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Gas-Phase Nitrate Radical Production Using Irradiated Ceric Ammonium Nitrate: Insights into Secondary Organic Aerosol Formation from Biogenic and Biomass Burning Precursors

Published as part of ACS Earth and Space Chemistry special issue "Hartmut Herrmann Festschrift".

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compounds (OVOCs) and secondary organic aerosol (SOA) formed from NO₃ oxidation of volatile organic compounds (VOCs) emitted by biogenic sources (isoprene, β -pinene, limonene, and β -caryophyllene) and biomass burning sources (phenol, guaiacol, and syringol). SOA yields and elemental ratios were typically within a factor of 2 and 10%, respectively, of those obtained in studies using conventional NO₃ sources. Maximum SOA yields obtained in our studies ranged from 0.02 (isoprene/NO₃) to 0.96 (β -caryophyllene/NO₃). The highest SOA oxygen-to-carbon ratios (O/C) ranged from 0.48 (β -caryophyllene/NO₃) to 1.61 (syringol/NO₃). Additionally, we characterized novel condensed-phase oxidation products from syringol/NO₃ reactions. Overall, the use of irradiated aqueous cerium nitrate as a source of gas-phase NO₃ may enable more widespread studies of NO₃-initiated oxidative aging, which has been less explored compared to that of hydroxyl radical chemistry.

KEYWORDS: secondary organic aerosol, nitrate radicals, oxidation flow reactor, aerosol mass spectrometry, proton transfer reaction mass spectrometry

1. INTRODUCTION

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> The importance of NO₃ as a nighttime atmospheric oxidant is well established.¹⁻⁴ It is formed when NO₂ reacts with O₃, producing NO₃ and O₂. This is followed by a temperaturedependent equilibrium between NO₃, NO₂ and dinitrogen pentoxide (N₂O₅). N₂O₅ readily hydrolyzes to form HNO₃ on wetted surfaces.⁵ Consequently, studies examining the NO₃ chemistry in a specific region necessarily must account for the local temperature, humidity, and particle surface area, among other factors. Laboratory studies of gas-phase NO₃ chemistry have traditionally relied on the same NO₂ + O₃ reactions or N₂O₅ thermal decomposition processes that occur in the atmosphere.⁶⁻¹⁰ Researchers have accommodated the techni-

nitric acid. In this study, we adapted the method to maintain stable NO_3 concentrations for over 24 h. We applied the method in laboratory oxidation flow reactor (OFR) experiments to measure the yield and chemical composition of oxygenated volatile organic

cal challenges associated with crystalline N_2O_5 , specifically that it must be stored under cold and dry conditions until use.

We recently developed a novel method for generating gasphase NO₃ by irradiating aerated aqueous solutions of ceric ammonium nitrate (CAN, $(NH_4)_2Ce(NO_3)_6$).¹¹ The method builds on the work of Thomas Martin and colleagues, who aimed to produce aqueous NO₃ for organic synthesis.^{12–17} In

Received:	October 3, 2024
Revised:	December 21, 2024
Accepted:	February 3, 2025

Article

approximately 3-6 mol L⁻¹ nitric acid (HNO₃), CAN primarily dissociates into NH_4^+ cations and hexanitratocerate $(Ce(NO_3)_{2^-}^{2^-})$ anions.¹² When exposed to ultraviolet light, $Ce(NO_3)_6^{2-}$ is reduced to $Ce(NO_3)_5^{2-}$, resulting in the generation of aqueous NO₃ as a primary photolysis product.¹ The NO₃ then evaporates into a carrier gas, achieving gasphase mixing ratios ranging from parts per billion to parts per million depending on operating conditions. The NO₃ concentration is mainly influenced by the concentrations of CAN and HNO₃, UV intensity, and irradiation wavelength. Because irradiation of $(NH_4)_2Ce(NO_3)_6$ and other ceric nitrates that are formed in solution (hereafter collectively referred to as "Ce^{IV}") generates aqueous NO₃, it is less affected by humidity than N2O5-based methods, where hydrolysis of N₂O₅ to HNO₃ can reduce the effectiveness of the source. One challenge with the use of Ce^{IV} irradiation as a NO₃ source is that it is depleted over short periods (1-2 h). This can be problematic for applications requiring sustained NO₃ generation over longer periods. To address this, we modified the method to enable the continuous injection of fresh Ce^{IV}.

The majority of laboratory SOA studies have involved the generation of ozone or hydroxyl radicals (OH) to mimic the daytime oxidation of gas-phase precursors. NO₃ oxidation of unsaturated species such as isoprene, monoterpenes, and sesquiterpenes that are emitted from biogenic sources, and phenols, methoxyphenols, and furans that are emitted from biomass burning sources, can also generate SOA.^{8,10,18} However, NO3-initiated SOA formation and oxidative aging are less well characterized than OH oxidation chemistry,³ in part due to the greater difficulty in producing NO₃ using conventional methods. In this study, we used irradiated Ce^{IV} as a NO₃ source to generate and characterize OVOCs and SOA from the NO₃ oxidation of VOCs emitted by biogenic and biomass-burning sources. Whenever possible, we compared the compositions and yields of OVOC and SOA obtained from our experiments with those obtained from the NO₃ oxidation of the same precursors in previous studies using conventional NO₃ sources.

2. EXPERIMENTAL SECTION

2.1. NO₃ Generation. NO₃ was generated by irradiating a mixture of 0.25 mol L⁻¹ Ce^{IV} and 3.0 mol L⁻¹ HNO₃ placed at the bottom of a 12.7 mm OD \times 11.1 mm ID FEP tube inside a photoreactor as described by Lambe et al.¹¹ The tube was surrounded by four vertically installed low-pressure UVA Hg lamps (λ_{max} = 369 nm, F436T5/BLC/4P-369, LCD Lighting, Inc.). A fluorescent dimming ballast (IZT-2S28-D, Advance Transformer Co.) regulated the current to the lamps, and the irradiance was adjusted by changing the ballast control voltage between 1.5 and 10 VDC. A zero air carrier gas flow of 1 L min⁻¹ was bubbled through a gas dispersion line made of 6.35 mm OD \times 4.8 mm ID FEP tubing into the irradiated Ce^{IV}/ HNO₃ mixture. After exiting the photoreactor, the NO₃containing carrier gas passed through a filter holder (Savillex, 401-21-47-10-21-2) with a 47 mm PTFE membrane filter (Pall Gelman, R2PJ047) to transmit NO₃¹⁹ while removing droplets produced in the bubbler. Based on previous iodide adduct chemical ionization mass spectrometer measurements,¹¹ we estimate that gas-phase HNO3 mixing ratios in the OFR were on the order of 1 ppmv.²⁰

At the end of each experiment, the lamps were turned off, the gas dispersion line was removed, and the FEP tubing and filter holder were flushed with distilled H_2O . We modified



Figure 1. Simplified representation of the photoreactor used to generate nitrate radicals (NO₃) via the irradiation of aqueous mixtures of ceric ammonium nitrates (Ce^{IV}) and nitric acid (HNO₃). Fresh Ce^{IV}/HNO₃ was continuously added to the photoreactor with a syringe pump, while the consumed solution was withdrawn with a second syringe pump. Air was bubbled through the solution to evaporate NO₃ into the gas phase.

higher than the removal rate to counteract the decreasing liquid level due to the evaporation of H_2O and HNO_3 . FEP transfer lines (3.175 mm OD) connected both syringe pumps to the photoreactor side ports, and an inline filter was placed upstream of the second syringe pump to remove solid cerous/ ceric nitrates from the liquid waste flow.

