first fragmentation and 2.5 mass units for the second ~~fragmentation~~one. In all cases, collision-induced dissociation (CID) was used to induce fragmentation.

2.4 Evaluation of MS/MS spectra

Elemental compositions were assigned with a mass tolerance of 6 ppm, including only the elements carbon, oxygen and hydrogen. The list of MS/MS fragments contains all *m/z* values smaller than the precursor ion which have a relative abundance above the chosen threshold of >1%. The same procedure was repeated with a background subtracted version of the spectrum. The final list of product ions is based on the background subtracted mass list, but additionally excludes *m/z* values which did not have an assigned elemental composition, which could be dismissed as product ions based on their assigned elemental composition or whose extracted ion chromatogram showed a poor overlap with the base peak chromatogram of the MS/MS measurement. While product ions and their relative abundances were selected based on the background subtracted mass list, the masses themselves were taken from the raw data as they showed higher mass accuracy. Since the chromatographic peaks of the two monoperoxy acids overlap (~~see~~ Fig. 3), special care was taken to separate the two spectra. Only the third of the chromatographic peaks furthest removed from their neighbour was used for the evaluation. In addition to the monomers, there were also dimeric adducts of monoperoxypinic acid detected at the same chromatographic peaks. Since they have the same retention time as the monomers, these compounds are ESI artefacts and not actually present in the sample. MS^3 spectra were taken for the mass of the dimeric monoperoxypinic acid adduct (*m/z* 403.16159), which is more prominent for isomer I. The resulting MS^3 spectrum of the dimeric adduct from the isomer I peak shows the same ~~fragments~~ product ions as the MS/MS spectrum of the monomer, but with lower abundances ~~of fragments which~~for those common to the two isomers ~~have in common~~. It was therefore taken to be closer to the pure spectrum of isomer I and used to characterise MS/MS fragmentations of that compound. Similarly, initial MS/MS conditions lead to low isolation efficiency of the deprotonated molecule of isomer I ~~quasimolecular ion~~ so that the MS/MS spectrum for isomer II was not significantly influenced by isomer I.

2.5 Data analysis of flow tube measurements

To investigate the presence of peroxypinic acid in the samples, extracted ion chromatograms of the peracid main ~~fragments~~ product ions were selected. If a peak was found at the appropriate retention time, its MS/MS spectrum~~a~~ was compared to that of the corresponding standard. The integrated peak of the extracted ion chromatogram of *m/z* 183.06 was used for the quantitative analysis of monoperoxypinic acid isomer II. It was normali~~z~~sed to the peak area of the main ~~fragment~~ product ion of camphoric acid, *m/z* 155.10, and to the mass loading of the filter.

3 Results and~~&~~ discussion

3.1 Liquid chromatography separation of the synthesi~~z~~sed standards

The chromatogram shows that pinic acid and its peroxy acid derivatives, synthesised as described above, elute from the HPLC column in order of decreasing polarity, with pinic acid eluting first, followed by the two monoperoxy pinic acids and finally diperoxypinic acid (Fig. 3). While the acid and diperoxy acid are clearly separated from the monoperoxy acids, the two monoperoxypinic acids strongly overlap due to similar polarities. Peaks were assigned based on deprotonated analyte ions ([M~~-~~ − H]~~$^-$~~$^-$), as well as the occurrence of different product ions~~fragmentations~~ for the two monoperoxypinic acid isomers.

3.2 Mass spectrometry of pinic acid and the synthesi~~z~~sed standards

All four analytes were detected as ~~quasimolecular~~ deprotonated molecules, i.e. [M~~-~~ − H]~~$^-$~~$^-$ ions (Fig. S18). In the case of pinic acid and the two monoperoxypinic isomers, the ~~quasimolecular ion~~deprotonated molecule is dominant in the chromatographic peak. In contrast, the mass spectrum of diperoxypinic acid was dominated by [M – H]$^-$~~[M-H]$^-$~~ ions of pinic and monoperoxypinic acid, which were about an order of magnitude more abundant than ~~the~~ that of diperoxypinic acid~~ [M-H]$^-$ ion~~. As described in previous papers (Harman et al., 2006; Steimer et al., 2017), this likely indicates ~~an~~ electrochemical reduction of the analyte (i.e., diperoxypinic acid) in the ion source. The pinic acid [M – H]$^-$~~quasimolecular~~ ion was also present in the monoperoxypinic acid spectra, although about an order of magnitude less abundant than that of~~the~~ monoperoxypinic acid~~ quasimolecular ion~~, which follows the trend of less efficient electroreduction of monoperoxy vs. diperoxy acids ~~observed~~ reported in our previous paper (Steimer et al., 2017). Tandem mass spectrometry was performed on all four analyte [M – H]$^-$~~[M-H]$^-$~~ ions, the results of which are summari~~z~~sed in Table 1~~Tab. 1~~. A graphic presentation of the MS/MS data can be found in the supplement (Fig. S19). The ~~fragments~~ product ions observed for~~ the~~ pinic acid~~ MS/MS~~ are in line with results from previous studies (Glasius et al., 1999; Yasmeen et al., 2011), where loss of CO_2 was observed as the main fragmentation process.

