Dr. Ammann,

In this document, we present, in the order the comments were raised by the reviewers, the changes made to the manuscript and/or our repliers to the reviewers. We believe that we have satisfactorily and completely responded to each and all reviewer issues and that the paper is now in a significantly improved form. We believe that the results provided in this paper represent a sizable step forward in atmospheric chemistry and hope you agree that it is now in a publishable form.

Sincerely,
Joel Rindelaub

Author comments are in **bold**.

**Anonymous Referee #1**
Received and published: 29 August 2016

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 NOx, 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.

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.

Thank you for the comment. Figures 1 and 6 have been updated to include the correct structure.

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 germinal 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.

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 D2O 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 13C and perhaps 1H-1H and/or 1H-13C two dimensional NMR spectra are needed to definitively identify the structure of the synthesis product.

Thank you for the very insightful comment. Supplemental Information (Section S1) was added describing the molecular assignment of the synthesized α-pinene-derived organic nitrate (APN) using 1H NMR, 13C NMR, FTIR, and chemical ionization mass spectrometry (CIMS).

It was determined, as the reviewer suggested, that the APN has olefinic functionality, thanks to supporting data from both 1H and 13C NMR spectra. DEPT-135 and DEPT 90 13C NMR were used to identify the connectivity of the carbon atoms. Also, similarity to the 13C NMR of the analogous diol, trans-soberol, was observed, indicating both compounds have the same carbon backbone.

In addition, FTIR was used to confirm organic nitrate functionality and CIMS was used to confirm the molecular weight of the proposed structure (215 g/mol).

These results indicate a very high confidence in the molecular assignment of the APN.

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.

Upon closer investigation of the data, campholenic aldehyde and pinocamphone could not be conclusively identified as reaction products. The identification of pinol, however, was accomplished via comparison to a known EI mass spectrum and published retention indices, as described in Supplemental Information Section S2.

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.

Thank you for the helpful comments. These issues have been addressed in the updated manuscript.
This work investigated the hydrolysis of a-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 pinocamphone 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 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 a-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.

For discussion related to specific acid catalysis and Jacobs et al. (2014), see the reply to Detailed Comment 5 posted below.

For discussion related to product identification and Bleier and Elrod (2013), see the reply to Detailed Comment 7 posted below.

In the very nice work of Darer et al. (2011), it is clearly shown in Figure 3 that the lifetime of the organic nitrate (for a pH of 0.83, according to our estimate) is approximately 1 h, rather than the 4 minutes (0.061 h) that they report. We wonder if this is a misprint. In any case, the following paragraph was added comparing our results to the previous studies, starting on page 5, line 18:

“The hydrolysis lifetimes measured for the APN are similar to those previously reported for tertiary hydroxyl nitrates. While not as short as the 0.019 h reported by Hu et al. (2011), the measured hydrolysis lifetimes of the APN are consistent with the data presented in Fig. 3 of Darer et al. (2011), which we estimate to display a lifetime of approximately 1 h at pH=0.8. However, a true comparison
of the measured hydrolysis rates is not possible, as solution pH values were not reported in either Darer et al. (2011) or Hu et al. (2011). Nonetheless, one possible explanation for the shorter lifetimes observed in previous work compared to this study may be related to the highly acidic hydrolysis conditions used in previous experiments, which employed the use of strong acids (i.e. acids with negative pK\textsubscript{a} values) ranging up to 2 M (Darer et al., 2011; Hu et al., 2011). If the organic nitrates studied in both Darer et al. (2011) and Hu et al. (2011) also proceeded via specific acid catalysis, a very low pH environment would likely have led to larger hydrolysis rates than those observed 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.

The hydrolysis product identification was accomplished by comparison to a known EI mass spectrum and published retention indices, as described in Supplemental Information Section S2.

Lastly, the organics nitrates discussed in this manuscript are from photooxidation under high NOx 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 that the results can be different for other types of organic nitrates (from NO3 chemistry).

Since the oxidation of other monoterpenes can lead to a greater distribution of primary/secondary organic nitrates, the terms “α-pinene-derived organic nitrate” and “tertiary” were specified as necessary. In addition, the following was added on page 7, line 13:

“It is important to note that organic nitrates formed from other oxidation processes, such as nitrate radical addition, may produce a larger degree of primary and secondary species that may be more resistant to hydrolysis than the tertiary organic nitrates formed during photooxidation of substituted alkenes (Nah et al., 2016).”

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.

The phrase in question was removed. Thank you.

The Boyd et al. (2015) reference was added. Darer et al. (2011) and Hu et al. (2011) were not added here because this line is referring to hydrolysis occurring in the aerosol phase rather than in bulk solution.

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.

The reaction rate of general acid catalysis is dependent on buffer concentration while specific acid catalysis rates do not depend on buffer concentration. Thus, the following was added on page 5, line 5:

“It is important to note, however, that Jacobs et al. (2014) did not observe an increase in hydrolysis rates with increasing buffer concentration, a result that is a defining characteristic of specific acid catalysis.”

4. Page 5, line 9. The authors noted that essentially identical kinetics were observed for primary and secondary nitrates, which 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.

The observed discrepancy is related to the stability of the carbocation intermediates (see second paragraph on page 5). In addition, the following was added on page 5, line 14:

“Since carbocation stability drives the rate of the unimolecular hydrolysis reaction, and rearrangements were not possible for the structures studied in Darer et al. (2011) and Hu et al. (2011), the observed hydrolysis rates in the previous studies followed a trend based on the degree of alkyl substitution, as opposed to this work and Jacobs et al. (2014).”

