

Interactive comment on “A new source of oxygenated organic aerosol and oligomers” by J. Liggio and S.-M. Li

Anonymous Referee #3

Received and published: 7 January 2013

General Comments

In this study the authors investigated the uptake of primary oxygenated VOCs onto acidic and neutralized sulfate particles. The experiments were conducted by exposing filtered urban ambient air to sulfate particles and measuring the addition of organic matter to the seeds using an aerosol mass spectrometer. Comparison of mass spectra and O/C ratios with previous studies indicate that the uptake was probably due to oxygenated VOCs directly emitted from vehicles. For the most acidic seed, organic growth appeared to be due in large part to oligomers formed from acid-catalyzed reactions of carbonyls. The study is an interesting one and suggests that future studies should consider the possibility that primary oxygenated VOCs can directly form aerosol, making it more difficult to determine the relative importance of SOA and POA to oxidized

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

organic aerosol. I think the paper is suitable for publication in ACP after the following comments/questions have been addressed.

Specific Comments

1. Page 29079, lines 3–6: Are these carbonyl measurements relative to total primary organic mass or the amount resolved by the analytical techniques?

2. Page 29080, lines 17–24: How is it known that there is less water available for hydration after adding NH_3 ? Studies by Zhou et al. (2006) *Env. Sci. Technol.*, 40, 7682, have shown for example that sulfuric acid reduces hydration of methylglyoxal, so perhaps in this case neutralizing the acid makes water more available for hydration.

Might the evaporation of OA be caused by the formation of solid ammonium sulfate, thus eliminating some of the sulfuric acid/water liquid phase into which organics were dissolved?

3. Page 29081: Shouldn't the products of reactions (1) and (2) be R-CH-C(OH)-R and $\text{R-C(OH)}_2\text{-R}$, respectively?

4. Page 29081: The occurrence of reaction (1) to any significant extent in ambient aerosol seems unlikely. In liquid particles in which such a reaction would occur, ozone would have easy access to the alkene C=C bond and so rapidly remove the alkenes as the equilibrium continued to shift to the left. Many studies of the heterogeneous kinetics of alkenes in particles (e.g., Morris et al. (2002) *Geophys. Res. Lett.*, 29, 71-1–71-4), typically liquid oleic acid, have shown that the reaction is sufficiently fast that in the atmosphere the lifetime of alkenes in liquid particles will be only a few minutes. Only when alkenes are in solid or glassy particles, which would presumably preclude the occurrence of reaction (1), are they inaccessible to ozone and so stable for longer periods of time.

5. Page 29081, lines 3-5: I've never seen it suggested that aldol condensation and acetal formation are irreversible (I don't know about cationic polymerizations). It may

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



take a while for oligomers that are formed by these reactions to dissociate, monomer-by-monomer, but I think this is possible.

6. Page 29081, lines 6–8: It seems like perhaps the reason the oligomers did not dissociate to monomers after adding NH_3 is not because the reactions are inherently irreversible, but that the acid needed to catalyze the reverse reactions had been neutralized. Catalysts are necessary for both forward and reverse reactions, so once oligomers are formed they should be stable in the absence of the catalyst. This is not necessarily the case for hemiacetals, however, since they can generally be formed with little or no strong acid present.

7. Page 29083: Considering the proposed importance of uptake of oxygenated primary VOC emissions to OA formation, do the authors know of any estimates of the ratios of volatile VOC reaction products relative to oxygenated primary VOCs in urban air? Unless there is something special about uptake of primary oxygenated emissions one would imagine that reaction products of most VOCs would be taken up similarly or probably more efficiently since they are often more highly oxygenated. It would be interesting to use this ratio to estimate the contribution of the uptake of volatile VOC reaction products to OA by multiplying it by the value of 0.14 ug/m^3 estimated for primary oxygenated VOCs.

8. Table 2: The PM ratios of Org/ SO_4 used here are high compared to the atmosphere. How might this affect the results of the experiments?

Technical Comments

1. Page 29075, line 20: I think this is supposed to be “41, 43, 44, 55, . . .”
2. Page 29079, line 20: “Aerosol” should be “aerosol”.
3. In a number of places the authors have written m/z 300/ SO_4 instead of m/z > 300/ SO_4 .
4. Throughout the paper the authors refer to “reversible or irreversible products”. I

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



take this to be shorthand for “products formed by reversible or irreversible reactions”, but I think the discussion would be clearer if the authors rewrote this text referring to reactions as reversible or irreversible and not products.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 29069, 2012.

ACPD

12, C11319–C11322,
2013

Interactive
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

C11322

