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Atmospheric Chemistry and Physics
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Interactive comment on "Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols" *by* L. D. Yee et al.

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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 1

This paper describes results from a series of simulation chamber experiments to inves-

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tigate the formation of secondary organic aerosol (SOA) resulting from photooxidation of phenol, guaiacol and syringol which are produced from biomass burning. State-of-the-art techniques have been used to help identify the gaseous and particulate phase products, which in turn facilitate mechanistic explanations for the SOA formation pathways.

A good number of experiments have been performed on each of the compounds and the on-line chemical characterization of gas phase products is nicely detailed. I think the work could have been improved further by performing some experiments in the presence of NOx, especially given that these phenolic compounds are present in plumes of biomass burning smoke. The article is well written and the results are presented in a clear and logical manner. The interpretation and discussion of the results is generally appropriate, however, the atmospheric reactivity of aromatic compounds is notoriously complex and at times the mechanistic explanations are somewhat speculative. Nevertheless, this is a very useful and informative piece of work that is of interest to the atmospheric chemistry community. I recommend publication following revision of the manuscript in line with the following comments.

Major Comments:

1. In section 4.2, three key gas-phase products observed by CIMS at m/z 145, 161 and 177 are assigned to carboxylic acids. The formation of acids as degradation products of aromatic compounds is unusual and requires more explanation. The authors state: ”From the time profiles of these CIMS ions, we predict that they are likely carboxylic acids...” without further justification. Based on a paper by Birdsall et al. (2010), the authors propose a possible reaction scheme in Figure 4. However, I could not find this type of reaction pathway in the cited paper, and although it does include the possible reaction of a bicyclic peroxy radical with HO2, this reaction produces an oxy radical, not an acid (Birdsall et al., 2010). In summary, I suggest the authors inspect the literature again and reconsider the possible mechanism for acid production.

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The authors make reference to Birdsall et al. (2010) because there is discussion of RO2 + HO2 → RO + OH + O2 (referenced therein as Equation 11) as a NOx-free reaction pathway that explains the observed ring-opened and ring-fragmented products. This reaction is shown in Figure 2 of Birdsall et al. (2010) resulting in the ring-opening of the OH-adduct alkoxy radical and subsequent formation of methylhexadienedial (a C6 dialdehyde). In the analogous pathway proposed for phenol, decomposition of the RO radical results in ring opening that maintains C6 backbone and depending on the site of OH addition, a carboxylic acid (due to ortho-OH addition). Isomeric hydroxy dialdehyde products would result from this ring-opening if the OH-addition was elsewhere. We are familiar with dialdehyde products as the result of bicyclic peroxy radical fragmentation products, however, these ions are likely C6 retaining. Because the time profiles of m/z 145, 161, and 177 rise within 1 hour of photooxidation (Figure 5), within the formation of up to three generations of OH adducts from phenol (Figure 3), it does not make sense to assume these ions come from isomeric OH adducts past trihydroxybenzene and that they rise linearly with time. If they were subsequent OH adducts, we would expect their time profiles to show some decay based on reaction with OH in the gas-phase as well as contribute to the particle-phase (as is evidenced by the plateau in the trihydroxybenzene signal at m/z 211 in Figure 3). We also know that the m/z 145 time profile (Figure 5) and m/z 211 time profile (Figure 3) are distinct, suggesting that while both ions are assigned to C6H6O3, they result from different chemical pathways.

To clarify, we have modified the discussion on page 3498, lines 7-15 to the following:

From the time profiles of these CIMS ions, we predict that they are likely carboxylic acids even though the proposed chemical formulae are isomeric to the aromatic OH adducts. That is, these ion signals grow linearly with time during the experiment duration and do not peak or plateau like their isomeric aromatic OH adducts. The peak/plateau of the signal from aromatic OH adducts is consistent with the proposed products' functionalities and potential to partition into the particle-phase, whereas these ring-opened products are of higher vapor pressure and may form throughout the experiment during continued oxidation of the phenolic products.