All neutral losses~~ fragments~~ observed for pinic acid also occurred for both of the monoperoxypinic acid isomers. However, as previously observed for aliphatic peroxy acids, there are additional loss processes present compared to the acid (Steimer et al., 2017), four of which are shared between the two isomers. Two of the resulting fragment ion types, [M~~-~~ − CH_2O_2]$^{-}$~~-~~ and [M − ~~-~~CH_4O_4]$^{-}$~~-~~, were observed in our previuous study for linear monoperoxydicarboxylic acids, while [M − ~~-~~$C_2H_2O_4$]$^{-}$~~-~~ was also observed for the only measured cyclic monoperoxydicarboxylic acid (monoperoxycamphoric acid) and [M − ~~-~~$C_2H_2O_3$]$^{-}$~~-~~ was not detected for any of the peroxy acids investigated in our previous study (Steimer et al., 2017).

The MS/MS spectra of the two isomers can be easily distinguished. While the main difference lies in the relative abundances of the various ~~fragment~~ product ions, the spectrum of isomer I also shows several ~~fragments~~ product ions not present for isomer II. Using~~,~~ this information, it was possible to determine that the electroreduction of diperoxypinic acid in the ion source predominantly leads to formation of isomer II. Based on the available literature (Szmigielski et al., 2006; Yasmeen et al., 2010, 2011), we suggest potential fragmentation pathways for the two isomers (Fig. S20). This allows the tentative assignment of isomer I and II as the monoperoxy pinic acid isomer with a methyl peroxycarboxyl substituent and a peroxycarboxyl substituent, respectively.

The diperoxypinic acid spectrum is dominated by loss of CHO_3, a process which was also observed for monoperoxycamphoric acid and monoperoxypinic acid isomer I. Two other relatively abundant neutral losses are peracid-specific fragments: H_2O_2, which was previously also observed in linear diperoxy acids, and $C_2H_2O_5$, which gives a minor contribution to the spectrum of monoperoxypinic acid isomer I.

In summary, the three peroxy acids synthesised here showed unique trends in fragmentation patterns for mono- and diperoxy acids, respectively. Some of these fragmentations were also observed for the 15 peroxy acids we characterised earlier (Steimer et al., 2017). The consistent fragmentation patterns of peroxy acids suggests that they might be suitable to identify unknown peroxy acids in SOA, e.g. as HOMs or ROS markers.

3.3 Flow tube experiments

The formation of peroxypinic acids in SOA formed through ozonolysis of α-pinene was investigated using the flow tube set up detailed above. The MS/MS spectra of the filter extracts showed presence of both monoperoxypinic acid isomers (both suggested to form during α-pinene ozonolysis (Docherty et al., 2005; Reinnig et al., 2009)), while there was no evidence of diperoxypinic acid formation. While both monoperoxypinic acid isomers were formed during α-pinene oxidation, the peak of isomer I was often too small for reliable integration, so that only isomer II was chosen for the following quantitative analyses. Even though isomer II could be reliably detected, it is only a minor product of the α-pinene oxidation, with about 1/5500 the peak area of pinic acid.