5. Page 6, line 8. The authors noted that campholenic aldehyde, pinol, and pinocamphone were identified as major products.

a. How is product identification verified? Did the authors synthesize authentic compounds of these products? Please clarify.

The hydrolysis product identification was accomplished by comparison to a known EI-MS spectrum and published retention indices, as described in Supplemental Information Section S2. It is important to note that upon closer investigation of the data, campholenic aldehyde and pinocamphone could not be conclusively identified as reaction products.
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 in the particle phase.

Unfortunately, only the reaction endpoints were available for GC-MS analysis. To clarify, the following was added on page 3, line 27:

“GC-MS data, which was used for product identification (see Section S2 in the Supplemental Information), was only available for data collected at the reaction endpoints.”

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 NOx 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 NOx 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.

Thank you for the comment. Section 4 (Discussion) was amended to include detailed discussion on the fate of organic nitrates. Starting on page 7, line 6:

“The reported hydrolysis lifetimes for atmospherically-relevant hydroxyl nitrates are generally shorter than those reported for oxidation reactions, which range from 2.5-28 h for gas phase OH radical oxidation and from 0.7-28 h for gas phase O₃ oxidation (Lee et al., 2014). Gas phase photolysis lifetimes have been reported from 0.50-1.0 h for carbonyl nitrates (Müller et al., 2014; Xiong et al., 2016) to ~107 h for mono-functional organic nitrates (Higgins et al., 2014). In comparison, previously reported tertiary organic nitrate hydrolysis lifetimes have been measured as short as 0.019 h (Hu et al., 2011), and as short as 0.14 h under acidic conditions in this study. This indicates that the partitioning of organic nitrates to the particle phase is likely a significant sink for atmospheric NOₓ that may critically diminish the potential for long range transport of NOₓ/ozone in the form of organic nitrates. It is important to note that organic nitrates formed from other oxidation processes, such as nitrate radical addition, may produce a larger degree of primary and secondary species that may be more resistant to hydrolysis than the tertiary organic nitrates formed during photooxidation of substituted alkenes (Nah et al., 2016).

To our knowledge, there are currently no reported photolysis or oxidation rate constant measurements for α-pinene-derived organic nitrates. However, using the EPI Suite available at the Environmental Protection Agency website (http://www.epa.gov/opptintr/exposure/pubs/episuite.htm), gas phase atmospheric lifetimes of APN were calculated to be 1.3 h and 0.64 h for OH radical and O₃ induced oxidation, respectively. Due to the lack of carbonyl functionality, it is expected that the APN photolysis rate is negligibly small. With recently reported aerosol pH values ranging from pH 0.5 to 3.0 in the southeastern US (Guo et al., 2015), the corresponding ambient hydrolysis lifetimes of the APN would be on the order of a half hour, which would indicate that particle phase hydrolysis is the principal atmospheric sink for α-pinene-derived organic nitrate compounds, in comparison to removal via photolysis and oxidation pathways. Hydrolysis in chamber experiments may be even faster as aerosol pH has recently been measured as low as pH ~0.68 for laboratory-generated particles (Rindelaub et al., 2016).”
7. Page 7, line 8. The author wrote “. . .Campholenic aldehyde has also been identified as the major product of the hydrolysis of another ⍺-pinene oxidation product, ⍺-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.

Further data analysis has concluded that campholenic aldehyde cannot be conclusively identified as a product of this study. The following was added regarding pinol formation on page 6, line 27:

“Pinol has also been observed as a product of α-pinene oxide hydrolysis (Bleier and Elrod, 2013), which is expected to proceed via the same tertiary carbocation intermediate as the APN hydrolysis.”

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.

Neither carveol nor sobrerol were observed in this study, which may be related to the relative thermodynamic stability of the products. As such, the following was added on page 6, line 28:

“In contrast to this study, Bleier and Elrod (2013) also observed the formation of sobrerol and carveol, the alternative S_n1 and E1 products, respectively, derived the tertiary carbocation. While it is peculiar that neither sobrerol nor carveol were detected in this study, the differentiation can at least partially be explained by the greater thermodynamic stability of pinol in comparison to both sobrerol and carveol (Bleier and Elrod, 2013).”

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).

Thank you for the comment. This line was replaced with the following on page 7, line 13:

“It is important to note that organic nitrates formed from other oxidation processes, such as nitrate radical addition, may produce a larger degree of primary and secondary species that may be more resistant to hydrolysis than the tertiary organic nitrates formed during photooxidation (Nah et al., 2016).”

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

Thank you for the observation. Figure 1 has been updated.
10. Figure 6. The chemical structure for pinol is incorrect.

