Reply to Referee #1

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General comments

The authors investigated volatility of secondary organic aerosol (SOA) from a-pinene oxidation using measurements of chemical composition of particles, evaporation upon heating and evaporation upon dilution. The topic is important in the field of atmospheric aerosols and well suited in Atmospheric Chemistry and Physics. The experimental work coupling different methods for investigating the volatility of SOA seems valid. I find that there are few aspects in the analysis and discussion of the results which should be improved/clarified before the manuscript can be published. Please find below my specific comments.

Reply

Thank you for your valuable comments; we appreciate the time and effort you have put into reviewing our paper. I have revised the manuscript based upon your input, as described below.

Specific comments

Comment 1

How large fraction of compounds are actually detected with PTR-MS? Is sticking of molecules on the filter affecting uncertainty of the resulting Csat?

Reply

We compared the mass concentration of gaseous products detected by the PTR-MS ($\Delta[\text{Gas}]_{\text{PTR-MS}}$) with the expected value, which was calculated from a difference between the amounts of consumed reactants and the SOAs formed ($\Delta[\text{M}]_{\text{c}} - [\text{SOA}]$). The results of runs 5, 6, 7, and 8 are summarized in Table R1. In run 6, for example, 0.31 ppmv of α-pinene and 0.27 ppmv of O_3 were consumed after a reaction time of 1 h, which corresponds to 2.3 mg m^{-3} in total. The amount of gaseous products detected by the PTR-MS was estimated to be 1.0 mg m^{-3}, using a calculated detection sensitivity (9.1 ncps/ppbv in this study) with a typical ion-molecular reaction rate constant (2×10^{-9} cm^3 molecule^{-1} s^{-1}) for all products. Since the amount of SOAs was 1.0 mg m^{-3}, the amount of gaseous products detected by the PTR-MS accounts for 77 % of ($\Delta[\text{M}]_{\text{c}} - [\text{SOA}]$). Except for run 7, gaseous products detected by the PTR-MS were 60−77% of the expected value ($\Delta[\text{M}]_{\text{c}} - [\text{SOA}]$).

The amount of products in the aerosol phase was estimated by summing ion signals of evaporated compounds during the heating of the sample filter. The results for runs 6 and 7 are listed in Table R1. About 30 % of SOAs measured by SMPS was detected by the PTR-MS.

We checked the time variations of the PTR-MS signals of m/z = 185 (pinonic acid) and 187 (pinic acid) after the aerosol sample filter was heated at 368 K (please see the specific comment 4 made by the other reviewer and Figure R2). The signals of m/z = 185 and 187 decreased to very low levels within 3 h, suggesting that the heating duration will be sufficient. Even though the PTR-MS signals decreased to zero after the heating, these compounds might be still adsorbed on the filter media. It might be difficult to determine the amount of compound remaining on filter. If 10% of the collected compound is not evaporated from the filter, we overestimate Csat and the result of $\log_{10}$ Csat shifts positively by 0.05 from that obtained when all compound is evaporated. If 20% of the collected compound is not evaporated, the result of $\log_{10}$ Csat shifts positively by 0.10. As far as we discuss the order of magnitude of Csat, the influence from sticking molecules will be small.

Comment 2

Particles were formed in different chambers in dry and 40% RH case: one with Teflon-coated walls and the other made of fluorinated ethylene polyethylene. At least Teflon walls are found previously to take up organic vapors. This can affect the composition (i.e. volatility distribution) of the particles and reduce the comparability of the dry and 40% RH experiments. Also, the SOA formation conditions have not been same in both types of experiments. The authors should discuss the effect of such possible sources of uncertainty in context of comparing the dry and 40% RH experiments. Also, please make it clear what was the RH in the evaporation section of the set-up when the particles formed at 40% RH were studied. I assume it was 40% (P4, L126).

Reply

We agree with your comments on potential differences in experimental conditions between experiments under dry and humid conditions. We discuss possible uncertainty in the context of comparing the dry and humid experiments in lines 336-337 in the revised manuscript as follows:

The results are not compared between dry and humid experiments here because the chamber systems differ between these experiments.

