The Acid-Catalyzed Hydrolysis of an α-Pinene-Derived Organic Nitrate: Kinetics, Products, Reaction Mechanisms, and Atmospheric Impact

Joel D. Rindelaub, Carlos H. Borca, Matthew A. Hostetler, Jonathan H. Slade, Mark A. Lipton, Lyudmila V. Slipchenko, Paul B. Shepson

Department of Chemistry, Purdue University, West Lafayette, IN, 47907, USA

Correspondence to: Joel D. Rindelaub (jrindela@purdue.edu), Paul B. Shepson (pshepson@purdue.edu)

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 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 (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 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 a 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 (IPCC, 2007), damages plants/crops (Fiscus et al., 2005), and is a lung irritant (EPA, 2011), the formation and fate of organic nitrates has implications for both climate and environmental health.

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). 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, 2016), are still very uncertain. While S$_N$2 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 nucleophlicity, 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 α-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 hydroxyl organic nitrate derived from α-pinene by injecting 10 µL of a given standard into a 100 mL buffered solution that was continuously mixed. The α-pinene-derived nitrate, shown in Fig. 1, was synthesized based on Pinto et al. (2007). 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 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. 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. FTIR analysis was accomplished by integrating the ~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.

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_2O), hydronium ion (H_3O^+), nitric acid (HNO_3), isobutyl nitrate (IBN), protonated
5 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,
10 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
15 (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.

20 ## 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 tertiary α-pinene-derived nitrate (APN), hydrolysis rate constants ranged from 3.2 x 10^{-5} s^{-1} at neutral pH (6.9) to 2.0 x 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
25 kinetics, and had rate constants smaller by more than two orders of magnitude relative to the APN, ranging from 1.23 x 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
30 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.

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 ωB97X-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 ωB97X-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 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 the identified product pinol using GC-MS (see Fig. 6), 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 unimolecular substitution (S_N1) or an elimination (E1) mechanism (Fig. 6; Bleier and Elrod, 2013). In this study, the reaction proceeded via an S_N1 pathway to form pinol by intramolecular attack from the secondary hydroxyl group to create a protonated pinol compound. The abstraction of the proton by water completed the acid-catalyzed reaction to create the final pinol product and H_3O^+.

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_N1 and E1 products, respectively, derived from 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).

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 (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).

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).

The formation of a relatively high vapor pressure product from α-pinene-derived nitrate hydrolysis, pinol, 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 is estimated to be three orders of magnitude greater than the original organic nitrate, based on calculations using the EPI Suite (see above). It is important to note that APN hydrolysis products

can have olefinic functionality, such as the case with pinol, and may react further in the particle phase, especially under acidic conditions, where sulfanation 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). Pinol has also been identified as a hydrolysis product of another α-pinene oxidation product, α-pinene oxide (Bleier and Elrod, 2013), thus, pinol may be an important tracer for the hydrolysis of α-pinene-derived species. Both the gas and particle phase fate of 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 that 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 α-pinene-derived organic nitrate, which has implications 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, the observed organic hydrolysis product, pinol, is 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, future work is needed to assess how the loss of particle phase organic nitrates impacts aerosol hygroscopicity.

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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	$(CH_3)_3COH + HNO_3 + H_3O^+$