Thank you for the observation. Figure 6 has been updated.
The Acid-Catalyzed Hydrolysis of an α-Pinene-Derived Organic Nitrate: Kinetics, Products, Reaction Mechanisms, and Atmospheric Impact

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Abstract. The production of atmospheric organic nitrates (RONO₂) has a large impact on air quality and climate, due to their contribution to secondary organic aerosol and influence on tropospheric ozone concentrations. Since organic nitrates control the fate of gas phase NOₓ (NO+NO₂), a byproduct of anthropogenic combustion processes, their atmospheric production and reactivity is of great interest. While the atmospheric reactivity of many relevant organic nitrates is still very uncertain, one significant reactive pathway, condensed phase hydrolysis, has recently been identified as a potential sink for organic nitrate species. The partitioning of gas phase organic nitrates to aerosol particles and subsequent hydrolysis likely removes the oxidized nitrogen from further atmospheric processing, due to large organic nitrate uptake to aerosols and proposed hydrolysis lifetimes, which may impact long range transport of NOₓ, a tropospheric ozone precursor. Despite the atmospheric importance, the hydrolysis rates and reaction mechanisms for atmospherically-derived organic nitrates are almost completely unknown, including those derived from α-pinene, a biogenic volatile organic compound (BVOC) that is one of the most significant precursors to biogenic secondary organic aerosol (BSOA). To better understand the chemistry that governs the fate of particle phase organic nitrates, this study elucidated the hydrolysis mechanism and rate constants for several organic nitrates, including an α-pinene-derived organic nitrate (APN). A positive trend in hydrolysis rate constants was observed with increasing solution acidity for all organic nitrates studied, with the tertiary APN lifetime ranging from 8.3 minutes at acidic pH (0.25) to 8.8 hours at neutral pH (6.9). Since ambient fine aerosol pH values are observed to be acidic, the reported lifetimes, which are much shorter than that of atmospheric fine aerosol, provide important insight into the fate of particle phase organic nitrates. Along with rate constant data, the product identification of the products campholenic aldehyde, pinol, and pinocamphone confirms a unimolecular specific acid-catalyzed mechanism is responsible for organic nitrate hydrolysis under acidic conditions, where carboxylation rearrangement is favored for α-pinene-derived species. The free energies and enthalpies of the isobutyl nitrate hydrolysis intermediates and products were calculated using a hybrid density functional (ωB97X-V) to support the proposed mechanisms. These findings provide valuable insight into the organic nitrate hydrolysis mechanism and its contribution to the fate of atmospheric NOₓ, aerosol phase processing, and BSOA composition.
1 Introduction

The atmospheric oxidation of biogenic volatile organic compounds (BVOCs), which have annual emission rates (~1100 Tg yr\(^{-1}\) total) roughly an order of magnitude larger than anthropogenic non-methane VOCs (Guenther et al., 1995), has a significant impact on air quality and climate. The production of secondary organic aerosol (SOA) from BVOC oxidation products influences the radiative balance of the planet, by directly interacting with both solar and terrestrial radiation, as well as indirectly through their role as cloud condensation nuclei (CCN; e.g. Ramanathan et al., 2001). Overall, the production of SOA from BVOCs has a cooling effect on global climate, estimated to have a combined radiative forcing as large as -1.5 W m\(^{-2}\) (Scott et al., 2014).

Additionally, the inhalation of SOA has significant impact on the human respiratory system and atmospheric aerosol concentrations are positively correlated with lung cancer and mortality rates (Raaschou-Nielsen et al., 2013). Despite the importance of SOA, the chemical mechanisms that explain the composition of aerosol particles and their chemical processes are still highly uncertain.

The gas phase oxidation of BVOCs also governs tropospheric ozone concentrations by controlling its precursor, NO\(_x\) (NO+NO\(_2\)). In the atmosphere, the most common atmospheric oxidant, the OH radical, can either abstract a hydrogen from or add to a BVOC, if it contains an olefinic functionality (e.g. \(\alpha\)-pinene), to create a peroxy radical from the rapid addition of molecular oxygen to the organic radical (Fig. 1). In high NO\(_x\) environments, such as areas within atmospheric transport of combustion emissions, nitric oxide can either add to the peroxy radical to form an organic nitrate (RONO\(_2\)) or it can be oxidized to create an alkoxy radical and NO\(_2\), which can readily photolyze to produce ozone (Fig. 1). The ratio of RONO\(_2\) production to NO\(_2\) production is referred to the organic nitrate branching ratio. Since ozone is a greenhouse gas
With respect to SOA production, among the most important BVOC-derived organic nitrates are products of α-pinene oxidation, due to their relatively low volatility and the very high annual global emission rate of α-pinene (~66 Tg yr$^{-1}$; Guenther et al., 2012). Under dry conditions, α-pinene-derived organic nitrates (APNs) can comprise a significant fraction of SOA mass (Xu et al., 2015; Rollins et al., 2010). At elevated relative humidity, when aerosol particles have increased liquid water content, organic nitrates can hydrolyze in the particle phase to eliminate the RONO$_2$ functionality (Liu et al., 2013; Rindelaub et al., 2015; Boyd et al., 2015; Bean and Hildebrandt Ruiz, 2016), leaving the nitrate ion within the particle. However, the products, mechanisms, and kinetics of the α-pinene-derived organic nitrate (APN) hydrolysis reactions are still unknown, negatively impacting our understanding of aerosol phase chemistry and the fate of atmospheric NO$_x$.

The conversion of the organic nitrate functionality to a non-volatile, largely unreactive nitrate ion via a substitution or elimination mechanism would lead to an effective sink of atmospheric NO$_x$ and reduce the potential for NO$_x$/O$_3$ transport. Recent results from Romer et al. (2016) indicate that the lifetime of atmospheric boundary layer NO$_x$ could be as low as ~2 hours, using an assumed short hydrolysis lifetime (Romer et al., 2016). The hydrolysis mechanism could also potentially impact SOA formation and cloud condensation nuclei activity. Thus the hydrolysis of organic nitrates, and the associated uncertainty, has a significant impact on our understanding of how BVOC-NO$_x$ interactions affect climate, air quality and health.

