Review of "Characterization of Organosulfates in Secondary Organic Aerosol Derived from the Photooxidation of Long-Chain Alkanes"

Reviewer's Summary:

The authors characterize organosulfates (OSs) from the laboratory oxidation of dodecane, decalin, and cyclodecane under varying conditions of humidity and two different seed types (non-acidified, acidified). They observe overlapping organosulfates in the laboratory experiments and on filters from Pasadena, USA and Lahore, Pakistan, concluding that OSs from the oxidation of anthropogenic precursors may contribute to urban SOA. The results are novel and would be of interest to the readers of ACP; however, I would not recommend this manuscript for publication because it is not well-written and the conclusions are highly speculative. In particular, the proposed chemical mechanisms from the laboratory experiments are not substantiated by a fundamental knowledge of the chemistry occurring in the reaction chambers used. The authors inconsistently address the fate of the RO2 radical within their laboratory experiments throughout the text and within the proposed mechanisms. There seems to be a mix of RO2 reacting with RO2, HO2, and NO, though they claim different regimes depending on what mechanism they are proposing to explain the OSs formed. For example, they state that reaction with NO is insignificant, yet they report a nitrate containing OS in the decalin system. They propose the formation of hydroperoxides in the case of dodecane experiments with high initial precursor concentrations and do not propose RO2 + RO2 chemistry, but for the C10 systems RO2 + RO2 reactions are proposed with some RO2 + HO2 reactions. They propose epoxide precursors in the C10 systems to OS formation, but not in the C12 system. In general, the proposed mechanisms are arbitrary and do not demonstrate careful control in the design of the experiments or understanding of the chemistry. This lack of understanding becomes clear because there are several areas where citations are used to support the current work, but the citations are used imprecisely and out of context. The manuscript would benefit from more clearly stated organizational structure (e.g. why some mechanisms are proposed in the main text versus the supplemental information). The authors should also clarify motivation in the experimental selection of two C10 cyclic alkane structures and one C12 straight chain structure. The brevity of the discussion of results on the OSs from dodecane photooxidation are quite brief relative to the other sections interpreting the results from decalin and cylodecane, and the effects of chemical structure are glossed over in brevity. Further, it is unclear if the conclusion that enhancement of OS yields are due to increased acidity of the seed aerosol is really due to acidity, rather than an effect of seeding the experiments with an atomized solution containing more sulfate. These concerns are outlined in detail below.

Major Comments:

1. Lines 58-61: These lines are specious in the use of citations and misleading. First, as written, these lines assert that the underestimate of global SOA is equivalent to an underestimate in urban SOA. Second, the references cited (Pye and Pouliot, 2012; Tkacik et al., 2012) do not specifically argue that the underestimate in predicted SOA is due to the omission of IVOCs. A better reference here based on the lines as written would be (Robinson et al., 2007). Pye and Pouliot, 2012 can be cited for exploring additional mechanisms (oligomer formation) from alkane and PAH in SOA formation, and Tkacik et al., 2012 can be cited for providing additional evidence that IVOCs may be a missing source in modeling urban SOA, but the authors need to reword these lines carefully and be more precise.

