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
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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 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 $^1$H NMR, $^{13}$C 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 $^1$H and $^{13}$C NMR spectra. DEPT-135 and DEPT 90 $^{13}$C NMR were used to identify the connectivity of the carbon atoms. Also, similarity to the $^{13}$C NMR of the analogous diol, trans-sobrerol, 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 $pK_a$ 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.**

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.

**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 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 $O_3$ 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 (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 $NO_x$ 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 $O_3$ 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 ($RONO_2$) 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 $NO_x$ ($NO+NO_2$), 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 $NO_x$, 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, product identification confirms a unimolecular specific acid-catalyzed mechanism is responsible for organic nitrate hydrolysis under acidic conditions. The free energies and enthalpies of the isobutyl nitrate hydrolysis intermediates and products were calculated using a hybrid density functional ($\omega$B97X-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 $NO_x$, 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. α-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

63  (IPCC, 2007), damages plants/crops (Fiscus et al., 2005), and is a lung irritant (EPA, 2011), the

64  formation and fate of organic nitrates has implications for both climate and environmental health.

65      With respect to SOA production, among the most important BVOC-derived organic nitrates

66  are products of α-pinene oxidation, due to their relatively low volatility and the very high annual

67  global emission rate of α-pinene (~66 Tg yr$^{-1}$; Guenther et al., 2012). ~~Under dry conditions,~~ ~~α-~~

68  ~~pinene~~Pinene-derived organic nitrates (APNs) can comprise a significant fraction of SOA mass

69  (Xu et al., 2015; Rollins et al., 2010). At elevated relative humidity, when aerosol particles have

70  increased liquid water content, organic nitrates can hydrolyze in the particle phase to eliminate

71  the RONO$_2$ functionality (Liu et al., 2013; Rindelaub et al., 2015; Boyd et al., 2015; Bean and

72  Hildebrandt Ruiz, 2016), leaving the nitrate ion within the particle. However, the products,

73  mechanisms, and kinetics of the α-pinene-derived organic nitrate (APN) hydrolysis reactions are

74  still unknown, negatively impacting our understanding of aerosol phase chemistry and the fate of

75  atmospheric NO$_x$.

76      The conversion of the organic nitrate functionality to a non-volatile, largely unreactive nitrate

77  ion via a substitution or elimination mechanism would lead to an effective sink of atmospheric

78  NO$_x$ and reduce the potential for NO$_x$/O$_3$ transport. Recent results from Romer et al. (2016)

79  indicate that the lifetime of atmospheric boundary layer NO$_x$ could be as low as ~2 hours, using

80  an assumed short hydrolysis lifetime (Romer et al., 2016). The hydrolysis mechanism could also

81  potentially impact SOA formation and cloud condensation nuclei activity. Thus the hydrolysis of

82  organic nitrates, and the associated uncertainty, has a significant impact on our understanding of

83  how BVOC-NO$_x$ interactions affect climate, air quality and health.

84      Despite much study of organic nitrate hydrolysis, the rates and mechanisms at low pH, which

85  is relevant to both ambient (e.g. Guo et al., 2015) and laboratory conditions (Rindelaub et al,

3

86   2016), are still very uncertain. While $S_N2$ mechanisms are believed to be more prevalent at high

87   pH (Baker and Easty, 1950; Boschan et al., 1955), recent studies suggest that unimolecular

88   mechanisms are responsible for the fate of organic nitrates under aqueous acidic conditions, due

89   to the polar protic solvent system, water's weak nucleophlicity, and the relatively large observed

90   hydrolysis rates for tertiary organic nitrates (Rindelaub et al., 2015). While the reaction is likely

91   acid-catalyzed, the catalysis mechanism is uncertain as both specific and general catalyzed

92   mechanisms have been proposed (Darer et al., 2011; Jacobs et al., 2014).

93      To better understand the organic nitrate hydrolysis mechanism and kinetics under acidic

94   conditions and the corresponding impact on atmospheric processes, hydrolysis reactions were

95   performed focusing on the fate of α-pinene-derived organic nitrates (APNs). The hydrolysis rate

96   constants, specific mechanism, and main product were determined for a laboratory-synthesized

97   APN. The hydrolysis of simple alkyl nitrates, isopropyl nitrate (IPN) and isobutyl nitrate (IBN),

98   were also studied to gain insight into the mechanisms of primary and secondary substituted

99   species, and to enable computational chemistry studies of the mechanism and energetics. The

100  results from this study help improve our understanding of organic nitrate chemistry, the fate of

101  atmospherically-relevant organic nitrates relating to climate and health, and can help explain

102  important mechanisms that impact aerosol phase chemistry.

103  **2 Experimental**

104  **2.1 Materials and methods**

105  Organic nitrate hydrolysis reactions were studied for isopropyl nitrate (Sigma Aldrich, >99%),

106  isobutyl nitrate (Sigma Aldrich, >97%), and a β-hydroxyl organic nitrate derived from α-pinene

107  by injecting 10 μL of a given standard into a 100 mL buffered solution that was continuously

108  mixed. The α-pinene-derived nitrate, shown in Fig. 1, was synthesized based on Pinto et al.

4

109  (2007). Briefly, α-pinene oxide was added to a 1.0 M solution of $Bi(NO_3)_3 \cdot 5H_2O$ in DCM, and

110  stirred for 1 hour under $N_2$ before purification using flash chromatography with a 20% ethyl

111  acetate in hexane solvent system. Product identification and purity were assessed using $^1$H and

112  $^{13}$C NMR (see Section S1 in the belowSupplemental Information).  Aliquots of 5 mL were taken

113  at varying time points from the reaction mixture and extracted with 5 mL of tetrachloroethylene

114  ($C_2Cl_4$) before analysis using FTIR for organic nitrate quantification. and GC-MS data, which

115  was used for product identification (see Section S2 in the Supplemental Information), was only

116  available for data collected at the reaction endpoints. for product identification. FT-IR analysis

117  was accomplished by integrating the ~1640 cm$^{-1}$ asymmetric –NO$_2$ stretch unique to organic

118  nitrates (Nielsen et al., 1995). The reaction solutions used were buffered at 10 mM with either a

119  sulfate, acetate, or phosphate buffer system. Hydrolysis reactions were studied at pH values 0.25,

120  1.0, 4.0, and 6.9.

