Responses to reviewers' comments for manuscript

α-pinene secondary organic aerosol at low temperature: Chemical composition and implications for particle viscosity

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We thank the Reviewers for their evaluation of the manuscript. Replies to the individual comments are directly added below them in italics. Please note that only references that are part of the replies to the comments are listed in the bibliography at the end of this document. References in copied text excerpts from the manuscript are not included in the bibliography. Page and line numbers refer to the original manuscript text.

Reviewer #1 *(responses in italics)*

This is a concise manuscript that presents necessary research into the Tmax interpretation from particle measurements utilising the FIGAERO ToF CIMS. I feel the results represent the work and analysis accurately, although I would suggest the following 2 points should be further investigated, as well as additional comments below.

1) I feel the application of a maximum calibration is inadequate for this work, or should be further investigated. The compounds measured are neither known to possess the

maximum sensitivity nor in any way validated by calibrations presented. The further discrepancy with minimal mass loadings between the AMS OA and CIMS CHOI further support inaccuracies in this determination. N2O5 has been determined to possess the maximum sensitivity in the CIMS (Lopez-Hilfiker et al., 2015) which possesses no similar functionality or mass. Calibration of a compound which can represent the products is necessary to validate any quantification from the CIMS measurements.

It is not the goal of this manuscript to quantify total mass loadings, but to discuss relative changes in mass spectra and maximum desorption temperatures of individual compounds due to varying temperature and relative humidity (RH) conditions. Our main results are therefore largely independent of absolute mass concentrations. We clearly state in the manuscript (paragraph 3.1) that the FIGAERO-CIMS mass loadings represent a lower limit. Having said this, the ratios of the FIGAERO-CIMS mass concentrations to total organic particle mass measured by AMS we present here are well in line with earlier determinations of this ratio for α-pinene SOA from the laboratory or field, where the collisional limit sensitivity was applied to FIGAERO-CIMS data (e.g. Lopez-Hilfiker et al., 2016; Mohr et al., 2017). In addition, Lee et al. (2014) showed that the sensitivity to individual organic acids of the FIGAERO-CIMS using I⁻ as reagent ion approaches the value of the collisional limit for larger molecules (m/Q 300 and larger), which make up the major fraction of the signal in our mass spectra.

2) A variation of RH and temperature is interpreted to change the Tmax of thermograms from CIMS. It would be possible to calibrate for inactive or isotopically labelled species in varying temperatures and RHs to isolate these variables and prove via independent tests that they are indeed responsible for variations in Tmax through changes in viscosity.

Earlier studies have shown that CIMS thermograms and corresponding Tmax are very reproducible under stable conditions (Lopez-Hilfiker et al., 2014). We therefore expect the observed variations in Tmax to result from the changes in particle viscosity. We agree with the reviewer that the separation of the temperature and RH variables is very important. As we explain in lines 343–348 (section 3.3) of our manuscript, the temperature in AIDA should not have an effect on the variation of Tmax for the different experiments, as it was always 223 K: "Since the temperature was 223 K in AIDA for

all experiments discussed here, the observed differences in Tmax, and presumed viscosity, cannot be directly explained by differences in temperature. In addition, during desorption of compounds with the FIGAERO, particles are actively heated (with heat transfer assumed to be immediate), and are not evaporating under equilibrium conditions. Presumed variations in particle viscosity based on observed variations in Tmax must therefore be due to variations in particle chemical composition, and/or RH differences". However, temperature may have played an indirect role for Tmax variations: The temperature during SOA formation in our experiments was either 223 or 296 K, which may have influenced the chemistry (chemical composition, oligomerization degree, etc.), and thus particle viscosity. We state this e.g. in lines 289–290: "[...] the differences observed in mass spectral patterns between the two types of experiments are a consequence of both temperature and precursor concentration differences." The influence of RH on Tmax variations is explained in the manuscript in e.g. lines 357–358, lines 362–365, and Fig. 8.

Line 13 – Change comma to semi-colon: Karlsruhe Institute of Technology; the Aerosol

Done.

Line 21 – insert "the" with "the filter for gases or utilising the filter for gases"

We replaced "with" by "coupled to a".

Line 45 – replace like with "such as"

Done.

Line 46 to 48 – Very short sentences. I advise to rephrase or extend

The two sentences were combined to one.

Line 56 – VOC should be VOCs

Corrected throughout the manuscript.

Line 60 - Give a range of upper contribution of SOA from monoterpene oxidation products

Due to a lack of published numbers, the sentence was changed to : "SOA from monoterpenes is very important in the boreal regions in summertime, and the fraction

*of total SOA mass from monoterpene oxidation products is estimated to be ~15 %
globally (Heald et al., 2008)."*

Line 63 – Superscript radical charge

*For clarification, the sentence was changed to: "The reactions of α-pinene with O_3,
and the radicals OH and NO_3 lead to […]".*

Line 66 – use O3 instead of ozone as already defined previously or maintain ozone
throughout

O_3 is used throughout the manuscript.

Line 77 – "SOA is a highly dynamic system" – It does have a highly dynamic system

but is phrased badly

*Sentence rephrased as following: "SOA is highly dynamic and continually evolves in
the atmosphere, becoming increasingly oxidized, less volatile, and more hygroscopic
[…]".*

Line 85 - I would restructure sentence not to start with "E.g."

*Sentence rephrased as following: "Water diffusion coefficients in the water-soluble
fraction of α-pinene SOA, were e.g. measured for temperatures between 240 and 280
K."*

Line 125 – Temperature should be temperatures

Corrected.

Line 130 – Instead of "right next to" describe distance or rephrase

*Sentence rephrased as following: "The APC (Aerosol Preparation and
Characterization) chamber (Möhler et al., 2008) is a 3.7 m^3 sized stainless steel vessel,
situated at a distance of 3 m from AIDA and connected to it by a 7 m stainless steel tube
of 24 mm inner diameter."*

Line 159 – Relative humidity (RH) has been defined a number of times in the paper so
the acronym can be used throughout rather than repetition

Corrected throughout the manuscript.

Line 177 – Can a correlation be quantified between AMS and SMPS?

Correlation coefficients and slopes were calculated for the experiments shown here, and the values were added to the manuscript as following: "(slopes are between 0.87−1.04 except for CD experiment (2.2) possibly due to the lower transmission efficiency in the aerodynamic lens of the AMS for sub-100-nm particles, Pearson's correlation coefficients are between 0.87−0.98 for the experiments presented here)."

Line 179 - 180 Capitalise all or none of the letters used for the instrument acronym

Corrected as suggested.

Line 181 – Restructure sentence

R: Sentence restructured as following: "During the gas phase measurement, gases were sampled via a Fluorinated Ethylene Propylene (FEP) tube of 0.83 m length while particles were simultaneously collected on a Teflon (Polytetrafluoroethylene, PTFE) filter [...]".

Line 191 – Why was the maximum sensitivity attributed to these products? Furthermore, was a calibration performed to define this or merely taken from another CIMS sensitivity?

Compare to the response to the first comment.

Line 192 – Were any backgrounds performed with no alpha pinene and varying ozone concentrations to quantify background oxidation of the chambers?

Each experiment was started by measuring background air and background particles in AIDA before addition of any trace gases. For type 2 experiments, we did not observe a significant background before the SOA transfer from the APC chamber and initial particle number concentrations were typically below 1 cm^{-3}. For type 1 experiments, O_3 was usually added first and α-pinene was added last. We observed only a small increases in both gas mixing ratio and particle mass ($<0.01 \mu g \text{ m}^{-3}$) after O_3 addition. However, these background concentrations were also negligible compared to the increase by the SOA generated (>1000 fold for particle mass). The following sentence was added in the manuscript: "[...] For type 2 experiments, backgrounds were negligible with initial particle number concentrations below 1 cm^{-3}. For type 1 experiments, we observed a small increase in both gas mixing ratio and particle mass

(<0.01 μg m⁻³) after O₃ addition, which was subtracted from the mass loadings presented here. However, the background and the increase induced by O₃ addition were negligible compared to the increase by the SOA mass (>1000 fold for particle mass)."

Line 195 – How was this calculated- can this temperature account for change in properties of deposited compounds on the filter? Can it be described how this was accounted in the interpretation of the results?

The temperature increase for the particle inlet can be calculated as described by Fitzer and Fritz (1989) using the dimensions of the stainless steel tube and the insulation material Armaflex, the corresponding heat conductivities, and the flowrate through the sampling tube. As we state in lines 195–197, due to the possible increase in temperature of the sample during deposition, we cannot entirely rule out partial evaporation of water or semi-volatile organic compounds. It is therefore possible that in our particle phase data highly volatile compounds may be slightly underestimated. Since temperature and sampling conditions were kept the same for all four experiments discussed in the manuscript, we assume the artefacts to be similar and thus our main results not to be affected by them. The corresponding reference was added to the manuscript.

Line 205 – Please provide a validation as to why the measurements were not wall loss corrected and why this is interpreted as not necessary

A detailed characterization of wall losses in the AIDA aluminum chamber using empirical data and the COSIMA model (Naumann, 2003) is subject of an upcoming publication. In our manuscript we are mostly interested in the relation between particle chemical composition and maximum desorption temperature (Tmax), which is completely independent of wall losses.

Line 213 to 214 – The AMS observes a lower limit range of total organic mass (67.5) than the CIMS (97.8), which I cannot see possible. I disagree with applying a maximum sensitivity, which I describe below, but also this surely should then result in a minimal concentration. Here it seems the CIMS can overestimate the low concentrations and underestimate/represent the high concentrations. The selective ionisation and change in sensitivity, as stated on line 221, would make the CIMS mass always less than the AMS as the maximum sensitivity is applied.

As we state in lines 225–228, the reason why the AMS observes lower organic mass concentrations (67.5 µg m^{-3}) than the CIMS (97.8 µg m^{-3}) for type 1 experiments is the reduced transmission of the aerodynamic lens for sub-100-nm particles (see the beginning of the CH experiment at time point t0 in Fig. 2C). After the particles have grown in size (Fig. 2D) the AMS observes more total organic mass (440.1 µg m^{-3}) than the CIMS (247.6 µg m^{-3}) due to selective ionization (the numbers were stated in lines 213–214). Please see our response to the first comment.

Line 224 – There must be more validation of applying the maximum sensitivity to all products. I would like to see a calibration of an available compound which is of similar mass or structure to that of the products observed. The maximum sensitivity is usually applied to halogens or non-collision limited species. None of this has bene exemplified here and I would therefore guess that this plays a much larger error in the concentration reported from the CIMS.

Please see our response to the first comment. The maximum sensitivity has been used for organic compounds measured by FIGAERO-CIMS using Iodide earlier (Mohr et al., 2017). In addition, Lopez-Hilfiker et al. (2015) state that " […] the maximum sensitivity provides a critical constraint on the sensitivity of a ToF-CIMS [using Iodide] towards a wide suite of routinely detected multifunctional organic molecules for which no calibration standards exist."

Line 240 – The loss due to evaporation could be quantified to a more accurate extent by running a double filter measurement by placing a filter further upstream of the current collection point. By performing a collection and desorbtion with two and one filters in line, some state of loss due could be accounted for.

We normally use a second filter upstream of the filter used for particle collection for particle zeroing, in order to know the contribution of gases potentially absorbing on the filter to the particle signal. For a more quantitative assessment of potential evaporation losses, a comparison of particle chemical composition (mass spectra) as a function of deposition time at the temperature conditions of our experiments would need to be performed, which however lies outside the scope of this paper.

Line 256 – Change biggest to largest or highest

Done.

Line 272 – Can error bars be added to this to illustrate a significant change between experiments

The average mass-weighted numC or numO values were calculated based on the sum of the product of carbon number or oxygen number of each compound multiplying the corresponding mass contribution of each compound. The only error bar that can be induced in this calculation is the uncertainty of the signal for each compound in the mass spectra. Assuming an uncertainty of 35 % for CIMS (Mohr et al., 2017), error bars were calculated and added for the average mass-weighted numC and numO as well as the mass contributions and concentrations for monomers and adducts in Figure 4, Figure 5, and Figure S2 respectively.

Line 294 – Thermograms has already defined, as well as Tmax

The repetitive definitions of thermograms and Tmax were removed.

Line 370 – I agree with all interpretation with respect to Tmax variation, although I would like to see this determined under controlled conditions. Would it not be possible to calibrate for a compound, for instance a C10 deuterated carboxylic acid loaded into the chamber with varying mass loadings, RH and temperature. I feel there could be more work after the campaign on repeating Tmax variation due to the factors determined to be significant as found by the chamber experiments.

We thank the reviewer for this suggestion, and we agree that more experiments might be needed in the future to further investigate particle viscosity and desorption behavior. However, using a single compound might not necessarily result in desired further clarification. As we state at several occasions in the manuscript (e.g. lines 335–338), our results show that Tmax is not purely a function of the compounds' vapor pressures or volatilities, but is influenced by diffusion limitations within the particles (particle viscosity) (Vaden et al., 2011; Yli-Juuti et al., 2017), interactions between particles deposited on the filter (particle matrix), and/or particle mass on the filter. Just adding a single compound to the AIDA chamber would not take the complex particle matrix resulting from SOA formation into account.

Reviewer #2 (*responses in italics*)

General comment:

The authors discuss the formation of α-pinene secondary organic aerosol within two environmental chambers and its chemical-physical characterisation. Two different kinds of experiments are described and they are meant to mimic different possible formation and evolution conditions of SOA in the atmosphere, at different temperatures and relative humidities. The formed aerosol was characterised with a series of different analytical techniques, that allow the measurement of size distribution of particles, chemical composition and degree of oligomerisation, desorption temperatures. Generally speaking, the formation of SOA at low temperature has been very little studied in the laboratory, because of evident experimental challenges that such measurements can present. I think that the potentiality of the authors' experimental setup in this respect is really interesting; the coupling of the two different types of experiments that they performed with the extensive chemical-physical characterisation of the formed α-pinene SOA provides some interesting and valuable insights in this relatively little investigated field of atmospheric aerosols research. That said, I find there are a few points within the manuscript needs to be clarified, especially in the final discussion that the authors present at the end of the paper, where the inferred viscosity of the formed SOA is discussed. If the authors can address my points and questions below, I would recommend the publication of the manuscript in Atmospheric Chemistry and Physics.

Specific comments:

Line 59-60: "The fraction of total SOA mass from monoterpene oxidation products is estimated to be ~15 % globally, and can be higher in 60 some regions (e.g. in the boreal forest) (Heald et al., 2008)". I think it would be worth mentioning here up to what kind of values the SOA from the oxidation of monoterpenes is estimated.

Due to a lack of published numbers, the sentence was changed to : "SOA from monoterpenes is very important in the boreal regions in summertime, and the fraction of total SOA mass from monoterpene oxidation products is estimated to be ~15 % globally (Heald et al., 2008)."

Line 123: "Here, we discuss a subset of the SOA15 dataset". This is not clear, do the authors mean that in this paper they are discussing a subset of 15 dataset, or a subset of a total of 15 experiments? I think it would be worth adding some information in the

manuscript on how many experiments of each kind are being discussed, possibly in Table 1 where all the different conditions for all the different types of experiments are summarised.

For clarification, the corresponding sentence was changed to: "Here, we discuss a subset (Table 1) of the large dataset of the SOA15 campaign that is based on experiments [...]".

Line 131: "was used to prepare SOA particles in a reproducible manner". Does this statement refer to the previous paper by Möhler et al. (2008) or is there data from this work that support this? Please add either the appropriate literature reference or report some data in support of this statement in the Supplement.

The corresponding reference (Wagner et al., 2017) was added.

Line 144: "a fraction of the SOA particles was then transferred to the dark AIDA chamber". Could please the authors provide a little bit more detail on how this transfer is done?

The SOA transfer to AIDA was done using a 7 m stainless steel tube with 24 mm inner diameter (this information was added to the manuscript). The transfer of particles is described in lines 143−146: "After a residence time of 1−1.5 h in the APC chamber, its pressure was increased by 5 hPa compared to AIDA and a fraction of the SOA particles was then transferred to the dark AIDA chamber kept at 223 K, 61 % RH (WDtoCH) or 30 % RH (WHtoCH), respectively, resulting in the particle number concentrations ranging between 1500−2200 cm^{-3} in the AIDA chamber."

