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Atmospheric
Chemistry
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Discussions

Interactive comment on "Fragmentation vs. functionalization: chemical aging and organic aerosol formation" *by* H. J. Chacon-Madrid and N. M. Donahue

Anonymous Referee #2

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The manuscript describes a well-designed series of experiments to probe the contributions of fragmentation and functionalisation to OA formation and transformation. The sequences of compounds are appropriately chosen and, within the scope of the study, appear suitable to address the stated goals. In general, I would support publication of the experimental results in this work in ACP, but I do have a couple of conceptual concerns:

A worry is the fundamental reliance on vapour pressure as the primary driver for SOA mass yield, via reversible equilibration. Given recent work, it is not immediately obvious that particle viscosity will allow equilibration within an aerosol particle's atmospheric

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lifetime. Page 13697 paragraph starting line 14 lays down a consequence of an assumption made in the paper that may not be realised in the atmosphere. Why would the mass yield be similar if mass transfer (particularly in evaporation) were condensed-phase diffusion limited? Surely there is no reason for species of identical vapour pressures to have identical mass transfer limitations - surely it would depend on the rate of change of viscosity of the particle with age? Can the authors comment on the impacts of such physical rather than chemical limitations?

page 13697 line 8: given the very active recent research on predicting vapour pressures and on the critical evaluation of estimation techniques to do this, along with the relative simplicity of the molecules in this study (relatively low degree of functionalisation), the existence of direct vapour pressure measurements of some of the molecules and its poor performance in some evaluations, it does not seem rigorous to use SIMPOL as the basis for the vapour pressures, even as a guide.

p13696 line 11: according to this, it seems that the definitions are not only distinguishing between functionalisation and fragmentation, but also between functionalisation and (fragmentation plus functionalisation). This will likely lay at the bottom of substantial confusion in the interpretation, depending on where (fragmentation plus functionalisation) takes place and the molar mass of the reactant molecule - i.e. substantial increase in volatility following cleavage in the middle of a molecule is much less likely to be offset by the functional groups added at the reaction site than cleavage near the end of the molecule. Can the authors comment on how a general framework for SOA ageing could possibly encompass the high number of possible vapour pressure trajectories following (fragmentation plus functionalisation) in real atmospheric mixtures?

p13698 line 15: the hypothesis is quite well-framed, but it is unclear how useful it can be in the context of the atmospheric degradation of complex mixtures of VOCs. Irrespective of whether the hypothesis is true, surely the oxidation state of the components in such a mixture will, at any snapshot in time, be so complex as to give no practical predictive capacity. I can see that sets of single components evolving in isolation in well-defined oxidative environments may follow a particular trend, but I have no idea how these can help us out in complex mixtures. Would the authors please comment on how generalisation of the results, even if perfect and unambiguous, can lead to predictions of differences in SOA production potential in the real world?

The experimental procedures are quite well described and seem appropriate (notwithstanding spikey blacklights), from precursor synthesis and injection, through wall loss characterisation and measurement protocol. It might be elucidating for a reader if the authors described the implications of the assumption of the OA condensation behaviour with respect to the dry inorganic seed. I have very little criticism of the experimental procedure which appears very rigorous and well-executed, or pf the reported results which appear robust and well interpreted within the context of the paper.

Whilst there are a number of useful general trends established, it is not clear that the results are sufficient for the establishment of a useful predictive framework. This is particularly true given the relatively narrow range of functionality investigated in this work. Can the authors give an indication of whether and how they would try to construct such a predictive framework based on the approach described? The paper describes a number of very useful experimental results, but seems to fizzle out before a strong set of conclusions can be made. I think this is a function of the complexity of the system, not allowing a simplified description of the system in terms of either O:C ratio or oxidation state. Can the authors please comment on how we should move forward given that a framework that describes components in terms of these variables and component volatility seems unable to provide a quantitative and predictive framework for aerosol formation and transformation.

minor: Abstract: "Understanding all these changes for all the species in detail is impossible" - currently impractical yes, impossible, no.

p 13694 line 24: what does "pre- cursor becomes larger as well as the extent of reaction" mean sentence beginning line 25 - what is a "rich" mechanism? Suggest "com-

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plex"

p13696 line 6: it would be better to state use accretion or oligomerisation consistently between the text and figure 1 line 19: it should be noted that not all accretion reactions (e.g. esterification) will lead to lower vapour pressures

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