The prevalence of these products may partially explain the absence of a strong signal from a hydroperoxide $C6H8O4$ at m/z 229. The alkylperoxy radical preferentially isomerizes to form the bicyclic peroxy radical and decomposes from a bicyclic alkoxy radical to <C6 fragments (often dicarbonyl) as mentioned above. However, Birdsall et al. (2010) observed evidence that the alkylperoxy radical may also participate in chemistry that regenerates OH and opens the ring (alternate route to alkoxy radical formation without first forming the bicyclic peroxy radical). This was found to be a more minor pathway also via $RO2 + HO2 \rightarrow RO + OH + O2$ for the case of toluene photooxidation. This results in an aromatic alkoxy radical and ring-opening to form methylhexadienedial, a C7 dialdehyde (preserving the carbon backbone). Though this route was more prominent under low [O2] conditions, Birdsall et al. (2010) also observed this product at pressures more similar to the atmosphere where bicyclic peroxy radical formation is expected to dominate and form dicarbonyl ring fragments. Thus, this ring-opening dicarbonyl pathway may also be present in this study, while minor compared to production of dicarbonyl fragments. Figure 4 outlines a potential mechanism employing this scheme to form these multifunctional C6 carboxylic acids from phenol, dihydroxybenzene, and trihydroxybenzene. The difference between the products proposed here and those of Birdsall et al. (2010) is that the hydroxy group placement results in carboxylic acid functionality. We note that depending on the hydroxy group placement on the ring, isomeric hydroxy dicarbonyl products are also likely and can contribute to these ion signals as well.

2. Epoxide formation is deemed to be very important for guaiacol (section 4.3.3) and syringol (section 4.4), but not for phenol. Any ideas why? This at least deserves some comment.

The authors do not mean to imply that epoxide formation is non-existent in the case of phenol. It is merely somewhat indeterminate from the current measurements and OH exposure for these experiments. From the CIMS measurements, the expected

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epoxide from phenol would be observed at m/z 227, but this is the same ion where 4HB is monitored (Table 3). The signal at m/z 227 is thus the sum of the signal from the epoxide and 4HB. The m/z 227 time profile (which was not plotted in Figure 3 for clarity) looks similar to m/z 211 THB, but is approximately one-fourth of the m/z 211 THB signal. The signal at m/z 227 has a plateau character similar to m/z 211 THB, and is consistent with expectations that 4HB contributes to the particle-phase, but we currently cannot separate the contribution from the epoxide. To clarify, we have rewritten page 3497, lines 11-12 to read, “A signal at m/z 227 was observed to have a similar profile as m/z 211, and may be attributed to tetra hydroxybenzene (4HB, Table 3) and an epoxide isomer ($C_6H_6O_4$). A plateau in the profile is consistent with 4HB also contributing to the particle phase. Individual contributions from 4HB and the epoxide could not be determined from the signal at m/z 227, which was approximately one-fourth of the signal at m/z 211 (not shown for clarity).” We have also added an additional footnote to Table 3 assignment of m/z 227 to note that an epoxide contribution likely exists.

3. The replacement of methoxy by OH is an interesting observation, however, the ensuing discussion could be improved (section 4.5). The authors refer to an article by Aihara et al. (1993) in which experiments were not performed in the gasphase, while at the same time omitting, possibly more relevant gas-phase studies where ipso addition of OH in aromatic systems is discussed. The authors should consult relevant gas-phase studies, e.g., by Noda et al. (J. Phys Chem A, 2009), Bohn et al. (PCCP, 2012) and Koch et al. (ACP, 2007) and discuss the possibility of straightforward elimination of a methoxy radical from the OH-aromatic adduct.

Thank you for directing the authors to these references. The authors agree that while Aihara et al., (1993) is not performed in the gas phase, it was presented because the particular species studied within had more chemically similar character (methoxy functionality). Having known of the dealkylation scheme in Noda et al., (2009), the authors felt at the time of manuscript writing that this scheme may not necessarily be the same for demethoxylation. That is, there may be differences in the RC-OCH3 behavior versus the RC-CH3 behavior. There is also controversy over the dealkylation as presented in Aschmann et al. (2010). However, with the referee's endorsement, we have included additional discussion in Section 4.5 to include the possibility of straightforward elimination of a methoxy radical via an analogous dealkylation scheme presented in Noda et al., (2009). Koch et al., (2007) presents several references in the introduction section that further provide evidence for cleavage of the ether bond in many liquid phase studies, but one gas-phase study of brominated diphenylethers by Raff and Hites (2006) is also presented which supports ipso addition responsible for the ether bond cleavage.

