Technical note: Gas-phase nitrate radical generation via irradiation of aerated ceric ammonium nitrate mixtures

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Abstract.

We present a novel photolytic source of gas-phase NO\textsubscript{3} suitable for use in atmospheric chemistry studies that has several advantages over traditional sources that utilize NO\textsubscript{2} + O\textsubscript{3} reactions and/or thermal dissociation of dinitrogen pentoxide (N\textsubscript{2}O\textsubscript{5}). The method generates NO\textsubscript{3} via irradiation of aerated aqueous solutions of ceric ammonium nitrate ((NH\textsubscript{4})\textsubscript{2}Ce(NO\textsubscript{3})\textsubscript{6}, “CAN”) and nitric acid (HNO\textsubscript{3}) or sodium nitrate (NaNO\textsubscript{3}). We present experimental and model characterization of the NO\textsubscript{3} formation potential of irradiated CAN/HNO\textsubscript{3} and CAN/NaNO\textsubscript{3} mixtures containing [CAN] = 10\textsuperscript{−3} to 1.0 M, [HNO\textsubscript{3}] = 1.0 to 6.0 M, [NaNO\textsubscript{3}] = 1.0 to 4.8 M, photon fluxes (I) ranging from 6.9×10\textsuperscript{14} to 1.0×10\textsuperscript{16} photons cm\textsuperscript{−2} s\textsuperscript{−1}, and irradiation wavelengths ranging from 254 to 421 nm. NO\textsubscript{3} mixing ratios ranging from parts per billion to parts per million by volume were achieved using this method. At the CAN solubility limit, maximum [NO\textsubscript{3}] was achieved using [HNO\textsubscript{3}] \approx 3.0 to 6.0 M and UVA radiation (\lambda\textsubscript{max} = 369 nm) in CAN/HNO\textsubscript{3} mixtures or [NaNO\textsubscript{3}] \geq 1.0 M and UVC radiation (\lambda\textsubscript{max} = 254 nm) in CAN/NaNO\textsubscript{3} mixtures. Other reactive nitrogen (NO\textsubscript{2}, N\textsubscript{2}O\textsubscript{4}, N\textsubscript{2}O\textsubscript{5}, N\textsubscript{2}O\textsubscript{6}, HNO\textsubscript{2}, HNO\textsubscript{3}, HNO\textsubscript{4}) and reactive oxygen (HO\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}) species obtained from the irradiation of ceric nitrate mixtures were measured using a NO\textsubscript{x} analyzer and an iodide adduct high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS). To assess the applicability of the method for studies of NO\textsubscript{3}-initiated oxidative aging processes, we generated and measured the chemical composition of oxygenated volatile organic compounds and secondary organic aerosols from the \beta-pinene + NO\textsubscript{3} reaction using a Filter Inlet for Gases and Aerosols (FIGAERO) coupled to the HR-ToF-CIMS.

1 Introduction

The importance of NO\textsubscript{3} as a nighttime atmospheric oxidant is well established (Wayne et al., 1991; Brown and Stutz, 2012; Ng et al., 2017; Wang et al., 2023). NO\textsubscript{3} is generated via the reaction NO\textsubscript{2} + O\textsubscript{3} \rightarrow NO\textsubscript{3} + O\textsubscript{2}, followed by achievement of
temperature-dependent equilibrium between NO$_3$, NO$_2$, and dinitrogen pentoxide (N$_2$O$_5$). N$_2$O$_5$ also hydrolyzes efficiently to HNO$_3$ on aqueous surfaces (Brown et al., 2004). Thus, any investigation of the influence of NO$_3$ chemistry in a specific source region necessarily must account for the local temperature, humidity, and particle surface area along with other factors. Despite these complications, for decades, laboratory studies investigating gas-phase NO$_3$ chemistry have utilized the same NO$_2$ + O$_3$ reactions and/or N$_2$O$_5$ thermal decomposition to produce NO$_3$ as occurs in the atmosphere, and accommodated the inherent limitations associated with N$_2$O$_5$; namely, that it must be stored under cold and dry conditions until use. Few viable alternative methods for the generation of gas-phase NO$_3$ have been identified. Reactions between fluorine atoms and nitric acid (F + HNO$_3$ → HF + NO$_3$), or chlorine atoms and chlorine nitrate (Cl + ClNO$_3$ → Cl$_2$ + NO$_3$) require handling and/or synthesizing hazardous halogen-containing compounds (Burrows et al., 1985; Bedjanian, 2019). F and Cl can also compete with NO$_3$ for the oxidation of target analytes, as can O$_3$ if its reaction with NO$_2$ is used as the NO$_3$ source.

In the 1960s and 1970s, following earlier research into the properties of ceric solutions (Meyer and Jacoby, 1901; Wylie, 1951; Hinsvark and Stone, 1956; Blaustein and Gryder, 1957), Thomas Martin and coworkers discovered that irradiating solutions containing ceric ammonium nitrate (CAN, (NH$_4$)$_2$Ce(NO$_3$)$_6$) generates aqueous NO$_3$ (Henshall, 1963; Martin et al., 1963, 1964; Glass and Martin, 1970; Martin and Glass, 1970; Martin and Stevens, 1978). In $\gtrsim$ 6M nitric acid (HNO$_3$), CAN is thought to dissociate primarily into NH$_4^+$ cations and hexanitratocerate (Ce(NO$_3$)$_6^{2-}$) anions (Henshall, 1963). The Ce(NO$_3$)$_6^{2-}$ is subsequently reduced to Ce(NO$_3$)$_5^{2-}$ upon irradiation by ultraviolet light, and NO$_3$ is generated as a primary photolysis product. A similar process occurs in other solvents, although the ensuing ceric composition in solution is complex and influenced by several factors. For example, in glacial acetic acid (CH$_3$COOH), CAN dissociates into primarily Ce(NO$_3$)$_4$ (Henshall, 1963). Additionally, ceric ions containing complexed hydroxyl (OH) or H$_2$O, CH$_3$COOH, or acetonitrile (CH$_3$CN) molecules are formed in aqueous, acetic acid, or CH$_3$CN media, respectively (Henshall, 1963; Glebov et al., 2021). Higher solution acidity and/or CAN concentration appears to promote the formation of Ce(NO$_3$)$_5^{2-}$ (Wylie, 1951) and ceric nitrate dimers (Blaustein and Gryder, 1957; Demars et al., 2015). The following generalized mechanism was proposed by Glass and Martin (1970) to describe ceric nitrate photochemistry:

\[
\begin{align*}
\text{Ce}^{(IV)} + h\nu & \rightarrow \text{Ce}^{(III)} + \text{NO}_3^3 \quad (R1) \\
\text{Ce}^{(III)} + \text{NO}_3 & \rightarrow \text{Ce}^{(IV)} \quad (R2) \\
\text{NO}_3 + \text{NO}_3 & \rightarrow \text{N}_2\text{O}_6 \quad (R3) \\
\text{N}_2\text{O}_6 + 2\text{Ce}^{(IV)} & \rightarrow 2\text{NO}_2 + \text{O}_2 + 2\text{Ce}^{(III)} \quad (R4) \\
\text{NO}_3 + \text{NO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 \quad (R5)
\end{align*}
\]