2.2. OVOC and SOA Generation and Measurement. The NO₃-containing carrier gas was injected into a dark Potential Aerosol Mass (PAM) oxidation flow reactor (OFR) (Aerodyne Research), which is a 13 L horizontal cylindrical chamber (46 cm long, 22 cm inner diameter) that was operated in continuous flow mode. The total carrier gas flow rate at the OFR inlet was 8 L min⁻¹, with an exhaust port open to atmosphere. A sample flow of 5.5 L min⁻¹ was pulled through the reactor to achieve a mean residence time in the OFR (τ_{OFR}) of approximately 140 s. The relative humidity and temperature inside the OFR ranged from 48.8 to 64.4% and 24.0 to 25.6 °C, respectively.

OVOCs and SOA were produced by the reaction of NO₃ with biogenic VOC (BVOC) and biomass burning VOC (BBVOC) precursors injected into the OFR at the mixing ratios shown in Table 1. Liquid solutions of the precursors, diluted to 10% (v/v) in carbon tetrachloride, chloroform, or acetonitrile (ACN) to achieve lower gas-phase mixing ratios than are achievable with undiluted solutions, were injected into the OFR carrier gas at room temperature at liquid flow rates ($Q_{VOC,l}$) ranging from 0.94 to 7.5 μ L h⁻¹ using a syringe pump (TriContinent C24000). The VOC mixing ratio entering the OFR, $r_{VOC,gr}$ was calculated using the ideal gas law²¹ (eq 1):

Table 1. BVOC and BBVOC Precursors Used in This Work

Compound	Structure	$k_{\rm NO_3} \times 10^{11}$	Mixing Ratio
		$[\rm cm^{3} \ s^{-1}]$	[ppbv]
Isoprene		0.0677^{76}	95,381
β -Pinene		0.251^{76}	30
Limonene		1.22^{76}	30
β -Caryophyllene	OH	1.80 ⁷⁷	21
Phenol	OCH ₂	0.364^{76}	109
Guaiacol	ОН	2.69^{78}	43, 85
Syringol	H ₃ COOCH ₃	15.8^{78}	72

$$r_{\text{VOC},g}(\text{ppb}) = \frac{Q_{\text{VOC},l}}{Q_{\text{carrier}}} \times \frac{\rho}{\text{MW}} \times \frac{RT}{P} \times r_{\text{VOC},L} \times \frac{10^7}{60}$$
(1)

Here, ρ (g cm⁻³) and MW (g mol⁻¹) are the liquid density and molecular weight of the pure VOC, respectively, *R* (8.314 J mol⁻¹ K⁻¹) is the universal gas constant, *T* (K) is temperature, *P* (hPa) is pressure, $r_{\text{VOC},l}$ is the VOC mixing ratio in solution, and 10⁷ is a combined conversion factor for pressure, volume, density, and time.

The VOC precursors, along with OVOCs that have proton affinities higher than H₂O, were measured with a Tofwerk/ Aerodyne Vocus proton-transfer-reaction time-of-flight mass spectrometer (hereafter referred to as "Vocus PTR") with H_3O^+ reagent ion chemistry²² and a resolving power of approximately 8000 (Th/Th). Particle number concentrations and size distributions were measured with a TSI scanning mobility particle sizer (SMPS). Ensemble aerosol mass spectra were measured with an Aerodyne long high-resolution time-offlight aerosol mass spectrometer (L-ToF-AMS). The molecular composition of syringol NO₃-SOA was analyzed using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-ToF, Tofwerk).²³ In this setup, the particle sample was passed through a charcoal denuder at 1 L min⁻¹ to remove gas-phase species and then ionized in a charged spray of droplets (50:50 H_2O/ACN , with 100 ppm of NaI) emitted

from a 50 μ m ID fused silica capillary heated to 220 °C. Soluble aerosol components were detected as Na⁺ and Na(ACN)_n⁺ adducts. A filter blanking system regularly switches between sampling filtered and unfiltered sample flow in a 50% duty cycle.

2.3. Analysis. 2.3.1. Photochemical Model. To constrain the integrated NO₃ exposure (NO_{3,exp}; defined as the product of the mean NO₃ concentration and residence time in the reactor) and the concentrations of radicals that affect the fate of organic peroxy radicals (RO₂) generated from VOC/NO₃ reactions, we developed separate aqueous and gas-phase photochemical box models using the KinSim chemical kinetic solver.²⁴ In this approach, [NO₃] was calculated at each 1 s time step in the model. All [NO₃] values over the calculated 140-s OFR residence time were then summed to determine NO_{3.exp}, without assuming that [NO₃] remained constant over time. Tables S1 and S2 summarize the reactions used to model concentrations of various species (e.g., Ce^{IV}, reactive oxygen, and reactive nitrogen compounds) in the photoreactor and the OFR. $RO_2 + RO_2$ reaction rate coefficients were calculated using a simplified parametrization.²⁵⁻²⁷ The reactions listed in Table S2 were also used to constrain the NO3,exp values in chamber studies from the literature that are summarized in Table S4.

For reactions listed in Table S1 that did not have published condensed-phase rate coefficients, we used gas-phase rate

coefficients with unit conversion. We assumed that aqueous HNO₃ completely dissociated into H⁺ and NO₃⁻, and we used condensed-phase rate coefficients where possible. OH penetration from the photoreactor into the OFR was considered negligible.¹¹ Similarly, the penetration of HNO₄ (formed from NO_2 + HO₂ reactions) into the OFR was assumed to be minimal. This assumption was supported by modeled NO₂ mixing ratios in the OFR that were derived from the room-temperature decomposition of HNO₄ into NO₂ and HO2. At the maximum NO3,exp/ these modeled NO2 values approached 200 ppbv, which exceeded NO₂ values previously measured under similar conditions by an order of magnitude.¹¹ Literature first-order wall loss rate coefficients of $k_{w,N_2O_5} = 0.01$ s^{-1} and $k_{w,NO_3} = 0.02 \ s^{-1}$ were used for OFR studies,^{11,28} and $k_{\rm w,N_2O_5} = 0$ and $k_{\rm w,NO_2} = 1.5 \times 10^{-3} \, {\rm s}^{-1}$ obtained by Mayorga et al.²⁹ were applied to chamber studies.

Inputs to the aqueous phase model included UV flux in the photoreactor at $\lambda = 369$ nm (I_{369}), [Ce^{IV}], and [HNO₃], while inputs to the gas-phase model included NO2, NO3, N2O5, HO_{2} and H_2O_2 concentrations emitted from the photoreactor, reduced by a factor of 8 due to dilution into the OFR carrier gas, assuming 100% penetration efficiency into the OFR. The gas phase model was run in two cases: one with VOC concentrations from Table 1 to calculate VOC consumption and RO₂ formation, and one without added VOC to calculate NO_{3,exp}. Model outputs were obtained over 140 s (OFR studies) or 3600 to 21800 s (chamber studies) at 1 s intervals. I_{369} values input to the aqueous phase model were adjusted to match VOC decay in the OFR (measured with the Vocus PTR), as closely as possible, constrained by the irradiance measured in the photoreactor without a $\mbox{Ce}^{\mbox{iV}}$ solution. The model-calculated I_{369} values ranged from approximately 3 × 10¹⁰ (1.5 VDC) to 1.5 × 10¹⁶ photons cm⁻² s⁻¹ (10 VDC). This 5 \times 10⁵-fold reduction in I_{369} between 10 and 1.5 VDC exceeded the measured 1073-fold reduction in irradiance in the absence of Ce^{IV}. We believe that the difference is due to the high optical depth of concentrated Ce^{IV} solutions. Our hypothesis is that in a concentrated solution of a strongly absorbing species, UV light penetrates less deeply before being fully absorbed. Consequently, at lower lamp voltages, the UV flux would be disproportionately reduced compared to the UV flux obtained at higher voltages, in which case the extent of this attenuation would be $[Ce^{IV}]$ -dependent.

