

Response to Reviewer 2

Reviewer comments are in **bold**. Author responses are in plain text. Excerpts from the manuscript are in *italics*. Modifications to the manuscript are in *blue italics*. Page and line numbers in the responses correspond to those in the original ACPD paper.

In this work, the authors presented results from oxidation experiments of aromatic compounds, toluene and 1,2,4-TMB. These aromatic compounds are important VOCs in urban areas, and their oxidation leads to significant ozone and secondary organic aerosol (SOA) formation. In this study the authors employed a number of new analytical techniques to measure the gas and particle phase composition, and compared to the latest version of Master Chemical Mechanism (MCM), which summarizes the current understanding about the mechanisms. Furthermore, the time trend analysis using gamma kinetic parameterization is a novel method to look at the multigenerational chemistry. This manuscript is well written, and I only have some minor suggestions. I recommend publication of this manuscript in ACP.

We would like to thank the reviewer for the positive reception of our work and constructive comments that helped us to improve our manuscript. In this document we provide our replies to the reviewer's comments.

1. It would be good to know on a bulk or general level, how these results improve the understanding of the chemistry. For example, I wonder what the carbon closure now is, with these new measurements. Figure 3 is probably a good place to show that.

The objective of this study is to evaluate the importance of various gas-phase oxidation pathways of aromatic compounds in terms of production of oxygenated low-volatile species (including HOMs) and SOA formation potential (P3 L5). Bulk organic carbon properties such as volatility, oxidation state, and reactivity, as well as carbon closure will be discussed in an accompanying paper currently under preparation.

2. Somewhat related: One key piece of information shown in Section 3.3 and Fig. 6 is that the total SOA mass measured by AMS and NH_4^+ CIMS compare very well, and so do the O/C ratios. This is an important discovery and should be highlighted in the abstract.

We agree with the reviewer that this is an important discovery. We underline this finding in Conclusions (P11 L28):

Many of these compounds are low in volatility and comprise a significant fraction (more than 25%) of SOA mass, which was measured using AMS and TD- NH_4^+ CIMS and the two measurements are in good agreement.

3. The multigenerational chemistry of many of the products is a key contribution. I expect that the accompanying paper describing the methods will be well received. There are some ambiguous ones that have non-integer m (e.g. 1.7-1.8). What is the general uncertainty in this analysis?

Noise can contribute to uncertainty in returned values of m . At low generations ($m=1-2$), the standard deviation of the fit is 0.1, while it can be higher (up to 0.8) at higher (3+) generations. Hence, it is possible

that the compounds with non-integer m are produced by more than one pathway with different number of reaction steps.

We add the following sentence to the manuscript (P6 L13):

At low generations ($m=1-2$), the standard deviation of the fit is 0.1, while it can be higher (up to 0.8) at higher (3+) generations (Koss et al., 2019).

4. Related to comment/question 3: I expect that some experiments with oxidation of later generation products would be very helpful. For example, oxidation of cresol (which is commercially available) should yield lower m for some of the products. Perhaps even examining the decrease in m would help apportion the relative amount for each generation. I think these are important experiments anyway given that the authors are claiming the importance of phenolic and benzaldehyde pathways in HOM production.

We agree with the reviewer that experiments with oxidation of later generation products (e.g., cresols and benzaldehydes) would be very helpful to further investigate different pathways in which highly oxygenated compounds are produced. While we plan to conduct these experiments in the future, we think that they are out of the scope of the current work.

5. The experiments were all conducted under RH of 2%. While I completely understand the rationale to create a well-controlled environment, it may be worthwhile to mention this is a potential limitation of this study and discuss implications. I do not see water playing an important role in the gas-phase chemistry, but could potentially shorten the lifetime of particle-phase hydroperoxides, epoxides and organic nitrates.

We add the following sentence as suggested (P3 L12):

The temperature of the chamber was controlled at 292 (+/- 1) K and approximately 2% relative humidity. All experiments were carried out under dry conditions (relative humidity, $RH \cong 2\%$, +/- 1%) to simplify gas- and particle-phase measurements. Higher RH can potentially shorten the lifetime of particle-phase hydroperoxides, epoxides and organonitrates (Li et al., 2018) as well as affect gas-particle partitioning kinetics and thermodynamics (Saukko et al., 2012).

Methods: I do not understand why the authors would use hexafluorobenzene as a tracer for both chamber wall loss and dilution of VOCs. I can see hexafluorobenzene is a good tracer for dilution, but I do not expect it to be lost to the chamber walls. Based on the chamber volume and air refilling rate, the dilution rate can be estimated. Is the hexafluorobenzene decaying faster than this dilution rate? If so, why is it being lost to the walls?

