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Interactive comment on “Secondary Organic Aerosol formation from phenolic compounds in the absence of NO_x” by S. Nakao et al.

Anonymous Referee #1

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Overall Comments

This manuscript describes a series of smog chamber experiments conducted in the UCR/CE-CERT chamber that were designed to examine SOA formation from benzene, toluene, m-xylene, and their corresponding phenolic compounds (these are known first-generation oxidation products from these monocyclic aromatic compounds). From the suite of experiments conducted, the authors are able to attribute that ~ 20% of the SOA from benzene, toluene, and m-xylene could be described by the further oxidation chemistry of the phenol derivatives. Gas-phase constituents were chemically characterized by both GC-FID and PTR-MS techniques. Aerosol-phase constituents were chemically characterized by off-line analyses of filter samples using ESI/APCI-HR-TOFMS as well as by an on-line PILS technique coupled to the same mass spectrometer used for

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the filter sample analyses. The authors claim that major signals (or ions) detected by both the online-PILS-ESI-TOFMS and off-line APCI/ESI-TOFMS corresponded to the first detection of bicyclic hydroperoxides in aromatic SOA (or in the particle phase). The authors make this assignment based on the fact that accurate mass data obtained from the APCI/ESI-HR-TOFMS technique indicate that these ions have elemental compositions similar to these particle-phase products. In addition, when the authors conduct high-NO experiments they find these signals substantially decrease, which seems to further support their hypothesis. Detailed chemical mechanisms leading to SOA formation from the oxidation of monocyclic aromatics (such as benzene, toluene, and the xylenes) have remained a bit of a mystery. Much of our uncertainty in the mechanism has resulted from our inability to chemically characterize aromatic SOA at the molecular level. Although there has been many heated discussions within our community about the necessity of chemical characterization efforts at the molecular level, it has been proven recently with other VOCs that these efforts provide important clues on the detailed mechanisms leading to SOA formation. Many of the existing analytical techniques are proving to not be useful or properly utilized in this effort either due to the harsh conditions of these existing techniques, the types of products formed being incompatible with the applied technique (e.g., constituents prone to hydrolysis during sample workup or chemical analyses or not ionizing), or the lack of chromatographic separation that allows for the unambiguous identification of certain products.

The authors of the present study employ a number of complimentary analytical techniques, as well as implementing the usage of PILS coupled to an ESI-HR-TOFMS instrument. I applaud the authors for their efforts; however, I feel there are a few mistakes made when using these techniques, especially when chemically characterizing the SOA constituents. These mistakes are critical since they guide the major conclusions of this study; specifically, the conclusion that bicyclic hydroperoxides are present in the aerosol phase and could be key intermediate species in forming SOA from aromatic oxidation. First, in Figures 7 and 8 the authors present ESI/APCI-HR-TOFMS data on filter samples. From these two data sets, it is quite clear that the authors di-

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rectly infused their aerosol samples into the ESI/APCI-HR_TOFMS instrument without chromatographic separation. One of the biggest problems with ESI (and APCI) is the fact that artifacts or adducts can occur very easily, allowing for the misinterpretation of the chemical composition. In addition, when directly infusing the entire sample matrix into the ESI/APCI-HR-TOFMS instrument certain compounds could not be detected due to their ionizations being suppressed due to the presence of compounds that have higher ionization efficiencies (e.g., surface active compounds on electrospray droplets). Thus, one of the concerns I have is how do the authors know in Figure 7 that these ions are not artifacts or adducts? Additionally, in Figure 8 you might not observe m/z 175 and 191 due to the fact that the nitroaromatics could have very high ionization efficiencies, and since there is no chromatographic separation they can suppress ion formation from compounds like m/z 175 and 191. Chromatographic separation would certainly resolve this issue. If you don't see compounds elute from the column this could mean that you are not employing the correct LC column or that you generated artifacts in the ESI-MS. As an example of my concern, If you simply inject phosphate, acetate, or sulfate into an ESI-MS instrument, you will easily generate a number of adducts that will spread across the m/z range in which you are scanning. This same argument would apply to the PILS data. The entire sample matrix introduced by the PILS onto the ESI/APCI-HR-TOFMS instrument will have the same issues. Thus, I'm not surprised that the PILS and off-line analyses corresponded so well. This artifact/adduct issue is a MAJOR concern for this paper and the authors need to clearly address this or back down their major conclusions as I feel this could unintentionally mislead readers on the mechanism.

