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

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Received: 7 July 2023 – Discussion started: 21 July 2023
Revised: 21 September 2023 – Accepted: 21 September 2023 – Published: 7 November 2023

Abstract. We present a novel photolytic source of gas-phase NO$_3$ suitable for use in atmospheric chemistry studies that has several advantages over traditional sources that utilize NO$_2$ + O$_3$ reactions and/or thermal dissociation of dinitrogen pentoxide (N$_2$O$_5$). The method generates NO$_3$ via irradiation of aerated aqueous solutions of ceric ammonium nitrate (CAN, (NH$_4$)$_2$Ce(NO$_3$)$_6$) and nitric acid (HNO$_3$) or sodium nitrate (NaNO$_3$). We present experimental and model characterization of the NO$_3$ formation potential of irradiated CAN / HNO$_3$ and CAN / NaNO$_3$ mixtures containing [CAN] = 10$^{-5}$ to 1.0 M, [HNO$_3$] = 1.0 to 6.0 M, [NaNO$_3$] = 1.0 to 4.8 M, photon fluxes ($I$) ranging from 6.9 × 10$^{14}$ to 1.0 × 10$^{16}$ photons cm$^{-2}$ s$^{-1}$, and irradiation wavelengths ranging from 254 to 421 nm. NO$_3$ 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$_3$] was achieved using [HNO$_3$] $\approx$ 3.0 to 6.0 M and UVA radiation ($\lambda_{\text{max}}$ = 369 nm) in CAN / HNO$_3$ mixtures or [NaNO$_3$] $\geq$ 1.0 M and UVC radiation ($\lambda_{\text{max}}$ = 254 nm) in CAN / NaNO$_3$ mixtures. Other reactive nitrogen (NO$_2$, N$_2$O$_4$, N$_2$O$_5$, N$_2$O$_6$, HNO$_2$, HNO$_3$, HNO$_4$) and reactive oxygen (HO$_2$, H$_2$O$_2$) species obtained from the irradiation of ceric nitrate mixtures were measured using a NO$_2$ 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$_3$-initiated oxidative aging processes, we generated and measured the chemical composition of oxygenated volatile organic compounds (OVOCs) and secondary organic aerosol (SOA) from the $\beta$-pinene + NO$_3$ reaction using a Filter Inlet for Gases and AEROsols (FIGAERO) coupled to the HR-ToF-CIMS.

1 Introduction

The importance of NO$_3$ 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$_3$ is generated via the reaction NO$_2$ + O$_3$ $\rightarrow$ NO$_3$ + O$_2$, 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...
NO₂ + O₃ reactions and/or N₂O₅ thermal decomposition to produce NO₃ as it occurs in the atmosphere and accommodated the inherent limitations associated with N₂O₅, namely, that it must be stored under cold and dry conditions until use. Few viable alternative methods for the generation of gas-phase NO₃ have been identified. Reactions between fluoro compounds (Burrows et al., 1985; Bedianian, 2019). F and Cl can also compete with NO₃ for the oxidation of target analytes, as can O₃ if its reaction with NO₂ is used as the NO₃ 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 Geyer, 1957), Thomas Martin and coworkers discovered that irradiating solutions containing ceric ammonium nitrate (CAN), (NH₄)₂Ce(NO₃)₆ generates aqueous NO₃ (Henshall, 1963; Martin et al., 1963, 1964; Glass and Martin, 1970; Martin and Glass, 1970; Martin and Stevens, 1978). In ≥ 6 M nitric acid (HNO₃), CAN is thought to dissociate primarily into NH₄⁺ cations and hexanitratocerate (Ce(NO₃)₆²⁻) anions (Henshall, 1963). The Ce(NO₃)₆²⁻ is subsequently reduced to Ce(NO₃)₃²⁻ upon irradiation by ultraviolet light, and NO₃ 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 (CH₃COOH), CAN dissociates into primarily Ce(NO₃)₄ (Henshall, 1963). Additionally, ceric ions containing complexed hydroxyl (OH) or H₂O, CH₃COOH, or acetonitrile (CH₃CN) molecules are formed in aqueous, acetic acid, or CH₃CN media, respectively (Henshall, 1963; Glebov et al., 2021). Higher solution acidity and/or CAN concentration appears to promote the formation of Ce(NO₃)₄²⁻ (Wylie, 1951) and ceric nitrate dimers (Blaustein and Geyer, 1957; Demars et al., 2015). The following generalized mechanism was proposed by Glass and Martin (1970) to describe ceric nitrate photochemistry:

\[
\begin{align*}
\text{Ce}^{(IV)} + h\nu & \rightarrow \text{Ce}^{(III)} + \text{NO}_3, \\
\text{Ce}^{(III)} + \text{NO}_3 & \rightarrow \text{Ce}^{(IV)}, \\
\text{NO}_3 + \text{NO}_3 & \rightarrow \text{N}_2\text{O}_6, \\
\text{N}_2\text{O}_6 + 2\text{Ce}^{(IV)} & \rightarrow 2\text{NO}_2 + \text{O}_2 + 2\text{Ce}^{(III)}, \\
\text{NO}_3 + \text{NO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3,
\end{align*}
\]

where Ce(IV) represents ceric nitrates as diverse as Ce(NO₃)₄, Ce(NO₃)₃²⁻, (NO₃)₃CeOCe(NO₃)₄²⁻, and (H₂O)₃(NO₃)₃CeOCe(NO₃)₃(H₂O)₃ that are potentially formed in solution (Blaustein and Geyer, 1957; Henshall, 1963; Demars et al., 2015). Similarly, Ce(III) represents cerous nitrates such as Ce(NO₃)₃ and Ce(NO₃)₅²⁻. The rate of Reaction (R2) is [HNO₃]-dependent (Martin and Glass, 1970), and the dinitrogen hexaoxide (N₂O₆) 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, 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 NO₃-initiated oxidative aging processes in solution; e.g., Alexander (2004). Given the potential simplicity of irradiating Ce(IV) mixtures relative to synthesizing and storing N₂O₅ under cold and dry conditions or reacting NO₂ + O₃ under carefully controlled conditions, Ce(IV) irradiation could in principle enable more widespread studies of NO₃ 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 NO₃. First, we designed a photoreactor that generates gas-phase NO₃ from irradiated CAN / HNO₃ and CAN / NaNO₃ mixtures. Second, we characterized NO₃ 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 oxygenated volatile organic compounds (OVOCs) and secondary organic aerosol (SOA) from the β-pinene + NO₃ 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 o.d. × 4.8 mm i.d. fluorinated ethylene propylene (FEP) tubing into approximately 10 mL of aqueous CAN / HNO₃ or CAN / NaNO₃ mixtures placed at the bottom of a 12.7 mm o.d. × 11.1 cm i.d. 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, R2P4047) to transmit NO₃ (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 the FEP tubing and filter holder were flushed with distilled H₂O to remove residual Ce(III) precipitate. Initial studies were conducted using a cavity-attenuated phase-shift (CAPS) NO₂ monitor operating at λ = 405 nm (Kebarabian et al., 2005) and a second retrofitted CAPS monitor operating at λ = 630 nm, which established that NO₂ and NO₃ 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\textsubscript{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 Fig. S1 in the Supplement. 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\textsubscript{3} (\( \lambda = 254 \) nm) or NO\textsubscript{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\textsubscript{2} photolysis measurements were conducted in the absence of oxygen to avoid O\textsubscript{3} formation. Photon flux values were then calculated using methods described in Lambe et al. (2019); maximum values of \( I_{254} = 1.0 \times 10^{16} \) 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 conductive 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\textsubscript{3} mixing ratios, a mixture of 10 VOC tracers with NO\textsubscript{3} reaction rate coefficients (\( k_{NO_3} \)) ranging from \( 3.01 \times 10^{-19} \) to \( 2.69 \times 10^{-11} \) cm\(^3\) molec\(^{-1}\) s\(^{-1}\) at \( T = 298 \) K (Table S1) was injected through a 10.2 cm length of 0.0125 cm i.d. Teflon tubing at a liquid flow rate of 0.94 µL h\(^{-1}\) 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\textsubscript{3} reactivity (\( NO_3 Remax \)), 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\textsubscript{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\textsubscript{3}O\textsuperscript{+} reagent ion chemistry (Krechmer et al., 2018) and \( \sim 8000 \) (Th / Th) resolving power. NO\textsubscript{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\textsubscript{3} injected into the OFR. Because NO\textsubscript{3} may additionally react with organic peroxy radicals (RO\textsubscript{2}) generated from VOC + NO\textsubscript{3} reactions as well as OVOCs, these calculated NO\textsubscript{3} concentrations represent lower