2.3.2. L-ToF-AMS, Vocus PTR, and EESI-ToF spectra. L-ToF-AMS spectra were analyzed using SQUIRREL/PIKA analysis software³⁰ which provided nonrefractory aerosol mass concentrations, high-resolution mass spectra, and elemental ratios (H/C, O/C, N/C) for the organic aerosol. Ions that were detected were incorporated into $C_x H_y^+$, $C_x H_y O^+$, $C_x H_y$ $\mathrm{O}^+_{>1},\ \mathrm{C}_x\mathrm{H}_y\mathrm{N}^+_n,\ \mathrm{NO}^+_z,\ \mathrm{and}\ \mathrm{NH}^+_y$ ion groups. The fraction of AMS signal attributed to particulate inorganic nitrates formed through $NH_3 + HNO_3 \rightarrow NH_4NO_3$ reactions was calculated using the equation $f_{\text{NO}_{3,\text{Inorg}}}$ = 3.44 $f_{\text{NH}_4^+}$, where $f_{\text{NH}_4^+}$ represents the fractions of the AMS signal detected as particulate ammonium. Using this method, the $f_{\rm NO_{3,\rm Inorg}}$ values calculated using this approach ranged from <1 to 25% of the total fraction of particulate nitrates (f_{NO_3}) . The difference between f_{NO_3} and $f_{\rm NO_{3,\rm Inorg}}$ was attributed to the presence of organic nitrates and/ or nitroaromatics present in the SOA. Elemental analysis followed the methods of Canagaratna et al.³¹ for H/C and O/

C and Aiken et al.³² for N/C, with O/C values including NO⁺ and NO₂⁺ signals associated with organic nitrates. N/C values were adjusted to account for contributions from inorganic nitrates, but the effect of inorganic nitrates on O/C values was minimal (<3%) and therefore was not corrected. In the results from Jaoui et al.,7 Xu et al.,33 and Nikkho et al.34 that are discussed in this paper, AMS spectra were reported, but elemental ratios were not determined. For the current study, mass spectra from those manuscripts were analyzed as described above to determine the corresponding elemental ratios. Vocus PTR and EESI-ToF spectra were analyzed using Tofware, yielding high-resolution mass spectra and ion formulas for products of reactions between sample components and H₃O⁺ (Vocus PTR), Na⁺ and/or Na(ACN)⁺ (EESI-ToF) that were detected as (M+H)⁺ (Vocus PTR), (M+Na)⁺ (EESI-ToF) and/or $(M+Na(ACN)_n)^+$ (EESI-ToF) adducts.

To aid in the interpretation of background-subtracted EESI-ToF spectra, positive matrix factorization (PMF) was used to classify EESI-ToF signals into groups of ions related to syringol/NO₃ reactions. EESI-ToF signals from m/z = 20-650were exported from Tofware and analyzed using the PMF Evaluation Tool (PET) version 3.08D.³⁵ PET was used to explore solutions containing between 1 and 10 factors and FPEAK = 0. Approximately 30 h of continuous EESI-ToF measurements were used to derive the PMF factors. The data indicated that 2-4 factors were sufficient to represent the syringol/NO3 oxidation chemistry. The low volatility of syringol and difficulty in stabilizing its concentration in the OFR made it challenging to separate the time-dependent variability in PMF factor apportionment from the naturally imprecise syringol conditions. Therefore, a PMF solution with two factors representing early and late-generation syringol NO₃-SOA components was selected for the analysis presented in Section 3.4.

2.3.3. SOA Yields. SOA mass yields were calculated as the ratio of SOA mass formed to the amount of precursor gas reacted.³⁶ SOA mass concentrations were determined from the integrated SMPS particle volume and material density, the latter of which was derived from H/C and O/C extracted from the AMS spectra.³⁷ SOA concentrations were not corrected for particulate inorganic nitrates because their contributions to AMS spectra were minor (<2%). The mass fraction remaining (MFR) of precursor gas was measured with the Vocus PTR and ranged from 0.97 to <0.01 depending on the precursor and [NO₃]. SOA yields were corrected for size-dependent particle wall losses in the OFR,³⁸ with correction factors ranging from 1.24 to 1.03 for mean volume-weighted particle diameters of approximately 52 nm (guaiacol NO₃–SOA) to 395 nm (isoprene NO₃–SOA).

SOA yield measurements obtained in OFRs may be biased low due to limited residence time for the condensation of lowvolatility organic compounds (LVOCs) generated from NO₃ oxidation of BVOC and BBVOC precursors. To address this, we applied a modified version of the LVOC fate correction model introduced by Palm et al.³⁹ The model uses input condensation sink, NO₃ exposure, OVOC/NO₃ rate coefficients (used as best available surrogates for LVOC/NO₃ rate coefficients, Table S5), and residence time values to calculate the fractional losses of LVOCs to OFR walls (F_{wall}), gas-phase oxidative loss with NO₃ (F_{NO_3}), condensation onto aerosols in the OFR (F_{cond}), and condensation onto downstream sampling line walls after exiting the OFR (F_{exit}).⁴⁰ The condensation

2.3.4. Analysis of Ambient PM Filter Samples. To complement laboratory syringol/NO₃ measurements (Section 3.4), targeted analysis for $C_8H_xO_y$ and $C_8H_xNO_y$ compounds was performed on Teflon filter samples of ambient particulate matter collected from urban inland (Atlanta, Georgia) and urban downwind coastal (Guilford, Connecticut, USA) locations.⁴² Integrated 12 h samples were collected during daytime and nighttime in intensive winter and summer campaigns. Filters were extracted with methanol and analyzed by using liquid chromatography coupled with electrospray ionization time-of-flight mass spectrometry (LC-ESI-ToF). Supplemental analysis of a subset of compounds detected in LC-ESI-ToF data using tandem mass spectrometry confirmed their molecular functionalities, while also indicating other compounds in the ambient air with the same molecular formulas, such as carboxylic acids and other oxygenated nonaromatic products.

3. RESULTS

This study used irradiated Ce^{IV} as a NO_3 source to generate and characterize OVOCs and SOA from the NO_3 oxidation of VOCs emitted by biogenic and biomass burning sources. First, we modeled the VOC and NO_3 concentration dynamics within the OFR. Second, we evaluated an adapted Ce^{IV} photoreactor capable of maintaining stable NO_3 concentrations over extended periods. Third, we used this method to measure the yields and elemental ratios of laboratory NO_3 –SOA. Finally, we characterized condensed-phase oxidation products from syringol/ NO_3 reactions and identified some of these compounds in nighttime ambient particulate matter samples.

3.1. Overview. Figure 2 shows modeled NO₃ concentrations for selected Ce^{IV} photoreactor conditions and OFR residence times without externally added VOC precursors. Over UV fluxes ranging from $I_{369} = 3 \times 10^{10}$ to 1.5×10^{16}



Figure 2. Modeled [NO₃] values obtained as a function of the Ce^{IV} photoreactor photon flux and OFR residence time (τ_{OFR}) in the absence of externally added VOC precursors. To display the abscissa on a logarithmic scale, the injection of NO₃ into the OFR is represented by $\tau_{OFR} = 0.1$ s instead of 0 s.

photons cm^{-2} s⁻¹, initial NO₃ mixing ratios in the OFR ranged from approximately 6–481 ppbv. For the 1.5×10^{16} photons $cm^{-2} s^{-1}$ condition, Figure S1 shows the fractional NO₃ loss $(F_{\rm NO_3})$ in the OFR at each 1 s time step caused by reactions with NO2, NO3, HO2, and wall losses. During the first second (1 s of residence time), the primary NO_3 loss pathway was its reaction with HO2, generated in the photoreactor and coinjected into the OFR ($F_{NO_3} = 0.67$). After 1 s, most NO₃ loss was due to reaction with NO₂ ($F_{\rm NO_3}$ = 0.85–0.91), followed by wall losses ($F_{NO_3} = 0.09-0.12$), NO₃+HO₂ reactions ($F_{\rm NO_3}$ < 0.02), and NO₃ + NO₃ reactions ($F_{\rm NO_3}$ < 0.006). Figures S2-S5 provide example model outputs of $[NO_3]$ and F_{NO_3} as functions of OFR residence time in the presence of externally added VOC precursors at the mixing ratios listed in Table 1. As expected, [NO₃] decreased compared to Figure 2 due to $NO_3 + VOC$ and $NO_3 + RO_2$ reactions, with the extent of suppression depending on the VOC concentration. In all scenarios, the NO₃ loss was dominated by reaction with NO₂, while NO₃ + RO₂ reactions and wall losses also played significant roles. In the 381-ppb isoprene case (Figure S2c,d), NO₃ was rapidly consumed, and subsequent NO₃ + VOC reactions depleted a significant fraction of the remaining NO_3 .

