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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 #2

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Wang and Hildebrandt Ruiz provide the results of chamber studies of the low NOx chlorine oxidation of isoprene, the most abundantly-emitted BVOC globally. The most valuable aspects of the work are the determination of SOA yields and application of ACSM and CIMS measurements to the study. The application of these new techniques provide a significant opportunity for an in-depth/detailed study of the SOA formation. I encourage the authors to delve further into the mechanistic details of the isoprene-Cl-SOA production, perhaps through comparison of ACSM mass spectra between experiments (or during an experiment) and more in-depth comparison of the gas-phase data with previous isoprene-Cl oxidation studies reported in the literature, as these activities may provide new insights. It may be useful to construct a schematic of possible

reaction/oxidation pathways with highlights of key molecules, particularly since the authors suggest that the major reaction products are similar to OH oxidation. At the very least, it would be helpful to discuss potential oxidation pathways further, by considering temporal trends in the various gas-phase species that suggest different generations of trace gases. Perhaps you could calculate the O:C ratios of these molecules and estimate associated vapor pressures for support and to consider partitioning to the particle phase. Overall, it seems like more information can likely be extracted from the ACSM and CIMS data.

Major Comments:

- Introduction: In motivating their laboratory study, the authors may wish to point out marine emissions of isoprene and the consideration of isoprene SOA from this source (e.g. Gantt et al 2010, Atmos. Environ.). The authors currently do not consider the potential for Cl oxidation of isoprene far from coasts (where NOx may also be low), which is a motivating factor for this work.

- Throughout the manuscript, chlorine incorporated into organic molecules appears to be referred to as "chloride", which chemically refers to Cl-, rather than chloro-organics, or organic chlorine. This reference to chloride is confusing as it makes the reader question whether the authors are indeed suggesting that inorganic chloride is present in the particle phase. This needs to be clarified throughout.

- Sec 2.2, Instrumentation, should be clarified in the main text in terms of the description of the CIMS, for which additional information is needed. Perhaps material from the supplemental information should be moved here, in addition to revisions for clarity. It is stated that proton transfer, charge exchange, and clustering are all used for chemical ionization, which is confusing since typically one pathway is chosen through specific conditions within the ion molecule region of the instrument. As worded, it sounds like these reaction pathways of analyte ion formation are all occurring simultaneously. It is also odd to me that the instrument doesn't seem to have been tuned for conditions of

primarily H3O+, rather than (H2O)nH3O+. What fraction of the signal was associated with H3O+, and how many n were observed? This would impact the resulting analyte ionization. When were (H2O)nH3O+ vs (H2O)nI- reagent ions used? Did this switch back and forth during experiments, or was one ion chemistry used per experiment? Were CIMS experiments conducted during all experiments, or only during C3 and C5?

- Page 5, First Paragraph: Was a decrease in reagent ion signal observed compared to below an experiment? This might suggest a non-linear response and concern that reagent ion reactions could be limited even if still in excess. Without calibration of the signals, this would make trends more difficult to assess if in a non-linear regime. The phrasing on lines 5-6 about this is not clear. Also, why wasn't at least isoprene calibrated for since each experiment started with a known mole ratio? It seems like that would be beneficial to this work and could probably even be done retroactively with knowledge of the experimental parameters. Was "significant depletion of reagent ion" (Page S3, Line 24) observed during any experiment?

- In the results and discussion, it would often be helpful, when possible, to give values in parentheses, rather than vague descriptors so that you don't require the reader to review and correctly interpret the graphs.

- Section 3.2 should either be moved after section 3.4 or moved to the supplemental information. This section does not contribute much to our understanding of Cl-SOA or precursors, as it primarily focuses on an issue with the ACSM method, which while important, doesn't seem to be the main focus of this work. Rather than only identifying a potential issue, could a chlorinated organic standard be purchased and aerosolized for characterization so that the authors could provide a solution to the problem as well? Similarly, nearly a full paragraph in the conclusions is dedicated to this subject, which detracts from the exciting science studied. Also, use of m/z 36 here is not intuitive when referring to chloride.

- Page 7, Lines 11-12: It is not clear, as written, if you then used a 2D model here.

- Please review rules for significant figures for numbers and fix throughout. Please note that when reporting error only one significant figure should be used, with the same number of decimal places used for the average and the error.

- Can you compare ACSM mass spectra at different points during an experiment to examine possible evidence of oxidative fragmentation or vapor wall loss (as discussed on Page 7, Lines 18-19)? Could ACSM mass spectra be compared between experiments to examine the potential for differences in SOA composition?

- A conclusion of the study is that "The effects of SOA aging must be described explicitly and separately from initial SOA formation." (Page 9, lines 16-17) Yet, few details are given in the results and discussion for what this explicit description is. Above I suggested possible ways to provide greater mechanistic information on the Cl-isoprene oxidation and subsequent SOA formation.

- Another conclusion of the study is "Similarities between chlorine-isoprene and OH-isoprene oxidation products suggest that air quality models may be able to lump the treatment of SOA produced from chlorine- and OH-initiated oxidation of isoprene." Yet this is difficult to discern as very little discussion was dedicated to this important topic. There also appears to be no quantitative information that would indicate similar yields associated with various reaction pathways. More in-depth interpretation and discussion of the data is required to support this statement.

Minor Comments:

- Page 2, Line 11: It is unclear why Riedel et al 2012 is cited here, since that is a coastal marine study.

- Page 4, Line 12: It is confusing to have several equations on the same line. It would be preferable to have one equation per line and number as such.

- Page 4, Lines 17-18: The words "low" and "high" are vague, and it would be useful to include at least approximate values in parentheses as well, for example, to aid in

interpretation of these descriptors.

- Page 6, lines 4-5: This sentence states "high reactivity of chlorine radicals toward isoprene and its reaction products" and therefore seems to contradict the earlier sentence on page 5, lines 27-28.

- Page 6, Line 10: The phrase "quantification proved to be difficult" is vague.

- Page 7, Lines 13-14: I would suggest deleting this sentence, as the previous paragraph already explained this and having this information here as well could confuse the reader.

- Page 7, Line 15: For clarity, I suggest adding the following to the end of the sentence "...literature values of OH oxidation under low and high NOx scenarios."

- Page 7, Line 16: Why was the highest observed SOA yield reported, rather than an average, for example?

- Page 7, Line 16: By "continuous cases", do you mean continuous Cl2 injection during an experiment? Make sure this is clear.

- Hypochlorous acid is generally written as HOCl. I'm not used to ClOH, as written throughout.

- Page 9, Lines 1-2: This sentence is commenting on the method, moreso than the science and could be moved to the methods section or supplemental.

- Page 9, Line 16: It isn't clear why this sentence is needed to be highlighted in the conclusions.

- Page 9, Lines 18-24: It would be useful to merge this short paragraph with the first paragraph of the conclusions section.

- Figure 3 caption: This figure does not explicitly show oxidation state as stated in the caption, which is misleading.

- Figure 5 caption: For clarification, I suggest adding the phrase "corresponding to low and high NOx OH oxidation" at the end of the first sentence.

- Figure 6 caption: It is not clear what is meant by "interfering ions" here.

- S1: Please provide references for this section of the SI.

- Page S3, Line 13: Why would instrument sensitivity change over time?

- Page S3, Line 16: k does not appear to be defined.

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