Referee # 2

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 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?

The point is well taken that we need to carefully establish that vapor pressure is a controlling property in SOA formation. However, there is an enormous body of experimental evidence that, all else being equal, precursors of lower vapor pressure will tend to generate more SOA than more volatile analogues. The experimental question under consideration here is whether chemically distinct precursors with similar vapor pressures will produce different amounts of SOA, and the answer is yes.

The comment refers largely to our interpretation of these experimental findings. There are decades of data supporting the applicability of partitioning theory to SOA experiments. It must be remembered that Odum's insight (Odum et al., 1996) was to use the partionable organic mass concentration (M_O in his notation, C_{OA} in ours) as an independent variable to plot SOA yield data. This organized seemingly random mass yield data in a consistent and theoretically sound way. The theoretical basis was partitioning theory. To our knowledge no other theoretically sound model has been proposed to supplant Odum's interpretation (one must consistently explain the rising and reproducible mass yields). There are numerous other examples of success for partitioning theory. These include systematic study of homologous sequences (e.g. Lim and Ziemann, 2009; Presto et al., 2010). When we have looked for continued condensation to particles after cessation of gas-phase chemistry (for example ozonolysis of limonene as presented in Fig. 7 of Pierce et al., 2008, or ozonolysis of a-pinene as presented in Fig. 3 of Presto et al., 2005) we have consistently failed to observe evidence of continued or delayed particle growth.

For all of the experiments described in this study, the SOA particles grew significantly during the first 1-2 hours, when OH radical levels were high, and then stopped growing. There was no discernable growth over the last hour of any experiment. This strongly suggests that the systems reached equilibrium over the several hour timescales of our experiments. We also feel the evidence is compelling that the SOA consists of a complex mixture. Indeed, we have probed the propensity of organic-aerosol systems to mix in many different ways over the past decade. This includes the interpretation of rising mass yields with increased product formation (i.e., partitioning theory under the Odum interpretation), but also via direct measurement of mixing of different aerosol systems with each other, and by probing the loss of primary aerosol species by surface OH reactions after substantial coating with SOA (which requires mixing of the two). Many different lines of evidence support the hypothesis that these systems consist of complex *mixtures at or near equilibrium.*

The recent findings referred to by the reviewer are indeed very intriguing (and definitely are broadly consistent with earlier findings from CMU reported by Grieshop et al., 2007 and Stanier et al., 2007). However, some statements in these recent papers suggest that partitioning theory requires that the aerosol particles be a liquid. That is false. Partitioning theory uses the sub-cooled liquid vapor pressure to estimate the interaction energy of a compound with an amorphous solvent. When we apply partitioning theory we do assume that the solvent is amorphous, and because we are finding the equilibrium state of the system we do naturally assume it is in equilibrium. Whether a given system actually reaches that equilibrium is an entirely different and of course interesting question. However, even if the system is in a highly viscous, glassy solvent, the basic equilibrium between the condensed phase and the gas phase will still be in play, and that equilibrium will be governed by the thermodynamics we attempt to describe in other publications (which are not especially relevant for this present publication).

Our working assumption is that the system will relax toward its equilibrium state with some time constant or set of time constants, and, in the case of growth, the particles will in general be somewhat smaller at a given instant than their equilibrium size (disequilibrium would lead to an underestimate of yields). At any given time we cannot invoke different mass accommodation coefficients for condensation and evaporation, as this would change the vapor pressure itself, which is controlled by the free energy of the products in the SOA solution.

There are really two possibilities under discussion. One is that particle viscosity may prevent equilibration on an experimental timescale, and the other is that viscosity may prevent equilibration on an atmospheric timescale. The relevant diffusion constants are about 10^{-14} cm^2 s^{-1} *for equilibration in 1h (note that a 100 nm object with such a viscosity is likely quite bouncy). We believe the first is more likely than the second, if for no other reason than the one originally brought to light by the seminal paper by Zobrist et al., 2008; water is a fantastic plasticizer. We at least find it hard to believe that most boundary layer air parcels will not encounter a sufficiently high RH to anneal toward their equilibrium mixing state, even if that mixing is delayed under some conditions. Obviously this fascinating topic deserves and is getting much more research attention.*

The bottom line is that, having never observed signs of continued, slow growth in our SOA formation experiments, we feel it is appropriate to acknowledge the question of mass-transfer limitations, confirm that observed SOA particle growth ended as the chemistry died out, and thus state that our observations are consistent with the SOA being in equilibrium at the end of our experiments. The question of an extended interpretation of those mass yields – what the volatility distribution of the products is, whether gas-phase chemistry predominates or whether accretion reactions in the condensed phase also contribute substantially to the ultimate volatility distribution, and consequently whether particle viscosity may play a role in subsequent particle dynamics – is beyond the scope of this work (which is fundamentally experimental and empirical). We will modify the manuscript to make this clear.