Figure 3 shows a 12-h time series where NO₃ was continuously generated in the photoreactor over a 12-h period and reacted with β -caryophyllene in the OFR to form SOA. In replicate experiments, NO_{3,exp} was systematically varied by adjusting the lamp voltage between 10 and 1.5 VDC every 30 min (Figure 3a) to change UV intensity and degree of oxidative aging. β -Caryophyllene concentrations were highest when the lamps were off and lowest above a lamp voltage set point of 2.5 VDC (Figure 3b). SOA concentrations formed between 2.5 and 10 VDC remained constant within uncertainties, suggesting that [NO₃] was constant within \pm 20%. Figure S6 shows an example 30-h time series where guaiacol was used as the precursor; at the highest lamp voltage set point, MFR < 0.01 throughout the experiment.

Figure 4 shows MFRs and SOA volume concentrations obtained after the NO₃ oxidation of each VOC in the OFR. In Figure 4a, SOA formation was not observed in experiments that used 95 ppbv isoprene. Under second-order reaction conditions, MFR values depend on [VOC] and [NO₃]. In scenarios with similar [VOC], the rate of VOC consumption was correlated with the NO₃ rate coefficient. For example, β -pinene and limonene required higher NO_{3,exp} than β -caryophyllene to achieve similar MFR (Figure 4b–d), while isoprene consumption was even slower due to its lower reactivity and higher concentration. Similar trends were observed for the BBVOCs, where phenol required higher NO_{3,exp} than guaiacol, and guaiacol required more than syringol.

BBVOCs decayed more slowly than BVOCs with similar NO₃ reactivity. For instance, β -pinene and phenol both had MFR > 0.6 at NO_{3,exp} values of 5.2 × 10¹² and 3.2 × 10¹³ cm⁻³ s, respectively, despite phenol's NO₃ rate coefficient being 1.5 times higher (Figure 4b,e and Table 1). Guaiacol and syringol concentrations also decayed slower than β -caryophyllene (Figure 4d,f,g) even though their NO₃ rate coefficients were 1.5 and 8.8 times faster, respectively. The higher mixing ratios of BBVOCs compared to those of β -pinene and β -caryophyllene may have contributed to their slower decay, as



Figure 3. Example application of the Ce^{IV} photoreactor to study SOA formation from the β -caryophyllene/NO₃ reaction. (a) Representative sequence of control voltage set points applied to the photoreactor lamps to vary [NO₃]. (b) Vocus PTR measurement of β -caryophyllene (C₁₅H₂₅⁺) and (c) SOA volume concentration obtained from the β -caryophyllene/NO₃ reaction. SOA concentrations formed between 2.5 and 10 VDC remained consistent within the uncertainties, suggesting that [NO₃] was constant within ±20%.



Figure 4. Mass fraction remaining (MFR) of (a) isoprene, (b) β pinene, (c) limonene, (d) β -caryophyllene, (e) phenol, (f) guaiacol, and (g) syringol measured with Vocus PTR at the exit of the OFR as a function of NO₃ exposure. SOA concentrations obtained from the NO₃ oxidation of each precursor are shown on the right ordinate. Error bars represent $\pm 1\sigma$ in the replicate measurements. Exponential fits are added to guide the eye. Additional figure notes for superscripts: ¹isoprene mixing ratio = 95 ppbv; ²isoprene mixing ratio = 381 ppbv; ³guaiacol mixing ratio = 43 ppbv; and ⁴guaiacol mixing ratio = 85 ppbv.

higher NO_{3,exp} would be needed to achieve a specific MFR, as was observed for isoprene (Figure 4). The amount of SOA formed also depended on the precursor. While 381 ppbv of isoprene (of which up to 306 ppbv was consumed) produced only 0.3 μ g m⁻³ of SOA, the reaction of NO₃ with 21 ppbv of β -caryophyllene generated up to 154 μ g m⁻³ of SOA. In several cases, the SOA concentration increased even after the precursor was fully consumed, most notably for limonene, guaiacol, and syringol, where SOA mass more than doubled after their MFR values were below 0.07 (Figure 4c,f,g). This suggests that increasing NO₃ also consumed early generation oxidation products and generated additional SOA,⁴³ highlighting the need to carefully consider the impact of NO_{3,exp} on SOA yields.

3.2. SOA Yields. Figure 5 presents SOA mass yields as a function of $NO_{3,exp}$ for the BVOC and BBVOC precursors studied, with the LVOC fate correction applied; SOA mass yields with and without this correction are shown in Figure S7 and Table S3. For comparison, results from chamber studies using N_2O_5 thermal decomposition or $NO_2 + O_3$ to generate NO_3 sources are also shown.^{6–10,29,33,44,45} Because $NO_{3,exp}$ values are not typically reported in chamber studies, they were calculated as described in Section 2.3.1. The corresponding ambient photochemical age shown on the top axis assumes a 24 h average NO_3 mixing ratio of 17.5 pptv (14 h at 30 pptv during nighttime and 10 h at 0 pptv during daytime⁴⁶).

Isoprene SOA yields were negligible ($\approx 3 \times 10^{-4}$; 0.02 with LVOC fate correction applied) between NO_{3,exp} = (1.2–1.7) × 10¹⁴ cm⁻³ s despite using mixing ratios comparable to or higher than chamber studies using seed particles, where isoprene SOA yields ranged from 0.02 to 0.24.^{6,7,33,45} For β -pinene, the SOA yield increased from 0.21 to 0.25 before slightly decreasing to 0.22. This yield was 33% lower than Fry et al.'s⁸ result at the same NO_{3,exp}, and 56–64% lower than yields of 0.50–0.61 at higher NO_{3,exp}, At NO_{3,exp} = 1.2 × 10¹⁴ cm⁻³ s, our limonene SOA yield of 0.50 was within 14% of



Figure 5. SOA mass yields obtained from NO₃ oxidation of (a) isoprene and β -pinene, (b) limonene and β -caryophyllene, and (c) phenol, guaiacol, and syringol as a function of NO₃ exposure. Corresponding ambient photochemical age shown on the top axis assumes a 24 h average NO₃ mixing ratio of 17.5 pptv⁴⁶). Representative error bars indicate estimated ±20% precision in SOA yield measurements and ±50% uncertainty in NO₃ exposure values. Additional figure notes for superscripts: ¹This work; ^aguaiacol mixing ratio = 43 ppbv; ^bguaiacol mixing ratio = 85 ppbv; ²Fry et al.;⁸ ³Boyd et al.;⁴⁵ ⁸Boyd et al.;^{44 9} Mayorga et al.;^{29 10} Meng et al.¹⁰