Your assumption on the RH of evaporation is correct. The RH of EDC was set to ~40% when particles formed at ~40%, whereas it was set to <1% when particles formed at <1%. We explain this in lines

136-138 of the revised manuscript as follows:

Prior to each dilution-evaporation experiment, clean air with a relative humidity identical to that in the SOA formation chamber was filled into the EDC.

We also explain this in the caption of Figure S1 of the supplementary material.

Comment 3

LC/MS measurements of composition: A. Can the SOA evaporate or react during the treatment of the filter sample? How much uncertainty does this cause to the measured composition? Especially, one would expect some of the semi-volatiles to evaporate when the filter extract is concentrated in nitrogen stream. If such effects are possible, the effect on the inferred SOA composition and VBS should be discussed. B. How large fraction of SOA compounds are expected to be detected with the method and do the compounds that are not detected cause uncertainty to the results? The ionization and transmission efficiencies are discussed on page 6 related to Csat distribution. Were the same efficiencies assumed when analyzing carbon number distributions? C. Based on Figure 3 there are rather large differences between runs 1 and 6 and between 7 and 8 although the oxidation conditions have been similar. This should be addressed in the discussion of the results.

Reply

A. We have added following text at lines 171–173 to discuss the effect of reactions during pre-treatment:

Monomers detected in a previous online study, $C_{10}H_{14-16}O_{7-11}$ (Ehn et al., 2017), are similar to those detected in our present offline analysis, suggesting that only a small portion of HOMs may decompose during pre-treatment.

Furthermore, we added the following sentence in lines 129–131 to discuss the effect of evaporation during pre-treatment:

In our previous paper (Sato et al., 2007), recovery of malic acid ($\log_{10} C^* \approx 2$) was determined to be > 90%, suggesting that evaporation loss during pre-treatment is negligible for molecules with $\log_{10} C^* \leq 2$.

B. If we apply pinonic acid-equivalent sensitivity for all product signals, the total mass of detected products will be estimated to be 153–273% of the total particle mass; suggesting that the sensitivity of pinonic acid is lower than an effective sensitivity for the total products. Because we do not know

the effective sensitivity for the total products, we cannot evaluate how large a fraction of SOA compounds is expected to be detected with the method. We agree with the comment. Undetected compounds would affect the volatility distributions determined from LC/MS data. We have added the following sentences in lines 314–317 of the revised manuscript:

The volatility distributions in Figures 4a, 4b, and 4c (LC/MS) have different shapes than Figure 4e (TD-AMS). The shapes of the volatility distributions obtained from LC/MS analysis may be affected by uncertainties in saturation concentration and sensitivity parameterizations as well as the existence of undetected molecules.

When we calculated carbon number distributions, we plotted the sum of raw signal intensities without using any efficiency (this is written in the caption of Fig.3). We revise the vertical axis title of this figure to "Sum of LC/MS signals (arb. units)". Furthermore, we add the following sentence in line 185 in the manuscript.

Note that the abundance was directly calculated from the summation of the signal intensities.

C.   We added the following sentences in lines 192–194:

There are differences between runs 1 and 6 and between runs 7 and 8, although the oxidation conditions are similar; these will be due to differences in initial reactant concentrations or uncertainties resulting from sensitivity variations.

Comment 4

Authors present the Csat distributions as sum of particle and gas phase (Figure 4) where particle phase is based on measured composition and gas phase is calculated assuming gas-particle equilibrium. Based on Figure 3, O/C is continuing to change at the end of the experiment suggesting that the system is not in equilibrium. Based on text on page 6 it's not clear if this was considered in the analysis when estimating abundance of gas phase compounds.

Reply

The equilibration time scale of gas–particle partitioning in this study is less than 1 h, as discussed in the reply to comment 3 made by the other reviewer. The O/C ratio increased from 0.340 to 0.355 for 1 h (i.e., 4% h^{-1}) during a filter sampling period in run 8. In other words, the variation of O/C is small ($\leq 4\%$) during the gas–particle equilibration; therefore, we can assume gas–particle equilibrium even though O/C is continuing to change at the end of the experiment.

Comment 5

The volatility distributions in Fig. 4 a-b have different shape compared to Fig. 4 c. Do authors have any ideas on what causes this?

