

Interactive comment on “Technical Note: Conversion of Isoprene Hydroxy Hydroperoxides (ISOPOOH) on Metal Environmental Simulation Chamber Walls” by Anne-Kathrin Bernhammer et al.

Anonymous Referee #1

Received and published: 22 November 2016

This manuscript provides a straightforward explanation of the potential for biases in measurements of functionalized volatile organic compounds (VOCs) made in environmental chambers containing metal surfaces. It had previously been reported that instrumental setups, particularly those containing heated metal, could interfere with VOC measurements by providing sites for heterogeneous reactions to occur; here, the authors provide evidence that such reactions can occur on metallic chamber walls as well. In this study, the authors use selective reagent ion mass spectrometry to measure the VOC products of isoprene ozonolysis in a stainless steel chamber, and compare those measurements to simulated concentrations of the same VOCs using a box

C1

model with chemistry from the Leeds MCM. Major discrepancies are found between measured and modeled concentrations of methyl vinyl ketone (MVK), methacrolein (MACR), formaldehyde, and ISOPOOH. Those discrepancies can largely be fixed by inclusion in the model of a decomposition reaction, in which ISOPOOH is catalytically converted on the chamber surface to formaldehyde and MVK or MACR (depending on the ISOPOOH isomer). The resulting conclusion - that decomposition on metal surfaces can represent a major loss process of ISOPOOH and can contribute markedly to increases in observed MVK and MACR concentrations in chamber experiments - is mostly insensitive to variations in assumptions in the model, such as OH concentrations and collision efficiency. It will be important to consider this effect and take it into account in future (and perhaps past) studies, and to investigate how it extends to other surfaces (e.g. plants), other experimental conditions (e.g. temperature and humidity), and other compounds (e.g. broader hydroperoxides).

General comments:

While the manuscript is qualitatively important in that it points out a previously unconsidered potential source of error in other studies involving hydroperoxides in metal chambers, in order for this to be quantitatively useful, it would be helpful to have some estimate of uncertainty. For example, correcting the product distributions of previous studies of isoprene photolysis or effectively designing new studies to avoid interferences in metal chambers will require estimates not just of the decomposition rate that best fit the measurements in the present study, but of the range of possible decomposition rates consistent with the measurements. Most useful, perhaps, would be upper and/or lower limits on the model parameters - e.g. collision efficiency and OH concentration - that might be extended to other studies. There are many elements where uncertainty enters into the results reported herein - modeled OH yields from ozonolysis, conversion efficiency of hydroperoxides on surfaces, measurement of compounds - and although some are treated individually in the manuscript (with Figures 2 and 6 showing how changing OH and conversion efficiency affect the model output), a more

C2

comprehensive treatment of the aggregated uncertainty in the conclusions would make the results more broadly applicable, and aid in extending the findings to other studies.

Along those lines, connecting these results to other studies and other systems will be key. Are there previous studies - particularly photooxidation product studies - in which metal surfaces have been used before, such that previously reported results may be called in to question or require adjustment based on the findings detailed herein? If so, some mention of those cases in the conclusion and implication sections would be warranted. Additionally, are there related systems that involve hydroperoxides to which this work might apply?

Content comments:

Page 5, line 27: How does this OH production rate compare with other estimates, and what effect does that have on the model? Similarly, it might be useful to perform some sensitivity studies, changing your modeled yields of not just OH but MVK and MACR from isoprene + O₃ (and isoprene + OH) and seeing how much that affects the results. It appears from a following paragraph (page 6, lines 7-13) and from Figure 2 that you performed some such studies; from those studies, can you conclude that the OH production rate used in the model was reasonable, or can you put any level of uncertainty on it?

Page 5, line 30: What does this [OH] number refer to? The modeled range of concentration present in the chamber when using the 26% yield number?

Page 7, line 5: The conversion efficiency per collision is another element in which it would be nice to look at the sensitivity of your results to the assumptions made. Figure 6 shows some of the model results if you loosen the assumption that conversion efficiency is not quantitative, but how do these values fit within the measurement uncertainty of MVK and MACR? How well does the modeled ISOPOOH match measurements? Using these values and the measurement uncertainty, can you estimate a range in which the conversion efficiency is likely to fall (or, perhaps more importantly, a

C3

lower limit)?

Page 7, line 8-10: Do you have a reference for the formation of unsaturated C₅-diols from ISOPOOH? In general, it would be nice to see the model-measurement discrepancy in ISOPOOH mixing ratios appear more in the results - say, in additional panels in Figure 3, or panel D of Figure 2. The formation of C₅-diols may cause further discrepancy between measurements and models, but if so, that discrepancy should be quantifiable; if it points to an additional loss process, how does that compare to the processes shown in Figure 5?

Page 7, line 15: Do you have a reference for the claim that uncharacterized wall production of formaldehyde is common in chamber experiments? If it is common enough to have been quantified in the past, is it possible to estimate whether that source could account for the missing fraction you observe?

Page 7 line 32 - page 8 line 1: Do you expect there are conditions under which the residence time on surfaces would be too short for the reaction to occur efficiently, or under which the limiting factor in ISOPOOH decomposition would be something other than the collision rate?

Minor copyediting comments:

Page 1, line 27: "affection" should perhaps be "affecting"

Page 2, line 29: "ISOPOOH decomposes isomer specific to smaller carbonyls" is unclear.

Page 3, line 11: "26 m electro polished stainless-steel " should read "26 m³ electropolished stainless steel"

Page 3, line 28: "being" is not needed

Page 3, line 31: parentheses not needed for this citation

Page 5, line 14: "rates" should be "rate" (or "plays" should be "play")

C4

Page 6, line 5: What do you mean by “makes up for”? Was there a 1.2-2 ppbv (50%) discrepancy in the modeled and observed MVK that is now accounted for? Or do you mean the total difference between measured and modeled MVK is 1.2-2 ppbv? And is that 50% of the modeled or measured total? Also, missing a “-“ between 0.6 and 1.2.

Page 7, line 3: “occurs” should perhaps be “are”

Page 7, line 14: what exactly does the 40% refer to? Is 5 ppbv equal to 40% of the average total formaldehyde signal?

Page 8, line 1: “ISOPPOOHs” should be “ISOPPOOH's”

Page 8, line 3: tense disagreement between “was” and “undergoes”

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-816, 2016.