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.

The different methods, such as SIMPOL, available in the literature to calculate vapor pressure can present poor performance (especially as the number of functionalities in a carbon backbone increase). However, the measured vapor pressure of molecules such as pinonaldehyde and cis-pinonic acid also possess a high level of uncertainty. Consequently, we use experimental data available and models for estimating vapor pressure.

Our preference for the simple formulation in SIMPOL is discussed in Donahue et al., 2011. It is partly because this is well matched to the simplicity of the Two Dimensional-Volatility Basis Set (Donahue et al., 2011), but also more broadly part of a "hypothesis of simplicity" related to the enormous number of product molecules we expect after several generations of SOA oxidation. The SIMPOL group contribution parameters are based on typical values for given functional groups, and we hypothesize that outliers from this are driven by atypical group-group interactions in certain molecules. Because SOA is generally comprised of a large ensemble of molecules, including structural isomers, we hypothesize that the SOA products will, on average, distribute in vapor pressure according to the simple group contribution predictions. Thus, to first order it is more useful to locate a precursor molecule where it "should" be absent unique behaviors.

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?

In order to avoid confusion, we defined only three mechanisms (functionalization, fragmentation and accretion) that lead the chemistry of VOCs and relate to aerosol formation. We have been consistently clear that fragmentation will almost always be followed by functionalization of any resulting radical fragments. An example is Fig. 4 in Jimenez et al., 2009. Carbon-carbon fragmentation does not always lead to higher vapor pressure products, but it can indeed decrease significantly product vapor pressures, enhancing SOA formation.

How a general framework for SOA aging could possibly work:

We are developing a framework that involves the competition between fragmentation, functionalization and accretion, among other mechanisms, that it is capable of predicting SOA formation. This is the 2D-Volatility Basis Set first introduced in Jimenez et al., 2009, and discussed in detail in Donahue et al., 2011. The main idea is to divide this 2D space in bins of volatility and oxidation state. Material is placed on such bins, and as the photo-oxidation occurs, it is moved in the 2D-VBS space. By using the thermodynamic framework described in Donahue et al., 2011 we can estimate the composition (C, H, O) of organics in any given bin. We then apply a ``kernel'' for non-fragmenting (functionalization) reactions and another ``kernel'' for fragmenting reactions. These kernels are built around a basic model of the functional groups added to molecules following each pathway, with different probabilities representing the strength of various pathways. Partitioning is calculated by using Donahue et al., 2006. An example of the 2D-VBS applied to a Lagrangian transport model is reported in Murphy et al., 2011. This modeling is in its early stages, and the mechanism becomes progressively less certain as the degree of functionalization (oxidation) rises in the space. While the behavior of each "bin" of necessity is based on *some sort of “grand average” representing typical ambient organics, our objective here is to probe the behavior of specific molecular structures in this space, in order that this “grand average” might be an average of actual data and not simply conjecture and extrapolation.*

It is also important to mention that such modeling and framework is outside of the scope of the current publication.

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?

This is probably the most important issue of our work. We agree completely that the systems presented are much simpler, by far, than the atmospheric photo-degradation of VOCs in the atmosphere. The reason to approach the problem of chemical atmospheric aging by inspecting one species at a time is to divide the problem into parts. We believe our project to be one piece of a very large puzzle that is likely to be investigated for years. Our intention is to give a first insight into the ability of oxygenated material to fragment more easily when compared to a fully reduced species.

The history of NMHC oxidation research is not one of individually unique mechanisms, but rather the emergence of various broad themes, most of which have been eloquently described by Roger Atkinson over the years. Indeed, our framework is built on the “hypothesis of simplicity” described above (though not everyone would describe it as overly simple). Time will tell whether it is suitably accurate for the real atmosphere, but there are indications from ambient data (for example the data described in Ng et al., 2010) that the idea that ambient organic aerosols exhibit some sort of broad average behavior may not be too farfetched.

We attempted to mention the big limitations of our project (page 13698, line 29, page 13699 lines 1-4); however, a stronger and clearer statement will be placed about such limitation in the Environmental Significance section.

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 behavior with respect to the dry inorganic seed. I have very little criticism of the experimental procedure, which appears very rigorous and well-executed, or of 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 particlarly 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.