3.3.1 Humid vs. dry conditions

The relative yields of monoperoxypinic acid under dry and humid ozonolysis conditions were investigated experimentally and *via* the AtChem box model (https://atchem.leeds.ac.uk). The complete reaction scheme for the degradation of α-pinene was extracted from the ~~Master Chemical Mechanism (~~MCM~~)~~ v3.3.1 (Jenkin et al., 1997; Saunders et al., 2003) via the MCM website (http://mcm.leeds.ac.uk/MCM). Gas-phase only simulations were performed for dark ozonolysis with [α-pinene]$_0$ = 300 ppm and $[O_3]_0$ = 20 ppm. It is known that the gas-phase formation of peroxy acids can proceed via HO_2 chemistry, without direct involvement of H_2O (Docherty et al., 2005; Eddingsaas et al., 2012). The calculated yield of monoperoxypinic acid per O_3 molecule was ~6 × 10^{-5} (~ 1.2 ppb) under dry conditions~~. This relative yield~~ and was insensitive to RH (0-100%) and initial precursor concentrations (1-300 ppm).~~,~~ This confirms ~~suggesting an~~ the unimportant role for water vapour in the gas-phase ~~mechanism~~formation of monoperoxypinic acid not only as a reactant, but also in terms of indirect effects on e.g. the concentrations of precursor species such as Criegee intermediates. The yield of monoperoxypinic acid was ~1/500 that of pinic acid in the simulations, compared to the experimental estimate above (~1/5500).

In the condensed phase, however, the formation of peracids from the carboxylic acid is reversible, with presence of liquid water shifting the equilibrium towards the acid (d’Ans and Frey, 1912; Parker et al., 1955). Increased humidity, leading to an increased fraction of water in ~~in~~ the particle phase, could therefore lead to less peroxypinic acid in α-pinene ozonolysis SOA. We proceeded with experiments to investigate whether humidity-dependent gas-particle partitioning and/or condensed-phase reactions, not accounted for in the model, could influence peroxy acid yields.

The concentration of monoperoxypinic acid isomer II in SOA was compared under dry (≤3% RH) and humid (~85% RH) conditions. The results of the comparison are shown in Fig. 4. Within the current limits of uncertainty, no difference in monoperoxypinic acid production was found for the two reaction conditions. This indicates that hydrolysis of monoperoxypinic acid is not a significant loss process under the studied conditions (i.e. reactant concentrations and reaction time). Available studies of the hydrolysis of peracetic acid show that its hydrolysis kinetics strongly depend on the reaction conditions, such as temperature and pH (Dul’neva and Moskvin, 2005; Yuan et al., 1997), leading to large variations in decomposition rates. The fact that the peroxypinic acid yield per SOA mass does not depend on humidity agrees with observations made by Docherty et al., (2005), who found no dependence of the organic peroxide yield per SOA mass on humidity. Previous studies of the humidity dependence of individual peroxy compounds were focused on small molecules predominantly residing in the gas phase (e.g. Hasson et al., 2001; Huang et al., 2013) and are therefore not directly comparable with our results. However, the fact that different correlations with humidity were found for different peroxy compounds demonstrates the need for investigation of individual compounds. The main factors limiting precision of ~~the~~ our measurement are low signal intensity, uncertainty of the measurement of filter mass loading and peroxypinic acid degradation on the filter, as described in the following section.

3.3.2 Peroxy acid degradation over time

We investigated the stability of monoperoxypinic acid isomer II in SOA over time when the filter was stored at room temperature after collection. In many studies ~~characterising~~ which characterise SOA composition in detail at~~on~~ a molecular level, filter samples, especially from field campaigns, are collected many hours to days or weeks before analysis. While these samples are usually kept at low temperatures for long-term storage, they are collected at room temperature, which can take longer than 24 h and there is often significant delay between sampling and storage. For thermally unstable compounds such as peroxides and peroxy acids, this might result in decomposition prior to analysis and thus risks underestimating the abundance of such compounds.

Monitoring of the amount of peroxy acid on the collected filters over almost three days clearly shows that this compound significantly degrades (Fig. 5). About 60% of monoperoxypinic acid is lost within the first five hours. Given that the measured samples were composites of four subsequently collected filters, the average age of the SOA sample before extraction is ca. 100 min. Therefore, a significant amount of monoperoxypinic acid will already have been lost at the time of analysis. Repeated measurements of the extracts over 22 hours showed that there is also a change in concentration over time in the liquid phase, however significantly less pronounced with a maximum of a factor two difference to the initial measurement. We therefore attempted to measure all extracts as soon as possible after extraction, using the same number of repeats. This was not always possible for the experiment shown as purple diamonds in Fig. 5, contributing to the uncertainty of the results.

