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Reactivity of a Carene-Derived Hydroxynitrate in Mixed Organic/Aqueous Matrices: Applying Synthetic Chemistry to Product Identification and Mechanistic Implications

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Abstract: β -hydroxynitrates (HN) are a major class of products formed during OH and NO₃ initiated oxidation of terpenes. Their production contributes significantly to secondary organic aerosol (SOA) formation and NO_x sequestration. However, studying the condensed phase reactions of this important class of molecules has been hindered by the lack of commercially available authentic standards. The goal of this work was to examine the influence of water concentration and solvent identity on product yields of a tertiary HN derived from 3-carene prepared in house. To assess the role of water on conversion chemistry, bulk-phase reactions were conducted in DMSO-*d*₆, a non-nucleophilic solvent, with a gradient of water concentrations, and analyzed with ¹H NMR. Product identifications were made by comparison with authentic standards prepared in house. Four major products were identified, including an unexpected diol produced from carbocation rearrangement, diol diastereomers, and *trans*-3-carene oxide, with varying yields as a function of water concentration. Product yields were also measured in two protic, nucleophilic solvents, MeOD-*d*₄ and EtOD-*d*₆. Finally, reactions with added chloride formed alkyl chloride products in yields approaching 30%. These results are among the first to highlight the complexities of nucleophilic reactions of hydroxynitrates in bulk, mixed aqueous/organic media and to identify new, unexpected products.

Keywords: hydroxynitrates 1; organic aerosol 2; hydrolysis 3

1. Introduction

The effects of aerosol on human health and the climate system have been well documented, and it is well established that the magnitude of the impact on each depends strongly on particle size and chemistry. The organic fraction of aerosol represents the most complex and poorly understood type of aerosol due to the wide range of processes and chemical species involved in its formation. Further, during its atmospheric lifetime, an aerosol particle is subjected to a myriad of physical and chemical processes that conspire to alter the chemical composition of the particle. Atmospheric condensed-phase reactivity is likely to differ substantially from the gas phase due to the drastic differences in molecular environments. Further, gas phase studies are disproportionately conducted relative to studies of condensed-phase reactions, hence this chemistry remains poorly understood.

Hydroxynitrates (HN) are one of the major classes of oxidation products formed in the atmosphere, following the OH or NO₃ radical-initiated oxidation of volatile organic compounds (VOCs) [1–5]. An example oxidation pathway for 3-carene, the bicyclic

monoterpene that is the focus of this study, begins with preferential addition at the secondary carbon to form the relatively more stable tertiary alkyl radical (Scheme 1). This species then rapidly couples with O_2 to form an alkylperoxy radical that undergoes a chain termination reaction with gas phase NO to form a tertiary β -hydroxynitrate (HN). The formation of HN has two major effects on air quality: (i) sequestering gas phase NO_x (NO and NO_2), which in turn impacts O_3 concentrations, [6–11] and (ii) significantly reducing the vapor pressure of the parent substrate and converting it into a semi-volatile species capable of contributing to secondary organic aerosol (SOA) [5,12–17]. Field measurements found that 5–23% of the molecules in SOA contain the nitrate functionality, which includes HN, highlighting their role in SOA formation [14,16,18]. While there is some understanding of HN production, our understanding of their fate in the condensed phase is limited, in part due to the absence of commercially available authentic standards.

Scheme 1. Example oxidation pathway of carene.

The dominant loss mechanisms of condensed-phase HN are believed to be deposition or hydrolysis, as direct photolysis is believed to proceed too slowly relative to the lifetime of an aerosol particle [19,20]. To date, a number of studies have implicated hydrolysis in the loss of organonitrates from the bulk, condensed-aqueous phase. These studies have primarily focused on smaller, water-soluble species [21–26]. Smog chamber studies have been completed with larger species and generally involve forming SOA from a gas phase precursor under high RH conditions [27–32]. The loss of nitrate traces from the particle phase is monitored once oxidation has ceased. From the perspective of the HN, these two systems represent vastly different molecular environments: water compared with a mixed, aqueous/organic solvent. It is unclear how matrix effects may impact the observed chemistry based on these previous studies.

