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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Chemical evolution of secondary organic aerosol from OH-initiated heterogeneous oxidation" *by* I. J. George and J. P. D. Abbatt

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Authors' Response to Referee Comments

We appreciate the constructive suggestions from both referees. We address all comments from both referees below.

Referee #1

Specific Comments:

1. Section 4: I suggest commenting on whether the differences observed in the effects of OH oxidation on POA and SOA particles might be due to differences in the reactive

uptake coefficients, since SOA has fewer H atoms for abstraction, or whether the differences in oxidation state of POA and SOA compounds impact the results via some other mechanism.

Authors' Reply: We have added the following text to Section 4 to discuss the point made by referee: "Another possibility for the less dramatic modification in particle properties of SOA during oxidation compared to model POA on the whole is slower kinetics of oxidation. It is currently unclear whether OH uptake remains constant as OA particles become more oxidized."

Technical Comments: 1. Figure 5. I suggest moving Figure A1 upwards so the baseline can be seen. Authors' Reply: We have modified Figure 5 as suggested.

Referee #2

Comments for discussion:

1. The different initial SOA types (SOA1, SOA2, SOA3) are a little confusing. They are shown in Table 1 but there isn't really a discussion of how they differ – this should be added when the Table is first referred to. In the results Section, findings with respect to "SOA" are discussed – does it mean all 3 SOA types had the same general behaviors? Do Figures 4-6 refer only to SOA1? It is also somewhat easy for the reader to confuse the different SOAs, the different AMS OA components (OOA1, HOA, etc.), and the PMF factors (A1, A2).

Authors' Reply: We have further clarified the differences between SOA types in Section 2 by adding the following text: "To study whether SOA precursor concentrations affect SOA composition and OH oxidation, AP and O3 were varied to either relatively high or low concentrations, i.e. the extreme values of the achievable experimental range of precursor concentrations in this work. SOA particles were produced under three sets of conditions by varying the SOA precursor gas mixing ratios: a) SOA1 particles produced under high AP (6.8 ppm), high O3 (75 ppm), b) SOA2 particles produced under high AP (5.3 ppm), low O3 (10 ppm), c) SOA3 particles produced under low AP (0.43 ppm), low O3 (11ppm)." We have also revised Figures 2 through 6 captions to clarify the types of SOA that the data represent.

2. A major strength of this work is the comparison of these OH oxidation experiments on SOA to the authors' previous experiments on oxidation of ambient OA and POA. However, the focus on oxidation of OA in ambient aerosols should be in the context of other important aging mechanisms, particularly since oxidation of SOA by OH appears to be a less efficient aging mechanism than others (see also comment 10).

Authors' Reply: This is a good point. We have evaluated OH-initiated heterogeneous oxidation as a mechanism of OOA formation in Section 4 and whether the timescales of this process make this aging important compared to other aging mechanisms. In particular, we state that SOA formation (or other mechanisms) is likely to be dominant close to VOC source regions, whereas the heterogeneous oxidation would be of higher relative importance in remote regions and aged particles, removed from sources. We have amended the following text to Section 4 to emphasize the importance of other aging mechanisms: "Although difficult to extrapolate from just one lab study, these results suggest that heterogeneous OH oxidation is not the dominant aging mechanism for the conversion of OA to the most highly oxidized form of OOA. Additional aging mechanisms, such as SOA formation, oxidative aging of semi-volatiles organics, cloud processing, and coagulation with particles containing soluble organics, likely also play an important role in the transformation of atmospheric organic aerosol to low-volatility OOA1."

3. The descriptions of changes observed in the AMS mass spectra can be difficult to follow. A "%" change is often described. Is this always a change in the mass concentration represented by that m/z, or just the raw signal? Does this change refer to the total aerosol mass derived from the AMS spectrum, or to the total OA component, or some other component? Listing the starting and final absolute values, in addition to this relative change would be helpful, particularly in the Abstract and Conclusions.

