Atmos. Chem. Phys. Discuss., 13, C912–C915, 2013
www.atmos-chem-phys-discuss.net/13/C912/2013/

Atmospheric
Chemistry
and Physics
Discussions

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

Anonymous Referee #3

Received and published: 3 April 2013

This paper describes a series of environmental chamber experiments and gas/particle-phase chemical analysis performed in order to elucidate the mechanisms of SOA formation from biomass burning intermediates: phenol, guaiacol, and syringol under low NOx conditions. Time-profiles of signals observed by the CIMS, in comparison with SOA mass, suggested that ring-fragment carboxylic acids were in equilibrium with SOA. Although vapor pressure of syringol is much lower than those of phenol and guaiacol (∼100 times lower than guaiacol), the SOA yield of syringol was significantly lower than the other two, which was ascribed to loss of carbon in methoxyphenol systems.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

This paper is clearly written and scientifically sound. I recommend publication after following points are addressed.

Major comments

1. Injection and quantification method of syringol needs to be evaluated. They stated "Guaiacol and syringol measurements obtained using the GC/FID were unreliable due to condensation loss in the sample loop; thus, the hydrocarbon concentration during these experiments was monitored using Chemical Ionization Mass Spectrometry (CIMS) in negative mode operation." How was CIMS calibrated? Was the same 55L Teflon bag used? Is there any significant loss of syringol in the injection system or on chamber wall (e.g., Loza et al. 2010; Matsunaga et al. 2010) that may bias quantification? Reactant loss may lead to under-prediction of SOA yields, which may affect their major conclusion on low SOA yield from syringol. Since syringol is solid at room temperature, additional description on how syringol was introduced into the chamber would be useful for future studies.

2. It is an interesting observation that some ring-fragment carboxylic acids followed SOA growth (e.g., m/z 185 FRAG in Fig.3, m/z 149 FRAG in Fig.7) better than other products (e.g., -OH addition products). Although authentic standards are not available, is there any approximation for the concentration of gas-phase carboxylic acids? Although carboxylic acids are often observed in particle phase (e.g., Sato et al., 2012), they are not commonly reported from gas-phase product analysis of aromatics (e.g., Calvert et al., 2002; Birdsall et al., 2011). Is this because previous studies (not using CIMS) missed gas-phase carboxylic acid?

3. Although "Atmospheric relevance" section discusses the impact of NO, NO2, and O3, no discussion on NO3 radical is given. Phenolic compounds react significantly with NO3 even at the trace level of daytime NO3 (e.g., Calvert et al., 2002, p.24, Figure 1-B-2: 86% of o-cresol in a polluted urban atmosphere reacts with NO3 in daytime) and ∼100% in nighttime. Although it may be reasonable to focus on low-NOx conditions in

this paper, caution must be given in extrapolating this finding to atmospheric models, especially because biomass burning continues in nighttime as well.

4. P.3497 Line 13: They showed that SOA is in equilibrium with m/z185 (Fig.3), which they propose to be the ring fragment C4H4O3, a carboxylic acid that forms from the decomposition of the bicyclic radical from phenol + OH. However, the time-profile of m/z185 seems unlikely for a 1st generation ring fragment; m/z185 increases only after m/z 211 (THB, 2nd generation product) started increasing. How come a 1st generation product increase after a 2nd generation product?

5. p.3498 Line 3: This paragraph needs more explanation. How does the time profiles of CIMS ions (m/z 145,161, and 177) suggest that they are carboxylic acids? How does “prevalence of these products” explain the absence of a hydroperoxides C6H8O4?

Minor comments

6. P.3489 Line 21, correct particle volume unit: μm3cm-3

7. Ion trap is described in detail in the experimental section but results are not shown anywhere explicitly. If no results from the ion trap are used for this paper, remove the description from the experimental section.

8. Dealkylation of aromatic hydrocarbon was discussed by Noda et al. (2009) and Aschmann et al. (2010). Aschmann et al. did not observe dealkylation. Discussion on methoxy loss could be improved in the context of these studies.

Reference

Aschmann, S. M., J. Arey and R. Atkinson, 2010. Extent of H-atom abstraction from OH + p-cymene and upper limits to the formation of cresols from OH + m-xylene and OH + p-cymene. Atmospheric Environment 44, 3970-3975.

Birdsall, A. W. and M. J. Elrod, 2011. Comprehensive NO-Dependent Study of the Products of the Oxidation of Atmospherically Relevant Aromatic Compounds. The

Journal of Physical Chemistry A 115:5397-5407.

Loza, C. L., A. W. H. Chan, M. M. Galloway, F. N. Keutsch, R. C. Flagan and J. H. Seinfeld, 2010. Characterization of vapor wall loss in laboratory chambers. Environmental Science & Technology 44:5074-5078.

Matsunaga, A. and P. J. Ziemann, 2010. Gas-wall partitioning of organic compounds in a teflon film chamber and potential effects on reaction product and aerosol yield measurements. Aerosol Science and Technology 44, 881-892.

Noda, J., R. Volkamer and M. J. Molina, 2009. Dealkylation of alkylbenzenes: A significant pathway in the toluene, o-, m-, p-xylene + OH reaction. J. Phys. Chem. A 113:9658-9666.

Sato, K., A. Takami, Y. Kato, T. Seta, Y. Fujitani, T. Hikida, A. Shimono and T. Imamura, 2012. AMS and LC/MS analyses of SOA from the photooxidation of benzene and 1,3,5-trimethylbenzene in the presence of NOx: effects of chemical structure on SOA aging. Atmos. Chem. Phys. 12:4667-4682.

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