Hydrolysis reactions can occur via two pathways depending on the substrate structure: (Scheme 2) a unimolecular S_N1 process where the NO_3^- leaves the substrate to generate a carbocation followed by nucleophilic addition of water, or (Scheme 3) a bimolecular S_N2 reaction where the water adds opposite to the $-ONO_2$, facilitating the release of an NO_3^- . Branched substrates, or those containing a bulky neighboring group that limits accessibility to the carbon containing the $-ONO_2$, tend to favor S_N1 reactions. Thus, we expect this pathway to dominate here as was suggested in other studies [23,24,32]. Nonetheless, both reaction pathways are sensitive to the identity of the solvent. S_N1 reactions tend to proceed faster in polar, protic solutions where the carbocation intermediate and the leaving group are stabilized. However, to the best of our knowledge, whether solvent effects impact product formation in the reaction of HNs has not been investigated directly.

Scheme 2. S_N1 hydrolysis mechanism.

Scheme 3. S_N2 hydrolysis mechanism.

The goal of this study was to examine bulk, condensed-phase reactivity of a tertiary carene-derived β -hydroxynitrate in several complementary systems. Reactions were con-

ducted in bulk by varying the concentration of water from a 100% aqueous solution to 0.6% water in an unreactive, non-nucleophilic solvent, DMSO- d_6 . Using authentic standards synthesized in house, we confirmed the identities of the major products from each reaction using ^1H NMR. Yields were determined as a function of water concentration to provide new insight into the most probable conversion mechanisms involved. Additional experiments in both neat and aqueous mixtures with MeOD- d_4 and EtOD- d_6 were run to achieve two aims. First, the mixtures should mimic a polar-protic matrix with enhanced solubility to enable homogeneous reaction mixtures. Methanol, for example, is commonly used as a solvent for aerosol sample extraction and preparation. Second, to determine the susceptibility of HN to nucleophilic reactions with species other than water. Finally, reactions with chloride, a strong nucleophile and atmospherically abundant species, were completed to probe the reactivity of HN towards inorganic nucleophiles. The results from this work are among the first which examine the reactivity of hydroxynitrates in bulk, single phase, mixed organic/aqueous matrices. Further, this work highlights the utility in applying synthetic chemistry and NMR to elucidate reaction mechanisms and identify new products in atmospheric chemistry.

2. Materials and Methods

2.1. General Methods

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. CHN **1** and *trans*-3-carene oxide **4** were prepared according to McKnight et al. [33]. Silica gel TLC plates (60 μm) with a fluorescent indicator (254 nm) were used to monitor the progress of the reactions; they were visualized using UV, anisaldehyde, or KMnO_4 stain. Purification was accomplished with silica gel column chromatography using a Teledyne Isco CombiFlash Lumen with 25 μm SiliCycle spherical silica gel columns. ^1H , ^{13}C , 1D-NOE, HSQC, and COSY NMR spectra were recorded on a Bruker AV 400 spectrometer and referenced to the protic residue of the deuterated solvent: chloroform- d (7.26 ppm), methanol- d_4 (3.31 ppm), ethanol- d_6 (3.56 ppm), or dimethyl sulfoxide- d_6 (2.50 ppm) unless otherwise noted. IR spectra were recorded on a ThermoNicolet IR 100 spectrometer using a Thunderdome attenuated total reflectance (ATR) sample accessory. High-resolution mass spectroscopy data was acquired via a Vanquish UHPLC/HPLC system coupled to Q Exactive Orbitrap MS with electrospray ionization in positive mode. Abbreviations include ethyl acetate (EtOAc), column volume (CV), retention factor (R_f), singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of triplets (tt), multiplet (m), broad (br), weak (w), medium (m), and strong (s). Selected, representative ^1H NMR signals which were used for product identification are given in Table 1. Full spectral characterization data are provided in the Supplemental Information. Yields are reported as the molar ratio of each product to the amount of CHN **1** reacted by the end of the experiment. Molar quantities were calculated from ^1H NMR integrations normalized to the number of equivalent hydrogens of unique signals from analytes (Table 1) and an internal standard, 1,2,3-trimethoxybenzene (d, 6.35 ppm, 2H) or 4-bromochlorobenzene (d, 7.37 ppm, 2H).