While Bohn et al. (PCCP, 2012) finds evidence for the reversibility of the OH adduct reaction with O2, the authors feel that this work does not necessarily provide evidence for an applicable mechanism involving direct methoxy radical elimination from methoxyphenol compounds. The mechanism of this reversibility involves removal of the O2 in the form of HO2, rather than removal of the OH group (analogous to a methoxy group for the current study). If "prompt" HO2 formation is considered an indicator of reverting the OH adduct back to a stable aromatic compound (e.g. benzene OH adduct +O2 → phenol + HO2), then this mechanism certainly applies in the currently proposed mechanism for forming series of OH addition products proposed here (i.e. G + OH, G + 2OH, G + 3OH, etc.). Still, Bohn et al. (2012) points out that beyond this mechanism, "prompt" HO2 formation can come from several other pathways including ring fragmentation pathways from the bicyclic peroxy radical as well as epoxide routes (also proposed in the current study). Thus, we do not feel that there is a concrete mechanism presented in this reference supporting direct elimination of a hydroxyl radical (for the case of benzene) or a methoxy radical (for the case of methoxyphenols) following OH addition.

Based on the insights of Noda et al., (2009) and Koch et al., (2007), we have added the following clarifications and discussion to Section 4.5:

Page 3504, Lines 19-21 have been replaced with the following:

While gas-phase aromatic chemistry is not completely understood Calvert et al. 2002, we propose possible explanations for these carbon loss pathways. Carbon loss from aromatic systems have been observed previously in the gas-phase, and is thought to be a result of ipso addition of OH at a substituent containing ring carbon and subsequent elimination of the substituent leaving a phenolic group. This is the case for alkylbenzenes, in which Noda et al., (2009) observed phenol formation from OH-intiated photooxidation of toluene and cresol formation from xylenes. Prior, Koch et al., (2007) provided evidence that the ipso addition of OH is relevant for the case of hexamethylbenzene. The extent by which these processes occur in the gas-phase is still unclear. The extent by which these processes occur in the gas-phase is still unclear, as Aschmann et al., (2010) does not observe the dealkylation as in Noda et al., (2009). Addition at the ipso position is generally considered to be a minor route $\leq$ 20% for the alkylbenzenes studied in Noda et al., (2009), though it could be that oxy substituents may influence the favorability of this route. Raff and Hites (2006) found that brominated diphenylethers also undergo ether cleavage, proposed as a result of ipso addition of OH. Thus, ipso addition of OH in the gas-phase may be more relevant for more highly-substituted and/or more complex substitutents on aromatics.

Koch et al., (2007) also pointed out several liquid-phase studies that find evidence of ether bond cleavage. Again, ipso addition of hydroxyl radical is cited as being responsible for ether bond cleavage (removal of an oxy substitutent) and C-C cleavage (removal of a methyl substituent) in some cases. Aihara et al., (1993) studied . . .

4. In sections 4.6 and 5 the authors imply that the formation of acids is important in SOA formation. For phenol however, the yields of gas-phase ring-retaining products is 80- 90% (Olariu et al., 2002, Berndt and Boge, 2003), indicating that the gas-phase yields of acids are certainly less than 15%. What does this say about the importance of gas-phase acid formation if the yield of SOA is significantly higher (up to 44%)?

In review of Referee 1 Major Comment 1 and Minor Comments 6-8, 13, 15, 17, and 19, the authors recognize that there is need for clarification of the formation of acids in both the gas-and particle-phases and these species' role in SOA formation from phenol. First, we agree that the yields of gas-phase acids are likely to be less than 15%, as we think acids form through two minor routes: 1) ring-opening of an alkoxy radical via the OH-adduct alkyperoxyradical reaction with HO2 ($RO2 + HO2 \rightarrow RO + OH + O2$) that leads to C6 acids (and isomeric dicarbonyls), and 2) ring-fragmentation of the bicyclic radical that generates mostly dicarbonyls consisting mostly of dialdehydes, but carboxylic acids as well, depending on substituent placement on the ring. While ring-retaining products have an 80-90% yield from phenol, the fate of those ring-retaining products in the presence of enough OH exposure can also result in acid production from the routes mentioned.

