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Organic Nitrate Contribution to New Particle Formation and Growth in Secondary Organic Aerosols from α -Pinene Ozonolysis

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Supporting Information

ABSTRACT: The chemical kinetics of organic nitrate production during new particle formation and growth of secondary organic aerosols (SOA) were investigated using the short-lived radioactive tracer ^{13}N in flow-reactor studies of α -pinene oxidation with ozone. Direct and quantitative measurements of the nitrogen content indicate that organic nitrates accounted for $\sim 40\%$ of SOA mass during initial particle formation, decreasing to $\sim 15\%$ upon particle growth to the accumulation-mode size range (>100 nm). Experiments with OH scavengers and kinetic model results suggest that organic peroxy radicals formed by α -pinene reacting with secondary OH from ozonolysis are key intermediates in the organic nitrate formation process. The direct reaction of α -pinene with NO_3 was found to be less important for particle-phase organic nitrate formation. The nitrogen content of SOA particles decreased slightly upon increase of relative humidity up to 80%. The experiments show a tight correlation between organic nitrate content and SOA particle-number concentrations, implying that the condensing organic nitrates are among the extremely low volatility organic compounds (ELVOC) that may play an important role in the nucleation and growth of atmospheric nanoparticles.

INTRODUCTION

Organic aerosol particles constitute a major fraction of air particulate matter, affecting climate and posing adverse effects on human health.^{1–5} These particles are either emitted directly by wood and fossil-fuel combustion, cooking, and natural sources⁶ or formed by oxidation of volatile organic compounds (VOCs) by atmospheric oxidants such as ozone (O₃), nitrate (NO₃), and hydroxyl (OH) radicals.^{7,8} NO₃ is an important night-time oxidant for VOCs but rapidly undergoes photolysis during day time.⁹ OH is the major atmospheric photochemical oxidant during daytime, whereas ozone contributes to VOC oxidation during both day and night-time. Ozonolysis reactions can produce OH in high yields, leading to simultaneous activity of both oxidation processes, even under dark conditions.^{10–13}

Nitrogen oxides (NO, NO₂ $\rightleftharpoons$ NO_x) are mainly emitted from fossil-fuel combustion and affect the chemical evolution of VOCs through the formation of organic nitrates.^{8,9,14} Organic nitrates are stable and function as a reservoir for the short-lived NO_x species under dry conditions, while in aqueous droplets, they can be rapidly converted to nitric acid (HNO₃).^{15–17} Deposition of organic nitrates into lung-lining fluid in the human respiratory tract might lead to the formation of HNO₃ by hydrolysis, a compound known to reduce pulmonary functions upon inhalation.¹⁸

The formation of organic nitrates hence affects the atmospheric nitrogen budget and alters the total aerosol mass yield from secondary sources.^{19–21} The presence of high levels

of both NO_x and O₃ generates a competition in VOC oxidation between the two oxidants, NO₃ and O₃. The NO₃ initiated oxidation of α -pinene showed low-SOA mass yields in previous laboratory experiments, in contrast to other monoterpenes, including β -pinene and limonene, producing aerosol in high yields.^{22–24} To our knowledge, the yield of organic nitrates in the dark ozonolysis of α -pinene has not yet been quantified.

Organic nitrogen compounds can be strong light absorbers, forming so-called brown carbon, which plays an important role in photochemistry and has a net warming effect on earth's climate.^{25–28} However, the formation, partitioning, and fate of nitrogen-containing organic compounds in SOA are still poorly understood. Organic nitrates can form in high quantities, as detected in field^{29–32} and laboratory^{33,34} samples, but quantification with online techniques remains a challenging task. A commonly used online technique is laser-induced fluorescence after the thermal conversion of organic nitrates to NO₂ (TD-LIF).^{23,34} Using mass spectrometric techniques, it is often difficult to detect organic nitrates reliably due to the thermal instability of the nitrate group,^{35,36} and organic nitrate contents must be inferred indirectly.³⁷ Fourier transform infrared (FTIR) spectroscopy³⁵ and high-resolution time-of-

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Table 1. Comparison of the Organic Nitrate Fraction Obtained in This Study to Other Aerosol Flow-Tube (AFT) and Environmental Chamber (EC) Experiments as Well as Field Data (field)^a