Despite much study of organic nitrate hydrolysis, the rates and mechanisms at low pH, which is relevant to both ambient (e.g. Guo et al., 2015) and laboratory conditions (Rindelaub et al.
are still very uncertain. While $S_N2$ mechanisms are believed to be more prevalent at high pH (Baker and Easty, 1950; Boschan et al., 1955), recent studies suggest that unimolecular mechanisms are responsible for the fate of organic nitrates under aqueous acidic conditions, due to the polar protic solvent system, water’s weak nucleophility, and the relatively large observed hydrolysis rates for tertiary organic nitrates (Rindelaub et al., 2015). While the reaction is likely acid-catalyzed, the catalysis mechanism is uncertain as both specific and general catalyzed mechanisms have been proposed (Darer et al., 2011; Jacobs et al., 2014).

To better understand the organic nitrate hydrolysis mechanism and kinetics under acidic conditions and the corresponding impact on atmospheric processes, hydrolysis reactions were performed focusing on the fate of $\alpha$-pinene-derived organic nitrates (APNs). The hydrolysis rate constants, specific mechanism, and main product were determined for a laboratory-synthesized APN. The hydrolysis of simple alkyl nitrates, isopropyl nitrate (IPN) and isobutyl nitrate (IBN), were also studied to gain insight into the mechanisms of primary and secondary substituted species, and to enable computational chemistry studies of the mechanism and energetics. The results from this study help improve our understanding of organic nitrate chemistry, the fate of atmospherically-relevant organic nitrates relating to climate and health, and can help explain important mechanisms that impact aerosol phase chemistry.

2 Experimental
2.1 Materials and methods

Organic nitrate hydrolysis reactions were studied for isopropyl nitrate (Sigma Aldrich, >99%), isobutyl nitrate (Sigma Aldrich, >97%), and a $\beta$-hydroxy organic nitrate derived from $\alpha$-pinene by injecting 10 $\mu$L of a given standard into a 100 mL buffered solution that was continuously mixed. The $\alpha$-pinene-derived nitrate, shown in Fig. 1, was synthesized based on Pinto et al.
Briefly, α-pinene oxide was added to a 1.0 M solution of Bi(NO$_3$)$_3$•5H$_2$O in DCM, and stirred for 1 hour under N$_2$ before purification using flash chromatography with a 20% ethyl acetate in hexane solvent system. Product identification and purity were assessed using $^1$H and $^{13}$C NMR (see Section S1 in the below Supplemental Information). Aliquots of 5 mL were taken at varying time points from the reaction mixture and extracted with 5 mL of tetrachloroethylene (C$_2$Cl$_4$) before analysis using FTIR for organic nitrate quantification, and GC-MS data, which was used for product identification (see Section S2 in the Supplemental Information), was only available for data collected at the reaction endpoints. FT-IR analysis was accomplished by integrating the $\sim$1640 cm$^{-1}$ asymmetric $–$NO$_2$ stretch unique to organic nitrates (Nielsen et al., 1995). The reaction solutions used were buffered at 10 mM with either a sulfate, acetate, or phosphate buffer system. Hydrolysis reactions were studied at pH values 0.25, 1.0, 4.0, and 6.9.

The chemical shifts, peak multiplicity and integration of the APN protons in the $^1$H NMR spectrum, using deuterated chloroform (CDCl$_3$) as a solvent, were as follows: (a) $\delta$ 5.6 (triplet, 1H), (b) $\delta$ 5.6 (singlet, 1H), (c) $\delta$ 2.4 (triplet of a triplet, 1H), (d) $\delta$ 2.2 (triplet, 1H), (e) $\delta$ 1.9 (doublet of a doublet, 2H), (f) $\delta$ 1.8 (singlet, 3H), (g) $\delta$ 1.6 (singlet, 3H), (h) $\delta$ 1.5 (singlet, 3H), (i) (doublet of a doublet, 2H).

2.2 Computational methods

The thermochemical calculations of a set of reactants, intermediates, and products involved in the proposed reaction pathways of isobutyl nitrate were explored using Density Functional Theory (DFT; Hohenberg and Kohn, 1964; Kohn and Sham, 1965). The set included water (H$_2$O), hydronium ion (H$_3$O$^+$), nitric acid (HNO$_3$), isobutyl nitrate (IBN), protonated isobutyl nitrate (IBHN$^+$), isobutyl ion (IB$^+$), tert-butyl ion (TB$^+$), isobutylene (2MP), tert-butyl alcohol
(TBA), and isobutyl alcohol (IBA), see Table 1. The reactions are assumed to run in an acidic environment, such that the hydronium ion is prevalent. First, a systematic torsional conformational search was performed on the structure of each molecule of the set, excepting water and hydronium ion. This procedure was performed in HyperChem (Hyperchem™ Professional 7.51, Hypercube, Inc.) with the Optimized Potentials for Liquid Simulations (OPLS) force field (Jorgensen and Tirado-Rives, 1988; Pranata et al., 1991). A maximum of 8 simultaneous variations was allowed, with angles changing every step by a maximum range of 180° at intervals of 15°. Similar structures were filtered, with an acceptance criterion set to 5 kcal mol⁻¹ above the lowest energy conformer. All the following calculations were carried out using the computational chemistry package Q-Chem 4.3 (Shao et al., 2015). Second, the lowest energy conformer was optimized employing the long-range corrected hybrid density functional ωB97X-V (Mardirossian and Head-Gordon, 2014), with the aug-cc-pVTZ basis set (Kendall et al., 1992), and Polarizable Continuum Model (PCM) of implicit aqueous solvent (Truong and Stefanovich, 1995; Barone and Cossie, 1998; Cossi et al., 2003). A high-accuracy grid was employed, as well as extremely tight convergence criteria. Third, frequency calculations were executed on the optimized structures to verify the convergence of the geometry optimizations, and also to determine if the molecule was a stable species or a reaction intermediate. These were run using the same setup described above, plus the inclusion of a thermochemical analysis upon completion of frequency calculations.

