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Atmospheric
Chemistry
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Discussions

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

Anonymous Referee #2

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

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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 NOx 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

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-Dihydroxybenezene, 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.

Although the authors report “SOA from biomass burning intermediates”, all experiments were carried out at low-NOx concentrations. While the authors seem to defend their work according to the chosen NOx concentrations within the atmospheric relevance section, a short summary within the introduction related to emission values, NOx 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, NOx values can be incredible high at biomass burning events. Mixing of air masses from smoldering fires (with aromatic emissions) and from the fire front (high CO, CO2 and NOX emissions) must be taken into account.

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.

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 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.

Minor and Technical Comments

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

p. 3489 line 14 – "dried air"; mixing ratio of the remaining water content? What are the concentrations of NOx species in the purified air?

p. 3489 line 25 – specify "low-NOx"

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

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.

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

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

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.

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

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

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.

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.

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?

p. 3496 line 9 – specify “generation”

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

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-Dihydroxybenezene, EUPHORE 4th Report 2001; Nieto-Gligorovski et al., 2008 and 2010; Tomas et al., Int. J. Chem. Kinet. 2003; . . .

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

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

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.

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?

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

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

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.

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.

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

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.

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?

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.

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.

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

p. 3509 line 4 – These low-NOx 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).

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