We thank the reviewers for their careful reading and helpful comments that improved the quality of our manuscript.

We understand the reviewer's concern about identification of bicyclic hydroperoxides using ESI/APCI-TOFMS. Although we kept the ESI/APCI-TOFMS results in the revised manuscript, we added the caveats of this technique and mentioned other possible structures such as ring-opened multi-functional compounds. However, we would like to emphasize that the formation of bicyclic hydroperoxide is not a novel mechanism; the formation of bicyclic peroxy radicals in gas-phase is widely accepted. The formation of bicyclic hydroperoxides and partitioning to SOA is already proposed by a previous modeling study (Johnson et al. 2005). This study proposes a possible extension of the aromatic hydrocarbon mechanism into phenolics based on previous studies. Although the ESI/APCI-TOFMS results are not unambiguous evidence to prove the mechanism, it is interesting to point out the major signals in the spectra match the bicyclic hydroperoxide and call for a need for further studies.

We'd like to also reemphasize the other major findings of this paper. This is the first study to quantitatively evaluate the significance of phenolic compounds in the aromatic SOA formation, and the conclusion that the phenolic route contributes a significant fraction (~20%), but not a majority of the SOA forming routes in low NO_x and high HO_2 conditions is helpful in interpreting SOA formation from aromatics. Furthermore, since SOA yield measurement of phenolic species are quite limited and there are no real-time density and O/C ratio measurement of phenolic SOA available, this will be of interest to readers of ACP.

Responses to specific comments are shown below.

Reviewer 1 comments:

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 directly 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?

Response: We agree that artifact formation and suppression of ionization are one of the major problems of ESI and APCI. We now clearly state this in the revised manuscript. We have confirmed that the use of acetic acid and formic acid as

mobile phase modifiers did not significantly change the major products distribution, indicating the major signals are not adducts from the acidic modifier. Also, the fact that there are series of products with the same number of carbons with the starting compounds (e.g., $C_6H_8O_6$ from phenol, $C_7H_{10}O_6$ from o-cresol, and $C_8H_{12}O_6$ from 2,4-DMP) strongly indicates artifact/adduct formation is unlikely at least for these species; if these species were adducts of two or more species, the number of carbon might exceed that of the reactants and the chance of seeing the obvious CH_2 (m/z14) shift is remote.

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.

Response: The concern about m/z175 and 191 was correct; when nitrophenolic species were separated by a LC column, m/z 175 and 191 were detected in a non-retained peak. This indicates that at least some fraction of $C_6H_8O_6$ analogs are formed through a non-peroxide route. We attempted column separation of $C_6H_8O_6$ analogs, but those species were too polar to be retained by reverse-phase columns. (Based on the highly oxidized formulae, it is not surprising that these species were not retained by reverse-phase column.) The column separation of these species would require another type of separation techniques (e.g., derivatization, normal phase). At this point, we report these signals without column separation and clarify further need for separation method development.

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.

Response: We agree that PILS – ESI/APCI-TOFMS will have the same issues. However, since the number of carbons for major

signals matches with that of reactants and there are obvious CH_2 shift between phenol and o-cresol, artifact formation is unlikely to be a major formation pathway for these signals. The detection of gas-phase catechol species only in PILS spectra is consistent with previous gas-phase studies on catechol formation from phenol. In addition, agreement between PILS and off-line filter indicates that the products are not likely artifacts from filter collection, which is also an interesting finding.

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 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).

Response: Since there is no additional evidence to back up the tentative identifications, product analysis using the PTR-MS is now omitted in the revised manuscript. For some experiments performed in the mezzanine chamber, PTR-MS was used to quantify the dimethylphenol. Our PTR-MS is unit mass resolution instrument (PTR-QMS). This is now stated in the experimental section.

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.