121  The chemical shifts, peak multiplicity and integration of the APN protons in the $^1$H NMR

122  spectrum, using deuterated chloroform (CDCl$_3$) as a solvent, were as follows: (a) δ 5.6 (triplet,

123  1H), (b) δ 5.6 (singlet, 1H), (c) δ 2.4 (triplet of a triplet, 1H), (d) δ 2.2 (triplet, 1H), (e) δ 1.9

124  (doublet of a doublet, 2H), (f) δ 1.8 (singlet, 3H), (g) δ 1.6 (singlet, 3H), (h) δ 1.5 (singlet, 3H),

125  (i) (doublet of a doublet, 2H).

126  **2.2 Computational methods**

127  The thermochemical calculations of a set of reactants, intermediates, and products involved in

128  the proposed reaction pathways of isobutyl nitrate were explored using Density Functional

129  Theory (DFT; Hohenberg and Kohn, 1964; Kohn and Sham, 1965). The set included water

130  ($H_2O$), hydronium ion ($H_3O^+$), nitric acid ($HNO_3$), isobutyl nitrate (IBN), protonated isobutyl

131  nitrate ($IBHN^+$), isobutyl ion ($IB^+$), *tert*-butyl ion ($TB^+$), isobutylene (2MP), *tert*-butyl alcohol

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132  (TBA), and isobutyl alcohol (IBA), see Table 1. The reactions are assumed to run in an acidic

133  environment, such that the hydronium ion is prevalent. First, a systematic torsional

134  conformational search was performed on the structure of each molecule of the set, excepting

135  water and hydronium ion. This procedure was performed in HyperChem (Hyperchem™

136  Professional 7.51, Hypercube, Inc.) with the Optimized Potentials for Liquid Simulations

137  (OPLS) force field (Jorgensen and Tirado-Rives, 1988; Pranata et al., 1991). A maximum of 8

138  simultaneous variations was allowed, with angles changing every step by a maximum range of

139  180° at intervals of 15°. Similar structures were filtered, with an acceptance criterion set to 5

140  kcal mol$^{-1}$ above the lowest energy conformer. All the following calculations were carried out

141  using the computational chemistry package Q-Chem 4.3 (Shao et al., 2015). Second, the lowest

142  energy conformer was optimized employing the long-range corrected hybrid density functional

143  $\omega$B97X-V (Mardirossian and Head-Gordon, 2014), with the aug-cc-pVTZ basis set (Kendall et

144  al., 1992), and Polarizable Continuum Model (PCM) of implicit aqueous solvent (Truong and

145  Stefanovich, 1995; Barone and Cossie, 1998; Cossi et al., 2003). A high-accuracy grid was

146  employed, as well as extremely tight convergence criteria. Third, frequency calculations were

147  executed on the optimized structures to verify the convergence of the geometry optimizations,

148  and also to determine if the molecule was a stable species or a reaction intermediate. These were

149  run using the same setup described above, plus the inclusion of a thermochemical analysis upon

150  completion of frequency calculations.

151  **3 Results**

152  In all experiments, the addition of an organic nitrate standard to aqueous solution resulted in

153  hydrolysis of the organic nitrate functionality, with first order loss rates that increased with

154  solution acidity (Figs. 2, 3). For the ~~secondary~~ tertiary α-pinene-derived nitrate (APN),

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155   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

156   (0.25). The hydrolysis rate constants for the secondary isopropyl nitrate and the primary isobutyl

157   nitrate displayed nearly identical kinetics, and had rate constants smaller by more than two

158   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

159   $10^{-5}$ s$^{-1}$ at low pH (0.25), when data from both experiments were averaged together.

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

161   APN had a condensed phase hydrolysis lifetime of 8.3 minutes at low pH, and a lifetime of 8.8

162   hours at neutral pH. Both of these hydrolysis lifetimes are much shorter than the lifetime of a

163   typical atmospheric aerosol particle. The average hydrolysis lifetimes of isopropyl nitrate and

164   isobutyl nitrate were much larger than those for APN, ranging from approximately 1 day at low

165   pH to greater than 8 months at neutral conditions.

166       The pH dependence of the observed rate constants indicates that the hydrolysis of organic

167   nitrates at low pH is a specific acid-catalyzed mechanism. In specific acid-catalyzed

168   mechanisms, the transfer of the H$^{+}$ ion from the acid to the reactant is reversible and occurs

169   before the rate determining step, consistent with a unimolecular mechanism. The observed

170   specific acid-catalyzed mechanism is in contrast to Jacobs et al. (2014), who report a general

171   acid-catalyzed mechanism for the hydrolysis of β-hydroxy organic nitrates. It is important to

172   note, however, that Jacobs et al. (2014) did not observe an increase in hydrolysis rates with

173   increasing buffer concentration, a result that is a defining characteristic of specific acid catalysis.

174   did not report the pH of their solutions, thus, a pH-dependent reaction may have been possible,

175   given their experimental parameters.

176       Previous studies indicate that organic nitrate hydrolysis rates increase with alkyl substitution

177   (Darer et al., 2011; Hu et al., 2011). However, in this study, essentially identical kinetics were

178  observed for the primary isobutyl nitrate and secondary isopropyl nitrate. This similarity can be

179  explained through inspection of the unimolecular hydrolysis mechanism. A proposed reaction

180  mechanism for the acid-catalyzed hydrolysis of IBN is shown in Fig. 4, where rearrangement to

181  a relatively stable *tert*-butyl carbocation drives the rate of the reaction. A similar observation

182  concerning the relatively large hydrolysis rate constant of a primary organic nitrate was recently

183  reported by Jacobs et al. (2014), who concluded that the resonance stabilization of a primary

184  carbocation increased the rate of a nucleophilic substitution reaction. Since carbocation stability

185  drives the rate of the unimolecular hydrolysis reaction, and rearrangements were not possible for

186  the structures studied in Darer et al. (2011) and Hu et al. (2011), the observed hydrolysis rates in

187  the previous studies followed a trend based on the degree of alkyl substitution, as opposed to this

188  work and Jacobs et al. (2014).

