Chemical Composition and Hydrolysis of Organic Nitrate Aerosol Formed from Hydroxyl and Nitrate Radical Oxidation of α-pinene and β-pinene

Masayuki Takeuchi1 and Nga L. Ng2,3*

1School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332, USA
2School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332, USA
3School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, 30332, USA

*Corresponding author: ng@chbe.gatech.edu

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Abstract

Atmospheric organic nitrate (ON) is thought to play a crucial role in the formation potential of ozone and aerosol, which are the leading air pollutants of concern across the world. Limited fundamental knowledge and understanding of the life cycles of ON currently hinders the ability to quantitatively assess its impacts on the formation of these pollutants. Although hydrolysis is currently considered as an important loss mechanism of ON based on prior field measurement studies, this process for atmospherically relevant ON has not been well constrained by fundamental laboratory studies. In this comprehensive study, we investigated the chemical composition and hydrolysis process of particulate ON (pON) formed from the oxidation of α-pinene and β-pinene by hydroxyl and nitrate radicals. For pON that undergoes hydrolysis, the hydrolysis lifetime is determined to be no more than 30 min for all systems explored. This is significantly shorter than those reported in previous chamber studies (i.e., 3-6 h) but is consistent with the reported lifetime from bulk solution measurement studies (i.e., 0.02-8.8 h). The discrepancy appears to stem from the choice of proxy used to estimate the hydrolysis lifetime. The measured hydrolyzable fractions of pON (FH) in the α-pinene+OH, β-pinene+OH, α-pinene+NO₃, and β-pinene+NO₃ systems are 23-32, 27-34, 9-17, and 9-15 %, respectively. While a very low FH for the nitrate radical oxidation system is expected based on prior studies, FH for the hydroxyl radical oxidation system is surprisingly lower than predicted in past studies. Overall, the hydrolysis lifetime as well as FH obtained in this study serve as experimentally constrained parameters that are required in regional and global chemical transport models to accurately evaluate the impacts of ON on nitrogen budget and formation of ozone and aerosol.
1. Introduction

The oxidation of biogenic volatile organic compounds (BVOC) by ozone (O\textsubscript{3}), hydroxyl radicals and nitrate radicals is a major source of secondary organic aerosol (SOA) globally (Kanakidou et al., 2005; Goldstein and Galbally, 2007; Spracklen et al., 2011). Many studies have pointed to the synergistic effects of anthropogenic emissions on biogenic SOA formation in the atmosphere (Weber et al., 2007; Carlton et al., 2010; Hoyle et al., 2011; Shilling et al., 2013; Xu et al., 2015a; Shrivastava et al., 2019). The oxidation of BVOC in environments with anthropogenic NO\textsubscript{x} emissions is an important mechanism for coupled biogenic-anthropogenic interactions. In the presence of NO\textsubscript{x}, the oxidation of BVOC can lead to the formation of organic nitrate (ON), a large component of reactive oxidized nitrogen. Results from ambient field measurements have revealed the ubiquitous presence of particulate ON (\textsubscript{p}ON), where it contributes to a large fraction of submicron organic aerosol at different sites worldwide (Fry et al., 2013; Xu et al., 2015b; Liu et al., 2012a; Rollins et al., 2012; Rollins et al., 2013; Lee et al., 2016; Kiendler-Scharr et al., 2016; Ng et al., 2017). These findings highlights the importance to understand the formation and fates of ON to accurately evaluate its roles in NO\textsubscript{x} recycling, O\textsubscript{3}, and SOA formation.

Monoterpenes (C\textsubscript{10}H\textsubscript{16}) is a major class of BVOC, with annual emissions of 157-177 Tg C yr\textsuperscript{-1} (Guenther et al., 2012). Laboratory studies have demonstrated that the nitrate radical oxidation of monoterpenes leads to a substantial formation of ON and SOA, with ON yields up to ~70% (Wangberg et al., 1997; Berndt and Boge, 1997; Griffin et al., 1999; Hallquist et al., 1999; Spittler et al., 2006; Fry et al., 2009; Fry et al., 2014; Boyd et al., 2015; Nah et al., 2016; Boyd et al., 2017; Slade et al., 2017; Claflin and Ziemann, 2018). For photooxidation of monoterpenes in the presence of NO\textsubscript{x}, ON yields as high as 26% have been reported for α-pinene (Noziere et al., 1999; Aschmann et al., 2002; Rindelaub et al., 2015). Monoterpene emissions do not depend strongly on light and typically continue at night, making them important ON and SOA precursors at any times of the day (daytime and nighttime) and throughout the year (different seasons). It has been shown that monoterpene-derived ON is prevalent in areas where there are substantial biogenic-anthropogenic interactions and oxidation of monoterpenes contributes to a large
fraction of SOA observed in the Southeastern U.S. (Xu et al., 2015a; Xu et al., 2015b; Lee et al., 2016; Zhang et al., 2018; Xu et al., 2018a).

One of the largest uncertainties in our understanding of monoterpene NO chemistry is the extent to which NO act as a permanent sink versus temporary reservoir of NOx (Takeuchi and Ng, 2018). This would depend on the fates of NO as they can either retain or release NOx upon further reactions. Once formed, gas-phase NO can undergo photolysis or hydroxyl radical oxidation to release NOx or partition into the particle phase. pON in turn can undergo further chemistry to release NOx or hydrolyze in the particle phase to form nitric acid (HNO3). Further, ON and HNO3 can be removed via dry and wet deposition. One important reaction of ON in the particle phase is hydrolysis in the presence of aerosol water, which is a mechanism for NOx loss (Day et al., 2010; Russell et al., 2011). Studies with bulk solutions showed that particle-phase hydrolysis of tertiary nitrate is fast with a lifetime of minutes, while primary and secondary nitrate is stable (Darer et al., 2011; Hu et al., 2011). However, the hydrolysis of pON in aerosol water is largely unconstrained. Results from field and modeling studies suggested a pON lifetime of a few hours (Pye et al., 2015; Lee et al., 2016; Fisher et al., 2016; Zare et al., 2018). A few recent laboratory chamber studies elicited a complex picture where pON formed from photochemical oxidation and nitrate radical oxidation of monoterpenes appear to experience different magnitudes of hydrolysis (Boyd et al., 2015; Rindelaub et al., 2015; Bean and Hildebrandt Ruiz, 2016; Boyd et al., 2017), likely due to the difference in the relative amount of primary, secondary, and tertiary nitrate in these oxidation systems. Overall, there are very limited studies on the further evolutions of ON produced from the oxidation of monoterpenes.