4 Conclusions

In this study, we successfully synthesi~~z~~sed three peroxypinic acids and showed that they can be distinguished from each other and the analogous carboxylic acid via their retention times in HPLC-MS and their specific MS/MS spectra. This technique can therefore be used to identify peroxypinic acids in SOA samples. We have shown that one of the peroxypinic acids, monoperoxypinic acid isomer II, was present in laboratory-generated α-pinene SOA. There was no observed effect of humidity on the production of monoperoxypinic acid from α-pinene, i.e. the reactions times in our flow tube set up were possibly too short to observe any potential decay due to hydrolysis. It was shown that monoperoxypinic acid quickly degrades, with about 60% lost within the first 5 hours. This demonstrates that filters need to be analysed as soon as possible after collection to avoid serious underestimation for such compounds, which presents a major problem particularly during field campaigns, where such immediate analysis is often not feasible. Ideally online techniques would need to be developed to quantify such unstable compounds in atmospheric aerosols.

Acknowledgement

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Table 1: MS/MS fragmentations of [M − ~~-~~H]$^{-}$ ions from pinic acid and its peroxyacid analogues.

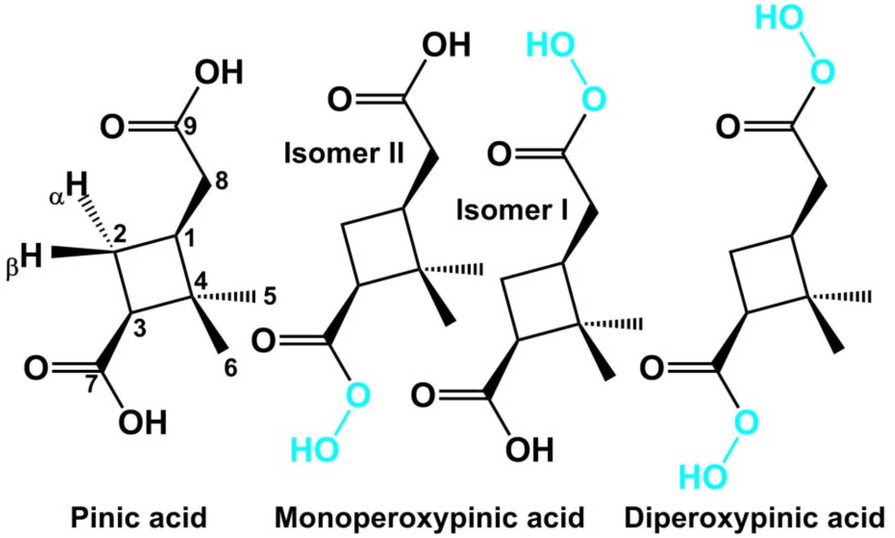
Compound	Deprotonated molecule [M − ~~-~~H]$^{-}$	*m/z* (Δ ppm)	Product ion *m/z* (rel. abund.)[a]	Neutral loss(es)

---

[a] Average of three MS/MS spectra, with exception of monoperoxypinic acid isomer I (average of two MS^3 spectra, see section 2.4 for discussion)

Pinic acid	$C_9H_{13}O_4^-$	185.08193 (-0.002)	141.09194 (100)	CO_2
			167.07127 (16)	H_2O
			123.08155 (4)	CH_2O_3
Monoperoxypinic acid isomer I	$C_9H_{13}O_5^-$	201.07706 (1.060)	111.08149 (100)	$C_2H_2O_4$
			155.07127 (38)	CH_2O_2
			139.07639 (37)	CH_2O_3
			140.08423 (10)	CHO_3
			157.08694 (8)	CO_2
			183.06619 (8)	H_2O
			127.07643 (5)	$C_2H_2O_3$
			84.02166 (3)	$C_5H_9O_3$
			115.00367 (3)	$C_5H_{10}O$
			129.05568 (3)	$C_3H_4O_2$
			99.04513 (2)	$C_4H_6O_3$
			111.04514 (2)	$C_3H_6O_3$
			121.06583 (2)	CH_4O_4
			184.07401 (1)	OH
			95.08662 (1)	$C_2H_2O_5$
Monoperoxypinic acid isomer II	$C_9H_{13}O_5^-$	201.07711 (1.293)	183.06605 (100)	H_2O
			157.08678 (35)	CO_2
			139.07625 (31)	CH_2O_3
			155.07116 (10)	CH_2O_2
			111.08142 (5)	$C_2H_2O_4$
			127.07635 (2)	$C_2H_2O_3$
			121.06577 (2)	CH_4O_4
Diperoxypinic acid	$C_9H_{13}O_6^-$	217.07232 (2.573)	156.07910 (100)	CHO_3
			155.07132 (16)	CH_2O_3
			111.08152 (13)	$C_2H_2O_5$
			183.06628 (7)	H_2O_2
			171.06625 (3)	CH_2O_2
			173.08189 (2)	CO_2
			199.06122 (1)	H_2O
			74.00093 (1)	$C_7H_{11}O_3$