Regarding condensation on dry inorganic seed:

The inorganic seeds (ammonium sulfate) serve different functions during our experimentation. They include, the ability to assess wall-losses (Hildebrandt et al., 2009), and also to create a somehow reproducible (regarding mass and number) size-distribution of particles on which condensation is enhanced. This allows us to have similar size-distributions among the different experiments, increasing consistency. We have ***never*** *observed inorganic seeds to influence SOA mass yields in our experiments (other than by preventing excessive wall losses). This may be because we use neutral ammonium sulfate at low relative humidity precisely because our objective for the seeds is for them not to influence the chemistry.*

It is important to mention that SOA formation can also proceed without initial inorganic seeds; however, the seeds allow a more reproducible and smoother particle growth, as wall losses are very high and somewhat erratic for freshly nucleated nanoparticles.

Construction of a predictive framework: *The predictive framework was discussed above. This work describes the beginning of a systematic exploration within that framework, not the end.*

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

*We will exchange the word "*impossible*" for "*impractical*".*

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

*The term "*precursor*" is used for molecule, but using "*precursor*" allows us to differentiate between a reactant and a product (this is because a product can indeed be a reactant at some point during continuous photo-oxidation). We will use the term "*a precursor-molecule*" instead of "*the precursor*".*

Regarding the fragment "…the extent of the reaction…*", we refer to how advanced is the extent of oxidation. The more oxidation has happened on a molecule, the more complex its mechanism becomes from that point and on. We will change the fragment to "*…the extent of oxidation…*".*

*We will exchange the word "*rich*" for "*complex*".*

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

*We will be consistent and use "*accretion*" in the text and Figure 1. We will make a comment that not all accretion reactions lead to lower vapor pressure.*

References to support answers:

1. Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics, Environ. Sci. Technol., 40, 2635-2643, 2006.
2. Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, Atmos. Chem. Phys., 10, 3303-3318, doi:3310.5194/acp-3311-3303-2011, 2011.
3. Grieshop, A. P., Donahue, N. M., and Robinson, A. L.: Is the gas-particle partitioning in alpha-pinene secondary organic aerosol reversible?, Geophys. Res. Lett., 34, L14810, 2007.
4. Hildebrandt, L., Donahue, N. M., and Pandis, S. N.: High formation of secondary organic aerosol from the photo-oxidation of toluene, Atmos. Chem. Phys., 9, 2973–2986, 2009.
5. Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E, Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, Science, 326, 1525-1529, 2009.
6. Lim, Y. B., and Ziemann, P. J.: Chemistry of Secondary Organic Aerosol Formation from OH Radical-Initiated Reactions of Linear, Branched, and Cyclic Alkanes in the Presence of NO_x, Aerosol Sci. Tech., 43, 604-619, 2009.
7. Murphy, B. N., Donahue, N. M., Fountoukis, C., and Pandis, S. N.: Simulating the oxygen content of ambient organic aerosol with the 2D volatility basis set, Atmos. Chem. Phys., 11, 7859–7873, 2011.
8. Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos. Chem. Phys., 10, 4625-4641, 2010.
9. Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H.: Gas/Particle Partitioning and Secondary Organic Aerosol Yields, Environ. Sci. Technol., 30, 2580-2585, 1996.
10. Pierce, J. R., Engelhart, G. J., Hildebrandt, L., Weitkamp, E. A., Pathak, R. K., Donahue, N. M., Robinson, A. L., Adams, P. J., and Pandis, S. N.: Constraining Particle Evolution from Wall Losses, Coagulation, and Condensation-Evaporation in Smog-Chamber Experiments: Optimal Estimation Based on Size Distribution Measurements, Aerosol Sci. Technol., 42, 1001-1015, 2008.
11. Presto, A. A., Huff Hartz, K. E., and Donahue, N. M.: Secondary Organic Aerosol Production from Terpene Ozonolysis. 1. Effect of UV Radiation, Environ. Sci. Technol., 39, 7036-7045, 2005.

12. Presto, A. A., Miracolo, M. A., Donahue, N. M., and Robinson, A. L.: Secondary Organic Aerosol Formation from High-NOx Photo-Oxidation of Low Volatility Precursors: n-Alkanes, Environ. Sci. Technol., 2010.
13. Stanier, C. O., Pathak, R. K., and Pandis, S. N.: Measurements of the Volatility of Aerosols from a-Pinene Ozonolysis, Environmental Science & Technology, 41, 2756-2763, 2007.
14. Zobrist, B., Marcolli, C., Pedernera, D. A., and Koop, T.: Do atmospheric aerosols form glasses?, Atmos. Chem. Phys., 8, 5221–5244, 2008.