Here, we present results from a laboratory chamber study on the chemical composition and hydrolysis process of pON formed from oxidation of α-pinene and β-pinene by hydroxyl and nitrate radicals. Specifically, we report the hydrolysis lifetimes and the fraction of hydrolyzable pON formed in the systems examined in this study. This comprehensive chamber study on the hydrolysis of pON produced from various oxidation pathways of monoterpenes and peroxy radical (RO2) fates provides the fundamental data to better constrain the role of hydrolysis in modulating pON concentrations and lifetimes in the atmosphere, their potential as a NOx loss pathway, and their impacts on overall nitrogen budget, O3 and SOA formation.
2. Methods

2.1. Chamber experiment design and procedure

A series of chamber experiments were performed in the Georgia Tech Environmental Chamber facility (Boyd et al., 2015) housing two 12 m³ Teflon reactors. Precursor volatile organic compounds (VOC) were α-pinene (99 %, Sigma-Aldrich) and β-pinene (99 %, Sigma-Aldrich) and the oxidation conditions of interest were hydroxyl and nitrate radical oxidation, which were represented as “daytime” and “nighttime” experiments, respectively. Specifically, four different systems of VOC and oxidation conditions were studied: α-pinene+OH, β-pinene+OH, α-pinene+NO₃, and β-pinene+NO₃. In order to infer the hydrolysis process, experiments were performed under low RH (i.e., ~5 %) or high RH (i.e., ~50-70 %) conditions and with effloresced or deliquesced seed particles for the same initial concentrations of precursor VOC and oxidant precursors. Temperature in the reactors was kept at room temperature (22-25°C). Experimental conditions are summarized in Table 1.

Prior to every experiment, the reactor was flushed with zero air (AADCO, 747-14) for at least a day. A typical experiment began with the injection of seed aerosol into the reactor by atomizing dilute ammonium sulfate (AS; 0.015 M) or sulfuric acid + magnesium sulfate (SA+MS; 0.01 + 0.005 M) aqueous solution. The seed aerosol was either directly atomized into the reactor or passed through a dryer before entering the reactor. The difference between efflorescence RH (~35 %) and deliquescence RH (~80 %) for AS aerosol is fairly large (Seinfeld and Pandis, 2016). Taking advantage of this property, it is possible to vary the amount of water in aerosol under the same RH in the reactor. Initial seed number and volume concentrations upon atomization for 20 min were approximately $2 \times 10^4$ cm⁻³ and $2 \times 10^{10}$ nm³ cm⁻³, respectively. A known amount of precursor VOC in the liquid form was transferred into a glass bulb, which was then evaporated and carried into the reactor by flowing zero air at 5 L min⁻¹ through the bulb. Although the measurement of the precursor VOC concentration was not available for all experiments, the target and measured concentrations in the experiments when the measurements were available were consistent.
For “daytime” experiments, an oxidant precursor (i.e., H₂O₂) was introduced to the reactor in the same manner as VOC except that the glass bulb was gently heated by a heat gun to help evaporate faster. During the injection of H₂O₂, a desired amount of NO was introduced into the reactor from a cylinder containing 500 ppm NO (Matheson). For Exp. 3-5, 5 ppm NO at 5 L min⁻¹ was continuously injected to the reactor until the SOA growth ceased. For Exp. 1, 2, 6, and 7, 15 ppm NO at 5 L min⁻¹ was injected for 5-20 min several times until the SOA growth ceased. The NO concentration was usually on the order of tens of ppb and always remained above a few ppb, making the bimolecular reaction with NO a favorable RO₂ reaction pathway. The experiment was initiated by turning on the irradiation of UV light approximately 20 min after the end of the last injection to ensure that particles and vapors were mixed well inside the reactor.

The procedure for “nighttime” experiments was the same until the end of the precursor VOC injection. An oxidant precursor (i.e., N₂O₅) was pre-made in a flow tube by simultaneously injecting 500 ppm NO₂ (Matheson) at 0.4 L min⁻¹ and ~250 ppm O₃ (Jelight 610) at 0.5 L min⁻¹. A simple kinetic box model was used to adjust the concentration of O₃ and flow rates of both NO₂ and O₃ to maximize the production of N₂O₅ and minimize the concentration of O₃, such that the VOC was dominantly oxidized by nitrate radicals. Once N₂O₅ entered the reactor, it thermally decomposed to generate NO₂ and nitrate radicals. VOC was usually depleted within the first 15 min of the experiment. For Exp. 8 and 14, the injection order of precursor VOC and oxidant precursor was switched such that the injection of VOC marked the beginning of the experiment. For Exp. 12 and 13, 25 ppm formaldehyde was added to the reactor to enhance the branching ratio of RO₂+HO₂ (Schwantes et al., 2015; Boyd et al., 2015) by injecting an appropriate amount of formalin solution (37% HCHO, Sigma-Aldrich) in the same manner as the injection of H₂O₂. We do not discuss the details of the effect of the injection order nor the effects of the RO₂ fate here as they had negligible impact on the results concerning hydrolysis.

2.2. Instrumentation and data analysis

A High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS; Aerodyne Research Inc.) measured the concentrations of non-refractory organics (Org), sulfate (SO₄), nitrate (NO₃),
ammonium (NH₄), and chloride (Chl) (DeCarlo et al., 2006). The data were analyzed using PIKA v1.16.

For the majority of nitrate-containing aerosol regardless of the class (i.e., inorganic or organic), the nitrate moiety (i.e., -NO₂, -ONO₂, and -O₂NO₂) was known to be thermally fragmented into NO⁺ and NO₂⁺ and was measured as NO₃ (Farmer et al., 2010). As many past studies have demonstrated the feasibility to separate the contribution of inorganic (NO₃,Inorg) and organic nitrate (NO₃,Org) to the measured NO₃ based on the ratio of NO⁺ and NO₂⁺ (Fry et al., 2009; Farmer et al., 2010; Xu et al., 2015b; Kiendler-Scharr et al., 2016; Fry et al., 2018), we used Eq. (1) presented in Farmer et al (2010) to obtain NO₃,Org. Rₐₙ (i.e., NO⁺/NO₂⁺ from ammonium nitrate) was obtained from the routine ionization efficiency calibration of HR-ToF-AMS using 300 nm ammonium nitrate particles. The drawback of this method is that Rₐₙ (i.e., NO⁺/NO₂⁺ from organic nitrate aerosol) could vary depending on the chemical composition (Xu et al., 2015b). In addition, a non-negligible contribution of ammonium nitrate could be expected in experiments with deliquesced seed aerosol owing to high solubility of HNO₃. Thus, we obtained the Rₐₙ measured in low RH experiments for each system of VOC and oxidation condition. In order to account for changes in Rₐₙ over time, Rₐₙ was scaled accordingly assuming that the ratio of Rₐₙ to Rₐₙ in the same system was constant (Fry et al., 2013). Rₐₙ, Rₐₙ, and Rₐₙ/Rₐₙ values obtained in this study were consistent with previously reported values (Fry et al., 2009; Bruns et al., 2010; Boyd et al., 2015; Nah et al., 2016) and are summarized in Table S1.

