

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

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We thank the referee for the suggestions and recommendations. Below are our responses to all comments.

1.) Reviewer: As the authors know well, acidity plays a MAJOR role for IEPOX uptake yielding isoprene SOA under low-NO_x 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 al. (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

C1

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.

Response: We have conducted four additional experiments, two with initial chlorine injection (Exp. A6 and A7) and two with continuous chlorine injection (Exp. C6 and C7). We observed significant increases in SOA concentrations when acidified seeding aerosol was used as well as increases in higher m/z mass fragments including m/z 82, which is generally associated with IEPOX-aerosol. We also observed lower gas-phase ion signals in the CIMS in acidified seed experiments compared to neutral seed experiments. Some of the changes made to the manuscript include,

Manuscript changes in Figure 1: Added time-series from Exp. C7, which used acidified seed particles for comparison with Exp. C2, which used neutral seed particles under otherwise similar experimental conditions. The figure shows that more SOA is formed in acidified seed experiments.

Manuscript changes in Table 1: Included the results from the four additional experiments. We also updated the wall loss-corrected SOA concentration and yields using updated relative ionization efficiency (RIE) values.

Manuscript changes in Section 3.1: “The data shown in Figure 1 and summarized

C2

in Table 1 also suggest that aerosol acidity promotes SOA formation: the SOA concentrations observed in acidified seed Exp. C7 are more than twice as high as SOA concentrations observed in neutral seed Exp. C2.”

Manuscript changes in Section 3.4: “Comparison of ACSM mass spectra (see Fig. S9) shows that the presence of acidic seed aerosol increases the contribution of organic ion fragments at m/z 82 (likely $C_5H_6O^+$) to the overall SOA mass (e.g. increases from 0.0055 in Exp. C2 to 0.0064 in Exp. C7; see Fig. S9), which is associated with IEPOX-derived OA (Budisulistiorini et al., 2013). Reduction in gas-phase product concentrations were also observed in the CIMS when the aerosol is acidic (see Fig. S10). These observations are consistent with increased partitioning of gas-phase products to the aerosol when the seed aerosol is acidic, resulting in the higher SOA concentrations shown in Fig. 1 and Table 1.”

Added Figure S9 to supplement: Additional figure comparing the ACSM unit-mass-resolution spectra obtained from neutral and acidified seed experiments

Added Figure S10 to supplement: Additional figure comparing the CIMS unit-mass-resolution spectra obtained from neutral and acidified seed experiments

Reviewer: 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.

Response: We have added additional details on our experimental protocol

Manuscript changes in Section 2.1: “Neutral seed particles were injected using an Aerosol Generation System (Brechtel, AGS Model 9200) with a 0.01 M ammonium sulfate solution; acidic seed injection used a solution containing 0.005 M ammonium sulfate and 0.0025 M sulfuric acid.”

2.) Reviewer: 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.

Response: We have attempted PMF analysis (without constraining factors) on these data but were unable to extract a factor related to IEPOX-OA. This is likely because the contribution of IEPOX-OA to total SOA mass from chlorine-initiated oxidation of isoprene, if present, is small. As mentioned in the revised manuscript, the observed f_{82} (the fraction of the total organic signal due to ions at m/z 82) is ~ 0.006 . Assuming that the IEPOX-OA factor would have an f_{82} value of 0.0132 based on the work of Budisulistiorini et al. (2013), the contribution of the IEPOX-OA to total OA in the present study would be at most 0.5%. It is considered infeasible to extract factors with such low contributions to total OA mass; for example, Ulbrich et al. (2009) suggest that only factors which contribute at least 5% to total OA mass can be extracted reliably using PMF. We have added this information to the revised manuscript.

Manuscript changes in Section 3.4: “Lastly, considering the observed f_{82} value (~ 0.006) and that typically associated with IEPOX-OA factors (0.013 \sim 0.022) (Budisulistiorini et al., 2013; Krechmer et al., 2015), IEPOX-OA is estimated to contribute

less than 0.5% to the total OA formed in these experiments. This suggests that the contribution of secondary OH chemistry to SOA formation initiated by chlorine radicals is minor.”

3.) Reviewer: 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.

Response: Additional references have been included.

4.) Reviewer: 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).

Response: Based on our CIMS measurements, multigenerational reaction pathways that could lead to hydroperoxide formation from continued oxidation of early C5 oxidation products are plausible. We show time series for some of these multifunctional chloroalkyl hydroperoxides in the updated Figure 6 and added a summary of a simplified suggested formation pathway in Figure 7 (an excerpt of which is attached to this response). References to previous work on hydroperoxide formation/oxidation under low NO_x are added as well.