ON/OA	precursor	method	references
15–40%	α -pinene	¹³ N tracer	AFT this study
50–80%	α -pinene ^c	¹³ N tracer	AFT this study
6–18%	α -pinene ^c	TD–LIF	AFT Rollins et al. ³⁴
9–27%	α -pinene ^c	FTIR	EC Noziere et al. ⁵³
45–74%	β -pinene ^b	HR-ToF-AMS	EC Boyd et al. ³⁸
56%	β -pinene ^b	TD–LIF	EC Fry et al. ²³
32–41%	β -pinene ^b	HR-ToF-AMS	EC Fry et al. ³³
36%	limonene ^c	TD–LIF	AFT Rollins et al. ³⁴
82%	limonene ^b	TD–LIF	EC Fry et al. ²³
25%	Δ -carene ^c	TD–LIF	AFT Rollins et al. ³⁴
56%	Δ -carene ^b	TD–LIF	EC Fry et al. ²³
22–23%		HR-ToF-AMS	field Lee et al. ⁶⁶
27–40%		TD–LIF	field Rollins et al. ³²
23–44%		HR-ToF-AMS	field Ayres et al. ³¹
19–32%		HR-ToF-AMS	field Xu et al. ⁶⁵
5–12%		HR-ToF-AMS	field Xu et al. ⁶⁷

^aNote that the ON fractions reported in this study are for dark ozonolysis of α -pinene, while most other laboratory studies looked into oxidation by NO₃ or photooxidation by OH, respectively. ^bFrom NO₃ oxidation. ^cFrom OH photooxidation.

flight mass spectrometry³⁸ (HR-ToF-MS) have been used as offline techniques to determine organic nitrogen contents. An overview on previous studies determining the nitrate content in various laboratory aerosol samples is given in Table 1.

In this study, we applied the short-lived radioactive tracer ¹³N to quantify the amount of organic nitrates produced and retained in SOA particles.³⁹ This online technique gives an accurate estimate of the total ¹³N that entered the particle phase and has been used previously to determine gas-particle kinetics and partitioning of nitrogen-containing compounds.^{39–44} Experimental conditions such as ozone and NO_x concentrations, relative humidity, light irradiation, and presence of OH scavengers were varied to investigate the kinetic mechanism using an aerosol flow-tube reactor. Box-model simulations based on the Master Chemical Mechanism (MCM)^{45,46} were conducted for interpretation of the experimental findings.

MATERIALS AND METHODS

PROTRAC. ¹³N decays radioactively with a half-life of ~10 min and is produced online by directing a 11 MeV proton beam through a flow-through gas target, utilizing the ¹⁶O(p, α)¹³N reaction of 10–15% O₂ in He by the PROTRAC (Production of Tracers for Atmospheric Chemistry) facility at Paul Scherrer Institute.^{39,43} The initial products are highly oxidized ¹³N species, which are subsequently reduced to ¹³NO over a molybdenum converter at 380 °C. ¹³NO is transported from the production site to the laboratory through a 580 m long polyvinylidene fluoride (PVDF) tube.

Flow-Tube Setup. SOA particles were produced by dark ozonolysis of α -pinene precursor gas (~1 ppm) in various mixtures of α -pinene, ozone, and NO in an aerosol-flow-tube system (Figure 1). Particles were nucleated homogeneously without seed particles. α -pinene was added to the flow system through a custom built gas diffusion source: in a temperature-controlled 200 mL glass flask, a flow of 50 mL min⁻¹ dry N₂

Figure 1. Schematic of the experimental setup. SOA particles were formed by α -pinene ozonolysis in the presence of ¹³NO and ¹⁴NO in an aerosol flow tube. Concentrations of ¹³N in the gas and particle phases were detected by γ detectors.

was directed over an α -pinene reservoir with a small orifice of variable size, leading to a stable and adjustable α -pinene concentration (i.e., gas-phase number mixing ratio) of 400–1500 ppb, as confirmed by proton-transfer mass spectrometry (PTR–MS). Ozone was generated by passing synthetic air (50 mL min⁻¹) through a quartz tube exposed to a UV source of adjustable intensity and monitored with a commercial ozone analyzer (Teledyne ML 9810). The ¹³NO containing gas flow (200 mL min⁻¹) is mixed with nonlabeled ¹⁴NO (0–100 mL min⁻¹) from a certified gas cylinder (10 ppm in N₂) to adjust the total NO concentration. The total volume flow through the flow tube system was set to 1.25 L min⁻¹. The length of the aerosol flow tube can be adjusted via movable inlets with a total reactor volume ranging between 0.7–5.5 L, corresponding to a reaction time between 0.5–5 min.