A Filter Inlet for Gases and AEROsols (FIGAERO) (Lopez-Hilfiker et al., 2014) coupled to a High Resolution Time-of-Flight Iodide Chemical Ionization Mass Spectrometer (HR-ToF-I-CIMS; Aerodyne Research Inc.) detected a suite of gaseous and particulate oxidized organic species as well as selected inorganic species (Bertram et al., 2011; Lee et al., 2014). The operation of FIGAERO-HR-ToF-I-CIMS was detailed in the previous studies (Nah et al., 2016; Sanchez et al., 2016). Reagent ions were generated by flowing a mixture of CH₃I and dry ultra high purity (UHP) N₂ (Airgas) through a polonium-210 source (NRD; Model P-2021). The instrument measured gaseous compounds by sampling air from the reactor at ~1.7 L min⁻¹ while collecting particles onto a Teflon filter. Upon completion of the collection period, collected particles were desorbed by temperature-programmed dry UHP N₂ flow and subsequently analyzed.
by HR-ToF-I-CIMS. Sensitivity could decrease if the amount of reagent ions were significantly depleted
and/or if the secondary chemistry in the ion-molecule reaction (IMR) chamber occurred at a significant
degree (Lee et al., 2014). To avoid changes in sensitivity among experiments, gas-phase sampling flow was
diluted with zero air immediately before the inlet such that the evaporation of aerosol was minimal. The
amount of aerosol collected on the filter was also adjusted by varying the sampling rate from 1 to 6 L min−1
depending on the aerosol mass concentrations inside the reactor. Overall, the fraction of reagent ions to
the total ions was kept above 80 %. In addition, iodide ion chemistry has been known to be affected by the
water vapor pressure inside the IMR owing to the difference in thermodynamics between I− and H2O− to
analyte compounds (Lee et al., 2014). In order to minimize changes in the water vapor pressure inside the
IMR, a small continuous flow of humidified UHP N2 (30-50 ccm) through a bubbler at a reduced pressure
was continuously added to the IMR directly. Therefore, while the instrument was not calibrated to report
the concentration of detected species, it was possible to quantitatively compare measured signal of each ion
among experiments because the instrument was operated under configurations that prevented undesired
changes in sensitivity. The data were analyzed using Tofware v2.5.11 and all the masses presented in this
study were I− adducts.

A Scanning Mobility Particle Sizer (SMPS) that consisted of a Differential Mobility Analyzer (TSI
3040) and a Condensation Particle Counter (TSI 3775) was operated under the low flow mode with the
sheath flow of 2 L min−1 to detect particles up to 1 µm in electrical mobility size. A Cavity Attenuated Phase
Shift spectroscopy (CAPS; Aerodyne Research Inc.) (Kebabian et al., 2005), an ultra-sensitivity NOx
analyzer (Teledyne M200EU), and an UV absorption O3 analyzer (Teledyne T400) measured NO2, NOx,
and O3, respectively. In selected experiments, a Gas Chromatograph coupled to Flame Ionization Detector
(GC-FID; Agilent) was used to make sure that a desired amount of a precursor VOC was injected. Except
CAPS, NOx analyzer, and O3 analyzer, all instruments had their own dedicated sampling line.

3. Results and discussion

3.1. Chemical composition of secondary organic aerosol
Shown in Fig. 1 are the mass spectra of particle-phase species obtained from FIGAERO-HR-ToF-I-CIMS at peak SOA growth. Many of the major species detected in this study are previously reported using the same or different technique (Eddingsaas et al., 2012; Claflin and Ziemann, 2018; Boyd et al., 2015; Nah et al., 2016; Lee et al., 2016; Romonosky et al., 2017). Concerning the chemical composition of SOA from each system, a more distinct difference is observed between different oxidation conditions (i.e., hydroxyl vs. nitrate radical oxidation) than between different precursor VOC (i.e., α-pinene vs. β-pinene). This is expected as α-pinene and β-pinene have the same chemical formula and very similar structures while the oxidation condition is distinctively different (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012).

For “daytime” experiments where hydroxyl radicals are the dominant oxidants, the contribution of ON (i.e., C_{x}H_{y}N_{z}O_{w}) and non-nitrated organics (i.e., C_{x}H_{y}O_{z}) are comparable and their contributions are well spread out over a wide range of masses. A large contribution of C_{x}H_{y}O_{z} is expected because the formation of ON is a minor pathway in RO_{2}+NO (Perring et al., 2013). In Eddingsaas et al. (2012), the major compounds reported in the α-pinene+OH system include C_{8}H_{12}O_{4-6} and C_{10}H_{16}O_{4-6}, which are also detected in our study. A suite of C_{10} ON from the chamber experiment of the α-pinene+OH system are reported in Lee et al. (2016) with the chemical formula of C_{10}H_{15,17,19}NO_{4-9}. All of these masses are detected in this study, though we observe a considerable contribution of C_{10} ON (i.e., C_{8}H_{9,11}NO_{6} and C_{9}H_{13,15,17}NO_{6}) as well as a small fraction of C_{10} dinitrate (i.e., C_{10}H_{14,16}N_{2}O_{9,10}) that has been rarely reported (Fig. 1a). This significant contribution from species containing C_{<10} indicates the large contribution of fragmentation process that is a preferred pathway in high NO conditions (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012; Perring et al., 2013). It is possible that these species with C_{<10} are thermally decomposed products during the thermal desorption process (Stark et al., 2017). However, it is unlikely that thermal decomposition plays a significant role for the SOA generated via hydroxyl radical oxidation of monoterpenes because the desorption temperature for these compounds (i.e., peaking at ~50-70 °C) are much lower than the temperature at which decarboxylation or dehydration reactions (>120 °C) are
expected to occur (Stark et al., 2017). SOA chemical composition of the β-pinene+OH system is similar to that of the α-pinene+OH system but with a larger contribution of C₇H₇O₇.

Another interesting observation in the α-/β-pinene+OH systems is that a selected class of compounds (i.e., C₁₀H₁₃(NO₅₋₈)) with the same H/C exhibit the same time evolutions regardless of the number of oxygen (Fig. S1). This observation is consistent with the autoxidation mechanism, in which highly oxidized molecules are formed in a short time scale (Ehn et al., 2014; Crounse et al., 2013; Jokinen et al., 2015). The detection of compounds with O >7 also supports the presence of autoxidation process; otherwise it is extremely difficult to produce highly oxidized molecules in a timescale of a few hydroxyl radical oxidation reactions. It is important to note that the concentration of NO in our experiments has been mostly kept on the order of tens of ppb over the course of the experiments by a continuous injection of dilute NO and, therefore, this result suggests that autoxidation is not a negligible pathway of RO₂ fate even at a moderately high NO level in laboratory experiments and in polluted ambient environments. Indeed, recent studies (Berndt et al., 2016; Xu et al., 2019; Pye et al., 2019) suggest that the autoxidation rate constant for the α-pinene+OH system could be up to a few per second, which is comparable to the NO level of ~10 ppb. The autoxidation rate constant as well as the role of NO in autoxidation based on this observation will be discussed in details in a forthcoming publication.