Line 147: "Figure 2", and Line 119. In panel A, which refers to the type 1 experiments, α-pinene was added over two separate steps. Could please the authors mention why? I think this is a quite important point, since in the discussion of the results the concentration of α-pinene and of SOA particles in the different kinds of experiments is often mentioned as a variable that influences the resulting chemical-physical properties of the produced aerosol (for example at Lines 283-291).

CH and CD are both type 1 experiments. Only for the CH experiment, α-pinene was added over two separate steps to increase SOA mass. This however will not influence the relationship between particle chemical composition and Tmax distribution.

Lines 155-157: Could the authors please mention how this 5% uncertainty in the quantification of the water vapours and the uncertainty of the dew point hygrometer reflects on the final uncertainty on the determined RH value?

Our TDL hygrometer has an accuracy of ±5 % in the water vapor pressure and our dew point mirror (MBW373LX) has an accuracy of ±0.1 °C corresponding to ±1 % in the water vapor pressure. Typically, both instruments agree within ±2 %. For the determination of the relative humidity, the temperature uncertainty needs to be taken into consideration and this is ± 0.3 °C expressed as the temperature inhomogeneity in the AIDA chamber under static conditions. This corresponds to ±3 % uncertainty in the water vapor pressure. Combining the observed uncertainties for water vapor pressure and temperature results in an uncertainty of ±5 % for the relative humidity. The following sentence was added in the manuscript: "Temperature (T) in the AIDA chamber was measured by home-made thermocouples (NiCrNi) and home-made PT 100 temperature sensors with an accuracy of ±3 %, […] a dew point mirror hygrometer (MBW373LX, MBW Calibration Ltd.) with an accuracy of ±1 % traceable to different national metrology standards including Federal Institution of Physical Technology (PTB), National Physical Laboratory (NPL), Federal Office of Metrology and Surveying (BEV) and NIST. Both instruments agree within ±2 %. Relative humidity (RH) in the AIDA chamber was calculated using the measured water vapor concentrations and temperature based on the saturation water vapor pressures given by Murphy and Koop (2005), resulting in an accuracy of ±5 %."

Line 176-177: "An AMS collection efficiency (CE) of 0.4-0.5 was used, except for the CH experiment where CE was 0.7, likely due to higher particle water content". What was this decision based on? Could the authors please explain this a little more in detail or provide a literature reference to support it?

AMS CE is expressed by the product of 3 terms, transmission efficiency of the aerodynamic lens for spherical particles (E_L), the loss of transmission due to particle nonsphericity which causes the particle beam to broaden (E_S), and the efficiency with which a particle that impacts the vaporizer is detected (Eb) (Huffman et al., 2005). It is influenced by aerosol composition and sampling line relative humidity (Middlebrook et al., 2012). We expect higher CE with higher relative humidity in the sampling line due to reduced bouncing of particles from the vaporizer. A CE of ~0.5 has been found for many AMS from both field and laboratory studies (e.g. Aiken et al., 2009; Takegawa

et al., 2005; Middlebrook et al., 2012; Robinson et al., 2017; Matthew et al., 2008), and comparison with ancillary data also indicate a CE close to 0.5 for our instrument. The corresponding reference was added to the manuscript.

Line 193: "For each experiment, backgrounds were determined by sampling from the AIDA chamber before adding any precursor gases". If the authors want to mention this aspect of their experimental procedure, which I think is quite important, could they please indicate what they measured on average in the background or give a literature reference if such measurements were previously published? Or provide some data about this in the Supplement?

Each experiment was started by measuring background air and background particles in AIDA before addition of any trace gases. For type 2 experiments, we did not observe a significant background before the SOA transfer from the APC chamber and initial particle number concentrations were typically below 1 cm^{-3}. For type 1 experiments, O$_3$ was usually added first and α-pinene was added last. We observed only a small increases in both gas mixing ratio and particle mass (<0.01μg m^{-3}) after O$_3$ addition. However, these background concentrations were also negligible compared to the increase by the SOA generated (>1000 fold for particle mass). The following sentence was added in the manuscript: "[...] For type 2 experiments, backgrounds were negligible with initial particle number concentrations below 1 cm^{-3}. For type 1 experiments, we observed a small increase in both gas mixing ratio and particle mass (<0.01 μg m^{-3}) after O$_3$ addition, which was subtracted from the mass loadings presented here. However, the background and the increase induced by O$_3$ addition were negligible compared to the increase by the SOA mass (>1000 fold for particle mass)."

Lines 283-291: I agree with the general conclusion of this paragraph, the authors state that from these results the importance of the experimental conditions when interpreting laboratory data is fundamental. As I mentioned in the comment on Line 147, I believe this discussion would benefit from the authors' explanation of why the concentration α-pinene was kept that much higher for type 1 experiments. If the two sets of experiments were performed at the same (or at a more comparable) VOC concentration this would not be a variable anymore and they would be able to completely discriminate the effects of α-pinene concentration from the effects of temperature on the chemical-physical properties of the formed SOA. Are the authors thinking of working in this direction?

We would like to mention that the α-pinene concentration was kept the same within the same experiment type (i.e. type 1 or type 2), but there were differences in α-pinene concentrations between type 1 and type 2 experiments (concentrations were by a factor of 3 higher for type 2 experiments). We are aware of the influence of the differences in precursor concentrations (e.g. lines 241–243, 289–290). However, even within each type of experiment, we also observed differences in mass spectral patterns, size distributions, degree of oligomerization, thermograms, etc. Therefore, we could not completely discriminate the effects of α-pinene concentration from the effects of temperature on the chemical-physical properties of the formed SOA. However, for future studies precursor conditions would be ideally be kept constant.

Line 299 and following discussion: "Here we show that thermograms may also be used for qualitative information on particle viscosity - My biggest concern with the author's claim that they can get some information on the particles' viscosity from thermograms regards what is actually the effect of viscosity at the high temperatures at which the thermograms are taken. The authors say: "at the higher temperatures where adducts desorb, particle matrix effects may become less important" (Lines 324-325), including particles viscosity. By heating up the deposited particles, the viscosity of the particles is going to change (decrease); even at the relatively low Tmax they measured at about 45 °C, is the viscosity of the particles still going to play a role in the rate of diffusion of the desorbed compounds? And what about when the temperature is even further increased? Is there a way the authors can support these claims more strongly?

We are limited in our possibilities of heating the particles to more than 200 °C due to the material of the FIGAERO (Teflon), which starts to melt at ~240 °C. We therefore cannot extend our studies to higher temperatures, unfortunately. Our empirical data on varying Tmax for the same individual compound for different experimental conditions indicate that indeed that there must be factors other than the vapor pressure of the respective compound that influence Tmax, even at those elevated temperatures applied in the FIGAERO. However, in line with the reviewer´s comment, and as stated in lines 323–325 in the manuscript: "Variation in Tmax of the sum of CHOI compounds was larger for monomers (Fig. 6C) than for adducts (Fig. 6D). Monomers are thus the more important contributors to the shifts in Tmax, likely because at the higher temperatures where adducts desorb, particle matrix effects may become less important."

Line 365: "Calculated particle water content derived from AMS measurements is prone

to large uncertainties (Engelhart et al., 2011); we observed a qualitative positive correlation with RH (data not shown)". If the authors want to mention this positive correlation I think it would be appropriate to show it in the Supplement, even if the water content quantification is characterised by a large uncertainty as they mention.

We agree with the reviewer that mentioning particle water content in the manuscript would warrant to show the data in the Supplement. However, as we are not confident enough with the quality of that data we have decided to remove that information from the manuscript.

Line 376: "The dependency of Tmax on filter mass loading was not linear, and for our FIGAERO reached a plateau at mass loadings of 2−4 µg.". Looking at the data reported in the Supplement in Figure S6 panels B and D, I do not think it is true that Tmax plateaus for CD experiments. Both the shape of the thermograms and the Tmax value change with different mass loading. This could mean that all the previous discussion on the CD experiments could be affected by the choice of sampling times (Table S1). Could please the authors comment on this aspect and rephrase this statement?

Figure S6 shows the sum thermograms of all CHOI compounds with different sampling time (which also means different mass loadings here). As described in the manuscript (lines 325−326), the sum of thermograms and its Tmax is highly influenced by compounds with large signal, we therefore also show a box and whisker diagram of Tmax distribution for CHOI compounds, CHOI monomers and adducts in the Supplement (Figure S7). In this figure we can observe that beyond filter mass loadings of 2−4 µg the curves level off (saturation effect).

Line 380: "In this study, α-pinene SOA physicochemical properties such as chemical composition, phase state, and viscosity were investigated". I would tone this down and rephrase this because of the very uncertain link between what is observed in the thermograms and the phase state/viscosity of the particles. Some aspects were actually investigated (size distributions, chemical composition, degree of oligomerisation, etc.) but the phase state/viscosity of the particles can just be supposed.

The sentence was rephrased as following: "In this study, α-pinene SOA physicochemical properties such as chemical composition, size distributions, and degree of oligomerization were investigated at low temperature (223 K) and different relative humidity (RH) [...]".

Technical comments:

Line 57: change "24.8 % mass contribution to global monoterpene emissions" to "24.8 % mass contribution to global monoterpenes emissions".

Corrected as suggested.

Line 183, 269 and 307: "Table 2". There is no Table 2 in the main manuscript, could please the authors double check this reference?

It is actually Table S1. Corrected throughout the manuscript.

Figures 4,5, S2, S5 and 7: It is a little confusing for the reader having the results for type 2 experiments often displayed before type 1 experiment. I think it would help the reader if the sequence of the data displayed in the figures reflected the sequence with which the different kinds of experiments are presented in the abstract and in section 2.1. Possibly adding a label "Type 1 (or 2)" would help the reader, too.

Labels were added in Figures 4, 5, S2, S5, 7 as suggested.

Figures S3 and S4: I don't think these figures are referred to at any point in the manuscript. If this is the case, could please the authors either add references to these figures in the main manuscript or add some more context to them in the Supplement?

Figures S3 and S4 are both referred in Section 3.3 in the manuscript (lines 305−306 for Figure S3 and lines 314−316 for Figure S4).

M. Claeys *(responses in italics)*

General comments:

My comments mainly relate to the chemical characterization of alpha-pinene SOA compounds, which could be elaborated in this manuscript. I found it interesting to see that the monomer $C_{10}H_{16}O_4$ and the dimer $C_{17}H_{26}O_8$ are major components of the alpha-pinene SOA system, and that the ratio monomers/oligomers is enhanced at the lower temperature.

We thank Prof. Claeys for her time in reading and commenting our manuscript. Replies

to the individual comments are directly added below them in italics.

Specific comments:

Line 68 - Introduction: The authors write: "The molecular formulae of organic species accounting for ~58-72 % of SOA mass from α-pinene ozonolysis have been identified, and can largely be grouped into monomers (C8-10H12-16O3-6, oxidation products from one α-pinene molecule) and dimers (C14-19H24-28O5-9, oxidation products from two α-pinene molecules) (Zhang et al., 2015)."

Since later in the manuscript results for the MW 358 dimer (C17H26O8) are selected, it would be worthwhile to also mention that major dimers of the alpha-pinene SOA system have been structurally elucidated. I suggest to add the following sentence: "Major dimers of the alpha-pinene SOA system have been structurally elucidated as a cis-pinyl-diaterpenyl ester (C17H26O8; MW 358) (Yasmeen et al., 2010) and a cispinyl-hydroxypinonyl ester (C19H28O7; MW 368) (Müller et al., 2008)."

Sentence added as suggested.

Line 302: The authors write: "Examples of the thermograms of a monomer (C10H16O4, molecular formula corresponding to hydroxy-pinonic acid), and an adduct (C17H26O8, molecular formula identified in SOA from α-pinene ozonolysis by e.g. Zhang et al., 2015; Mohr et al., 2017) both clustered with I- at t0 are shown in Fig. 6A-B."

With regard to the monomer C10H16O4, it would be worthwhile to consult the recent article by Zhang et al. (2017). These authors have studied HOMs in the alpha-pinene ozonolysis system and provided evidence for the formation of isomeric hydroxypinonic acids, with the hydroxy group at different positions of the pinonic acid skeleton, i.e., the 7- and 5-positions.

With regard to the C17H26O8 compound, it would be relevant to also mention the chemical structure. I suggest to do this as follows: "…. and a diester [C17H26O8, molecular structure identified in SOA from α-pinene ozonolysis as a cispinyl-diaterpenyl ester (Yasmeen et al., 2010) and molecular formula identified in SOA from α-pinene ozonolysis by e.g. Zhang et al., 2015; Mohr et al., 2017] both clustered ……"

Sentence corrected as suggested.

Line 308: The authors write: "For experiment CD, the C10H16O4I1 – thermograms

exhibited a multi-modal shape, indicative of contributions from isomers having different vapor pressures, or thermal decomposition of larger molecules. "

As already mentioned above, there is indeed evidence for different isomeric hydroxypinonic acids (Zhang et al., 2017), but decomposition of dimers is also a possibility. It is noted that the MW 368 diester, elucidated as a cis-pinyl-hydroxypinonyl, has a cis-pinic and 7-hydroxypinonic acid residue. In this respect, it would be interesting to examine the thermogram of cis-pinic acid (MW 186). Furthermore, it would also be worthwhile to examine the thermogram of terpenylic acid (MW 172), which could result from the degradation of the MW 358 diester.

According to Prof. Claeys suggestion we re-examined the data and indeed also found multi-mode thermograms for cis-pinic acid (MW 186) and terpenylic acid (MW 172). The following sentence was added in the manuscript: "[…] Different isomeric hydroxypinonic acids were found in α-pinene SOA (Zhang et al., 2017) and the decomposition of cis-pinyl-hydroxypinonyl diester could have a cis-pinic and 7-hydroxypinonic acid residue (Müller et al., 2008)."

Line 410: It is not clear what the authors mean by "adduct". I think they mean "oligomer", which is chemically more correct. The dimeric esters with MW 358 and 368, for example, are covalent dimers.

We changed the definition of adducts in lines 261–262 to: "[…] (this definition includes dimers, trimers, and oligomers in general)".

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α-pinene secondary organic aerosol at low temperature: Chemical composition and implications for particle viscosity

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Abstract. Chemical composition, size distributions, and ~~viscosity~~ degree of oligomerization of secondary organic aerosol (SOA) from α-pinene ($C_{10}H_{16}$) ozonolysis were investigated for low temperature conditions (223 K). Two types of experiments were performed using two simulation chambers at the Karlsruhe Institute of Technology~~,~~: the Aerosol Preparation and Characterization chamber (APC), and the Aerosol Interaction and Dynamics in the Atmosphere chamber (AIDA). Experiment type 1 simulated SOA formation at upper tropospheric conditions: SOA was generated in the AIDA chamber directly at 223 K, 61 % relative humidity (RH) (experiment termed "cold humid", CH), or for comparison at 6 % RH (experiment termed "cold dry", CD) conditions. Experiment type 2 simulated SOA uplifting: SOA was formed in the APC chamber at room temperature (296 K), <1 % RH (experiment termed "warm dry", WD) or 21 % RH (experiment termed "warm humid", WH) conditions, and then partially transferred to the AIDA chamber kept at 223 K, and 61 % RH (WDtoCH) or 30 % RH (WHtoCH), respectively. Precursor concentrations varied between 0.7 and 2.2 ppm α-pinene, and 2.3 and 1.8 ppm ozone for type 1 and type 2 experiments, respectively. Among other instrumentation, a chemical ionization mass spectrometer (CIMS) ~~with~~ coupled to a filter inlet for gases and aerosols (FIGAERO), deploying I⁻ as reagent ion, was used for SOA chemical composition analysis.

For type 1 experiments with lower α-pinene concentration and cold SOA formation temperature (223 K), smaller particles of 100−300 nm vacuum aerodynamic diameter (d_{va}) and higher mass fractions (>40 %) of adducts (molecules with more than 10 carbon atoms) of α-pinene oxidation products were observed. For type 2 experiments with higher α-pinene concentration and warm SOA formation temperature (296 K), larger particles (~500 nm d_{va}) with smaller mass fractions of adducts (<35 %) were produced.

We also observed differences (up to 20 ℃) in maximum desorption temperature (T_{max}) of individual compounds desorbing from the particles deposited on the FIGAERO Teflon filter for different experiments, indicating that T_{max} is not purely a function of a compound's vapor pressure or volatility, but is also influenced by diffusion limitations within the particles (particle viscosity), interactions between particles deposited on the filter (particle matrix), and/or particle mass on the filter. Highest T_{max} were observed for SOA under dry conditions and with higher adduct mass fraction; lowest T_{max} for SOA under humid conditions and with ~~lowest~~ lower adduct mass fraction. The observations indicate that particle viscosity may be influenced by intra- and inter-molecular hydrogen bonding between oligomers, and particle water uptake, even under such low temperature conditions.

