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Interactive comment on “Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis” by M. I. Jacobs et al.

Anonymous Referee #2

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Overall Comment and Recommendation:

The authors of this manuscript synthesized 3 of 8 isoprene-derived hydroxynitrates (4-hydroxy-3-nitroxy isoprene, 4,3-HNI; E-1-hydroxy-4-nitroxy isoprene, E-1,4-HNI; Z-1-hydroxy-4-nitroxy isoprene, Z-1,4-HNI) and subsequently determined the OH rate constant and reaction products from 4,3-HNI oxidation in a flow tube interfaced to PTR-CIMS. In addition, the authors examined the hydrolysis rate in bulk aqueous solutions (representing aerosol processes) for 4,3-HNI and E/Z-1,4-HNI isomers using their previously established NMR technique. The study presented here was well conducted and described by the authors. This manuscript will certainly be of large interest to the read-

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ers of Atmospheric Chemistry and Physics, especially since 3 of the 8 possible HNI isomers were synthesized and examined for their potential gas- and aerosol-phase reactions. Notably, the authors found that a minor but significant yield of IEPOX was formed from the OH-initiated oxidation of 4,3-HNI. The observation of IEPOX formation from the HNI + OH reaction is interesting and could help to explain prior observations. For example, in Surratt et al. (2010, PNAS) it was found under initially high-NO conditions that the organosulfate derivative of IEPOX was detected at m/z 215 by LC/ESI-MS (see Figure 4, top panel from that paper). Further recent work by Budisulistiorini et al. (2013, ES&T) in downtown Atlanta observed a substantial fraction of IEPOX-derived SOA by online aerosol mass spectrometry (i.e., ACSM); specifically they found on average during summer that IEPOX-derived SOA contributed 33% of the total OA mass measured in downtown Atlanta. Of course, some of the IEPOX-derived SOA was likely transported from upwind locations, but this new work does suggest that IEPOX-derived SOA from IEPOX formed by HNI + OH could be contributing as well in areas like urban Atlanta that is impacted by both large isoprene and vehicular NO_x emissions. Furthermore, this work makes the important conclusion that traditional descriptions of high- and low-NO_x conditions may longer be appropriate in describing the formation of SOA from isoprene. For example, it might be more appropriate to describe it as IEPOX-favorable conditions. Overall, I support this manuscript for publication in Atmospheric Chemistry and Physics. I noted the short comment posted in the discussion by the Caltech group (Lee et al.) that they have also observed IEPOX from the OH-initiated oxidation of HNI at similar yields as predicted by Jacobs et al. here at atmospheric pressure. This was a concern I had when originally reading this manuscript, but knowing the Caltech group has explored this at near atmospheric pressure conditions further supports the significance of the work presented here. Before publication, I request that the authors address the following specific and minor comments listed below.

Specific Comments:

1.) Flow tube uncertainties: Was your flow tube coated with any type of halocarbon

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wax, acting to prevent substantial losses of certain gaseous products, such as the IEPOX? This seems important and I wonder if the authors have any sense of their losses and how well these have been characterized within their flow tube? How might potential losses of compounds or compounds on the walls of the flowtube that come back into the gas phase over time affect the results presented here? I think the authors need to carefully describe any potential uncertainties.

2.) PTR-CIMS measurements: One thing that I do worry about is what is the potential formation of other isomers that correspond to the same m/z (i.e., m/z 119) detected by the PTR-CIMS? Since your CIMS is a quadrupole you can't rule out other isomers at m/z 119 contributing to this signal, such as ISOPOOH (Paulot et al., 2009, Science), C5-alkene triols (Wang et al., 2005, RCM), and 3-methyltetrahydrofuran-3,4-diols (Lin et al., 2012). In my group we have found we can detect all of these isomers at the same m/z using acetate and iodide CIMS. Not that I'm saying your measurements are bad, but that is the problem with your quad and my group's TOFMS, we can't do MS/MS experiments like the Caltech group to better isolate which isomers are contributing to these ion signals and also determine the fractions in which they do. I think you have to at least mention some where in the text that this is a limitation of your MS measurements and could certainly affect the yields you report if isomers are co-present by some unknown or unrecognized chemistry.

3.) Hydrolysis kinetics: I'm curious, why didn't the authors also consider using H₂SO₄ in their hydrolysis experiments since that might be more relevant than HClO₄? Would different acids potentially matter due to differences in nucleophiles?

4.) Assumption of Equal Response Factors for PTR-CIMS: How valid is this assumption? Have the authors done tests with standards to confirm this or are they referring to prior work? If the latter, then please cite the relevant work. I suspect this may not be a good assumption based on my own group's recent work with calibrating our CIMS with different authentic standards.

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5.) Context of your findings with organic nitrates observed previously in SOA: From the hydrolysis and OH oxidation studies presented here, I wonder if the authors can put these findings into context for organic nitrates observed previously by Surratt et al. (2006, JPCA; 2010, PNAS)? Organic nitrate oligomers were observed previously in isoprene SOA produced in the presence of NO_x and I wonder if instead that 4,3-HNI (or another isomer) is oxidized in the gas phase that yields a C₄ backbone organic nitrate product that could condense and then be incorporated in aerosol oligomerization processes? For example, I'm thinking if it condenses into the aerosol phase then it might be available to act as a nucleophile for methacrylic acid epoxide (MAE) (Lin et al., 2013, PNAS), and thus, helping to explain the formation of oligomeric nitrates previously observed.

Minor Comments:

- 1.) Introduction, Page 12123, Line 19: Citations are needed for this statement.
- 2.) Section 2.4.4, Page 12129, Line 1: missing a subscript O for "[4,3-HNI]_t,"
- 3.) Section 2.4.4, Page 12129, Line 2: missing a subscript O for "t,"
- 4.) Section 2.4.4., Page 12129, Line 11: Don't you mean [4,3-HNI] instead of epoxide?
- 5.) Section 2.4.5., Page 12130, Line 9: I would insert "mass" before the word "spectra" to be more specific.
- 6.) Section 2.4.5., Page 12130, Lines 23-24: I'm assuming you weren't able to measure the OH reaction rate of 4,3-HNI and its products at 760 torr due to experimental limitations, right? Maybe say that specifically here?
- 7.) Section 3.2, Page 12132, Lines 23-25: When the authors say overlap problem for the E and Z isomers, does this mean you synthesized them as a 1:1 mixture? Please clarify.
- 8.) Section 3.3.1., Page 12134, Lines 18-20: Do the authors mean to say "data for

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each competitor were plotted together"?

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