where Ce$^{(IV)}$ represents ceric nitrates as diverse as Ce(NO$_3$)$_4$, Ce(NO$_3$)$_6^{2-}$, (NO$_3$)$_5$CeOCe(NO$_3$)$_5^{2-}$, and (H$_2$O)$_3$(NO$_3$)$_3$CeOCe(NO$_3$)$_3$(H$_2$O)$_3$ that are potentially formed in solution (Henshall, 1963; Blaustein and Gryder, 1957; Demars et al., 2015). Similarly, Ce$^{(III)}$ represents cerous nitrates such as Ce(NO$_3$)$_3$ and Ce(NO$_3$)$_5^{2-}$. The rate of Reaction R2 is [HNO$_3$]-dependent (Martin and Glass, 1970), and the dinitrogen hexaoxide (N$_2$O$_6$) intermediate was proposed on the basis of supporting observations without direct measurements (Glass and Martin, 1970).
CAN is used routinely as an oxidizing agent in organic synthesis due to its widespread availability and low cost, high oxidative potential, and low toxicity (Nair and Deepthi, 2007). However, its usage in atmospheric chemistry to date is limited to studies of NO$_3$-initiated oxidative aging processes in solution, e.g. Alexander (2004). Given the potential simplicity of irradiating Ce(IV) mixtures relative to synthesizing and storing N$_2$O$_5$ under cold and dry conditions or reacting NO$_2$ + O$_3$ under carefully controlled conditions, Ce(IV) irradiation could in principle enable more widespread studies of NO$_3$ oxidation chemistry, which is understudied compared to OH chemistry (Ng et al., 2017). Here, for the first time, we investigated the use of Ce(IV) irradiation as a source of gas-phase NO$_3$. First, we designed a photoreactor that generates gas-phase NO$_3$ from irradiated CAN/HNO$_3$ and CAN/NaNO$_3$ mixtures. Second, we characterized NO$_3$ concentrations achieved over a range of reactor operating conditions and mixture composition. Third, we characterized gas-phase reactive nitrogen and reactive oxygen species generated following Ce(IV) irradiation. Fourth, we demonstrated application of the method to generate and characterize OVOCs and SOA from the $\beta$-pinene + NO$_3$ reaction.

2 Methods

2.1 Photoreactor design and operation

Figure 1 shows a schematic of the experimental setup used in this study. A zero air carrier gas flow of 0.5 L min$^{-1}$ was bubbled through a gas dispersion line consisting of 6.35 mm OD x 4.8 mm ID FEP tubing into approximately 10 mL of aqueous CAN/HNO$_3$ or CAN/NaNO$_3$ mixtures placed at the bottom of a 12.7 mm OD x 11.1 cm ID FEP tube. The FEP tube was surrounded by low-pressure mercury fluorescent lamps installed vertically in a custom enclosure. These lamps had a 35.6 cm illuminated length. At these operating conditions, the calculated gas transit time in the illuminated portion of the reactor was approximately 3 s. After exiting the photoreactor, the carrier gas flow was passed through a filter holder (Savillex, 401-21-47-10-21-2) containing a 47 mm PTFE membrane filter (Pall Gelman, R2PJ047) to transmit NO$_3$ (Wagner et al., 2011) while removing stray droplets from the sample flow. At the end of each experiment, the lamps were turned off, the gas dispersion line was removed from the top of the reactor, and FEP tubing and filter holder were flushed with distilled H$_2$O to remove residual Ce(III) precipitate. Initial studies were conducted using a Cavity Attenuated Phase Shift (CAPS) NO$_2$ monitor operating at $\lambda$ = 405 nm (Kebabian et al., 2005) and a second retrofitted CAPS monitor operating at $\lambda$ = 630 nm which established that NO$_2$ and NO$_3$ were produced from irradiated Ce(IV). Subsequent studies described in the next section used a 2B Technologies Model 405 analyzer to measure NO and NO$_2$ (Birks et al., 2018).

Depending on the specific experiment, lamps with peak emission output centered at $\lambda$ = 254, 313, 369, or 421 nm, respectively (GPH436TL/4P, Light Sources, Inc.; F436T5/NBUVB/4P-313, F436T5/BLC/4P-369, F436T5/SDI/4P-421, LCD Lighting, Inc.) were used. Emission spectra from the manufacturer are shown in Figure S1. A fluorescent dimming ballast (IZT-2S28-D, Advance Transformer Co.) was used to regulate current applied to the lamps. To quantify the photon flux $I_\lambda$ in the photoreactor for studies that used $\lambda$ = 254, 313, or 369 nm radiation, we measured the rate of externally added O$_3$ ($\lambda$ = 254 nm) or NO$_2$ photolysis ($\lambda$ = 313 or 369 nm) as a function of lamp voltage under dry conditions (RH < 5%). The photon flux was not quantified in studies that used $\lambda$ = 421 nm radiation. NO$_2$ photolysis measurements were conducted in the absence
of oxygen to avoid O$_3$ formation. Photon flux values were then calculated using methods described in Lambe et al. (2019); maximum $I_{254} = 1.0 \times 10^{16}$ photons cm$^{-2}$ s$^{-1}$, $I_{313} = 6.0 \times 10^{15}$ photons cm$^{-2}$ s$^{-1}$, and $I_{369} = 7.0 \times 10^{15}$ photons cm$^{-2}$ s$^{-1}$ were obtained.

### 2.2 Characterization studies

In one set of experiments, the 0.5 L min$^{-1}$ photoreactor effluent was mixed with a 6.5 L min$^{-1}$ zero air carrier gas and injected into a dark Potential Aerosol Mass oxidation flow reactor (OFR; Aerodyne Research, Inc.), which is a horizontal 13 L Teflon-coated aluminum cylindrical chamber operated in continuous flow mode. Approximately 6.5 L min$^{-1}$ of sample flow was pulled from the reactor, resulting in a calculated mean residence time in the OFR ($\tau_{OFR}$) of approximately 120 s. To constrain NO$_3$ mixing ratios, a mixture of 10 VOC tracers with NO$_3$ reaction rate coefficients ($k_{NO_3}$) ranging from $3.01 \times 10^{-19}$ to $2.69 \times 10^{-11}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ at $T = 298$ K (Table S1) was injected through a 10.2 cm length of 0.0152 cm ID Teflon tubing at a liquid flow rate of 0.94 $\mu$L hr$^{-1}$ using a syringe pump. The tracer mixture was then evaporated into a 1 L min$^{-1}$ zero air carrier gas prior to injection into the OFR. The total external NO$_3$ reactivity (NO$_3$R$_{ext}$), which is the summed product of each tracer mixing ratio and its $k_{NO_3}$, was approximately 5 s$^{-1}$. VOCs with proton affinities greater than that of H$_2$O were chosen to enable their measurement with a Tofwerk/Aerodyne Vocus proton transfer-reaction time-of-flight mass spectrometer (hereafter referred to as “Vocus PTR”) operated using H$_3$O$^+$ reagent ion chemistry (Krechmer et al., 2018) and $\sim$ 8000 (Th/Th) resolving power. NO$_3$ mixing ratios were calculated from the measured decrease in VOC mixing ratios using the Vocus PTR. Here, we assumed that the total concentration of reacted VOCs was equal to the concentration of NO$_3$ injected into the OFR. Because NO$_3$ may additionally react with organic peroxy radicals (RO$_2$) generated from VOC + NO$_3$ reactions as well as OVOCs, these calculated NO$_3$ concentrations represent lower limits. Modeling calculations suggest that the fractional consumption of NO$_3$ by RO$_2$ ranged from $<$0.01 to 0.17 over the range of conditions that were studied (Fig. S2). A subset of OVOCs generated from VOC + NO$_3$ reactions that had proton affinities greater than that of H$_2$O were also detected with the Vocus PTR.