189      The hydrolysis lifetimes measured for the APN are similar to those previously reported for

190  tertiary hydroxyl nitrates. While not as short as the 0.019 h reported by Hu et al. (2011), the

191  measured hydrolysis lifetimes of the APN are consistent with the data presented in Fig. 3 of

192  Darer et al. (2011), which we estimate to display a lifetime of approximately 1 h at pH=0.8.

193  However, a true comparison of the measured hydrolysis rates is not possible, as solution pH

194  values were not reported in either Darer et al. (2011) or Hu et al. (2011). Nonetheless, one

195  possible explanation for the shorter lifetimes observed in previous work compared to this study

196  may be related to the highly acidic hydrolysis conditions used in previous experiments, which

197  employed the use of strong acids (i.e. acids with negative $pK_a$ values) ranging up to 2 M (Darer

198  et al., 2011; Hu et al., 2011). If the organic nitrates studied in both Darer et al. (2011) and Hu et

199  al. (2011) also proceeded via specific acid catalysis, a very low pH environment would likely

200  have led to larger hydrolysis rates than those observed in this study.

201    To further support the unimolecular reaction mechanism of organic nitrate hydrolysis,

202    theoretical enthalpy and free energy profiles of the proposed isobutyl nitrate reaction mechanism

203    are presented in Fig. 5, (a) and (b), respectively. Based on extensive benchmarks,

204    thermochemical calculations in the gas phase at the $\omega$B97X-V/aug-cc-pVTZ level of theory are

205    accurate up to ~3.6 kcal mol$^{-1}$ (Mardirossian and Head-Gordon, 2014). According to recent

206    literature, the $\omega$B97X-V/aug-cc-pVTZ level of theory offers an excellent balance between

207    computational cost and accuracy (Chan and Radom, 2011; Chan and Radom, 2012). Therefore,

208    the main source of potential inaccuracies in our calculations is the use of a PCM implicit solvent,

209    which is known to provide a less rigorous description of charged species (Takano and Houk,

210    2005). However, the uncertainty due to using PCM is not quantifiable without calculations

211    involving an explicit solvent model, the pursuit of which is beyond the scope of the present

212    study.

213    According to the DFT calculations, the isobutyl ion (IB$^+$) corresponds to a saddle point of the

214    energy profile, thus it is considered a metastable reaction intermediate, rather than a stable

215    species. Due to the instability of the primary isobutyl carbocation (IB$^+$), it is likely that a 1,2

216    hydride shift occurs in concert with bond cleavage of the nitrate group to create the tertiary

217    carbocation intermediate (TB$^+$). In addition, geometry optimizations and frequency calculations

218    indicated that protonation of isobutyl nitrate (IBN) occurs on the terminal oxygen of the nitrate

219    rather than the oxygen of the nitrate ester, as shown in Fig. 4, because the latter produces a

220    metastable species.

221    Comparing the enthalpy and free energy results, it is observed that both the zero-point

222    vibrational energy and entropic contributions play important roles in determining the most

223    probable products.

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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 for 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 product the identified

producteation 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 will can either proceed

via an intramolecular unimolecular substitution ($S_N1$) or an elimination (E1) mechanism or

intramolecular rearrangement (Fig. 6; Bleier and Elrod, 2013). In this study, Following the E1

reaction proceeded via an $S_N1$ pathway will lead to the formation ofto form pinocamphonepinol

by intramolecular attack from the secondary hydroxyl group to create a protonated pinol

246 compound. The abstraction of the proton by water will complete the acid-catalyzed reaction to

247 create the final pinol product and $H_3O^+$.

248    Pinol has also been observed as a product of α-pinene oxide hydrolysis (Bleier and Elrod,

249 2013), which is expected to proceed via the same tertiary carbocation intermediate as the APN

250 hydrolysis. In contrast to this study, Bleier and Elrod (2013) also observed the formation of

251 sobrerol and carveol, the alternative $S_N1$ and E1 products, respectively, derived the tertiary

252 carbocation. While it is peculiar that neither sobrerol nor carveol were detected in this study, the

253 differentiation can at least partially be explained by the greater thermodynamic stability of pinol

254 in comparison to both sobrerol and carveol (Bleier and Elrod, 2013). In this mechanism, water

255 will abstract a β proton from the tertiary carbocation intermediate, forming a double bond. The

256 resulting olefinic alcohol product will be in equilibrium with pinocamphone through keto-enol

257 tautomerization.

258    Rearrangement of the α-pinene-derived tertiary carbocation will lead to the formation of

259 either pinol or campholenic aldehyde (Fig. 6). Pinol is formed after the four-membered ring of

260 the 3° α-pinene-derived carbocation fragments to form a double bond and another tertiary

261 carbocation. This rearrangement will be followed by intramolecular attack from the secondary

262 hydroxyl group to create a protonated pinol compound. The abstraction of the proton by water

263 will complete the acid-catalyzed reaction to create the final pinol product and $H_3O^+$.

264    The major product of APN, campholenic aldehyde, which accounted for over 90% of the total

265 peak area from all products, is formed by rearrangement of the α-pinene-derived tertiary

266 carbocation intermediate to form a secondary carbocation (Fig. 6). The conversion of a tertiary

267 carbocation to a secondary carbocation is usually uphill by about ~10 kcal mol$^{-1}$, however, if the

268 rearrangement leads to the formation of a product much lower in energy, this barrier is not

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269  prohibitive (Carey and Sunberg, 2007). In this case, the rearrangement of the less stable

270  bicyclo[3.1.1]heptane system to the more stable bicyclo[2.2.1]heptane system compensates for

271  the energetic difference between secondary and tertiary carbocations. After rearrangement to

272  form the secondary carbocation, fragmentation occurs via a retro-Prins reaction to create a

273  cyclopentene and an aldehyde. The final product, campholenic aldehyde, is formed after water

274  abstracts the remaining acidic proton, reforming $H_3O^+$ and completing the acid-catalyzed

275  reaction.

## 4 Discussion

277  As discussed above, particle phase and cloud water hydrolysis is an important reaction

278  concerning the atmospheric fate of organic nitrates. The conversion of the $RONO_2$ functional

279  group within the aerosol phase to the nitrate ion, which has negligible vapor pressure and will

280  exist within particles depending on pH, will reduce the potential of further reactions re-releasing

281  gas phase $NO_x$ to the atmosphere, such as through organic nitrate photolysis and/or oxidation.

282      The reported hydrolysis lifetimes for atmospherically-relevant hydroxyl nitrates are

283  generally shorter than those reported for oxidation reactions, which range from 2.5-28 h for gas

284  phase OH radical oxidation and from 0.7-28 h for gas phase $O_3$ oxidation (Lee et al., 2014). Gas

285  phase photolysis lifetimes have been reported from 0.50-1.0 h for carbonyl nitrates (Müller et al.,

286  2014; Xiong et al., 2016) to ~107 h for mono-functional organic nitrates (Higgins et al., 2014).