Authors' Reply: We agree that reporting percentage changes in fractional numbers can be confusing. We have tried to adapt our wording to make these changes easier to understand, and we have added absolute changes and initial values in numbers when possible for clarification (see Abstract, Sections 3.1 and 4).

4. For the CCN activation curves polydisperse SOA was introduced into the flow tube, while in other experiments monodisperse SOA only was used. This could introduce a wide range of changes in response to oxidation and subsequent particle properties; was this investigated? Some of the variability in Fig 9 may be due to more heterogeneity with particle size being introduced after oxidation (see next comment). Were the other aerosol properties for the CCN experiments similar to those from experiments using monodisperse aerosol? More attention should be devoted in the text to this key C1467 difference as it is easy to overlook presently.

Authors' Reply: The referee brings up a good point. We restricted our experiments to one size of particles only, apart from the CCN experiments where polydisperse SOA were oxidized. This would be a highly worthy project for a subsequent publication, i.e. to study the size-dependence of this chemistry. We expect heterogeneous oxidation to be somewhat more efficient for smaller particles as they have greater surface area to volume ratios. We now raise this point in Section 3.2 and added the following text: "Note that we have made the assumption in these experiments that the hygroscopicities of SOA particles are initially constant with particle size. We observed relatively broad CCN activation curves however, suggesting that there is some variability in hygroscopicities with particle size that may have contributed to variability in our results. Although the mass spectra for SOA particles did not change significantly under the Hg Lamp and O3 Dark control conditions, it is possible that particle composition could still have been altered on a molecular level that may impact the CCN activity, as the extent of the changes may vary with particle size. This may explain why the variability in the CCN activation results appears to increase when SOA particles are exposed to UV light (Hg Lamp), O3 Dark as well as OH, but more work is needed to confirm this. Furthermore, because oxidation rates may vary with particle size, there may also be chemical variability from size to size in the oxidized polydisperse aerosol. Another possibility is that not all particles receive the same level of OH exposure in the flow reactor."

That being said, we do have limited AMS data taken during the CCN experiments that show that the F44 fractions for 100 nm being somewhat higher than for 200 nm particles for the same level of OH exposure. Some of the variability in the data in Figure 9 could well be due to this effect, as now stated in Section 3.2 (see above comment)

5. Size-selecting particles post-reaction in the flow tube from a polydisperse aerosol for CCN analysis passes particles that may have a range of particle aging and associated physicochemical properties yet the same mobility diameter. Did you observe evidence of this? Were the slopes of the CCN activation curves relatively steep, or were they broad\ indicating a range of particle hygroscopicity (and thus chemistry), and/or particle shape? Are SS-scans not possible with the TGDC used here?

Authors' Reply: This question follows on from the previous point raised by the second Reviewer. Our CCN activation curves were indeed quite broad, suggesting particle size dependent variability on composition (see above comment). Yet, we do not have direct evidence to confirm this. Another possibility is that not all particles receive the same level of OH exposure in the flow reactor. Supersaturation scans were theoretically possible, but much more time consuming with our Thermal Gradient Diffusion Chamber, which is not automated. And so, we did not perform such experiments as a function of supersaturation. Ideally, more work should be done to study size resolve changes in particle properties of OA. See revised text from Comment 4.

6. The approximate nature of the O/C ratios determined from the AMS data should be more clearly emphasized. Aiken et al.'s ratios from ambient measurements were applied to the m/z 44 data in this study as the c-TOF-AMS cannot measure the elemental composition directly. This assumes those relationships are valid for the lab system studied here, which may not be the case.

Authors' Reply: We agree. We have added an additional sentence in Section 3.1 to note the assumption made here: "Because we do not have direct measurements of elemental composition of the SOA particles in this work, we make the assumption that the relationship between O/C ratios to F44 from Aiken et al. (2008) holds true for the laboratory SOA in this work as it does for chamber and ambient SOA in that study.".

7. What mass fraction of the total OA do each component, and the two PMF factors represent? What is the residual mass not accounted for by these components? Does the AMS OA mass concentration agree with that measured from the SMPS?