3 Results

In all experiments, the addition of an organic nitrate standard to aqueous solution resulted in hydrolysis of the organic nitrate functionality, with first order loss rates that increased with solution acidity (Figs. 2, 3). For the secondary-tertiary α-pinene-derived nitrate (APN),
hydrolysis rate constants ranged from $3.2 \times 10^{-5}$ s$^{-1}$ at neutral pH (6.9) to $2.0 \times 10^{-3}$ s$^{-1}$ at low pH (0.25). The hydrolysis rate constants for the secondary isopropyl nitrate and the primary isobutyl nitrate displayed nearly identical kinetics, and had rate constants smaller by more than two orders of magnitude relative to the APN, ranging from $1.23 \times 10^{-7}$ s$^{-1}$ at neutral pH (6.9) to 1.1 x $10^{-5}$ s$^{-1}$ at low pH (0.25), when data from both experiments were averaged together.

The corresponding hydrolysis lifetimes for the organic nitrates studied are shown in Table 2.

APN had a condensed phase hydrolysis lifetime of 8.3 minutes at low pH, and a lifetime of 8.8 hours at neutral pH. Both of these hydrolysis lifetimes are much shorter than the lifetime of a typical atmospheric aerosol particle. The average hydrolysis lifetimes of isopropyl nitrate and isobutyl nitrate were much larger than those for APN, ranging from approximately 1 day at low pH to greater than 8 months at neutral conditions.

The pH dependence of the observed rate constants indicates that the hydrolysis of organic nitrates at low pH is a specific acid-catalyzed mechanism. In specific acid-catalyzed mechanisms, the transfer of the H$^+$ ion from the acid to the reactant is reversible and occurs before the rate determining step, consistent with a unimolecular mechanism. The observed specific acid-catalyzed mechanism is in contrast to Jacobs et al. (2014), who report a general acid-catalyzed mechanism for the hydrolysis of β-hydroxy organic nitrates. It is important to note, however, that Jacobs et al. (2014) did not observe an increase in hydrolysis rates with increasing buffer concentration, a result that is a defining characteristic of specific acid catalysis. did not report the pH of their solutions, thus, a pH dependent reaction may have been possible, given their experimental parameters.

Previous studies indicate that organic nitrate hydrolysis rates increase with alkyl substitution (Darer et al., 2011; Hu et al., 2011). However, in this study, essentially identical kinetics were
observed for the primary isobutyl nitrate and secondary isopropyl nitrate. This similarity can be explained through inspection of the unimolecular hydrolysis mechanism. A proposed reaction mechanism for the acid-catalyzed hydrolysis of IBN is shown in Fig. 4, where rearrangement to a relatively stable tert-butyl carbocation drives the rate of the reaction. A similar observation concerning the relatively large hydrolysis rate constant of a primary organic nitrate was recently reported by Jacobs et al. (2014), who concluded that the resonance stabilization of a primary carbocation increased the rate of a nucleophilic substitution reaction. Since carbocation stability drives the rate of the unimolecular hydrolysis reaction, and rearrangements were not possible for the structures studied in Darer et al. (2011) and Hu et al. (2011), the observed hydrolysis rates in the previous studies followed a trend based on the degree of alkyl substitution, as opposed to this work and Jacobs et al. (2014).

The hydrolysis lifetimes measured for the APN are similar to those previously reported for tertiary hydroxyl nitrates. While not as short as the 0.019 h reported by Hu et al. (2011), the measured hydrolysis lifetimes of the APN are consistent with the data presented in Fig. 3 of Darer et al. (2011), which we estimate to display a lifetime of approximately 1 h at pH=0.8. However, a true comparison of the measured hydrolysis rates is not possible, as solution pH values were not reported in either Darer et al. (2011) or Hu et al. (2011). Nonetheless, one possible explanation for the shorter lifetimes observed in previous work compared to this study may be related to the highly acidic hydrolysis conditions used in previous experiments, which employed the use of strong acids (i.e. acids with negative $pK_a$ values) ranging up to 2 M (Darer et al., 2011; Hu et al., 2011). If the organic nitrates studied in both Darer et al. (2011) and Hu et al. (2011) also proceeded via specific acid catalysis, a very low pH environment would likely have led to larger hydrolysis rates than those observed in this study.
To further support the unimolecular reaction mechanism of organic nitrate hydrolysis, theoretical enthalpy and free energy profiles of the proposed isobutyl nitrate reaction mechanism are presented in Fig. 5, (a) and (b), respectively. Based on extensive benchmarks, thermochemical calculations in the gas phase at the $\omega$B97X-V/aug-cc-pVTZ level of theory are accurate up to ~3.6 kcal mol$^{-1}$ (Mardirossian and Head-Gordon, 2014). According to recent literature, the $\omega$B97X-V/aug-cc-pVTZ level of theory offers an excellent balance between computational cost and accuracy (Chan and Radom, 2011; Chan and Radom, 2012). Therefore, the main source of potential inaccuracies in our calculations is the use of a PCM implicit solvent, which is known to provide a less rigorous description of charged species (Takano and Houk, 2005). However, the uncertainty due to using PCM is not quantifiable without calculations involving an explicit solvent model, the pursuit of which is beyond the scope of the present study.