287  In comparison, previously reported tertiary organic nitrate hydrolysis lifetimes have been

288  measured as short as 0.019 h under neutral conditions (Hu et al., 2011) and as short as 0.14 h

289  under acidic conditions in this study, indicating that the partitioning of organic nitrates to the

290  particle phase is likely a significant sink for atmospheric $NO_x$ that may critically diminish the

291  potential for long range transport of $NO_x$/ozone in the form of organic nitrates. It is important to

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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 $O_3$ 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 $NO_x$ in forested boundary layers and, at low aerosol pH, protonation of the resultant $NO_3^-$ can represent a dominant source of atmospheric $HNO_3$ (Romer et al., 2016).

314   As discussed above, particle phase and cloud water hydrolysis is an important reaction

315   concerning the atmospheric fate of organic nitrates. The consumption of the $RONO_2$ functional

316   group within the aerosol phase has an impact on the fate of atmospheric $NO_x$ and its contribution

317   to ozone concentrations. The rapid conversion of the $RONO_2$ functional group to the nitrate ion,

318   which has negligible vapor pressure and will exist within particles depending on pH, indicates

319   that the partitioning of atmospheric organic nitrates to aerosol particles is not likely to induce

320   further reactions capable of re-releasing gas phase $NO_x$ to the atmosphere, which will greatly

321   diminish the potential for long range transport of $NO_x$ in the form of organic nitrates.

322      Additionally, with recently reported aerosol pH values ranging from pH 0.5 to 3.0 in the

323   southeastern US (Guo et al., 2015), the corresponding ambient hydrolysis lifetimes of APNs

324   would be on the order of a half hour, further indicating that particle phase hydrolysis is a likely

325   efficient sink for atmospheric organic nitrate compounds. Hydrolysis in chamber experiments

326   may be even faster as aerosol pH has recently been measured as low as pH -0.68 for laboratory

327   generated particles (Rindelaub et al., 2016). In addition, many other α-pinene and monoterpene

328   derived derived organic nitrates are expected to be tertiary (Peeters et al., 2001), which are likely

329   more reactive than the APN studied within these experiments and will have larger hydrolysis

330   rates. This also indicates that the current ambient measurements of particle phase organic nitrate

331   concentrations may be underestimating the atmospheric production of organic nitrates, due to the

332   likely large degree of aerosol phase hydrolysis. Indeed, this chemistry can represent a dominant

333   fate of $NO_x$ in forested boundary layers and, at low aerosol pH, protonation of the resultant $NO_3^-$

334   can represent a dominant source of atmospheric $HNO_3$ (Romer et al., 2016).

335      The formation of a relatively high vapor pressure products from α-pinene-derived nitrate

336   hydrolysis, such as pinoleampholenic aldehyde, may lead to a reduction in aerosol mass by the

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337 partitioning of products back into the gas phase, lowering particle mass concentrations. For

338 instance, the calculated vapor pressure of pinolcampholenic aldehyde is estimated to be three

339 orders of magnitude greater than the original organic nitrate, based on calculations using the EPI

340 Suite (see above). available at the Environmental Protection Agency website

341 (http://www.epa.gov/opptintr/exposure/pubs/episuite.htm). It is important to note that APN

342 hydrolysis products can have olefinic functionality, such as the case with pinol campholenic

343 aldehyde and pinol, and may react further in the particle phase, especially under acidic

344 conditions, where sulfoanation and/or oligomerization can occur. Photo-induced chemistry

345 occurring to aerosol phase products may result in oxidation at the double bond (Bateman et al.,

346 2011). Campholenic aldehydePinol has also been identified as a hydrolysis the major product of

347 the hydrolysis of another α-pinene oxidation product, α-pinene oxide (Bleier and Elrod, 2013),

348 thus, campholenic aldehydepinol may be an important tracer for the hydrolysis of α-pinene-

349 derived species. Both the gas and particle phase fate of campholenic aldehydepinol warrant

350 further study.

351     The identification of organic nitrate hydrolysis products is important not only to our

352 understanding of the atmosphere but also to our chemical understanding of the organic nitrate

353 hydrolysis mechanism. Research regarding RONO$_2$ hydrolysis under acidic conditions has been

354 limited and suggests that nucleophilic substitution is the dominant reaction pathway. This study

355 shows that through the unimolecular mechanism, elimination and elimination and intramolecular

356 rearrangement/attack are also likely reactive pathways and should be considered when

357 identifying aerosol phase chemical processes and potential tracers of atmospherically relevant

358 compounds.

359 **5 Conclusions**

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A specific acid-catalyzed hydrolysis mechanism was determined for an α-pinene-derived organic nitrate, which has implications ~~into~~ for 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 α-pinene-derived organic nitrate further emphasizes the likelihood of particle phase hydrolysis being a sink for organic nitrates and, transitively, atmospheric $NO_x$. 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 $NO_x$ and, thus, decreased ozone transport. However, ~~some of the~~the observed organic hydrolysis product~~s~~ , pinol, is ~~are~~ relatively volatile and may partition back to the gas phase, decreasing organic aerosol mass. In addition to the investigation of α-pinene-derived organic nitrate photolysis and oxidation, f~~F~~uture work is needed to assess how the loss of particle phase organic nitrates impacts ~~cloud condensation nuclei and environmental health~~aerosol hygroscopicity.

**References**

Baker, J.W. and Easty, D.M.: Hydrolysis of organic nitrates, Nature, 166, 156, 1950.

Barone, V. and Cossie, M.: Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model, J. Phys. Chem. A, 102, 1995–2001, 1998.

16

Bateman, A.P., Nizkorodov, S.A., Laskin, J. and Laskin, A.: Photolytic processing of secondary organic aerosols dissolved in cloud droplets, Phys. Chem. Chem. Phys., 13, 12199–12212, 2001.

Bean, J.K. and Hildebrandt Ruiz, L.: Gas–particle partitioning and hydrolysis of organic nitrates formed from the oxidation of α-pinene in environmental chamber experiments., Atmos. Chem. Phys., 16, 2175-2184, 2016.

Bleier, D.B. and Elrod, M.J.: Kinetics and Thermodynamics of Atmospherically Relevant Aqueous Phase Reactions of α-Pinene Oxide, J. Phys. Chem. A, 117, 4223-4232, 2013.

Boschan, R., Merrow, R.T. and van Dolah, R.: The chemistry of nitrate esters, Chem. Rev., 55, 485-510, 1955.