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

pH	IPN	IBN	APN
		Lifetime	
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
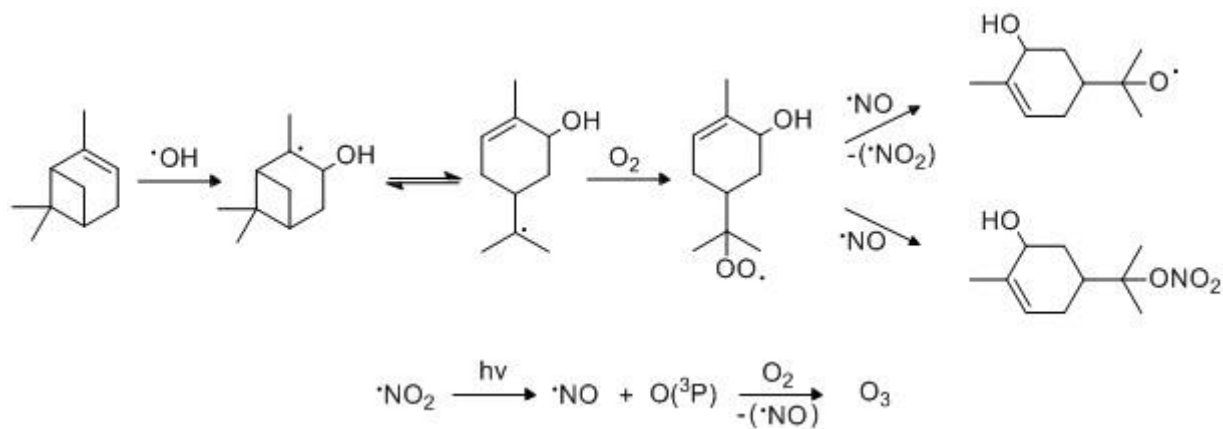
Figure 1: The formation of atmospheric organic nitrates and ozone from the gas phase oxidation of α-pinene, initiated by the OH radical.
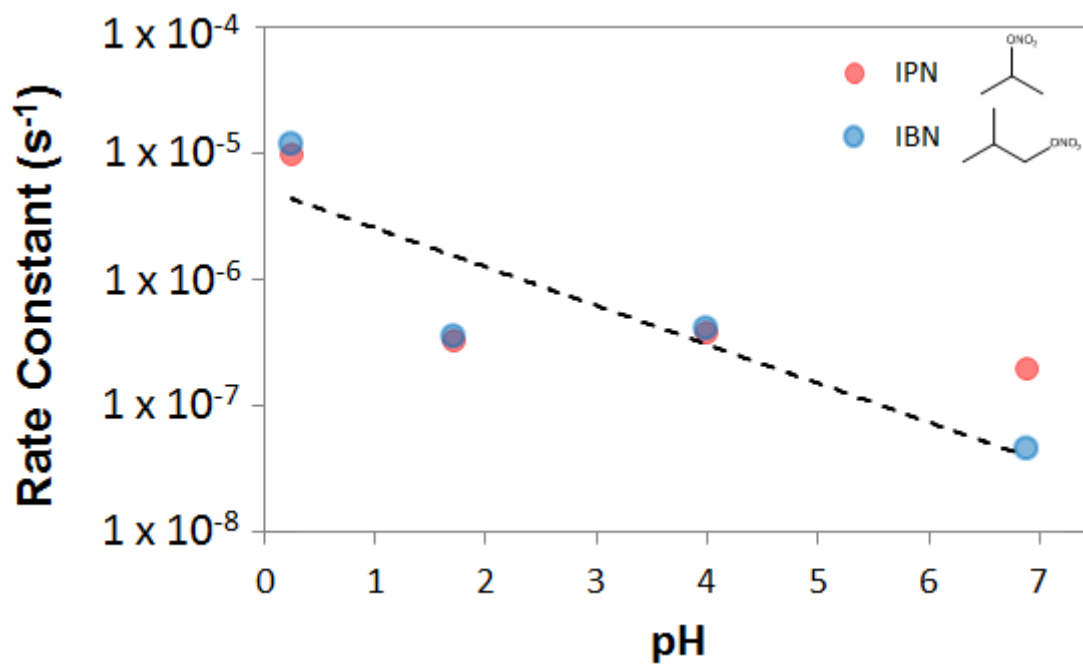
Figure 2: The hydrolysis rate constants (s⁻¹) for isopropyl nitrate (IPN; red) and isobutyl nitrate (IBN; blue) as a function of solution pH.
