

Responses to each reviewer comment are in bold font.

Reviewer(s)' Comments to Author:

Reviewer 1:

This paper presents measurements of the kinetics of the reaction of isoprene-derived hydroxynitrates with OH radicals using relative rate techniques, including measurements of the product yields and ab initio calculations of the potential energy surface for the reaction. In addition, the authors present measurements of the kinetics of hydrolysis of these hydroxynitrates. Understanding the fate of these nitrates is important given the significance of isoprene emissions to atmospheric chemistry as they may be an important sink of NO_x under “high NO_x” conditions. The authors find that an isoprene epoxide previously believed to be produced only under “low NO_x” conditions is a minor but a significant product of the OH radical reaction with 4-hydroxy-3-nitroxy isoprene (4,3-HNI) isomer that has been shown to be an important precursor to the formation of secondary organic aerosols. Based on the product analysis, the authors propose a mechanism for oxidation of this hydroxynitrate that results in the release of approximately 30% of the NO_x sequestered through the formation of epoxides and other products. This is a new result that suggests that the chemistry of isoprene emissions is more subtle than previously thought.

The experiments are well designed and the paper is well written and suitable for publication in ACP after the authors have addressed the following comments:

1) The authors suggest that the overall rate constant for the OH + 4,3-HNI isomer is likely at the high-pressure limit similar to that observed for the OH + isoprene reaction (page 12137). However, the observed pressure dependence of the epoxide product seems to suggest that reaction may not be at the high pressure limit, as the rate of collisional quenching and reaction of the energized OH-4,3-HNI adduct (reactions R8 and R10) are slow relative to formation of IEPOX (reaction R9) at low pressure. It is not clear whether the authors measured the overall rate constant as a function of pressure to demonstrate that the measured rate constant is independent of pressure, and that dissociation of the energized complex back to reactants (reaction R7) is slow relative to formation of products (R8 -R10). Given the observed pressure dependence of IEPOX production, it would be valuable to measure the overall rate constant at different pressures to ensure that the overall rate constant is indeed at its high pressure limit at 100 Torr.

Response: Our measured OH reaction rate constant at 100 Torr was found to be nearly identical to the atmospheric pressure rate constant previously reported (Lee et al., 2014). Since a comparison of these two measurements suggests that the 100 Torr rate constant measurement is already at the high pressure limit, further pressure dependent rate constant measurements were deemed unnecessary. This explicit argument has been added to Section 3.3.1 of the revised manuscript.

2) The authors calculate the relative yields of IEPOX, MVKN and HAC from the oxidation of 4,3-HNI at atmospheric pressure based on the measured yields at 50 Torr and the observed pressure dependence of the IEPOX yield, assuming that the ratio of MVKN to HAC formation is constant as a function of pressure, which was experimentally observed (page 12139). A similar method was used to calculate the product yields from the oxidation 1,2-HNB at atmospheric pressure (page 12140). However, the ratio of the measured yields of MVKN and HAC are not the same at the different pressures Table 2). The paper would benefit from an expanded discussion and clarification of the calculated yields. Did the

authors measure the yields of MVKN and HAC at different pressures? Including the measured yields of all the products as a function of pressure would give more confidence in the calculated yields at atmospheric pressure.

Response: MVKN and HAC were monitored at each of the pressures and, on average, the ratio of their yields was observed to be constant. We have revised the manuscript to include the average ratios of the product yields with their statistical uncertainties. For 4,3-HNI this average MVKN:HAC product ratio was 4.01 ± 0.98 , and for 1,2-HNB the average C3-C4 bond splitting:C2-C3 bond splitting ratio was 5.8 ± 1.6 .

Minor comments:

Abstract/Introduction: There is no mention of the measurements of 1,2-HNB oxidation in the Abstract or Introduction. It was unclear why the hydrolysis rate constants for this compound were measured in section 2.3 until the motivation for the measurements was discussed in section 2.5.2. A brief statement in the introduction as to why these measurements were included would help to clarify the motivation for including these measurements.