Behind the reactor, the gas flow was split 3-fold between a scanning mobility particle sizer (SMPS) system to determine the particle-size distribution and two separate detection systems for ¹³N species. The total concentration of ¹³N in the gas and particle phase combined was detected with a packed Co-oxide tube that traps particles and also efficiently binds all gas-phase NO_y species ($\equiv$ NO_x, NO₃, HNO₃, N₂O₅, and organic nitrates). The Co-oxide (dominated by Co₃O₄) packing was obtained by soaking firebricks in saturated Co-nitrate solution followed by baking at 700 °C.³⁹ For the quantification of ¹³N in the particle phase alone, particles were collected on a glass-fiber filter after removing all gas-phase species by a charcoal denuder. CsI scintillation counters (Carroll and Ramsey) were placed behind both a Co-oxide trap and glass fiber filter, and the flux of ¹³N into both traps was measured at 1 min time resolution. ¹³N is a well-known positron (β^+) emitter, and the generated positrons annihilate with an electron under the emission of two γ -photons, which were measured by the scintillation counters. The inversion method to derive incoming ¹³N from integrated γ -ray signals is described in detail elsewhere.⁴⁰ All experiments were performed at room temperature (295 K).

Mass Fraction of Organic Nitrates. The mass fraction of organic nitrates RONO₂ in the particle phase (w_{ON}) was determined by comparison of the measured particle phase ¹³N signal intensity (I_p) to the gas-phase ¹³N signal intensity in the absence of the α -pinene ozonolysis reaction ($I_{g,0}$), measured at the Co-oxide trap. $I_{g,0}$ constitutes the entirety of undecayed ¹³N at the end of the flow reactor and can easily be correlated to the initial NO gas-phase concentration $c_{\text{NO},0}$. $I_p/I_{g,0} \times c_{\text{NO},0}$ hence provides an absolute number concentration of nitrogen atoms in the particle phase. We assume that particle-phase nitrogen was dominated by organic nitrates and the contribution of inorganic nitrogen (e.g., HNO₃ and N₂O₅) was very small, as confirmed by RH-dependent experiments. Increase in humidity

should favor inorganic nitrate formation by N_2O_5 hydrolysis to form HNO_3 , which was not observed with the ^{13}N signal. Moreover, the box-model simulations have shown that N_2O_5 did not accumulate in significant amounts, as outlined below. In fact, the ^{13}N signals at both detectors were reduced at elevated relative humidity, probably due to the more efficient loss of HNO_3 and N_2O_5 to the flow-reactor walls under humid conditions.⁴¹ There are also potential wall loss effects of O_3 , NO_2 , and NO_3 , which have been considered in the kinetic box model described below. Raw data from a typical experiment is showcased in Figure S1. For each data point, the flow tube system was flushed with synthetic air for 20–30 min until the ^{13}N signal intensity ($I_{\text{g},0}$, black solid line in Figure S1) stabilized. After the simultaneous addition of all reactants, I_{p} (black solid line in Figure S1) was determined once a steady state in SMPS and scintillation counter signal was reached. With knowledge of the aerosol mass concentration, m_{SOA} , and assuming that each organic nitrate molecule contains only a single $-\text{ONO}_2$ function, w_{ON} can be determined by

$$w_{\text{ON}} = \frac{I_{\text{p}} M_{\text{ON}} c_{\text{NO}_2,0}}{B \lambda I_{\text{g},0} N_{\text{A}} m_{\text{SOA}}} \quad (1)$$

where N_{A} is Avogadro's number. The molar mass M_{ON} was assumed to be $250 \pm 50 \text{ g mol}^{-1}$, which was chosen considering the high abundance of nitrated products in the range of 200–250 g mol^{-1} in the MCM^{45,46} and observations of highly functionalized nitrated compounds exceeding molar masses of 300 g mol^{-1} in regions dominated by monoterpene SOA.⁴⁷ Sum formulas of typical nitrated products from α -pinene ozonolysis are given in Table S1. The scintillation counters register radioactive decay on the basis of the γ quanta generated upon annihilation of the positrons emitted. Because the distance to the scintillation counter and shape of the particle filter versus the Co-oxide trap differ, a proportionality constant B is used to consider the different detector geometries and minor differences in the sensitivity of individual detectors. B was determined to be 0.66 in separate experiments in which a glass fiber filter was loaded with ^{13}N -labeled aerosol and transferred multiple times between both detector setups. A fraction of the aerosol is lost in the charcoal denuder and hence affects the measured particle-phase signal I_{p} . The fraction was found to be independent of particle size and can thus be accounted for with a simple scaling factor $\lambda = 0.59$, as determined by SMPS.