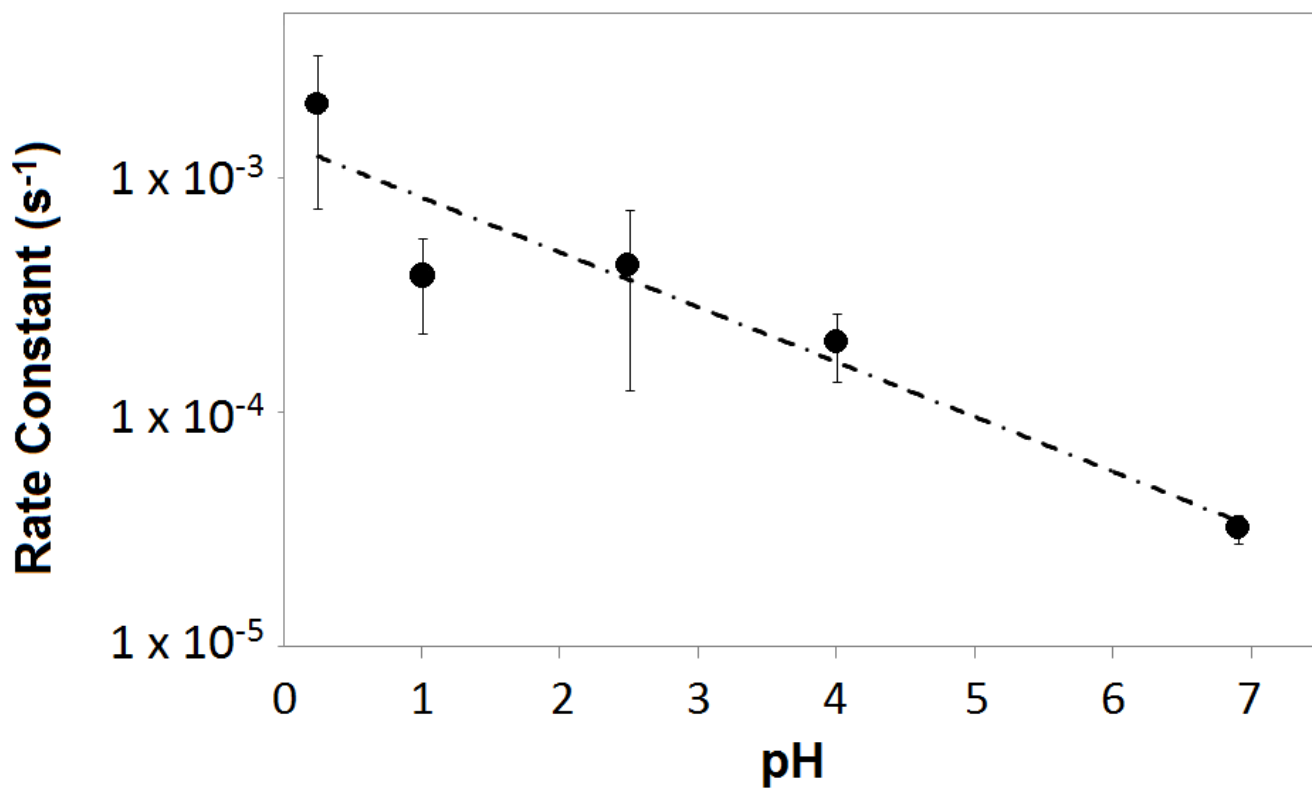
Figure 3: The hydrolysis rate constants (s^{-1}) for the α-pinene-derived nitrate as a function of solution pH. The error bars correspond to one standard deviation of replicate measurements.
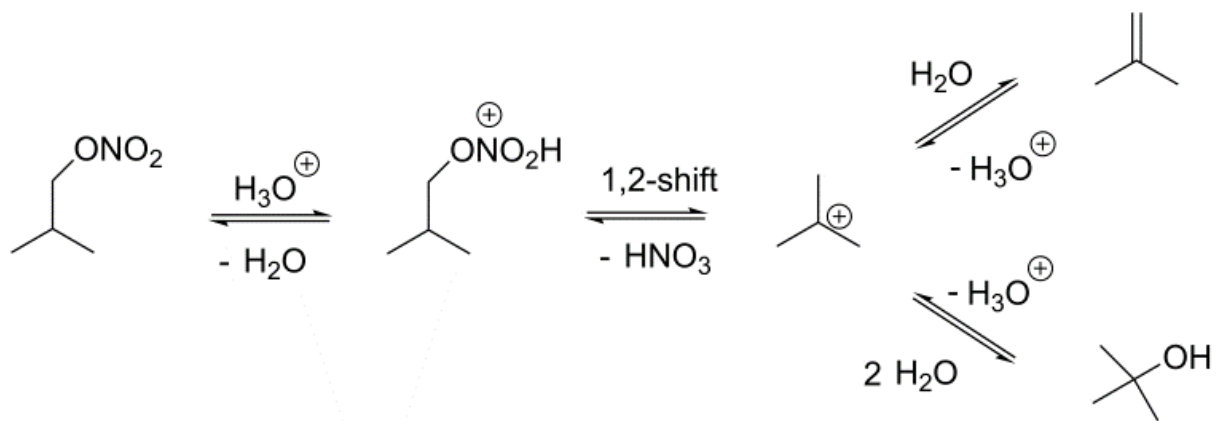
Figure 4: The proposed unimolecular mechanism for isobutyl nitrate (IBN) demonstrating the specific acid-catalysis and 1,2 hydride shift rearrangement.