Our results suggest that particle physicochemical properties such as viscosity and oligomer content mutually influence each other, and that variation in T_{max} of particle desorptions may provide implications for particle viscosity and particle matrix

effects. The differences in particle physicochemical properties observed between our different experiments demonstrate the
40   importance of taking experimental conditions into consideration when interpreting data from laboratory studies or using them as input in climate models.

1 Introduction

Atmospheric aerosols have adverse impacts on human health (Nel, 2005; Rückerl et al., 2011) and rank among the main drivers of anthropogenic climate change (IPCC, 2013). Organic compounds make up a large fraction (20−90 %) of submicron
45   particulate mass (Zhang et al., 2007; Murphy et al., 2006; Jimenez et al., 2009; Ehn et al., 2014). Organic aerosol (OA) particles can be directly emitted into the atmosphere from sources ~~like~~ such as fossil fuel combustion and forest fires (primary organic aerosol, POA), or be formed in the atmosphere from the oxidation of gas-phase precursors (secondary organic aerosol, SOA). SOA dominates the global budget of OA (Shrivastava et al., 2015)~~.~~, and its ~~Gaseous~~ gaseous ~~SOA~~ precursors (volatile organic compounds, VOCs) can be of both biogenic and anthropogenic origin. In the atmosphere, VOCs are oxidized by the hydroxyl
50   radical (OH), ozone (O_3), or the nitrate radical (NO_3) into semi-volatile, low volatile and/or extremely low volatile organic compounds (SVOC, LVOC/ELVOC), which can partition into the particle phase and lead to the formation of SOA (Jimenez et al., 2009; Hallquist et al., 2009; Jokinen et al., 2015; Ehn et al., 2014). Due to the wealth of precursors and formation mechanisms in both the gas and particle phase, SOA is very complex and can contain thousands of compounds with a wide range of functionalities, volatilities, and other physicochemical properties (Hallquist et al., 2009; Nozière et al., 2015).

55   Global estimates indicate that biogenic VOCs emissions (539 Tg C a^{-1}) dominate over anthropogenic VOCs emissions (16 Tg C a^{-1}), and that the global SOA production from biogenic VOCs (22.9 Tg C a^{-1}) outreaches that from anthropogenic VOCs (1.4 Tg C a^{-1}) as well (Heald et al., 2008). An important class of biogenic VOCs are monoterpenes ($C_{10}H_{16}$), emitted in substantial amounts (43 Tg C a^{-1}, Heald et al., 2008) by vegetation (e.g. many coniferous trees, notably the pine). One of the most abundant monoterpenes is α-pinene (24.8 % mass contribution to global monoterpenes emissions, Kanakidou et al.,
60   2005). SOA from monoterpenes is very important in the boreal regions in summertime, and ~~The~~ the fraction of total SOA mass from monoterpene oxidation products is estimated to be ~15 % globally~~, and can be higher in some regions (e.g. in the boreal forest)~~ (Heald et al., 2008).

      SOA formation from α-pinene has been studied extensively in smog chambers (e.g. Kristensen et al., 2016; Denjean et al., 2015; McVay et al., 2016), although studies covering a wide temperature range are rare (Saathoff et al., 2009; Donahue et al.,
65   2012). The reactions of α-pinene with O_3, and the radicals OH– and NO_3 ~~radicals~~ lead to a large suite of oxygenated reaction products including aldehydes, oxy-aldehydes, carboxylic acids, oxy-carboxylic acids, hydroxy-carboxylic acids, dicarboxylic acids, organic nitrates etc. (Winterhalter et al., 2003; Kanakidou et al., 2005). Aerosol yields vary for the different oxidants, and the most important process with regard to aerosol mass formation from the oxidation of α-pinene is the reaction with O_3~~ozone~~ (Kanakidou et al., 2005).

70   The molecular formulae of organic species accounting for ~58−72 % of SOA mass from α-pinene ozonolysis have been identified, and can largely be grouped into monomers ($C_{8–10}H_{12–16}O_{3–6}$, oxidation products from one α-pinene molecule) and dimers ($C_{14–19}H_{24–28}O_{5–9}$, oxidation products from two α-pinene molecules) (Zhang et al., 2015). Major dimers of the α-pinene SOA system have been structurally elucidated as a cis-pinyl-diaterpenyl ester ($C_{17}H_{26}O_8$; MW 358) (Yasmeen et al., 2010) and a cis-pinyl-hydroxypinonyl ester ($C_{19}H_{28}O_7$; MW 368) (Müller et al., 2008). Autoxidation processes can form highly oxidized
75   molecules (HOM, elemental oxygen to carbon ratios of 0.7−1.3, Ehn et al., 2012), both monomers and dimers, which have been shown to play an important role in atmospheric new particle formation (Ehn et al., 2014). Less oxygenated dimers (e.g. esters and other accretion products), some of which have similarly low volatility as HOM and for many of which formation mechanisms are still not known, are major products in aerosol particles from α-pinene ozonolysis, and have been proposed as

key components in organic particle growth in field and laboratory (Kristensen et al., 2014; Kristensen et al., 2016; Tröstl et al., 2016; Zhang et al., 2015; Mohr et al., 2017).

SOA is a-highly dynamic ~~system between the gas and particle phase that~~ and continually evolves ~~during residence time~~ in the atmosphere, becoming increasingly oxidized, less volatile, and more hygroscopic (Jimenez et al., 2009). As a consequence, SOA residence time in the atmosphere at different temperature (T) and relative humidity (RH) conditions strongly influences the particles' physicochemical properties such as phase state, and thus their effects on air quality and climate (Tsigaridis et al., 2006; Jimenez et al., 2009; Shiraiwa et al., 2017). Biogenic SOA has been shown to exist in phase states ranging from liquid to amorphous (semi-)solid in the atmosphere (Virtanen et al., 2010; Bateman et al., 2016; Shiraiwa et al., 2017). The phase state can affect gas uptake, gas-particle partitioning, diffusion, the particles' ability to act as cloud condensation nuclei (CCN) and/or ice nuclei (IN), as well as the particles' lifetime in the atmosphere (Shiraiwa et al., 2011; Price et al., 2015; Lienhard et al., 2015). ~~E.g. w~~Water diffusion coefficients in the water-soluble fraction of α-pinene SOA were e.g. measured for temperatures ~~conditions~~ between 240 and 280 K. The results showed that water diffusion slowed down as temperature decreased, indicating increasing viscosity of SOA particles (Price et al., 2015). Diffusivity of organic molecules in SOA particles can show similar behavior, leading to large equilibration times under dry conditions (Shiraiwa et al., 2011) and/or cool conditions (Bastelberger et al., 2017). Observations of particle shape transformations (Järvinen et al., 2016), coalescence times (Pajunoja et al., 2014), and the particle bounce factor (BF) (Virtanen et al., 2010; Pajunoja et al., 2015) are other parameters used to indicate the phase state and viscosity of particles. At dry conditions and at temperatures close to room temperature, the viscosity of α-pinene SOA is assumed to range from 10^5 to (higher than) 10^8 Pa s (Song et al., 2016; Renbaum-Wolff et al., 2013; Pajunoja et al., 2014), which corresponds to a semisolid state (Shiraiwa et al., 2011), whereas at a RH of about 90 % and room temperature its consistency is comparable to that of honey (~10 Pa s) (Renbaum-Wolff et al., 2013). Generally, SOA is more viscous in cool and dry conditions (shown e.g. for α-pinene SOA at temperatures ranging from 235 K to 295 K and RH ranging from 35 to 90 %, Song et al., 2016; Järvinen et al., 2016; Shiraiwa et al., 2011; Wang et al., 2015; Kidd et al., 2014).

Differences in α-pinene SOA chemical composition were observed for different SOA formation temperatures and RH conditions, such as lower oligomer content at higher RH (up to 87 %, Kidd et al., 2014), or lower temperature (285 K, Zhang et al., 2015). Given that the differences in physicochemical properties of SOA particles observed as a function of temperature and RH only cover part of the range of atmospheric values, it is of great importance for our understanding of SOA climate effects to increase efforts in the investigation of SOA evolution at atmospherically relevant conditions, especially at low temperature. More knowledge on SOA at temperature and RH conditions that are representative of the upper troposphere, where SOA can be transported to or formed in-situ, is required in order to understand their potential importance for phase state, morphology, and chemical composition, and thus ultimately SOA cloud formation potential (Zhang et al., 2015; Virtanen et al., 2010; Lienhard et al., 2015; Frege et al., 2017). However, such studies, particularly of SOA at low temperature, are still scarce.

In the present work, we investigate the chemical composition, size distributions, and ~~viscosity~~ degree of oligomerization of α-pinene SOA formed at four different conditions corresponding to temperatures of 223 K and 296 K and RH between <1 % and 61 % in order to simulate SOA uplifting to and SOA formation in the upper troposphere. Samples for chemical ionization mass spectrometric analysis were taken from the AIDA chamber at 223 K and collected on Teflon filters at two different times after starting the experiments. We discuss differences in these mass spectra and corresponding molecular desorption profiles when heating the filters from room temperature to 200 °C as well as possible implications for mutual interactions between particle chemical composition and viscosity.

2 Methodology

2.1 Environmental chambers and experimental design

The data for this study were acquired during a two-month measurement campaign (SOA15) in October and November 2015 at environmental chambers of the Institute of Meteorology and Climate Research (IMK) at the Karlsruhe Institute of Technology (KIT). The measurement campaign investigated yields, physical properties, and chemical composition of SOA from α-pinene ozonolysis as a function of precursor concentration, temperature and relative humidity (RH), as well as the ice nucleation abilities of the SOA particles (Wagner et al., 2017). The focus on ice cloud formation allowed the investigation of the particles' physicochemical properties at temperatures as low as 223 K (representative of conditions in the upper troposphere at 8−12 km altitude in mid-latitudes), a range where detailed characterization is largely missing. Here, we discuss a subset (Table 1) of the large dataset of the SOA15 campaign dataset that is based on experiments investigating the influence and mutual interaction of particle chemical composition and viscosity shortly after SOA formation and after a residence time of ~3.5 h which were formed at different temperatures (223−296 K) and RH (<1−61 %) conditions using both environmental chambers available at IMK (see Fig. 1).

The AIDA (Aerosol Interaction and Dynamics in the Atmosphere) aerosol and cloud chamber is an 84.3 m^3 sized aluminum vessel. It can be operated in a temperature range of 183 to 333 K, a pressure range of 1 to 1000 hPa, RH from close to 0 to 200 %, and different warming and cooling rates (Schnaiter et al., 2016; Möhler et al., 2003; Saathoff et al., 2009).

The APC (Aerosol Preparation and Characterization) chamber (Möhler et al., 2008) is a 3.7 m^3 sized stainless steel vessel, right next to situated at a distance of 3 m from AIDA and connected with to it by a 7 m stainless steel tube of 24 mm inner diameter. The APC chamber can only be operated at room temperature (296 K) and was used to prepare SOA particles in a reproducible manner (Wagner et al., 2017).

We present two types of chamber experiments (Fig. 1): For the first type, SOA from α-pinene ozonolysis was directly formed at 223 K in the AIDA chamber. For the second type, SOA was first produced in the APC chamber kept at room temperature and then transferred to the AIDA chamber kept at 223 K. The second type of experiment thus represents a simplified simulation of particle formation in the boundary layer and subsequent uplifting of particles to higher altitudes with lower temperature conditions. We stress here that for both types of experiments, the particles were sampled from the cold AIDA chamber for chemical analysis. The detailed conditions for these two types of experiments are listed in Table 1. During the first type of chamber experiment, SOA was formed by reaction of an excess of O_3 ozone (initially 2.3 ppm generated by silent discharge in pure oxygen, Semozon 030.2 discharge generator, Sorbios GmbH) with α-pinene (initially 0.714 ppm, 99 %, Aldrich) in the dark AIDA chamber at 223 K, 61 % RH (experiment termed "cold humid", CH) or 6 % RH (experiment termed "cold dry", CD) conditions. For the second type of chamber experiment, SOA was first formed with an excess of O_3 ozone (initially 1.8 ppm) and 2.2 ppm α-pinene in the dark APC chamber at room temperature (296 K), <1 % RH (experiment termed "warm dry", WD) or 21 % RH (experiment termed "warm humid", WH) conditions. After a residence time of 1−1.5 h in the APC chamber, its pressure was increased by 5 hPa compared to AIDA and a fraction of the SOA particles was then transferred to the dark AIDA chamber kept at 223 K, 61 % RH (WDtoCH) or 30 % RH (WHtoCH), respectively, resulting in the particle number concentrations ranging between 1500−2200 cm^{-3} in the AIDA chamber. No OH scavenger was used during SOA formation, and RH was kept constant in AIDA during the course of the experiments. The time series of total particle mass for experiment type 1 (particles formed in-situ in AIDA, CH) and experiment type 2 (aerosols formed in APC and transferred to AIDA, WDtoCH) are shown in Fig. 2. The times t0 (right after SOA formation (CD, CH) or SOA transfer (WDtoCH, WHtoCH)) and t1 (~3.5 h later) indicate the points in experiment time which were used for the investigation of the physicochemical evolution of α-pinene SOA.

2.2 Temperature and relative humidity measurements

160   Temperature (T) in the AIDA chamber was measured by home-made thermocouples (NiCrNi) and home-made PT 100
       temperature sensors with an accuracy of ± 3 %, which are regularly calibrated with reference sensors traceable to standards
       of the National Institute of Standards and Technology (NIST). Under static conditions, gas temperature in the AIDA chamber
       deviated by less than 0.3 K in time and in space. Water vapor concentrations in the AIDA chamber were measured by a home-
       made tunable diode laser (TDL) spectrometer with an accuracy of ± 5 % (Fahey et al., 2014; Skrotzki et al., 2013), as well as
165   a dew point mirror hygrometer (MBW373LX, MBW Calibration Ltd.) with an accuracy of ± 1 % traceable to different national
       metrology standards including Federal Institution of Physical Technology (PTB), National Physical Laboratory (NPL), Federal
       Office of Metrology and Surveying (BEV) and NIST. Both instruments agree within ± 2 %. Relative humidity (RH) in the
       AIDA chamber was calculated using the measured water vapor concentrations and temperature based on the saturation water
       vapor pressures given by Murphy and Koop (Murphy and Koop, 2005), resulting in an accuracy of ± 5 %.

170   **2.3 Particle and gas measurements**

       Number concentrations of SOA particles formed in APC or AIDA were recorded with two condensation particle counters
       (CPC3022, CPC3010, TSI Inc.) outside the temperature controlled housing of the chambers via stainless steel tubes extending
       35 cm into the AIDA chamber. The absolute uncertainty of the number concentrations is estimated to be ± 20 % by comparison
       of the different CPCs with each other and with an electrometer (3068, TSI Inc.). Particle size distributions were sampled in
175   the same way from both chambers with scanning mobility particle sizers (SMPS, DMA 3071 connected to a CPC 3010, TSI
       Inc.). Mass concentrations were derived from integrated number size distributions and their conversions to mass using their
       corresponding calculated particle density ($1.3-1.5$ kg m^{-3}). Particle densities were calculated using the ratio of vacuum
       dynamic diameter (d_{va}) measured by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne
       Research Inc., hereafter AMS) and mobility diameter (d_m) measured by the SMPS, assuming particle sphericity (shape factor
180   = 1). O_3Ozone concentrations were measured by an O_3ozone monitor (O_3 41M, Environment S.A.). The AMS was connected
       to the AIDA chamber by a stainless steel tube of 1.35 m length (flowrate 0.1 l min^{-1}, residence time 1.6 s). It was equipped
       with a high-pressure lens (HPL) (Williams et al., 2013) and continuously measured total organic particle mass as a function of
       size (up to 2.5 μm particle aerodynamic diameter) at a time resolution of 0.5 min. Elemental oxygen to carbon (O:C) and
       hydrogen to carbon (H:C) ratios were derived using the EALight_1_06 procedure in the AMS data analysis software package
185   SQUIRREL (version 1.57H) (Canagaratna et al., 2015). An AMS collection efficiency (CE) of $0.4-0.5$ was used, except for
       the CH experiment where CE was 0.7, likely due to higher particle water content (Middlebrook et al., 2012). AMS mass
       concentrations compare well with the total mass derived from SMPS (slopes are between $0.87-1.04$ except for CD experiment
       (2.2) possibly due to the lower transmission efficiency in the aerodynamic lens of the AMS for sub-100-nm particles, Pearson's
       correlation coefficients are between $0.87-0.98$ for the experiments presented here). Individual organic compounds in both the
190   gas and particle phase were measured with a Filter Inlet for Gases and AEROsols coupled to a hHigh-rResolution tTime-of-
       fFlight cChemical iIonization mMass sSpectrometer (FIGAERO-HR-ToF-CIMS, Aerodyne Research Inc., hereafter CIMS)
       deploying iodide ions (I$^-$) as reagent ions (Lopez-Hilfiker et al., 2014; Lee et al., 2014). With the FIGAERODuring the gas
       phase measurement, gases were measured sampled via a 0.83 m Fluorinated Ethylene Propylene (FEP) tube of 0.83 m length
       while particles were simultaneously collected on a Teflon (Polytetrafluoroethylene, PTFE) filter via a separate sampling port
195   (stainless steel tube of 0.66 m length, flowrate 5 l min^{-1}, residence time 0.9 s). At regular intervals ($5-20$ min, see Table 2S1),
       the gas phase measurement was switched off and particles on the filter were desorbed by a flow of ultra-high purity (99.999
       %) nitrogen heated from room temperature to 200 °C over the course of 35 min. The resulting mass spectral signal evolutions
       as a function of desorption temperature are termed thermograms (Lopez-Hilfiker et al., 2014). Single mode thermograms of a
       compound with signal maxima occurring at distinct desorption temperatures (T_{max}), which correlate with the compound's
200   enthalpy of sublimation, can be used to infer its saturation vapor pressure (Lopez-Hilfiker et al., 2015; Mohr et al., 2017).