In contrast, the signals of C₅HₓNₓOₓ are dominant in the nitrate radical oxidation condition, indicating that the production of ON is greatly favored over non-nitrated organics. This observation is consistent with a direct addition of a nitrate functional group to a double bond (Wayne et al., 1991; Ng et al., 2017), whereas the formation of ON in the hydroxyl radical oxidation condition is a minor channel of RO₂+NO reaction (Perring et al., 2013). Moreover, the contribution from species containing C<10 is minimal. This is because unlike hydroxyl radical oxidation, a hydrogen subtraction reaction by a nitrate radical is less efficient and, thus, multi-generation oxidation is unlikely to occur within the timescale of experiments (Wayne et al., 1991; Ng et al., 2017). This means that once the precursor VOC undergoes functionalization upon the initial nitrate radical oxidation, it is not likely to experience fragmentation during
Unlike “daytime” SOA, the distribution of masses is dominated by a few signature ions, such as C_{10}H_{13}NO_{5,6} and C_{20}H_{32}N_{2}O_{8-10} (Fig. 1c and 1d). In Boyd et al. (2015), Nah et al. (2016), and Lee et al. (2016), the major species reported in the $\alpha$/-$\beta$-pinene+NO$_3$ systems are monomeric nitrate aerosol (i.e., C_{10}H_{13,15,17,19}NO_{4-10}), while in this study a substantial contribution of dimeric species (i.e., C_{20}H_{32}N_{2}O_{8-11}) is observed. The abundant presence of dimeric compounds has been previously observed in some studies on nitrate radical oxidation of $\alpha$/-$\beta$-pinene (Romonosky et al., 2017; Claflin and Ziemann, 2018) and particle-phase reactions to produce such dimers have been proposed by Claflin and Ziemann (2018). Many of the reported species in Claflin and Ziemann (2018) except the trimeric species (mass scan range not extended to trimeric species in our study) are observed in our study. One major difference between Claflin and Ziemann (2018) and this study is the substantial presence of monomeric nitrate aerosol (i.e., 30-60% by signal) in this study. This difference may be attributed to the difference in the amount of available monomeric blocks to form dimer species. Assuming reversible dimerization process, the concentration of dimer species shall be proportional to the square of monomer concentration, such that the monomer to dimer ratio increases in a quadratic manner as the available monomer concentration decreases. Since the amount of SOA formed in Claflin and Ziemann (2018) is approximately two orders of magnitude higher than that in this study, the concentration of monomers in the particle-phase is higher, favoring a more efficient formation of dimeric species. Together, these results suggest that the contribution of dimeric nitrate aerosol could vary greatly depending on the concentrations of monomeric blocks at the specific time and location.

Previous field studies have reported the mass spectra of ambient C_{10} $\sigma$ON obtained by FIGAERO-HR-ToF-I-CIMS in rural Alabama site during the Southern Oxidant and Aerosol Study (SOAS) (Lee et al., 2016) and in rural forest in Germany (Zhang et al., 2018). A comparison of the ambient mass spectra with those obtained in this study reveals that average ambient $\sigma$ON resembles “daytime” $\sigma$ON more than “nighttime” $\sigma$ON (Fig. S2). $\sigma$ON from “daytime” experiments has a distribution of masses centered around C_{10}H_{13,15,17}NO_{7}, which is consistent with the ambient measurement data. On the other hand, nitrate radical
oxidation does not seem to oxidize organic species enough that the distribution of masses is skewed towards a less-oxidized region (i.e., C_{10}H_{13,15,17}NO_{5,6}). However, it is difficult to draw a quantitative conclusion simply based on this comparison because O_3, another important oxidant at night, is not studied. Moreover, an average lifetime of aerosol could extend up to a week and thus ambient aerosol is continuously exposed to further oxidation while the experiments here are more applicable to freshly formed aerosol. In addition, the use of C_{10}ON alone may not be a good representative of monoterpenes-derived ON as 42-74% of ON in this study contains fewer or more than 10 carbon (Table S2). Nonetheless, the chemical composition of aerosol generated in this study is comparable to those in the atmosphere and, thus, the results shall be directly applicable to relevant ambient conditions.

3.2. Hydrolysis of particulate organic nitrate

3.2.1. Proxy used to evaluate hydrolysis process

Various proxies using HR-ToF-AMS data have been used to infer ON hydrolysis in previous studies. In Bean and Hildebrandt Ruiz (2016), NO_3 measured by an Aerosol Chemical Speciation Monitor (ACSM, practically similar to how AMS operates and measures aerosol species) (Ng et al., 2011) is normalized to SO_4 as a means to account for particle wall-loss and is fitted by an exponential function to estimate the ON hydrolysis rate. On the other hand, Boyd et al. (2015) normalize NO_3 measured by HR-ToF-AMS to Org and attribute the relative decay of NO_3/Org between humid (RH ~50%) to dry (RH <5%) conditions to hydrolysis. Other approaches include the SMPS-derived particle wall-loss correction of NO_3 measured by HR-ToF-AMS followed by fitting its decay trend (Liu et al., 2012b) and the determination of fraction of total (i.e., gas and particle) ON to the precursor VOC consumed as a function of RH using a Fourier-Transform InfraRed spectroscopy (FTIR). Below, we systematically examine the use of different proxies using HR-ToF-AMS data to infer hydrolysis and discuss how the corresponding results are interpreted.

Figure 2 shows the time series of Org, NO_3, SO_4, and NH_4 measured by HR-TOF-AMS for α-pinene+NO_3 system. There is a substantial difference in NO_3 for the same VOC system but under different
reactor RH and phase state of seed particles (Exp. 10 and 11), while Org and SO4 concentrations are similar. The spike in NO3 in high RH wet seed experiment (Fig. 2b) is attributed to the uptake of N2O5 and/or dissolution of HNO3 into aqueous aerosol followed by neutralization with ammonia to produce ammonium nitrate. This is consistent with the sharp increase in molar ratio of NH4/SO4 to higher than 2, which is the theoretical value for AS particles. It is also possible that inorganic nitrate is generated via hydrolysis of gaseous ON that is too volatile to condense but is soluble enough to dissolve in aqueous aerosol and, thus, only appears in high RH experiments. Since we do not have a way to quantitatively differentiate the contribution of the aforementioned sources, the focus of this study is on hydrolysis of pON that is condensed driven by volatility. However, further study is required to investigate the hydrolysis of volatile yet soluble gaseous ON, and the approach must be different from the comparison between low and high RH experiments to obtain meaningful results.

To evaluate the extent of pON hydrolysis, the contributions of inorganic nitrate (NO3\textsubscript{Inorg}) and organic nitrate (NO3\textsubscript{Org}) to the measured NO3 need to be calculated. Firstly, NO3\textsubscript{Org} is estimated by subtracting NO3 associated with excess NH4. Secondly, NO3\textsubscript{Org} is derived from NO+/NO2+ approach (Sect. 2.2.). Figure S3 shows the comparison of NO3\textsubscript{Org} estimated by these two independent methods for the α-pinene+NO3 system. It is clear that NO3\textsubscript{Org} from both methods are consistent and that there is a considerable contribution of NO3\textsubscript{Inorg} to NO3 in the experiment. We note the contribution of NO3\textsubscript{Inorg} to NO3 can vary depending on experimental conditions with a range from to 28 to 90 % for all experiments in this study. Nevertheless, these results demonstrate that for laboratory experiments with high RH and wet seeds, when using HR-ToF-AMS data to infer hydrolysis, it is important to separate the measured NO3 into NO3\textsubscript{Inorg} and NO3\textsubscript{Org}.

