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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Isoprene nitrates: preparation, separation, identification, yields, and atmospheric chemistry" *by* A. L. Lockwood et al.

Anonymous Referee #1

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The OH-initiated oxidation of isoprene in the presence of NO can lead to potentially 8 different hydroxy nitrate isomers. This manuscript describes the preparation and identification of three different isoprene-derived hydroxy nitrates. These compounds are then used as standards in the interpretation of GC-MS data obtained from the oxidation of isoprene in an environmental chamber. All eight possible hydroxy nitrate products formed in the oxidation of isoprene are identified and quantified for the first time. This isomer-specific data provides interesting details concerning the stability of the peroxy radical intermediates and the measured overall hydroxy nitrate yield helps to narrow the experimental uncertainty in the production of these important temporary peroxy and NOx reservoirs (which are critical in the modeling of the production tropospheric ozone production by isoprene). Therefore, I expect that this work will be of great interest to the atmospheric chemistry community.

The work has been carefully planned and executed, and the analysis is logical (especially where some speculative assignments are required). However, there are a number of issues related to the clarity of the prose of the manuscript as well as some missing details that the authors should consider before preparing a final version of the manuscript.

p. 10626, line 4: "isoprene nitrates" should be properly defined as "isoprene hydroxy nitrates" in the abstract before explicitly switching to the short hand notation "isoprene nitrates" in the main body of the manuscript.

p. 10626, line 11: The author's "isoprene nitrate" nomenclature is used, but not defined in the abstract, so that it will be meaningless to readers who are browsing the abstract. Perhaps replace with: "Three isomers dominated the observed isoprene oxidation product distribution: two different hydroxy nitrates (with the hydroxy group at the terminal chain position in both cases) formed from reaction at each of the double bonds in isoprene and a hydroxy nitrate formed from the allylic rearrangement of the isoprene backbone."

p. 10628, line 1: It would be helpful to give a figure that shows this oxidation process. It's confusing to refer to the oxidation products of the oxidation products of isoprene. This is a pretty important point, since one of the main findings of the work is that the INs are fleeting species...

p. 10632, line 17: Typo: "Isoprene (concentrations were) determined. . .."

p. 10633, line 23: Is the reason that only 3 isomers are expected is that the tertiary carbocation intermediate is particularly stable? In other words, is this the explanation for why (2,1)-IN is not formed in this synthesis?

p. 10634, line 6: "unresolved" would be a more accurate word choice than "unseparated"

p. 10634, line 18: This sentence is confusing because "yields" clearly refers to the

photochemical experiments, but this sentence falls in the middle of a discussion concerning the synthesized INs.

p. 10634, lines 24-25: There should be more discussion of the unidentified peaks in Figure 4. It sounds like the authors think they know what the longer retention time peaks are so they might as well put this information in the manuscript. Do the authors have ideas for the shorter retention time peaks? Are the INs falling apart in the GC column?

p. 10636 line 8: What are the assumptions in the OH + IN correction calculation? How reliable are the predicted rate constants likely to be?

p. 10639, line 6: "These values. . ." Based on the language that follows, I think that the authors are referring to rate constants, rather than lifetimes. This should be clarified.

p. 10644, Table 1: It would be much more clear if the authors included separate columns for the OH and O3 lifetimes rather than a single column of lifetimes (It's not at all obvious which INs have lifetimes dictated by OH reactivity vs. O3 reactivity).

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 10625, 2010.