Multi-mode thermograms indicate contributions from isomers having different vapor pressures, or thermal fragmentation of larger molecules during the heating of the filter (Lopez-Hilfiker et al., 2015). Integration of thermograms of individual compounds yielded their total signal in counts per deposition, which were converted to mass concentrations using a sensitivity of 22 counts s^{-1} ppt^{-1} (collisional limit, Lopez-Hilfiker et al., 2016). For each experiment, backgrounds were determined by sampling from the AIDA chamber before adding any precursor gases. For type 2 experiments, backgrounds were negligible with initial particle number concentrations below 1 cm^{-3}. For type 1 experiments, we observed a small increase in both gas mixing ratio and particle mass (<0.01 µg m^{-3}) after O_3 addition, which was subtracted from the mass loadings presented here. However, the background and the increase induced by O_3 addition were negligible compared to the increase by the SOA mass (>1000 fold for particle mass).

All instruments were set up at room temperature, outside the temperature-controlled housing of AIDA. Despite inlet insulation with Armaflex, we calculated a theoretical temperature increase (Fitzer and Fritz, 1989) of ~15 K for the particle inlet of the CIMS (the FIGAERO filter was thus presumably at 238 K during deposition), and cannot entirely rule out partial evaporation of water or semivolatile organic compounds, which is taken into account in our interpretation of results.

3 Results and discussion

3.1 Organic particle mass and size distribution

Figure 2A−B shows the time series of total particle mass derived from SMPS size distributions, total organic particle mass measured by AMS, and total mass of particulate oxygenated hydrocarbons ($C_{x>1}H_{y>1}O_{z>1}$ detected as clustered with I^-, termed CHOI compounds) measured by CIMS for both types of experiments. Panel A depicts the CH experiment, representative of experiment type 1, where particles were directly formed in AIDA. Panel B represents experiment type 2, where aerosol was formed in the APC and transferred to AIDA (here the WDtoCH example, see Table 1). Please nNote that the data were not wall-loss corrected. Gaps in the AMS time series were due to filter measurements. To investigate the evolution of the SOA particles' physicochemical properties with time, we chose two points in time during the experiments, t0 and t1. t0 is the first FIGAERO filter deposition from AIDA after particle formation (experiment type 1) or particle transfer (experiment type 2), while t1 is approximately 3.5 h later. Averaged concentrations of total organics, total CHOI compounds, as well as elemental oxygen to carbon (O:C) ratios at t0 and t1, together with an overview of the experimental conditions including temperature (T), relative humidity (RH), and added precursor (α-pinene and O_3) concentrations for all experiments discussed here (WDtoCH, WHtoCH, CH, and CD) are listed in Table 1. Particle size distributions measured by AMS for all four experiments at t0 and t1 are shown in Fig. 2C-D.

For SOA formed in AIDA (type 1 experiments), mean total organic mass concentrations at t0 and t1 were in the range of 67.5−440.1 µg m^{-3}, and mean total concentrations of CHOI compounds 97.8−247.6 µg m^{-3}. When particles were transferred from the APC chamber (type 2 experiments), organic and CHOI mass concentrations in AIDA reached values of 48.5−64.2 µg m^{-3} and 23.3−40.7 µg m^{-3}, respectively. We stress here that even though particle mass concentrations in AIDA were higher for the experiments of type 1 (particles formed at 223 K directly in AIDA), the α-pinene concentration for the type 2 experiments was higher by a factor of ~3 (Fig. 2A−B and Table 1). This also led to larger particle sizes for the type 2 experiments. Due to additional α-pinene addition between t0 and t1 only for the CH experiment, we observed a step increase of total particle mass for this experiment (Fig. 2A).

The discrepancies between AMS and CIMS concentrations are likely due to the CIMS with I^- as reagent ion being more sensitive to more polar oxygenated organic compounds (Lee et al., 2014) and thus only a potential subset of organic compounds measured by AMS. Evaporation losses of particulate compounds during filter deposition in the FIGAERO may play a minor role. In addition, by using the collisional limit for the CIMS data, we apply maximum sensitivity and thus present lower limits

of CHOI compounds. The differences between the AMS and SMPS derived mass concentrations in Fig. 2A are likely due to the lower transmission of sub-~~200~~100-nm particles in the aerodynamic lens of the AMS used here. The AMS measured lower concentrations than the SMPS at the beginning of the CH experiment (Fig. 2A), when the newly formed particles were much smaller (see Fig. 2C) compared to later in the experiment when they had grown in size (see Fig. 2D). For the WDtoCH
245 experiment (Fig. 2B) with larger particles transferred from the APC to the AIDA chamber, AMS and SMPS derived mass concentrations agree very well. The slightly decreasing trend observed during both experiments was due to wall losses (Donahue et al., 2012).

3.2 Chemical characterization of SOA particles

3.2.1 Elemental oxygen to carbon ratios

250 Elemental oxygen to carbon (O:C) ratios were calculated using both AMS and CIMS data. The mean AMS O:C ratios for SOA formed in APC and AIDA were 0.34−0.36 and 0.26−0.30, respectively (Table 1). This is representative of O:C ratios for relatively fresh SOA measured in ambient studies (Mohr et al., 2012; Ge et al., 2012; Canagaratna et al., 2015). For CHOI compounds measured by CIMS, the calculated mean O:C ratios for SOA formed in APC and AIDA were 0.59−0.66 and 0.56−0.61, respectively. The AMS O:C ratio is expected to be lower than that of the CHOI compounds measured by iodide
255 CIMS, as the latter is selective towards polar oxygenated compounds. The potential loss of semivolatiles from the filter during FIGAERO deposition may additionally increase the mass-averaged O:C ratio of compounds measured with this instrument. The O:C ratios of SOA formed in the APC were slightly higher than those formed in AIDA, likely a result of the difference in precursor concentrations and temperature and thus partitioning behavior of semivolatile SOA compounds during formation between the particles and chamber walls. We rule out a dilution effect when transferring particles from APC to AIDA, since
260 the dilution factor was orders of magnitude smaller than the decrease in saturation vapor pressure due to the temperature reduction from APC (296 K) to AIDA (223 K), and confirmed by the absence of a change in particle size after transfer. For all experiments, O:C ratios remained largely constant from t0 to t1.

3.2.2 FIGAERO-CIMS mass spectra

Mass spectra of integrated desorptions from the CIMS are compared for the four experiments and two points in time, t0 and
265 t1. Mass spectra shown were normalized to the sum of signal of all detected CHOI compounds. The corresponding mass loadings and sampling times (particle collection on filter) for the four experiments are listed in Table S1. Figure 3A shows a comparison of mass spectral patterns for the experiments WDtoCH and CD, 3B for WHtoCH and CD, and 3C for CH and CD, all at t0 (the same comparisons for t1 are to be found in Fig. S1). Overall, the mass spectral patterns across all experimental conditions and points in time were relatively similar. Monomers ($C_mH_yO_z$ compounds, $m\leq10$), dimers ($C_nH_yO_z$ compounds,
270 $11\leq n\leq20$), and even trimers ($C_pH_yO_z$ compounds, $21\leq p\leq30$) clustered with I$^-$ were observed in the mass spectra at t0 and t1 for all occasions.

Monomers dominated the overall signal of detected compounds, with the ~~biggest~~ largest signal at m/z 327 (mainly $C_{10}H_{16}O_4I^-$, likely hydroxy-pinonic acid clustered with I$^-$). As we can see from Fig. 3, relatively higher contributions of monomers were measured at t0 for experiments WDtoCH and WHtoCH compared to CD. The difference in relative monomer
275 contributions for experiments CH and CD was less distinct. At the same time, relatively larger contributions from dimers and trimers (inserts in Fig. 3) were observed for the experiment CD (and to a lesser extent for the CH). This was also the case for t1 (Fig. S1).

Figure 4 shows the relative mass contributions of monomers and adducts (this definition includes ~~including~~ dimers, ~~and~~ trimers, and oligomers in general) for the four experiments at both time points. As already observed in the mass spectral
280 patterns, larger relative mass contributions from monomers were measured for the type 2 experiments (WDtoCH, WHtoCH),

and larger relative mass contributions from adducts for the type 1 experiments (CH, CD). There was no significant change for the relative contributions and absolute concentrations of adducts (Fig. S2) between t0 and t1 for type 2 experiments (WDtoCH, WHtoCH). For type 1 experiments (CH and CD), absolute concentrations of monomers and adducts (Fig. S2) were increasing from t0 to t1 due to the addition of α-pinene after t0 and hence the continuing production of oxidation products and particle mass (compare Fig. 2). However, the relative contributions of monomers for type 1 experiments were increasing from t0 to t1, which may be partially influenced by smaller FIGAERO sampling time and thus less evaporation losses of semivolatiles at t1 (see Table 2 S1 and supplement), but mostly by increased condensation of semivolatiles or lower-molecular-weight products with increasing particle size (compare Fig. 2C−D).

Figure 5 shows the average mass-weighted number of carbon atoms (numC) and oxygen atoms (numO) for CHOI compounds for the four experiments at t0 and t1. The corresponding average mass-weighted compounds' formulae for SOA generated in APC and AIDA were $C_{10-12}H_yO_{6-7}$ and $C_{11-13}H_yO_{6-7}$, respectively. Slightly bigger numC were observed for type 1 experiments (CH, CD) than type 2 experiments, with the largest value for experiment CD, followed by CH and WHtoCH. NumC was smallest for WDtoCH. There was no obvious trend for numO.

In summary, smaller particles with slightly lower O:C ratios, bigger carbon numbers and relatively more mass from adducts were observed for type 1 experiments (CH, CD), which had lower α-pinene concentration and colder formation temperature (223 K) compared to the type 2 experiments. For type 2 experiments (WDtoCH, WHtoCH), higher α-pinene concentration (by a factor of ~3) and warmer formation temperature (296 K) produced larger particles with slightly higher O:C ratios, smaller carbon numbers and relatively more mass from monomers. The slightly higher O:C ratio in type 2 experiments is thus not due to bigger oxygen numbers, but due to smaller carbon numbers (Fig. 5), indicating that relatively more small oxygenated molecules were formed for type 2 experiments. This is likely due to higher α-pinene concentration and faster oxidation at 296 K leading to rapid condensation of monomers, providing enough gaseous oxidation products for the equilibrium of semivolatiles to be shifted to the particle phase. Type 1 experiments, on the other hand, were performed with lower α-pinene concentration, and particles were formed in-situ, favoring higher contributions of larger ELVOC/LVOC compounds, especially at the early stages of particle growth (Tröstl et al., 2016). At the same time, the low temperature conditions may also have shifted equilibrium to the particle phase and led to condensation of compounds with relatively lower degree of oxygenation (compared to warm temperature conditions). Overall, the differences observed in mass spectral patterns between the two types of experiments are a consequence of both temperature and precursor concentration differences. They underline the importance of experiment conditions when interpreting laboratory data or modelling.

3.3 Thermograms: Variation in T_{max} of SOA compounds for different experiments

In addition to information on mass spectral patterns and mass loadings when peaks are integrated, the FIGAERO also provides signal curves as a function of desorption temperature (referred to as thermograms). These thermograms result from the thermal desorption of particles deposited on the Teflon filter in the FIGAERO (Lopez-Hilfiker et al., 2014). Single mode thermograms of a compound with a signal maximum occurring at a distinct desorption temperature (Although T_{max}) can be used to infer the compound's saturation vapor pressure (Lopez-Hilfiker et al., 2015; Mohr et al., 2017). However, evaporative behavior and inferred volatility of a particle-bound compound are also influenced by the particles' physical phase state, particle phase diffusivity and viscosity (Yli-Juuti et al., 2017). Here we show that thermograms may also be used for qualitative information on particle viscosity.

Thermograms resulting from the thermal desorption of deposited SOA particles from the four experiments CH, CD, WDtoCH, and WHtoCH at both time points t0 and t1 were analyzed. Examples of the thermograms of a monomer ($C_{10}H_{16}O_4$, molecular formula corresponding to hydroxy-pinonic acid identified by Zhang et al., 2017), and an adduct ($C_{17}H_{26}O_8$, molecular structure identified in SOA from α-pinene ozonolysis as a cispinyl-diaterpenyl ester by Yasmeen et al., 2010 and molecular formula identified in SOA from α-pinene ozonolysis by e.g. Zhang et al., 2015; Mohr et al., 2017) both clustered

with I⁻ at t0 are shown in Fig. 6A−B. Panel C shows the sum of thermograms of all monomers, panel D the sum of all adduct thermograms at t0. The same plots for t1 can be found in Fig. S3. Thermograms and sums of thermograms were normalized to their maximum values. The corresponding mass loadings and sampling times (particle collection on filter) for the four experiments are listed in Table ~~2~~S1. For experiment CD, the $C_{10}H_{16}O_4I_1^-$ thermograms exhibited a multi-modal shape, indicative of contributions from isomers having different vapor pressures, or thermal decomposition of larger molecules. Different isomeric hydroxypinonic acids were found in α-pinene SOA (Zhang et al., 2017) and the decomposition of cis-pinyl-hydroxypinonyl diester could have a cis-pinic and 7-hydroxypinonic acid residue (Müller et al., 2008). Based on previous FIGAERO data analyses (Lopez-Hilfiker et al., 2015; D'Ambro et al., 2017; Wang et al., 2016), we can safely presume that the first mode corresponds to the monomer.

Figure 6A−B shows that T_{max} of an individual compound varied by up to 20 °C, depending on experimental conditions. It has been shown earlier that thermograms and corresponding T_{max} are highly reproducible for stable conditions (Lopez-Hilfiker et al., 2014). In our instrument, T_{max} varied by 2 °C at most for the monomer, $C_{10}H_{16}O_4$, and another adduct, $C_{16}H_{24}O_6$ (molecular formula identified in SOA from α-pinene ozonolysis by e.g. Zhang et al., 2015) both clustered with I⁻, for 6 subsequent thermograms under stable conditions, respectively (Fig. S4). The variation in T_{max} as a function of experiment types observed here thus indicates that the shape of thermogram for a given compound and given FIGAERO configuration is not only defined by the compound's enthalpy of evaporation. For both $C_{10}H_{16}O_4I_1^-$ and $C_{17}H_{26}O_8I_1^-$ thermograms, T_{max} was highest for experiment CD, followed by WHtoCH, and CH, WDtoCH. Similar trends were observed for all compounds measured by the FIGAERO-CIMS, as shown by the sums of thermograms of all monomer compounds (Fig. 6C), or sums of thermograms of all adduct compounds (Fig. 6D). Sum T_{max} of monomers and adducts varied from 46 °C (experiment WDtoCH) to 74 °C (experiment CH) and 93 °C (experiment WHtoCH) to 104 °C (experiment CD), respectively.