2. Line 65: References here should include Yee et al., 2013 which more specifically addresses analogous to Lim and Ziemann, 2005 the products and mechanisms of C12 alkanes of varying structures.
3. Line 66: Tkacik et al., 2012 should be included here for presenting yields from several alkane systems.
4. Line 71: For this discussion on structure and fragmentation, additional reference should be cited (Lambe et al., 2012).
5. Line 107: The authors assert that acid-catalyzed reactive uptake has not been reported for the oxidation of alkanes. This is not true. Atkinson, Lim, and Ziemann have shown that alkane oxidation leading to 1,4-hydroxy carbonyls convert to cyclic hemiacetals in an acid-catalyzed multi-phase process (Dibble, 2007; Atkinson et al., 2008; Lim and Ziemann, 2009a, 2009b). Schilling Fahnestock et al., 2015 also report the effect of acidity on SOA formation from C12 alkanes.
6. Lines 123-124: Can the authors give more background on these two sites to orient the reader also with the motivation/purpose of this study? What types of sites are these—urban with what type of emissions profiles and surrounded by vegetation, etc.?
7. Line 222-223: It would be helpful to label the 1,3-dodecanone sulfate in Figure 1 to aid the reader. The authors should be careful with their naming convention here (i.e. 1,3-), as this particular isomer certainly is not the only potential isomer and is not the only isomer specified in Yee et al., 2012 and Yee et al, 2013.
8. Lines 226-230: The reference cited, Ruehl et al., 2013, is improperly used here. Ruehl et al., 2013 describes the heterogenous oxidation of octacosane and finds a strong preference for OH attack at the terminal carbons. The current work, however, is gas-phase oxidation, so the specificity of the isomers as listed in lines 228-229 should be rethought. Further, the naming convention for these isomers are inconsistent with the naming convention in line 222-223. It seems as though the 1, 3-dodecanone denotes the 1 position as the ketone, whereas here the reference to 2, 4-, 3,5-, and 4,6- and other isomers suggests the 1 position is likely the carbon at the end of the dodecane chain.
9. Lines 234-237: This is a poorly worded sentence. It is unclear in relation to the context of the current work, and there is imprecise use of citations. Hydroperoxides can undergo further oxidation by reaction with OH, but to generate alkoxy radicals from hydroperoxides, that would likely include photolysis. The authors need to address the extent of photolysis in the experiments then. Or are the authors referring to reactions of RO2 + NO to generate alkoxy radicals? If so, then the authors need to address the extent of RO2 + NO occurring in the experiments. If the former, rewrite as, "First-generation hydroperoxides can undergo further oxidation by reaction with OH to form low-volatility, more highly oxidized products, or can be photolyzed to alkoxy radicals (RO) to form more highly volatile products." The use of Carasquillo et al., 2014 here is inappropriate to discuss the oxidation of hydroperoxides as written. Carasquillo et al., 2014 describe the fate of differing alkoxy radical structures and how it affects SOA yield. The authors need to clarify what they are trying to say here and how it relates to the mechanism proposed in Figure 1.
10. Lines 237-243: The authors can cite Raff and Finlayson-Pitts, 2010 for IPN as an OH radical source, but it cannot be cited to fully account for the chemical conditions (i.e. the fate of RO_2) in the current experiments without considering the differences between their experiment and that

of Raff and Finlayson-Pitts, 2010. The authors should report NO_x levels in these experiments to verify the claim that RO_2 + NO reactions are minimal. Also, how is O_3 formed in these experiments? The authors need to calculate (considering the relatively high levels of initial hydrocarbon), the relative fate of RO_2 between reaction with RO_2, HO_2, and NO. The proposal that OS-279 stems from hydroperoxide species in Figure 1 seems least inappropriate if RO_2 fate is really dominated by reaction with RO_2 and/or NO.

