

Interactive
Comment

***Interactive comment on* “Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols” by L. D. Yee et al.**

L. D. Yee et al.

lyee@caltech.edu

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The authors would like to thank all referees for their helpful comments and suggestions for improving this manuscript. Responses to all referee comments are below and many revisions to the manuscript have been made. All references to specific sections, pages, and line numbers in author responses to the referee comments are based on those of the current discussion manuscript format.

Referee 2

The authors Yee et al. present with their article “Secondary organic aerosol formation

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from biomass burning intermediates: phenol and methoxyphenol” a well-structured and sophisticated work within the area of aromatic compounds and secondary biomass burning aerosol. Various experiments are presented based on phenol, guaiacol and syringol gas-phase oxidation with OH radicals in an aerosol smog-chamber. The authors report aerosol formation yields, gas- and particle-phase products measured using CIMS and different MS-based offline methods as well as proposed reaction schemas for the three different precursors. Based on their results, a chemical pathway for the loss of carbon in methoxyphenol systems and an explanation for the observed yields are given. Finally, the obtained results are concluded according to the atmospheric relevance of their work. The work of Yee et al. is based on a comprehensive amount of smog-chamber runs with state-of-the-art gas- and particle-phase analytics. The article is clearly structured and well written. With this article, the authors significantly contribute to the BBOA and aromatic SOA discussion. As outlined in the comment sections, this work could be improved by several major and minor additions, e.g. a detailed introduction on pre-existing work and relevance to the presented one; a detailed discussion on NO_x conditions at biomass burning events; a simplification of some figures. However, I recommend publication of this paper in ACP after taking the comments below into account.

Major Comments:

1. While the entire manuscript is very detailed, the introduction section is extremely short. A tight overview on pre-existing work on BBOA, aromatic SOA, olefinic aerosol, would be helpful to underline the importance of the conclusions of this article (e.g. Coeur-Tourneur et al., *Atmos. Environ.*, 2009; Ofner et al., *Z. Phys. Chem.*, 2010; Ofner et al., *ACP*, 2011; Olariu et al., *Atmospheric Ozone Degradation Reaction of 1,2-Dihydroxybenzene*, EUPHORE 4th Report 2001; Nieto-Gligorovski et al., 2008 and 2010; Tomas et al., *Int. J. Chem. Kinet.* 2003). A comprehensive picture of performed work with relations to the present work would assist a general picture on aromatic BBOA chemistry.

Thank you for the literature recommendations. The introduction has been revised to add a concise overview of the recommended references and context for the current study in aromatic BBOA chemistry.

2. Although the authors report “SOA from biomass burning intermediates”, all experiments were carried out at low-NO_x concentrations. While the authors seem to defend their work according to the chosen NO_x concentrations within the atmospheric relevance section, a short summary within the introduction related to emission values, NO_x concentrations related to different biomass burning events would be helpful (e.g. Iinuma et al. (Environ. Sci. Technol., 2010), Veres et al. (J. Geophys. Res., 2010), Akagi et al. (ACP, 2012)). Depending on the temperatures, NO_x values can be incredibly high at biomass burning events. Mixing of air masses from smoldering fires (with aromatic emissions) and from the fire front (high CO, CO₂ and NO_x emissions) must be taken into account.

This is a very valid point, and we have added a short summary from the suggested references in the introduction section to include discussion on the importance of NO_x. We also stress that the current study is an idealization of certain chemical conditions including NO_x < 10 ppb such that a controlled study can be done in the RO₂ + HO₂ chemical regime. This provides additional insight into aromatics chemistry in general, and many aromatic systems have similar product distributions in the absence and presence of NO_x (Olariu et al. 2002; Sato et al., 2007).