Variation in T_{max} of the sum of CHOI compounds was larger for monomers (Fig. 6C) than for adducts (Fig. 6D). Monomers are thus the more important contributors to the shifts in T_{max}, likely because at the higher temperatures where adducts desorb, particle matrix effects may become less important. Since the sum of thermograms and its T_{max} is highly influenced by compounds with large signal, we also show a box and whisker diagram of T_{max} for monomers and adducts (Fig. S5). The median T_{max} values showed similar variation as the T_{max} values based on thermogram sums. Examples of the T_{max} distribution of individual CHOI compounds in numO/numC space at t0 are shown in Fig. 7 for the WDtoCH and CD experiments. Points were color-coded by T_{max}. Compounds with nominal molecular formulae $C_{8-10}H_yO_{4-6}I^-$ were the main contributors to mass concentrations (data not shown), and thus also aggregated T_{max} values. Generally, T_{max} for CHOI compounds ranged from 25 to 165 °C, and increased with carbon numbers and oxygen numbers of compounds, as is to be expected given the relationship between enthalpy of evaporation and volatility of a compound (Lopez-Hilfiker et al., 2015; Mohr et al., 2017). The comparison between WDtoCH (Fig. 7A) and CD (Fig. 7B) experiments, however, showed differences in T_{max} values for most compounds. T_{max} values, especially of a lot of compounds with nominal molecular formulae $C_{5-10}H_yO_{1-10}I^-$ and $C_{15-25}H_yO_{11-20}I^-$, were higher for the CD experiment. The similar behavior in variation in T_{max} of most compounds measured by FIGAERO-CIMS indicates that T_{max} is not purely a function of the compounds' vapor pressures or volatilities, but is influenced by diffusion limitations within the particles (particle viscosity) (Vaden et al., 2011; Yli-Juuti et al., 2017), interactions between particles deposited on the filter (particle matrix), and/or particle mass on the filter. In the following we will discuss these implications in more detail.

Mass transport limitations within SOA particles, often measured or modelled as evaporation rates of specific compounds (Yli-Juuti et al., 2017; Wilson et al., 2015; Roldin et al., 2014), have been related to the particle viscosity (Vaden et al., 2011; Yli-Juuti et al., 2017). Particle viscosity is highly influenced by temperature and ~~relative humidity (~~RH~~)~~ (Shiraiwa et al., 2017; Kidd et al., 2014), with higher viscosities at cool and/or dry conditions (Shiraiwa et al., 2011). Since the temperature was 223 K in AIDA for all experiments discussed here, the observed differences in T_{max}, and presumed viscosity, cannot be directly explained by differences in temperature. In addition, during desorption of compounds with the FIGAERO, particles are actively

heated (with heat transfer assumed to be immediate), and are not evaporating under equilibrium conditions. Presumed variations in particle viscosity based on observed variations in T_{max} must therefore be due to variations in particle chemical composition, and/or RH differences.

The biggest T_{max} difference in Fig. 6 was between WDtoCH and CD experiments, which was in accordance with the largest differences in mass spectra as discussed above (see Fig. 3A and 4). This is indicative of a relationship between T_{max} in the thermograms and particle chemical composition. It has been shown earlier that the chemical properties of particulate compounds influence particle viscosity (Kidd et al., 2014; Hosny et al., 2016). Viscosity is expected to be higher with higher oligomer content, due to inter-component hydrogen bonding, especially at low RH (Kidd et al., 2014). This is in accordance with our results, which showed highest T_{max} values for the CD experiment, which also had the highest contribution from adducts.

RH is an additional parameter that greatly influences particle viscosity (Kidd et al., 2014; Hosny et al., 2016; Renbaum-Wolff et al., 2013). Even though the fact that the SOA particles might be dried very quickly by the dry heated nitrogen during particle desorption, we suppose that RH might have a "memory effect" and still influence T_{max}. RH conditions during the four experiments presented here ranged from 6 % (CD), 30 % (WHtoCH) to 61 % (WDtoCH and CH). Note that these were the conditions of the measurement time in the AIDA chamber; for WDtoCH and WHtoCH, the RH conditions during SOA formation in the APC chamber were 1% and 21%, respectively. We thus need to differentiate between $RH_{formation}$ and $RH_{measurement}$. As shown in Fig. 8, there was no trend between $RH_{formation}$ and T_{max}, indicating that the RH during particle formation did not play an important role in the observed viscosity variation. However, we observed a negative correlation of $RH_{measurement}$ and T_{max} of all monomer compounds at t0, indicating that even under low temperature conditions of 223 K there is particle water uptake, and an influence of RH on viscosity. ~~Calculated particle water content derived from AMS measurements is prone to large uncertainties (Engelhart et al., 2011); we observed a qualitative positive correlation with RH (data not shown).~~ Particle water uptake thus seems to influence particle viscosity even at such low temperature and on such short timescales (few hours). To what extent RH and particle water uptake, or chemical properties and adduct content, and their respective influence on water uptake via increased hygroscopicity, contribute to the observed differences in T_{max} and presumed viscosity, we can only speculate. In the CH and WDtoCH experiments, $RH_{measurement}$ was ~60 % for both. The adduct mass fraction was only slightly higher for SOA in the CH experiment, and so was T_{max} and thus potentially particle viscosity. More controlled studies at low temperature are needed to separate these effects.

We also noticed that different mass loadings on the filter due to different sampling times and/or sample concentrations influenced the shape of thermograms and thus T_{max}. T_{max} increased as a function of mass loading on the filter, likely due to the increase in heat capacity of the increasing mass of the particle matrix, and potential interactions between the particles. The dependency of T_{max} on filter mass loading was not linear, and for our FIGAERO reached a plateau at mass loadings of 2−4 µg. Our results are therefore not affected by the mass loading effect, but we recommend taking it into account in analyses that involve T_{max}. A detailed discussion can be found in the supplement.

4 Conclusions and atmospheric implications

In this study, α-pinene SOA physicochemical properties such as chemical composition, ~~phase state~~size distributions, and ~~viscosity~~ degree of oligomerization were investigated at low temperature (223 K) and different relative humidity (RH) using two simulation chambers (APC and AIDA). Two types of experiments were performed: For type 1 experiments, SOA was directly generated in the AIDA chamber kept at 223 K, 61 % RH (experiment termed "cold humid", CH) or 6 % RH (experiment termed "cold dry", CD) conditions. For type 2 experiments, SOA was formed in the APC chamber at room temperature (296 K), <1 % RH (experiment termed "warm dry", WD) or 21 % RH (experiment termed "warm humid", WH)

conditions, and then partially transferred to the AIDA chamber kept at 223 K, 61 % RH (WDtoCH) or 30 % RH (WHtoCH) conditions, respectively, to simulate SOA uplifting.

For type 1 experiments (CH, CD) with lower α-pinene concentration and cold SOA formation temperature (223 K), smaller particles with relatively more mass from adducts were observed. For type 2 experiments (WDtoCH, WHtoCH) with higher α-pinene concentration (by a factor of ~3) and warm SOA formation temperature (296 K), larger particles with relatively more mass from monomers were produced. The differences observed in mass spectral patterns between the two types of experiments are likely a consequence of both temperature and precursor concentration differences. Higher α-pinene concentration and faster oxidation at 296 K during SOA formation in the APC chamber shift the gas-particle equilibrium to the particles, resulting in larger mass fractions of semivolatile and/or monomer compounds. Low temperature conditions in the AIDA chamber during SOA formation on the other hand may result in condensation of compounds with a relatively lower degree of oxygenation. Our results show that depending on where SOA formation takes place in the atmosphere (e.g. boundary layer or upper troposphere), chemical properties can vary, and with that reactivity and lifetime.

In addition to the differences in mass spectral patterns for the different experiments, we also observed differences in the shape of thermograms resulting from the desorption of SOA particles collected on the FIGAERO filter: T_{max} of an individual compound in the thermograms varied by up to 20 °C depending on experimental conditions, indicating that T_{max} is not only influenced by a compound´s vapor pressure or volatility, but also by diffusion limitations within the particles (particle viscosity). For both $C_{10}H_{16}O_4I_1^-$ and $C_{17}H_{26}O_8I_1^-$ thermograms, T_{max} was highest for experiment CD, followed by WHtoCH, and CH, WDtoCH. We observed higher T_{max} for α-pinene SOA particles with higher oligomer mass fractions, indicating the potential role of intra- and inter-molecular hydrogen bonds between these large and highly functionalized molecules for the increase in particle viscosity (Kidd et al., 2014). Furthermore, T_{max} was negatively correlated with RH in the particle reservoir and particle water content, suggesting that hygroscopic properties and water uptake are important factors even at such low temperature. We also demonstrated an effect of mass deposited on the FIGAERO filter on T_{max}, which needs to be taken into account for further studies relying on T_{max}.

The results suggest that particle physicochemical properties such as viscosity and oligomer content mutually influence each other. More controlled experiments at low temperature are needed to separate the direct effects of RH and particle water uptake, or chemical properties such as adduct content (i.e. oligomer content), and the indirect effects of chemical properties on water uptake via changes in hygroscopicity on the observed differences in T_{max} and presumed viscosity. The differences in SOA physicochemical properties observed in our set of experiments as a function of temperature, RH, and precursor conditions demonstrates the importance of ambient and laboratory measurements at a wide range of atmospherically relevant conditions, and of taking experimental conditions into careful consideration when interpreting laboratory studies or using them as input in climate models.

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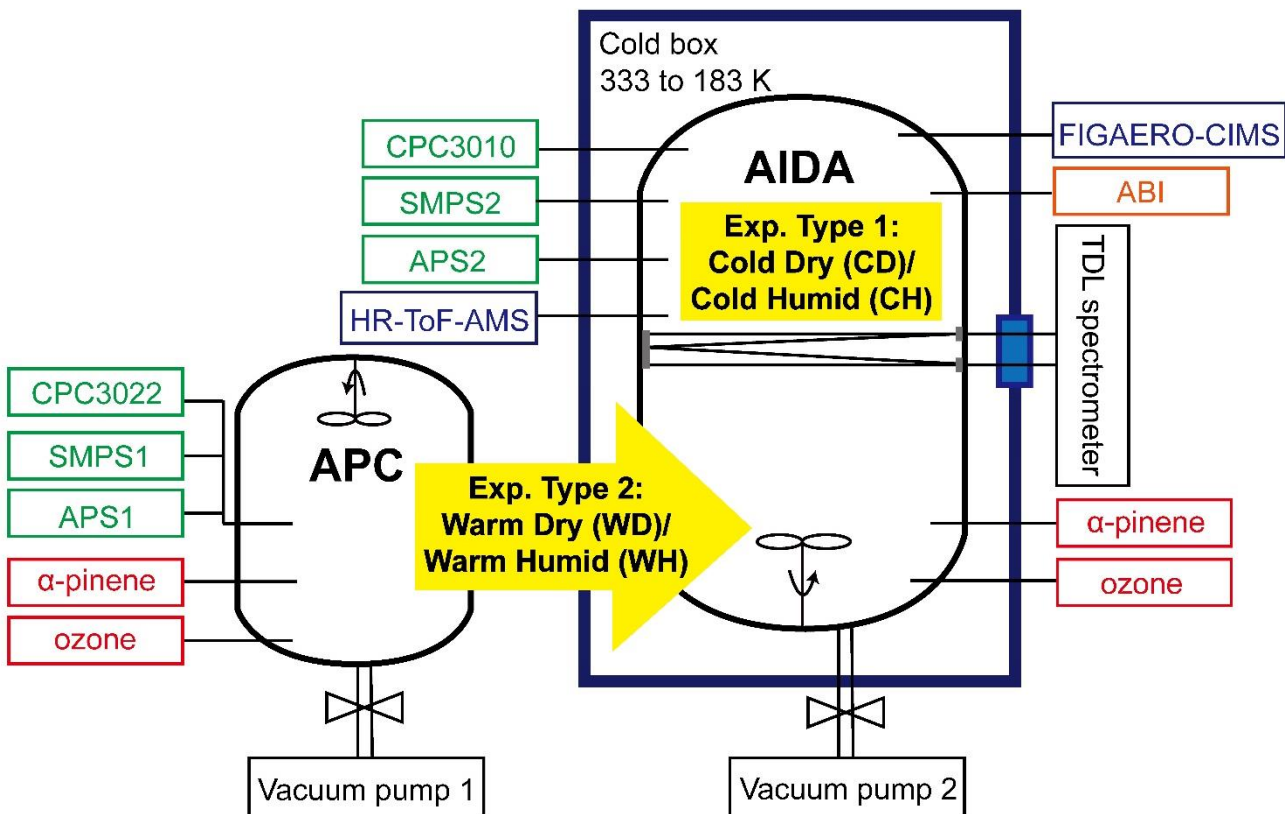
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Figure 1. Brief schematic and conditions for the two types of experiments (modified from Wagner et al., 2017). Both chambers at IMK (APC and AIDA) were used in this study. Instruments are annotated in green, blue or orange, and precursor gases in red. More detailed information for the instruments and precursor gases are explained in the text.
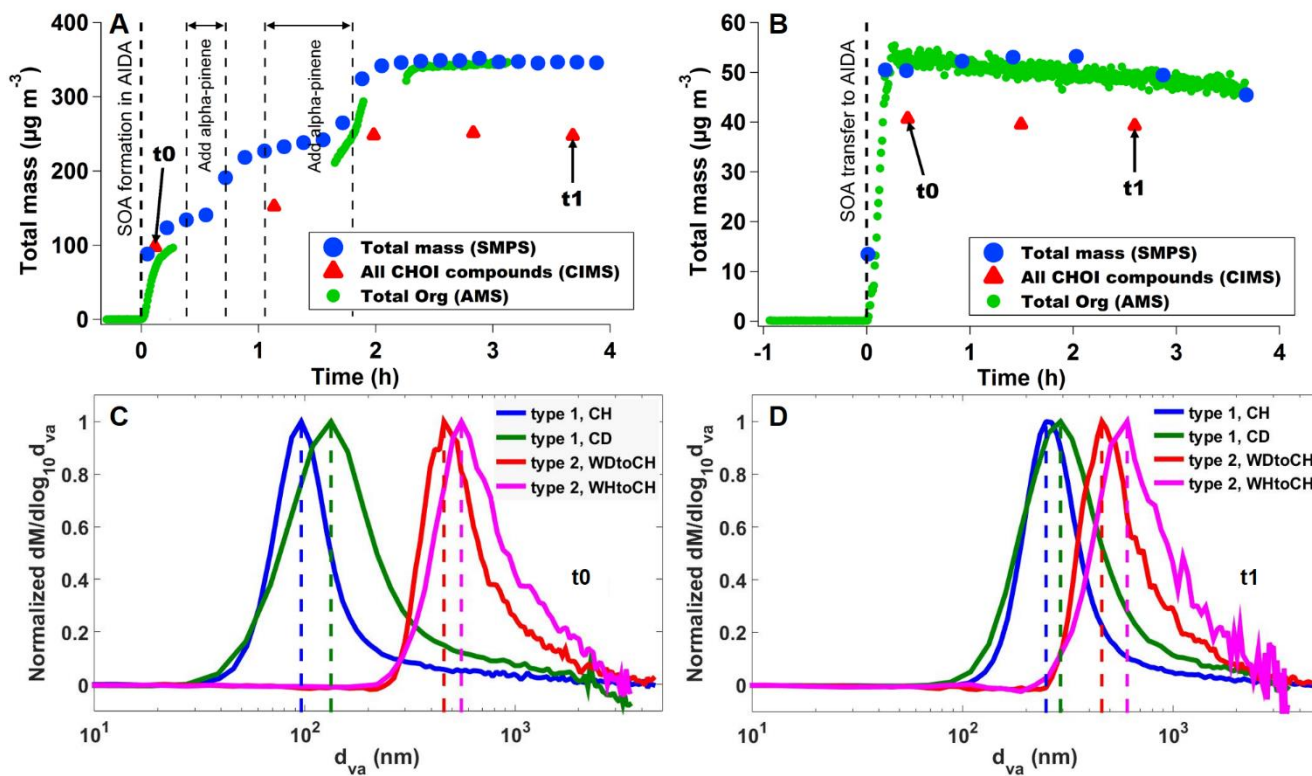
Figure 2. (A) Particle mass concentrations derived from SMPS size distributions (blue circles), CHOI mass concentrations measured by CIMS (red triangles), and organic mass concentrations measured by AMS (green circles) representative for type 1 experiments (here CH), (B) representative for type 2 experiments (here WDtoCH). Data were not wall loss corrected. t0 and t1 indicate points in time used for comparisons in this study. (C) Averaged size distributions measured by AMS at t0, and (D) t1 for the four experiments.

