

***Interactive comment on “Technical Note:
Preparation and purification of atmospherically
relevant α -hydroxynitrate esters of monoterpenes”
by Elena Ali McKnight et al.***

Anonymous Referee #1

Received and published: 14 August 2019

General comments

This manuscript describes the synthesis and characterization of a number of hydroxy nitrate esters of monoterpene compounds. Specifically, the work refines a previously identified route to hydroxy nitrate esters – reaction of epoxide precursors with bismuth nitrate – and shows that it is a general pathway to a variety of potentially important nitrate esters. Because of the need for analytical standards for organic nitrates, this work will be of interest to readers of Atmospheric Chemistry and Physics. I recommend publication after the authors consider the following suggestions for improvement of the manuscript.

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Specific comments

p. 2 line 24: The cited work was not controversial - it was a case of scientific fraud. I would change this last clause to "and has been subject of a retracted study."

p. 3 line 7: It seems as if the column chromatography method is critical to the success of this work (intractable mixtures turn out to be tractable). Is this particular system critical to this success? I'm not familiar with it.

p. 3 line 25: ^{13}C NMR data is very useful when using reference data to analyze complex mixtures. I see that some species have ^{13}C characterization, and some don't (like this species). It would strengthen the utility of this work if as much ^{13}C characterization were included.

p. 7 line 1: There should be a reference to the numbering system here (or preceding this section) and the information given that the structures are given later in the paper. I also think the name should include monoterpene precursor to help keep track of the various species.

p. 19 line 18: The authors should expand on how their results bear on previous work. Generally, it would be valuable to point out that these reactions generally lead to ring opening of the bicyclic backbone of the monoterpene. The atmospheric chemistry literature contains a number of proposed monoterpene epoxide reaction products in which the bicyclic backbone is retained (for example, see Duporte, G et al. Experimental Study of the Formation of Organosulfates from α -Pinene Oxidation. Part I: Product Identification, Formation Mechanisms and Effect of Relative Humidity. The Journal of Physical Chemistry A 2016, 120 (40), 7909–7923) even though the synthetic literature shows that this is not usually the case. Specifically, it should be pointed out that Rindelaub's compounds 1 and 2 are the present work's compounds 17 and 22, and some comparison of the two methods should be given. The authors should also summarize the species for which they were not able to isolate compounds (such as several tertiary nitrates, which have previously been shown to highly susceptible to hydrolysis) since

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this is valuable information concerning the potential stability of these compounds in the atmosphere.

Technical corrections

p. 2 line 10: typo (incomplete citation)

p. 11 line 1: type: add "oxide" to heading name

Figure 7, Compounds 23 and 24: It is very difficult to see the dashed line bonds to the nitrate groups.

p. 16 line 3: typo: slashed "o" should be lower case

p. 16 line 12: typo: author name is currently in all capital letters

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-690>, 2019.