In a separate set of experiments, the photoreactor effluent was diluted into 4 L min$^{-1}$ zero air carrier gas and sampled with an Aerodyne iodide-adduct high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS; hereafter referred to as “CIMS”; Bertram et al. (2011)) and the NO$_x$ analyzer. The CIMS was operated at a $\sim$ 4000 (Th/Th) resolving power. Iodide-adduct reagent ion chemistry was used due to its high sensitivity and selectivity towards nitrogen oxides and multifunctional organic nitrates (Lee et al., 2014). To demonstrate application of the method to study NO$_3$-initiated oxidative aging processes, the chemical composition of $\beta$-pinene + NO$_3$ gas-and condensed-phase oxidation products was measured with a Filter Inlet for Gases and Aerosols (FIGAERO) coupled to the CIMS (Lopez-Hilfiker et al., 2013). Gas sampling and simultaneous particle collection was performed for 1 min intervals, followed by thermal desorption of the particle sample from a PTFE filter membrane (15 min ramp from room temperature to 200°C, 10 min holding time, 8 min cooldown to room temperature).
2.3 Photochemical model

To supplement our measurements, and to characterize aqueous phase concentrations of species produced in the photoreactor that were not measured, we developed a photochemical box model that was implemented in the KinSim chemical kinetic solver (Peng and Jimenez, 2019). The KinSim mechanism shown in Table S2 contains reactions to model concentrations of Ce(IV), Ce(III), NO, NO2, NO3, N2O3, N2O4, N2O5, HNO2, HNO3, HNO4, H, O, OH, HO2, and H2O2. We assumed that HNO3 that was present in solution prior to irradiation completely dissociated into H+ and NO3−. When possible, we used condensed-phase rate coefficients in the mechanism. For reactions that we assumed occurred but did not have published condensed-phase rate coefficients (e.g. NO3 + OH → NO2 + HO2) we used published gas-phase rate coefficients instead with no modifications. UV/Vis extinction cross sections (σext) of CAN/HNO3 and CAN/NaNO3 mixtures were separately obtained between λ = 200 and 600 nm using an Agilent Cary 5000 UV/Vis/NIR spectrophotometer. Because of the high absorptivity and concentrations of the mixtures, samples were prepared in a 0.01 mm short-path-length cuvette (20/C-Q-0.01, Starna) to minimize saturation of the photodetector relative to a cuvette with a standard 10 mm path length. Even with the cuvette that was used, CAN dilution was necessary in some cases in order to obtain σext without photodetector saturation at shorter wavelengths. Spectra were obtained as a function of [CAN] (0.047 to 0.526 M), [HNO3] (0 to 6.0 M), and [NaNO3] (0 to 4.0 M) to cover the approximate range of mixture compositions that were characterized in Section 2.2. The σext-values of the mixtures were then calculated using the Beer-Lambert law and applied in the KinSim mechanism. Model outputs were obtained over a total experimental time of 14400 s at 1 s intervals.

3 Results and Discussion

The maximum NO3 quantum yield (ϕNO3) of UVA-irradiated CAN/HNO3 mixtures is obtained at 6.0 M HNO3 (Martin and Stevens, 1978); thus, this mixture composition served as the basis from which additional characterization studies were conducted. We found that 0.5 M CAN was the approximate solubility limit in 6.0 M HNO3 at 25°C. Because 1.1 M CAN is the solubility limit in H2O and CAN is almost nearly in HNO3 (Martin and Glass, 1970), 0.7 M CAN is the estimated solubility limit in 6.0 M HNO3 in the absence of changes in ceric nitrate composition in solution. Thus, the reduction in CAN solubility (0.7 M → 0.5 M) observed in our studies was presumably associated with significant conversion of CAN to dimeric ceric nitrates in 6.0 M HNO3 (Blaustein and Gryder, 1957; Demars et al., 2015).

3.1 NO3 characterization studies

Figure 2a shows time series of thiophene (C4H4S), 2,3-dihydrobenzofuran (C8H8O), cis-3-hexenyl acetate (C8H14O2), isoprene (C5H8), dimethyl sulfide (C2H6S), 2,5-dimethylthiophene (C6H8S), α-pinene (C10H16), and guaiacol (C7H8O2) concentrations following injection into the OFR and exposure to NO3 generated in the photoreactor from irradiation of a mixture of 0.5 M CAN and 6.0 M HNO3 at I369 = 7×1015 photons cm−2 s−1. Here, concentrations of each VOC were first normalized
to the acetonitrile concentration to correct for changes in the syringe pump output over time and then normalized to the VOC concentration prior to NO₃ exposure. Aside from C₆H₈S, whose relative decay was less pronounced than expected (Table S1), and butanal (C₄H₈O, not shown), whose signal decreased by approximately 30% and did not recover for reasons that are unclear, the oxidative loss of each tracer increased with increasing $k_{NO₃}$. Maximum tracer consumption was observed at the beginning of the experiment due to maximum NO₃ production from Ce(IV) irradiation. As the experiment progressed and Ce(IV) was reduced to Ce(III), the NO₃ concentration and corresponding VOC oxidative loss decreased. Compared to the other VOCs, the initial increase in C₁₀H₁₆ and C₇H₈O₂ concentrations over the first 2 hours was delayed because of their higher $k_{NO₃}$ values that resulted in >95% consumption and lower sensitivity to changes in [NO₃] in the initial stage of the experiment. To confirm that VOC degradation shown in Fig. 2a was due to reaction with NO₃, Figure S3 shows the relative NO₃ rate coefficients obtained from the decay of C₄H₄S, C₈H₈O, and C₈H₁₄O₂ measured with the Vocus PTR. We measured relative rate coefficients of 3.59 between C₈H₈O and C₄H₄S and 6.92 between C₈H₁₄O₂ and C₄H₄S, which are in agreement with relative rate coefficient values of 3.44±1.20 and 7.68±2.84 calculated from their absolute NO₃ rate coefficients (Atkinson, 1991; D’Anna et al., 2001). Time series of ions corresponding to nitrothiophene (C₄H₃NO₂S), C₅H₇NO₄₋₆ and C₁₀H₁₅NO₅₋₆ organic nitrates, and nitroguaiacol (C₇H₇NO₄), which are known NO₃ oxidation products of C₄H₄S, C₅H₈, C₁₀H₁₆, and C₇H₈O₂ (Atkinson et al., 1990; Jenkin et al., 2003; Saunders et al., 2003; Cabañas et al., 2005), along with C₈H₅NO₄₋₆ and C₈H₁₃NO₅₋₆ ions that may be associated with NO₃ oxidation products of C₈H₈O and C₈H₁₄O₂, respectively, were anticorrelated with those of their respective VOC precursors (Figure S4). Tracer decay experiments similar to the one shown in Figure S3 were used to obtain results that are discussed in more detail in Sections 3.2, 3.3, and 3.4.