2.2. NMR Scale Reaction Procedures

2.2.1. Reaction in 0.6% D_2O in DMSO- d_6

All steps were carried out under argon unless otherwise stated. DMSO- d_6 was dried by vacuum distillation over CaH_2 (65 $^\circ\text{C}$, 9 mm Hg) and stored in a Schlenk flask in a desiccator chamber when not in use. 1-bromo-4-chlorobenzene (61 mg) was dried by P_2O_5 in a desiccator for 3 days. Dry DMSO- d_6 (8.5 mL) was transferred to the dry 1-bromo-4-chlorobenzene to make the internal standard solution (37 mM). A solution of D_2O (40 μL) in dry DMSO- d_6 (3.82 mL) was also prepared (0.57 M D_2O). The 1-bromo-4-chlorobenzene solution (0.4 mL, 37 mM) and D_2O solution (0.4 mL, 0.57 M) were mixed with dried CHN **1** (5 mg), then transferred to an NMR tube. The reaction progress was monitored by ^1H NMR until completion (at least 90% consumption of starting material).

Table 1. Product structures and selected identifying ^1H NMR signals in $\text{DMSO-}d_6$. 1 Hydrogen atoms corresponding to the identifying signals are indicated in blue.

ID	Structure	^1H NMR (ppm)
<i>trans</i> -2		3.11 (dd)
<i>cis</i> -2		3.41 (dd)
3		0.14 (dt)
4		2.79 (brs)
5		3.43 (dd) ²
6		3.42 (dd) ³
<i>trans</i> -7		3.33 (dd)
<i>cis</i> -7		3.94 (t)

¹ Full spectral data are provided in the Supplemental Information. ² $\text{MeOD-}d_4$. ³ $\text{EtOD-}d_6$.

2.2.2. Reactions in 4.2–50% D_2O / $\text{DMSO-}d_6$

A known mass of 1-bromo-4-chlorobenzene or 1,2,3-trimethoxybenzene (internal standard) was dissolved in varying concentrations of D_2O in $\text{DMSO-}d_6$. This solution (0.7 mL) was mixed with CHN 1 (5–6 mg), then transferred to an NMR tube. The reaction progress was monitored by ^1H NMR until completion.

2.2.3. Reactions in 100% H_2O

CHN 1 (101 mg, 0.469 mmol) was suspended in D.I. water (5 mL, 0.09 M), then stirred at room temperature for 16 h. The reaction mixture was quenched with 0.5 M NaOH (0.938 mL, 1 equivalent), then concentrated in vacuo. ^1H NMR (CDCl_3) was used to evaluate the product distribution of the reaction.

2.2.4. Reactions with MeOD- d_4

A known mass of 1-bromo-4-chlorobenzene or 1, 2, 3-trimethoxybenzene (internal standard) was dissolved in MeOD- d_4 or 16.7% (v/v) D₂O/MeOD- d_4 . This solution (0.7 mL) was mixed with CHN 1 (5–6 mg), and then transferred to an NMR tube. The reaction progress was monitored by ¹H NMR until completion.

2.2.5. Reactions with EtOD- d_6

A known mass of 1-bromo-4-chlorobenzene or 1, 2, 3-trimethoxybenzene (internal standard) was dissolved in EtOD- d_6 or 16.7% (v/v) D₂O/EtOD- d_6 . This solution (0.7 mL) was mixed with CHN 1 (5–6 mg), and then transferred to an NMR tube. The reaction progress was monitored by ¹H NMR until completion.

2.2.6. Reactions with NaCl

A known mass of 1-bromo-4-chlorobenzene (internal standard) was dissolved in a solution of NaCl (1 or 5 equivalent) in 8.4% (v/v) D₂O/DMSO- d_6 . This solution (0.7 mL) was mixed with CHN 1 (5–6 mg), and then transferred to an NMR tube. The reaction progress was monitored by ¹H NMR until completion.