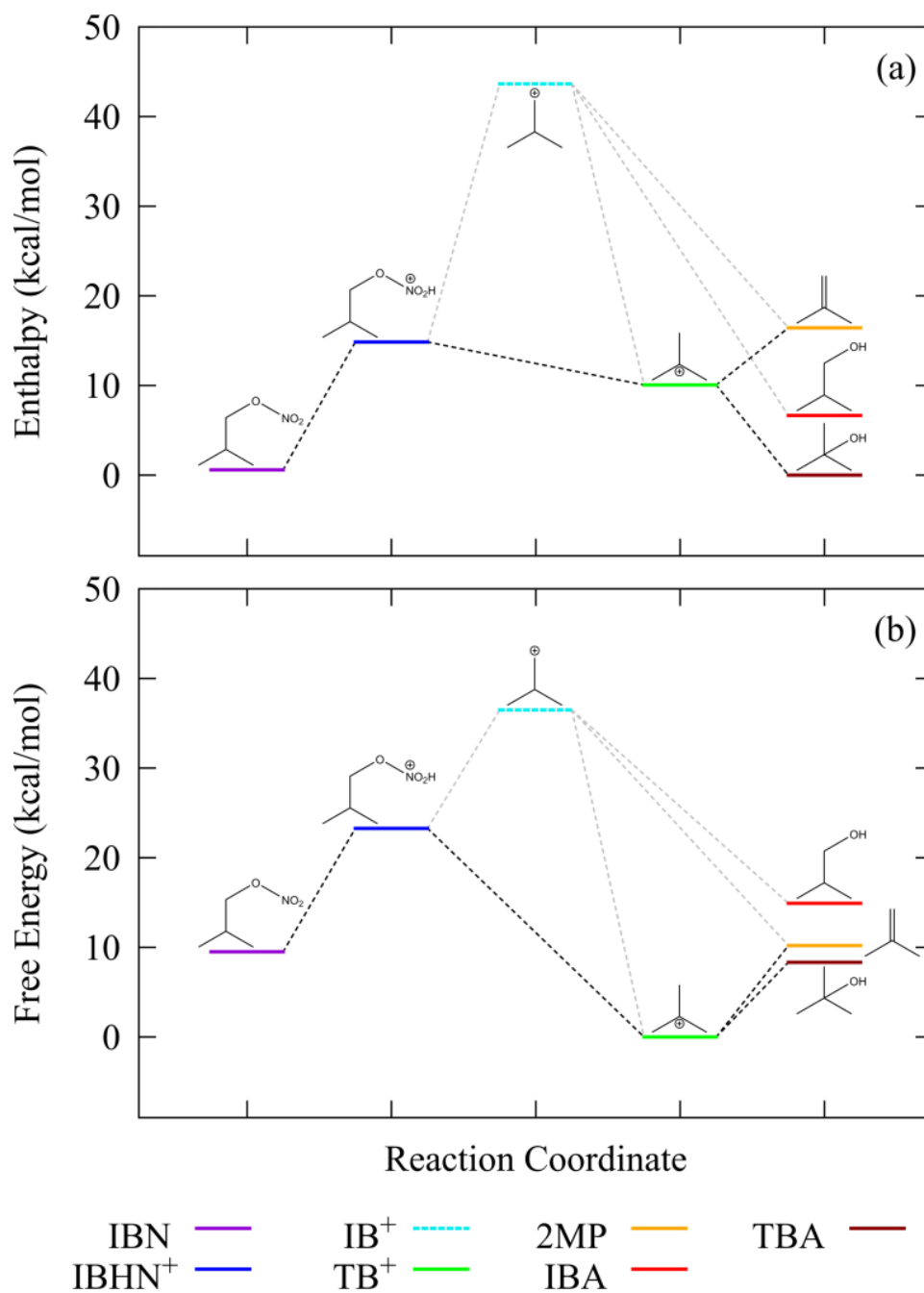
Figure 5: The calculated relative free energies of the intermediates and products of the proposed acid-catalyzed isobutyl nitrate hydrolysis mechanism. See Table 1 for calculation stoichiometry. The reaction is not likely to proceed through the IB⁺ intermediate, due to the instability of the carbocation.
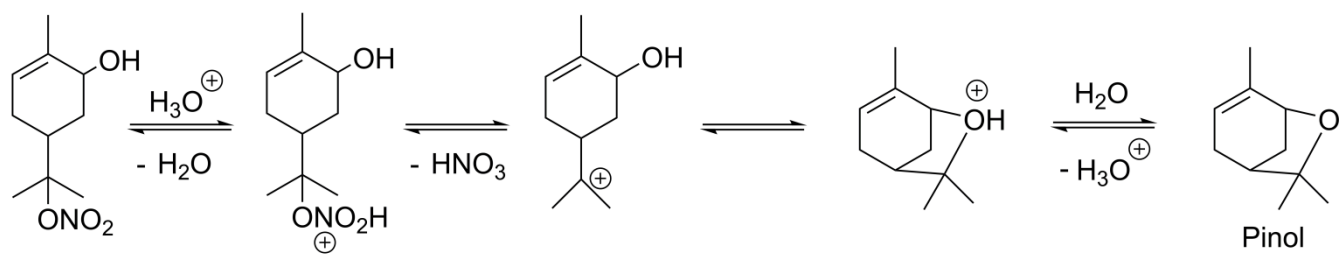
Figure 6. The proposed acid-catalyzed hydrolysis mechanism of an α-pinene-derived nitrate.