### 3.2 Effect of irradiation wavelength

Figure 3a shows normalized [NO₃] values obtained following irradiation of mixtures containing CAN and 6.0 M HNO₃ or 4.8 M NaNO₃ as a function of irradiation wavelength. In CAN/HNO₃ mixtures, [NO₃] was a factor of 2.4-3.5 higher following irradiation at $\lambda = 369$ compared to the other wavelengths. On the other hand, [NO₃] decreased with increasing irradiation wavelength following irradiation of CAN/NaNO₃ mixtures; at $\lambda = 254$ nm, [NO₃] was a factor of 3.2-42 times higher than at the other irradiation wavelengths that were used. These differences in [NO₃] were larger than the differences in calibrated photon flux values at the maximum output of each lamp type (±40%; Sect. 2.1). Different Ce(IV) in CAN/HNO₃ and CAN/NaNO₃ mixtures may have influenced these trends, as suggested by their UV/Vis spectra (Fig. 3b). The $\sigma_{ext}$ curves of CAN/HNO₃ mixtures were generally larger, broader, and red-shifted relative to those of CAN/NaNO₃ mixtures, with the extent of red-shifting increasing with increasing [HNO₃], possibly due to higher yields of Ce(NO₃)$_{2}^{2-}$ and/or ceric nitrate dimers (Blaustein and Gryder, 1957; Henshall, 1963; Demars et al., 2015). For $\lambda > 250$ nm, CAN/HNO₃ mixtures had $\sigma_{ext,max}$ values between $\lambda = 306 - 311$ nm, whereas CAN/NaNO₃ solutions had $\sigma_{ext,max}$ values at $\lambda = 296$ nm. However, if [NO₃] was simply proportional to $\sigma_{ext}$, irradiation of CAN/HNO₃ mixtures at $\lambda = 313$ nm should have produced the highest [NO₃]; this was not the case. Instead, model calculations suggest that higher [NO₂] obtained from significantly faster photolysis of HNO₃ at $\lambda = 254$ and 313 nm relative to $\lambda > 350$ nm suppressed NO₃ downstream of the photoreactor when shorter irradiation wavelengths were used (Sander et al. (2011), Table S2). At a photon flux of $10^{16}$ photons cm$^{-2}$ s$^{-1}$, model-calculated [NO₃]
values were within ± 13% of each other for irradiation wavelengths ranging from λ = 254 to 369 nm. However, higher [NO2] values obtained following Ce(IV) irradiation at λ = 254 and 313 nm suppressed NO3 by >96% relative to the λ = 369 nm case during 120 s of simulated NO2 + NO3 reactions in the OFR. Thus, although the measured NO3 suppression at these other irradiation wavelengths was less substantial than the model output, the measurement and model trends, along with achievement of maximum [NO3] following λ = 254 nm irradiation of CAN/NaNO3 mixtures that had lower [HNO3], qualitatively support this explanation for the wavelength-dependent NO3 yields observed in CAN/HNO3 mixtures.

### 3.3 Effect of mixture composition

To characterize the influence of individual reagents on NO3 formation, tracer decay experiments similar to the measurements shown in Figure 2 were repeated as a function of [CAN], [HNO3], and [NaNO3]. Figure 4a shows [NO3] obtained from irradiated 6.0 M HNO3 solutions containing 0.001 to 0.5 M CAN \( (I_{369} = 7 \times 10^{15} \text{ photons cm}^{-2} \text{ s}^{-1}) \), and irradiated 1.0 M NaNO3 solutions containing 0.5 to 1.0 M CAN \( (I_{254} = 1 \times 10^{16} \text{ photons cm}^{-2} \text{ s}^{-1}) \). Results were normalized to [NO3] achieved with solutions containing 0.5 M CAN and 6.0 M HNO3. Control experiments conducted with irradiated 6.0 M HNO3 or 1.0 M NaNO3 solutions at \( I_{254} = 1 \times 10^{16} \text{ photons cm}^{-2} \text{ s}^{-1} \) in the absence of CAN suggest that a fraction of the NO3 obtained in CAN mixtures was generated via the reactions HNO3 + hν → OH + NO2 and HNO3 + OH → NO3 + H2O. The remaining NO3 was clearly obtained from CAN irradiation because [NO3] increased with increasing [CAN], as expected from Reaction R1. Overall, [NO3] increased by approximately a factor of 3 as [CAN] was increased from 0.001 to 0.5 M in 6.0 M HNO3.

Figure 4b shows [NO3] obtained in irradiated solutions containing 0.5 M CAN as a function of [HNO3] ranging from 1.0 to 6.0 M or [NaNO3] ranging from 1.0 to 4.8 M at the same \( I_{369} \) and \( I_{254} \) values used to obtain results shown in Fig. 4a. Irradiated CAN solutions containing 3.0 M and 6.0 M HNO3 generated the same [NO3] concentrations within measurement uncertainties, presumably because the NO3 quantum yield (\( \phi_{NO3} \)) ranged from 0.92-1.00 over this range of acidity (Martin and Stevens, 1978; Wine et al., 1988). [NO3] decreased by a factor of 2 as [HNO3] was decreased from 3.0 M to 1.0 M, consistent with a reduction in \( \phi_{NO3} \) from 0.92 to 0.46 (Martin and Stevens, 1978). On the other hand, in irradiated CAN/NaNO3 mixtures with uncharacterized \( \phi_{NO3} \), [NO3] was constant within measurement uncertainties between 1.0 and 4.8 M NaNO3.

Other mixture components that were tested or considered included substitution of CH3CN in place of H2O and HNO3, ammonium nitrate (NH4NO3) instead of NaNO3, ceric potassium nitrate (K2Ce(NO3)6) instead of CAN, and addition of sodium persulfate (Na2S2O8) to generate additional NO3 via \( S_2O_8^{2-} + h\nu \rightarrow 2SO_4^- \) followed by \( SO_4^- + NO_3^- \rightarrow NO_3 + SO_4^{2-} \) (Gaillard de Sémainville et al., 2007). CAN/CH3CN mixtures are commonly used in organic synthesis applications, perhaps even more so than CAN/HNO3 (Baciocchi et al., 1988; Choidini et al., 1993; Alexander, 2004). In limited testing, CAN/CH3CN appeared to generate significantly less NO3 than CAN/HNO3 or CAN/NaNO3, possibly due to lower \( \phi_{NO3} \) of irradiated Ce(IV)-CH3CN complexes (Glebov et al., 2021) and/or suppression of NO3 due to its reaction with CH3CN in solution. K2Ce(NO3)6 is less widely available and less water-soluble than CAN and so was not considered further. Irradiation of CAN/NH4NO3 and CAN/NaNO3 mixtures generated similar [NO3], but we prefer NaNO3 due to its lower volatility.
Finally, ternary mixtures containing 0.5 M CAN + 2.0 M NaNO₃ + 0.5 M Na₂S₂O₈ irradiated at λ = 254 nm generated negligible additional NO₃ compared to binary CAN/NaNO₃ mixtures.

3.4 Effect of photon flux

Figure 5 shows normalized [NO₃] values obtained from irradiated mixtures of 0.5 M CAN & 6.0 M HNO₃ (λ = 369 nm) and 0.5 M CAN & 1.0 M NaNO₃ (λ = 254 nm) as a function of photon flux ranging from 6.9×10¹⁴ to 7.5×10¹⁵ photons cm⁻² s⁻¹. Results for both CAN/HNO₃ and CAN/NaNO₃ mixtures were normalized to [NO₃] achieved with 0.5 M CAN, 6.0 M HNO₃ and I₃₆⁹ = 6.8×10¹⁵ photons cm⁻² s⁻¹. Symbols are colored by the NO₃ lifetime (τ_NO₃), defined here as the time it took for [NO₃] to experience one e-fold decay relative to the maximum [NO₃] that was measured. Figure 5 shows that [NO₃] increased with increasing photon flux, consistent with the fact that it is a primary photolysis product, along with a concurrent decrease in τ_NO₃ due to faster reduction of Ce(IV) to Ce(III). For the CAN/HNO₃ system, [NO₃] increased by a factor of 1.5 as I₃₆⁹ was increased from 6.9×10¹⁴ to 6.8×10¹⁵ photons cm⁻² s⁻¹, in agreement with the model-calculated increase in [NO₃] within measurement uncertainty. τ_NO₃ decreased from 9 to 5 hr. For the CAN/NaNO₃ system, [NO₃] increased by a factor of 1.9 as I₂₅⁴ was increased from 1.0×10¹⁵ to 7.5×10¹⁵ photons cm⁻² s⁻¹, and τ_NO₃ decreased from 10 to 3 hr.