Response: The contribution to the other 80% is highly unknown. Since the experiments were performed in dry conditions (dew points <-40°C), aqueous-phase chemistry is unlikely to contribute the major fraction. The importance of glyoxal and

aqueous reaction is a focus of our on-going subsequent work and beyond the scope of this manuscript.

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.

Response: Comparison of PTR-MS time series and PM volume did not yield useful information. Most of the products have increasing trend similar to PM volume. Since product identification using unit mass resolution is highly uncertain, PTR-MS product time-series is not shown in the revised manuscript.

Minor/Technical Questions:
1.) Experimental Section.

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.).

Response: Experiments were performed in dry condition (dew point below -40C). This is now stated in the experimental section.

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.

Response: Agilent tuning mix (G1969-85020) was used to calibrate the ESI/APCI-TOFMS.

3.) Experimental Section.
Why was acetonitrile chosen was the filter extraction solvent? What about methanol?
Were tests made to evaluate which solvent is best for the aromatic SOA?

Response: Bateman et al. (ES&T, 2008, 42, 7341-7346) reported that methanol can react with carbonyls or carboxylic acids in SOA, and hence acetonitrile is the preferred solvent for SOA extraction. Our tests indicated that use of methanol or acetonitrile did not alter the major signals. The detailed

investigation of solvent as done by Bateman et al. is not the focus of this study.

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.

Response: Now PILS-ESI-TOFMS is described in more detail.

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?

Response: Nucleation only. This is now stated in the experimental section.

6.) Results and Discussion. Section 3.1.
How was wall-loss corrections done for the aerosol? Please provide details either here or in experimental section.

Response: Exponential decay rate of particle number is applied to calculate particle volume wall loss. This is now stated in the experimental section. Details available in Carter et al. (2005).

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.

Response: Phenol, cresol and some of dimethylphenol were measured by GC-FID. Dimethylphenol in mezzanine chamber experiments was measured by PTR-MS as stated in the experimental section.

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

Response: NO_x-free regime was chosen in this study to simplify the mechanism when evaluating the contribution of phenolic species in aromatic SOA. When NO_x is present, there could be significant amount of nitrate radicals due to the short wavelength of blacklights (peak intensity at 350 nm). The reaction of nitrate radical and phenolic species is much faster than that of aromatic hydrocarbons, and hence the evaluation of phenolic route as in section 3.3 becomes more complex. Furthermore, the change in NO_2/NO ratio during experiments would complicate the direct comparison of aromatic experiment and phenolic experiment. Evaluation of phenolic route in NO_x-free condition is a vital step toward further evaluation in the presence of NO_x.

Reviewer2:

the chemical formulae suggested from the ESI/APCI-TOFMS data are not sufficient enough to prove the existence of the bicyclic hydroperoxides in SOA. Before this work can be published in ACP, the authors are requested to perform additional analytical work to provide much more solid evidence to substantiate the findings shown in the current version of manuscript.

Response: As described in the response to reviewer 1, we now clearly state that this is not unambiguous identification and just a tentative assignment of structure. Since the presence of bicyclic peroxides are widely accepted by the gas-phase mechanism community and bicyclic hydroperoxides are already used as one of the model SOA precursors, we would like to keep the ESI/APCI-TOFMS results and point out these species deserve further studies.

Specific comments:
P2026-P2027: The last paragraph of the introduction is not well written and it does not connect well with the rest of the introduction. It is difficult for me to understand from this paragraph if the authors aim to evaluate "phonelic hydroperoxides" or simply "phenolic compounds" as intermediates for aromatic SOA formation. In my opinion, the last paragraph does not indicate the focus of the present study well.

Response: The introduction is modified as requested.

P2026, L14: 'first possible detection'. Can the authors provide concrete evidence for the detection of bicyclic hydroperoxides? It is hard to elucidate molecular structures

(not chemical formulae) simply from direct infusion ESI/APCI-TOFMS analysis. This is also the same for PTR-MS data which has much lower mass resolution than the ESI/APCI-TOFMS data. Such sentence should be reserved for those molecules that are positively identified from the comparison to authentic standard compounds or NMR analysis. MSMS, post-column derivatization or NMR data is desirable to prove the presence of bicyclic hydroperoxides.