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and Ng, N. L.: Secondary organic aerosol formation from the β-pinene+NO3 system: effect of humidity and peroxy radical fate, Atmos. Chem. Phys., 15, 7497-7522, 2015.

Carey, F.A. and Sunberg, R.J. Advanced Organic Chemistry, Part A: Structure and Mechanisms, 5th ed. Springer: New York, 2007, p. 440.

Chan, B. and Radom, L.: Approaches for Obtaining Accurate Rate Constants for Hydrogen Abstraction by a Chlorine Atom, J. Phys. Chem. A, 116, 3745–3752, 2012.

Chan, B. and Radom, L.: Assessment of theoretical procedures for hydrogen-atom abstraction by chlorine, and related reactions, Theor. Chem. Acc., 130, 251-260, 2011.

Cossi, M., Rega, N., Scalmani, G. and Barone, V.: Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model, J. Comput. Chem., 24, 669-681, 2003.

Darer, A.I.; Cole-Filipiak, N.C.; O'Connor, A.E.; Elrod, M.J. Thermodynamics and kinetics of the hydrolysis of atmospherically relevant organonitrates and organosulfates, Environ. Sci. Technol., 45, 1895–1902, 2011.

EPA: Second External Review Draft of the Integrated Science Assessment of Ozone and related Photochemical Oxidants. Research Triangle Park, N.C: Environmental Protection Agency, 2011 (Report no. EPA/600/R-10/076B).

Fiscus, E.D., Booker, F.L. and Burkey, K.O.: Crop responses to ozone: uptake, modes of action, carbon assimilation and partitioning, Plant Cell Environ., 28, 997–1011, 2005.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L.; Lerdau, M., Mckay, W. A., Pierce, T., Scholes, Ste inbrecher, B. R., Tallamraju, R., Taylor, J. and Zimmerman, P.: A global model of natural volatile organic compound emissions. J. Geophys. Res., 100, 8873–8892, 1995.

Guenther, A.B., Jiang, X., Heald, C.L., Sakulyanontvittaya, T., Duhl, T., Emmons, L.K. and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471-1492, 2012.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K.M., Capps, S.L., Hite Jr., J.R., Carlton, A.G., Lee, S.-H., Bergin, M.H., Ng, N.L., Nenes, A. and Weber, R.J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228, 2015.

Higgins, C.M., Evans, L.A., Lloyd-Jones, G.C., Shallcross, D.E., Tew, D.P., and Orr-Ewing, A.J.: Quantum Yields for Photochemical Production of NO2 from Organic Nitrates at Tropospherically Relevant Wavelengths, J. Phys. Chem. A, 118, 2756–2764, 2014.

Hohenberg P., Kohn, W.: Inhomogeneous electron gas, Phys. Rev., 136, B864, 1964.

Hu, K.S., Darer, A.I., and Elrod, M.J.: Thermodynamics and kinetics of the hydrolysis of atmospherically relevant organonitrates and organosulfates, Atmos. Chem. Phys., 11, 8307-8320, 2011.

HyperChem(TM) Professional 7.51, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA.

IPCC 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, (Eds: S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, H. L. Miller). Cambridge University Press, Cambridge, UK and New York, USA, 2007.

Jacobs, M.I., Burke, W.J. and Elrod, M.J.: Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis, Atmos. Chem. Phys., 14, 8933-8946, 2014.

Jorgensen, W.L. and Tirado-Rives, J.: The OPLS [optimized potentials for liquid simulations] potential functions for proteins, energy minimizations for crystals of cyclic peptides and crambin, J. Am. Chem. Soc., 110, 1657–1666, 1988.

Kendall, R.A., Dunning, T.H. and Harrison, R.J.: Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions, J. Chem. Phys., 96, 6796-6806, 1992.

Kohn, W. and Sham, L. J.: Self-Consistent Equations Including Exchange and Correlation Effects. Phys Rev., 140, A1133, 1965.

Lee, L., Teng, A.P., Wennberg, P.O., Crounse, J.D., and Cohen, R.C.: On rates and mechanisms of OH and O3 Reactions with isoprene-derived hydroxyl nitrates, J. Phys. Chem. A, 118, 1622–1637, 2014.

Liu, S., Shilling, J.E., Song, C., Hiranuma, N., Zaveri, R.A. and Russell, L.M.: Hydrolysis of Organonitrate Functional Groups in Aerosol Particles, Aerosol Sci. Technol., 46, 1359-1369, 2012.

Mardirossian, N., and Head-Gordon, M.: ωB97X-V: A 10-parameter, range-separated hybrid, generalized gradient approximation density functional with nonlocal correlation, designed by a survival-of-the-fittest strategy, Phys. Chem. Chem. Phys., 16, 9904-9924, 2014.

Müller, J.-F., Peeters, J., and Stavrakou, T.: Fast photolysis of carbonyl nitrates from isoprene, Atmos. Chem. Phys., 14, 2497-2508, 2014.

Nah, T., Sanchez, J., Boyd, C.M., and Ng, N.L.: Photochemical Aging of α‑pinene and β‑pinene Secondary Organic Aerosol formed from Nitrate Radical Oxidation, Environ. Sci. Technol., 50, 222−231, 2016.