According to the DFT calculations, the isobutyl ion (IB$^+$) corresponds to a saddle point of the energy profile, thus it is considered a metastable reaction intermediate, rather than a stable species. Due to the instability of the primary isobutyl carbocation (IB$^+$), it is likely that a 1,2 hydride shift occurs in concert with bond cleavage of the nitrate group to create the tertiary carbocation intermediate (TB$^+$). In addition, geometry optimizations and frequency calculations indicated that protonation of isobutyl nitrate (IBN) occurs on the terminal oxygen of the nitrate rather than the oxygen of the nitrate ester, as shown in Fig. 4, because the latter produces a metastable species.

Comparing the enthalpy and free energy results, it is observed that both the zero-point vibrational energy and entropic contributions play important roles in determining the most probable products.
Without those contributions, a barrier to reach the isobutyl ion is significantly higher and the overall reaction would be much slower. The entropic contribution also impacts the probability of producing isobutylene via an elimination mechanism, among other products. In any case, computations suggest that the energetically favored product is the nucleophilic substitution product, tert-butyl alcohol (TBA). The difference in calculated free energy of the TB$^+$ intermediate and the final products is likely within the uncertainty of using an implicit solvation model for charged species.

The much larger observed hydrolysis rate constants of APN, as well as that for a secondary β-hydroxynitrate from the Jacobs et al. (2014) study, compared to the IPN/IBN systems is related to carbocation stability in the unimolecular mechanism. Due to its relative size, the α-pinene-derived carbocation will have greater charge stabilization. Further reaction of the tertiary carbocation intermediate readily occurs, as indicated from the identified product pinol using GC-MS (see Fig. 6). Thus, the creation of these products from APN hydrolysis further confirming the unimolecular nature of the organic nitrate hydrolysis under acidic conditions. While theoretical calculations were not conducted for this system, the experimental data and supporting theoretical calculations of IBN hydrolysis indicate that the unimolecular mechanism is favored for organic nitrates in acidic environments.

Once the α-pinene-derived tertiary carbocation is formed, the reaction can either proceed via an intramolecular unimolecular substitution (S$_\text{N}1$) or an elimination (E1) mechanism or intramolecular rearrangement (Fig. 6; Bleier and Elrod, 2013). In this study, following the E1 reaction proceeded via an S$_\text{N}1$ pathway will lead to the formation of a form pinocamphonepinol by intramolecular attack from the secondary hydroxyl group to create a protonated pinol.
compound. The abstraction of the proton by water will complete the acid-catalyzed reaction to create the final pinol product and H$_3$O$^+$. Pinol has also been observed as a product of α-pinene oxide hydrolysis (Bleier and Elrod, 2013), which is expected to proceed via the same tertiary carbocation intermediate as the APN hydrolysis. In contrast to this study, Bleier and Elrod (2013) also observed the formation of sobrerol and carveol, the alternative S$_N$1 and E1 products, respectively, derived the tertiary carbocation. While it is peculiar that neither sobrerol nor carveol were detected in this study, the differentiation can at least partially be explained by the greater thermodynamic stability of pinol in comparison to both sobrerol and carveol (Bleier and Elrod, 2013). In this mechanism, water will abstract a β-proton from the tertiary carbocation intermediate, forming a double bond. The resulting olefinic alcohol product will be in equilibrium with pinocamphone through keto-enol tautomerization.

Rearrangement of the α-pinene-derived tertiary carbocation will lead to the formation of either pinol or campholenic aldehyde (Fig. 6). Pinol is formed after the four-membered ring of the 3° α-pinene-derived carbocation fragments to form a double bond and another tertiary carbocation. This rearrangement will be followed by intramolecular attack from the secondary hydroxyl group to create a protonated pinol compound. The abstraction of the proton by water will complete the acid-catalyzed reaction to create the final pinol product and H$_3$O$^+$. The major product of APN, campholenic aldehyde, which accounted for over 90% of the total peak area from all products, is formed by rearrangement of the α-pinene-derived tertiary carbocation intermediate to form a secondary carbocation (Fig. 6). The conversion of a tertiary carbocation to a secondary carbocation is usually uphill by about ~10 kcal mol$^{-1}$, however, if the rearrangement leads to the formation of a product much lower in energy, this barrier is not
prohibitive (Carey and Sunberg, 2007). In this case, the rearrangement of the less stable bicyclo[3.1.1]heptane system to the more stable bicyclo[2.2.1]heptane system compensates for the energetic difference between secondary and tertiary carbocations. After rearrangement to form the secondary carbocation, fragmentation occurs via a retro-Prins reaction to create a cyclopentene and an aldehyde. The final product, campholenic aldehyde, is formed after water abstracts the remaining acidic proton, reforming \( \text{H}_2\text{O}^+ \) and completing the acid-catalyzed reaction.

4 Discussion

As discussed above, particle phase and cloud water hydrolysis is an important reaction concerning the atmospheric fate of organic nitrates. The conversion of the RONO$_2$ functional group within the aerosol phase to the nitrate ion, which has negligible vapor pressure and will exist within particles depending on pH, will reduce the potential of further reactions re-releasing gas phase NO$_x$ to the atmosphere, such as through organic nitrate photolysis and/or oxidation.