While the gas-phase acid formation is a minor route, we track the gas-phase traces of these acids as a way of monitoring chemical development of the system. That is, we use them as an important indicator of when SOA forms as in the discussion of Section 5 regarding the different ring-fragments that follow the SOA mass trace for phenol and guaiacol. It is unclear if the C6 ring-opened acids contribute to the particle-phase (without additional particle-phase analyses) via gas-to-particle partitioning, however we believe that it is very likely that the high O:C and <C6 ring-fragmented dicarbonyls may contribute to the particle-phase and/or oxidize further to generate more highly-oxidized acids that are in the particle-phase. This mechanism is more in line with those generally proposed for aromatics photooxidation and observation of carboxylic acids in the particle-phase. This is also why the <C6 ring-fragments are used to track the SOA mass, rather than the proposed ring-opened acids (C6 retaining).

Still, C7 dicarboxylic acids observed by Sato et al. (2007) from toluene oxidation were a large signal from the particle-phase, and the proposed mechanisms of formation involved novel three-step pathway through an epoxy route and a two-step pathway through toluene oxide to generate dicarboxylic acids. Ofner et al. (2010) also found that the SOA-formation process from catechol involves ring-opened carboxylic acid deriviatives that are part of highly hydroxylated olefin structures. Thus, it seems as

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though ring-opened carboxylic acids may play a significant role in SOA formation and resulting yields from phenolic compounds.

In light of the current discussion, we have revised Section 4.6, lines 18-20, to read, “This is consistent with the necessity of further oxidation of ring-opened dicarbonyl fragments and ring-opened acids to explain the presence of highly oxidized species observed in the guaiacol filter analyses. Ofner et al., (2010) found that the SOA-formation process from catechol involves ring-opened carboxylic acid deriviatives that are part of highly hydroxylated olefin structures, which supports the organic acid functionality observed in the current related systems.”

Minor Comments:

1. Page 3489, line 26: Insert details about the lamps used to photolyze H2O2

We have included a description as follows, "There are three hundred 40W black lights, Sylvania 350BL, with an emission spectrum that peaks at 340-350 nm wavelength. Based on the irradiance spectrum of the lights and the absorption cross section of H2O2 (Sander et al. 2011), this results in a photolysis rate constant, jH2O2 = 2.9 x 10^6 s^{-1}.”

2. Page 3492, line 1: Were the lamps switched off when the maximum aerosol concentration was reached?

No, they were turned off afterwards. We have added a statement of clarification, “. . .as determined by the DMA. Lights were turned off after the filter sampling period was complete.”

3. Page 3495, line 1: Overstatement. . .the yields of SOA from syringol are not substantially lower than those of phenol and guaiacol.

We have removed the word, “substantially” from this line.

4. Page 3496, line 5: Avoid using “m/z’s”, e.g., by changing the words in the sentence.

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There are several other instances of this in the manuscript.

We have changed or restructured all of these instances in the manuscript to avoid the use of “m/z’s”.

5. Page 3496, line 9; The use of the term “a generation” is not clear to me. Should a different term be used?

We do intend to use the term “a generation” to refer to each stage of chemical oxidation initiated by OH reaction with a stable (non-radical) species. A chemical generation would include the subsequent intermediate reactions of radical species following OH addition or photolysis of a non-radical species (e.g. R. + O2, RO2 + HO2), but we do not consider these reactions individually to be additional generations. That is, a first-generation product is any stable product formed following OH reaction with the parent compound. A second-generation product is any stable product formed following OH reaction with one of the first-generation products. We differentiate generations to generally keep track of the number of OH radicals are used to reach a stage of chemical development.

6. Page 3497, line 16: The peak for m/z 135 is assigned to an enol. Is this compound stable?

In light of Referee 1 Minor comments 7 and 8 below, we have reassigned the peak at m/z 135 to a dicarbonyl product, dihydroxy-butenedial.