Once NO3 is separated into NO3\textsubscript{Inorg} and NO3\textsubscript{Org}, we evaluate whether the normalization of NO3\textsubscript{Org} to SO4 and Org provides a consistent decay trend. Photooxidation of α-pinene (Exp. 3-5) is used as a case system. As hydrolysis is a reaction where liquid water is directly involved in, it is expected that the rate of hydrolysis will change proportionally as a function of aerosol water content. Based on the hygroscopicity...
parameter for AS (κ = 0.53) (Petters and Kreidenweis, 2007) and for ambient LO-OOA (κ = 0.08) (Cerully et al., 2015) that has a substantial contribution from \( \rho \)ON (Xu et al., 2015a), estimated aerosol water contents at peak SOA growth in Exp. 3-5 are approximately 0, 1, and 26 µg m\(^{-3}\), respectively. Figure S4 illustrates that AS seed particles are indeed effloresced in Exp. 4 (high RH, dry AS) but not in Exp. 5 (high RH, wet AS). These mass concentrations of aerosol water translate to 0, 6, and 36 mol L\(^{-1}\), respectively, under the assumption that SOA is miscible with liquid water. It is speculated that SOA formed in Exp. 3-5 are miscible with water because (1) the measured O/C ratio in HR-ToF-AMS (Canagaratna et al., 2015) is close to 0.7, which is near the lower end but above the liquid-liquid phase separation condition (Song et al., 2012) and (2) there is evidence of aqueous-phase reactions which highly depend on the availability of aerosol water, as discussed in Sect. 3.3. Thus, the decay rate of NO\(_3\),\( _{\text{Org}}\) normalized to SO\(_4\) and/or Org between Exp. 4 and Exp. 5 shall differ by a factor of 6 based on the molar concentrations of aerosol water.

Figure 3a shows the mass ratio of NO\(_3\),\( _{\text{Org}}\)/SO\(_4\) and the decay rate as a characteristic time in Exp. 3-5. The characteristic times of Exp. 4 and 5 (4.4 vs. 4.0 h) do not differ regardless of the molar concentrations of aerosol water, suggesting that the decreasing trend in NO\(_3\),\( _{\text{Org}}\)/SO\(_4\) may not be due to changes in aerosol water content and \( \rho \)ON hydrolysis, but arise from the difference in the reactor humidity alone. A comparison of NO\(_3\),\( _{\text{Org}}\)/SO\(_4\) and NO\(_3\),\( _{\text{Org}}\)/Org also reveals that these two proxies capture a different range of decay mechanisms. Figure 3b shows the relative decay trend of NO\(_3\),\( _{\text{Org}}\)/SO\(_4\) and NO\(_3\),\( _{\text{Org}}\)/Org between Exp. 4 (high RH) and Exp. 3 (low RH). If hydrolysis is a dominant decay mechanism of \( \rho \)ON, the trend of NO\(_3\),\( _{\text{Org}}\)/Org would be identical to that of NO\(_3\),\( _{\text{Org}}\)/SO\(_4\). This is because the organic moiety of hydrolysis product is generally considered to have a substituted alcohol group (Boschan et al., 1955) and to have a relatively similar vapor pressure and shall remain in the particle phase (Pankow and Asher, 2008). However, the measured decay trend of the two proxies is greatly different. It is possible that some organic moiety of hydrolysis product could be significantly more volatile and repartition back to the gas phase (Rindelaub et al., 2016; Bean and Hildebrandt Ruiz, 2016) and, thus, both organics and HNO\(_3\) formed from hydrolysis evaporate. In this case, not only NO\(_3\),\( _{\text{Org}}\) but also some fraction of Org would decrease because Org measured by HR-ToF-AMS includes the contribution from the organic part of \( \rho \)ON. This will lead to the relatively
smaller decrease in NO$_3$$_{\text{Org/Org}}$ compared to NO$_3$$_{\text{Org/SO}_4}$. We can reconstruct the decay rate of NO$_3$$_{\text{Org/Org}}$ assuming 1) the decay rate of NO$_3$$_{\text{Org/SO}_4}$ is solely due to hydrolysis of pON and 2) the maximum contribution of pON to OA is 35% (see Fig. 4 and discussions below). The reconstructed decay rate of NO$_3$$_{\text{Org/Org}}$ is shown in Fig. 3b. As observed in the figure, the decay rate of the reconstructed NO$_3$$_{\text{Org/Org}}$ is much larger than the measured NO$_3$$_{\text{Org/Org}}$. This suggests that hydrolysis is not the only loss process reflected in the decreasing trend of NO$_3$$_{\text{Org/SO}_4}$, while NO$_3$$_{\text{Org/Org}}$ is likely a better proxy that isolates hydrolysis from other loss processes. The likely important loss process manifested in NO$_3$$_{\text{Org/SO}_4}$ is the loss of organic vapors to the walls of the rector (Matsunaga and Ziemann, 2010; Krechmer et al., 2016; Huang et al., 2018; Loza et al., 2010; Mcvay et al., 2014; Zhang et al., 2015; Zhang et al., 2014; La et al., 2016). For example, Huang et al. (2018) observe that the decay of isoprene hydroxyl nitrate depends on the reactor humidity. Therefore, NO$_3$$_{\text{Org/Org}}$ is a better proxy to infer hydrolysis of pON than others.

3.2.2. Hydrolysis lifetime of particulate organic nitrate

In order for the data to be easily comparable with those reported in models or using other technique, the use of general terms instead of the AMS specific terms (i.e., NO$_3$$_{\text{Org}}$ and Org) can be convenient. We define pON as the total mass concentration of particulate organic nitrate (includes organics part and nitrate part of the ON compounds) and OA as the total mass concentration of organic aerosol (includes nitrate and non-nitrated organics). The inclusion of nitrate mass in OA is important as the contribution of nitrate functional groups to the total organic aerosol concentration is large. The conversion method from NO$_3$$_{\text{Org/Org}}$ into pON/OA is illustrated in Eq. (1).

$$\frac{p\text{ON}}{OA} = \left(\frac{\text{NO}_{3,\text{Org}}}{\text{Org}}\right) \times \left(\frac{\text{MW}_{p\text{ON}}}{\text{MW}_{\text{NO}_3}}\right)$$

(1)

MW$_{p\text{ON}}$ represents the average molecular weight of pON per nitrate functional group estimated from FIGAERO-HR-ToF-ICIMS data, and MW$_{\text{NO}_3}$ indicates the molecular weight of nitrate (i.e., 62 g mol$^{-1}$). Since MW$_{p\text{ON}}$ does not significantly vary during the course of experiments (i.e., relative standard deviation...
of <1.2 %), the average value is applied to each experiment. The variability of MW\textsubscript{\text{pON}} among different systems is also found to be small, ranging from 229 to 238 g mol\(^{-1}\) and, thus, an average MW\textsubscript{\text{pON}} is used for experiments where FIGAERO-HR-ToF-I-CIMS data are not available. Figure 4 shows the time-series data of \(\gamma\text{ON}/\text{OA}\) for all the systems investigated in this study.