limits. Modeling calculations suggest that the fractional consumption of NO\textsubscript{3} by RO\textsubscript{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\textsubscript{3} reactions that had proton affinities greater than that of H\textsubscript{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\textsubscript{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\textsubscript{3}-initiated oxidative aging processes, the chemical composition of \( \beta \)-pinene + NO\textsubscript{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., 2014). Gas sampling and simultaneous particle collection were 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 cool down 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, H2O, 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 aside from unit conversion. Gas-phase wall loss rates of NO3, NO2, and OH species were not explicitly considered in the mechanism. 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 absorbivity 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 Sect. 2.2. The σext values of the mixture 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 nearly insoluble 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 (C9H14O2), isoprene (C5H8), dimethyl sulhide (C2H6S), 2,5-dimethylthiophene (C6H7S), 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 λ600 = 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 C4H4S, 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 kNO3. 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 h was delayed because of their higher kNO3 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, Fig. S3 shows the relative NO3 rate coefficients obtained from the decay of C4H4S, C5H8, and C6H14O2 measured with the Vocus PTR. We measured relative rate coefficients of 3.59 between C5H8O and C10H16 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), C3H7NO4+6 and C10H13NO5+6 organic nitrates, and nitroguaicic acid (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 C8H16O7NO4+6 and C8H13NO5−6 ions that may be associated with NO3 oxidation products of C5H8O and C6H14O2, respectively, were anticorrelated with those of their respective VOC precursors (Fig. S4). Tracer decay experiments, similar to
Different Ce salts may have influenced these trends, as suggested by their UV-vis spectra (Fig. 3b). The $\sigma_{\text{ext}}$ curves of CAN/HNO$_3$ mixtures were generally larger, broader, and redshifted relative to those of CAN/NaNO$_3$ mixtures, with the extent of red shifting increasing with larger [HNO$_3$], possibly due to higher yields of Ce(NO$_3$)$_2^{2-}$ and/or ceric nitrate dimers (Blaustein and Gryder, 1957; Henshall, 1963; Demars et al., 2015). For $\lambda > 250\,\text{nm}$, CAN/HNO$_3$ mixtures had $\sigma_{\text{ext, max}}$ values between $\lambda = 306$–311 nm, whereas CAN/NaNO$_3$ solutions had $\sigma_{\text{ext, max}}$ values at $\lambda = 296\,\text{nm}$. However, if [NO$_3$] was simply proportional to $\sigma_{\text{ext}}$, irradiation of CAN/HNO$_3$ mixtures at $\lambda = 313\,\text{nm}$ should have produced the highest [NO$_3$]; this was not the case. Instead, model calculations suggest that higher [NO$_3$] obtained from significantly faster photolysis of HNO$_3$ at $\lambda = 254$ and 313 nm relative to $\lambda > 350\,\text{nm}$ suppressed NO$_3$ 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 [NO$_3$] values were within ±13% of each other for irradiation wavelengths ranging from $\lambda = 254$ to 369 nm. However, higher [NO$_3$] values obtained following Ce(IV) irradiation at $\lambda = 254$ and 313 nm suppressed NO$_3$ by >96% relative to the $\lambda = 369\,\text{nm}$ case during 120 s of simulated NO$_2$ + NO$_3$ reactions in the OFR. Thus, although the measured NO$_3$ suppression at these other irradiation wavelengths was less substantial than the model output, the measurement and model trends, along with achievement of maximum [NO$_3$] following $\lambda = 254\,\text{nm}$ irradiation of CAN/NaNO$_3$ mixtures that had lower [HNO$_3$], qualitatively support this explanation for the wavelength-dependent NO$_3$ yields observed in CAN/HNO$_3$ mixtures.