11. Table 2: The authors never describe the origin of the C7 (OS-209) and C9 (OS-237) organosulfates observed in the dodecane system and also observed in the ambient samples. This is another indication that fragmentation pathways are at play, potentially through RO2 + NO reactions in the system. The authors need to be careful in explaining the fate of the RO2 radical in their experiments and whether the ambient observation of these OSs can really be attributed to dodecane chemistry in the atmosphere when they may clearly originate from other precursors. The authors need to also describe the potential influence of monoterpenes at the sites they have taken samples from to preclude OS origin from biogenic precursors, as they say themselves that C10 monoterpene OSs are isomeric to some proposed in the C10 alkane systems. How good is RT matching/SICs for confirming that the laboratory generated OSs are really the same as those in ambient data? What measurements in these locations suggest that decalin, cylodecane, and dodecane are prevalent here?
12. Lines 246-247: The citation of Claeys et al., 2004 is inappropriate here. The authors propose that "heterogenous chemistry of gas-phase organic peroxide" is a mechanism for OS and tetrol formation, citing Claeys et al., 2004. Yet, Claeys et al., 2004 state, "The mechanism we suggest, reaction with hydrogen peroxide under acidic conditions in the aerosol liquid phase…," which is not consistent with the heterogeneous mechanism proposed in the current work and in Riva et al., 2015b. The difference in humidity should also affect the distribution of hydroperoxide compounds in the gas/particle phase. The authors should address this in the context of mechanistic explanations for their observations.
13. Lines 256: Several citations should be added here. Include reference to works by Lim and Ziemann, Lambe et al., Yee et al., Loza et al., Tkacik et al.
14. Lines 284-286: The mechanism described in text corresponds with the pathway in Figure S8, pathway c, not pathway a. Authors should rewrite these lines to describe pathway a. It also becomes clear here that the authors are not consistent with description of the chemistry proceeding in the chamber. In Figure S8, the fate of RO2 is initially reaction with RO2, but then in pathway a, it shifts to RO2+HO2. The selected pathways seem arbitrary to explain the proposed structure in Figure 2a.
15. Line 290: It is unclear whether the analytical technique is sufficient for seeing hydroperoxide moieties on molecules as they are included in the proposed structures. Were hydroperoxide standards such as t-buytylhydroperoxide or cumene hydroperoxide run using this method to verify that the hydroperoxide moiety can be retained on the column? Or is there something about the organosulfates that allow for this? The authors should address this in the experimental methods section as well.
16. Lines 295-296: The work of Yee et al., 2013 and Schilling Fahnestock et al., 2015 do not test decalin, so they should not be cited here to support proposed formation of a 1-hydroperoxy radical in the decalin system used in the current work. While the mechanisms laid out in Atkinson, 2000 can apply here, as worded it seems as if the authors are proposing the particular

alkoxyl radical ($C_{10}H_{17}O^{\cdot}$) was discussed in the reference. Reword the sentence/omit the reference.

17. Line 298/Figure 3: To guide the reader it would be beneficial to update the mechanism in Figure 3 with the same label of tCARBROOH next to intermediate the authors are referring to
18. Lines 298/Figure 3: Do the authors see evidence of an analogous product in the case of decalin, as the OS-279 that was observed in the dodecane case? The proposed mechanism of carbonyl hydroperoxide heterogenous reactive uptake followed by OS formation should also be considered for the decalin tCARBROOH as well and supported by the measurements/compared on the basis of volatility differences due to carbon number/ring structure and the impact of reactive uptake versus partitioning to the particle phase.
19. Lines 299-301: The mechanism of RO_2 radical isomerization/auto-oxidation is a special case in which the RO_2 radical lifetime is long enough for this to take place (e.g. remote areas). Please also refer to and reference (Peeters et al., 2009; Crounse et al., 2011; Orlando and Tyndall, 2012). The authors need to justify why the basis of their proposed mechanisms for OS formation rely on this pathway when the initial fate of RO_2 radicals in their systems are presented as RO_2 + RO_2 (e.g. Figures 3, 4, and S8). Is it RO2 + RO2, RO2 + HO2, RO2 + NO, RO2 isomerization?
20. Lines 301-305: The authors should address the extent of photolysis reactions affecting the fate of the proposed hydroperoxides and aldehydes in the system.
21. Line 306: “previously unreported” is unclear. Do the authors mean previously unreported in ambient data or previously unreported from similar experiments?
22. Line 311: As worded, OS-267, is proposed to originate from further oxidation of OS-269, but the arrows drawn in Figure 3 are inconsistent suggesting origin from the epoxide. Please clarify.
23. Line 327/Figure 4: The description of Ring cleavage of the C10 alkoxy radical is not consistent with the “ISO”/isomerization descriptor in Figure 4. Please clarify that pathway.
24. Line 340: Figure 1d does not exist. Clarify the reference.
25. Lines 343-345: Sentence is awkward beginning with “Pathway c”, and from what figure? Clarify that it is Figure 4. Again, citation of Atkinson, 2000 seems inappropriate as the sentence is written.
26. Lines 343-345/Figure 4, pathway c: Here the authors propose that RO2 + NO chemistry is occurring to form a nitrate containing OS. This contradicts the authors’ earlier statement in lines 237-243 stating that the RO2 + NO reactions are not significant in their experimental setup. The authors need to handle in more detail the fate of RO2 under the unclear experimental conditions.
27. Lines 349-364: Why is discussion of OS-281 and OS-297 featured here, when discussion of OS-265 is discussed near the beginning of Section 3.2? Since they are all referenced in Figure S8, their chemistry should be discussed together from the same mechanistic precursors.
28. Section 3.2: Authors should clarify the main mechanistic differences and relative importance between Figure S8, Figure 3, and Figure 4, and the flow of products to be discussed at the beginning of Section 3.2. Currently as written, the flow of Section 3.2 is very arbitrary when choosing different OS products to discuss.
29. Lines 377-380: Incorrect use of citations here. Yee et al., 2012 do not propose RO2 + RO2 chemistry and therefore a “precedent” has not been established. The authors should not be citing Atkinson, 2000; Yee et al., 2012 and Raff and Finlayson-Pitts, 2010 to speak for the