Kinetic Box Model. A simple gas-phase box model is used to quantify important species in the oxidation of α -pinene on the time scale of the flow-tube experiment. We adopt the HO_x and NO_y chemistry from the MCM that consists of 12 reactants in 24 chemical reactions (Table S2).^{45,46} We added a simplified mechanism of SOA formation, which is based on MCM but lumps individual compounds into bins of compound classes with similar properties. The added mechanism consists of seven additional reactants in 23 chemical reactions (Table 2 and Figure S2). These reactants include two types of reactive oxygen intermediates (ROI)^{5,43} in the form of organic peroxy radicals (RO_2) and alkoxy radicals (RO), which are formed upon initial reaction of α -pinene with O_3 and OH and can be interconverted. All stable, non-nitrated products are lumped into an *organics* bin and assumed inert toward further oxidation. Molecules in an *organic nitrates* bin are formed either via the oxidation of α -pinene with NO_3 or via the reaction of RO_2 with NO . Following the major reaction pathways in MCM, we

Table 2. Lumped Reaction Mechanism of α -Pinene Dark Ozonolysis and Reaction Rates at 295 K

no.	reaction	reaction rate
R1	$\text{O}_3 + \alpha\text{-pinene} \rightarrow \text{RO}_2^{\text{I}} + \text{OH}$	$k_1 = 0.85 \times 9.2 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$
R2	$\text{O}_3 + \alpha\text{-pinene} \rightarrow \text{RO}_2^{\text{II}}$	$k_2 = 0.15 \times 9.2 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$
R3	$\text{OH} + \alpha\text{-pinene} \rightarrow \text{RO}_2^{\text{II}}$	$k_3 = 5.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
R4	$\text{NO}_3 + \alpha\text{-pinene} \rightarrow \text{RO}_2^{\text{III}}$	$k_4 = 6.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
R5	$\text{NO} + \text{RO}_2^{\text{I}} \rightarrow \text{NO}_2 + \text{RO}^{\text{I}}$	$k_5 = 9.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
R6	$\text{NO}_3 + \text{RO}_2^{\text{I}} \rightarrow \text{NO}_2 + \text{RO}^{\text{I}}$	$k_6 = 2.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
R7	$\text{HO}_2 + \text{RO}_2^{\text{I}} \rightarrow \text{organics}$	$k_7 = 2.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
R8	$\text{NO} + \text{RO}_2^{\text{II}} \rightarrow \text{organic nitrates}$	$k_8 = 0.17 \times 9.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
R9	$\text{NO} + \text{RO}_2^{\text{II}} \rightarrow \text{NO}_2 + \text{RO}^{\text{I}}$	$k_9 = 0.83 \times 9.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
R10	$\text{NO}_3 + \text{RO}_2^{\text{II}} \rightarrow \text{NO}_2 + \text{RO}^{\text{I}}$	$k_{10} = 2.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
R11	$\text{HO}_2 + \text{RO}_2^{\text{II}} \rightarrow \text{organics}$	$k_{11} = 2.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
R12	$\text{NO} + \text{RO}_2^{\text{III}} \rightarrow \text{NO}_2 + \text{RO}^{\text{II}}$	$k_{12} = 9.1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
R13	$\text{NO}_3 + \text{RO}_2^{\text{III}} \rightarrow \text{NO}_2 + \text{RO}^{\text{II}}$	$k_{13} = 2.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
R14	$\text{HO}_2 + \text{RO}_2^{\text{III}} \rightarrow \text{organic nitrates}$	$k_{14} = 2.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
R15	$\text{RO}_2^{\text{I}} \rightarrow \text{RO}^{\text{I}}$	$k_{15} = [\text{RO}_2] \times 0.7 \times 1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
R16	$\text{RO}_2^{\text{I}} \rightarrow \text{organics}$	$k_{16} = [\text{RO}_2] \times 0.3 \times 1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
R17	$\text{RO}_2^{\text{II}} \rightarrow \text{RO}^{\text{I}}$	$k_{17} = [\text{RO}_2] \times 0.7 \times 1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$
R18	$\text{RO}_2^{\text{II}} \rightarrow \text{organics}$	$k_{18} = [\text{RO}_2] \times 0.3 \times 1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$
R19	$\text{RO}_2^{\text{III}} \rightarrow \text{RO}^{\text{II}}$	$k_{19} = [\text{RO}_2] \times 0.8 \times 1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$
R20	$\text{RO}_2^{\text{III}} \rightarrow \text{organic nitrates}$	$k_{20} = [\text{RO}_2] \times 0.2 \times 1 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$
R21	$\text{RO}^{\text{I}} \rightarrow \text{organics} + \text{HO}_2$	$k_{21} = 1 \times 10^6 \text{ s}^{-1}$
R22	$\text{RO}^{\text{I}} \rightarrow \text{RO}_2^{\text{II}}$	$k_{22} = 1 \times 10^6 \text{ s}^{-1}$
R23	$\text{RO}^{\text{II}} \rightarrow \text{organics} + \text{NO}_2$	$k_{23} = 1 \times 10^6 \text{ s}^{-1}$
R24	$\text{RO}^{\text{II}} \rightarrow \text{RO}_2^{\text{III}}$	$k_{24} = 1 \times 10^6 \text{ s}^{-1}$

