

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 #2

Received and published: 14 October 2016

This work investigated the hydrolysis of α -pinene derived organic nitrate (APN), isopropyl nitrate, and isobutyl nitrate in solutions of varying pH. It was found that the hydrolysis rate constant increases with solution acidity for all compounds studied. The lifetime of APN with respect to hydrolysis increases from 8.3 min to 8.8 hr for solutions with pH = 0.25 and pH = 6.9, respectively. Campholenic aldehyde, pinol, and pinocampone were identified as hydrolysis products. Theoretical calculations were performed for the hydrolysis mechanisms for isobutyl nitrate using Density Function Theory, and analogous mechanisms were then proposed for the hydrolysis of APN. A unimolecular specific acid-catalyzed mechanism was proposed.

The manuscript is generally well-written. The work will be of interest to the atmospheric

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research community and will add to the growing recent studies on organic nitrate formation and fates. The results are interesting and have important implications. I have several main comments:

Firstly, the manuscript should provide more context and carefully compare and contrast the results from this study to prior published work. Instead of just briefly mentioning prior literature, the authors should discuss any discrepancies in more detail. For instance, with Jacobs et al. (ACP, 2014) with respect to the specific acid-catalyzed mechanism, with Darer et al. (ES&T, 2011) and Hu et al. (ACP, 2011) with respect to the hydrolysis rates of primary/secondary organic nitrates, etc. Further, the results reported here are quite similar to the work by Bleier and Elrod (J Phys Chem A, 2013), who investigated the hydrolysis of α -pinene oxide under acidic conditions. However, other than mentioning that campholenic aldehyde is also identified as a major product in Bleier and Elrod, there is no further discussion regarding similarities/differences between their results and those reported in Bleier and Elrod. This should be addressed. Bleier and Elrod have also identified other products (pinol, etc) and proposed reaction mechanisms for the formation of these products. In this regard, it'd be important for the authors to specify clearly what is new in this study.

Secondly, the authors did not provide specific details on how the hydrolysis products are identified and verified. Since this is an essential part of the manuscript and affects all the discussions on the proposed mechanisms, this info needs to be included in the revised manuscript.

Lastly, the organics nitrates discussed in this manuscript are from photooxidation under high NO_x condition; however, nitrate radical oxidation of BVOC is another important source of organic nitrates (Ng et al., ACPD, 2016), where the relative abundance of primary/secondary/tertiary organic nitrates and their fates can be different from those formed from OH oxidation. When discussing “hydrolysis of organic nitrates” throughout the manuscript, it is important that the authors make it clear regarding the specific origins of the organic nitrates in relevant discussions in the manuscript, and comment

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that the results can be different for other types of organic nitrates (from NO₃ chemistry).

I recommend publication of the manuscript after the authors address the comments.

Detailed Comments

1. Page 2, line 23. I do not think the authors need to specify “under dry conditions”, since organic nitrates are typically detected and can comprise a large fraction of ambient SOA mass even under humid ambient and lab conditions.

2. Page 2, line 26. For hydrolysis of organic nitrates, here, it would be appropriate to cite Darer et al., (2011), Hu et al., (2011), and Boyd et al., (2015) as well.

3. Page 5, line 8. The specific acid-catalyzed mechanism proposed here is in contrast to that in Jacobs et al. The authors noted that in Jacobs et al. the solution pH was not reported. The authors are correct that the pH values were not reported, however, according Jacobs et al, “The hydrolysis of the hydroxynitrate isomers was monitored in a variety of acid concentrations (0 to 2 M HClO₄), and, regardless of the acid concentration, the rate of hydrolysis remained constant”. With this, it would seem that the range of pH values in Jacobs et al. is comparable to this study? If so, the authors need to evaluate and discuss this discrepancy more extensively.

4. Page 5, line 9. The authors noted that essentially identical kinetics were observed for primary and secondary nitrates, which in in contrast to Darer et al. and Hu et al. where hydrolysis rates increase with alkyl substitution. What is the cause of this discrepancy? Because of different mechanisms? Please discuss in more detail.

5. Page 6, line 8. The authors noted that campholenic aldehyde, pinol, and pinocampone were identified as major products. a. How is product identification verified? Did the authors synthesize authentic compounds of these products? Please clarify. b. As samples at different time points were analyzed (page 3 line 25), please include time dependent data for these products in the revised manuscript, which can offer insights into the dynamics of the formation of these species and/or potential further reactions

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in the particle phase.

6. Page 7, first paragraph. The authors wrote “. . . partitioning of atmospheric organic nitrates to aerosol particles is not likely to induce further reactions capable of releasing gas phase NO_x to the atmosphere. . . .” Other than hydrolysis, organic nitrates can also be photolyzed and/or react with OH further, and depending on the VOC, they can also release NO_x back to the atmosphere upon photooxidation (e.g., Nah et al., ES&T, 2016). The authors should modify the text and take both hydrolysis and photooxidation into account when discussing organic nitrates fates and implications of their work.

7. Page 7, line 8. The author wrote “. . . Campholenic aldehyde has also been identified as the major product of the hydrolysis of another α -pinene oxidation product, α -pinene oxide (Bleier and Elrod, 2013). . .”.

a. Other than campholenic aldehyde, just like this study, Bleier and Elrod also identified pinol as a product in their study. Bleier and Elrod also proposed reaction mechanisms for the formation of campholenic aldehyde and pinol. The authors should also mention these results from Bleier and Elrod in their manuscript. b. Bleier and Elrod identified trans-carveol and trans-sobrerol as hydrolysis products in their study. It did not appear that these products are identified in this study? What is the cause of this discrepancy? The experiments in Bleier and Elrod were also conducted under acidic conditions. c. Overall, as this work is quite similar to that by Bleier and Elrod, the authors should compare and contrast their results to those from Bleier and Elrod in more detail, e.g., products, formation mechanisms, etc, and specifically clarify what is new in this study.

8. Page 7, line 13, I think the authors should make it clear that this is the case of organic nitrates formed from photooxidation. For organic nitrates formed from nitrate radical oxidation, the relative amount of primary/secondary/tertiary nitrates and their overall hydrolysis could be different (Boyd et al., ACP, 2015).

9. Figure 1 and Figure 6. Which organic nitrate did the authors synthesize?

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10. Figure 6. The chemical structure for pinol is incorrect.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-726, 2016.