Authors' Reply: The PMF factors A1 and A2 represented on average 66 and 34% of the sum of masses of the PMF factors A1 and A2 before oxidation, where the summed OA mass of the PMF factors is within 3% of measured OA mass. The correlation for all data of measured and summed PMF factor masses OA mass gives an R2 of 0.9999 and slope of 1.002. We now state this in Section 3.1: "The relative changes in the mass fractions of the PMF A1 and A2 factors of the summed PMF factor organic mass concentrations (i.e. these organic mass concentrations were correlated with measured values with slope = 1.002 and R2 = 0.9999) due to OH exposure are shown in Figure 6. The HOA-like A1 PMF factor, representing 66($\pm$2)% of SOA1 organic mass before oxidation..."

The AMS measured organic mass was consistently lower than the SMPS measured mass based on mobility size assuming a collection efficiency of unity for the SOA particles during AMS sampling. The collection efficiency is likely lower for SOA particles, however. We focused on relative changes in volume and mass due to oxidation, so that this difference does not impact our results.

8. Does Eqn. 3 work well for your previous oxidation experiments of POA or ambient aerosol? It doesn't seem so surprising that ambient aerosol measurements do not accurately describe these lab studies, since you have already indicated (as have others) that lab-generated SOA does not have the same AMS-derived composition / properties

as ambient aerosol.

Authors' Reply: The Reviewer brings up a good point and so we have removed that paragraph and comparison to the predictions of Equation 3, given that laboratory and ambient data do not necessarily overlap in chemical properties.

9. Why are SOA1 and SOA2 discussed in more detail than SOA3? SOA3 is omitted from Figure 9 and is not discussed in the text.

Authors' Reply: We performed CCN experiments focusing on SOA1 and SOA2 only due mainly to time constraints, and because the SOA types were so similar. We have now stated more clearly that CCN experiments were carried out for only these SOA types in Section 3.2: "Given the similarity in SOA types, SOA3 was not studied."

10. In the Implications section, it is pointed out that for a (rather substantial) 2 week equivalent of OH exposure, the O/C increased by 0.04. Comparing with Figure 4 in the cited Jimenez et al. 2010 paper, this change is very small and certainly explains very little about the postulated "aging" of organic aerosol in the atmosphere. It's not C1468 clear to me how it can be concluded from the work presented here that "It is likely that heterogeneous oxidation will be a significant aging process leading to OOA formation from POA and SOA in remote regions. . ."?

Authors' Reply: We have altered the Abstract and Conclusions sections to indicate that in regions close to source regions, other oxidation mechanisms – such as SOA formation – are likely to dominate whereas heterogeneous oxidation is likely to be of higher relative importance away from such sources. That being said, it is challenging to rank the relative importance of these mechanisms given that extrapolation from the lab to the field is difficult, dependent upon such things as particle size, NOx conditions, SOA precursors concentrations, etc.

Minor points:

11. Pg. 3267: Robinson et al. (2007) , and Jimenez et al. (2009) are appropriate citations to include in recent characterizations of ambient OA. Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, Science, 315, 1259-1262, 2007.

Authors' Reply: We have added these references as suggested.

12. Pg. 3267: The Introduction omits condensed-phase processes including oligomerization and other aqueous phase reactions as possible aging pathways.

Authors' Reply: We have added text to introduce these additional aging processes in Section 1: "Atmospheric chemical aging of OA includes coagulation with aged particles, condensation of soluble inorganic species and oxidized organic gases to form SOA, condensed-phase reactions within the particle leading to oligomer formation, cloud processing and multi-phase reactions, and heterogeneous oxidation of OA by gas-phase oxidants (e.g. OH, O3, NO3, Cl)."

13. Pg. 3267, line 29: Petters et al. concluded that oxidation of OA was unlikely to be an efficient pathway for increasing aerosol hygroscopicity significantly and that other processes such as condensation of inorganic species likely dominated hygroscopicity changes in the atmosphere. A similar comment applies to the Atmospheric Implications section.