The reported hydrolysis lifetimes for atmospherically-relevant hydroxyl nitrates are generally shorter than those reported for oxidation reactions, which range from 2.5-28 h for gas phase OH radical oxidation and from 0.7-28 h for gas phase O$_3$ oxidation (Lee et al., 2014). Gas phase photolysis lifetimes have been reported from 0.50-1.0 h for carbonyl nitrates (Müller et al., 2014; Xiong et al., 2016) to ~107 h for mono-functional organic nitrates (Higgins et al., 2014).

In comparison, previously reported tertiary organic nitrate hydrolysis lifetimes have been measured as short as 0.019 h under neutral conditions (Hu et al., 2011) and as short as 0.14 h under acidic conditions in this study, indicating that the partitioning of organic nitrates to the particle phase is likely a significant sink for atmospheric NO$_x$ that may critically diminish the potential for long range transport of NO$_x$/ozone in the form of organic nitrates. It is important to
note that organic nitrates formed from other oxidation processes, such as nitrate radical addition, may produce a larger degree of primary and secondary species that may be more resistant to hydrolysis than the tertiary organic nitrates formed during photooxidation of substituted alkenes (Nah et al., 2016).

To our knowledge, there are currently no reported photolysis or oxidation rate constant measurements for α-pinene-derived organic nitrates. However, using the EPI Suite available at the Environmental Protection Agency website (http://www.epa.gov/opptintr/exposure/pubs/episuite.htm), gas phase atmospheric lifetimes of APN were calculated to be 1.3 h and 0.64 h for OH radical and O₃ induced oxidation, respectively. Due to the lack of carbonyl functionality, it is expected that the APN photolysis rate is negligibly small. With recently reported aerosol pH values ranging from pH 0.5 to 3.0 in the southeastern US (Guo et al., 2015), the corresponding ambient hydrolysis lifetimes of the APN would be on the order of a half hour, which would indicate that particle phase hydrolysis is the principal atmospheric sink for α-pinene-derived organic nitrate compounds, in comparison to removal via photolysis and oxidation pathways. Hydrolysis in chamber experiments may be even faster as aerosol pH has recently been measured as low as pH -0.68 for laboratory-generated particles (Rindelaub et al., 2016).

Due to the likely large degree of aerosol phase hydrolysis, current ambient measurements of particle phase organic nitrate concentrations may be underestimating the atmospheric production of organic nitrates. Indeed, this chemistry can represent a dominant fate of NOₓ in forested boundary layers and, at low aerosol pH, protonation of the resultant NO₃⁻ can represent a dominant source of atmospheric HNO₃ (Romer et al., 2016).
As discussed above, particle phase and cloud water hydrolysis is an important reaction concerning the atmospheric fate of organic nitrates. The consumption of the RONO₂-functional group within the aerosol phase has an impact on the fate of atmospheric NOₓ and its contribution to ozone concentrations. The rapid conversion of the RONO₂-functional group to the nitrate ion, which has negligible vapor pressure and will exist within particles depending on pH, indicates that the partitioning of atmospheric organic nitrates to aerosol particles is not likely to induce further reactions capable of re-releasing gas phase NOₓ to the atmosphere, which will greatly diminish the potential for long-range transport of NOₓ in the form of organic nitrates.

Additionally, with recently reported aerosol pH values ranging from pH 0.5 to 3.0 in the southeastern US (Guo et al., 2015), the corresponding ambient hydrolysis lifetimes of APNs would be on the order of a half hour, further indicating that particle phase hydrolysis is a likely efficient sink for atmospheric organic nitrate compounds. Hydrolysis in chamber experiments may be even faster as aerosol pH has recently been measured as low as pH -0.68 for laboratory-generated particles (Rindelaub et al., 2016). In addition, many other α-pinene and monoterpene-derived organic nitrates are expected to be tertiary (Peeters et al., 2001), which are likely more reactive than the APN studied within these experiments and will have larger hydrolysis rates. This also indicates that the current ambient measurements of particle phase organic nitrate concentrations may be underestimating the atmospheric production of organic nitrates, due to the likely large degree of aerosol phase hydrolysis. Indeed, this chemistry can represent a dominant fate of NOₓ in forested boundary layers and, at low aerosol pH, protonation of the resultant NO₃⁻ can represent a dominant source of atmospheric HNO₃ (Romer et al., 2016).

The formation of a relatively high vapor pressure product from α-pinene-derived nitrate hydrolysis, such as pinoleampholenic aldehyde, may lead to a reduction in aerosol mass by the
partitioning of products back into the gas phase, lowering particle mass concentrations. For instance, the calculated vapor pressure of pinol-campholenic aldehyde is estimated to be three orders of magnitude greater than the original organic nitrate, based on calculations using the EPI Suite (see above), available at the Environmental Protection Agency website (http://www.epa.gov/opptintr/exposure/pubs/episuite.htm). It is important to note that APN hydrolysis products can have olefinic functionality, such as the case with pinol-campholenic aldehyde and pinol, and may react further in the particle phase, especially under acidic conditions, where sulfonation and/or oligomerization can occur. Photo-induced chemistry occurring to aerosol phase products may result in oxidation at the double bond (Bateman et al., 2011). Campholenic aldehyde pinol has also been identified as a hydrolysis the major product of the hydrolysis of another α-pinene oxidation product, α-pinene oxide (Bleier and Elrod, 2013), thus, campholenic aldehyde pinol may be an important tracer for the hydrolysis of α-pinene-derived species. Both the gas and particle phase fate of campholenic aldehyde pinol warrant further study.