Reply

In the revised manuscript, we discussed the volatility distribution of LC/MS further, and we calculated additional results employing a third saturation concentration parameterization method (Fig. 4c). We also check the sensitivity of transmission efficiency (Fig. 4d). We compared the results in Figs. 4a, 4b, 4c, and 4d with the results of TD-AMS (Fig. 4e), and discussed potential reasons for the difference in the shape of the volatility distribution. We added the following explanations in lines 314–318 of the manuscript:

The volatility distributions in Figures 4a, 4b, 4c, and 4d (LC/MS) have different shapes than Figure 4e (TD-AMS). The shapes of the volatility distributions obtained from LC/MS analysis may be affected by uncertainties in saturation concentration and sensitivity parameterizations as well as the existence of undetected molecules. The shape of the volatility distributions obtained from the TD-AMS may be influenced by heat-induced reactions.

Comment 6

Heat induced evaporation (Figure S3 and P7 L248-260): The variation of MFR at T=50C seem rather large for cases with OH scavenger (black markers). Did the authors look into what could cause this variation? Authors state that "Although the effects of OH scavengers, photochemical aging, and relative humidity on particle volatility were studied, the thermograms showed that all SOA results were similar to each other, within experimental uncertainties." Can the variation between the black markers be something else than experimental uncertainty? In that case there could be some effect of OH scavenger, aging and RH hidden in the data points.

Reply

A probable reason of data variations is the error of thermodenuder temperature. If this is the case, all TD-AMS data have errors of similar level; therefore, we cannot discuss further on the effect of OH scavenger, aging, and RH. We added the following sentences in lines 300–302:

The variations between black symbols at 50 ° C are greater than those at higher temperatures. A major reason for such variations may be the difference between the sensor temperature and the TD effective temperature.

Comment 7

"The present results indicate that gas/particle partitioning was virtually irreversible even though the VFR continued to decrease after 3 h." (P7, 282) This is unclear. What do the authors mean by irreversibility here?

Reply

What we describe here is that SOA mass concentration after dilution does not agree with that predicted by the yield curve measured in SOA growth experiments. This sentence was also highlighted by the other reviewer. We have decided to remove this sentence in the new manuscript. Please see also our reply to comment 3 made by the other reviewer.

Comment 8

"To the best of our knowledge, this study is the first to arrive at the results described above." (P8, L291) Please be more specific here. Not all the results described in the manuscript are as new as this suggests. Highly oxidized and/or long carbon chain compounds and slow evaporation are detected in earlier studies also, e.g. in the references of the current manuscript.

We revised sentences in lines 359–362 of the manuscript as follows:

To the best of our knowledge, this study is the first to analyse HOMs by column separation and to compare the product volatility distribution determined by chemical analysis with those determined by particle evaporation measurements. The HOM detection by column separation is a valuable contribution to the current research because this technique could potentially be applied to molecular identification.

Comment 9

Please consider revising the title "Lower than expected volatility of secondary organic aerosols formed during -pinene ozonolysis". The evaporation of particles was indeed slower than expected based on the yield experiments. However, considering Vaden et al. (2011, ACP) and other studies since then (which authors reference in the manuscript), I don't think "lower than expected" is anymore valid. With this I do not by any means suggest that the current study would not be important. It is definitely a topic which is worth of extensive research. However, the current title suggests that the authors find even lower volatility than Vaden et al. and other studies have found, which doesn't seem to be the case.

Reply

We agree with this comment and replaced the title with the following new title:

Comment 10

Figure S2 and Table S2. These include only a small number of compounds and different compounds for different methods. It is not clear why these specific compounds were chosen for these comparisons.

Reply

The results calculated by EVAPORATION are employed for the fitting by a 1D function. Chemical structure information is necessary for predictions of saturation concentration, thus α-pinene oxidation products of which chemical structures have been previously suggested, including semi-volatile compounds, highly oxygenated molecules, and dimers, were selected for EVAPORATION calculations. We assumed that the results of parameterization were applicable to all products detected by LC/MS. EVAPORATION data were validated against the results of a different calculation method, the SPARC online calculator (Hilal et al., 2003), and experimental results of PTR-MS. The SPARC data were calculated for α-pinene oxidation products which have already been identified in previous studies. All compounds selected in the SPARC calculations are included in the group of compounds selected for the EVAPORATION calculations. The PTR-MS results include only data for compounds that are detected in the region $151 \leq m/z \leq 229$; gas compounds are only detected by PTR-MS in the region $m/z \leq 229$; and to avoid interference from fragment ions, we only used results of $m/z \geq 151$. The PTR-MS data include results of both identified and unidentified products. We added the following sentences in lines 228–233 of the manuscript and added a brief explanation in the caption of Figure S2 of the supplementary material:

Chemical structure information is necessary for predictions of saturation concentration, thus α-pinene oxidation products for which chemical structures have been previously suggested, including semi-volatile compounds, highly oxygenated molecules, and dimers, were selected for EVAPORATION calculations. We assumed that the results of parameterization were applicable to all products detected by LC/MS. EVAPORATION data were validated against the results of a different calculation method, the SPARC online calculator (Hilal et al., 2003), and experimental results of PTR-MS.

In addition, we added the following sentences in lines 112–115 of the manuscript:

The ion signals of m/z 151–229 were only used for the evaluations of saturation concentration. The signals of $m/z < 151$ were not used because there would be interference from fragment ions. The signals of $m/z > 229$ were not detected due to the low sensitivity of the quadruple mass spectrometer.

Technical comment 1

P1, L22: "Atmospheric fine aerosols are believed to negatively affect climate (IPCC, 2013): : :" Is this a typo? What do authors mean by 'negatively affect climate'?

Reply

We removed "negatively" from the sentence.

Technical comment 2

P1, L39: "Wilson et al., 2014" should probably be 2015.

Reply

You are correct: we revised it.

Technical comment 3

P2, L41-43: ": : :however, later research showed that the evaporation process is strongly influenced by the particle phase state, and suggested that dilution results cannot be simply interpreted by gas/particle partitioning." Please add reference to this statement.

Reply

We have revised this paragraph in response to specific comment 1 made by the other reviewer. We added references at appropriate places in the revised text.

Technical comment 4

P5, L179: "The highest relative abundance was observed in the photochemical aging experiment,: : :" Please specify which compounds you refer to.

Reply

We specified the compounds we refer to in the revised manuscript.

Technical comment 5

P5, L191: ": : :that such dimerization will occur prior to the formation of the latter."Please clarify this sentence.

Reply

To clarify this, we revised the sentence in lines 208−209 of the manuscript as follows:

The results suggest that dimers will be formed from less-oxygenated monomers instead of HOMs, and that dimerization will occur prior to the formation of monomer HOMs.

Technical comment 6

P7, L271: "Although evaporation is assumed to occur instantaneously in VBS models,: : :" Did you mean equilibrium partitioning models? VBS is often used also for representing dynamics of condensation/evaporation.

Reply

Yes, we do. We replaced VBS models with "equilibrium partitioning models" here.

Technical comment 7

P8, L297: ": : :and photochemical aging in gas phase would be slower than that expected in the model." Please clarify this sentence. It is not clear how this conclusion was reached.

We totally revised this paragraph according to specific comment 12 by the other reviewer. This sentence was removed in the revised manuscript.

Technical comment 8

Figure S2. At the start of figure caption, please change "MW" to "Molecular weight (MW)" for clarity.

Reply

We have revised it accordingly.

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Table R1. A summary of the amounts of consumed reactants, gaseous products, and SOAs.

	Run 5	Run 6	Run 7	Run 8
$\Delta[\alpha\text{-pinene}]$ (ppmv)	0.10	0.31	0.30	0.14
$\Delta[O_3]$ (ppmv)	0.08	0.27	0.19	0.15
$\Delta[M]_c$ (mg m^{-3})	0.72	2.3	2.0	1.1
[SOA] (mg m^{-3})	0.22	0.96	0.86	0.30
$\Delta[M]_c - [SOA]$ (mg m^{-3})	0.50	1.3	1.1	0.8
$\Delta[Gas]_{PTR\text{-}MS}$ (mg m^{-3})	0.33	1.0	1.2	0.48
$\Delta[Aerosol]_{PTR\text{-}MS}$ (mg m^{-3})	a	0.30	0.25	a

a: The filter sample was not analyzed by the PTR-MS.