Authors' Reply: We have added a sentence to Section 1 on this topic: "We do note though that Petters et al. (2006) have concluded that such mechanisms of increasing aerosol hygroscopicity are likely to be less important than other aging processes, such as condensation of soluble inorganics."

14. Pg. 3268, line 1: "initially CCN-inactive": In general I don't like this terminology because it is not precise. Even an insoluble wettable particle can be "CCN active" if it is large enough or exposed to high enough superaturations. I recommend this phrase be modified; some suggestions: "initially CCN-inactive at particles sizes XX

and supersaturations less than YY"; or perhaps a simpler way to express the idea is "initially having kappa _0".

Authors' Reply: We have qualified the phrase CCN-inactive as suggested in Section 1: "Chemical aging has recently been shown to enhance hygroscopicity of OA, e.g. increasing the cloud condensation nucleus (CCN) activity of model POA particles that are initially CCN inactive for particle sizes < 200 nm at supersaturations <1% (Broekhuizen et al., 2004; Petters et al., 2006; Shilling et al., 2007; George et al., 2009)."

15. Pg. 3268, line 5: Please clarify that Zhang et al. measured only the OA composition from non-refractory submicron aerosol components, not the entire aerosol mass. Authors' Reply: We have amended the sentence as suggested in Section 1.

16. Pg. 3268: "There is a growing consensus that SOA formation dominates over the aging process over timescales of several hours (Jimenez et al., 2009)." What is intended to be conveyed – that more SOA mass forms from gas-phase oxidation and subsequent gas-to-particle partitioning than from heterogeneous oxidation of POA/HOA -> SOA/OOA? Authors' Reply: This is what is meant by the sentence. We modified this sentence for further clarity: "There is a growing consensus that SOA formation dominates over the aging process leading to an enhanced oxidation state of OA over timescales of several hours, given that heterogeneous oxidation is too slow to impact aerosol chemistry on these timescales (Jimenez et al., 2009)."

17. Pg. 3270, line 14: How efficient was the denuder at removing the precursor VOCs? Authors' Reply: We have measured the efficiency of the charcoal trap to remove volatile organic compounds sampled from room air with a Proton Transfer Reaction Mass Spectrometer (PTR-MS). We found that it reduced the levels of aromatics to the instrument's detection limit and the levels of small ketones and aldehydes by a factor of 3 or greater, but had little effect on small acids such as formic acid. Based on these results, we expect that the a-pinene will be efficiently trapped by the charcoal.

18. Pg. 3275, line 9: "F44 and F55 were altered by +21% and −7%, respectively". Do

these refer to relative mass concentrations changes for that specific m/z?

Authors' Reply: The percentage changes refer to changes in the F44 and F55 values, which are fractions of m/z 44 and 55 out of total organic mass, as defined in the preceding paragraph. These values are shown in the organic mass spectra of the three SOA types in Figure 1. We have amended the sentence in Section 3.1 for clarity: "Taking the trend for all SOA types, the F44 and F55 fractions were altered by +21% and -7% from initial values, respectively…"

19. Pg. 3275, line 21: I'm not sure where this small "1 to 2% on an absolute scale" change comes from; please explain what numbers are being used here. This is an important point that warrants further discussion.

Authors' Reply: Our wording here can be confusing as noted in Comment 3, so we have expressed the changes in F44 fractions due to aging as values and not percentages here to reduce confusion.

20. Pg. 3277, line 5: typo: "presently" should be "presented"

Authors' Reply: This typo has been corrected.

21. Pg. 3278, line 23: what are the causes of the high variability?

Authors' Reply: We did not systematically investigate the source of this variability, but it is likely arising from a combination of small changes in lines losses, volatility changes at 600 degrees in the AMS due to composition changes from each SOA production source, etc.