We used hexafluorobenzene as a tracer for the dilution of VOCs, not as a tracer for vapour-phase wall loss. The reviewer is correct that a highly volatile compound like hexafluorobenzene is not expected to be lost to the chamber walls. The hexafluorobenzene loss rate was consistent with the known chamber volume and dilution air flow. Vapour wall loss was quantified using the “rapid burst” method (Krechmer et al., 2016), and the rate constant of this process $k_{\text{wall loss}}$ was estimated to be $5 \cdot 10^{-4} \text{ s}^{-1}$.

To make this point clearer, we edit the following sentences:

P4 L32: ~~The chamber wall loss and dilution term for volatile compounds was estimated based on the concentration of the dilution tracer, hexafluorobenzene.~~

P5 L4: ~~The OH concentration was determined using the decay of the aromatic precursor, accounting for losses from dilution and chamber wall deposition.~~

We also update equation 1:

$$[\text{ArVOC}]_t = [\text{ArVOC}]_0 \cdot \exp(-k_{\text{ArVOC}+\text{OH}} \cdot [\text{OH}]_{\text{exposure}}]_t - k_{\text{physical loss ArVOC dilution}} \cdot t) \quad (1)$$

CO and formaldehyde were mentioned in methods, but no results were presented.

CO and formaldehyde will be discussed in further details in the accompanying paper under preparation. Since they play no role in the present paper, we remove the sentence describing CO and formaldehyde measurements from the manuscript (P4 L17).

Methods: Particle-phase compounds were quantified using I⁻ CIMS, but for the gas phase compounds the authors claim I⁻ CIMS is quite uncertain. Are the uncertainties in quantification the same for both phases?

Particle-phase compounds were quantified using both the FIGAERO-HRToF-I⁻-CIMS and a second PTR3 equipped with an aerosol inlet comprising a gas-phase denuder and a thermal desorption unit (TD-NH₄⁺ CIMS). Total organic mass and O:C ratio measured by TD-NH₄⁺ CIMS are in good agreement with the AMS measurements (P10 L21). As for FIGAERO-HRToF-I⁻-CIMS, uncertainties of the particle-phase measurements are similar to the gas-phase measurements.

We add the following clarification to the manuscript (P4 L24):

Uncertainties of the particle-phase CIMS measurements are similar to the corresponding uncertainties of the gas-phase CIMS instruments.

Section 2.4: how large are the time steps?

The time step Δt was five minutes which corresponds to the switching period between two ionization modes of PTR3 (P4 L5).

Section 3.1: Is it possible that the epoxide was not detected because of thermal decomposition for the particle phase measurements, or fragmentation during ionization?

The reviewer raises an interesting point. While it is possible that the epoxide was decomposed or fragmented during ionization, we think that it should have been detected using the instrumentation implemented in this study. We calibrated PTR3 NH₄⁺ CIMS and H₃O⁺ CIMS for isoprene epoxydiol (trans-IEPOX) and observed very little fragmentation in NH₄⁺ CIMS comparing to H₃O⁺ CIMS (Fig. R1).

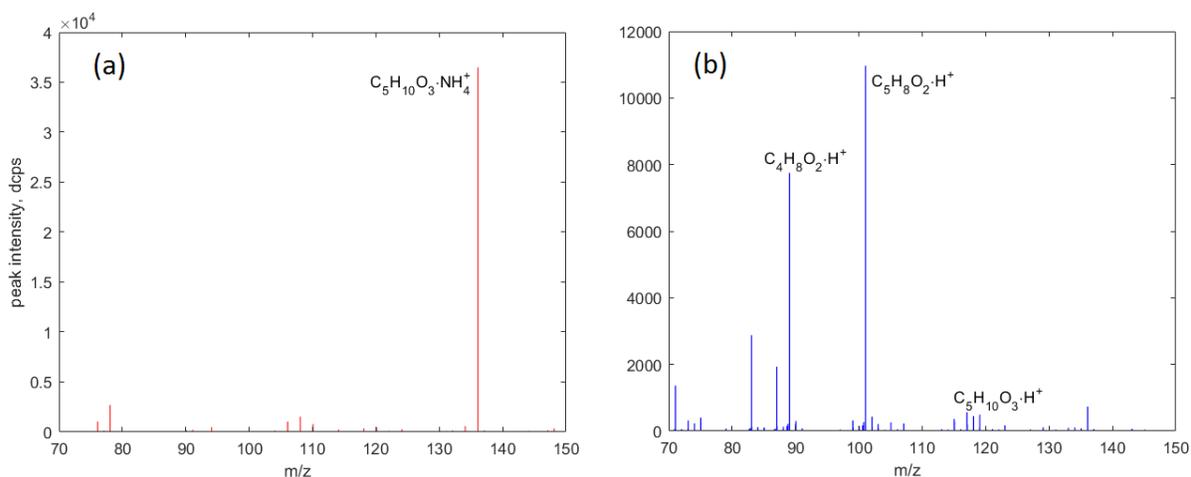


Figure R1: High-resolution mass-spectra obtained during calibration of trans-IEPOX in (a) PTR3 NH_4^+ CIMS and (b) PTR3 H_3O^+ CIMS.