For reference, we have added an appendix section to the manuscript that presents the results of experiments conducted in the presence of NO_x (using HONO as the oxidant precursor) that were a part of this study, but omitted in the current manuscript. We have also outlined the reasons for this omission in the original manuscript which are both technical and scientific in nature including: 1) The actual experimental conditions resulted in hundreds of ppb levels of NO_x, which are much higher than those reported. For example, Iinuma et al. (2010) biomass burning co-located NO_x measurements are on the order of 20 ppb. Thus, the product distributions in these experiments result

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in favored nitro-products, but do not necessarily represent the more relevant chemical development in the atmosphere. NO_x levels can also become depleted several hours later (via NO₂ incorporation into PAN species) or with dilution via transport of a plume as observed in Akagi et al., (2012). Thus, experiments in the absence or at levels of NO_x < 10 ppb can still be representative of product distributions at lower NO_x levels (< 30 ppb). 2) Interference of HONO response on our NO_x analyzer made it more difficult to report more precise NO levels. 3) Before photooxidation commenced, we observed a likely nitro-product that formed once HONO was introduced to the reactors, presumably a reaction of methoxyphenol with HONO and/or NO_x (by-product of the HONO synthesis) in the dark to form a nitro-product. This was not observed in Lauraguais et al., (2012) for the case of syringol and CH₃ONO in the dark. While direct HONO/NO_x reaction with the methoxyphenol compounds may be of atmospheric relevance, this complicated the chemical system that we started with and made it difficult to constrain the chemistry for the later observed product distributions.

3. O:C and other ratios are mentioned in the text but not graphically displayed. Even the evolution of the averaged carbon oxidation state (Kroll et al., nature, 2011) could assist the suggested reaction schemes. Also the evolution of the aerosol formation yields would allow a further interpretation. Some difficult parts of the manuscript could be obviously assisted by clear and simple graphs. The theoretical part of the “Novel chemical pathways for carbon loss” should also be assisted using a graphical interpretation.

Thank you for these suggestions. The O:C ratios are graphically displayed in Chhabra et al., 2011, but we have added the use of carbon oxidation state as recommended to assist with the chemical discussion in this study. We also have included a simple graphical interpretation of the thermochemistry proposed for methoxy loss in the methoxyphenol systems.

4. Other figures should be simplified or combined. Fig. 1 and 2 could be rearranged. The missing phenolic yields should be added. In general, displaying the evolution of

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the yields as a function of the aerosol mass would be more significant. The authors should think on simplifying figures like 3, 7 and 9. If there is now other information in figure 5 than the permanent increase of acid and fragment concentrations, the authors could think on skipping this figure.

The authors have combined Figures 1 and 2 and added the phenol growth curves as well. Figures 1 and 2 for the guaiacol and syringol growth curves, respectively, were originally kept separate because syringol experiments employ higher initial organic loadings, and would obscure the details of the guaiacol growth curves at lower organic loading. To combine phenol, guaiacol, and syringol growth curves on the same plot, we have scaled growth curves from the syringol experiments by a factor of 0.5 in both coordinates and noted this in the text and caption for the new figure.

The authors have also added a figure showing the evolution of the yields as a function of the organic aerosol mass generated. We have added descriptions in the text under Section 3.

The authors have removed Figure 5 and adjusted the reference in text, page 3498, line 18-20 to, “All CIMS traces for proposed ring opening acids and ring fragments share a similar trend of constant linear growth over time (not shown). Many of these trend with the aerosol mass (e.g. m/z 185 mentioned earlier), indicating that aerosol growth continues to proceed with the generation of ring opening and fragmentation processes.”

Minor and Technical Comments:

1. Tab. 1 – References for physico-chemical properties (boiling points and vapour pressures)

The authors have added footnotes for the reference (U.S. EPA Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11, 2012).

2. p. 3489 line 14 – “dried air”; mixing ratio of the remaining water content? What are the concentrations of NO_x species in the purified air?

We have added the levels for the purified air entering the chamber, “(RH < 5%, NO_x < 2ppb)” to this line.

3. p. 3489 line 25 – specify “low-NO_x”

We have added the description here, “We refer to the reaction conditions of these experiments as “low-NO_x” because there is no intentional injection of NO_x ([NO_x]₀ < 5 ppb, the lower detection limit of the NO_x analyzer).

4. p. 3490 line 10 and Table 2: please add the relative humidity and specify the LDL of the different analysers within the table.

These changes have been made to the manuscript within the text and in footnotes for Table 2. We added the sentence, p. 3490, line 15, “The lower detection limits (LDL) of the utilized analyzers are 5% RH, 2 ppb O₃, and 5 ppb NO_x.”

