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Atmospheric Chemistry and Physics Discussions

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 #1

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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 NOx under "high NOx" conditions. The authors find that an isoprene epoxide previously believed to be produced only under "low NOx" conditions is a minor but a significant product of the OH radical reaction with 4-hydroxy-3-nitroxy

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Interactive Discussion
Discussion Paper

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 NOx 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.

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

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(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.

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.

Page 12129, line 7: ln([epoxide]$_{t,0}$/[epoxide]$_{t,OH}$) should probably read ln([4,3-HNI]$_{t,0}$/ln[4,3-HNI]$_{t,OH}$)

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

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 12121, 2014.