Atmos. Chem. Phys. Discuss., 11, C9089–C9093, 2011
www.atmos-chem-phys-discuss.net/11/C9089/2011/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Aqueous phase processing of secondary organic aerosols" *by* Yao Liu et al.

Anonymous Referee #2

Received and published: 19 September 2011

General comments:

This paper investigated the aqueous phase processing of secondary organic aerosols (SOA) generated from gas-phase oxidation of isoprene, α-pinene and TMB using a smog chamber. The SOA collected on the filters were extracted by water and subsequently oxidized by H2O2 under dark condition and OH radicals in the presence of light using a photochemical reactor. Numerous online and offline analytical techniques including AMS, TD-API-AMS, HPLC-API-MS, API-MS2, IC-MS, SMPS and HTDMA were employed for physical and chemical characterizations of the chamber SOA and nebulised filter extracts. This is one of a few studies to investigate the aqueous phase oxidation of a complex organic aerosols, and the presented results are interesting. However, the objective of the paper is not clear, and some of the results can be discussed in

more details. Some expected results (e.g., TD-API-AMS spectra in a positive mode, and aqueous oxidation of TMB SOA) were omitted in the manuscript without providing any explanations. Furthermore, the reproducibility of the data for α-pinene and TMB aqueous oxidation is another concern. The specific comments are shown below.

Specific comments:

1. Introduction: Page 21492, line 19-20: The sentence describing the objective is too general. Actually, the overall goal of this paper is not clear after reading through the paper.

2. The experimental section is confusing. It is not clear that which instruments were employed to analyze organic aerosols from the smog chamber and nebulized solution droplets from the aqueous-phase photooxidation reactor. Figure 1 should show all the instruments being used. After read through the text, I think CPC and AMS were connected to the smog chamber, and IC-MS was utilized for aqueous characterizations as well. To make readers easier to follow, the authors should make it clear in each subsection and Figure 1. I also suggest to reorganize the flow of this section by moving the descriptions of both online and offline characterization after Section 2.5.

3. Page 21498, line 9-18: The criteria used to decide the initial H2O2 concentration was presented in this paragraph. So, what is the expected OH levels in each experiment?

4. AMS measurements: (a) The arrows shown in Figure 2 may be misleading. They give an impression that the evolution of organic compositions during aqueous oxidation are following their trajectories on the f44-f43 space. Some recent studies have demonstrated that the aging pathways of lab and ambient SOA usually have a curvature in another direction (i.e., f44 increase continuously and f43 initial increase and then decrease via oxidative aging) (Ng et al., 2010; Lambe et al., 2011; and Lee et al., 2011a). (b) What are the reasons to omit the discussion of all TMB samples and the "dark H2O2" samples of isoprene SOA. Please either state the reason or discuss the

data in this section.

5. HTDMA measurements:(a) The f44/f43 ratio can generally explain the observed changes in organic hygroscopicity after aqueous processing. Nevertheless, it is possible to further examine whether there is any correlation between organic kappa and O:C ratio, which can be determined by the elemental analysis of HR-AMS data or estimated from the relationship between f44 and O:C established by Aiken et al. (2008). It would be interesting to compare the results with the correlations recently reported by Lambe et al. (2011) and Massoli et al. (2011). (b) Page 21503, line 5-6: The concentration of TMB SOA in aqueous solution (> 0.9 mg/L) is much higher than that of isoprene SOA (0.4 mg/L). What is the possible reason to have low AMS signal for nebulised TMB SOA extracts? Is it related to the water solubility or volatility of the SOA?

6. Section 3.3: (a) I think the smog chamber was operated in batch mode, and hence the chamber SOA composition should keep changing throughout the experiment. I am wondering if the authors attempted to determine the 2-h average TD-API-AMS spectra of chamber SOA measured on-line. Because the TD-API-AMS spectra of nebulised aqueous extracts also represents the 2-h average organic composition, this approach may improve all spectral correlations between chamber SOA and their corresponding aqueous extracts (Figure 4). (b) What are the results of AMS analysis and TD-API-AMS operated in positive mode for biogenic SOA and negative mode for TMB SOA? Are they come up with the same conclusion made in this section? (c) The meaning of the last paragraph is not clear.