For “nighttime” experiments, the relative ratio of \(\text{C}_x\text{H}_y\text{N}_{1-2}\text{O}_z\) and \(\text{C}_x\text{H}_y\text{O}_z\) obtained from FIGAERO-HR-ToF-I-CIMS data in Fig. 1 does not appear to match well with \(\gamma\text{ON}/\text{OA}\) from HR-ToF-AMS data. For example, the signals are dominated by \(\text{C}_x\text{H}_y\text{N}_{1-2}\text{O}_z\) in the \(\beta\)-pinene+NO\(_3\) system, as shown in Fig. 1d, while \(\gamma\text{ON}/\text{OA}\) is at most 0.5, as shown in Fig. 4d. The discrepancy would be attributed to the overestimation of Org (in particular, \(\text{C}_x\text{H}_y\) family) in HR-ToF-AMS and/or underestimation of \(\text{C}_x\text{H}_y\text{O}_z\) in FIGAERO-HR-ToF-I-CIMS. Relative ionization efficiency (RIE) of less-oxidized organic species in HR-ToF-AMS is experimentally measured to be higher at least by a factor of 2 (Xu et al., 2018b). As previously reported (Boyd et al., 2015), the HR-ToF-AMS mass spectrum of SOA formed from \(\beta\)-pinene+NO\(_3\) contains significant amounts of \(\text{C}_x\text{H}_y\) fragments, indicating the less-oxidized nature of SOA from \(\beta\)-pinene+NO\(_3\). For example, if the true RIE of Org by \(\beta\)-pinene+NO\(_3\) SOA were to be a factor of 2 higher than the default RIE of Org (i.e., 1.4), the reported concentration of Org would have been overestimated by a factor of 2, such that actual \(\gamma\text{ON}/\text{OA}\) would have been higher than reported in Fig. 4d. On the other hand, an iodide reagent ion is not quite selective to detect less oxidized species, which could overestimate the contribution of \(\gamma\text{ON}\) to OA (Aljawhary et al., 2013). Nonetheless, this discrepancy between HR-ToF-AMS and FIGAERO-HR-ToF-I-CIMS data, however, should not affect the results regarding the hydrolysis lifetime and hydrolyzable fraction of \(\gamma\text{ON}\) presented later.

As illustrated in Fig. 4, the time series of \(\gamma\text{ON}/\text{OA}\) stabilizes fairly quickly in most of the experiments, regardless of RH and/or the phase state of seed aerosol. This suggests that the timescale of \(\gamma\text{ON}\) hydrolysis in the systems studied is significantly shorter or longer than the timescale of our experiments. It is also evident from Fig. 4 that \(\gamma\text{ON}/\text{OA}\) in high RH experiments are always lower than that in low RH experiments. These two observations imply that the rate of \(\gamma\text{ON}\) hydrolysis may be fast enough that the decay trend of \(\gamma\text{ON}\) compared to OA is not visibly manifested, though a clear difference of \(\gamma\text{ON}/\text{OA}\)
between low and high RH experiments is exhibited as a result of fast hydrolysis. Since no sudden, drastic change in pON/OA is observed except for a few initial data points, we conclude that the hydrolysis lifetime of hydrolyzable pON for α-β-pinene derived ON shall be no more than 30 min (i.e., 3 data points in Fig. 4). Particle acidity is found to enhance the rate of hydrolysis in prior study (Rindelaub et al., 2016), though no clear difference is observed between experiments with AS and SA+MS seed particles (i.e., Exp. 5 and 2). pON formed from hydroxyl and nitrate radical oxidation of α-pinene and β-pinene may not require a low pH to undergo hydrolysis at a rate comparable to the timescale of chamber experiments.

Comparing with the results from past chamber studies reporting a pON hydrolysis lifetime of 3 to 6 h (Liu et al., 2012b; Bean and Hildebrandt Ruiz, 2016; Boyd et al., 2015), our estimated hydrolysis lifetime is substantially shorter, but is consistent with the range (i.e., 1 min to 8.8 h) reported in studies using the bulk solution (Darer et al., 2011; Hu et al., 2011; Jacobs et al., 2014; Rindelaub et al., 2016) (Fig. 5). In Liu et al. (2012) and Bean and Hildebrandt Ruiz (2016), the hydrolysis lifetime is derived from the decay rate of NO3 corrected for the particle wall loss or normalized to SO4. As demonstrated in Sect. 3.2.1., this NO3/ SO4 decay rate is likely affected by other loss processes, such as vapor wall loss, and, thus, is not a good proxy to estimate the hydrolysis lifetime. The apparent discrepancy does not stem from the contradiction in the obtained data itself but rather in the data interpretation. Indeed, the lifetime estimated based on the decay of NO3,Org/ SO4 in our study is 4 h (Fig. 3a) that is consistent with 6 and 3 h reported in Liu et al. (2012) and Bean and Hildebrandt Ruiz (2016). On the other hand, in Boyd et al. (2015) the hydrolysis lifetime is estimated based on the decay rate of NO3/Org. The discrepancy in the reported hydrolysis lifetime here could be attributed to the fact that NO3 is not separated into NO3,Org and NO3,Inorg.

Figure S5 shows our data analyzed in the same manner as Boyd et al. (2015). The lifetime calculated based on the decay is 2.2 h, which is close to the reported 3 h (Boyd et al., 2015). The reduction of NO3/Org in Fig. S5 (~30 %) is greater than in Boyd et al. (2015) (10 %), which could be because (1) the amount of N2O5, a source of inorganic nitrate, used in our study is slightly larger and (2) RH in our study is higher by 10-20 %, which may have allowed greater uptake of N2O5 to produce inorganic nitrate.
In previous bulk solution studies where the concentration of interested organic nitrate (in particular hydroxyl nitrate) in aqueous solution rather than in aerosol water is monitored over time, it is unlikely that the data interpretation is affected by other loss processes present in chamber experiments, such as vapor wall-loss. It is also common to monitor the organic moiety of hydrolysis product (Darer et al., 2011), while it is extremely difficult in chamber experiments where hundreds of organic species are present at the same time, leading to the difficulty in accurately measuring the hydrolysis lifetime in chamber experiments. Based on the comprehensive analysis we demonstrate above on evaluating pON hydrolysis in chamber experiments, we recommend the use of the hydrolysis lifetime reported in this study, which is no more than 30 min, for pON formed from α-pinene and β-pinene.

3.2.3. Hydrolyzable fraction of particulate organic nitrate

The fraction of hydrolyzable pON (FH) can be directly estimated from the difference in pON/OA between low and high RH experiments shown in Fig. 4. Although we show that hydrolysis is substantially faster than the timescale of chamber experiments in our study, there still appears a clear difference in pON/OA between high RH experiments but with a different phase state of seed aerosol (i.e., Exp. 4 and 5). The difference mass spectra among Exp. 3-5 obtained from FIGAERO-HR-ToF-I-CIMS reveal that the difference in pON/OA between Exp. 4 and 5 does not arise from the reduction in pON but from the increase in non-nitrated organics (Fig. 6). The reason for this OA increase with the abundant presence of aerosol water is speculated to be uptake and other aqueous-phase reactions than hydrolysis and is briefly discussed in Sect. 3.3. Thus, the absolute difference in pON/OA between low RH, dry seed and high RH, dry seed experiments best indicates FH. Depending on the fate of the organic moiety of the hydrolysis product (i.e., stay in the particle phase or repartition back to the gas phase), FH varies. Since we are unable to determine the fate of hydrolysis product, an upper and lower limit of FH are reported as a range of FH. For the α-pinene+OH system, 23-32% of pON formed undergoes hydrolysis within the timescale of the experiments. For the other systems with no experiment under high RH with dry seed aerosol, the same level of additional
contribution from non-nitrated organics encountered in $\alpha$-pinene+OH system is assumed and $F_H$ is scaled accordingly. For the $\beta$-pinene+OH, $\alpha$-pinene+NO$_3$, and $\beta$-pinene+NO$_3$ systems, 27-34, 9-17, and 9-15 % of $p$ON are found hydrolyzable within the timescale of the experiments. Table 2 summarizes the hydrolysis lifetime and $F_H$ in the systems explored in this study.

