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Comment

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

Anonymous Referee #2

Received and published: 10 April 2010

George and Abbatt describe heterogeneous oxidation experiments in which SOA produced from the ozonolysis of α -pinene is subjected to further oxidation by OH radicals. A previously described aerosol flow tube system was used to control the aerosol's exposure to OH. Physicochemical properties of the aged aerosol that were measured included changes in particle density, volume, hygroscopicity, and chemical composition, as represented by unit mass fragments measured by an AMS. This work is an interesting study of the possibility of further oxidation of oxidized SOA by the hydroxyl radical. The paper will be of interest to a wide range of ACP's readership. The experiments were properly conducted and described, the paper is well written overall and should be accepted for publication after the following minor comments have been

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addressed.

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).

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).

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.

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

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difference as it is easy to overlook presently.

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?

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.

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?

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.

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.

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

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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. . .”?

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.

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

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.

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 supersaturations. 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”.

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.

16. Pg. 3268: “There is a growing consensus that SOA formation dominates over

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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?

17. Pg. 3270, line 14: How efficient was the denuder at removing the precursor VOCs?

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?

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.

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

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

22. Pg. 3279: The hygroscopicity of lab-generated α -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

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F. Stratmann, Atmos. Chem. Phys., 9, 3999-4009, 2009.

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

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

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

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.

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.

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

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.

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

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