5. p. 3490 line 20f – Why was the method switched and CIMS not used for all experiments? The authors should specify the used methods and different LDLs (related to the method of measuring) within Table 2.

We have added further clarification regarding the reason for using the GC-FID for phenol measurements and the CIMS for measurement of the methoxyphenol compounds. The following text has been added after page 3490, line 23, “The LDL for phenol on the GC-FID was determined to be ~ 1 ppb from calibrations.”

The following discussion has been added page 3491 following line 15: Calibrations of guaiacol and syringol on the CIMS were performed similar to those of phenol on the GC-FID by preparing 55 L Teflon chamber standards of varying concentrations of the methoxyphenol compounds. The LDL for guaiacol on the CIMS was established to be 100 ppt and that for syringol to be 500 ppt. While phenol was detected at both the transfer (m/z 113) and the cluster product (m/z 179), a calibration curve was not made because a photooxidation product in the phenol system interfered significantly at m/z 113.

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6. p. 3492 line 19 – demonstrating the gradient elution program in a graph would be more descriptive than in the text.

The authors agree, though this particular program is technical regarding the instrumentation methods used. As such we do not feel it necessitates another figure for the manuscript as it would not present data or scientific insight to the focus of the paper.

7. p. 3493 line 15 – the authors could think about calculating also the averaged carbon oxidation states (as mentioned above) and presenting them graphically.

Thank you for this suggestion. We have implemented this change as mentioned in our response to Referee 2, Major Comment 3.

8. p. 3494 line 4: As the growth curves are not perfect lines, the calculated yields are depending on the chosen concentration ranges; Hence, the authors should add the calculated errors to the yields in talbe 2. Further the authors could think about plotting the evolution of the yields as a function the aerosol mass.

The authors have calculated the errors and included them in Table 2. We have also included a plot of the evolution of the yields as a function of the aerosol mass.

9. p. 3494 line 6 – specify the method of wall-loss correction (reference)

The authors have included references for this method and have revised this line to read, “To calculate the mass concentration of the SOA, the SOA volumes established by DMA measurements are wall-loss corrected following procedures in Keywood et al. (2004); Ng et al. (2007) and then multiplied by the SOA density, as determined by the AMS in seed-free (nucleation) experiments.”

10. p. 3494 line 11 – as mentioned above, the averaged carbon oxidation states could be interesting as well.

This has been address per the above Referee 2, Major Comment 3 and Minor Comment 7.

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11. p. 3494 line 19 – Why do the authors not present the growth curves of phenol. For a consequent presentation of the results, these data should be published.

The authors did not present these originally due to the greater uncertainty that arose for the phenol hydrocarbon measurement and because other studies have presented yield curves previously. However, with the recommendation from Referee 2, Major Comment 4, we have added the growth curves of the phenol experiments with those of syringol and guaiacol in one figure.

12. p. 3494 line 24 “fall on a line” – This is only an optical illusion and depending on the scaling of the plots. The authors should resign this statement and mention the errors and deviations, which are an indication of the reproducibility of the experiments. Fig. 1 and 2: The authors could think about combining these two figures and adding the phenol growth curves. Further, demonstrating the evolution of the yields as a function of the formed aerosol mass could also be interesting for all three species.

The authors have resigned this statement and have refocused the discussion accordingly. The figure changes have also been implemented in response to Referee 2, Major Comment 4.

13. p. 3495 line 3 – “boiling point and vapour pressure” – The authors should cite a reference for this general statement. Are the boiling point and the initial vapour pressure really an indication for the aerosol formation potential?

This statement has been revised to read, “One might expect that the relatively higher boiling point and lower vapor pressure of syringol might suggest enhanced ability of it or its photooxidation products to partition to the particle-phase, as vapor pressure is a key component in calculating the partitioning coefficient (Pankow, 1994).”

14. p. 3496 line 9 – specify “generation”

We have added the word “chemical” in front of “generation” to specify that we are referring to chemical generations.

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15. p. 3496 line 16 – “many of the transfer products are likely acidic” – Is there a reference available; the authors could also refer to the related tables.

We have added the reference Huey et al. (1996) following that line and a reference to Tables 3-5.