$F_H$ has been only reported in several studies (Liu et al., 2012b; Boyd et al., 2015; Zare et al., 2018). The determination of $F_H$ is essential because the assumption that all $p$ON hydrolyzes biases the relative importance of hydrolysis among the loss mechanisms of $p$ON and NOx. Boyd et al. (2015) report that $F_H$ of $p$ON formed via $\beta$-pinene+NO$_3$ is $\sim$10 %, which is in a good agreement with our range of 9-15 %. From a perspective of predicted molecular structures of $p$ON, $<5$ % of $p$ON from $\beta$-pinene+NO$_3$ are tertiary (Claflin and Ziemann, 2018) that is expected to undergo hydrolysis in minutes (Darer et al., 2011; Hu et al., 2011). In our study, a considerable contribution of monomeric (C$_{10}$) $p$ON is observed (Fig. 1d), while dimeric (C$_{20}$) $p$ON is dominant in Claflin and Ziemann (2018). This may indicate that monomeric $p$ON is more susceptible to hydrolysis such that $F_H$ in this study is slightly higher than expected based on the proposed molecular structures of $p$ON in Claflin and Ziemann (2018).

$F_H$ for $\alpha$-$\beta$-pinene+OH systems are higher than those from $\alpha$-$\beta$-pinene+NO$_3$ systems. This trend is consistent with the understanding that $p$ON via hydroxyl radical oxidation have a larger fraction of tertiary nitrate groups, which are significantly more susceptible to hydrolysis (Darer et al., 2011; Hu et al., 2011) than those formed via nitrate radical oxidation (Ng et al., 2017). Although the relative trend of $F_H$ between $\alpha$-$\beta$-pinene+OH and $\alpha$-$\beta$-pinene+NO$_3$ systems is consistent, the magnitude of $F_H$ in the $\alpha$-$\beta$-pinene+OH system appears to be smaller than expected based on the tertiary nitrate fraction estimated via the explicit gas-phase chemical mechanism (Browne et al., 2013; Zare et al., 2018). In previous studies, $F_H$ are estimated to be 62 and 92 % for $\alpha$-$\beta$-pinene+OH systems, respectively. However, our results indicate $F_H$ is 23-32 and 27-34 % for the same systems (Fig. 5). The chemical mechanism used in Browne et al. (2013) and Zare et al. (2018) are based on the Master Chemical Mechanism (MCM) that is well known in the degradation chemistry of VOC in the gas phase (Jenkin et al., 1997; Saunders et al., 2003). However, the
same mechanism performs poorly in regards to the chemical composition of SOA (Faxon et al., 2018) as well as the prediction of SOA formation (Ruggeri et al., 2016; Boyd et al., 2017) when equipped with gas-particle partitioning modules based on the absorptive gas-particle partitioning theory (Pankow, 1994). It is, therefore, reasonable to argue that the chemical composition of \( \rho \)ON could greatly differ from that of total ON predicted by the MCM. Thus, \( F_H \) reported in this study provides the fundamental experimental constraints on \( \rho \)ON hydrolysis, that can be used in regional and global models for elucidating potential impacts of ON on nitrogen budget and formation of ozone and aerosol.

### 3.3 Signature of other aqueous-phase reactions than hydrolysis

As briefly discussed in the above section, the presence of elevated level of aerosol water seems to have enhanced the contribution of small (i.e., \( C_{\sim 9} \)) but more-oxidized organic species to SOA. As shown in Fig. 5c, the enhancement is observed for a variety of non-nitrated organic aerosol including \( C_4H_6O_4 \), \( C_5H_8O_5 \), \( C_7H_{10}O_4 \), and \( C_8H_{10}O_4 \), while \( \rho \)ON overall neither increase nor decrease. \( C_5H_6O_5 \) has been reported as a product of the aqueous-phase reaction of \( \alpha \)-pinene derived compounds (Aljawhary et al., 2016). Other compounds, such as \( C_4H_8O_4 \), \( C_7H_{10}O_5 \), and \( C_8H_{10}O_5 \), also appear to result from the aqueous processing because compounds with similar chemical formulae but with slightly higher degrees of oxidation (i.e., \( C_4H_8O_5 \), \( C_7H_{10}O_5 \), and \( C_8H_{10}O_5 \)) are reported in Aljwhary et al. (2016). The reason for this less oxidized nature of SOA in this study may be attributed to our experiments being performed in moderately high NO conditions that promotes a higher contribution of a carbonyl group than a hydroperoxyl group, which is preferred in low NO conditions. In Aljwhary et al. (2016), the starting compound is a product in low NO conditions (pinonic acid, \( C_{10}H_{16}O_3 \)). Thus, it is reasonable that products of the aqueous processing in this study are slightly less oxidized than observed in Aljwhary et al. (2016).

The enhancement of non-nitrated organic aerosol in FIGAERO-HR-ToF-I-CIMS may be due to aqueous processing of species in the particles in the presence of aerosol water. This can come from further reactions of semi/low-volatile species in the particle phase, or reactive uptake of volatile (but highly water-soluble) species into the aerosol followed by subsequent aqueous-phase reactions to form low-volatility
products (Ervens et al., 2011). A comparison of the average thermogram at peak SOA growth among Exp. 3-5 indicates a higher contribution of low-volatility compounds in Exp. 5 than in Exp. 3 and 4, as illustrated by the bimodal peaks (Fig. S6). Given the same degree of gas-phase oxidation expected among Exp. 3-5, these results show that aqueous chemistry in wet aerosol contributes to the further formation of low-volatility compounds. Overall, the highest average degree of oxidation (O/C = 0.77) is observed in high RH wet aerosol experiment (Expt. 5). The effect of particle water on monoterpane SOA formation warrants further studies.

3.4 Atmospheric implications

There is emerging evidence that monoterpane SOA greatly contribute to atmospheric aerosol in the Southeastern U.S. (Zhang et al., 2018; Xu et al., 2018a). ON is no exception; a substantial fraction of α,β-ON is considered to be from monoterpenes (Lee et al., 2016; Huang et al., 2019; Xu et al., 2015a). While C10 ON measured in FIGAERO-HR-ToF-I-CIMS is a good tracer of monoterpane derived α,β-ON, we show that a fair amount of α,β-pinene α,β-ON is found as C<10 or C>20 depending on the oxidation condition. This implies that the contribution of monoterpane derived α,β-ON could be substantially underestimated when only considering C10 α,β-ON. Fraction of α,β-ON with different number of carbon reported in this study (Table S2) is a useful parameter to quantitatively determine the contribution of monoterpenes derived α,β-ON to total α,β-ON.