experimental conditions in the current work. The mechanism of RO2 + RO2 → RO can be supported by work on general atmospheric chemistry mechanisms including Atkinson, 2000 and many other works, and so if this mechanistic pathway is to be cited, than many other works should be cited as well.

30. Line 379: Inconsistent citation here compared to line 300 for similar mechanistic argument.
31. Figure S14: Why do the authors propose in the case of cyclodecane formation of the hydroperoxide from RO2 + HO2 pathways and subsequent chemistry thereof, but not in the case of decalin in any of Figures 3, 4, and S8? Further, Figure S14 outlines a mechanism from further reaction of the hydroperoxide to get to an epoxide that then enters the particle phase to produce OS-251 and OS-249. This seems like a plausible analogous mechanism to propose for the case of dodecane rather than reactive uptake of a carbonyl hydroperoxide. Why do the authors propose different mechanisms between dodecane and cyclodecane to generate the similar analogs (OS-279, OS-249)?
32. Section 3.4: This section is weak and little effort is made to really describe the chemical differences between the systems to interpret the findings. There should be comparisons of vapor pressures of the precursors and carbon numbers and discussion of previously published yields from these compounds to support the discussion. How does quantification using the available OS surrogate standards potentially affect the OS quantification across these systems/factoring in different sensitivities?
33. Line 400: The authors claim that "the presence of acidic aerosols significantly increase OS formation in most cases". However, is this just an effect of using an atomized solution with more sulfate (0.06M ammonium sulfate + 0.06M sulfuric acid) in the acidic case versus only 0.06M ammonium sulfate in the non-acidified case? It may be a concerted effect of more available sulfate in the "acidic" case as well as acidity.
34. Line 484: The authors return to claim that the experiments are conducted under dominant "RO2/HO2" chemistry—this is contradictory to the formation of OS-326 containing a nitrate group.
35. Lines 484-486: Enhancement of OS due to acidified ammonium sulfate seed needs to be addressed with regard to the effect of just having introduced more sulfate into the experiments compared to the non-acidified case. See earlier Major Comment, 33.
36. Lines 491-496: The "novel pathway" involving reactive uptake of hydroperoxides is not well-substantiated in the current work and is mostly speculation. The vapor pressure alone of the carbonyl hydroperoxide makes it a potential candidate to partition to the particle phase, not via reactive uptake. There are no direct measurements of hydroperoxides in the gas phase, and insufficient discussion on if hydroperoxides are detected in the particle phase using the UPLC technique. Further, if reactive uptake is at play, why have the authors not seen the corresponding decalin analog of carbonyl hydroperoxide?