18

460  Nielsen, T., Egelov, A.H., Granby, K. and Skov, H.: Observations on particulate organic nitrates
461      and unidentified components of NOy, Atmos. Environ., 29, 1757-1769, 1995.
462  Peeters, J., Vereecken, L. and Fantechi, G.: The detailed mechanism of the OH-initiated
463      atmospheric oxidation of alpha-pinene: a theoretical study, Phys. Chem. Chem. Phys., 3,
464      5489-5504, 2001.
465  Pinto, R.M.A., Salvador, J.A.R. and Le Roux, C.: Bismuth(III) salts mediated regioselective ring
466      opening of epoxides: an easy route to halohydrins and betahydroxy nitrates, Tetrahedron, 63,
467      9221-9228, 2007.
468  Pranata, J., Wierschke, S.G. and Jorgensen, W.L.: OPLS potential functions for nucleotide bases.
469      Relative association constants of hydrogen-bonded base pairs in chloroform, J. Am. Chem.
470      Soc., 113, 2810–2819, 1991.
471  Raaschou-Nielsen, O., Andersen, Z. J.,  Beelen, R., Samoli, E., Stafoggia, M., Weinmayr, G.,
472      Hoffmann, B., Fischer, P., Nieuwenhuijsen, M. J., Brunekreef, B., Xun, W. W.,
473      Katsouyanni, K., Dimakopoulou, K., Sommar, J., Forsberg, B., Modig, L., Oudin, A.,
474      Oftedal, B., Schwarze, P. E., Nafstad, P., De Faire, U., Pedersen, N. L. Ostenson, C. G.,
475      Fratiglioni, L., Penell, J., Korek, M., Pershagen, G., Eriksen, K. T., Sorensen, M.,
476      Tjonneland, A., Ellermann, T., Eeftens, M., Peeters, P. H.,  Meliefste, K., Wang, M., Bueno-
477      de-Mesquita, B., Key, T. J., de Hoogh, K., Concin, H., Nagel, A. Vilier, S. Grioni, V.
478      Krogh, M. Y. Tsai, F. Ricceri, C. Sacerdote, C. Galassi, E. Migliore, A. Ranzi, G., Cesaroni,
479      G., Badaloni, C., Forastiere, F., Tamayo, I., Amiano, P., Dorronsoro, M., Trichopoulou, A.,
480      Bamia, C., Vineis, P. and Hoek, G.: Air pollution and lung cancer incidence in 17 European
481      cohorts: prospective analyses from the European Study of Cohorts for Air Pollution Effects
482      (ESCAPE), Lancet Oncol., 14, 813-822, 2013.
483  Ramanathan. V., Crutzen, P. J., Kiehl, J. T. and Rosenfeld, D.: Aerosols, Climate, and the
484      Hydrological Cycle, Science, 294, 2119-2124, 2001.
485  Rindelaub, J.D., McAvey, K.M. and Shepson, P.B.: The photochemical production of organic
486      nitrates from α-pinene and loss via acid-dependent particle phase hydrolysis. Atmos.
487      Environ., 100, 193-201, 2015.
488  Rindelaub, J.D., Craig, R.L., Nandy, L., Bondy, A.L., Dutcher, C.S., Shepson, P.B. and Ault,
489      A.P.: Direct Measurement of pH in Individual Particles via Raman Microspectroscopy and
490      Variation in Acidity with Relative Humidity, J. Phys. Chem. A, 120, 911-917, 2016.
491  Rollins, A.W., Smith, J.D., Wilson, K.R. and Cohen, R.C.: Real Time In Situ Detection of
492      Organic Nitrates in Atmospheric Aerosols, Environ. Sci. Technol., 44, 5540-5545, 2010.
493  Romer, P.S, Duffey, K.C., Wooldridge, P.J., Allen, H.M., Ayers, B.R., Brown, S.S., Brune,
494      W.H., Crounse, J.D., de Gouw, J., Draper, D.C., Feiner, P.A., Fry, J.L., Goldstein, A.H.,
495      Koss, A., Misztal, P.K., Nguyen, T.B., Olson, K., Teng, A.P., Wennberg, P.O., Wild, R.J.,
496      Zhang, L. and Cohen, R.C.: The lifetime of nitrogen oxides in an isoprene-dominated forest.
497      Atmos. Chem. Phys., 16, 7623-7637, 2016.
498  Scott, C. E., A. Rap, D. V. Spracklen, P. M., Forster, K. S., Carslaw, G. W., Mann, K. J.,
499      Pringle, N., Kivekas, M., Kulmala, H., Lihavainen, H. and Tunved, P.: The direct and

indirect radiative effects of biogenic secondary organic aerosol, Atmos. Chem. Phys., 14, 447-470, 2014.

Shao, Y. et al.: Advances in molecular quantum chemistry contained in the Q-Chem 4 program package, Mol. Phys., 113, 184-215, 2015.

Takano, Y. and Houk, K.N.: Benchmarking the Conductor-like Polarizable Continuum Model (CPCM) for Aqueous Solvation Free Energies of Neutral and Ionic Organic Molecules, J. Chem. Theory Comput., 1, 70–77, 2005.

Truong, T.N. and Stefanovich, E.V.: A new method for incorporating solvent effect into the classical, ab initio molecular orbital and density functional theory frameworks for arbitrary shape cavity, Chem. Phys. Lett., 240, 253-260, 1995.

Xiong, F., Borca, C.H., Slipchenko, L.V., and P.B. Shepson: Photochemical degradation of isoprene-derived 4,1-nitroxy enal, Atmos. Chem. Phys., 16, 5595-5610, 2016.

Xu, L., Suresh, S., Guo, H., Weber, R. J. and Ng, N. L.: Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates, Atmos. Chem. Phys., 15, 7307-7336, 2015.

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518       **Table 1**. Stoichiometry of the calculated states.

| State | Species Included |
|---|---|
| IBN | $(CH_3)_2CHCH_2ONO_2 + H_3O^+ + H_2O$ |
| $IBHN^+$ | $(CH_3)_2CHCH_2ONO_2H^+ + 2H_2O$ |
| $IB^+$ | $(CH_3)_2CHCH_2^+ + HNO_3 + 2H_2O$ |
| $TB^+$ | $(CH_3)_2C^+CH_3 + HNO_3 + 2H_2O$ |
| 2MP | $(CH_3)_2C=CH_2 + HNO_3 + H_3O^+ + H_2O$ |
| IBA | $(CH_3)_2CHCH_2OH + HNO_3 + H_3O^+$ |
| TBA | $(CH_3)_3COH + HNO_3 + H_3O^+$ |

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**Table 2**. The hydrolysis lifetimes of isopropyl nitrate (IPN), isobutyl nitrate (IBN), and the α-
pinene-derived nitrate (APN) at varying pH.

| pH | Lifetime | | |
|---|---|---|---|
| | IPN | IBN | APN |
| 0.25 | 28 h | 23 h | 8.3 min |
| 1.0 | -- | -- | 44 min |
| 1.7 | 35 d | 33 d | -- |
| 2.5 | -- | -- | 33 min |
| 4.0 | 30 d | 28 d | 1.3 h |
| 6.9 | > 8 mo | > 8 mo | 8.8 h |

