

Interactive comment on “Chemistry of α -pinene and naphthalene oxidation products generated in a Potential Aerosol Mass (PAM) chamber as measured by acetate chemical ionization mass spectrometry” by P. S. Chhabra et al.

Anonymous Referee #2

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This work attempts to build on a growing body of laboratory studies in which hydrocarbon oxidation experiments in the laboratory are used as a guide to tune models and analysis methods aimed at improving our understanding of organic aerosol formation processes. The data analysis methods presented here, although some significant improvements are desired, is an improvement on previous studies aimed at the interpretation of CIMS TOF measurements, and will be helpful moving forward in relating field observations to laboratory investigations. I find the presentation of the manuscript clear and concise, however, I have some major concerns regarding the publication of

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quantitative information which contains errors that are, as presented, of an entirely unknown magnitude to both the reader as well as, it would seem, the authors.

While I find the laboratory work and modeling to be of sufficient quality to merit publication, I am hesitant to sign off on this manuscript for publication in Atmospheric Measurement Techniques for several reasons. The majority of the analysis, conclusions, as well as validations of the results rely on approximations that when compounded could potentially result in significant over/under approximations of the gas and particle phase concentrations. It is wildly unjustified in both previous as well as this current publication to apply a constant sensitivity factor across the entire observable mass range. Variation in ionization efficiencies aside, the formation of an acetate cluster ion, as the primary mechanism of ionization, occurs with a dramatically different efficiency than proton abstraction reactions. Furthermore, the treatment of cluster ions in this work is likely inappropriate, and nearly impossible (as the research was done) to quantify the errors associated with the cluster ion correction applied here. I acknowledge that the authors are open about the assumptions made in this work; however, regard any mass loading, yields, or quantitative data reported here as mere speculation. Agreement is in many cases is somewhat misleading considering that the results are in many examples justified by comparison to other published works using similar flawed methods. This is a problem that is becoming systemic with TOF-CIMS measurements, and one that is continuing to be addressed by statements such as “We ignore such non-linearity here but note that they should be studied in the future.” In my opinion, in order to be considered for publication this work requires a more detailed discussion on the magnitude of the errors from using the many approximations used as well as quantification of the errors associated with all mass yields and other numerical figures reported within this work. Without a thorough treatment of the errors in this analysis, the reader is unable to easily understand the accuracy of the values and subsequent discussion, which in turn makes this study of little use as a model for understanding real atmospheric oxidation. If in fact the authors are comfortable with the methods and results reported, then they should be able to place more finite bounds on the reported numbers. Un-

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derstanding and applying aerosol formation mechanisms from gas phase oxidation is frequently slowed significantly by debates of what quantitative mass yields are correct leading to inefficient progress. This problem will be further exacerbated by a lack of understanding as to the accuracy of published values.

Major comments:

p6392, line 6-7: Am I right in understanding that the OH oxidation experiments were performed with 5 ppm of ozone and the ozone experiments we performed using only 1 ppm more? I find this to odd as that would mean the ozone exposure in both scenarios is very similar. Would this not allow a large amount of ozonolysis products to be observed during the OH experiments?

p6392, line 11: Please be more specific as to what mass was used to monitor DCOOH. At unit mass resolution the authors should consider the contribution of other species to the ion at m/z 46. Any production of OH with trace amounts of NO will likely result in HONO, which also will be detected at m/z 46. Under certain conditions with the acetate ion CIMS, NO₂ is also detected at m/z 46 with relatively good efficiency depending on ionizer conditions. One would also expect some contribution of any HO₂NO₂ that may be formed in the chamber. If in fact you did use unit mass resolution to monitor this ion have you considered the following? How may production of any of these species effect you calculation of OH exposure? Have you modulated the DCOOH during an experiment to test if any other interference were present on this ion?

p6393, line 27: How exactly did you approximate that < 7% of even mass signal is due to organic ions? This merits a bit more discussion.

p6394, line 24: While I can understand that the correction, as you have applied it, may only contribute a couple percent to the error on the bulk composition, this is not the actual error of this treatment of the ion clusters and is a misleading statement. Statements like this only serve to mislead the reader as to the true errors associated with a significant assumption such as this. It is essential to your quantitative analysis

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that you represent the true errors of involved in this work.

p6395, line 3: How can you be certain that you are removing the proper background considering that you have no clean spectra of naphthalene? Is the Van Krevelen diagram not also affected by the contamination?

p6398, line 6: There is currently a lot of unknowns regarding the nearly ubiquitous production of these small acids from the oxidation of practically all organics in chamber studies, specifically I am thinking formic and acetic acid. Yet, the authors seemingly make this statement in a rather matter of fact manner. The mechanism for the formation of these acids is currently completely unknown and not an insignificant gap in available knowledge, considering the magnitude of secondary formation of small acids observed in the atmosphere via unknown processes. If the authors wish to make a statement like this, and other places throughout the paper, I believe a bit more justification is required. Perhaps the authors would like to comment on the oxidative fragmentation mechanism they believe is forming these small acids.

p6403, line 10: I am under the impression that the measurements made here were in the gas phase, with particle phase 'concentrations' calculated using vapor pressures and partitioning theory. As such, there are no acetate-CIMS signals measured for particle phase species. Am I misunderstanding something here? Are we looking at volatilized particle contents or gas phase products? This should be better explained not only here but also much earlier in the paper.

Figure 2. The figure displays unit mass resolution however the ions identified are given as high mass resolution species. There need to be agreement here. Please change the mass spectra to high mass resolution or the masses to unit.

Minor Comments:

p6386, line 17: add comma after "yields", delete "and" before O/C, and add comma after "O/C".

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p6388, line 25: organics to organic

p6390, line 23: delete "or"

p6392, line 14: The unit molec cm⁻³ s, in my opinion should be expressed as moles s cm⁻³.

P6392, line 14: approximate and ~ express the same thing therefore "approximately ~" is redundant.

P6403, line 19: add comma after "yields" and a second comma after "study".

P6403, line 20: should "approximately" be "corresponding"?

P6403, line 22: remove comma before "for 10 to 100"

P6403, line 23: add comma after "mass"

Table 1. Can you include errors on the VOC concentrations used?

Table 2. From the figure description one has no idea why there is a column labeled "Constant (1.79)".

Figure 3. The smaller numbers in the figure space are near impossible to see. Please consider scaling up the lower end of the size scale to make these more observable.

Supplemental Figure 3 and 4. These identities contained here and throughout the manuscript are in most cases best guesses as an identity based on previous literature and assumptions about the molecular formula. I think that this point needs to be stressed a bit more in the manuscript in order to be more transparent about the potential for misidentifications here.

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