Table 1. Experimental conditions and precursor concentrations for the four experiments discussed in this study: CH, CD (type 1), and WDtoCH, WHtoCH (type 2). Total organic mass, CHOI mass concentrations, and elemental oxygen to carbon (O:C) ratios are given for t0 and t1. ~~Relative humidity (~~RH (with respect to water)~~)~~ values from the APC chamber were measured at room temperature (296 K).

Exp. name	SOA position	T (K)	RH (%)	α-pinene added (ppm)	O_3 ~~Ozone~~ added (ppm)	Total Org (μg m^{-3})	Total CHOI (μg m^{-3})	O:C
CH	AIDA	223	61.0	0.714	2.3	67.5/319.5	97.8/247.6	0.26/0.30
CD	AIDA	223	6.0~~2~~	0.714	2.3	260.1/440.1	110.6/160.4	0.28/0.29
WDtoCH	APC → AIDA	296 → 223	<1 → 60.6	2.2	1.8	50.9/48.5	40.7/39.3	0.34/0.34
WHtoCH	APC → AIDA	296 → 223	21 → 30.3	2.2	1.8	64.2/58.4	23.4/23.3	0.36/0.37
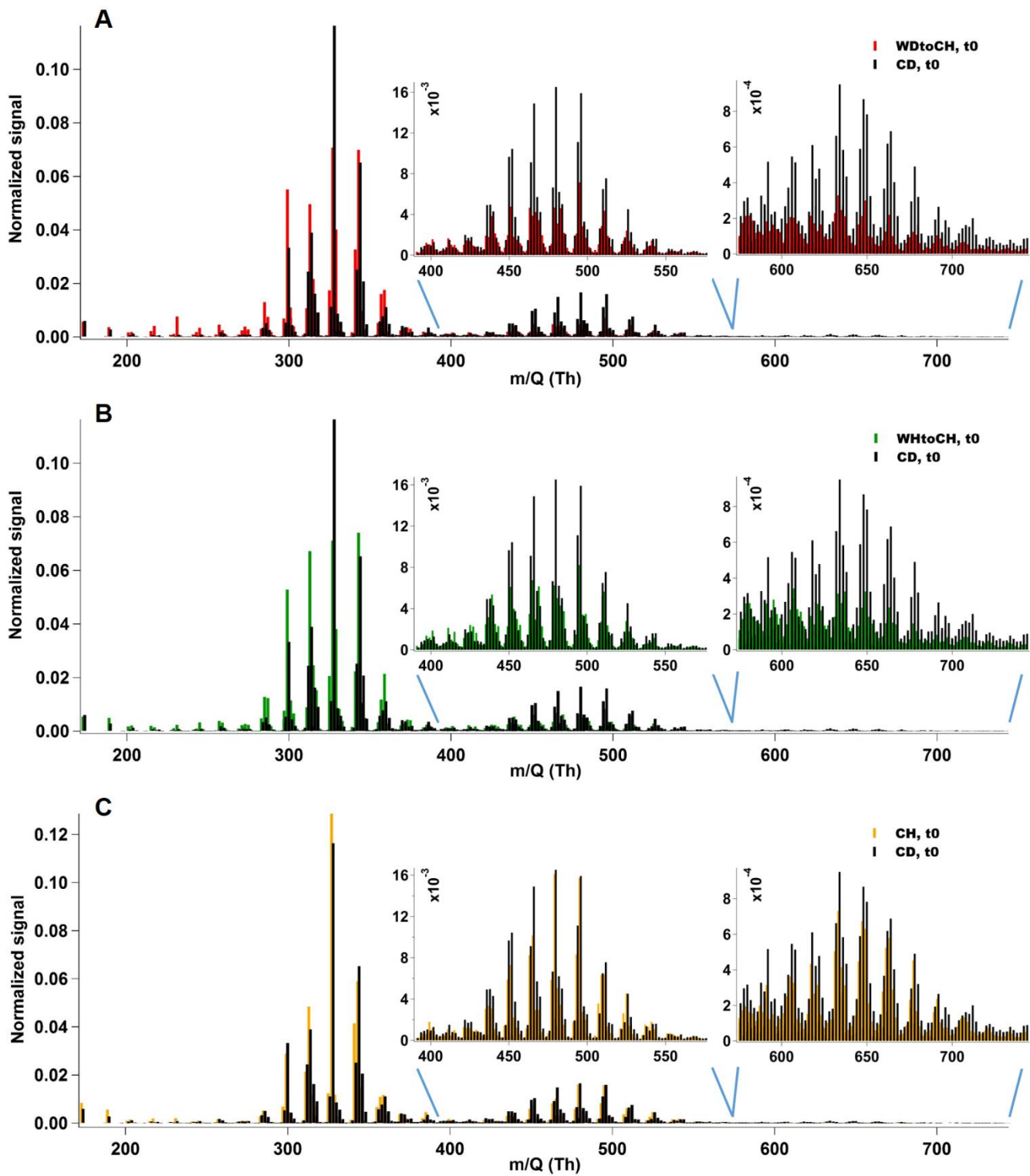
Figure 3. FIGAERO-CIMS mass spectra (normalized to the sum of signal of all detected CHOI compounds) of experiments WDtoCH and CD (A), WHtoCH and CD (B), CH and CD (C) at t0. Inserts show enlarged regions of dimers (left) and trimers (right).
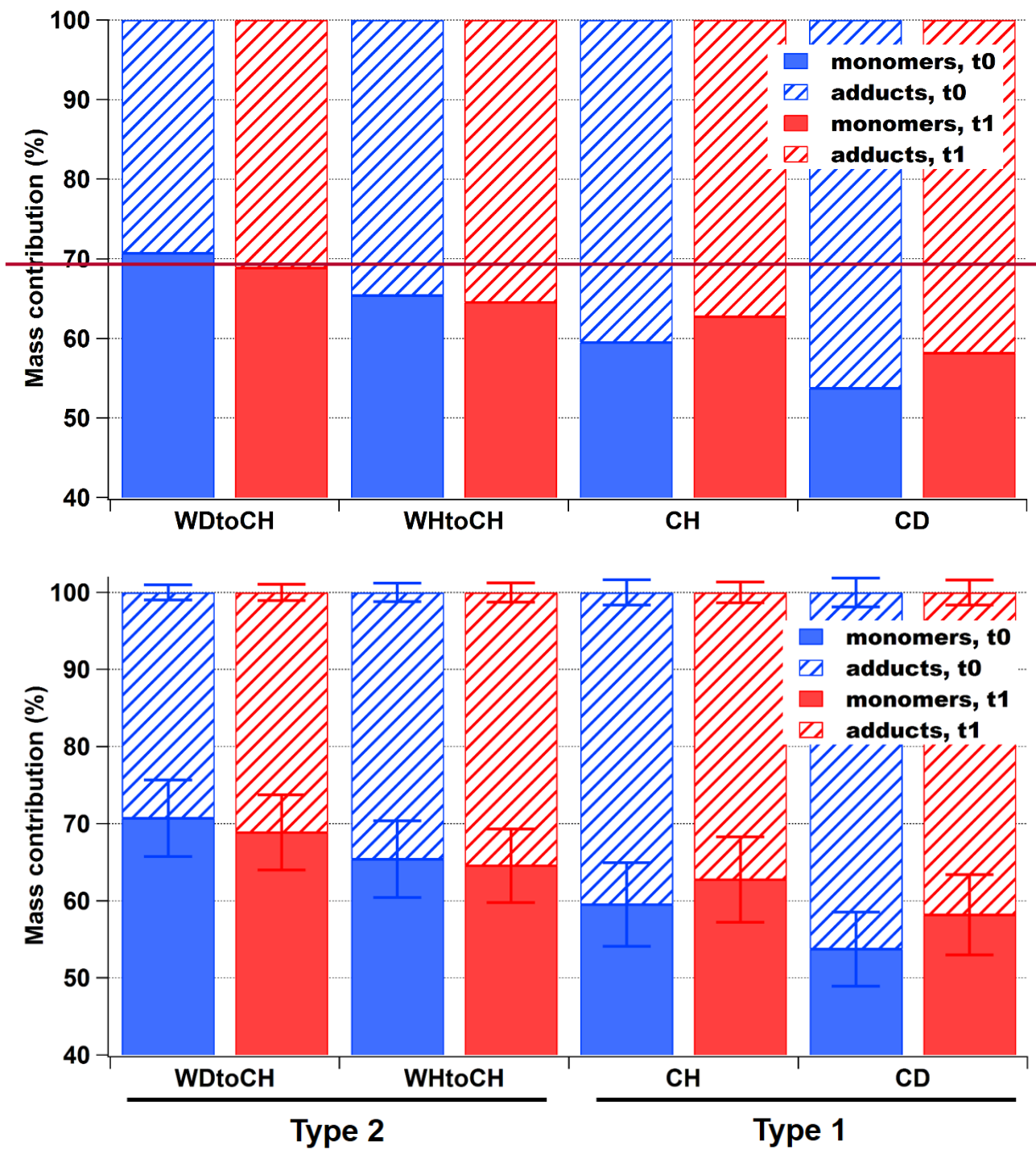
Figure 4. Relative mass contributions of monomers and adducts with error bars at t0 (blue) and t1 (red).
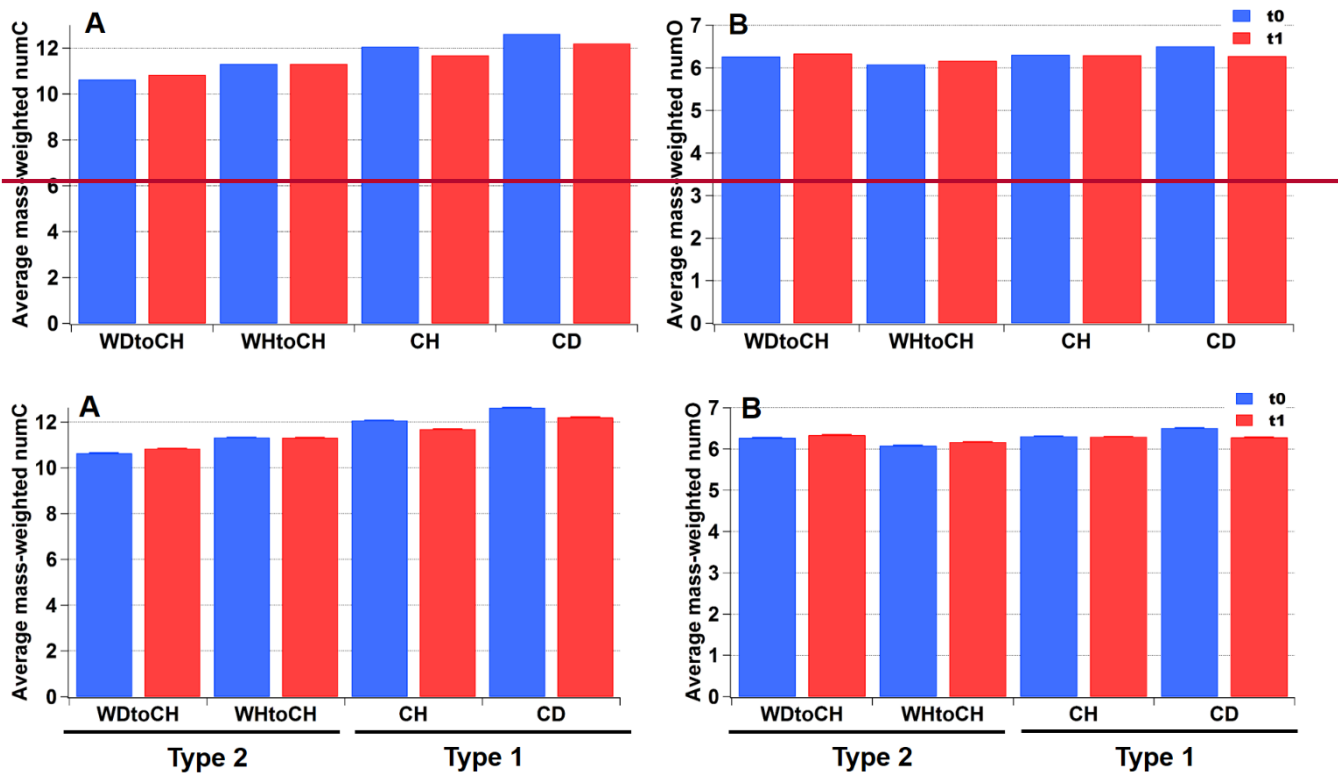
Figure 5. (A) Average mass-weighted number of carbon atoms (numC) and (B) oxygen atoms (numO) with error bars at t0 (blue) and t1 (red).
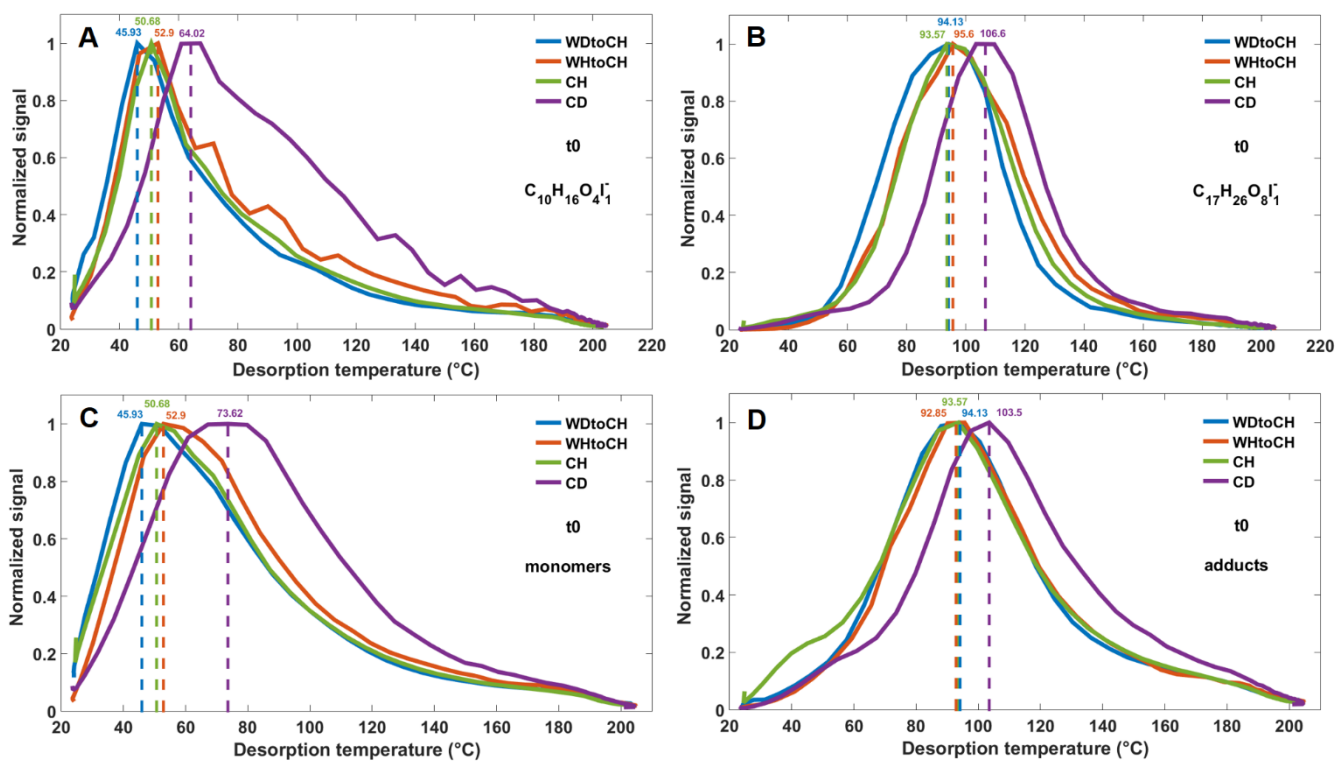
Figure 6. Thermograms of a monomer, $C_{10}H_{16}O_4$ (A) and an adduct, $C_{17}H_{26}O_8$ (B) both clustered with I^- at t0, and sum thermograms of monomers (C) and adducts (D) at t0. Dashed lines refer to the corresponding T_{max}.
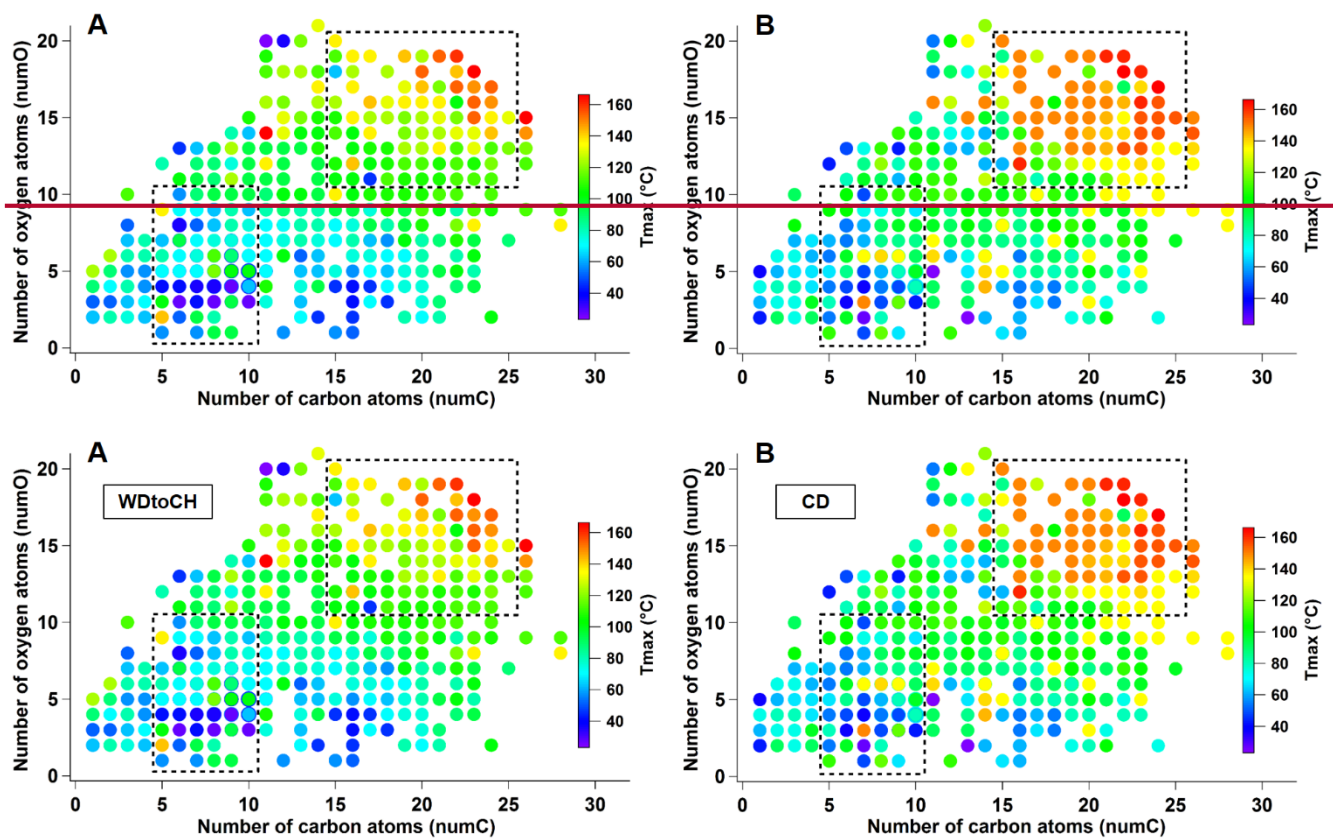
Figure 7. T_{max} distribution for individual CHOI compounds of WDtoCH (A) and CD (B) experiments at t0 according to number of oxygen atoms (numO) vs Number of carbon atoms (numC). Dashed boxes specify the compounds with nominal molecular formulae $C_{5–10}H_yO_{1–10}I^-$ and $C_{15–25}H_yO_{11–20}I^-$ which had bigger T_{max} differences.
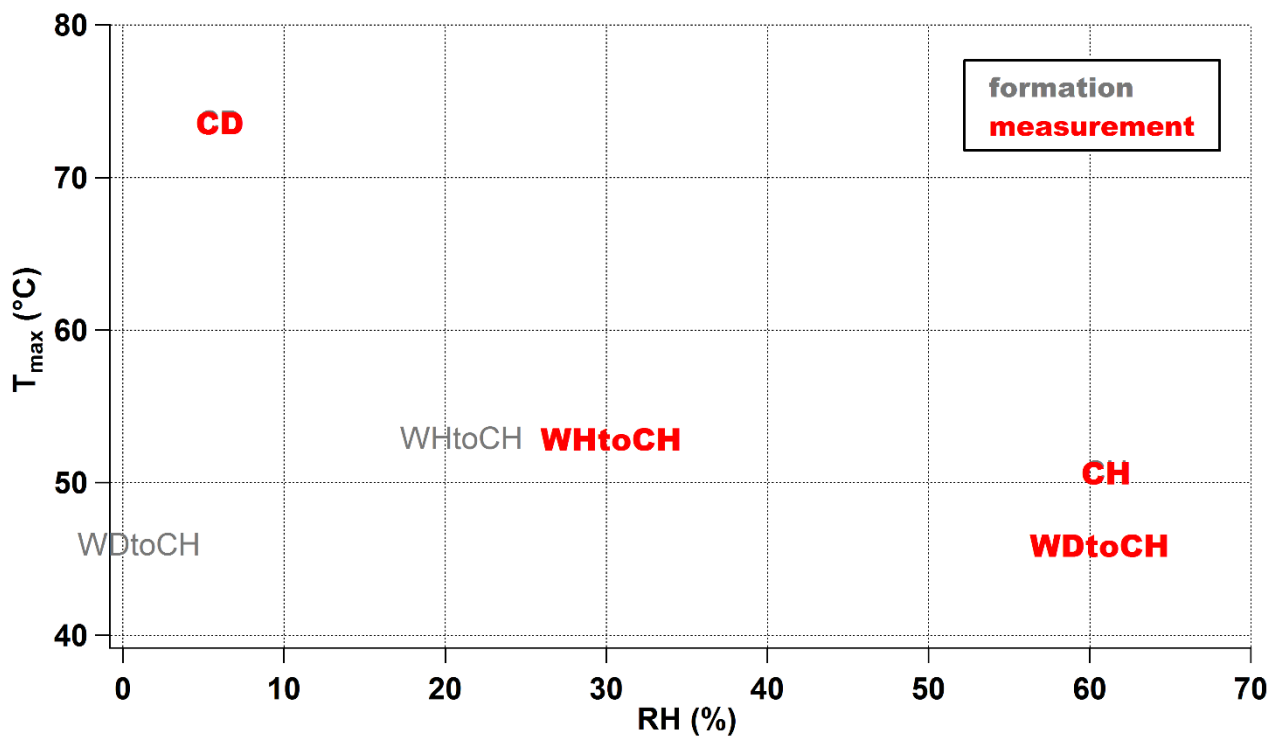
Figure 8. Relationship of $RH_{formation}$ (gray), $RH_{measurement}$ (red) and T_{max} of all CHOI monomer compounds for four experiments at t0.