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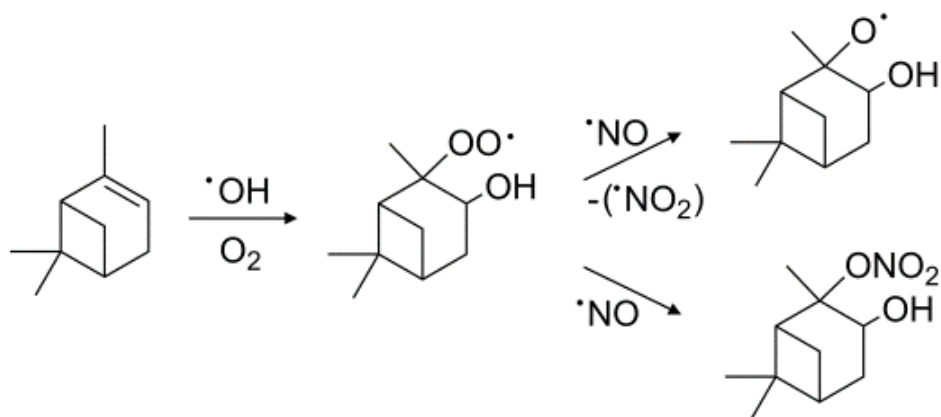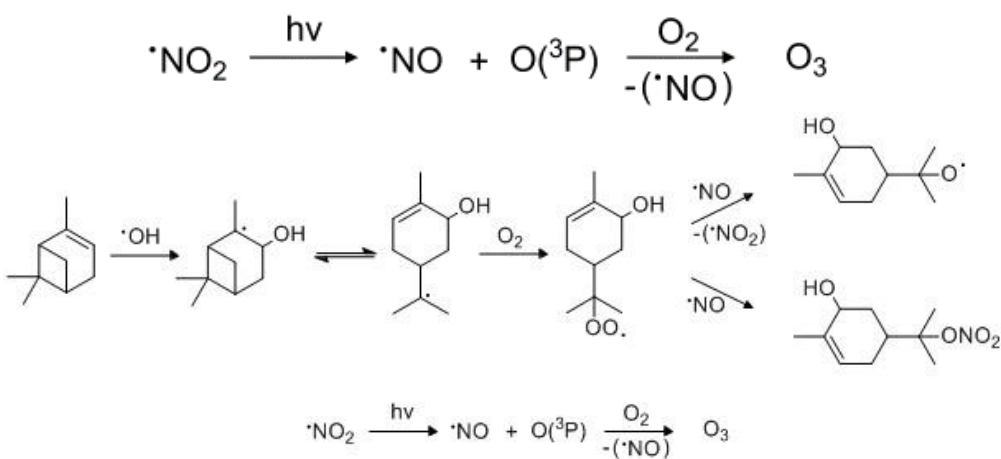
Figure 1. The formation of atmospheric organic nitrates and ozone from the gas phase oxidation
of α-pinene, initiated by the OH radical.