To examine concentrations of NO₃ and a subset of additional gas-phase photolysis products obtained over a wider range of conditions, Figure 6 plots model-calculated [NO₃], NO₂:NO₃, HO₂:NO₃, and N₂O₅:NO₃ values as a function of photon flux ranging from 1×10¹⁴ to 1×10¹⁷ photons cm⁻² s⁻¹ following λ = 254, 313, 369 and 421 nm irradiation of a mixture of 0.5 M CAN and 6.0 M HNO₃. Figure 6a also plots the measured [NO₃] obtained from irradiation of a mixture of 0.5 M CAN and 6.0 M HNO₃ at I₃₆⁹ = 7×10¹⁵ photons cm⁻² s⁻¹ (Fig. 2) after correcting for dilution between the photoreactor and the OFR (Sect. 2.2) and application of a NO₃ wall loss rate coefficient of 0.2 s⁻¹ within the photoreactor (Dubé et al., 2006). At this photon flux value, the model-calculated [NO₃] = 1.4 ppmv agrees with [NO₃] = 1.7 ± 0.6 ppmv obtained from measurements. When considering only the primary photochemical process (Reactions R1-R5), maximum [NO₃] values within ± 10% of each other were achieved at photon fluxes ranging from 5×10¹⁵ (λ = 313 nm) to 4×10¹⁶ photons cm⁻² s⁻¹ (λ = 421 nm). [NO₃] values decreased at higher photon flux values due to conversion of NO₃ to NO₂ via photolysis. As shown in Fig. 6b, significant additional NO₂ production was obtained via HNO₃ photolysis at shorter irradiation wavelengths above I ≈ 10¹⁵ photons cm⁻² s⁻¹, resulting in NO₂:NO₃ > 10 (λ = 254 nm) and 1 (λ = 313 nm). Given additional reaction time downstream of the photoreactor, high NO₂ may suppress NO₃ (Sect. 3.2) and increase N₂O₅:NO₃ beyond the range of values shown in Fig. 6c. We also calculated OH:NO₃ and HO₂:NO₃ following irradiation of CAN/HNO₃ mixtures over the range of conditions shown in Figure 6. Aqueous OH:NO₃ ≈ 0.1 and did not change significantly as a function of photon flux or irradiation wavelength, and aqueous HO₂:NO₃ values ranged from 0.05 (λ = 254 nm) to 0.25 (λ ≥ 369 nm). While OH influenced aqueous-phase chemistry inside the photoreactor via formation of reactive oxygen species (Sect. 3.5), OH probably did not influence downstream gas-phase chemistry due to significant wall losses inside the photoreactor: assuming a lower-limit OH wall loss rate coefficient of 5 s⁻¹ (Schwab et al., 1989), the estimated OH penetration efficiency through the reactor was less than 10⁻⁶.
3.5 Characterization of reactive nitrogen and reactive oxygen photolysis products

Figure 7 shows time series of reactive nitrogen and reactive oxygen species detected following irradiation of the same mixture of 0.5 M CAN and 1.0 M NaNO₃ \((I_{254} \approx 10^{16} \text{ photons cm}^{-2} \text{ s}^{-1})\), shown here because the signal-to-noise in CIMS measurements of irradiated CAN/NaNO₃ mixtures was generally better than in measurements of irradiated CAN/HNO₃ mixtures due to reagent ion depletion by HNO₃. A time series of \([\text{NO}_3^-]\) obtained separately from VOC tracer decay measurements under similar irradiation conditions is also shown. The NO₂ and NO₃ mixing ratios reached maximum values of 26 and 58 ppbv shortly after the lights were turned on (Fig. 7a), suggesting an initial \(\text{NO}_2:\text{NO}_3 \approx 0.45\) (Fig. 4). Multiple reactions may generate NO₂, including Reaction R3, HNO₃ and/or NO₃ photolysis, and other reactions listed in Table S2. While NO₂ and/or HNO₂ photolysis generated NO, its concentration was negligible in these experiments.

Figure 7b shows time series of \(\text{IN}_2\text{O}_5^-\) and \(\text{IN}_2\text{O}_6^-\) signals measured with the CIMS. \(\text{IN}_2\text{O}_5^-\) was formed from NO₂ + NO₃ \(\rightarrow\) N₂O₅ reactions in the photoreactor and N₂O₅ + I⁻ \(\rightarrow\) IN₂O₅⁻ reactions in the CIMS IMR. As expected, \(\text{IN}_2\text{O}_5^-\) followed a similar profile as NO₂ and NO₃. \(\text{IN}_2\text{O}_6^-\) was either generated from NO₃ + NO₃ \(\rightarrow\) N₂O₆ reactions in the photoreactor (Glass and Martin, 1970) followed by N₂O₆ + I⁻ \(\rightarrow\) IN₂O₆⁻ reactions in the IMR, or from the following series of reactions in the IMR: HNO₃ + IO⁻ \(\rightarrow\) NO₃⁻ + HOI, HOI + NO₃⁻ \(\rightarrow\) INO₃ + OH⁻, and INO₃ + NO₃⁻ \(\rightarrow\) IN₂O₆⁻ (Ganske et al., 2019). To further explore the plausibility of N₂O₆ formation in this system, we conducted a theoretical investigation of the gas-phase NO₃ + NO₃ \(\rightarrow\) N₂O₆ reaction and found that this reaction is exothermic, even more so than NO₃ + NO₃ \(\rightarrow\) N₂O₅. Additional details regarding this analysis are provided in Sect. S1.

Figure 7c shows time series of IHNO₂⁻, HNO₂NO₃⁻, IHNO₃⁻, and HNO₄NO₃⁻. These ions are associated with nitrous acid (HNO₂) and peroxynitric acid (HNO₄) respectively (Veres et al., 2015). Because rapid formation of HNO₂⁻ ions was observed following Ce(IV) irradiation, and because IO⁻ signals were relatively low (Sect. S2.1), we hypothesize that I⁻ + NO₃ and/or I⁻ + HNO₃ reactions were the main source of NO₃⁻ (Lee et al., 2014; Dörich et al., 2021), and that subsequent competitive NO₃⁻ + HNO₂⁻ and I⁻ + HNO₂⁻ reactions in the IMR generated both IHNO₂⁻ and HNO₂⁻NO₃⁻. HNO₄ was generated following the reactions HNO₃ + hv \(\rightarrow\) OH + NO₂, OH + NO₃ \(\rightarrow\) HO₂ + NO₂, and HO₂ + NO₂ \(\rightarrow\) HNO₄. This hypothesis is supported by the similarity between NO₂ and IHNO₂⁻ time series coupled with the relatively constant concentrations of HO₂ generated via OH + OH \(\rightarrow\) H₂O₂ and OH + H₂O₂ \(\rightarrow\) HO₂ + H₂O reactions. H₂O₂, detected as IH₂O₂⁻, also behaved similarly as IHNO₂⁻ (Figure 7d). HNO₂ had a different temporal profile than the other nitrogen oxides: IHNO₂⁻ increased throughout the experiment, and HNO₂NO₃⁻ increased and then decreased. We hypothesize that NO₂+NO₂ \(\rightarrow\) N₂O₄ and N₂O₄+H₂O \(\rightarrow\) HNO₂+HNO₃ reactions were the main source of HNO₂ (Sect. S2.2).

Figure S13 shows time series of the same ions plotted in Figure 7 following irradiation of a solution containing 0.5 M CAN and 3.0 M HNO₃ \((I_{369} \approx 7 \times 10^{15} \text{ photons cm}^{-2} \text{ s}^{-1})\). Here, 3.0 M HNO₃ was used because 6.0 M HNO₃ depleted the CIMS reagent ion too much (IHNO₂⁻:I⁻ \(\approx 15\)) to achieve signal-to-noise that was sufficient for comparison to CAN/NaNO₃ mixtures (IHNO₂⁻:I⁻ \(\approx 3\)). The same gas-phase nitrogen oxides and reactive oxygen species were observed in this reaction system as with the irradiated CAN/NaNO₃ mixture. The relative yields of each compound plotted in Figures 7 and S13 were within a factor of 3 of each other, although signals of nitrogen oxides and reactive oxygen species obtained from irradiated
CAN/HNO₃ mixtures decreased at a slower rate than the same compounds obtained from irradiated CAN/NaNO₃ mixtures. These trends may be due to different Ce(IV) composition (Fig. 3 and Sect. 3.2) and/or enhanced rate of Ce(III) + NO₃ → Ce(IV) reactions in HNO₃ relative to NaNO₃ (Reaction R2).