7. Page 3498, lines 1-2: why are the products at m/z 185, 135 and 107 assigned to carboxylic acids?

These carboxylic acids are potential isomers for ring fragments that result from the bicyclic radical decomposition of phenol OH-initiated photooxidation. They are isomeric with hydroxy dicarbonyl structures as well. The potential structure for m/z 185 shown in Table 3 results from ring-fragmentation of the para-isomer (i.e. OH-attack of phenol at the para position). This is also isomeric to hydroxyl-butenedial (not the carboxylic acid shown for m/z 185), which is more likely to form from ring-fragmentation of the ortho-isomer. Although we only show one isomer in Table 3, for consistency with the text (as brought up in Referee 1's Minor comment 8), we have revised Table 3 to show hydroxyl-butenedial rather than the carboxylic acid form. The m/z 135 structure also results in a dicarbonyl structure, but again, a carboxylic acid group can result based on the position of OH-attack and where the peroxide bridge forms. This particular structure can form from several different pathways, one example being the OH oxidation of catechol, where OH attacks para to one of the phenolic groups. The dialdehyde with two hydroxy groups, a dicarboxylic acid, and the current isomer shown in Table 3 for m/z 135 are all potential structures. Though we state that these proposed structures result from assuming initial OH-attack at a position ortho or para to the phenolic group, we have adjusted the table to display the structure that is more likely (due to OH attack favored at the ortho-position). We have revised Table 3 to show dihydroxy-butenedial for the proposed structure for m/z 135. In retrospect, we have removed m/z 107 because while it is likely an acid structure, its mechanism of formation was thought to be a product of CO2 removal of a C4 acetyl radical in the more minor H-abstraction route of phenol photooxidation, which we do not discuss in great detail here.

We have also modified the discussion, page 3498, lines 14-17 to reflect this change: Figure 3 also shows that the SOA is in equilibrium with m/z 185, which we propose to be the ring fragment $C_4H_4O_3$, hydroxy butenedial, that forms from the decomposition of the bicyclic radical from phenol + OH. Another dicarbonyl, $C_4H_4O_4$, is monitored at m/z 135, which could be the analogous ring fragment from dihydroxybenzene + OH. These products approach the high O:C ratios characteristic of the SOA in this system.

8. Page 3501, lines 1-3: $C_4H_4O_3$ at m/z 185 is attributed to an acid in Table 3, but here it is stated that it is hydroxy-butenedial, an aldehyde. In fact the ring fragmentation products for phenol are all acids (Table 3), while those for guaiacol are mainly carbonyls (Table 4, Figure 6). Is something amiss here?

Please note the response to comment 7 above which addresses the potential for isomeric carboxylic acids and dicarbonyls to be ring fragments from these compounds. Each m/z is the sum of the signal from all isomers (e.g. contributions from the carboxylic acids and the dicarbonyls), and only one isomer structure is shown per m/z in Table 3.

9. Page 3502, line 3: Loss of a methyl radical from this species seems unlikely.

The authors have revised this portion of the mechanism to follow a similar pathway presented in Collins et al., (2005) for the OH-initiated oxidation of diisopropylether under low-NOx conditions. This involves formation of a hydroperoxide that is photolyzed to form an alkoxy radical. Due to the substitution at this carbon, this results in elimination of the methoxy group and formation of a ketone group. The text on page 3502, lines 1-4 have been replaced with the description, "In the event that the radical placement occurs on the carbon containing the methoxy group during formation of the bicyclic radical, carbon loss may occur by removal of a methoxy group. The ether alky radical will react with O2 to generate an ether alkyl peroxy radical. Collins et al., (2005) proposed that photooxidation of diisopropyl ether in the absence of NOx (with RO2 + HO2 reactions dominating) likely resulted in the formation of hydroperoxide species that could then undergo decomposition, photolysis, or reaction with OH. Photolysis of the hydroperoxy group in the current methoxyphenol case would result in an alkoxy radical and elimination of the methoxy group to form a ketone. This leads to formation of a C6 bicyclic ketone product as outlined in Pathway 3b of Fig. 6. The mechanism and structure for this particle-phase product remain tentative, as the proposed structure may be unstable and participate in additional condensation reactions."

10. Page 3502, lines 6-18: Ofner et al. (ACP, 2011) investigated the SOA formed from guaiacol. This paper should be cited here.