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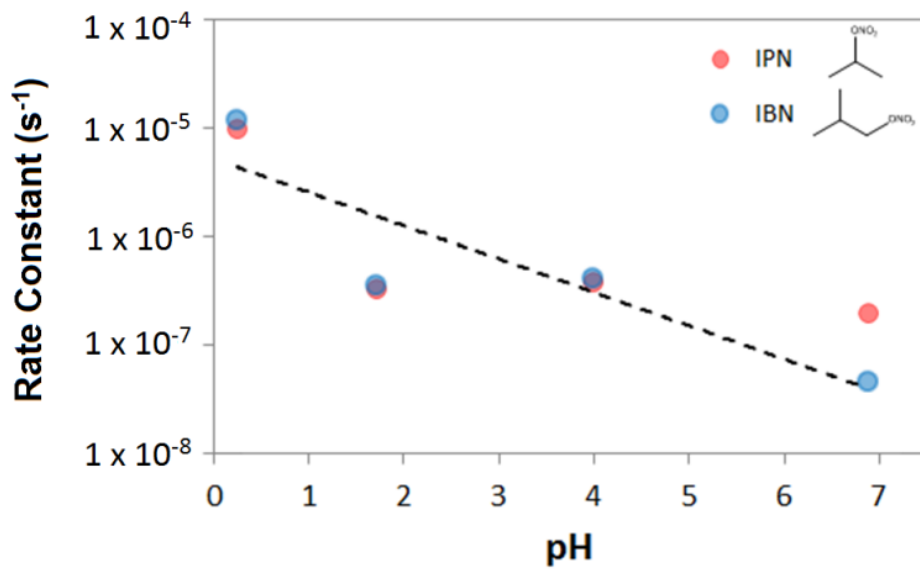
**Figure 2**. The hydrolysis rate constants ($s^{-1}$) for isopropyl nitrate (IPN; red) and isobutyl nitrate (IBN; blue) as a function of solution pH.
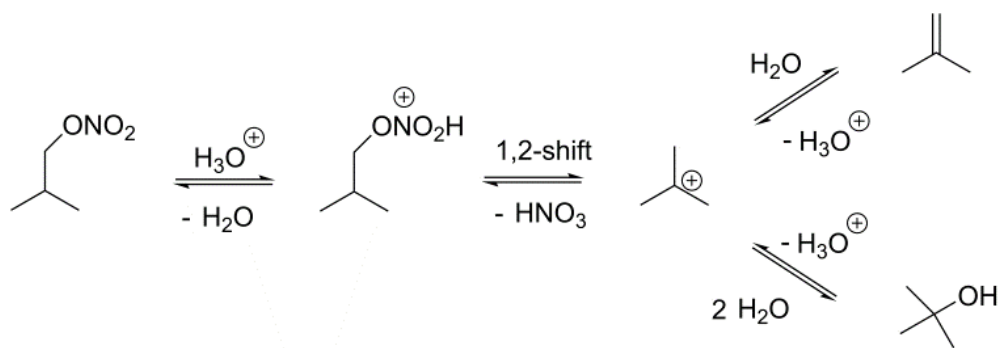
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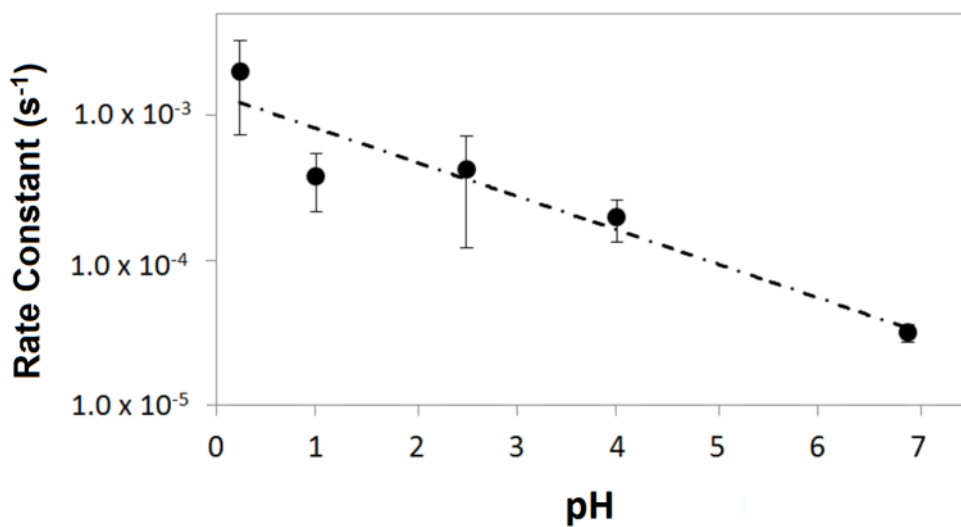
**Figure 3**. The hydrolysis rate constants ($s^{-1}$) for the α-pinene-derived nitrate as a function of
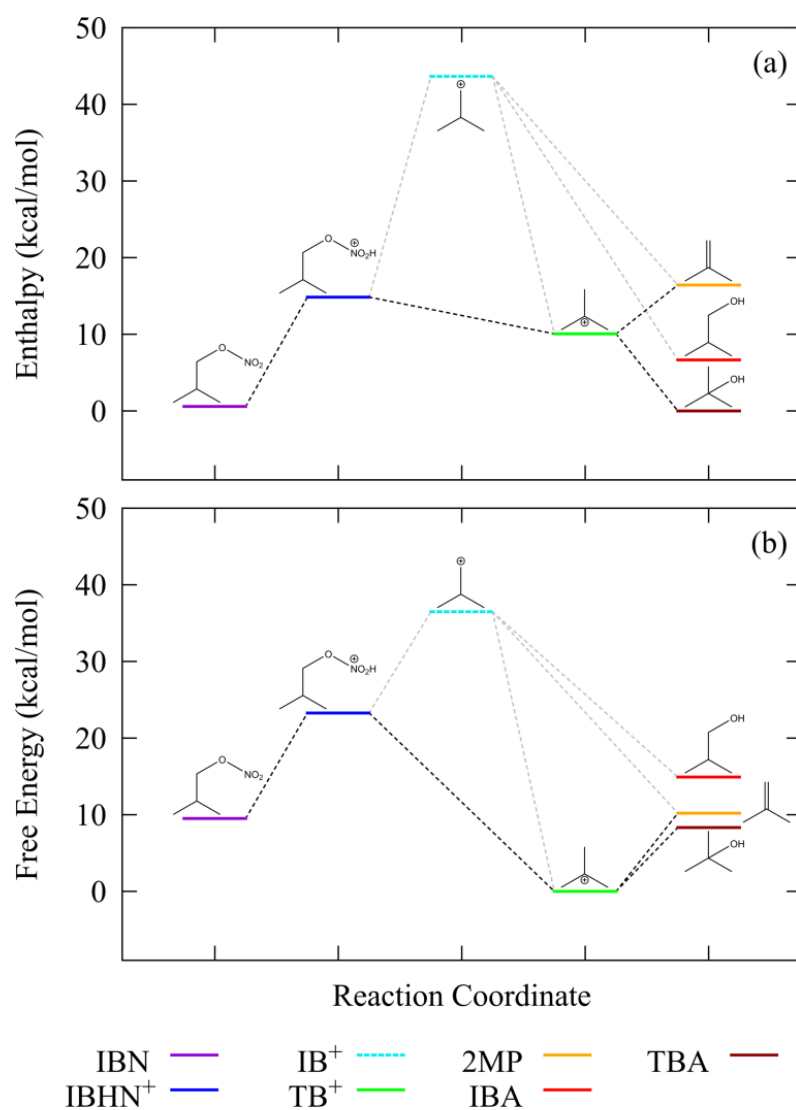solution pH. The error bars correspond to one standard deviation of replicate measurements.

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545  **Figure 4**. The proposed unimolecular mechanism for isobutyl nitrate (IBN) demonstrating the
546  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.

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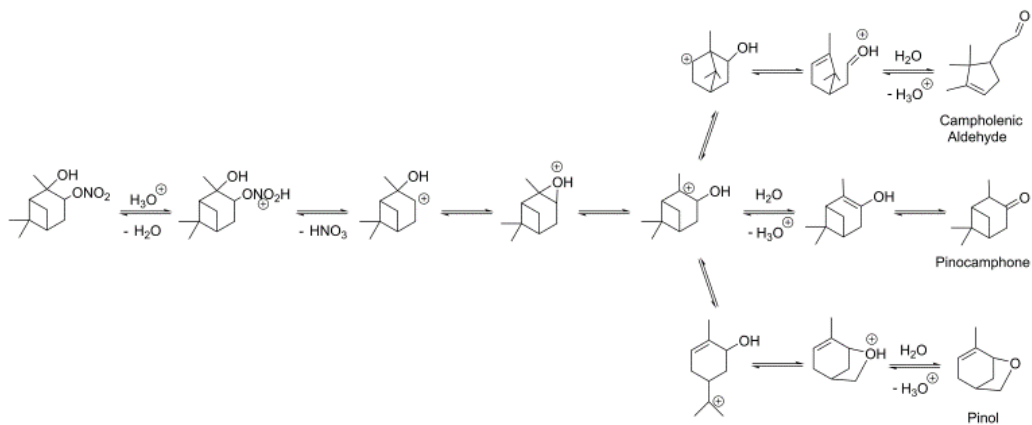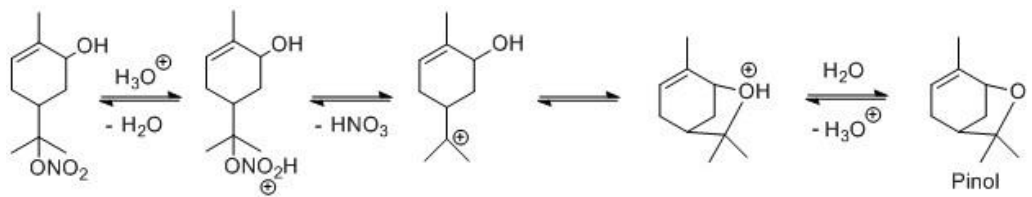
**Figure 6**. The proposed acid-catalyzed hydrolysis mechanism of an α-pinene-derived nitrate.

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