3. Results

We began our investigations by attempting to synthesize diol 2 by treating CHN 1 with water. The reaction of CHN 1 in pure water was challenging to observe in situ by ¹H NMR because CHN 1 has a low aqueous solubility (<0.4 mM) [34] that is below the threshold necessary for this technique (>5 mM). Bulk aqueous-phase reactions were instead conducted as a slurry in H₂O. The NMR spectrum of the reaction mixture after 16 h contained one major product (diol 3). Notably, we did not observe signals consistent with the *trans*- & *cis*-diols 2 produced from the direct nucleophilic addition of water to the carbocation (Figure 1). Instead, the major product was identified as diol 3. The structure of diol 3 was confirmed by isolation of this product using column chromatography and comparison of the NMR spectra with literature data [35].

Figure 1. Product formation from CHN 1 in D₂O/DMSO- d_6 mixtures.

The likely mechanism for the formation of rearrangement diol 3 is given in Figure 1. Following the formation of the carbocation, rearrangement occurs, forming an acyclic propyl group that can accommodate the positive charge in the absence of the ring strain. The rearranged tertiary carbocation then undergoes substitution with water to yield the tertiary diol 3. As a dynamic, heterogeneous system, product yields were not determined by ¹H NMR integrations of the bulk reaction mixture, but instead by measuring the molar ratio of diol 3 recovered after purification by column chromatography to the starting amount of CHN 1 added to the reaction mixture (entry 1, Table 2). The experimental procedure for the purification and isolation of this material is described in the Supplemental Information.

Table 2. Product yields from the conversion of CHN **1** with varying % D₂O in DMSO-*d*₆. Yields are reported as averages with standard deviations obtained from triplicate measurements or not determined (n.d.) because the signal was below detection.

Entry	%D ₂ O	<i>cis</i> -2	<i>trans</i> -2	3	4
1	100 ¹	n.d.	n.d.	0.68 ²	n.d.
2	50	n.d.	0.33 ³	0.67 ³	n.d.
3	25	0.25 ± 0.02	0.21 ± 0.01	0.13 ± 0.03	0.03 ± 0.00
4	16.7	0.42 ± 0.04	0.22 ± 0.01	0.02 ± 0.01	0.04 ± 0.01
5	8.4	0.46 ± 0.04	0.10 ± 0.01	0.02 ± 0.03	0.05 ± 0.01
6	4.2	0.53 ± 0.01	0.10 ± 0.01	n.d.	0.04 ± 0.00
7	0.6	0.91 ± 0.02	n.d.	n.d.	0.08 ± 0.05

¹ Reaction was run in H₂O; ² a single isolated yield after column chromatography; and ³ a single run completed.

Given this unexpected result and the limited solubility in pure water, we explored the condensed-phase reactivity of CHN **1** in bulk deuterated solvent mixtures. The final products were analyzed by ¹H NMR relative to an internal standard. It was critical to compare our data with reference spectra collected using authentic standards that were synthesized in house to identify each specific product in the NMR because chemical shifts are heavily influenced by the identity of the matrix. Three solvents were investigated: DMSO, a polar aprotic, non-nucleophilic solvent, as well as polar protic alcohols, methanol and ethanol.

3.1. HN Reactivity in a Single-Phase Mixed D₂O/DMSO-*d*₆ Solution

Condensed-phase reactions of CHN were run in mixtures of D₂O in DMSO-*d*₆. Reactions were run with the addition of controlled amounts of D₂O to assess the role that a changing solvent identity had on product yields at the following concentrations: 50%, 25%, 16.7%, 8.4%, 4.2%, and 0.6% (Table 2). In this set of reactions, we observed four products that appeared in varying yields depending on the matrix composition (see Table 1 for representative ¹H NMR signals, Figure 2 and page 44 of the SI for ¹H NMR). There were two diol diastereomers (*trans*-2 and *cis*-2, 3.11 and 3.41 ppm), the re-arrangement diol **3** (0.14 ppm), and epoxide **4** (2.79 ppm). The yields of each product were determined by integration of a characteristic signal (Table 1) relative to an internal standard. Yields were measured at the completion of the experiment, after five hours or when at least 90% of the CHN **1** had been converted to product (Table 2).

Figure 2. ¹H NMR spectra of CHN **1** reactions in (a) 50%; (b) 25%; and (c) 0.6% D₂O/DMSO-*d*₆ mixtures.

