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Atmospheric Chemistry and Physics Discussions

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.

(a) Reviewer: p.5, line 1: The limitations of estimating O:C, H:C, and the oxidation state of carbon from f44 based on empirical correlations should be briefly discussed. For example, equation S-1 in section S2 may underestimate O:C values substantially in environments dominated by NOx-free isoprene chemistry (Canagaratna et al., 2015). Also, the presence of heteroatoms may introduce deviations from equation S-3 in section S2 when estimating the oxidation state of carbon (Kroll et al., 2011).

Response: We have added discussion of the limitations of the empirical correlation and ACSM data to the revised manuscript

Manuscript changes in Section 2.3: "The empirical correlations were derived using a comprehensive collection of AMS datasets but may underestimate O:C values for SOA formed under low NOx conditions from isoprene or toluene (Canagaratna et al., 2015). Variability in f43 and f44 among different ACSMs have also been reported. (Crenn et al., 2015)."

Manuscript changes in Section S2: "Deviation from Eq. (S3) could occur due to the presence of peroxide groups or heteroatom groups, such as select chloroalkyl hydroperoxide compounds identified in CIMS measurements (Kroll et al., 2011).

(b) Reviewer: p.5, line 13: The separation of experiments A1-A5 and experiments H1/H2 seems to be somewhat arbitrary. In my opinion, experiment H1 should be experiment A6, and the much higher maximum yield of this experiment should be part of the discussion of section 3.3. Experiment H2 is a technical experiment to "...explore the ability of the ACSM to detect organic chloride" (supplement, section S4). I was confused to find information about H2 in Table 1, and I recommend to remove it from the table and just explain the character of this experiment in the supplement.

Response: We agree with the referee's recommendation. We have re-designated experiment H1 as experiment A8 and have conducted two additional initial chlorine injection experiments which are now designated as A6 and A7. Experiment H2 is now designated as experiment S1. Experimental details for Exp. S1 are now described in-text within supplement section S4.

(c) Reviewer: p.5, line 21: Chlorinated organic compounds have also been identified in ambient aerosol samples from Western Australia by ion cyclotron mass spectrometry (Kamilli et al., 2016), with a higher abundance of chlorinated organic compounds in daytime samples when photochemistry is active.

Response: A reference to this work has been added in section 3.1 of the revised manuscript.

d) Reviewer: p.7, line 19: The VOC:Cl2 ratios may be expected to be much higher under atmospheric conditions than in the presented experiments. Do the authors have some insight, or could they speculate about how the yields may change for larger isoprene:Cl2 ratios? Also, when presenting the highest observed SOA yields, why do the authors exclude experiment A1 for the average yield of the initial injection experiments?

Response: We have added discussion on a potential correlation between the VOC:Cl2 ratio and SOA yields, as well as details that may be of interest to modelers. The yield calculated from experiment A1 was in fact used in calculating the average initial chlorine experiment SOA yields in the discussion paper. The text "A2-A5" was a typographical error and has now been corrected to "A1-A5." Based on new calibration results we have also updated the relative ionization efficiency (RIE) values used in ACSM data analysis, which resulted in lower calculated yield values.

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 experiments). Thus, yields form continuous injection experiments should be used in air-quality models which do not explicitly account for fragmentation reactions."

e) Reviewer: p.8, line 8: When discussing secondary OH chemistry, the authors mention potentially unidentified HOx production pathways other than HO2 production during formation of CMBO. It would be extremely interesting to have at least a semi-quantitative estimate of the contributions of chlorine-initiated secondary OH chemistry vs. OH chemistry from other sources, potentially also due to chamber wall effects.

Response: We have carried out some chamber box modeling and expanded the discussion of HOx chemistry. Model results show that chlorine chemistry accounts for the majority of HO2 production when sufficient isoprene is present. Overall, chlorine radicals consume over 99% of the isoprene. Secondary OH-isoprene chemistry has very minor contribution to the overall photooxidation chemistry in these experiments.

Manuscript changes in Section 2.1: "Background effects were estimated using the SAPRC chamber modeling software (http://www.engr.ucr.edu/∼carter/SAPRC/) in combination with the Carbon Bond 6 (CB6r2) chemical mechanism which was modified to include basic gas phase inorganic chlorine chemistry in addition to Cl2 and ClNO2 photolysis (Sarwar et al., 2012; Yarwood et al., 2010). Wall effects are represented within the model by a constant emission of nitrous acid (HONO) from the chamber walls on the order of 0.1 ppb min-1, which was determined separately in chamber characterization experiments (Carter et al., 2005)."

Manuscript changes in Section 3.4: "The SAPRC chamber model results indicate that more than 99% of the isoprene reacts with Cl; secondary OH chemistry is therefore only a very minor pathway in these experiments. Model results also show that HO2 production is dominated by isoprene-chlorine chemistry when sufficient isoprene is present, whereas wall effects dominate HO2 production (>60 %) after all isoprene has been consumed. It is worth noting that the model does not explicitly represent Cl-initiated oxidation of reaction products, which can produce additional HOx radicals. Therefore, we expect the actual secondary OH chemistry to be more important than the current model estimation."

Technical Comments and Responses

-Reviewer: in manuscript: p.2, line 16 and p.7, line.27: When referring to isomers of CMBO, these should be isomers of chloromethylbutenone, e.g. 1-chloro-3-methyl-3-butene-2-one, not "isomers of 3-methyl-3-butene-2-one".

Response: We have corrected the naming

-Reviewer: p.3, line 23: Change "relatively ionization efficiencies" to "relative ionization efficiencies".

Response: We have corrected the typographical error.

-Reviewer: p.4, line 10: The reference should read "Odum et al., 1996".

Response: We have corrected the reference.

-Reviewer: p.9, line 4: Change "produced form" to "produced from". p.9, line 6: Change "chlorine-initiation oxidation" to "chlorine-initiated oxidation".

Response: We have corrected the typographical errors

-Reviewer: p.18, Table 1: I don't understand the value of the VOC:Cl2 ratio in experiment H2.

Response: Wrong precursor concentrations were reported for Exp. H2. We have corrected the errors in the revised manuscript.

-Reviewer: p.3, line 7: Change "number of water cluster" to "number of water clusters". p.4, line 7: Remove "greater than" before "44 % overestimation could be expected".

Response: We have modified the texts as suggested.

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