distinguish three different RO_2 radicals: RO_2^{I} are produced from α -pinene ozonolysis and are unable to form organic nitrates, and RO_2^{II} are mainly formed from OH oxidation of α -pinene and RO_2^{III} contain a nitrate group. OH is produced secondarily during α -pinene ozonolysis, R1.^{10,11,48} Branching between R1 and R2 returns a production efficiency of OH of 85%, which is in line with previous observations.⁴⁹ RO radicals are formed by the reaction of RO_2 with NO , NO_3 , or RO_2 , leading to recycling of HO_2 via reaction R21. We distinguish non-nitrated (RO^{I}) and nitrated (RO^{II}) forms of RO radicals. When possible, reaction rates were directly adopted from MCM. When reaction rates differed between individual species in a compound class (R8, R9, and R15–R20 in Table 2), an intermediate or representative reaction rate was used in the lumped model.

The formation of peroxyacyl nitrates (PANs) has been neglected for simplicity because these reactions would have prompted an even more detailed oxidation mechanism, and PANs are not expected to contribute to SOA mass significantly due to their high vapor pressures.⁵⁰ The wall loss of a subset of compounds (i.e., O_3 , NO_2 , NO_3 , HNO_3 , and N_2O_5) was accounted for using an uptake coefficient γ (Table S3). A substantial fraction of the low-volatility oxidation products (organics and organic nitrates) may also be lost to the reactor walls⁵¹ (as the reactor-wall surface exceeds the aerosol surface considerably), but inclusion of these losses does not affect the merely qualitative result of the calculations and has thus been

neglected. Limitations due to mixing of gas flows and condensation onto particles was also neglected in the calculation.

To validate the lumped model, we performed calculations including the full MCM mechanism, which returned a good correlation between both approaches (Figure S3). The lumped model with only 23 distinct reactions is thus a valid approximation of the complex explicit mechanism with 894 reactions and suffices for the general mechanistic considerations in this study. Given the comparability of both calculations, such a simplified mechanism may increase the feasibility of more resource intensive calculations such as multiphase chemistry models or regional climate models in future studies.

RESULTS AND DISCUSSION

Quantification of Organic Nitrate. Figure 2a shows the time evolution of particle-number concentration (blue circles) and aerosol mass concentration (orange hexagons) as determined by the SMPS system, assuming an average density of 1.25 g cm^{-3} for SOA compounds.^{20,52} The intensity of the ^{13}N particle-phase signal (green squares) was normalized by the ^{13}N gas-phase signal intensity in the absence of the α -pinene ozonolysis, and the numerical value of the normalized signal thus directly represents the fraction of original NO_x that entered the particle phase. In this typical experiment, 1.6 ppm ozone was added in 2-fold excess to 800 ppb NO because both species react quickly on the time scale of a few seconds, in situ forming NO_2 . α -Pinene was added in slight excess (1 ppm) to minimize potential nonozonolysis reactions between ozone and organics. Typical experiments reached SOA mass concentrations of up to $500 \mu\text{g m}^{-3}$, with a number mean diameter of $\sim 120 \text{ nm}$ and a mass mean diameter of $\sim 250 \text{ nm}$. Note that due to experimental constraints on the reaction time and detection sensitivity, the concentrations used in this experiment are larger than typically observed in the atmosphere.