Fry et al.'s⁸ yield of 0.44 at NO_{3,exp} = 1.4×10^{14} cm⁻³ s. The highest limonene SOA yield we measured was 0.72 at NO_{3,exp} = 1.7×10^{14} cm³ s, but yields were still increasing, suggesting that maximum yields may occur at higher NO_{3,exp}. Our maximum β -caryophyllene SOA yield was 0.96, and the yield decreased to 0.80–0.93 between (0.66–1.2) × 10^{14} cm⁻³ s, which is within 10% of other reported yields at similar NO_{3,exp}.^{7,8} Notably, other studies obtained maximum SOA yields of 1.5 at NO_{3,exp} = (3.0–3.8) × 10^{14} cm⁻³ s prior to the yield decreasing to 0.91, suggesting possible NO₃-induced fragmentation of the SOA at higher exposures. Qualitatively similar trends have been observed extensively in studies of OH-initiated SOA formation and oxidative aging at high OH exposure.^{47–49}

Figure 5c shows the SOA yields for phenol, guaiacol, and syringol. Phenol and guaiacol SOA yields reached 0.058 and 0.18 at $NO_{3,exp} = 1.2 \times 10^{14}$ cm⁻³ s, compared to yields of 0.05 and 0.12 calculated from measurements by Mayorga et al.²⁹ at $NO_{3,exp} = 1.9 \times 10^{14}$ cm⁻³ s. Guaiacol SOA yields ranging from 0.08 to 0.21 were obtained by Meng et al.¹⁰ at higher $NO_{3,exp}$.

Our study is the first to report syringol NO₃–SOA yields, with a maximum value of 0.42 obtained at NO₃ = 1.2×10^{14} cm⁻³ s, which is significantly higher than yields of phenol and guaiacol NO₃–SOA. In contrast, syringol OH-SOA yields measured by Yee et al.⁵⁰ ranged from 0.25 to 0.37, which were lower than the OH-SOA yields of phenol (0.24–0.44) and guaiacol (0.44–0.50).

3.3. Elemental Composition of NO₃–SOA. *3.3.1. H/C and O/C.* Van Krevelen diagrams,⁵¹ which plot H/C against O/C, are commonly used to analyze SOA formation and oxidative aging.⁵² During oxidative aging, particularly when initiated by H atom abstraction, O/C increases while H/C decreases as oxygen-containing functional groups are added to the carbon backbone. In this study, Van Krevelen diagrams are used to compare the elemental ratios of NO₃–SOA produced from different precursors using irradiated Ce^{IV} as the NO₃ source. Data from studies using N₂O₅ thermal decomposition and NO₂ + O₃ reactions are included for comparison. AMS spectra used to derive the O/C and H/C are shown in Figures S8 and S9.

Figure 6a shows the H/C and the O/C for SOA derived from BVOCs. For β -pinene SOA, O/C, and H/C range from 0.47 to 0.69 and 1.64 to 1.60, respectively, compared to O/C =0.33 to 0.35 obtained by Boyd et al.⁹ without considering contributions from organic nitrate fragments. Limonene SOA O/C and H/C range from 0.55 to 0.70 and from 1.67 to 1.57. These values may reflect contributions of known condensedphase monoterpene/NO3 oxidation products with similar O/C and H/C, such as $C_{10}H_{15,17}NO_{5-8}$ and $C_{20}H_{32}N_2O_{8-12}$.^{11,53–55} β -caryophyllene SOA had O/C and H/C ranging from 0.32 to 0.48 and 1.62 to 1.57, respectively, compared to O/C = 0.48and H/C = 1.65 obtained by Jaoui et al.⁷ On the other hand, whereas chamber-generated isoprene NO₃-SOA had O/C and H/C ranging from 1.09 to 1.43 and 1.90 to 1.98, respectively,^{7,33} OFR-generated isoprene NO₃-SOA had O/ C ranging from 0.81 to 0.87 and H/C ranging from 1.77 to 1.87. This difference is likely associated with the relatively low reactivity of isoprene toward NO₃ (Table 1) coupled with the higher NO3,exp values used in isoprene NO3-SOA chamber studies (Figure 5).

Figure 6b shows H/C as a function of the O/C ratio for NO₃–SOA generated from BBVOC precursors. In general, BBVOC-derived NO₃–SOA had higher O/C than BVOC-derived NO₃–SOA. O/C and H/C for phenol NO₃–SOA ranged from 0.87 to 0.93 and 1.47 to 1.51. O/C and H/C values for guaiacol NO₃–SOA ranged from 0.77 to 1.17 and 1.64 to 1.44, and O/C and H/C values for syringol OH-SOA ranged from 0.93 to 1.61 and 1.54 to 1.72. SOA elemental ratios of our least-oxidized guaiacol NO₃–SOA agreed within approximately 10% (O/C) and 22% (H/C) of those obtained by Nikkho et al.³⁴ for chamber-generated guaiacol NO₃–SOA with O/C = 0.73 and H/C = 1.35.

The rate at which H/C changed relative to O/C, Δ (H/C)/ Δ (O/C), can provide information about functional groups that may have formed following NO₃ oxidation.⁵² Average (H/C)/(O/C) slopes were obtained from the data shown in Figure 6a-c and are summarized in Table 2. (H/C)/(O/C) slopes ranged from -0.67 (limonene NO₃-SOA) to 0.80 (phenol NO₃-SOA) when calculated from the differences between H/C and O/C of the least- and most-oxidized NO₃-SOA for each precursor. When (H/C)/(O/C) slopes are instead calculated from the differences between H/C and O/C of the gas-phase precursor and the most-oxidized SOA, values



Figure 6. (a) and (b) H/C versus O/C and (c) and (d) N/C versus O/C of NO₃–SOA formed from BVOC and BBVOC precursors. H/C, O/C, and N/C were calculated from AMS spectra of SOA (Section 2.3). Oxygen from AMS NO⁺ and NO₂⁺ signals were assumed to be from organic nitrates and/or nitroaromatics present in the SOA and counted toward O/C. Open black symbols represent elemental ratios of unoxidized BVOC/BBVOC precursors. Additional figure notes for superscripts: ¹This work; ^aguaiacol mixing ratio = 43 ppbv; ^bguaiacol mixing ratio = 85 ppbv; data from ²Xu et al., ³³ ³Jaoui et al., ⁷ and ⁴Nikkho et al.³⁴ analyzed as described in Section 2.3.

ranged from -0.07 (β -caryophyllene NO₃-SOA) to 0.66 (phenol NO₃-SOA). Overall, these (H/C)/(O/C) slopes are higher than (H/C)/(O/C) slopes achieved following OH oxidation of the same precursors.^{56,57} Whereas H atom abstraction is often a significant pathway for OH-initiated reactions, it occurs to a lesser extent with NO₃-initiated reactions, where NO_3 addition to C=C bonds to generate nitrogen-containing RO₂ is usually the initial step.^{25,58-1} Subsequent $RO_2 + HO_2/RO_2$ reactions that generate alcohols/ peroxides in the absence of C-C bond cleavage would then increase H/C. Notably, phenol and methoxyphenol NO₃-SOA had (H/C)/(O/C) slopes ranging from 0.38 to 0.66 despite the fact that H atom abstraction by NO₃, which would yield negative (H/C)/(O/C) values, is presumed to be the dominant gas-phase reaction pathway in these systems.^{10,29,61,6}

