

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

Anonymous Referee #2

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Review of Liggio and Li “A new source of oxygenated organic aerosol and oligomers”

General Comments

In this manuscript, the authors perform chamber experiments examining the uptake of oxygenated organics from filtered ambient urban air onto neutral and acidic sulfate seed particles. The authors measure fast, but relatively small uptake of oxygenated gases onto neutralized seed aerosol that scaled with seed mass. In the presence of acidic sulfate aerosol, the authors measure continuous uptake of more substantial amounts of organic. Simultaneously, they observe changes in the OA mass spectra and O:C consistent with formation of high-MW oligomers. The manuscript is relatively clearly written and the subject will be of interest to readers of ACP. A chemical mechanism explaining the uptake on the acidic particles is presented and is supported by the

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data. These observations are also broadly consistent with literature studies showing organic oligomerization reactions in acidic aerosol and with current understanding of organic aerosol (OA) formation.

The more surprising results come from the observations of uptake of organics onto neutral seed aerosol, which make up the bulk of the experiments presented in the manuscript. For these experiments, the authors do not present a mechanism that can explain their observations, which are difficult to interpret in the context of the current understanding of OA formation. Given the lack of an explanation for their neutral-seed observations, it is difficult to rule out that the data are an experimental artifact. The authors should offer some plausible mechanistic explanation for dilute organic gases condensing or reacting on the neutral seed aerosol. The explanation the authors currently offer is reported to be of minor importance just a few pages earlier in the manuscript. Providing additional experimental detail, such as the phase of the neutral seed particles, the total aerosol loading involved, and the additional details on the gas-phase hydrocarbons, would potentially clarify possible mechanisms and convince readers and reviewer(s) that their observations are applicable to the atmosphere. After these revisions, the manuscript should be publishable in ACP.

Major Specific Comments

As the manuscript is currently written, it is difficult to assess whether the OA formation/condensation observed on the neutral seed experiments is a robust phenomenon one could expect to occur in the ambient atmosphere or a result of an experimental artifact. I'm having a hard time interpreting their observations in the context of what is current known about OA formation. Currently, the authors suggest that hydration of olefins under acidic conditions may explain the uptake (P29079, lines 6-11). However, on P29077, lines 17-23 the authors argue that the importance of reactive uptake on acidic seed is minor. The authors also argue that incorporation of organic during nucleation of the sulfate seed is unimportant and that repartitioning of organics from the filtered aerosol to the seed aerosol is unimportant. Finally, the authors report that

there was little or no oxidant present in the system. In the absence of reactive uptake or incorporation of organics in the nucleation process or gas-phase oxidation, it is difficult to understand how significant amount of organics would condense onto/into a non-absorbing inorganic phase under sub-saturated conditions and the absence of any chemical reaction. Their observations are particularly hard to reconcile with the fact that these gases apparently didn't partition to the ambient sulfate and organic aerosol (at least at significant levels) despite being more concentrated in the ambient air and with the fact that the gases that condensed in the experiments are less oxygenated and presumably more volatile than the ambient OA. The authors should propose some mechanism, similar to what is presented for the acidic seed experiments, to explain their observations.

Below are further suggestions for revisions the authors could make to the manuscript which would help understand the uptake mechanism and strengthen their assertion that uptake of primary organic gases onto neutral seed is an important atmospheric process.

1) The authors should include a discussion of the seed phase. The acidic seed particles are clearly liquid, but the phase of the neutral seed is ambiguous. Based on the reported CE (.22 in some experiments) and the RH, I infer that the seed is solid. However, if the reported RH's are sometimes above the efflorescence point so it is possible the seed is a metastable liquid if it initially formed as a liquid. The phase is relevant as it is very difficult to understand how dry, essentially unreactive inorganic seed particles would uptake organics in the absence of any reaction. If however, the particles were in a metastable state, I can see hygroscopic gases dissolving into the aqueous layer, though timescale seems wrong (see below).

2) The authors should comment on organic uptake timescales since it provided important clues into the uptake mechanism. The timescale (<2 minutes) indicates that the equilibration time is extremely fast, faster even than the timescales that would be required mixing processes. It is also difficult to imagine any condensed-phase reaction

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process coming to completion on this rapid a timescale. How long did it take for the formation of sulfate seed to come to completion? Is it on the same timescale?

3) The manuscript would benefit from showing data before injection of the SO₃ gas. Showing the data before injection of the SO₃ gas would allow readers to assess the instrument's ability to measure a zero and visualize the organic deposition timescale. It would also help understand the timing of the NH₃ and SO₃ injections.

4) Please state the length of time between injection of the ammonium gas and the SO₃ gas. Do the reviewers notice organic formation from ammonium addition alone? Can the authors comment on the possibility that the large excess of ammonia gas is driving the organic condensation? Is possible that the large excess of ammonia gas is reacting with alkanolic acids to form salts? The authors state that amine formation was not observed in the gas phase, but they could partition rapidly to the condensed phase. Was significant nitrogen observed in particle-phase?

5) Can the authors observe any changes in the PTR-MS concentrations when organic uptake/condensation occurs? Are there any clues from the PTR-MS about what species are partitioning to the condensed phase?

My other major comment is in regard to the terminology the reviewers use to describe the OA. In the abstract and in the conclusions, the authors seem to assert that the organics formed are primary organic aerosol (e.g., P 29083, lines 12-16). In the case of uptake onto the acidic seed aerosol, this is clearly not the case as heterogeneous chemistry drives uptake. I would argue that the OA should be classified as secondary because the primary gases undergo chemical transformation. In the case of the neutral seed experiments, the terminology is more ambiguous until the mechanism is constrained. Ordinarily I would consider this a minor and somewhat pedantic point, but the authors ascribe significant importance to the distinction between POA and SOA in the manuscript, so they should clarify the language.

Minor Comments and Technical Corrections

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Can the authors comment on the neutralization of the seed? The observed ammonium:sulfate ratios are significantly below 2 in many of the experiments despite the large excess of ammonia in the gas phase. The measured ratios in some experiments (E4, E8, E14) appear to deviate from the expected value by a factor larger than experimental error.

The text annotations within figures 2, 3, and 6 are small and difficult to read when printed.

Tables 1 and 2 – Separating the control, acidic seed, and neutral seed experiments with a line and a label (like is done to separate the control experiments from the rest in T2) would make it easier for the reader to understand the data.

Table 2. Can the authors also list the final organic concentrations? It would be particularly useful for the acidic seed experiments where significant uptake after 2 minutes is observed.

Page 29071, lines 15-20. Kroll et al. (2011) should be cited. Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E., and Worsnop, D. R.: Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol, *Nat. Chem.*, 3, 133-139, 10.1038/nchem.948, 2011.

The authors' observations also have implications for other chamber experiments. Many chamber SOA experiments employ dry AS seed particles, and none that I am aware of have reported organic uptake before an oxidant was introduced, though the precursor gases are admittedly different. However, crystalline AS seed is generally believed to be inert in these experiments and the processes the authors identify could affect chamber experiment employing AS seed once oxidation is initiated. The authors may want to comment on this potential artifact.

Did the authors take any steps to remove oxidants present in the ambient air from being

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injected to the chamber? Can the authors comment on oxidant levels? I would expect that some ozone would have passed through the filters and made it into the chamber.

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