At 50% D₂O (entry 2, Table 2; Figure 2a) the mixture was dominated by the rearrangement product **3** (0.67) and *trans*-diol **2** (0.33). Due to solubility constraints, this reaction was also a dynamic heterogeneous mixture. However, the observed trend which transitions from favoring the expected diol to rearrangement diol **3** is consistent with the results in pure water where it was the dominant product. As the concentration of D₂O was decreased, there was a shift in the product distribution. At 25% D₂O (entry 3, Table 2; Figure 2b), the *cis*-diol **2** appeared in near equal amounts to *trans*-diol **2** (0.25 to 0.21, respectively). A small amount of rearrangement diol **3** (0.13) and epoxide **4** (0.03) also appeared. At lower concentrations of water, the *cis*-diol **2** becomes the major product, with no observable *trans*-diol **2** at 0.6% D₂O (entry 7, Table 2; Figure 2c). The epoxide concurrently increased to a maximum yield of 0.08.

3.2. HN Reactivity in Single-Phase D₂O/Alcohol Solutions

Reactivity studies of CHN **1** in mixtures of alcoholic solvents and water were run. Ethanol and methanol were chosen as polar protic solvents that are weak nucleophiles ($pK_a \sim 16$) capable of adding to a CHN **1** carbocation (Figure 3). Additionally, these commonly used extraction solvents were examined as simple models for smaller, low volatility, oxidized species, even though neither are believed to exist in appreciable amounts in ambient aerosol particles due to their high C^* .

Figure 3. Product formation from CHN **1** in D₂O/MeOD-*d*₄ and EtOD-*d*₆ mixtures.

Complete consumption of CHN **1** in 16.7% D₂O in MeOD-*d*₄ was observed to occur within 4 h at 30 °C as evidenced by a decrease in the -CH₃ singlet (1.80 ppm). From the NMR spectrum of the final product mixture (entry 1, Table 3), we were able to identify two prominent new signals corresponding to the same rearrangement diol **3** observed in the D₂O reactions (0.39, 4.00 ppm), an ether product **5** (0.27, 3.55 ppm), as well as a minor amount of *trans*-diol **2** (0.19, 1.98 ppm). An authentic standard of ether **5** was prepared by stirring epoxide **4** in a solution of methanol with an equivalent of bismuth nitrate (Scheme 4) [33]. Spectral data of the authentic material was compared with the reaction mixture to confirm the identity of **5**. In pure methanol, CHN **1** mainly produced **5** (0.51) after 20 h at 30 °C, formed by the addition of methanol to the CHN carbocation (entry 2, Table 3). While care was taken to exclude water, methanol is highly hygroscopic, and as a result adventitious water reacted with CHN **1** to form the rearrangement diol **3** with a yield of 0.20. Finally, minor signals corresponding to the epoxide **4** were observed, but the signal-to-noise ratio was too low for quantification.

Table 3. Product yields from the conversion of CHN **1** with varying % D₂O in alcoholic solvents. Yields are reported as averages and standard deviations obtained from triplicate measurements or not determined (n.d.) because the signal was below detection.

Entry	% D ₂ O	Solvent	5 or 6	<i>Cis</i> -2	<i>Trans</i> -2	3	4
1	16.7	MeOD- <i>d</i> ₄	0.27 ± 0.02	n.d.	0.19 ± 0.02	0.39 ± 0.02	n.d.
2	0		0.51 ± 0.06	n.d.	n.d.	0.20 ± 0.03	n.d.
3	16.7	EtOD- <i>d</i> ₆	n.d.	0.05 ± 0.03	0.30 ± 0.01	0.24 ± 0.02	0.04 ± 0.04
4	0		n.d.	0.36 ± 0.01	0.13 ± 0.03	0.09 ± 0.01	n.d.

Scheme 4. Bismuth-mediated methanolysis of CHN 1.