16. p. 3497 lines 13ff: “carboxylic acids”: The authors should address the related literature like e.g.: Coeur-Tourneur et al., *Atmos. Environ.*, 2009; Ofner et al., *Z. Phys. Chem.*, 2010; Ofner et al., *ACP*, 2011; Olariu et al., *Atmospheric Ozone Degradation Reaction of 1,2-Dihydroxybenzene*, EUPHORE 4th Report 2001; Nieto-Gligorovski et al., 2008 and 2010; Tomas et al., *Int. J. Chem. Kinet.* 2003;

We thank Referee 2 for directing our attention to these references. In light of the corrections made for Referee 1 Minor Comment 7, which included reassigning these ions to the more common isomeric dicarbonyl products, we have shifted the focus on carboxylic acids to section 4.3.5 in line with Referee 1 Minor Comment 10 (Ofner studies). We have added reference to Olariu et al., (2001) and Tomas et al. (2003) in Section 4.6 in line with discussion of the Ofner 2010 study to enrich the discussion on acid production, though we omitted Nieto-Gligorovski as we do not have evidence of heterogeneous oxidation at this time. The revised discussion is as follows:

Previous study on the ozonolysis of 1,2-dihydroxybenzene showed that several carbonyls existed in both the gas and particle phases (Olariu, 2001). Carboxylic acids believed to be ring fragments, as well as muconic acid, a ring-opened C6 dicarboxylic acid, were also identified. Muconic acid was also identified in the particle phase from benzenediol ozonolysis Tomas et al. (2003). These results support the current observations that many dicarbonyl species in general trend with the SOA mass, suggesting that they are semi-volatile in nature.

17. p. 3498 line 13 – The authors should state the differences of their reaction schema to the cited one of Birdsall et al. 2010

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The authors have addressed this in response to Referee 1, Major Comment 1.

18. p. 3498 line 20 – Is there any detailed understanding of the system coupled to this statement?

We have added this description, “Many of these trend with the aerosol mass (e.g. m/z 185 mentioned earlier), indicating that aerosol growth continues to proceed with the generation of ring opening and fragmentation processes.”

19. Fig. 3: What means “ m/z 129 x 0.15 DHB”? Please clarify this definition. The combination of all these data in only one complex figure could be a little bit confusing.

We have added in the caption that this signal has been scaled (multiplied by 0.15) to fit on the scale with other trends. Unfortunately, these plots are complex, but it is important to keep the time profiles together to understand the stages of chemical development in the gas-phase and how they may coincide with aerosol growth.

20. Fig. 5: “ m/z 145 x 0.2 ACID1” – What does this mean? What is ACID1,2,3 and FRAG, FRAG, FRAG. Are the authors able to present proposed molecular formulas?

In light of Referee 2, Major Comment 4, this figure has been removed from the figure.

21. p. 3500 line 4 “OH addition” and p. 3500 line 17 “O:C ratio” see e.g. Ofner et al., ACP, 2011.

We have added a description to compare this O:C ratio with those of Ofner et al., ACP (2011). We have added, p. 3500, after line 19, “Ofner et al., (2011) found O:C ratios of 0.3 - 1, which were attributed to products that are likely highly oxygenated benzenes and conjugated olefins.”

22. Fig. 7 As mentioned for fig. 3, this figure is complex as well. Maybe a simplification is possible?

The authors agree that this figure can be complex, but we do believe that showing the chemical complexity and simultaneous development is appropriate here. The current

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supporting text of this figure does focus on stepping through each trace so the gas- and particle-phase development can be linked with the mechanism in Figure 6.

23. p. 3502 line 3 - The proposed peroxide is unlikely very stable. This intermediate is also suitable for condensation like reactions with other molecules. The authors could think about adding a simplified version of this channel to the reaction schema.

The authors agree that this compound is likely unstable and may participate in particle-phase chemistry. Due to the uncertainty of the gas-phase mechanism, however, we have noted its structure as a tentative assignment though the molecular formula is consistent with a particle-phase product. This revision is addressed in Referee Comment 1, Minor Comment 9.

24. p. 3502 line 18: for O:C ratios from ICR-FT/MS measurements and related FTIR analysis of functional groups of organic aerosol from guaiacol see Ofner et al., ACP, 2011.