Thank you for suggesting this reference. We have cited this reference in a discussion at the end of line 18 as follows: Previous study by Ofner et al. (2011) reports that the most important functional groups of generated SOA from guaiacol and catechol include carboxylic acids, carboxylic anhydrides and lactones or esters. While carboxylic acids can form as ring fragmentation products depending on the particular conformation of the bicyclic radical, the observation of carboxylic anhydrides and lactones suggests potential for additional intra- and inter-molecular reactions that may occur in the particle-phase involving the carbonyl and methoxy groups of SOA products. Ofner et al. (2011) also observes the degradation of the methoxy group during SOA formation from guaiacol, and finds this degradation to be more pronounced under wet conditions. This supports additional chemistry (likely in the particle phase) that goes beyond the proposed gas-phase products in Figure 6.

11. Page 3505, lines 7-21: Presumably the photolytic elimination of a methoxy radical was investigated in test experiments on the photolysis of guaiacol and syringol. In other words, this information should be known to the authors.

Unfortunately, direct photolysis of the methoxyphenol compounds was not tested for. We have reason to believe that since the hydrocarbon decays are within reasonable agreement with measured rate coefficients Coeur-Tourneur et al., (2010) for guaiacol (and Lauraguais et al., (2012) for syringol, that photolysis is not a significant contribution. 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. Additional comment on possibilities for estimating the photolysis rate is presented in response to Referee 2, Minor Comment 28.

12. Page 3507, line 11; “alpha” or “ipso”?

We do intend the use of “alpha” here, but to clarify, we have modified this line to read, “However, with the additional methoxy groups, OH attack at the alpha-unsubstituted carbons to the methoxy groups becomes competitive and changes the potential for maintaining aromaticity in the methoxyphenol systems.”

13. Page 3508, line 24: Acid formation in the gas or particle phase?

We have revised page 3508, lines 24 and 29 to clarify acid formation in the particle phase, as well as clarify the mechanism of acid-formation from further oxidation of carbonyl ring fragments. Page 3508, line 24 has been modified to read, “This may also partially explain why the syringol SOA yield is lower if particle-phase acid formation from carbonyl ring fragments drives the SOA growth.” Page 3508, line 29 has been revised to, “This could be due to the lack of OH addition to the ring on syringol in critical positions that lead to SOA formation via ring-fragmentation pathways and acid formation.”

14. Page 3518, Table 2: Define V0 and Vf.

We have added a footnote “b” to Table 2 to define V0 and Vf as the following, “b V0 is initial seed volume; Vf is final volume (seed + organic aerosol), as measured by DMA”.

15. Page 3520, Table 4: Structure for product with m/z 175 is not an acid

Yes, the structure proposed is not an acid, as the particular conformation of the alkylperoxy radical in Figure 6 leads to a dialdehyde structure for m/z 175. The authors mean to imply in Table 4 that the mechanistic pathway is analogous to that proposed for ring opening acids pathway for phenol (Figure 4). That is, RO2 + HO2 → ring opening product + OH + O2. An isomeric acidic structure can be achieved by following the oxidation shown in Figure 6, but from a different resonance structure. To clarify this pathway more broadly, we have renamed this pathway in Tables 3, 4, and 6 from “ring opening acid” to, “ring opening product,” and have also changed the reference in the mechanism in Figure 6 to reflect this nomenclature.

16. Page 3520, Table 4: Product with m/z 107 is different to that for phenol (Table 3). Is this correct?

Yes, we believe this to be the more likely contribution to signal at m/z 107 for the guaiacol experiments based on the mechanism. However, we keep in mind that signal

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at a particular m/z is the sum of signal from all isomers that the CIMS is sensitive to at that m/z. It is possible that the acid assigned to m/z 107 in the phenol case and its isomers may also be present (in minor amounts) since we observe some evidence of a dihydroxybenzene route from guaiacol photooxidation. Again, we only present one isomer in these Tables, though there are several possibilities based on where OH-attack occurs, resonance, and substituent group effects.

17. Page 3522, Table 6: Product with m/z 205 is not an acid

This comment has now been addressed in our response to minor comment 15.

18. Page 3526, Figure 4: The second horizontal arrows have HO2 under them. Is this correct?

Thank you for catching this error. The HO2 has been removed from underneath the second horizontal arrows.

19. Page 3528, Figure 6: The product with m/z 175 is not an acid.

This comment has now been addressed in our response to minor comment 15.

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