Minor Comments:

1. Line 30: "Both studies strongly support formation of OSs" is awkward. Reword, for example, "Both studies strongly support that OSs can form from the gas-phase oxidation of anthropogenic precursors…"
2. Line 48: Change "aerosol" to "particles", as aerosol is technically defined as both gas + particle.

3. Line 76: Insert comma after “2015)”.
4. Line 82: Insert comma after “NO_3”.
5. Line 83: Change comma to semi-colon after “2007,”.
6. Line 90: Delete “of”.
7. Line 103: Change “reduce” to “reduces”.
8. Line 136: Check misprint on the high humidity range listed as “(4-60%)”.
9. Line 220: Insert after “)”, “, hereafter referred to as OS-279, ”.
10. Line 268: “ion at *m/z* 265.0749” should be “ion at *m/z* 265.0752” according to Figure 2.
11. Line 315: Add in “Figure 3, pathway a” to be clear.
12. Line 345: Change “identical” to “analogous” as the sequence of reactions are certainly not identical as shown in Figure 4.
13. Line 350: Change chemical formula to include S for OS-281.
14. Line 352: Rewrite the sentence. The radical reacts with O2, followed by 1,6 H shift, etc.
15. Lines 362-363: Rewrite the awkward phrasing, “which be reactively taken up to give a sulfate ester”.
16. Lines 371-374: Poor grammar. Rewrite sentence.
17. Line 379: “hydroperoxydes” is spelled wrong.
18. Line 459: Add “of” after “oxidation”.
19. Line 482: Add “,” after “cyclododecane”.

Additional References:

Atkinson, R.; Arey, J.; Aschmann, S. M. Atmospheric Chemistry of Alkanes: Review and Recent Developments. *Atmos. Environ.* **2008**, *42* (23), 5859–5871.

Crounse, J. D.; Paulot, F.; Kjaergaard, H. G.; Wennberg, P. O. Peroxy Radical Isomerization in the Oxidation of Isoprene. *Phys. Chem. Chem. Phys.* **2011**, *13* (30), 13607–13613.

Dibble, T. S. Cyclization of 1,4-Hydroxycarbonyls Is Not a Homogenous Gas Phase Process. *Chem. Phys. Lett.* **2007**, *447* (1-3), 5–9.

Lambe, A. T.; Onasch, T. B.; Croasdale, D. R.; Wright, J. P.; Martin, A. T.; Franklin, J. P.; Massoli, P.; Kroll, J. H.; Canagaratna, M. R.; Brune, W. H.; et al. Transitions from Functionalization to Fragmentation Reactions of Laboratory Secondary Organic Aerosol (SOA) Generated from the OH Oxidation of Alkane Precursors. *Environ. Sci. Technol.* **2012**, *46* (10), 5430–5437.

Lim, Y. Bin; Ziemann, P. J. Chemistry of Secondary Organic Aerosol Formation from OH Radical-Initiated Reactions of Linear, Branched, and Cyclic Alkanes in the Presence of NOx. *Aerosol Sci. Technol.* **2009a**, *43*, 604–619.

Lim, Y. Bin; Ziemann, P. J. Kinetics of the Heterogeneous Conversion of 1,4-Hydroxycarbonyls to Cyclic Hemiacetals and Dihydrofurans on Organic Aerosol Particles. *Phys. Chem. Chem. Phys.* **2009b**, *11* (36), 8029–8039.

Orlando, J. J.; Tyndall, G. S. Laboratory Studies of Organic Peroxy Radical Chemistry: An Overview with Emphasis on Recent Issues of Atmospheric Significance. *Chem. Soc. Rev.* **2012**, *41* (19), 6294.

Peeters, J.; Nguyen, T. L.; Vereecken, L. HO X Radical Regeneration in the Oxidation of Isoprene W. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5935–5939.

Robinson, A. L.; Donahue, N. M.; Shrivastava, M. K.; Weitkamp, E. a; Sage, A. M.; Grieshop, A. P.; Lane, T. E.; Pierce, J. R.; Pandis, S. N. Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging. *Science* **2007**, *315* (5816), 1259–1262.