Second, I'm concerned with the proposal that the PTR-MS can observe bicyclic ketones. The reason for this concern is proton transfer reactions can easily cause compounds to fragment down or even adduct with H₂O. In order to further prove this hypothesis, it would be important to synthesize this bicyclic ketone (which I admit is probably not possible here or easy to do) or obtain a reasonable surrogate (at least some organic peroxide) and directly analyze it by the PTR-MS. This should further prove or

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disprove that you can observe these kinds of compounds by PTR-MS. It was never directly stated in the manuscript, but could the authors clarify if this PTR-MS instrument is a unit or high mass resolution instrument? In any case, we need to be extremely careful not to assign chemical structures to nominal mass ions or even from elemental compositions obtained from accurate mass measurements until further complimentary chemical evidence is provided (e.g., running a standard or MS/MS data).

Another major question I have for the authors is what could the other 80% of the SOA mass be attributed to? Could this be something like aqueous-phase chemistry of ring-opening oxidation products (like glyoxal or methylglyoxal), heterogeneous chemistry, or something else unknown? As the authors probably know well, there has been much work on the aqueous-phase chemistry of some of these ring-opening products from aromatic oxidation. I think some discussion of the other potential reaction routes leading to the 80% of the SOA mass not ascribed by the phenolic route is warranted.

Lastly, in order to gain further insights into the intermediates that might lead to SOA formation from these compounds, did the authors consider correlating their abundant ions detected by the PTR-MS to their AMS total organic mass data? This might provide some clues as to which gas-phase ions appear to play a role in SOA formation from these compounds. It could be that the further oxidation of some of these first- or later-generation compounds (ions) play a role in forming SOA, or that heterogeneous chemistry is important, or a combination of both gas- and aerosol-phase chemistry.

Based on the major comments/questions I have above, I recommend that this manuscript be reconsidered after major revisions by the authors. In addition to the major comments outlined above, I kindly ask that the authors consider my minor/technical questions below.

Minor/Technical Questions:

1.) Experimental Section.

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What was the RH of these experiments? This should be clearly stated somewhere in the experimental section. I ask this since RH has been shown to be an important in SOA formation from certain aromatics (e.g., Kamens et al., 2011, Atmos. Environ.).

2.) Experimental Section.

What standard compounds were used for the accurate mass determinations when using the ESI/APCI-TOFMS instrument? This should be clearly stated here.

3.) Experimental Section.

Why was acetonitrile chosen as the filter extraction solvent? What about methanol? Were tests made to evaluate which solvent is best for the aromatic SOA?

4.) Experimental Section.

It is not appropriate to leave out details of the PILS-ESI-TOFMS method, especially since the paper cited is not even published (that is the paper is under construction). The authors need to include some of the details here since there is no instrument paper yet available.

5.) Experimental Section.

Please indicate in the experimental section as to whether these experiments were nucleation only or had seed aerosol present. If seed aerosol was used, what type of aerosol?

6.) Results and Discussion. Section 3.1.

How were wall-loss corrections done for the aerosol? Please provide details either here or in experimental section.

7.) Results and Discussion. Section 3.3.

To be absolutely clear, please indicate here whether GC-FID or PTR-MS was used to measure the amount of reacted phenol.

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8.) The authors indicate in the introduction that SOA formation from aromatics are important in urban locations. However, this study is focused on the NO_x-free regime. This raises the question as to what one expects to be important for aromatic oxidation; specifically, is high-NO_x or low-NO_x conditions more atmospherically relevant for SOA formation from aromatics? Are aromatics around long enough to be transported to lower-NO_x (or NO_x-free) regimes? The authors clearly state in the introduction that SOA formation from aromatics is generally higher under low-NO_x regimes. Is this the main reason for focusing on this regime in this study?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 2025, 2011.

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