Table S1. Particle mass loadings (µg) on the filter and corresponding sampling times (min) at t0 and t1.

Exp. name	t0		t1	
	Mass loadings (µg)	Sampling time (min)	Mass loadings (µg)	Sampling time (min)
WDtoCH	4.07	20	3.93	20
WHtoCH	2.34	20	2.33	20
CH	6.60	13.5	6.19	5
CD	11.06	20	4.01	5

	t0		t1	
	Mass loadings (µg)	Sampling time (min)	Mass loadings (µg)	Sampling time (min)
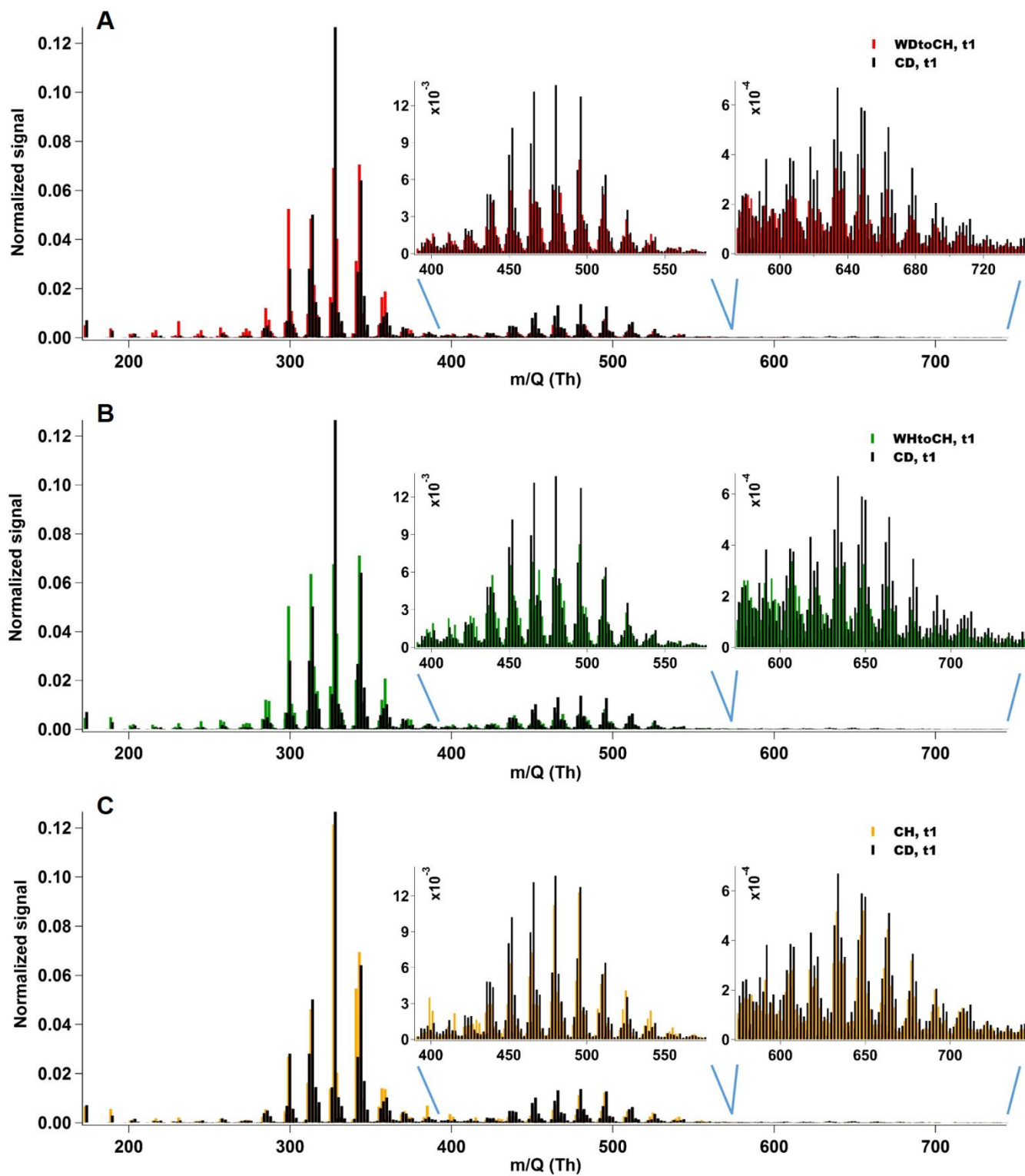
Figure S1. FIGAERO-CIMS mass spectra (normalized to the sum of signal of all detected CHOI compounds) of experiments WDtoCH and CD (A), WHtoCH and CD (B), CH and CD (C) at t1. Inserts show enlarged regions of dimers (left) and trimers (right).
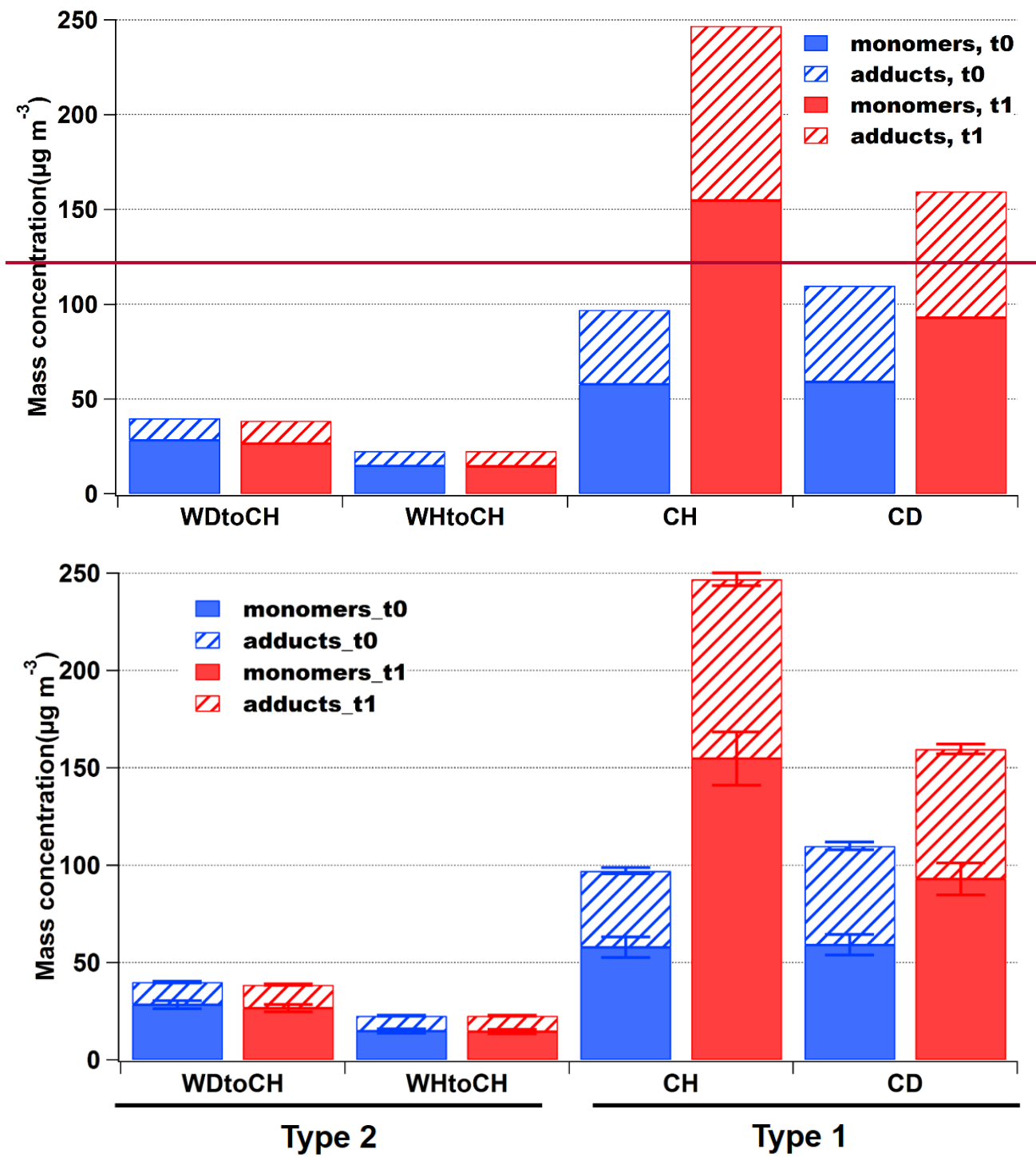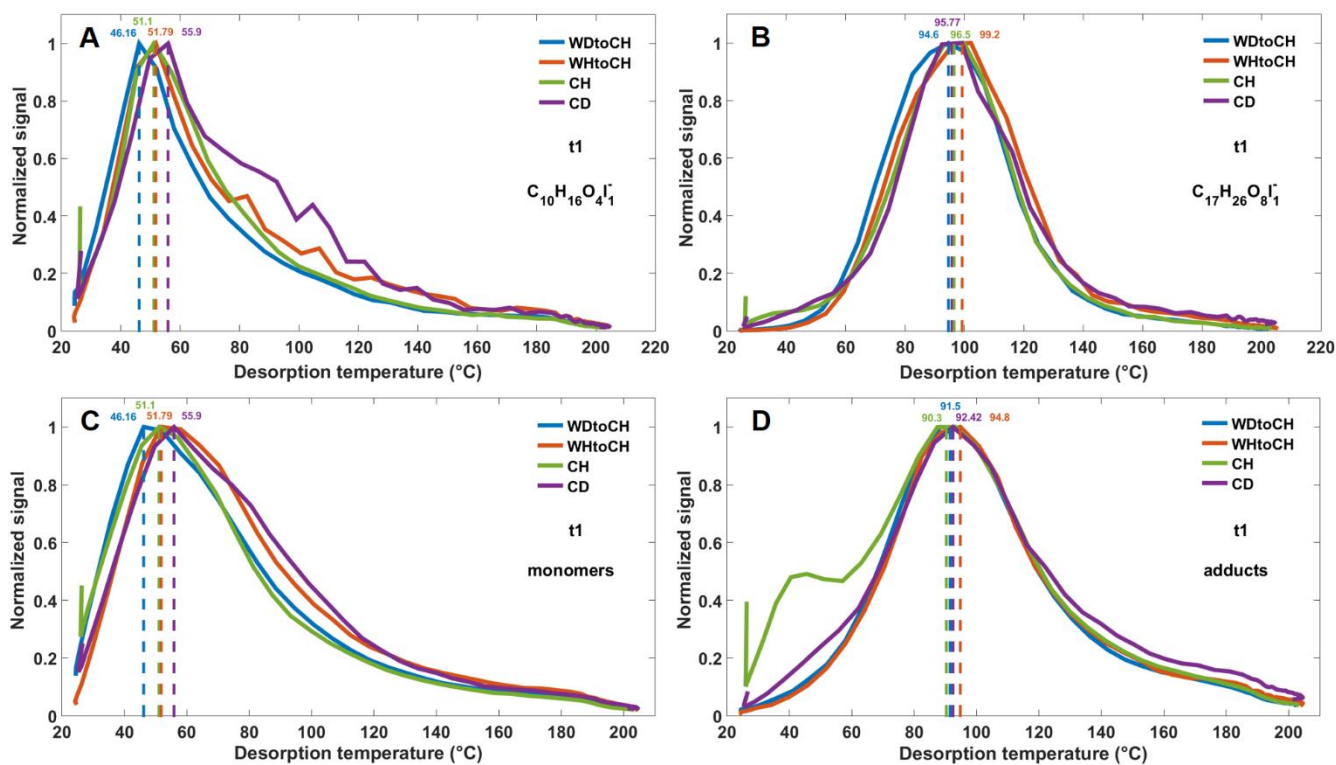
Figure S2. Absolute mass concentrations of monomers and adducts with error bars at t0 (blue) and t1 (red).