As shown in Figure 2a, the SOA mass increased almost linearly with time throughout the experiment. The ^{13}N particle-phase signal increased strongest in the early stages of the experiment when the SOA concentration was still very low, indicating that the nitrated products must exhibit a low volatility. The ^{13}N signal ceased to increase after $\sim 200 \text{ s}$, correlating well with the particle number concentration. This behavior was reproduced in several experiments (cf. Figure S4), suggesting a relationship between the formation of nitrogen-containing compounds and new particle formation. This observation is in line with previous suggestions that organic nitrates may contribute significantly in atmospheric new-particle-formation events, especially over forested regions.⁴⁷

Figure 2b shows the time evolution of the particle-phase nitrogen content in the particle-phase w_{ON} . w_{ON} was as high as 40% in the beginning and reduced to 15% toward the end of the experiment as the production of organic nitrates ceased and the total SOA mass continued to increase. These are the first measurements of w_{ON} for dark ozonolysis in the literature so far but can be compared to experiments of OH photooxidation and NO_3 -induced oxidation, which have been extensively studied, as is summarized in Table 1. Individual reported nitrate contents span wide ranges, representing experimental uncertainty. Compared to other precursors such as limonene and β -pinene, α -pinene produces significantly less organic nitrate. Field studies confirm the high contribution of organic nitrate formation to SOA mass, reaching as high as 44%,³¹ which is in

Figure 2. (A) SOA mass concentration (orange hexagons), aerosol particle-number concentration (blue circles), and the normalized ^{13}N signal (green squares) in the particle phase as a function of reaction time in the flow-tube reactor upon mixing of 1600 ppb O_3 , 800 ppb NO, and 1000 ppb α -pinene. The solid lines are to guide the eye. (B) Organic nitrate content w_{ON} (red triangles) as a function of reaction time in the flow-tube reactor, assuming one nitrate group per organic molecule with a molar mass of $250 \pm 50 \text{ g mol}^{-1}$ (eq 1).

line with the organic nitrate content of freshly nucleated SOA in this study.³¹

As discussed below, the deceleration in organic nitrate production during the course of the experiments is most likely due to depletion of NO in the reactor. In the atmosphere, NO is unlikely to be totally scavenged by ozone during daytime due to the continuous emission of NO_x and photolysis of NO_2 . Such a scenario could not be simulated in the flow-tube experiments because the high ozone concentrations, which are necessary to produce a large enough amount of organic aerosol, drives the equilibrium strongly toward NO_2 , even under the light conditions possible in our flow-tube setup. Irradiation with UV light (centered around 354 nm) had, in fact, no significant effect within experimental error on both produced SOA mass and strength of the ^{13}N signal (Figure S4).

The addition of an excess of 50 ppm cyclohexane as OH scavenger led to a complete shutdown of new particle formation. Experiments including ammonium sulfate seed particles revealed a strong suppression of SOA mass and the ^{13}N signal once cyclohexane was added. SOA production could be recovered upon increase of ozone concentrations, but the ^{13}N signal stayed low at an elevated background level, as shown

in Table S4. This suggests that the major pathway of organic nitrate formation occurs via the α -pinene–OH reaction, which is in line with the reaction mechanism proposed in Table 2.

We thus expect organic nitrate formation to be strong under day light conditions, i.e., during OH photooxidation. We performed a separate set of OH photooxidation experiments by in situ photolysis of HONO (see Figure S5 for experimental details). As outlined in Figure S5B, the organic nitrate mass fractions stabilized at $\sim 50\%$ in the flow-tube reactor. This augmented value is higher than previously determined for the OH photooxidation of α -pinene^{34,53} but in line with the proposed reaction mechanism because only RO₂ radicals produced in OH oxidation (RO₂^{II}) contribute to organic nitrate formation.^{45,46} A possible reason for the discrepancy between previous studies and this study might be the larger concentration of NO in our experiments, as it is also in situ produced from HONO photolysis, which was expected to limit organic nitrate formation in previous studies.³⁴ In the atmosphere and under daylight conditions, NO exists in a photostationary state and is only scavenged at high ozone concentrations. Hence, the high organic nitrate contents of up to 44% found in field samples (Table 1) can be understood as a result of both ozonolysis and photooxidation but will also include organic nitrates produced via nighttime NO₃ oxidation. Although oxidation of α -pinene by NO₃ is known to produce anomalously low amounts of SOA and was thus less relevant in the experiments of this study, this reaction pathway can contribute strongly to the production of organic nitrates for other biogenic precursors.^{23,38} Note that in the OH photooxidation experiment, as opposed to the ozonolysis experiments, new particle formation could not be directly correlated to the ¹³N signal (Figure S5a).

