

Interactive comment on “The Acid-Catalyzed Hydrolysis of an α -Pinene-Derived Organic Nitrate: Kinetics, Products, Reaction Mechanisms, and Atmospheric Impact” by Joel D. Rindelaub et al.

Anonymous Referee #1

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This manuscript describes bulk solution experiments aimed at understanding the possible aerosol phase hydrolysis of organic nitrates derived from alpha-pinene under conditions of varying acidity. The main finding of the work is that the kinetics of the hydrolysis process is fast compared to aerosol lifetimes, and is acid-catalyzed, indicating that the process will be even faster for low pH aerosol particles. This finding would be important in that it suggests that aerosol phase partitioning of organic nitrates may be an important sink for NO_x, with a correspondingly important impact on the accuracy of atmospheric chemical models.

However, there are two aspects that lead me to be concerned that the authors have not definitively identified the chemical species that they have studied.

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One aspect is a problem with the manuscript itself. While I think that that the authors are claiming that they have synthesized and studied the secondary organonitrate depicted in Figure 6 from hints in the text discussion, there is really no discussion of how the authors determined which of the isomers they determined they had actually synthesized, and Figure 1 confusingly shows the tertiary organonitrate.

The other aspect is more fundamental. I don't believe that the ^1H NMR chemical shifts reported for the organonitrate species are obviously consistent with either of the two possible isomers. In particular, two chemically inequivalent protons with chemical shifts of about 5.6 ppm are reported. Muthuramu et al. *ES&T* 1993, 27, 1117-1124 demonstrated that protons that are geminal to nitrate groups for simple hydroxynitrates shift about 1.2 ppm higher compared to protons that are bonded to carbons with a geminal hydroxyl group instead (for example, compare the relevant proton in 2-nitrooxy-3-hydroxybutane to 2,3-butanediol), while the hydroxyl protons themselves shift to a lower chemical shift value in the hydroxynitrates as compared to the diols. This information, in conjunction with the NMR spectrum for pinanediol, can be used to predict the proton chemical shifts for the proposed organonitrates. Zhu et al. *J. Med. Chem.* 2009, 52, 4192–4199 reported the ^1H NMR spectrum for the two stereoisomers of pinanediol. For both stereoisomers, the proton on the secondary carbon bonded to a hydroxyl group is observed at about 4.0 ppm. The hydroxyl group protons are observed, depending on the particular stereoisomer, between 2.8 and 3.5 ppm. All of the other protons are observed at chemical shifts of 2.5 ppm or less. Therefore, for the proposed secondary organonitrate structure, one would expect a single proton chemical shift at about 5.2 ppm ($4.0 + 1.2$ ppm), which is reasonably consistent with one of the 5.6 ppm peaks reported in the present work. However, no other peaks above about 3.5 ppm would be expected for the secondary organonitrate species. For the tertiary organonitrate species, no peaks at all in the 5-6 ppm range would be expected. On the other hand, chemical shifts in the 5-6 ppm range have been observed for a number of ring-opened olefinic reaction products of alpha-pinene oxide (Bleier et al. *JPCA*, 2013, 117, 4223-4232), the reagent used to prepare the reactant in the present work.

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Therefore, I think the presence of the second 5.6 ppm peak opens up the possibility that the authors have prepared an organonitrate species with a double bond, and it is the reaction of this species that they have actually studied. Of course, it is possible that the proposed secondary organonitrate species has a very unusual ^1H spectrum that can't be predicted by the process described above, and the authors have in fact correctly identified the reactant structure (perhaps the authors have additional unreported information, such as a ^1H spectrum taken in D_2O that indicates that one of the 5.6 ppm peaks is the hydroxyl proton with an anomalously large chemical shift value?). In any case, there certainly isn't enough data reported in the manuscript for such an assignment to be considered definitive. It is probably the case that one dimensional ^{13}C and perhaps ^1H - ^1H and/or ^1H - ^{13}C two dimensional NMR spectra are needed to definitively identify the structure of the synthesis product.

Additionally, the authors report that campholenic aldehyde, pinol, and pinocamphone reaction products were identified via GC-MS methods. Since none of these species are commercially available as standards, it's not clear to me how definitive identification of the reaction products was made.

Because neither the reactant nor the products of the main chemical reaction under study have been convincingly identified, I believe that these issues must be addressed in a revised manuscript.

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