We have added this reference to support this statement, “However, since many corresponding signals are not observed in the CIMS, it is also possible that a number of these highly oxygenated (> O₅) species may be formed in the particle phase, as evidenced in Ofner et al., (2011) for aerosol from guaiacol and catechol.”

25. Fig. 9 – see comments related to fig. 3 and 7

The authors agree that this figure can be complex, but we do believe that showing the chemical complexity and simultaneous development is appropriate here. Splitting Figure 9 into two panels was also done to support the step by step explanations of the complex syringol chemistry.

26. p. 3502 l. 24 – Comparing the SOA mass curves would be easier if the authors present them within one graph and even calculate and plot the deviation between the single curves.

The authors do not intend for the SOA mass curves alone to be compared across

systems. The discussion here focuses on the relative start of SOA formation (and the trend of SOA mass) with the gas-phase products, several of which are analogous across systems. That is, phenol SOA growth is clearly delayed until three generations of oxidation have been achieved (trihydroxybenzene is present), whereas syringol and guaiacol SOA are immediately formed.

27. p. 3503 l. 3 – Which transfer product do the authors mean? In table 4 for the CIMS ions only one acid (m/z 175) is marked as transfer product for guaiacol and in table 6 it's also only one (m/z 149)? Where is the enhancement towards greater acidity?

We have clarified this as, "...transfer product (m/z 173)". This is the ion resulting from syringol as a result of F transfer instead of ionization via the CF_3O^- cluster described earlier p. 3502 lines 25-26. The analogous products we refer to across guaiacol and syringol systems that become increasingly more acidic include those listed in Tables 3 and 4, selected entries paired here:

1) G (Cluster), S (Transfer)

2) G+OH (Cluster), S+OH (Transfer)

3) G+2OH (Cluster), S + 2OH (Transfer contribution at m/z 205, but since epoxide is there, cluster product is used to track solely S + 2OH)

28. p. 3505 l. 12-13 - The authors should provide a reference for the solar simulator in the chamber. Based on photon flux measurements of the chamber, the photolysis rate of the methoxy group of guaiacol could be calculated and compared to the experimental data.

Authors have provided a reference for the UV lights as addressed in Referee 1, Minor Comment 1. Direct photolysis of the methoxyphenol compounds was not tested for. Photolysis rate would have to be proxied using absorption cross sections from related simple ether compounds, for which many are not available for the relevant wavelength range for our UV lights. Otherwise, photolysis rate would have to be proxied from the

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experimental methoxyphenol decay accounting for both reaction with OH and photolysis. Rate coefficients for reaction with OH are known from Coeur-Tourneur et al., (2010) for guaiacol and Lauraguais et al., (2012) for syringol. The rate coefficient for guaiacol + OH is in agreement with the experimental data, so it would be difficult to parse out the photolysis rate without testing for it directly. Coeur-Tourneur et al., (2010) and Lauraguais et al., (2012) both found no evidence of photolysis of guaiacol and syringol, respectively, though their irradiance spectrum was from 380 nm – 800 nm, just above the estimated wavelength (340 nm) corresponding to the estimated energy necessary for ether bond cleavage and removal of the methoxy group.

29. p. 3506 and 3507 – The authors should underline their estimations related to the standard enthalpies of formation using a graphical presentation of their calculations and conclusions.

The authors have included a simple graphic also addressed in Referee 2, Major Comment 3.

30. p. 3508 l. 20 – The averaged carbon oxidation state would assist the definition of “highly oxidized species”.

We have implemented this change in accordance with Referee 2 Major Comment 3 and Minor Comment 7 to assist with the chemical interpretation of “highly oxidized species.”

31. p. 3509 line 4 – These low-NO_x conditions are not typical for biomass burning events. Iinuma et al. (Environ. Sci. Technol., 2010) report Methyl-Nitrocatechols as tracers for BBOA. Veres et al. (J. Geophys. Res., 2010) report HONO emissions up to 300 ppb. See also Akagi et al. (ACP, 2012).

We have updated the discussion here to highlight the context of this study in spite of the conditions being low-NO_x, similar to our address of Referee 2, Major Comment 2.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 3485, 2013.