

Interactive comment on “Size dependent chemical ageing of oleic acid aerosol under dry and humidified conditions” by S. Al-Kindi et al.

Anonymous Referee #1

Received and published: 26 April 2016

The manuscript entitled, “Size Dependent Chemical Ageing of Oleic Acid Aerosol under Dry and Humidified Conditions,” by Al-Kinki et al. focuses assigning reaction products of the ozonolysis of oleic acid using ATOFMS. Exploring the chemical aging of organic particles relevant in the environment (or as proxy for structural similar systems) and developing new strategies for their quantitative analysis is certainly of fundamental interest. Given the complexity of atmospheric aerosol, laboratory experiments on confined systems are required for developing a better understanding of the complex processes occurring in airborne particles. Oleic acid (OL) + O₃ has been extensively studied and there are key elements of the reaction mechanism that are still not understood and may involve the complex evolution of organic diffusion constants with extent of oxidation. The authors present a very detailed experimental description of the apparatus and have gone to impressive lengths to make the ATOFMS mass spectra, to

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the extent possible, quantitative. The mass spectral assignments are plausible and the authors present, in most cases, reasonable mechanistic routes for the formation of the high molecular weight products. Since this reaction has been extensively studied, and is a subject of an extensive data evaluation and review paper by Zahardis and Petrucci, the expectation is elevated for any new paper reporting and interpreting results on this reaction in light of the extensive existing literature. The main weakness of the work, which should be addressed by the authors, is the absence of interpreting the observed products within a full kinetic framework (especially in light of previous literature) as detailed below.

1. The connection between the SMPS measurements of particle size (dry and wet) are disconnected from the main theme of the paper which is chemical composition via ATOFMS. The ATOFMS instrument sizes by aerodynamic flight time, so it is not clear what additional information is provided by the SMPS? The authors observed the expected decrease in size previously observed in many other studies. The difference between dry and wet size reduction is insignificant statistically. Therefore, the authors should either better justify the inclusion of the SMPS data and discussion for the main focus of the paper or remove it for brevity.

2. Much of the mechanistic discussion is predicated on the size dependent concentrations shown in Fig. 7 and 8, which doesn't adequately normalize for extent of reaction (# of reactive collisions), since at a single ozone exposure the concentration (even without secondary chemistry) of OL will be size dependent. So any mechanistic conclusions based upon particle size drawn from Fig. 7 and 8 is ambiguous at best. For example, page 23 line 2 it is not unsurprising that larger particles contain more unreacted OL than smaller particles; this is exactly what you would expect kinetically given the difference in the number of OL molecules vs. size and the differences in surface area vs. size. So this observation alone is not sufficient to conclude that limited OL or O₃ diffusivity is the cause. This conclusion originally reported by Smith 2002 was drawn only after the full particle size kinetics ([OL] vs. ozone exposure) was measured and

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reactive uptake coefficients were computed and were then found to be size dependent. Later on page 23 line 13-14 the authors conclude that the molar ratio of O₃:OL is smaller for larger particles. . . .in order to explain larger OL for bigger particles in Fig. 7 and 8. Again I don't see how this works since at a fixed ozone concentration larger particles (due to S/V ratio) will always have a less extent of reaction than smaller particles. Furthermore, the authors state that ozone is not appreciably diminished inside their reactor when particles are present. So it is not clear how this small molar ratio of O₃:OL works then. Won't the Henry's law constant imply that the [O₃] is independent of size? Again on page 24 line 15-16 there is a statement about lower concentration of OL in smaller particles. . . . but again this could just arise from a larger extent of reaction for smaller particle than larger ones at a single ozone concentration. It may well be the case that different chemistries are operative in larger particles (secondary chemistry) but such a comparison needs to be done by first eliminating the trivial size dependence due to kinetics. Furthermore, I don't observe any consistent monotonic trend in OL (or ON, NN, HMW) vs. size for example. The authors should address this. The quantity of OL (fig. 7 and 8) oscillates as a function of size, suggesting simply measurement error or uncertainty rather than a robust trend in secondary chemistry/diffusion as a function of size. Some error analysis needs to be shown and included in Fig. 7 and 8.