			127.07646 (1)	$C_2H_2O_4$



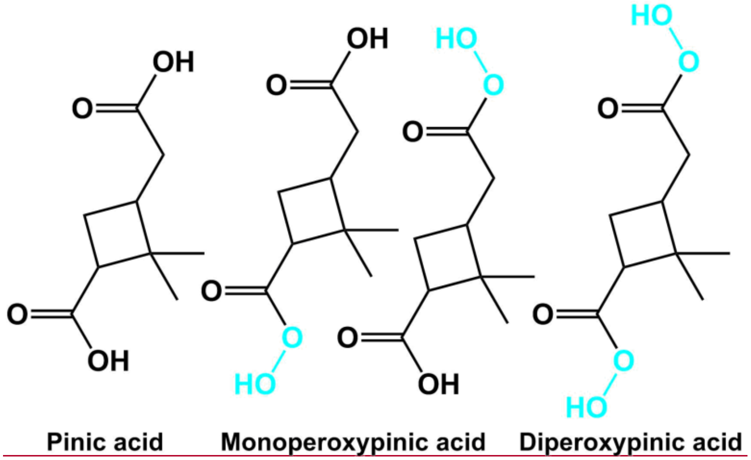


Figure 1 Structures of *cis-*pinic acid and its peroxy acid derivatives synthesised and characterised in this study.

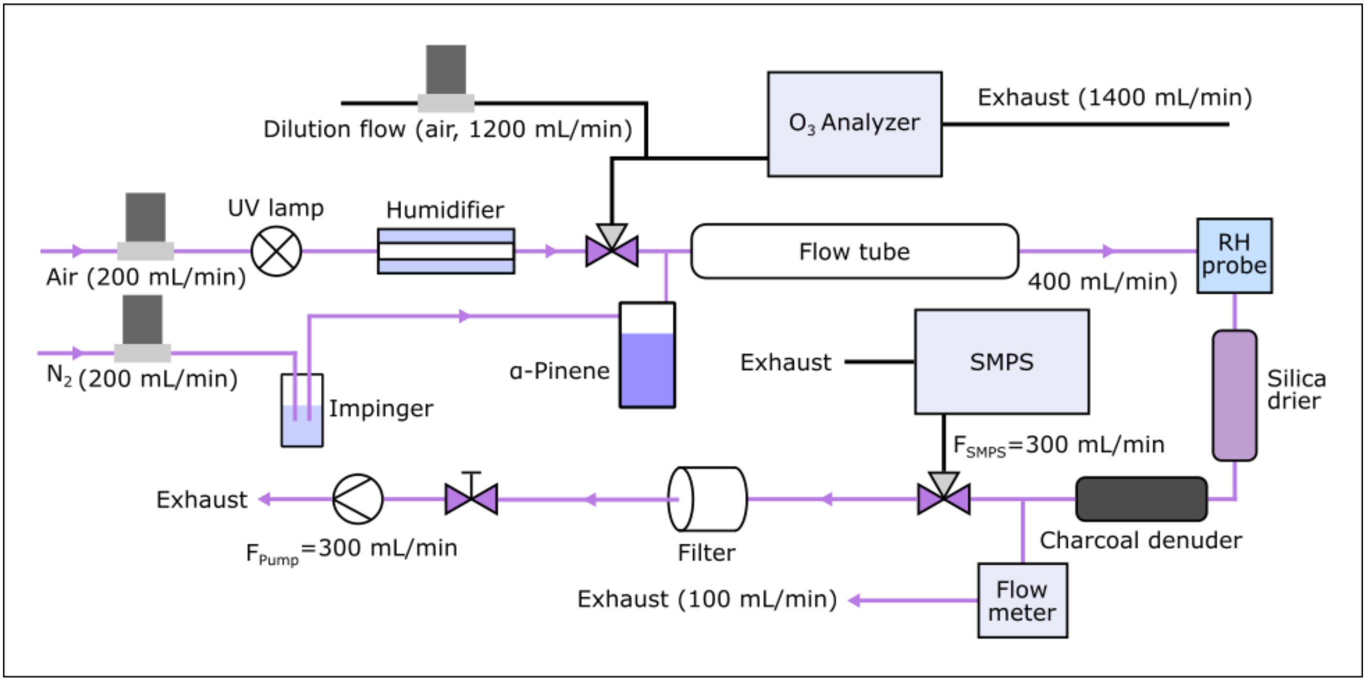
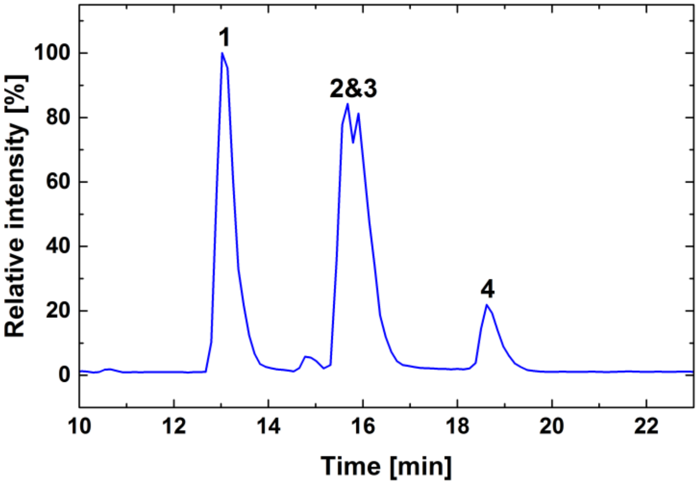