### 3.6 OVOC/SOA generation from β-pinene + NO₃

To demonstrate proof of principle for NO₃-initiated oxidative aging studies, we generated NO₃ via irradiation of a mixture of 0.5 M CAN and 3.0 M HNO₃ (I₃₆₉ = 7×10¹⁵ photons cm⁻² s⁻¹), reacted it with β-pinene in a dark OFR, and obtained FIGAERO-CIMS spectra of gas- and condensed-phase β-pinene + NO₃ oxidation products (Sect. 2.2). Figure 8a shows a spectrum of gas-phase β-pinene/NO₃ oxidation products detected between m/Q = 320 and 420, where the majority of the signal was observed; signals shown are unmodified (M+I)⁻ formulas. The largest ion detected was at m/Q = 356 (IC₁₀H₁₅NO₁⁻), which represents a major first-generation dicarbonyl nitrate oxidation product with a relative abundance of 0.31 and a calculated saturation vapor pressure of 2×10⁻⁷ atm (C* = 1900 µg m⁻³; Claflin (2018)). Other ions corresponding to first-generation hydroxycarbonyl nitrate (IC₁₀H₁₇NO₁⁻, C* = 95 µg m⁻³), tricarbonyl nitrate (IC₁₀H₁₅NO₅⁻, C* = 35 µg m⁻³), hydroxycarbonyl nitrate (IC₁₀H₁₇NO₆⁻, C* = 4.7 µg m⁻³), and hydroxycarbonyl nitrate acid (IC₁₀H₁₇NO₇⁻, C* = 0.29 µg m⁻³) products were detected in addition to IC₅H₁₃NO₅⁻ and a suite of additional previously characterized C₈ and C₉ organic nitrates (Nah et al., 2016; Takeuchi and Ng, 2019; Shen et al., 2021). The IC₁₀H₁₆N₂O⁻ hydroxy dinitrate, which was also previously observed in FIGAERO-CIMS spectra of α-pinene/NO₃ SOA (Nah et al., 2016), was generated via an unknown reaction pathway. Because model-calculated NO:NO₃ was on the order of 10⁻⁵ under these conditions, its formation from the RO₂ + NO₃ reaction seems more likely (Orlando and Tyndall, 2012). Overall, the high molar yield and vapor pressure of C₁₀H₁₅NO₅ (Claflin, 2018) are consistent with it having the highest relative abundance in the gas phase (Fig. 8a), whereas the other C₁₀ β-pinene oxidation products were semivolatile under our experimental conditions.

Figure 9a shows a spectrum of condensed-phase β-pinene/NO₃ oxidation products obtained with the FIGAERO-CIMS; signals were averaged over the entire thermal desorption cycle and are plotted on logarithmic scale and represent unmodified (M+I)⁻ formulas. To aid interpretation of the major features of the spectrum, bands of ion signals corresponding to IC₁₀H₁₅NOₓ⁻, IC₂₀H₃₂N₂Oₓ⁻, and IC₃₀H₄₇N₃Oₓ⁻ oxidation products were highlighted and colored by the number of oxygen atoms in their chemical formulas. Here, the largest ion detected was at m/Q = 372 (IC₁₀H₁₅NO₆⁻), which is the condensed-phase component of the same tricarbonyl nitrate detected in the gas-phase (Fig. 8a). IC₁₀H₁₅NO₅⁻ and IC₁₀H₁₅NO₇₋₉ signals were also detected. The second largest ion signal was measured at m/Q = 571 (IC₂₀H₃₂N₂O⁻), an acetal dimer obtained from the condensed-phase reaction of two C₁₀H₁₇NO₅ monomers followed by H₂O elimination (Claflin and Ziemann, 2018). Similar accretion reactions between other C₁₀ organic nitrates yielded IC₂₀H₃₂N₂O⁻ and IC₂₀H₃₂N₂O₁₀⁻ signals. Likewise, reactions between C₁₀ monomers and C₂₀ dimers generated C₃₀ trimers detected between m/Q = 768 - 864 (IC₃₀H₄₇N₃O₁₂₋₁₈). The largest trimer-related ion, IC₃₀H₄₇N₃O₁₂, was generated from C₁₀H₁₇NO₄ + C₂₀H₃₂NO₉ - H₂O or C₁₀H₁₇NO₅ + C₂₀H₃₂NO₈ - H₂O reactions (Claflin and Ziemann, 2018). A fourth cluster of ion signals at m/Q > 984 was also observed. Unambiguous assignment of chemical formulae to these signals was challenging due to the limited range of
the CIMS m/z calibration and lack of available information about C\(_{\geq 30}\) \(\beta\)-pinene/NO\(_3\) oxidation products. However, it seems plausible that these signals are associated with tetraters.

To compare our results with those obtained using a conventional NO\(_3\) generation method (room temperature N\(_2\)O\(_5\) thermal decomposition) in an environmental chamber study, Figures 8b and 9b show reference gas- and condensed-phase FIGAERO-\(\Gamma^-\)-CIMS spectra of OVOCs and SOA generated from NO\(_3\) oxidation of \(\beta\)-pinene in the Georgia Tech environmental chamber (Takeuchi and Ng, 2019). The spectra obtained here and by Takeuchi and Ng (2019) exhibit an overall high degree of similarity, with linear correlation coefficients of 0.87 and 0.96 between the respective gas- and condensed-phase spectra. Clusters of IC\(_{10}\)H\(_{15}\)NO\(_x^-\), IC\(_{26}\)H\(_{32}\)NO\(_2\)O\(_x^-\), and IC\(_{30}\)H\(_{47}\)N\(_3\)O\(_x^-\) ion signals were present in both Figs. 9a and 9b. The main differences between the gas-phase spectra shown in Figs. 8a and 9a were the different abundances of IC\(_{10}\)H\(_{17}\)NO\(_4^-\), a first-generation hydroxynitrate product (Claflin and Ziemann, 2018), and IC\(_{16}\)H\(_{16}\)N\(_2\)O\(_7^-\). Because C\(_{10}\)H\(_{17}\)NO\(_4\) is formed from RO\(_2\)+RO\(_2\) reactions (DeVault et al., 2022) and is sufficiently volatile (C\(_*\) = 750 \(\mu\)g m\(^{-3}\)) to partition into the gas phase (Claflin, 2018), differences in gas-phase C\(_{10}\)H\(_{17}\)NO\(_4\) and C\(_{10}\)H\(_{16}\)N\(_2\)O\(_7\) yields were likely related to differences in the relative importance of RO\(_2\)+RO\(_2\) versus RO\(_2\)+NO\(_3\) reaction pathways in the study by Takeuchi and Ng (2019) compared to this work.