22. Pg. 3279: The hygroscopicity of lab-generated a-pinene+ozone SOA was also studied by Prenni et al. (2007) and more recently Wex et al. (2009) and Petters et al. (2009): Prenni, A.J., Petters, M.D., Kreidenweis, S.M., DeMott, P.J. and Ziemann, P.J., (2007), Cloud droplet activation of secondary organic aerosol, Journal of Geophysical Research, vol. 112, D10223, doi:10.1029/2006JD007963. Towards closing the gap between hygroscopic growth and activation for secondary organic aerosol: Part 1 –

Evidence from measurements. H. Wex, M. D. Petters, C. M. Carrico, E. Hallbauer, A. Massling, G. R. McMeeking, L. Poulain, Z. Wu, S. M. Kreidenweis, and F. Stratmann, Atmos. Chem. Phys., 9, 3987-3997, 2009. Towards closing the gap between hygroscopic growth and activation for secondary organic aerosol – Part 2: Theoretical approaches. M. D. Petters, H. Wex, C. M. Carrico, E. Hallbauer, A. Massling, G. R. McMeeking, L. Poulain, Z. Wu, S. M. Kreidenweis, and F. Stratmann, Atmos. Chem. Phys., 9, 3999-4009, 2009.

Authors' Reply: We have added the first two references.

23. Pg. 3279, line 16: Reference to Fig 8 should be Fig 9.

Authors' Reply: Typo has been corrected.

24. Pg. 3280, line 17: Typos: should be "values derived. . . were more significantly"

Authors' Reply: Typo has been corrected.

25. Pg. 3281, line 29: "additional aging mechanisms" such as?

Authors' Reply: We have added text to clarify additional aging mechanisms mentioned in Section 4: "Additional aging mechanisms, such as SOA formation, oxidative aging of semi-volatiles organics, cloud processing, and coagulation with particles containing soluble organics, likely also play an important role in the transformation of atmospheric organic aerosol to low-volatility OOA1."

26. Pg. 3282, line 12: "The modification in SOA hygroscopicity from OH oxidation was more subtle compared to hygroscopicity changes observed in previous work with model POA". POA starts at a much smaller kappa value, and in this regime kappa is much more sensitive to small increases in the volume fraction of hygroscopic material. Thus it is not surprising that POA exhibited much larger changes in hygroscopicity (kappa) than SOA did. These details should be included for readers less familiar with the kappa hygroscopicity framework.

Authors' Reply: This is an important point that we have included in the discussion of our CCN activity results in Section 3.2: "Because POA is initially hydrophobic (kappa ~ 0), its hygroscopicity is much more sensitive to the addition of small amounts of soluble material and surface tension reduction than SOA particles of relatively moderate hygroscopicity." and in Section 4: "This is due to the fact that POA particles have low initial oxygen content (O/C <0.1), minor changes from oxidation will obviously have a greater impact on their overall composition than for SOA particles."

27. Pg. 3282, line 16: "Although OH oxidation may not significantly alter CCN activity of OOA". A brief statement about the larger potential roles that other aging pathways, condensation of inorganic components in particular, have on increasing aerosol hygroscopicity could be included here.

Authors' Reply: We have added a general statement in Section 4 on the role of other aging processes in conversion of POA to CCN: "Close to source regions, it is now becoming clear that other particle aging pathways, such as condensation of inorganic material and SOA, will likely dominate the conversion of POA to more hydrophilic and CCN active OA."

28. Table 1: F44 is % of what, mass concentration? Was RH always zero for SOA generation?

Authors' Reply: F44 is now defined in Table 1 caption. All SOA particles in this experiment were produced under dry conditions as stated in Section 2.1.

29. Fig. 9: How were the error bars estimated and why do they show such large variation? State in the caption the supersaturation at which these measurements were performed.

Authors' Reply: We have amended Figure 9 caption to explain the error bars and define the supersaturation. The nature of the variability in the data is not fully clear. As was suggested in the previous comments, it may be that the particle hygroscopicity and related properties become more variable with particle size under certain flow tube conditions. See response to Comment 4.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 3265, 2010.