Unlike methanol, the reaction of CHN 1 in EtOD- d_6 at 30 °C was a longer reaction, than in methanol, reaching 90% conversion after one day. The major product in pure EtOD- d_6 (entry 4, Table 3) was *cis*-diol 2 (0.36), with smaller amounts of *trans*-diol 2 (0.13) and rearrangement diol 3 (0.09). The spectral data from the reactions of CHN 1 in EtOD- d_6 were compared with the authentic standards for diols 2, 3, and epoxide 4. We were surprised that ether 6 was not detected in the reaction mixture. In order to confirm the absence of ether 6, an authentic standard was prepared by mixing *trans*-carene oxide with bismuth tribromide in ethanol (Scheme 5). Relative stereochemistry of 6 was confirmed via 1D NOE experiments. With the addition of 16.7% water to the reaction mixture (entry 3, Table 3), the product distribution switched to a majority of *trans*-diol 2 (0.30) and rearrangement diol 3 (0.24). A trace amount of *cis*-diol 2 (0.05) and epoxide 4 (0.04) were detected. Ether 6 was also not detected in this reaction.

Scheme 5. Bismuth-mediated ethanolysis of epoxide 4.

3.3. CHN Reactivity in D_2O /DMSO- d_6 Solutions Containing Cl^-

Given the propensity of CHN 1 to react with methanol, we were curious to explore the reactivity with chloride (Figure 4), a ubiquitous species present in aerosol from a number of natural and anthropogenic sources [36]. The addition of a single equivalent of NaCl generated a mixture of *cis*-diol 2 (0.49) and *cis*-alkyl chloride 7 (0.19). Minor amounts of the *trans*-isomers of 2 and 7, as well as trace amounts of 3 and 4 were detected (entry 1, Table 4). Increasing the amount of NaCl to five equivalents reduced the amount of *cis*-diol 2 produced (0.27), and increased the complexity of the mixture (entry 2, Table 4). Nearly equivalent amounts of *trans*- and *cis*-alkyl chloride 7 were produced, along with trace amounts of 3 and 4.

Figure 4. Product formation from the reaction of CHN 1 with Cl^- in 8.4% D_2O /DMSO- d_6 .

Table 4. Product yields from the conversion of CHN 1 with varying equivalents of NaCl in 8% D₂O/DMSO-*d*₆. Yields are reported as averages and standard deviations obtained from triplicate measurements.

Entry	<i>n</i> Molar Equiv. NaCl	<i>Trans</i> -7	<i>Cis</i> -7	<i>Cis</i> -2	<i>Trans</i> -2	3	4
1	1	0.06 ± 0.01	0.19 ± 0.09	0.49 ± 0.25	0.08 ± 0.02	0.04 ± 0.03	0.03 ± 0.02
2	5	0.16 ± 0.08	0.18 ± 0.09	0.27 ± 0.15	0.08 ± 0.03	0.06 ± 0.03	0.02 ± 0.01

4. Discussion

In this study, we examined the role of solution composition and water concentration on product formation from the hydrolysis of a tertiary carene-derived β-hydroxynitrate. Using authentic standards prepared in house and ¹H NMR, we quantified the yields of four major products that formed in different proportions as a function of water concentration: *cis*- and *trans*-diol diastereomers 2, an atmospherically unidentified rearrangement diol 3, and an epoxide 4. We note that the final product mixtures from reactions with less than 50% water were complex and we were able to account for approximately 40–60% of the CHN 1 that was consumed. We observed a number of minor signals between 4.60–5.75 ppm which could correspond to allylic alcohol and alkenyl hydrogens. It is plausible that elimination pathways could account for the mass balance discrepancy. Work to confirm the identity of these minor products with synthetic standards is ongoing in our groups.

At the lowest water concentration, the *cis*-diol 2 was the major product (0.91), from the addition of water to the carbocation formed through loss of nitrate. While the S_N1 reaction producing *cis*-diol 2 may also produce *trans*-diol 2, the steric bulk from the methyl-substituted cyclopropane ring likely hinders attack from that face, and hence the single diastereomer was favored. From 0.6–50% D₂O, we observed an increase in the yields for both the *trans*-diol 2 and the rearrangement diol 3, and a coincident decrease in the *cis*-diol 2. Between 25% and 50% D₂O, the yields of rearrangement diol 3 increased by a factor of five. Some turnover point exists between 50% and 100% D₂O where the *trans*-diol 2 ceases to form.