To further investigate the fate of RO\(_2\) generated from VOC + NO\(_3\) reactions as a function of CAN irradiation conditions, we calculated the fractional oxidative loss of generic alkyl and acyl RO\(_2\) species due to reaction with HO\(_2\), NO\(_3\) and NO\(_2\) (\(F_{RO_2+HO_2}\), \(F_{RO_2+NO_3}\), \(F_{RO_2+NO_2}\)) using Equations 1-3:

\[
F_{RO_2+HO_2} = \frac{k_{RO_2+HO_2}[HO_2]}{k_{RO_2+HO_2}[HO_2] + k_{RO_2+NO_3}[NO_3] + k_{RO_2+NO_2}[NO_2]} (1)
\]

\[
F_{RO_2+NO_3} = \frac{k_{RO_2+NO_3}[NO_3]}{k_{RO_2+HO_2}[HO_2] + k_{RO_2+NO_3}[NO_3] + k_{RO_2+NO_2}[NO_2]} (2)
\]

\[
F_{RO_2+NO_2} = \frac{k_{RO_2+NO_2}[NO_2]}{k_{RO_2+HO_2}[HO_2] + k_{RO_2+NO_3}[NO_3] + k_{RO_2+NO_2}[NO_2]} (3)
\]

Here, \(k_{RO_2+HO_2}\), \(k_{RO_2+NO_3}\), and \(k_{RO_2+NO_2}\) are reaction rate coefficients for the corresponding RO\(_2\) + HO\(_2\), RO\(_2\) + NO\(_3\) and RO\(_2\) + NO\(_2\) forward reactions whose values are summarized in Table S3. Several simplifying assumptions were made. First, we assumed that RO\(_2\) + NO reactions were negligible. Second, we did not consider RO\(_2\) isomerization/autooxidation and RO\(_2\) + RO\(_2\) reactions that are influenced by external factors. Third, we set \(F_{RO_2+NO_2}\) = 0 for alkyl-RO\(_2\)-generated RO\(_2\)NO\(_2\), which thermally decompose on timescales of seconds or less (Orlando and Tyndall, 2012). Fourth, we assumed that vapor wall losses of acyl-RO\(_2\)-generated RO\(_2\)NO\(_2\) were a minor RO\(_2\) sink because the OFR residence time (\(\tau_{OFR}\) \(\approx\) 120 s, Sect. 2.2) was significantly shorter than their estimated wall loss timescale (\(\tau_{wall}\) \(\approx\) 400 s, Palm et al. (2016)). Figure 10 shows calculated \(F_{RO_2+HO_2}\), \(F_{RO_2+NO_3}\), and \(F_{RO_2+NO_2}\) values for alkyl-RO\(_2\) and acyl-RO\(_2\) as a function of photon flux over the range of NO\(_3\) generation conditions presented in Fig. 6. For alkyl-RO\(_2\), \(F_{RO_2+HO_2}\) decreased and \(F_{RO_2+NO_3}\) increased with increasing photon flux and decreasing irradiation wavelength. On the other hand, for acyl-RO\(_2\), \(F_{RO_2+NO_2}\) increased while
$F_{\text{RO}_2 + \text{HO}_2}$ and $F_{\text{RO}_2 + \text{NO}_3}$ decreased over the same irradiation conditions. Overall, at the optimal NO$_3$ generation conditions (e.g. $\lambda = 369 \text{ nm}$ and $I_{369} \approx 10^{16} \text{ photons cm}^{-2} \text{ s}^{-1}$), our calculations suggest that $F_{\text{RO}_2 + \text{HO}_2} \approx F_{\text{RO}_2 + \text{NO}_3}$ (Fig. 10c) and that $F_{\text{RO}_2 + \text{HO}_2} \approx F_{\text{RO}_2 + \text{NO}_3} \approx F_{\text{RO}_2 + \text{NO}_2}$ was significant for acyl-RO$_2$ (Fig. 10g).

4 Conclusions

Ce$^{(IV)}$ irradiation complements NO$_2 + \text{O}_3$ reactions and N$_2$O$_5$ thermal dissociation as a customizable photolytic NO$_3$ source. Important method parameters were [CAN], [HNO$_3$] or [NaNO$_3$], UV intensity, and irradiation wavelength. By contrast, important parameters for NO$_2 + \text{O}_3$ and N$_2$O$_5$-based methods are [O$_3$], [NO$_2$], temperature, and humidity. Because Ce$^{(IV)}$ irradiation already generates NO$_3$ in aqueous solution, its performance is not hindered by humidity to the same extent (if at all) as N$_2$O$_5$-based methods, where hydrolysis of N$_2$O$_5$ to HNO$_3$ decreases the efficacy of the source. Additionally, the NO$_3 + \text{H}_2\text{O}$ reaction rate in solution or on surfaces is slow relative to other NO$_3$ loss pathways. Another advantage of Ce$^{(IV)}$ irradiation is that it does not involve the use of O$_3$ as a reagent, therefore eliminating the possibility of competing O$_3$ and NO$_3$ oxidation of compounds that are reactive towards both oxidants if NO$_2 + \text{O}_3$ reactions and/or online N$_2$O$_5$ synthesis are used as the NO$_3$ source (Lambe et al., 2020). To identify optimal operating conditions for maximizing [NO$_3$], we characterized concentrations of NO$_3$ at [CAN] = $10^{-3}$ to 1 M, [HNO$_3$] = 1.0 to 6.0 M, [NaNO$_3$] = 1.0 to 4.8 M, photon flux = $6.9 \times 10^{14}$ to $1.0 \times 10^{16}$ photons cm$^{-2}$ s$^{-1}$, and irradiation wavelengths of $\lambda = 254, 313, 369, \text{or } 421 \text{ nm}$. With CAN/HNO$_3$ mixtures, maximum [NO$_3$] was achieved with [CAN] $\approx 0.5$ M, [HNO$_3$] $\approx 3.0$ to 6.0 M, and $I_{369} = 8 \times 10^{15}$ photons cm$^{-2}$ s$^{-1}$ (4.3 mW cm$^{-2}$). With CAN/NaNO$_3$ mixtures, maximum [NO$_3$] was achieved with [CAN] $\approx 1.0$ M, [NaNO$_3$] $\geq 1.0$ M, and $I_{254} \approx 1 \times 10^{16}$ photons cm$^{-2}$ s$^{-1}$ (7.8 mW cm$^{-2}$). Thus, for applications such as environmental chamber or OFR studies of NO$_3$-initiated oxidative aging processes, where significant NO$_3$ production over relatively short time periods is beneficial, irradiation of concentrated Ce$^{(IV)}$ solutions at high photon flux is advantageous. Other applications that require sustained NO$_3$ production at lower concentrations and/or over longer time periods may benefit from using lower [Ce$^{(IV)}$] and photon flux. Overall, because Ce$^{(IV)}$ irradiation generates NO$_3$ at room temperature using widely-available, low-cost reagents and light sources (including high power light-emitting diodes in addition to, or instead of, UV fluorescent lamps) it is easier to apply than other NO$_3$ generation techniques - especially in field studies - and it may therefore enable more widespread studies of NO$_3$ oxidation chemistry. Adapting a photoreactor to operate with continuous injection of fresh Ce$^{(IV)}$ or alternative photolytic NO$_3$ precursors (e.g. Hering et al. (2015)) rather than in batch mode as was done here may further enhance its performance and will be investigated in future work.

*Code and data availability.* Data and KinSim mechanisms presented in this manuscript are available upon request. The KinSim kinetic solver is freely available at http://tinyurl.com/kinsim-release.
Author contributions. AL, BB, and PL conceived and planned the experiments. AL, BB, MA, and PL carried out the experiments. AL conceived, planned, and carried out the KinSim model simulations. NO and PZ conceived, planned, and carried out the quantum chemical calculations. AL, BB, MT, NO, PZ, MC, DW, and PL contributed to the interpretation of the results. AL took the lead in writing the manuscript. All authors provided feedback on the manuscript.

Competing interests. At least one of the coauthors is a member of the editorial board of Atmospheric Chemistry and Physics.