Dependence on Environmental Parameters. We investigated the dependence of particle-phase nitrogen on relative humidity, NO_x and O₃ concentrations. Organic nitrates are known to undergo hydrolysis under humid conditions.^{15,16} Figure 3a shows the ¹³N signal measured at three different relative humidities: 0, 30 and 80% RH. The ¹³N particle-phase signal was further normalized by the produced SOA mass because both signals showed the same scattering pattern between repetitions of the same experiment, indicating uniform nitrogen content. For every humidity displayed in Figure 3a, three full time dependencies have been measured, and the data points represent averages from all runs. Increased relative humidity led to a slight but significant decrease in the ¹³N signal. It has to be noted that the duration of the experiment is shorter than the expected atmospheric lifetime of tertiary organic nitrates toward hydrolysis of several hours.^{16,17,54} Primary and secondary nitrates are not expected to hydrolyze at atmospheric time scales.⁵⁵ The small dependence of the ¹³N signal on relative humidity found in this study is thus expected to be more pronounced at atmospheric time scales.¹⁷

In a similar fashion, the NO_x concentrations were varied systematically between 1–100 ppb, yielding practically no difference in SOA mass, particle number, and ¹³N signal, as shown in Figure 3b. Note that in these experiments, the concentrations of NO were much smaller than the O₃ concentration (1350 ppb), so that O₃ remained largely unaffected from immediate titration with NO upon mixing in the flow tube. Varying the O₃ concentration in our experiments strongly affected the mass of non-nitrated organics and, only to a slighter extent, the particle-number concentration and particle-phase nitrogen signal (Figure S6). Note that those

Figure 3. (A) Humidity dependence and (B) ¹⁴NO concentration dependence of the ¹³N signal in the particle phase as a function of reaction time in the flow-tube reactor, normalized by the produced SOA mass. Error bars denote standard deviations between multiple executions of the same experiment. Solid lines are least-squares fits to the data to guide the eye.

experiments were performed under low-NO_x conditions, where only trace amounts of labeled nitrogen were present in the system.

Box-Model Calculations. We applied the kinetic box model to showcase that the data can be qualitatively described with a simple kinetic mechanism. Panels a and b of Figure 4a show the concentration profiles of all major gas-phase species under typical experimental conditions with initial concentrations of 1600 ppb O₃, 1000 ppb α -pinene, and 800 ppb NO. NO (light blue solid line, Figure 4a) is quickly titrated by ozone and RO₂ and drops below 1 ppb after 25 s of the experiment. In this period, a large fraction of the total organic nitrate is formed through the RO₂ + NO channel (light green dashed line, Figure 4b), with most RO₂ originating from the α -pinene + OH reaction. After this point, organic nitrates are mostly produced through the α -pinene + NO₃ channel, leading to a slow but steady increase of the total organic nitrate concentration (dark green solid line). The concentration of in-situ-produced NO₃ stays in the low ppt range. These modeling results are consistent with the experimental observations, where formation of organic nitrates almost ceased after an initial period of fast growth. Predominant formation of organic nitrates via the α -pinene + OH channel at the beginning of the experiment may explain the correlation to new particle formation seen in Figure 2a: organic compounds formed via RO₂ radicals are known to

Figure 4. Modeling results showing the gas-phase concentrations of a selection of important (A) inorganic and (B) organic compounds tracked by the lumped chemistry box model. The dark green line represents all organic nitrates produced, whereas the dashed light green line shows only organic nitrates produced via the $RO_2 + NO$ channel, hence excluding the α -pinene + NO_3 channel.

form highly oxidized multifunctional molecules by autooxidation, which may play a major role in new particle formation.^{47,56,57}

In the model calculations, organic nitrates constituted up to ~26% of the total number of stable organic molecules in the gas phase (red solid line, Figure 4b), which is on the same order as the particle-phase composition determined in the ^{13}N tracer experiments, and shows the same temporal evolution as it drops to ~7% after 2 min of reaction time. The calculation results deviate from the experiment as organic nitrates were continuously produced via the α -pinene + NO_3 channel in the calculations (dark green solid line, Figure 4b), while in the experiments, no further organic nitrate was detected (Figure 2a), but rather, they followed the behavior of organic nitrates produced via the $RO_2 + NO$ channel (light green dashed line, Figure 4b). Note that the time-dependent particle-phase composition depends not only on the concentrations and vapor pressure of the reaction products but also on their gas and bulk diffusivities in the case of nonequilibrium SOA partitioning: the nitrate-rich organic material condensed onto particles in the early stages of the experiment might not partition back to the gas phase on the time scale of the experiment if organic particles adopt an amorphous solid state.^{58,59} In MCM, many stable organic nitrates formed via the α -pinene + NO_3 channel are first-generation products, which may be too volatile to partition into the particle phase in significant amounts and are assumed to play only a minor role in the initial particle nucleation.⁵⁹ This observation is consistent with previous results, such as those by Fry et al.²³ and Draper et al.,²⁴ who observed no aerosol formation from NO_3 oxidation