3. Smith et al. 2002 observe that the uptake coefficient decreases with increasing size. How is this observation reconciled with the present study in which formation of HMW species is observed in large particles, since the mechanisms presented for HMW formation involve the consumption of more than one OL molecule (i.e. secondary chemistry, see R1 and Scheme 2). Thus it would seem from the present results, that larger effective uptakes are expected for larger sized particles (more secondary chemistry since there are additional sinks for OL, rather than just O₃) which would be exactly the opposite trend observed by Smith et al. Size dependent kinetic measurements would offer a tangible way to connect the formation of HMW with previous size dependent uptake coefficient measurements of Smith et al.

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4. It is not clear to me why, given the experimental setup (ATOMS, SMPS, AFT) why the authors did not measure the OL decay kinetics and product formation kinetics vs. Ozone exposure. This would have addressed #2 above as well as provided needed evidence for some of the proposed reaction mechanisms described throughout the manuscript. This would be entirely new by providing a potential new connection between reactive uptake, particle size, HMW, and diffusive limitations. Furthermore, there should be distinctive kinetic signatures based upon the proposed reaction mechanism. For example, the formation of NN via the decomposition of the primary ozonide (route 1 scheme 2) would be expected to have a different kinetic evolution than NN formed via the reaction of CI1 addition to the OL double bond and subsequent decomposition (as shown in scheme 2). Since the former NN pathway only involves consumption of 1 OL in contrast to the latter which requires for its formation the consumption of 2 OL. This is also true for example in Scheme 3, where AA is formed by CI1 + ON but also could be formed by isomerization CI1 directly.

In summary, the logical arguments about mechanisms based upon difference in OL concentration (and other products) in small and large particles does not necessarily follow, given the way the experiments were performed (all sized measured at a single ozone concentration) and the lack of full kinetic measurements ([OL] vs. Ozone exposure) is needed to compare the same extent of reaction for each particle size. Although it is clear the authors observe some new HMW species whose identification is important for the community, the manuscript needs to be significantly revised for clarity, and further kinetic measurements might be required.

Minor Comments:

1. The split axis, while certainly convenient, makes it very difficult for the reader to ascertain the true relative intensities of the peaks in the mass spectra shown in Figs. 5 and 6. Please reformat these figures with insets (not split axes) of relevant regions so that the reader can, as much as possible, see the raw data.

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2. Scheme 3: Elimination of H₂O doesn't give the product shown. Do you mean elimination of OH radicals? Intermediates steps are needed to show how H₂O is formed.
3. Define what NBS stands for at its first usage page 10 line 17.
4. The ozone concentration is reported at the exit of the generator. Is this the same as the ozone concentration in the flow tube. This should be clarified.
5. The authors should discuss the possibility or not of ion-molecule reactions in the laser ionization region potentially contributing to the mass observed.
6. Check Scheme 2 for consistency regarding upper and lower cases and order of name, mass etc.
7. The first part of the paper, comprising the experimental description, contains a very detailed description of the single experimental components and can be shortened for better readability.
8. P. 9, l 4-6. Redundant, since it won't be referred to at any time in the paper.
9. Panel description (a, b, c) is missing in Figure 2.
10. The comparison of NBS and NBS + OL (Figure S1b) shows next to the OL and OL dimer two additional peaks in the positive spectrum. Can you comment on their origin?
11. Figure 3: change labeling of y-axis. Upper/lower cases in title is inconsistent with other figures, the tick label 0.0 is inconvenient, as is the position of the title. Why are the assignments for the positive ion spectrum of NN and 4-ON missing? Also the OL spectrum is different from the one in the SI, the peak around $m/z = 60$ is missing, although it does not originate from NBS.
12. Can you make an assumption about the nature of peaks in the positive ion spectrum in Figure 5?
13. Define AAHP (p.21).

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14. Panel description (a) is missing in Figure 7.
15. Typographical errors are noted on: p. 2 line 15, 18; p. 4, l. 23; p. 5, l. 2 (2x); p. 7, l. 17, 23; p. 8, l. 16; p. 10, l. 3; p.16, l. 1; p.21, l. 13; p. 25, l 5; p. 41

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-230, 2016.

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