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Figure 1. Overview of experiments conducted in this study. Aqueous mixtures of ceric ammonium nitrate (CAN) and nitric acid (HNO₃) or sodium nitrate (NaNO₃) were irradiated in a photoreactor to generate nitrate radicals (NO₃⁻) in solution. Air was bubbled through the solution to evaporate NO₃⁻ and other volatile photolysis products into the gas phase. The photoreactor effluent was then (i) injected into a dark oxidation flow reactor (OFR) along with a VOC mixture to characterize [NO₃⁻] via tracer decay measurements using a Vocus proton transfer-reaction time-of-flight mass spectrometer (PTR-ToF) (ii) sampled with an iodide adduct high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) (iii) injected into a dark OFR to characterize β-pinene/NO₃ oxidation products with a Filter Inlet for Gases and Aerosols (FIGAERO) coupled to the HR-ToF-CIMS. Supporting measurements were obtained using a NOₓ analyzer.
Figure 2. Example results from an experiment in which a mixture of 0.5 M CAN and 6.0 M HNO₃ was irradiated to generate NO₃ ($\lambda_{\text{max}} = 369$ nm, $I_{369} = 7 \times 10^{15}$ photons cm$^{-2}$ s$^{-1}$) that was injected into the OFR along with a reactive VOC tracer mixture. (a) Time series of the fractional consumption of VOC tracers measured with the Vocus following irradiation: thiophene ($C_4H_4S$), 2,3-dihydrobenzofuran ($C_8H_8O$), cis-3-hexenyl-1-acetate ($C_8H_{14}O_2$), isoprene ($C_5H_8$), dimethyl sulfide ($C_2H_6S$), 2,5-dimethylthiophene ($C_6H_{16}$), $\alpha$-pinene ($C_{10}H_{16}$), guaiacol ($C_7H_8O_2$). Signals of each tracer were normalized to their initial concentrations prior to NO₃ exposure and to acetonitrile concentrations to account for changes in the syringe pump output. (b) Time series of $[\text{NO}_3]$ calculated from (a) and Tab. S1.
Figure 3. (a) [NO₃] values obtained from irradiated CAN & 6.0 M HNO₃ and CAN & 4.8 M NaNO₃ mixtures as a function of irradiation wavelength. Results were normalized to [NO₃] achieved with irradiation of CAN/HNO₃ mixtures at λ = 369 nm or CAN/NaNO₃ mixtures at λ = 254 nm. Error bars represent ±1σ uncertainty in binned [NO₃] values. (b) Extinction cross sections (σ_{ext}) of CAN/HNO₃ and CAN/NaNO₃ mixtures (for details see Sect. 2.3). The black dot corresponds to data from Wine et al. (1988).
Figure 4. $[\text{NO}_3]$ obtained from (a) irradiated 6.0 M HNO$_3$ solutions containing 0.001 to 0.5 M CAN ($I_{369} = 7 \times 10^{15}$ photons cm$^{-2}$ s$^{-1}$), and irradiated 1.0 M NaNO$_3$ solutions containing 0.5 to 1.0 M CAN ($I_{254} = 1 \times 10^{16}$ photons cm$^{-2}$ s$^{-1}$). (b) irradiated 0.5 M CAN solutions containing 1.0 to 6.0 M [HNO$_3$] or 1.0 to 4.8 M [NaNO$_3$] at the same $I_{369}$ and $I_{254}$ values used to obtain results shown in (a). Results were normalized to $[\text{NO}_3]$ achieved with mixtures of 0.5 M CAN and 6.0 M HNO$_3$. Error bars represent estimated ±35% uncertainty in $[\text{NO}_3]$ values obtained from CAN/HNO$_3$ mixtures, ±15% uncertainty in $[\text{NO}_3]$ values obtained from CAN/NaNO$_3$ mixtures, and ±10% uncertainty in [CAN], [HNO$_3$], and [NaNO$_3$] values.
Figure 5. Normalized $[\text{NO}_3]$ values obtained from irradiated mixtures of 0.5 M CAN and 6.0 M HNO$_3$ ($\lambda = 369$ nm) or 0.5 M CAN and 1.0 M NaNO$_3$ ($\lambda = 254$ nm) as a function of photon flux ranging from $6.9 \times 10^{14}$ to $7.5 \times 10^{15}$ photons cm$^{-2}$ s$^{-1}$. Results were normalized to $[\text{NO}_3]$ achieved with 0.5 M CAN, 6.0 M HNO$_3$ and $I_{369} = 6.8 \times 10^{15}$ photons cm$^{-2}$ s$^{-1}$. Symbols are colored by the time it took for $[\text{NO}_3]$ to experience one e-fold decay relative to the maximum $[\text{NO}_3]$ that was measured ($\tau_{\text{NO}_3}$). Error bars represent estimated $\pm 35\%$ uncertainty in $[\text{NO}_3]$ values obtained from CAN/HNO$_3$ mixtures, $\pm 15\%$ uncertainty in $[\text{NO}_3]$ values obtained from CAN/NaNO$_3$ mixtures, and $\pm 30\%$ uncertainty in photon flux values.
Figure 6. Model-calculated (a) [NO$_3$], (b) NO$_2$:NO$_3$, (c) HO$_2$:NO$_3$, and (d) N$_2$O$_5$:NO$_3$ values in solution as a function of photon flux ranging from $1 \times 10^{14}$ to $1 \times 10^{17}$ photons cm$^{-2}$ s$^{-1}$ following $\lambda = 254, 313, 369$ and 421 nm irradiation of a mixture containing 0.5 M CAN and 6.0 M HNO$_3$. [NO$_3$] obtained from measurements shown in Fig. 2 is plotted in (a). For details see Sect. 2.3 and Tab. S2.
Figure 7. Time series of (a) NO$_2$ and NO$_3$, (b) N$_2$O$_5$ and N$_2$O$_6$, (c) HNO$_2$ and HNO$_4$, and (d) HO$_2$ and H$_2$O$_2$ detected following irradiation of a mixture containing 0.5 M CAN and 1.0 M NaNO$_3$. N$_2$O$_5$, N$_2$O$_6$, HO$_2$ and H$_2$O$_2$ were detected as I$^-$ adducts, and HNO$_2$ and HNO$_4$ were detected as both I$^-$ and NO$_3^-$ adducts with HR-ToF-CIMS. CIMS signals detected as iodide adducts were normalized to the I$^-$ signal prior to the start of the experiment, and CIMS signals detected as nitrate adducts were normalized to the maximum NO$_3^-$ obtained during the experiment (see Fig. S5).
Figure 8. HR-ToF-CIMS spectra of gas-phase $\beta$-pinene/NO$_3$ oxidation products obtained following $\beta$-pinene reaction with NO$_3$ generated via (a) irradiation of a mixture of 0.5 M CAN and 3.0 M HNO$_3$ and subsequent injection into the OFR (b) thermal decomposition of N$_2$O$_5$ injected into the Georgia Tech environmental chamber. Signals shown are unmodified (M+I)$^-$ formulas.
Figure 9. FIGAERO-HR-ToF-CIMS spectra of condensed-phase β-pinene/NO₃ oxidation products obtained following β-pinene reaction with NO₃ generated via (a) irradiation of a mixture of 0.5 M CAN and 3.0 M HNO₃ and subsequent injection into an OFR (b) thermal decomposition of N₂O₅ injected into the Georgia Tech environmental chamber. Signals shown are unmodified (M+I)⁻ formulas. Bands of ion signals corresponding to C₁₀H₁₅NOₓ, C₂₀H₃₂N₂Oₓ, and C₃₀H₄₇N₃Oₓ oxidation products are highlighted and colored by the number of oxygen atoms in their chemical formulas.
Figure 10. Fractional oxidative loss of alkyl and acyl organic peroxy radicals (RO$_2$) due to reaction with HO$_2$, NO$_3$ and NO$_2$ ($F_{RO_2+HO_2}$, $F_{RO_2+NO_3}$ and $F_{RO_2+NO_2}$) generated following $\lambda =$ (a), (e) 254 (b), (f) 313 (c), (g) 369 (d), (h) 421 nm irradiation of a mixture containing 0.5 M CAN and 6.0 M HNO$_3$ as a function of photon flux ranging from $1 \times 10^{14}$ to $1 \times 10^{17}$ photons cm$^{-2}$ s$^{-1}$. 