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Interactive comment on "Secondary organic aerosol from chlorine-initiated oxidation of isoprene" *by* Dongyu S. Wang and Lea Hildebrandt Ruiz

Anonymous Referee #4

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Summary and Recommendation:

This is an interesting study that examines the potential of SOA formation from chlorine radical (Cl)-initiated oxidation of isoprene. I've spent many years examining the detailed chemical processes of isoprene oxidation leading to SOA formation, and to my knowledge, this does appear to be the first examination of the role of Cl radicals in forming SOA. The paper is concise and will be of great interest to the readers of ACP. I'm particularly interested in this work as my group has recently been examining the potential of isoprene SOA in marine aerosols, especially from remote regions where NOx levels are likely low. As one of the reviewers recommended in the quick review

stage, I think it is important to more clearly stress where this chemistry might be relevant that you are examining in here in your chamber studies. I stress this point as we definitely measure isoprene SOA tracers related to low-NOx pathways in remote marine aerosols (work yet to be published). Field studies have also demonstrated this, such as Fu et al. (JGR, 2011) and Hu et al. (Scientific Reports, 2013). However, one thing that is interesting to us is could other oxidants play a role. This study seems to suggest this!

I have a few major points that need to be addressed before publication can be fully considered. Due to the nature of these major points, I think the manuscript should be accepted with major revisions noted. Once the authors can address these, I will certainly support publication in ACP. Briefly, I'll summarize that I think the chamber experiments could have included other conditions (like higher RH or more acidic aerosol) to examine SOA potential from isoprene oxidation, more references should have been cited, and importantly I think that PMF/ME-2 analyses of the ACSM data set should have been considered in order to estimate if IEPOX-derived SOA or non-IEPOX SOA dominated to the SOA mass. This sort of mass closure would reveal or provide more context on what other potential pathways/products are missing (such as organochlorine products).

Major Points to Consider:

1.) As the authors know well, acidity plays a MAJOR role for IEPOX uptake yielding isoprene SOA under low-NOx conditions. This was conclusively demonstrated with authentic IEPOX for the first time by Lin et al. (2012, ES&T); however, Wang et al. (2005, RCM), Surratt et a. (2006, JPCA), Paulot et al. (2009, Science), and Surratt et al. (2010, PNAS) were some of the first studies to propose for the existence of IEPOX even though an authentic standard did not exist at that time to study its reactive uptake. Since then, kinetic studies have demonstrated that acidity plays a key role in IEPOX producing substantial amounts of SOA (Gaston et al., 2014, ES&T; Riedel et al., 2015, ES&T Letters; Riedel et al., ACP, 2016). If ammonium sulfate aerosol is wet,

due to a high enough RH, then ammonium sulfate can take up IEPOX to yield SOA if the reaction time scales are long enough (Nguyen et al., 2014, ACP).

With this reminder above, I wonder why the authors did not consider also conducting experiments at elevated RH and increased acidities with the ammonium sulfate seed aerosol? I can imagine if the chemistry applies to remote marine locations, the aerosol may be more wet and/or acidic (especially if there are sufficient DMS emissions). Jon Abbatt's group also showed recently in Wong et al. (2015, ES&T) that deliquesced ammonium sulfate particles can yield a lot of SOA through a non-IEPOX route. So this could be something important to consider.

By the way, the authors don't appear to say how the ammonium sulfate aerosol were injected into the chamber? What was the concentration of your atomizing solution? This should be added to the experimental section.

2.) PMF/ME-2 analyses of your SOA composition using the ACSM data:

As the authors likely know, Lin et al. (2012, ES&T), and more specifically Budisulistiorini et al. (2013, ES&T), demonstrated that AMS and ACSM, respectively, datasets can resolve IEPOX-OA factor when PMF is applied. Why didn't the authors consider conducting PMF in their analyses to constrain how much of the SOA is from IEPOX? You could run PMF with the IEPOX-OA factor constrained using the reference MS library (so this would be ME-2).

Furthermore, Krechmer et al. (2015, ES&T) did this for the non-IEPOX SOA pathway. He used his reference mass spectrum for the non-IEPOX SOA to constrain its importance to field aerosol collected during the 2013 SOAS campaign! Riva et al. (2016, ES&T) also showed that authentic ISOPOOH makes SOA without needing IEPOX due to the low-volatility nature of the multifunctional hydroperoxides produced!

Since you don't use offline chemical analyses to measure molecular-level SOA components, I think it is worth while conducting PMF/ME-2 analyses to see if that can help

constrain the different pathways yielding the total SOA mass. I hope the authors might agree with this suggestion.

3.) Please go through carefully and make sure certain references are not missing throughout the text. I mention a few of these in my minor comments below.

4.) I know it isn't a focus in this manuscript, but it would be very powerful if molecular tracers could be identified for Cl-initiated radicals yielding SOA. The authors mention using the ACSM to try to constrain the organochlorine budget, but seemed to have trouble with this due to interference issues. This is why I suggested conducting PMF/ME-2 analyses above in # 2. However, does the CIMS data (especially the iodide reagent ion chemistry) suggest the presence of low-volatility hydroperoxides that contain chlorine in them? From OH radical studies by Krechmer et al. (2015, ES&T), Riva et al. (2016, ES&T), and Liu et al. (2016, ES&T), they all measured low-volatility multifunctional hydroperoxides that made sufficient amounts of SOA (that don't require aerosol acidity like IEPOX).

5.) When reviewing Table 1, I realized it wasn't well explained in the text why the different injection methods were used. What did these methods explicitly tell you? For modelers, this Table might be very difficult for them to judge which yields should be used. Also, related to my point # 1 above, modelers seeing these yields may question if these yields are accurate to remote low-NOx regions where Cl radical chemistry might matter. Can the authors offer which yield may be the most appropriate to use?

Finally, I'm assuming these various injection methods were used to gain some insights into vapor wall losses? It remains unclear to me how exactly vapor wall losses were dealt with (if at all) in reporting the SOA yields shown in Table 1.

Minor Comments:

1.) Abstract, Page 1, Line 12: Remove "%" after "8." You don't need this.

2.) Methods, Page 2, Line 32: Insert a space between "exceeding100"

3.) Section 3.4, Page 7, Line 27: You write "3-methyl-3-butene-2-one (CMBO) [(C5H7OCl)H+]." This appears to be named incorrectly. Please name according to IUPAC.

4.) Section 3.4, Page 7, Line 31: I would reference Kroll et al. (2006, ES&T) and Surratt et al. (2006, JPCA) as one of the initial references to demonstrates MACR oxidation is a source of SOA.

5.) Section 3.4, Page 8, Line 26: The authors should reference Lin et al. (2012, ES&T)

6.) Section 3.4, Page 8, Line 27: The authors should also reference Gaston et al. (2014, ES&T) and Riedel et al. (2015, ES&T Letters)