The identification of organic nitrate hydrolysis products is important not only to our understanding of the atmosphere but also to our chemical understanding of the organic nitrate hydrolysis mechanism. Research regarding RONO$_2$ hydrolysis under acidic conditions has been limited and suggests that nucleophilic substitution is the dominant reaction pathway. This study shows that through the unimolecular mechanism, elimination and intramolecular rearrangement/attack are also likely reactive pathways and should be considered when identifying aerosol phase chemical processes and potential tracers of atmospherically relevant compounds.

5 Conclusions


A specific acid-catalyzed hydrolysis mechanism was determined for an \( \alpha \)-pinene-derived organic nitrate, which has implications into atmospheric air quality and climate. This finding, along with supporting theoretical calculations of the isobutyl nitrate hydrolysis mechanism, helps broaden our chemical understanding of the hydrolysis mechanism of organic nitrates. The hydrolysis rates observed for the organic nitrates studied increased with solution acidity and the large rates observed for the \( \alpha \)-pinene-derived organic nitrate further emphasizes the likelihood of particle phase hydrolysis being a sink for organic nitrates and, transitively, atmospheric \( \text{NO}_x \). It also highlights the importance of ambient aerosol pH measurements. The hydrolysis of organic nitrates within the particle phase will lead to a decreased effective lifetime for \( \text{NO}_x \) and, thus, decreased ozone transport. However, some of the observed organic hydrolysis products, pinol, is relatively volatile and may partition back to the gas phase, decreasing organic aerosol mass. In addition to the investigation of \( \alpha \)-pinene-derived organic nitrate photolysis and oxidation, future work is needed to assess how the loss of particle phase organic nitrates impacts cloud condensation nuclei and environmental health.

Acknowledgements. This research was supported in part through computational resources provided by Information Technology at Purdue University. P.B.S. acknowledges support from the National Science Foundation (grant AGS-1228496) and L.V.S. acknowledges support from the National Science Foundation (grants CHE-1465154).

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Table 1. Stoichiometry of the calculated states.

<table>
<thead>
<tr>
<th>State</th>
<th>Species Included</th>
</tr>
</thead>
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<tr>
<td>IBN</td>
<td>(CH$_3$)$_2$CHCHONO$_2$ + H$_3$O$^+$ + H$_2$O</td>
</tr>
<tr>
<td>IBHN$^+$</td>
<td>(CH$_3$)$_2$CHCHONO$_2$H$^+$ + 2H$_2$O</td>
</tr>
<tr>
<td>IB$^+$</td>
<td>(CH$_3$)$_2$CHCH$_2$ + HNO$_3$ + 2H$_2$O</td>
</tr>
<tr>
<td>TB$^+$</td>
<td>(CH$_3$)$_2$C=CH + HNO$_3$ + 2H$_2$O</td>
</tr>
<tr>
<td>2MP</td>
<td>(CH$_3$)$_2$C=CH + HNO$_3$ + H$_3$O$^+$ + H$_2$O</td>
</tr>
<tr>
<td>IBA</td>
<td>(CH$_3$)$_2$CHCH$_2$OH + HNO$_3$ + H$_3$O$^+$</td>
</tr>
<tr>
<td>TBA</td>
<td>(CH$_3$)$_3$COH + HNO$_3$ + H$_3$O$^+$</td>
</tr>
</tbody>
</table>
Table 2. The hydrolysis lifetimes of isopropyl nitrate (IPN), isobutyl nitrate (IBN), and the α-pinene-derived nitrate (APN) at varying pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>IPN</th>
<th>IBN</th>
<th>APN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>28 h</td>
<td>23 h</td>
<td>8.3 min</td>
</tr>
<tr>
<td>1.0</td>
<td>--</td>
<td>--</td>
<td>44 min</td>
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<tr>
<td>1.7</td>
<td>35 d</td>
<td>33 d</td>
<td>--</td>
</tr>
<tr>
<td>2.5</td>
<td>--</td>
<td>--</td>
<td>33 min</td>
</tr>
<tr>
<td>4.0</td>
<td>30 d</td>
<td>28 d</td>
<td>1.3 h</td>
</tr>
<tr>
<td>6.9</td>
<td>&gt; 8 mo</td>
<td>&gt; 8 mo</td>
<td>8.8 h</td>
</tr>
</tbody>
</table>
Figure 1. The formation of atmospheric organic nitrates and ozone from the gas phase oxidation of α-pinene, initiated by the OH radical.
Figure 2. The hydrolysis rate constants (s$^{-1}$) for isopropyl nitrate (IPN; red) and isobutyl nitrate (IBN; blue) as a function of solution pH.
Figure 3. The hydrolysis rate constants ($s^{-1}$) for the $\alpha$-pinene-derived nitrate as a function of solution pH. The error bars correspond to one standard deviation of replicate measurements.
Figure 4. The proposed unimolecular mechanism for isobutyl nitrate (IBN) demonstrating the specific acid-catalysis and 1,2 hydride shift rearrangement.
Figure 5. The calculated relative free energies of the intermediates and products of the proposed acid-catalyzed isobutyl nitrate hydrolysis mechanism. See Table 1 for calculation stoichiometry.

The reaction is not likely to proceed through the IB⁺ intermediate, due to the instability of the carbocation.
Figure 6. The proposed acid-catalyzed hydrolysis mechanism of an α-pinene-derived nitrate.