In addition, we studied thermal decomposition of OVOCs extracted from alpha-pinene SOA by measuring their peak intensities using TD- NH_4^+ CIMS. Signals of many species increased at moderate temperatures ($T < 160^\circ\text{C}$) and levelled out or decreased at higher temperatures ($T > 180^\circ\text{C}$), as shown in Fig. R2. Therefore, we chose the TDU temperature to be 180°C , as at this temperature all particles were evaporated while thermal decomposition of labile species was relatively small.

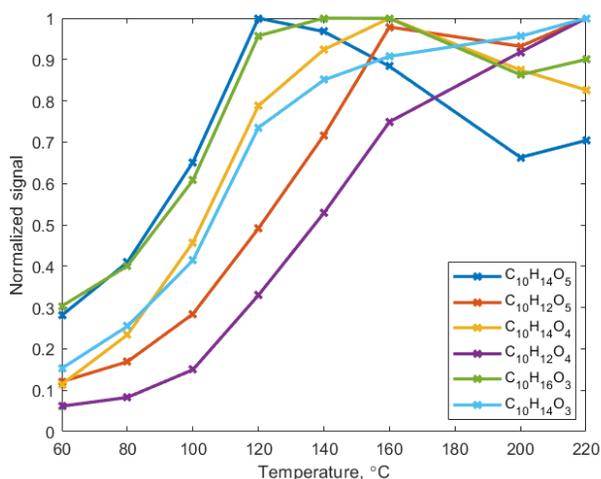


Figure R2: Thermograms of select OVOCs extracted from alpha-pinene ozonolysis SOA.

Hence, we think that toluene and 1,2,4-TMB epoxides should be detectable using NH_4^+ CIMS.

Section 3.2.1, Line 13: BPR has been defined earlier.

We thank the reviewer for spotting this typo in the manuscript and remove the abbreviation (“BPR”) from the manuscript (P7 L13).

Section 3.2.1 Line 29-30: Presumably the lifetimes are calculated using generic $\text{RO}_2 + \text{NO}$ and $\text{RO}_2 + \text{HO}_2$ rate constants? What rate constants were used?

The rate constants were estimated using information from MCM v3.3.1.

For toluene:

$$k_{\text{RO}_2+\text{HO}_2} = 2.05 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, k_{\text{RO}_2+\text{NO}} = 9.26 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

For 1,2,4-TMB:

$$k_{\text{RO}_2+\text{HO}_2} = 2.22 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, k_{\text{RO}_2+\text{NO}} = 9.26 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Tables 1-3: what are the uncertainties in m from the fits?

Noise can contribute to uncertainty in returned values of m .

We add the following sentence to the manuscript (P6 L13):

At low generations ($m=1-2$), the standard deviation of the fit is 0.1, while it can be higher (up to 0.8) at higher ($3+$) generations (Koss et al., 2019).

Figure 6: why is there a discontinuity at 14 hours of exposure for toluene? Was more OH precursor added? Similarly there seems to be one as well for TMB at 4 h.

During experiments, additional injections of HONO were added to the chamber to roughly maintain the OH levels (Fig. S1). Discontinuities in particle-phase signals are indeed caused by the additional HONO injections.

References

Krechmer, J.E., Pagonis, D., Ziemann, P.J., and Jimenez, J.L.: Quantification of Gas-Wall Partitioning in Teflon Environmental Chambers Using Rapid Bursts of Low-Volatility Oxidized Species Generated in Situ, Environ. Sci. Technol. 50(11), 5757–5765, <https://doi.org/10.1021/acs.est.6b00606>, 2016.

Li, Z., Smith, K. A., and Cappa, C. D.: Influence of relative humidity on the heterogeneous oxidation of secondary organic aerosol, Atmos. Chem. Phys., 18, 14585–14608, <https://doi.org/10.5194/acp-18-14585-2018>, 2018.

Saukko, E., Lambe, A. T., Massoli, P., Koop, T., Wright, J. P., Croasdale, D. R., Pedernera, D. A., Onasch, T. B., Laaksonen, A., Davidovits, P., Worsnop, D. R., and Virtanen, A.: Humidity-dependent phase state of SOA particles from biogenic and anthropogenic precursors, Atmos. Chem. Phys., 12, 7517–7529, <https://doi.org/10.5194/acp-12-7517-2012>, 2012.