3.3.2. N/C. Nitrogen-containing oxidation products are often examined as major products associated with NO₃–SOA.

Figure 6c,d shows N/C versus O/C for the NO₃-SOA discussed earlier. For β -pinene and limonene SOA, the N/C ranges from 0.054 to 0.062 and 0.066 to 0.073, respectively. These values are in agreement with β -pinene SOA N/C ratios ranging from 0.063 to 0.091 reported by He et al.⁶³ but are lower than N/C values of 0.074 and 0.104 of β -pinene SOA and limonene SOA studied by Boyd et al.^{9,44} and of $C_{10}H_{15,17}NO_{5-8}$ and $C_{20}H_{32}N_2O_{8-12}$ oxidation products that we hypothesize are formed in high yields in monoterpene NO₃-SOA.^{11,53-55} This suggests that oxidation products without nitrogen atoms are also formed in significant yields in our experiments. β -caryophyllene SOA has N/C ranging from 0.058 to 0.061, in agreement with N/C = 0.060 to 0.069 reported by He et al.⁶³ but lower than N/C = 0.086 measured by Jaoui et al.⁷ The larger N/C measured by Jaoui et al.⁷ may have resulted from increased NO₃ addition to both double bonds at higher NO_{3.exp}. Isoprene SOA has N/C \approx 0.09–0.10, compared to N/C between 0.18 to 0.28 measured in other studies.^{7,33,63} This difference is likely due to the rapid suppression of NO₃ at the isoprene mixing ratios that were used (Table 1 and Figure S2) and the lower NO_3 exposure used compared to other studies, which, taken together, reduced the extent of multigenerational aging and yields of di/trinitrates in this study.^{33,64} BBVOC-derived NO₃-SOA generally has higher N/C than BVOC-derived NO₃-SOA. For example, phenol, guaiacol, and syringol NO₃-SOA have N/C ranging from 0.078 to 0.099, 0.079 to 0.13, and 0.049 to 0.13, respectively. The N/C of our least-oxidized guaiacol NO3-SOA agrees within 20% of the N/C value obtained by Nikkho et al.³⁴

The change in N/C relative to that in the O/C, $\Delta(N/C)/$ $\Delta(O/C)$, also provides insight into the functional groups formed during NO₃ oxidation. A (N/C)/(O/C) slope of 0 indicates the addition of non-nitrogen-containing functional groups, while a slope of 0.5 indicates the addition of nitro groups $(-NO_2)$. Slopes of 0.20 to 0.25 suggest the formation of organic nitrates along with peroxide or alcohol functional groups following NO_3 addition to C=C bonds, or combinations of nitro groups and non-nitrogen-containing oxygenated groups. Average (N/C)/(O/C) slopes, shown in Table 2, range from -0.35 (phenol SOA) to 0.067 (guaiacol SOA) when calculated between the least- and most-oxidized NO₃-SOA. For BVOC- and phenol-derived SOA, $\Delta(N/C)$ <0.01 across the range of NO3 exposures that were used, indicating a limited extent of direct NO3 addition to earlygeneration oxidation products following the first oxidation step. Thus, for these systems, this calculation does not accurately reflect the overall change in elemental composition following NO₃ oxidation of the precursors. However, when

`able 2. Average $\Delta({ m H/C})/\Delta({ m O/C})$ and $\Delta({ m N/C})/\Delta({ m O/C})$	C) Values Calculated from	the SOA Elemental R	Ratios (Figure 6)'
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NO ₃ -SOA precursor	$\Delta(H/C)/\Delta(O/C)$ (precursor+SOA)	$\Delta(H/C)/\Delta(O/C)$ (SOA only)	$\Delta(N/C)/\Delta(O/C)$ (precursor+SOA)	$\Delta(N/C)/\Delta(O/C)$ (SOA only)
isoprene	0.31		0.12	
β -pinene	0	-0.18	0.091	0.024
limonene	-0.037	-0.67	0.093	-0.050
β -caryophyllene	-0.067	-0.31	0.13	0.017
phenol	0.66	0.80	0.10	-0.35
guaiacol ¹	0.45	-0.28	0.12	0.041
guaiacol ²	0.42	0.05	0.12	0.058
syringol	0.38	0.26	0.13	0.11

^aAdditional table notes for superscripts: ¹guaiacol mixing ratio = 43 ppbv; ²guaiacol mixing ratio = 85 ppbv.

comparing gas-phase precursors to the most oxidized SOA, the slopes range from 0.09 (β -pinene and limonene SOA) to 0.16 (isoprene SOA), suggesting significant yields of both nitrogenand non-nitrogen-containing products. To investigate this further, as a case study, the molecular composition of syringol NO₃–SOA was characterized with EESI-ToF, and the results are presented in the following section.

3.4. Molecular Characterization of Syringol NO₃– SOA. Yang et al.⁶² identified nitrosyringol ($C_8H_9NO_5$) and 2,6-dimethoxyquinone ($C_8H_8O_4$) as key gas-phase products of the syringol/NO₃ reaction. Our study confirmed these findings, as these compounds were also detected in significant amounts with the Vocus PTR, although their low volatility and potential surface interactions with inlet tubing made it difficult to draw definitive conclusions about how their yields varied with NO₃ exposure (Figure S10). Minor signals for other compounds such as $C_8H_8O_5$ and $C_8H_{10}O_5$ were also detected with the Vocus PTR. Figure 7 shows the composition of EESI-



Figure 7. (a) EESI-ToF signals of syringol NO₃–SOA factors isolated using positive matrix factorization as a function of NO₃ exposure; (b) and (c) composition of C_8 and C_{16} syringol/NO₃ oxidation products measured with EESI-ToF and categorized by oxygen and nitrogen content.

ToF spectra for two syringol NO₃–SOA factors isolated using PMF (Section 2.3), categorized by oxygen and nitrogen content. Along with C₈ species, previous studies of gas-phase syringol/OH and syringol/NO₃ reactions found C₆ and C₇ fragmentation products in the gas phase after methoxy group loss.^{50,62} In this study, ion formulas assigned to EESI-ToF spectra were dominated by C₈H_xN₀₋₂O_y and C₁₆H_xN₀₋₄O_y

signals. The largest C₈ signals detected in syringol NO₃–SOA at lower NO_{3,exp} were associated with C₈H₁₀O₄, C₈H₁₂O₅, C₈H₉NO₈, C₈H₁₁NO₉, C₈H₁₁NO₁₀, C₈H₁₃NO₁₀, and C₈H₁₄N₂O₁₂ (Figure 7a). At higher NO_{3,exp}, C₈H₉NO₈, C₈H₁₁NO₉, and C₈H₁₃NO₁₀ remained abundant, but C₈H₁₀O₄ and C₈H₁₂O₅ decreased, while C₈H₁₂O₇, C₈H₉NO₁₄ and C₈H₁₀N₂O₁₁ increased. Methoxy group loss via fragmentation reactions would have yielded C₆ and C₇ oxidation products, which contributed to a minor fraction of the signal at representative mass-to-charge ratios of the EESI-ToF spectra (Figures S11–S18). Additionally, the observed increase in the SOA H/C (Figure 6) and the AMS signal detected at m/z = 31 (CH₃O⁺; Figure S19) suggest that methoxy group loss was minor.