Figure 2: Flow tube setup for oxidation under humid conditions. The pink lines show the gas and aerosol flow path during sample collection, when O_3 analyser and SMPS are not connected.



5 **Figure 3: Base peak chromatogram of the synthesised mixture, showing the separation of pinic acid (1), monoperoxypinic acid isomers I and II (2, 3) and diperoxypinic acid (4).**

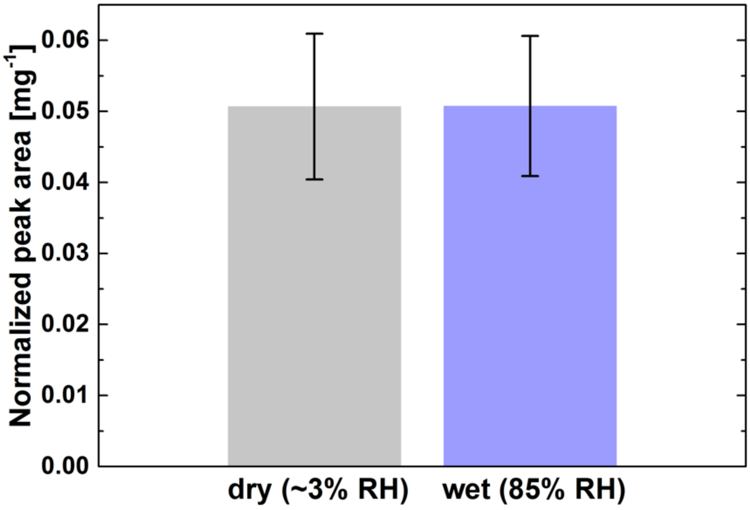


Figure 4: Monoperoxypinic acid isomer II as a product of α-pinene oxidation under dry and humid conditions; error bars show the standard deviation between repeat measurements. The peak area was normali~~z~~sed to the peak area of the internal standard and the aerosol mass on the filter.

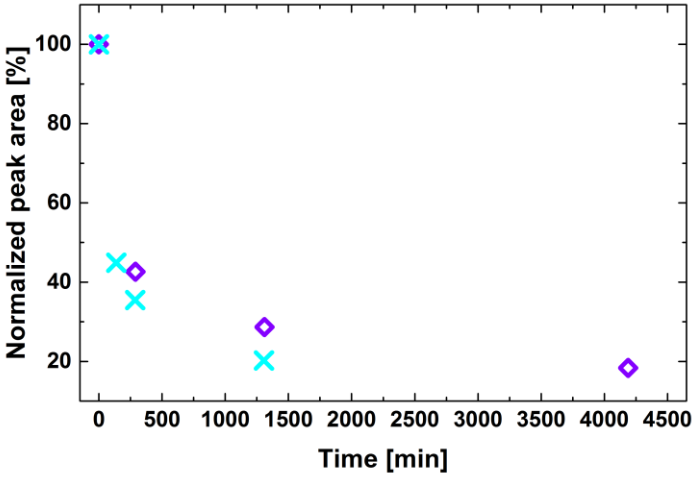


Figure 5 : Degradation of monoperoxypinic acid isomer II on the filter illustrating its short lifetime of only a few hours. Diamonds and crosses represent two different repeats of the degradation experiment.