Response: We now clearly state that the identification is tentative and awaits further analytical evaluation. We have removed the statement accordingly.

P2027, L1: "Low NOx conditions" should be "low NOx and high HOx conditions".

Response: Done

P2030, L1: 'achieved done' → 'achieved'

Response: Done

P2030, L5: What are the reasons to use mixed mode ionization? Do the authors see significantly different data from ESI/TOFMS or APCI/TOFMS data? Most of phenolic compounds can be detected using ESI/TOFMS. Since no chromatographic separation was employed before the ESI/APCI-TOFMS detection, the TOFMS data provided in this study likely suffers from the artifact formation in the ion source. How confident are the authors that the ESI/APCI-TOFMS data are free from the ion source artifacts?

Response: Mixed mode is used to detect as many species as possible. However, in effect, the results of ESI and ESI/APCI were the same. APCI yielded lower sensitivity compared to ESI in this study.

P2030, L7: 'negative polarity mode' → 'negative ion mode'

Response: Done.

P2030, L9: 'Time-of-Flight' or 'ToF' → 'TOFMS'

Response: Done

P2030, L9: 'a online' → 'an online'

Response: Done

P2030, L10: 'PILS-TOF' → 'PILS-TOFMS'

Response: Done

P2030, L15: 'Table 2' → 'Table 1'

Response: Done

P2030, L15: Experimental conditions and artifact formation. The mixing ratio of H2O2 is an inherited problem. Extremely high mixing ratio of HO2 radical may steer towards the formation of peroxy compounds. The authors need to discuss a potential issue arising from high H2O2 mixing ratio.

Response: Although there are concerns about high H_2O_2 mixing ratio, H_2O_2 is widely used in evaluating reaction mechanism in low NO_x conditions. H_2O_2 was used to simplify chemical mechanism (low NO_x and NO_3 radical) and to facilitate quantitative evaluation of phenolic SOA formation route in aromatic SOA formation. This condition needs to be considered as a simplified system.

P2032: The section 3 is split into a number of small subsections that are less than 10 lines. Most of these sections are rather descriptive and do not provide detailed interpretation of the data.

Response: Done

P2032, L12: 'studies(Table 2)' → 'studies (Table 2)'

Response: Done

P2032, L13: 'Boge' → 'Böge'

Response: Done

P2033, L13: The authors assume that the m/z data obtained from the PTR-MS is [M + H]+. It is known that the proton transfer reactions in the ion source do form ions other than [M + H]+ ions due to fragmentation or H2O adduction formation. In addition, have the authors considered a potential artifact formation from the reaction of OH radicals in the ion source? It is often ignored - the formation of H3O+· yields an equivalent amount of OH radical in theory (N2 +· + H2O → N2 + H2O+· , H2O+· + H2O → H3O+· + OH-).

Response: We agree that there could be artifact formation and product identification by unit mass resolution is highly uncertain. We have removed text on identification of products by PTR-MS.

P2033, L15: 'A m/z 171' → 'An m/z 171'

Response: The section is removed.

P2034, L23: 'C6H8O6 formation' → 'C6H8O6 compound'

Response: Done

P2035, L7: Can the authors suggest the formation mechanisms for these compounds? It's hard to imagine OH addition for these compounds.

Response: PTR-MS identification section removed (see above).

P2035, L9 "3.8 Implication": This section does not add much to the manuscript. I feel 'Outlook' more suitable than 'Implication' for this section. - I suggest combining this section with the conclusions.

Response: Removed.

P2042 Table 1: Please provide higher resolution images for chemical structures.

Response: Done.

P2045 Table 3: 'Phenolicroute' → 'Phenolic route'

Response: Done.