We hypothesize that $C_8H_{10}O_4$ and $C_8H_{12}O_5$ represent oxidation products that are generated via the addition of one and two alcohol groups to syringol, with potential structures shown in Table 3. $C_8H_{10}O_4$ could also form from the conversion of syringol's alcohol group into a peroxide group. Because these products do not contain nitrogen atoms, we hypothesize that they are generated following H-atom abstraction by NO₃ to produce an alkyl radical, followed by a reaction with O_2 to generate RO_2 and subsequent isomerization, RO₂+RO₂, and/or RO₂+HO₂ reactions (e.g., Figure S20). C₈H₉NO₈, C₈H₁₁NO₉, and C₈H₁₁NO₁₀ are likely formed following NO3 addition to syringol to generate a nitrogen-containing RO_2 (Figure S21). These then react with other RO₂ to form C₈H₉NO₈ and C₈H₁₁NO₉ or with HO₂ to form C₈H₁₁NO₁₀, plus other species. This process is similar to the formation of $C_6H_7NO_7$ and $C_6H_7NO_7$ from phenol/NO₃ chemistry,^{27,58,60} but with two additional methoxy groups added for the syringol/NO₃ derivatives (Table 3). C₈H₁₂O₇ may be a ring-closed product with two alcohols and one peroxide group added to syringol or a ring-opened product with two alcohols and one carboxylic acid. Given the high ring strain of the proposed ring-closed structure and the high abundance of m/z = 44 (CO₂⁺), a marker for decarboxylated organic acids⁶⁵ in the AMS spectra of syringol NO₃-SOA (Figure S9), we believe that the ring-opened product is more likely. We hypothesize that C₈H₁₄N₂O₁₂ is a ring-opened dinitrate formed after two NO₃ additions to syringol along with two alcohols and one carbonyl group (Table 3). Additionally, m/z = 29 (CHO⁺), a marker for alcohols,³¹ is the largest signal in the AMS spectrum of syringol SOA (Figure S9), supporting the presence of multiple alcohol functional groups in the condensed-phase syringol/NO3 oxidation products.

The largest C_{16} signals detected by EESI-ToF at lower $NO_{3,exp}$ were $C_{16}H_{18}O_7$, $C_{16}H_{19}NO_{11}$, and $C_{16}H_{18}N_2O_{13-15}$. Potential condensed-phase accretion reactions involving syringol/NO₃ oxidation products detected by Vocus PTR (e.g., $C_8H_9NO_5$) and EESI-ToF (e.g., $C_8H_{10}O_4$, $C_8H_{12}O_7$, $C_8H_{11}NO_9$, $C_8H_{11}NO_{10}$) include

$$C_{8}H_{10}O_{4} + C_{8}H_{10}O_{4} \xrightarrow{-H_{2}O} C_{16}H_{18}O_{7}$$

$$C_{8}H_{9}NO_{5} + C_{8}H_{12}O_{7} \xrightarrow{-H_{2}O} C_{16}H_{19}NO_{11}$$

$$C_{8}H_{9}NO_{5} + C_{8}H_{11}NO_{9} \xrightarrow{-H_{2}O} C_{16}H_{18}N_{2}O_{13}$$

$$C_{8}H_{9}NO_{5} + C_{8}H_{11}NO_{10} \xrightarrow{-H_{2}O} C_{16}H_{18}N_{2}O_{14}$$

Table 3. Proposed Structures for a Subset of Gas- and Condensed-Phase Syringol/NO₃ Oxidation Products Detected with Vocus PTR at $(M+H)^+$ and EESI-ToF at $(M+Na)^+$ and/or $(M+Na(ACN)_n)^+$ Ions

Formula	Structure	Technique
$\mathrm{C_8H_8O_4}$		Vocus PTR
$\rm C_8H_9NO_5$		Vocus PTR
$\mathrm{C_8H_{10}O_4}$	or o	EESI-ToF
$\mathrm{C_8H_{12}O_5}$	HO OH	EESI-ToF
$\mathrm{C_8H_{12}O_7}$	но он он	EESI-ToF
$\rm C_8H_9NO_8$		EESI-ToF
$\rm C_8H_{11}NO_9$		EESI-ToF
$\mathrm{C_8H_{11}NO_{10}}$		EESI-ToF
$\mathrm{C_8H_{13}NO_{10}}$		EESI-ToF
$C_8H_{14}N_2O_{12}$		EESI-ToF

At higher NO_{3,exp}, the yields of $C_{16}H_{18}O_{16-24}$, $C_{16}H_{17,19}NO_{18-21}$, and $C_{16}H_{18}N_2O_{21-23}$ increased, likely forming from various combinations of $C_8H_{10}O_{4-12}$ and $C_8H_9O_{5-14}$ monomers in the condensed phase such as

$$C_{8}H_{10}O_{12} + C_{8}H_{10}O_{12} \xrightarrow{-H_{2}O} C_{16}H_{18}O_{23}$$

$$C_{8}H_{10}O_{12} + C_{8}H_{9}NO_{8} \xrightarrow{-H_{2}O} C_{16}H_{17}NO_{19}$$

$$C_{8}H_{10}O_{12} + C_{8}H_{11}NO_{9} \xrightarrow{-H_{2}O} C_{16}H_{19}NO_{20}$$

$$C_{8}H_{11}NO_{9} + C_{8}H_{9}NO_{14} \xrightarrow{-H_{2}O} C_{16}H_{18}N_{2}O_{22}$$

Although other C_8 products and reaction pathways likely contributed to the formation of C_{16} dimers, this partial list highlights the importance of multiphase methoxyphenol/NO₃ oxidation chemistry in syringol NO₃–SOA formation.

Several prominent syringol/NO3 oxidation products, including C₈H₉NO₅, C₈H₈O₄, C₈H₁₀O₄ and C₈H₁₂O₅, were detected in ambient particulate matter at both urban inland (Atlanta, Georgia, USA) and urban downwind coastal (Guilford, Connecticut, USA) field sites during winter. At the Guilford site, C₈H₉NO₅ was detected in 43% of the winter nighttime samples. It co-occurred with C₈H₈O₄ on 30% of these nights and with $C_8H_{12}O_5$ on 100% of them, with mean ion abundance ratios of $C_8H_8O_4/C_8H_9NO_5 = 0.84 \pm 1.15$ and $C_8H_{12}O_5/$ $C_8H_9NO_5 = 0.71 \pm 0.58$. $C_8H_9NO_5$, $C_8H_8O_4$, and $C_8H_{12}O_5$ were observed only at night during winter, while C8H10O4, which is also a known OH oxidation product of syringol,⁵⁰ was detected in summer both at night and occasionally during the day. At the Atlanta site, C₈H₉NO₅ was detected in 50% of winter nighttime samples, co-occurring with C8H8O4 and C₈H₁₂O₅ on 50% of those nights with mean ion abundance ratios $C_8H_8O_4/C_8H_9NO_5 = 1.77 \pm 0.75$ and $C_8H_{12}O_5/$ $C_8H_9NO_5 = 1.21 \pm 0.85$. In the winter, as at the Guilford site, these species were detected exclusively at night. In contrast, $C_8H_{10}O_4$ and $C_8H_{12}O_5$ appeared occasionally during both day and night in summer.

3.5. Discussion. The chemical composition and yield of SOA produced in this study were likely influenced by several factors: (1) the physicochemical properties and concentration of precursors, which affect gas-to-condensed phase partitioning, (2) condensation sink, (3) aerosol liquid water content, (4) oxidant exposure, and (5) the fate of RO_2 . Systematic studies of the influence of humidity on NO3-SOA yield and composition are extremely limited^{44,54} due to the reduced effectiveness of N₂O₅-based NO₃ sources in humid conditions, as N2O5 hydrolyzes to HNO3 on wet surfaces; the use of irradiated Ce^{IV} as a NO₃ source circumvents this limitation. Our results suggest that NO₃ exposure, which is typically not calculated or reported in laboratory NO3-SOA studies, can significantly influence the NO₃-SOA yield and composition, especially for less reactive precursors like isoprene and/or systems undergoing multiple generations of NO₃ oxidation.³³ While inorganic seed particles are typically used to enhance the condensation sink and/or the aerosol liquid water content in chamber studies,⁶⁶ no seeds were used in this work. Thus, an approach such as the LVOC fate analysis (Section 2.3) was required to correct yields for residence-time-limited LVOC condensation, especially for more volatile precursors, such as isoprene and phenol.