7. Section 3.4: (a) It is necessary to extend the discussion of the α-pinene results in this section. In particular, Figure 5 shows the positive spectral differences to demonstrate the formation of aqueous oxidation products. Similarly, the negative differences should be able to indicate the consumption of some specific SOA materials during the oxidation. Although the comparison is only qualitative, this information may improve our understanding on aqueous oxidation mechanism of α-pinene SOA. (b) Again, what are the results of TD-API-AMS operated in positive mode for both isoprene and α-pinene

SOA? I expect to have the TMB results in this section too.

8. Page 21508, line 22-28: Lee et al. (2011b) recently showed that the reaction between glyoxal and H2O2 can produce 2-hydroxy-2-hydroperoxyethanal (HHPE), which can be decomposed in the presence of UV light. Therefore, 1-HEHP was possibly produced via the reaction between acetaldehyde and H2O2.

9. Section 3.5.2: Some high mass peaks were observed in the "dark H2O2" samples (Figure S2). Furthermore, Tan et al. (2009, 2010) did not observe significant formation of oligomer in their experiment when cloud-relevant concentration (10-6 M) of glyoxal and methylglyoxal were used. Compared to Tan et al. (2009, 2010) (10 mM), much higher initial H2O2 concentration (100 mM) was used in the aqueous oxidation of isoprene SOA. For the case of α-pinene, the initial H2O2 concentration was only 15 mM and no formation of oligomers was observed. Is it possible that high H2O2 (and probably OH radical) concentration also favours the oligomerization process?

Minor comments:

1. Page 21494, line 5: What kind of filter was used for aerosol collection?

2. Page 21494, line 17: Please change "AMS" to "AMS: Aerosol mass spectrometer"

3. Page 21500, line 7-9: Please briefly explain how to calculate the organic concentrations in aqueous solution from the SMPS data.

4. Page 21506, line 5: I am not sure if "HPLC-MS" used here is equal to the "HPLC-API-MS" mentioned in the experimental section. If yes, please use "HPLC-API-MS" throughout the paper.

5. Table 2: (a) Please add a few columns to indicate the production pathways of the identified organics (e.g., chamber vs. aqueous oxidation). (b) The chemical structures shown in Page 21523 are not well displayed.

References:

1. Aiken, A. C. et al. (2008), O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol., 42, 4478-4485.

2. Lambe, A. T., et al. (2011), Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA), Atmospheric Chemistry and Physics, 11, 8913-8928.

3. Lee, A. K. Y., et al. (2011a), Aqueous OH oxidation of ambient organic aerosol and cloud water organics: Formation of highly oxidized products, Geophys. Res. Lett.,38, L11805 doi:10.1029/2011GL047439.

4. Lee, A. K. Y., et al. (2011b), Aqueous-phase oxidation of glyoxal: Application of a novel analytical approach employing aerosol mass spectrometry and complementary off-line techniques, Journal of Physical Chemistry A, doi: 10.1021/jp204099g.

5. Massoli, P., et al. (2010), Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles, Geophys. Res. Lett., 37, L24801, doi:10.1029/2010GL045258.

6. Ng, N. L., et al. (2010), Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos. Chem. Phys., 10, 4625-4641.

7. Tan, Y., et al. (2009), Effects of Precursor Concentration and Acidic Sulfate in Aqueous Glyoxal-OH Radical Oxidation and Implications for Secondary Organic Aerosol, Environ. Sci. Technol., 43, 8105-8112.

8. Tan, Y., et al. (2010), SOA from methylglyoxal in clouds and wet aerosols: Measurement and prediction of key products, Atmos. Environ., 44, 5218-5226.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 21489, 2011.