Response: We have added the following sentence to the end of the Introduction section of the revised manuscript: “The oxidation and hydrolysis kinetics of a similar, unsaturated hydroxynitrate (1-hydroxy-2-nitroxy-3-butene (1,2-HNB)) were also investigated in order to explore the generality of mechanisms gleaned from similar study of the isoprene-derived species.”

Page 12129, line 7: $\ln([epoxide]_t,0/[epoxide]_t,OH)$ should probably read $\ln([4,3-HNI]_t,0/\ln[4,3-HNI]_t,OH)$

Response: This typo has been corrected.

Page 12138, line 22: There appears to be a typo in this equation – the α probably should be an =.

Response: The proportionality symbol is correct. If the expression were an equality, several constants relating to ideal gas unit conversions would need to be present. Since the main purpose of the expression is show the linearity as a function of pressure, we felt the equality expression was distractingly complex.

Reviewer 2:

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 readers 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 no 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 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 flow tube 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.

Response: The following text was added to end of Section 2.4.5 of the revised manuscript: “At the experimental pressures and timescales, it has also been shown that the flow tube acts as a nearly wall-less reactor (Seeley et al., 1993), which helps to ensure that the measured relative gas phase concentrations are representative of the true relative product yields. Nonetheless, the flow tube was also coated with halocarbon wax to further reduce gas-wall interactions and care was taken to ensure that product signals were fully equilibrated at each point in the measurement.”

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.

Response: We've added the following statement to Section 2.4.5 of the revised manuscript to explain the possibility of having more than one product at a given mass: "Different isomeric species with the same m/z ratio cannot be distinguished with this quadrupole-based CIMS instrument; therefore the proposed products are those that are easiest to rationalize in the context of the proposed mechanism and the experimental conditions." However, as a 2nd generation OH oxidation product, ISOPOOH should not form under our conditions of very high HNI concentrations. We also don't consider C5-alkene triols and 3-methyltetrahydrofuran-3,4-diols as likely species since the current evidence suggests that these are species produced on SOA and not via gas phase processes.

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?

Response: HClO₄ was used to avoid adding a nucleophile (such as SO₄²⁻) that could compete with water in the nucleophilic reactions of HNI. Therefore, our measurements were intended to be relevant to a situation in which water is the dominant nucleophile.

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.

Response: We have not extensively investigated response factors for the kind of multifunctional species observed as products of the HNI oxidation (this is difficult due to the low, unknown vapor pressures of these species). However, since all product species have OH functionality, and previous work has shown that a variety of alcohol species have virtually identical PTR rate constants (this citation has been added to the revised manuscript in Section 2.4.5), we believe that this assumption is a reasonable one.

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.

Response: The reviewer's proposed reaction of MAE with MVKN on SOA is certainly possible. However, since MVKN does not have the same molecular formula repeat unit as a ring-opened nitrate addition product of MAE, it doesn't seem likely that MVKN is involved in the formation of the oligomeric nitrates reported by Lin et al.

Minor Comments:

1) Introduction, Page 12123, Line 19: Citations are needed for this statement.

Response: We believe that this generic statement about the addition of nitrate functional groups to hydrocarbons leading to reduced volatility and increased hydrophilicity follows from general intermolecular interaction principles and does not merit a specific citation.

2) Section 2.4.4, Page 12129, Line 1: missing a subscript O for "[4,3-HNI]_t,"

Response: This typo has been corrected.

3) Section 2.4.4, Page 12129, Line 2: missing a subscript O for "t,"

Response: This is not a typo.

4) Section 2.4.4., Page 12129, Line 11: Don't you mean [4,3-HNI] instead of epoxide?

Response: This typo has been corrected.

5) Section 2.4.5., Page 12130, Line 9: I would insert "mass" before the word "spectra" to be more specific.

Response: "mass" was added.

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?

Response: We have added: "Due to the pressure-dependent efficiency of the microwave discharge source, measurements could not be performed at pressures greater than 400 Torr."

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.

Response: In the supplement (page S6-7) we mention that primarily E-1,4-HNI was formed, not a 1:1 mixture.

8) Section 3.3.1., Page 12134, Lines 18-20: Do the authors mean to say "data for each competitor were plotted together"?

Response: This typo has been corrected.