To investigate the fate of RO₂ generated from BVOC/ BBVOC + NO₃ reactions, we calculated the fractional loss of generic alkyl RO₂ due to reactions with HO₂, NO₃ and RO₂ $(F_{RO_2+HO_2}, F_{RO_2+NO_3}, F_{RO_2+RO_2})$ in the OFR using the approach outlined in Section 2.3.1 and the modeled reactions and kinetic data summarized in Table S2. We assumed that $RO_2 + NO_2^{67}$ reactions were negligible and we did not quantify the rate of RO_2 isomerization/autoxidation reactions, which likely occur but to an uncertain extent.⁶⁸ Figure 8 shows



Figure 8. Fractional loss of organic peroxy radicals (RO_2) generated from the NO₃ oxidation of BVOC and BBVOC precursors due to the reaction with NO₃, HO₂, and RO₂. Reactions and kinetic rate coefficients used in these calculations are listed in Table S2.

that $F_{\rm RO_2+HO_2}$ and $F_{\rm RO_2+RO_2}$ decreased while $F_{\rm RO_2+NO_3}$ increased as a function of NO_{3,exp}. Above NO_{3,exp} $\approx 4.3 \times 10^{13}$ cm⁻³ s, where SOA yields for most precursors approached or reached their maximum values, $F_{\rm RO_2+NO_3}$ usually exceeded 0.70. In isoprene/NO₃ studies, $F_{\rm RO_2+RO_2}$ and $F_{\rm RO_2+RO_2}$ were competitive due to the higher isoprene concentration that was used to promote NO₃–SOA formation along with a faster assumed RO₂+RO₂ rate coefficient.⁶⁹ Other laboratory studies of BVOC/NO₃-derived SOA often do not quantify the RO₂ loss pathways. However, $F_{\rm RO_2+RO_3}$ is typically greater than, or comparable to, $F_{\rm RO_2+RO_2}^{9,33}$ with $F_{\rm RO_2+HO_2}$ sometimes assumed to be the dominant RO₂ loss pathway.^{9,45}

NO₃ oxidative aging studies often rely on nitrogencontaining molecular tracers formed from the addition of NO₃ to unsaturated precursors or the addition of NO₂ to alkyl radicals. Otherwise, isolating the competing influence of O₃ and NO₃ at night can be difficult.⁷⁰ However, in our syringol NO₃–SOA studies, about half of the C₈ oxidation products detected did not contain nitrogen atoms, which challenge this approach. For example, major products like C₈H₁₂O₅ and C₈H₁₀O₄, which are also produced from syringol/OH reactions,⁵⁰ were prevalent at lower NO_{3,exp}. One alternative explanation is that competitive OH and NO₃ oxidation occurred in the OFR. However, based on experiments with other BVOC and BBVOC precursors, our results suggest that OH oxidation was minimal in these studies. Isoprene, which has the slowest NO₃ reaction rate among the BVOC precursors studied and an OH reaction rate similar to β caryophyllene (within a factor of 2⁷¹), decayed more slowly than the other BVOCs as NO_{3,exp} increased (Figure 4). Comparisons of the elemental composition of isoprene NO₃– SOA and OH-SOA also showed distinct differences in their H/ C and O/C (Figure S22). Additionally, SOA yields from syringol/NO₃ reactions were significantly higher than those from phenol/NO₃ and guaiacol/NO₃, while syringol OH-SOA yields measured by Yee et al.⁵⁰ were lower than those of phenol/OH and guaiacol/OH. These findings, along with the detection of C₈H₁₀O₄ and C₈H₁₂O₅ in ambient samples concurrently with C₈H₉NO₅ (Section 3.4), suggest that our results reflect unique syringol/NO₃ chemistry rather than experimental artifacts.

4. CONCLUSIONS

In this study, we applied Ce^{IV} irradiation as a NO₃ source to investigate the NO₃-SOA formation and oxidative aging of representative BVOC and BBVOC precursors. Modifications to the method enable applications similar to those of an environmental chamber using conventional NO₃ sources. SOA yields and elemental ratios were typically within a factor of 2 and 10%, respectively, of those determined in previous studies using N_2O_5 thermal decomposition or $NO_2 + O_3$ reactions to generate NO₃. This suggests that both approaches are suitable for simulating atmospheric NO₃ chemistry. Advantages of Ce^{IV} irradiation include (1) reduced sensitivity to humidity compared to N2O5-based methods, where hydrolysis to HNO₃ lowers source efficacy and (2) it avoids the use of O_3 , thereby eliminating the possibility of competing O_3 and NO₃ oxidation of compounds that are reactive toward both oxidants. However, due to the higher reactivity of NO3 compared to N2O5, achieving uniform mixing in large environmental chambers remains a challenge.⁷² Moreover, the method requires careful consideration of potential artifacts from elevated HNO₃ concentrations. Substituting HNO₃ with sodium nitrate in aqueous ceric ammonium nitrate mixtures may help mitigate this issue¹¹ and warrants further investigation.

Our results highlight the high SOA formation potential of low-volatility BVOCs and BBVOCs like β -caryophyllene and syringol, which had maximum NO₃-SOA yields of 0.96 and 0.42, respectively. These yields are comparable to, or even higher than, yields of SOA obtained from OH oxidation of the same precursors.^{7,50} However, multiple nights of equivalent atmospheric NO3 exposure were needed to form SOA from more volatile precursors like isoprene, which reacts comparatively slowly with NO₃. Enhancing the condensation sink and increasing $F_{\rm RO_2+RO_2}$ also appear to significantly impact isoprene NO₃-SOA yields.^{33,45,64,73} Given that atmospheric NO3 mixing ratios range from several pptv to several hundred pptv,³ the potential for NO₃–SOA formation from BVOC and BBVOC precursors varies from minimal to significant over a single night in polluted areas. In addition to measuring syringol NO₃-SOA yields for the first time, our work identifies several unique aspects of this system worth further investigation, including SOA components with (1) O/C ranging from 0.5 to 1.6 (2) H/C between 1.1 and 1.7 that increase with NO_3 exposure, and (3) a complex distribution of C_8 and C_{16} oxidation products containing anywhere from zero to four nitrogen atoms and four to 25 oxygen atoms per molecule. Future studies that simulate day-night oxidation cycles for

BVOC/BBVOC precursors will help clarify the relative roles of OH- and NO_3-initiated oxidative aging in OVOC/SOA formation. $^{74-77}$

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspace-chem.4c00293.

Time series of guaiacol signals measured with Vocus PTR during a guaiacol/NO₃ experiment; SOA yield values plotted with and without LVOC fate correction applied; AMS spectra of NO₃–SOA up to m/z = 120; time series of syringol, dimethoxybenzoquinone, and nitrosyringol signals measured with Vocus PTR during a syringol/NO₃ experiment; AMS CH₃O⁺ signals measured in NO₃–SOA as a function of NO₃ exposure; Van Krevelen diagram comparing H/C and O/C of isoprene OH-SOA and NO₃–SOA; reactions and kinetic data used in aqueous-phase and gas-phase KinSim mechanisms; summary of literature NO₃–SOA yield studies used for comparison with results from this work (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Atmospheric Chemistry Program of the National Science Foundation: grants AGS-2131368 to Aerodyne Research, AGS-2131458 to the Georgia Institute of Technology, and AGS-1764126 and AGS-2131084 to Yale University. AL thanks John Jayne and Douglas Worsnop (Aerodyne Research), Quanfu He (Forschungszentrum Jülich), and Sepehr Nikkho (University of British Columbia) for helpful discussions. JD and DG thank Taekyu Joo (Korea U.) for help with Atlanta offline LC-ESI-ToF sample collection. Chemical mechanistic information used in this manuscript was adapted from the Master Chemical Mechanism, MCM v3.3.1,^{25,58–60} via the website www.mcm.york.ac.uk. The views expressed in this paper are those of the author(s) and do not necessarily represent the views or the policies of the U.S. Environmental Protection Agency.

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