Figure S3. Thermograms of a monomer, $C_{10}H_{16}O_4$ (A) and an adduct, $C_{17}H_{26}O_8$ (B) both clustered with I^- at t1; sum thermograms of monomers (C) and adducts (D) at t1. Dashed lines refer to the corresponding T_{max}.
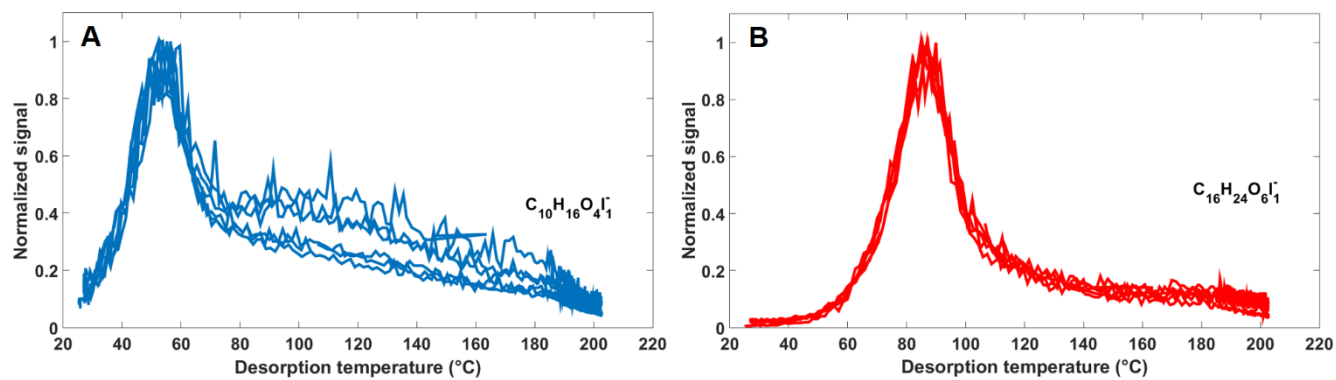
Figure S4. Thermograms of a monomer, $C_{10}H_{16}O_4$ (A) and an adduct, $C_{16}H_{24}O_6$ (B) both clustered with I^- under stable conditions.
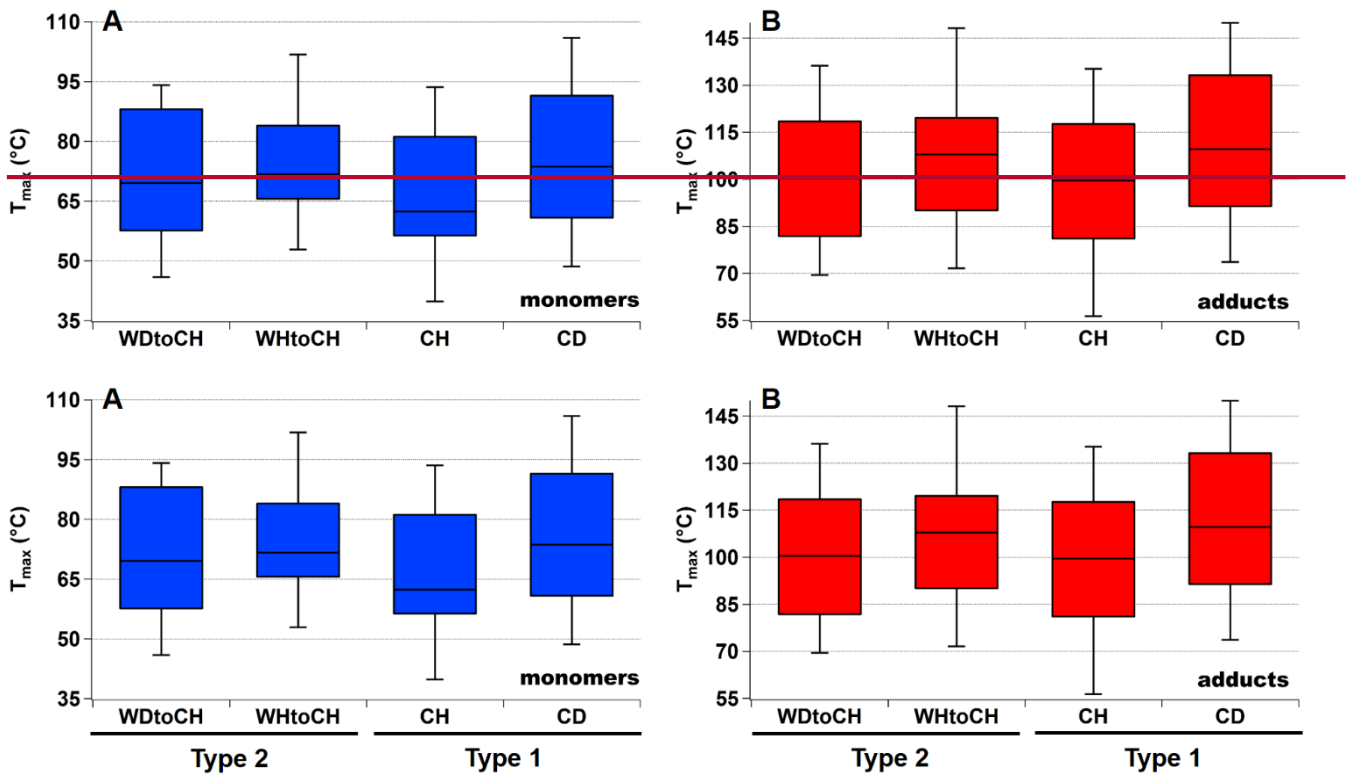
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Figure S5. T_{max} box plot for monomers (A) and adducts (B) for four experiments at t0.

Mass loading effects

Different mass loadings on the filter due to different sampling times and/or sample concentrations influence thermogram shapes and thus T_{max}. Thermograms of the sums of all CHOI compounds, monomers and adducts for different filter mass loadings for WHtoCH and CD experiments were compared (Figure S6). The corresponding filter mass loadings are listed in Table S2. The box plot of T_{max} of all CHOI compounds, monomers and adducts increased with increasing mass loading on the filter (Figure S7). Beyond filter mass loadings of 2−4 µg the curves levelled off (saturation effect). Potential reasons for the observed effect of filter mass loading on T_{max} values are increased heat capacity of the increasing mass of the particle matrix, particle-particle interactions, and diffusion limitations due to several particle layers.

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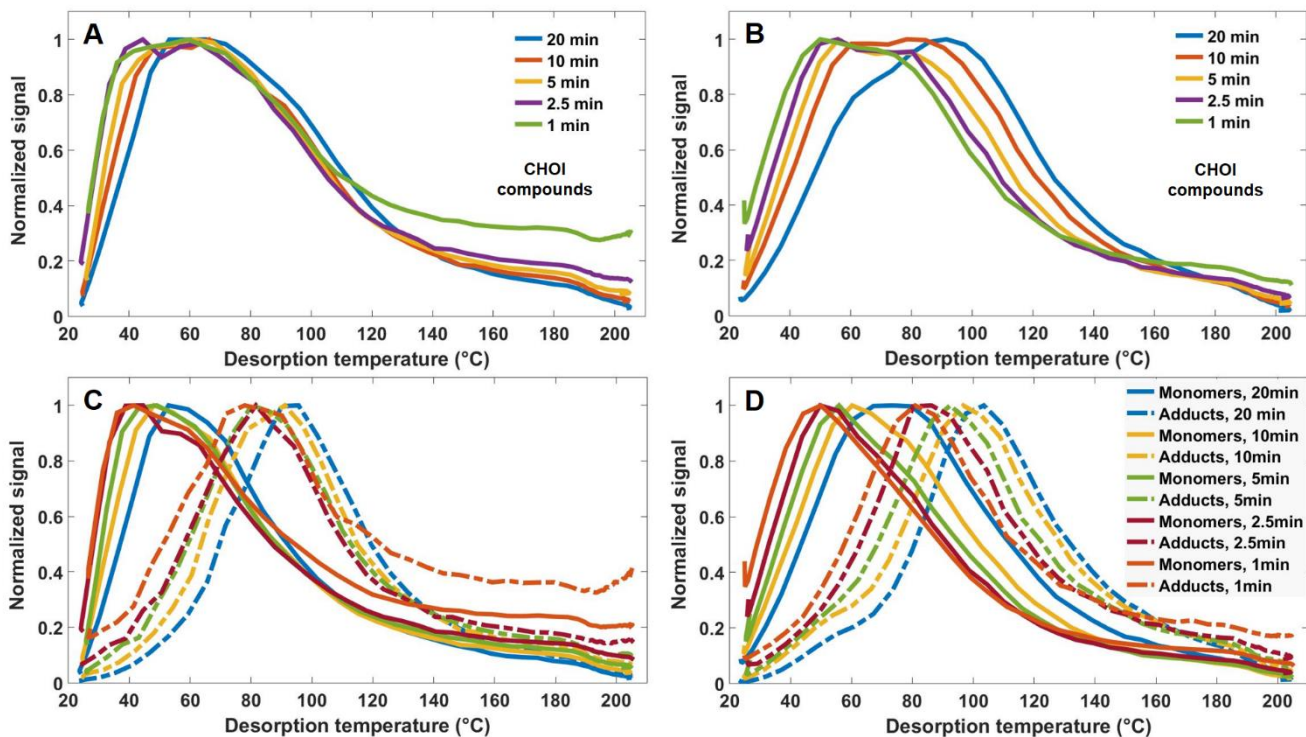
Figure S6. Sum thermograms of CHOI compounds with different sampling time for WHtoCH (A) and CD (B) experiments, and sum thermograms of monomers (solid lines) and adducts (dashed lines) for WHtoCH (C) and CD (D) experiments.

Table S2. Mass loadings (μg) on the filter with different sampling time for WHtoCH and CD experiments.

Exp. name	Mass loadings (μg)				
	20 min	10 min	5 min	2.5 min	1 min
WHtoCH	2.36	1.24	0.60	0.38	0.20
CD	11.06	7.25	4.01	2.08	0.94
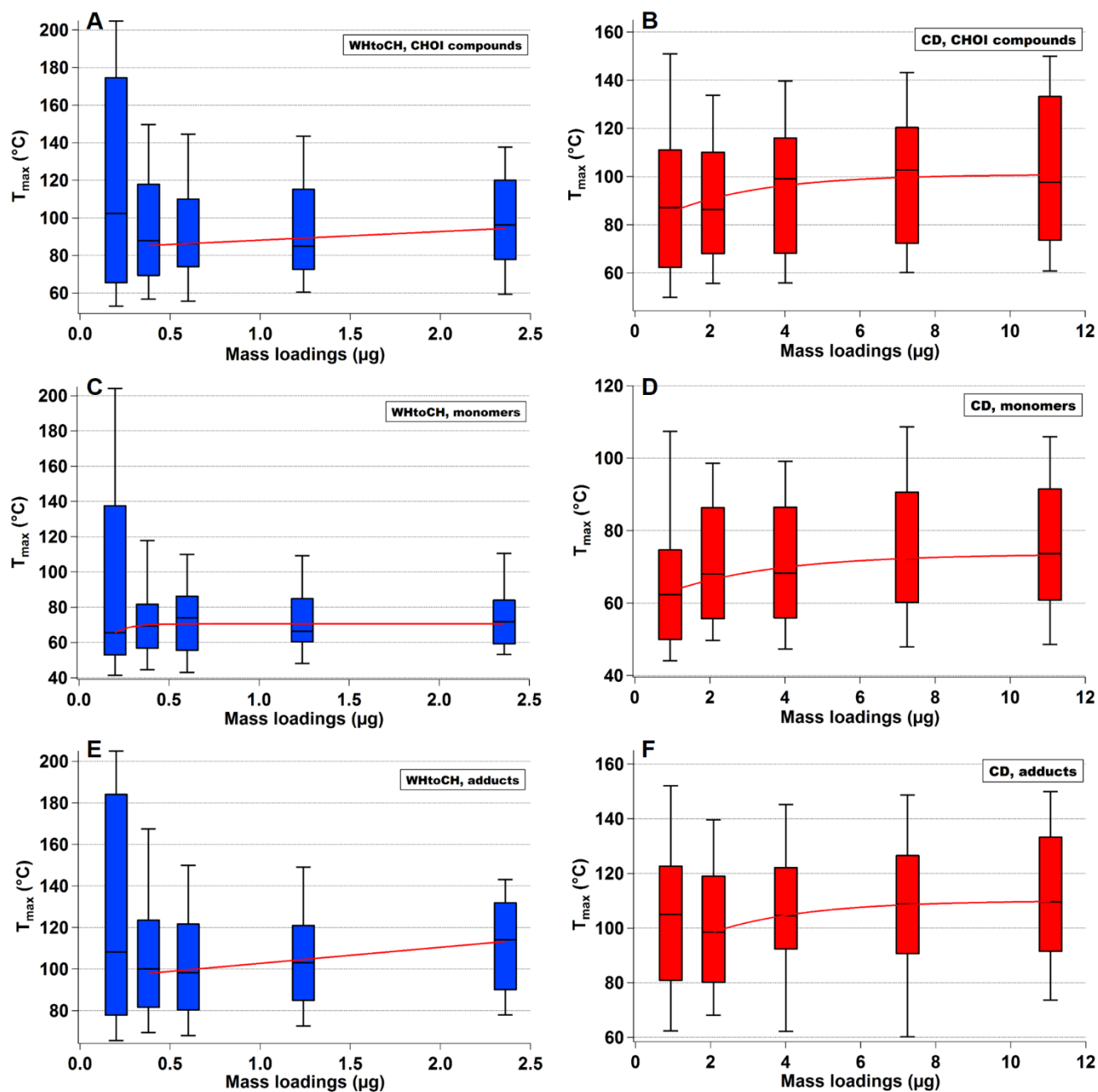
Figure S7. Box plot of T_{max} at different mass loadings for CHOI compounds (A–B), monomers (C–D) and adducts (E–F) for WHtoCH (left) and CD (right) experiments. Red lines refer to the exponential curves fitted for the median T_{max} in (A–D) and (F) except for linear fit in (E).

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