Manuscript changes in Figure 6a and 6b: Updated with chloroalkyl hydroperoxides observed in both CIMS modes that match mechanistic expectations

Manuscript changes in Figure 7: Replaced with a summary of simplified (only one

C5

isomer is shown) reaction pathways that could give rise to the observed hydroperoxide species.

Manuscript changes in Section 3.4: “Multifunctional, low volatility hydroperoxides produced from non-IEPOX OH-isoprene reaction pathways under low NO_x condition have been found to contribute to SOA formation (Krechmer et al., 2015; Liu et al., 2016; Riva et al., 2016), and the same can be expected of the chloroalkyl hydroperoxide species identified in this work including C₅H₇ClO₃ and C₅H₈Cl₂O₃.”

(5). Reviewer: 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?

Response: The different injection methods were used to separate SOA formation from the effects of vapor wall loss. We have added some clarifying text.

Manuscript changes in Section 2.1: “Initial Cl₂ experiments were performed to achieve rapid oxidation of isoprene and to separate initial SOA formation from effects of vapor wall loss. Because chlorine radicals are not expected to regenerate, continuous Cl₂ injection experiments were performed to provide a steady Cl radical source to control the extent of gas-phase reactions.”

Manuscript changes in Section 3.1: “After extended photooxidation (T>100 mins), SOA concentrations achieved via initial chlorine injection and continuous chlorine injection differ by less than 8 μg m⁻³ (< 20% of total SOA mass at the time for Exp. C2), which could be attributed to vapor wall loss of early generation low-volatility products.”

Reviewer: 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-NO_x regions where Cl radical chemistry might matter. Can the authors offer which yield may be the most appropriate to use?

C6

Response: We have added the following qualifications and recommendations.

Manuscript changes in Section 3.3: "Under atmospheric conditions, the VOC to chlorine ratio will usually be higher than those used in these experiments. Previous studies on chlorine-initiated SOA formation from toluene (Cai et al., 2008) and limonene (Cai and Griffin, 2006) suggest that SOA yield decreases with higher VOC-to-chlorine ratio. While we do not observe a clear correlation between SOA yield and isoprene-chlorine ratios used in this work (0.49-1.22), such dependence could be present over a wider range of this ratio. For air quality models, the use of the continuous case yield, which is similar to recently reported OH-oxidation yields (Liu et al., 2016; Xu et al., 2014), is more appropriate because the isoprene-to-chlorine ratio is closer to atmospheric conditions. Furthermore, the SOA yields from continuous injection experiments account for fragmentation reactions in the atmosphere (which occur throughout the experiment). Thus, yields from continuous injection experiments should be used in air-quality models which do not explicitly account for fragmentation reactions."

Reviewer: 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.

Response: The different injection methods were indeed used to separate the effects of vapor wall loss from SOA formation, as clarified above. The wall loss correction method used accounts for depositional particle loss, as well as organic vapor loss to the deposited particles. Essentially, the correction method assumes that organic aerosols lost to the chamber wall would still participate in equilibrium partitioning as if they were suspended. Loss of organic vapor to the clean Teflon[®] surface is not accounted for here. This was described in more concise terms in the manuscript,

From Section 2.3: "Assuming internal mixing of particles and that organic vapor can condense onto suspended and wall-deposited particles alike, we corrected for particle wall loss and the loss of organic vapors onto wall-deposited particles using the organic-

C7

to-sulfate ratio (Hildebrandt et al., 2009)"

Minor comments

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

Response: We have removed "%"

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

Response: We have fixed this typographical error.

3.) Reviewer: 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.

Response: We have corrected the naming to 1-chloro-3-methyl-3-butene-2-one

4.) Reviewer: 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.

Response: We have modified the references as suggested.

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

Response: We have added the suggested reference.

6.) Reviewer: 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)

Response: We have added the suggested references.

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C8

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C9

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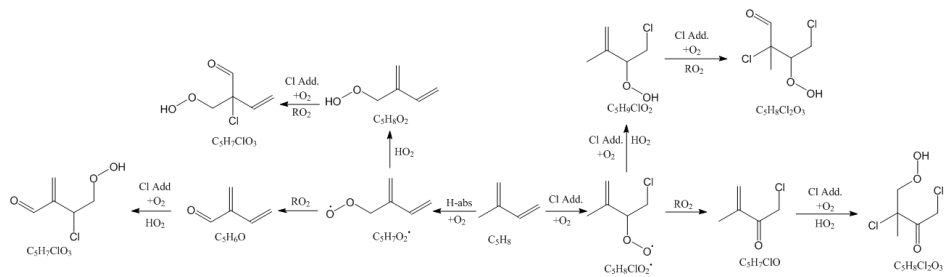


Fig. 1. Excerpt from Figure 7 showing potential hydroperoxide formation pathways