of α -pinene. Further evidence against the significant contribution of the α -pinene + NO_3 channel to SOA mass comes from experiments under UV irradiation, showing a negligible effect of UV light on the ^{13}N signal during experiments (Figure S4). NO_3 photolyses readily at wavelengths in the visible part of the light spectrum.⁶⁰ Organic nitrates from the α -pinene + NO_3 channel are thus expected to decrease upon irradiation with UV light.

Future studies would benefit from a more detailed kinetic model, which includes a comprehensive chemical mechanism and also treats the full process of gas-phase oxidation, partitioning into the particle phase, and potential subsequent particle-phase chemistry.⁶¹ Such complex models would, however, need a much larger set of kinetic data than that available in this study to constrain the multitude of model input parameters necessary to describe all important processes.^{62,63} The lumped model developed in this study may help to describe the multiphase chemistry of SOA formation in future studies because it strongly reduces the complexity of the chemical mechanism while correctly describing the concentrations of all important gas-phase reactants.

In conclusion, nitrogen containing compounds account for a significant fraction of α -pinene SOA. Using a radioactive tracer method, we found that organic nitrates constitute up to 40% of aerosol mass, with a pronounced influence during the initial formation period of particles. Experiments using OH scavengers showed low particle-phase nitrogen, suggesting that organic nitrate formation is mostly achieved through oxidation with OH to form RO_2 radicals and subsequent reaction with NO, as summarized in Figure 5. Organic nitrates

Figure 5. Schematic representation of the key processes explaining the experimental observations. α -Pinene reacts with ozone to Criegee intermediates (CI), which, under elimination of OH, decompose into semivolatile and low-volatile organic compounds (SVOC and LVOC). OH also reacts with α -pinene under the formation of RO_2 radicals that may react with NO to form organic nitrates ($RONO_2$), which are assumed to be of extremely low volatility, or non-nitrated low-volatility and extremely low volatility compounds (LVOC and ELVOC). ELVOCs from the OH oxidation of α -pinene might facilitate particle nucleation and, along with other oxidation products, lead to particle growth through condensation. The organic nitrate content ranges between 40% for freshly nucleated particles and 15% for particles in the accumulation-mode size range.

originating from OH oxidation may be extremely low-volatility compounds (ELVOCs), as suggested by the strong abundance of particle-phase nitrates at low aerosol-mass loadings and the tight correlation between organic nitrate content and particle number: strongly reduced particle formation rates in the presence of OH scavengers suggest that organic nitrates and other non-nitrated ELVOCs from OH-initiated oxidation may play an important role in facilitating particle nucleation and initial nanoparticle growth.

Strong formation of organic nitrates can significantly affect the atmospheric NO_x budget by reacting as reservoir species or

by providing a pathway for the deposition of particles and, hence, the removal of NO_y .¹⁷ Because they are present in large amounts in organic aerosol, organic nitrates deposited in the lungs might have implications for human health because they release nitric acid upon hydrolysis. This is especially true in regions with a large contribution of biogenic SOA from monoterpene oxidation to the total aerosol burden, such as the Pacific Northwest, Mountain West, and the southeastern United States.^{64,65}

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00961.

Experimental details on OH photooxidation experiments and calculations with the extended gas-phase chemistry mechanism. Molar mass of typical nitrated products for α -pinene ozonolysis (Table S1); HO_x and NO_y gas phase chemistry mechanism (Table S2); uptake coefficients for reactor wall losses (Table S3); and experimental data on OH scavenger experiments (Table S4). Experimental raw data from a typical experiment in the flow tube reactor (Figure S1); schematic representation of the reaction mechanism (Figure S2); comparison between lumped and explicit chemistry model (Figure S3); experimental data on UV irradiation experiments (Figure S4); experimental data on OH photooxidation (Figure S5); and experimental data on ozone concentration dependence experiments (Figure S6). (PDF)

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Notes

The authors declare no competing financial interest.

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