Many previous modeling studies using ambient measurement data as constraints report that the lifetime of α,β-ON is likely several hours (Pye et al., 2015; Fisher et al., 2016; Lee et al., 2016; Zare et al., 2018). Hydrolysis of α,β-ON is used as a dominant loss process with the lifetime of several hours to improve the concentration of modeled OA (Pye et al., 2015) and to improve the concentrations of gaseous and particulate ON (Fisher et al., 2016). If the ambient α,β-ON concentration is indeed governed by a loss process with a few hours of lifetime, our results imply that the particle-phase hydrolysis may not be the only dominant loss process because the hydrolysis lifetime reported in this study is significantly shorter. Other potential but less-studied loss mechanisms of ON and α,β-ON include deposition (Nguyen et al., 2015), photolysis (Muller et al., 2014), and aqueous photooxidation (Romonosky et al., 2017; Nah et al., 2016).
For instance, enhanced photolysis rate is observed for carbonyl nitrate derived from isoprene (Muller et al., 2014), while no similar study is available for monoterpene derived ON in literature. Also, it has been demonstrated that different monoterpene ON can have drastically different photochemical fates (Nah et al., 2016). Taken together, results from this study highlight the importance to investigate other potential loss processes of monoterpene derived ON.

Aside from the hydrolysis lifetime, many modeling studies assume $F_H$ as unity (Pye et al., 2015; Fisher et al., 2016; Lee et al., 2016). Even when $F_H$ is considered, the value of $F_H$ used in other studies is still substantially higher than estimated in this study (Browne et al., 2013; Zare et al., 2018). The use of higher $F_H$ would result in overestimating the contribution of hydrolysis as a loss process of ON and NOx. While hydrolysis is considered as a permanent sink of NOx, many other loss processes, such as further hydroxyl radical oxidation and photolysis, are considered as a temporary reservoir of NOx. If the relative importance of ON fates in models was not accurate, the role of ON in NOx cycling and the formation potential of ozone could have been inaccurately interpreted. Therefore, results from this study regarding the hydrolysis lifetime and $F_H$ serve as experimentally constrained parameters for chemical transport models to accurately evaluate the role of ON in regards to nitrogen budget and the formation of ozone and fine aerosol.

**Author contribution**

M.T. designed and performed the research and analyzed the data with substantial inputs from N.L.N. M.T. and N.L.N. wrote the manuscript.

**Acknowledgements**

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Figure 1. FIGAERO-HR-ToF-I-CIMS mass spectra of SOA in (a) \( \alpha \)-pinene+OH from Exp. 3, (b) \( \beta \)-pinene+OH from Exp. 6, (c) \( \alpha \)-pinene+NO\(_3\) from Exp. 10, and (d) \( \beta \)-pinene+NO\(_3\) from Exp. 14. Top portion of each panel represents \( C_xH_yN_{1-2}O_z \), whereas bottom represents \( C_xH_yO_z \). Bars are colored by the number of carbon as noted in the legend. Prominent masses are labeled with the corresponding chemical formulae without an iodide ion.
Figure 2. (a, b) NO$_3$ concentration and the molar ratio of NH$_4$ to SO$_4$ and (c, d) concentrations of Org, SO$_4$, and NH$_4$ measured by HR-ToF-AMS. Data presented in Panels (a) and (c) are from Exp. 10 (low RH, dry AS), while those in Panels (b) and (d) are from Exp. 11 (high RH, wet AS). These two experiments are essentially the same except for RH and phase state of seed aerosol.
Figure 3. (a) Time-series data of NO$_{3,\text{Org/SO}}^-$ from Exp. 3-5 ($\alpha$-pinene+OH) and the exponential fits with corresponding characteristic times. (b) NO$_{3,\text{Org/Org}}^-$, NO$_{3,\text{Org/SO}}^-$, reconstructed NO$_{3,\text{Org/Org}}^-$ based on the decay rate of NO$_{3,\text{Org/SO}}^-$. 
Figure 4. Time-series data of $p_{\text{ON/OA}}$ in (a) $\alpha$-pinene+OH from Exp. 1-5, (b) $\beta$-pinene+OH from Exp. 6-7, (c) $\alpha$-pinene+$\text{NO}_3$ from Exp. 8-13, and (d) $\beta$-pinene+$\text{NO}_3$ from Exp. 14-15. Data points are colored by conditions concerning reactor RH and phase state of seed aerosol. For $\alpha$-pinene+$\text{NO}_3$, data points are also shaped differently depending on the expected dominant RO$_2$ fate.
Figure 5. Comparison of hydrolysis lifetime of organic nitrate and hydrolyzable fraction of pON in literature. “Chamber” refers to laboratory studies of organic nitrate aerosol via chamber experiments, “Bulk” refers to laboratory studies of organic nitrate compounds using bulk solution measurements, and “Model” refers to modeling studies using ambient measurement data as constraints. Data points are colored by the system of VOC and oxidant condition explored in this study and are alphabetized based on the reference. Pink shaded regions are ranges reported in literature, while blue shaded regions are ranges reported in this study.
Figure 6. FIGAERO-HR-ToF-I-CIMS difference mass spectra of SOA in α-pinene+OH. (a) Exp. 4 (high RH, dry AS) minus Exp. 3 (low RH, dry AS). (b) Exp. 5 (high RH, wet AS) minus Exp. 3 (low RH, dry AS). (c) Exp. 5 (high RH, wet AS) minus Exp. 4 (high RH, dry AS). Bars are colored by the difference in chemical composition (i.e., red for C_{x}H_{y}O_{z} and blue for C_{x}H_{y}N_{1-2}O_{z}). Prominent masses are labeled with the corresponding chemical formulae without an iodide ion.
Table 1. Summary of experimental conditions considered in this study.

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<th>Exp.</th>
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<th>Oxidant precursor</th>
<th>Reactor RH</th>
<th>Seed</th>
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<td>Effloresced AS$^b$</td>
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<td>N$_2$O$_5$ (80 ppb)</td>
<td>~60-70 %</td>
<td>Deliquesced SA+MS</td>
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<td>Effloresced AS</td>
</tr>
<tr>
<td>13</td>
<td>α-pinene (12 ppb)</td>
<td>N$_2$O$_5$ (80 ppb), HCHO (25 ppm)</td>
<td>~60-70 %</td>
<td>Deliquesced AS</td>
</tr>
<tr>
<td>14</td>
<td>β-pinene (12 ppb)</td>
<td>N$_2$O$_5$ (80 ppb)</td>
<td>~5 %</td>
<td>Effloresced AS</td>
</tr>
<tr>
<td>15</td>
<td>β-pinene (12 ppb)</td>
<td>N$_2$O$_5$ (80 ppb)</td>
<td>~60-70 %</td>
<td>Deliquesced SA+MS</td>
</tr>
</tbody>
</table>

$^a$The target for the initial reactor RH is ~70 %. However, the irradiation of UV light increases the reactor temperature by several degree Celsius and hence decreases RH.

$^b$Ammonium sulfate

$^c$Sulfuric acid and magnesium sulfate
Table 2. Hydrolysis lifetime and corresponding fraction of hydrolyzable \(p\)ON.

| System             | Hydrolysis lifetime | Hydrolyzable fraction (F\(h\))
|--------------------|---------------------|-------------------------------
| \(\alpha\)-pinene+OH | <30 min             | 23–32 %                       |
| \(\beta\)-pinene+OH   | <30 min             | 27–34 %                       |
| \(\alpha\)-pinene+NO\(_3\) | <30 min             | 9–17 %                        |
| \(\beta\)-pinene+NO\(_3\) | <30 min             | 9–15 %                        |

\(a\)Lower or higher limit of hydrolyzable \(p\)ON fraction is based on the assumptions that organic moiety of hydrolysis products remains in aerosol or partitions back to the gas phase.
References


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