

General Comments

This paper describes results from a series of simulation chamber experiments to investigate the formation of secondary organic aerosol (SOA) resulting from photo-oxidation 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 NO_x, 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.
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.
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 gas-phase, 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.

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%)?

Minor Comments

1. Page 3489, line 26: Insert details about the lamps used to photolyze H₂O₂
2. Page 3492, line 1: Were the lamps switched off when the maximum aerosol concentration was reached?
3. Page 3495, line 1: Overstatement...the yields of SOA from syringol are not substantially lower than those of phenol and guaiacol.
4. Page 3496, line 5: Avoid using “m/z’s”, e.g., by changing the words in the sentence. There are several other instances of this in the manuscript.
5. Page 3496, line 9; The use of the term “a generation” is not clear to me. Should a different term be used?
6. Page 3497, line 16: The peak for m/z 135 is assigned to an enol. Is this compound stable?
7. Page 3498, lines 1-2: why are the products at m/z 185, 135 and 107 assigned to carboxylic acids?
8. Page 3501, lines 1-3: C₄H₄O₃ 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?
9. Page 3502, line 3: Loss of a methyl radical from this species seems unlikely.
10. Page 3502, lines 6-18: Ofner et al. (ACP, 2011) investigated the SOA formed from guaiacol. This paper should be cited here.
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.
12. Page 3507, line 11; “alpha” or “ipso”?
13. Page 3508, line 24: Acid formation in the gas or particle phase?
14. Page 3518, Table 2: Define V₀ and V_f.
15. Page 3520, Table 4: Structure for product with m/z 175 is not an acid
16. Page 3520, Table 4: Product with m/z 107 is different to that for phenol (Table 3). Is this correct?
17. Page 3522, Table 6: Product with m/z 205 is not an acid
18. Page 3526, Figure 4: The second horizontal arrows have HO₂ under them. Is this correct?
19. Page 3528, Figure 6: The product with m/z 175 is not an acid.