With increased %D₂O, the solvent composition became more polar and protic; both changes served to stabilize the carbocation intermediate and the NO₃[−] leaving group, allowing for other reaction pathways to become favorable. These effects were especially pronounced at 25% D₂O when the carbocation formed from CHN 1 was sufficiently stabilized to undergo a rearrangement to form a tertiary propyl carbocation which then hydrolyzes to the rearrangement diol 3 (Figure 1). These results were consistent with those obtained from the 16.7% D₂O experiments run in ethanol and methanol. Both solutions provided a higher degree of carbocation stabilization through hydrogen bonding than the DMSO system and as a result we observed that the major diol product was the re-arrangement diol 3, followed by the *trans*-diol 2 product. These results were more consistent with those obtained at higher % D₂O experiments conducted in DMSO. Finally, the epoxide 4 was always a minor product (<0.08) with yields that were fairly insensitive to water concentrations below 50% D₂O. The epoxide 4 may also undergo hydrolysis to form the diol diastereomers 2 (Figure 1), and may explain why, to our knowledge, this species has not been reported in ambient measurements. It is plausible that this reaction pathway was faster at high water concentrations (50 and 100%).

The results from the mixed aqueous/DMSO studies clearly demonstrated how the identity of the solvent matrix, a proxy for aerosol particles, has a direct impact on the relative yields of each of the three isomers. Differences in the relative stereochemistry of the diols are likely to have subtle influences on the condensed-phase fate of each diastereomer. Moreover, while the rearrangement isomer 3 has an identical elemental composition to the other species, it is predicted to have different physiochemical properties. The vicinal -OH groups present on the diol diastereomers 2 result in stronger intramolecular H-bonding, and increases the C* of these isomers relative to the rearrangement diol 3 [17]. This has implications for an enhanced volatilization from the aerosol phase. Furthermore, reactivity with the OH radical was estimated to be a factor of two slower for the re-arrangement diol 3 than the diastereomer diols 2 [34]. These data indicate that the species may have

different atmospheric lifetimes. These results may have significant implications for the evolution of the chemical composition of the aerosol as well as the fate of later generation carene oxidation products.

The set of experiments run in pure, single-phase methanol and ethanol, and with added chloride provide new insight into the susceptibility of CHN 1 to reactions with other nucleophiles. Most notable was the identification of ether methanolysis product 5, from the addition of methanol to the carbocation in high yield (0.51) and the absence of the analogous ethanolysis product 6. Both species have roughly equivalent pK_a values, however, the steric bulk of the ethyl group likely hindered attack on the carbocation, preventing the ethanolysis product from forming. Given their high C^* , we do not anticipate that either solvent will be present in appreciable amounts in the condensed phase under ambient conditions. These results, however, suggest that great care should be taken when choosing solvents for aerosol collection and extraction as nitrate-containing species are extremely susceptible to degradation in alcoholic solvents.

Further, while kinetic measurements were not the focus of this study, we note that nearly complete conversion of CHN 1 to products in methanol and ethanol occurred within one day at 30 °C in “pure solvent,” and within four hours when 16.7% water was added. Additional experiments with other solvents are necessary to identify which provide the greatest stability for analytical measurements. Finally, the reactions run with the addition of the chloride ion in one or five molar equivalents relative to CHN 1 highlight the role inorganic nucleophiles may play in the reactions of HN. The combined yields of both chloride diastereomers was 0.25 to 0.44 for the one and five molar equivalent solutions, respectively, which were competitive with the formation of the diols at 8% D_2O . We note that organosulfates have been identified as products from epoxides treated with sulfuric acid [18]. Together with our results, these pathways represent a potentially important pathway for the degradation of HN in the atmosphere.

This study relied heavily on synthetic chemistry to prepare and characterize the products from a reaction that we had initially expected to be straight forward, the hydrolysis of a hydroxynitrate ester. We observed that the reaction was actually much more complex than we originally believed and that our initial hypothesis was incorrect. Importantly, these findings would not have been possible without the use of authentic standards and an analytical technique that could clearly differentiate and identify isomeric species. Resolving diastereomers is not possible with the conventional EI or CIMS mass spectrometry commonly used in atmospheric chemistry, nor would the identification of the rearrangement diol be straight forward. This work highlights the power of using synthesis and NMR for product identification and mechanism elucidation to improve our understanding of how aerosol species evolve in the atmosphere.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/atmos12121617/s1>, Synthetic procedures for the preparation of authentic standards, full spectral characterization data, and NMR of reaction mixtures.

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