3.3 Effect of mixture composition

To characterize the influence of individual reagents on NO$_3$ formation, tracer decay experiments similar to the measurements shown in Fig. 2 were repeated as a function of [CAN], [HNO$_3$], and [NaNO$_3$]. Figure 4a shows [NO$_3$] obtained from 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$^{-1}$). Results were normalized to [NO$_3$] achieved with solutions containing 0.5 M CAN and 6.0 M HNO$_3$. Control experiments conducted with irradiated 6.0 M HNO$_3$ or 1.0 M NaNO$_3$ solutions at $I_{254} = 1 \times 10^{16}$ photons cm$^{-2}$ s$^{-1}$ in the absence of CAN suggest that a fraction of the NO$_3$ obtained in CAN mixtures was generated via the reactions HNO$_3 + h\nu \rightarrow$ OH + NO$_2$ and HNO$_3 + \text{OH} \rightarrow$ NO$_3$ + H$_2$O. The remaining NO$_3$ was clearly obtained from CAN irradiation because [NO$_3$] increased with increasing [CAN], as expected from Reaction (R1). Overall, [NO$_3$] increased by approximately a factor of 3 as [CAN] was increased from 0.001 to 0.5 M in 6.0 M HNO$_3$.

Figure 4b shows [NO$_3$] obtained in irradiated solutions containing 0.5 M CAN as a function of [HNO$_3$] 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 and 6.0 M HNO₃ generated the same [NO₃] concentrations within measurement uncertainties, presumably because the NO₃ quantum yield (\( \phi_{NO_3} \)) 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 to 1.0 M, consistent with a reduction in \( \phi_{NO_3} \) from 0.92 to 0.46 (Martin and Stevens, 1978). On the other hand, in irradiated CAN / NaNO₃ mixtures with uncharacterized \( \phi_{NO_3} \), [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 \( S_2O_5^{2-} + h\nu \rightarrow 2SO_4^{2-} \) followed by \( SO_4^{2-} + NO_3^- \rightarrow NO_3^- + SO_2^{2-} \) (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 \( \phi_{NO_3} \) 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 therefore 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 \( \lambda = 254 \text{ nm} \) 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 (1) 0.5 M CAN and 6.0 M HNO₃ (\( \lambda = 369 \text{ nm} \)) and (2) 0.5 M CAN and 1.0 M NaNO₃.
as a function of photon flux ranging from 1.0 × 10⁻¹⁵ to 4.0 × 10⁻¹⁰ photons cm⁻² s⁻¹. Symbols are colored by the time it took for [NO₃] to experience one e-folding decay relative to the maximum [NO₃] that was measured (τNO₃). Error bars represent estimated ±35% uncertainty in [NO₃] values obtained from CAN/HNO₃ mixtures, ±15% uncertainty in [NO₃] values obtained from CAN/NaNO₃ mixtures, and ±30% uncertainty in photon flux values.

(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 (τNO₃), defined here as the time it took for [NO₃] to experience one e-folding 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 τNO₃ due to faster reduction of Ce⁶⁺ to Ce³⁺. 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. τNO₃ decreased from 9 to 5 h. 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 τNO₃ decreased from 10 to 3 h.

To examine concentrations of NO₃ and a subset of additional gas-phase photolysis products obtained over a wider range of conditions, Fig. 6 plots model-calculated [NO₃], NO₂ : NO₃, HO₂ : NO₃, and N₂O₅ : NO₃ values as a function of photon flux ranging from 1.0 × 10¹⁴ to 1.0 × 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) as well as 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 4.0 × 10¹⁰ 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 Fig. 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 (I₂₅₄ ≈ 10¹⁰ photons cm⁻² s⁻¹), shown here because the signal-to-noise ratio 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 [NO₃] 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 NO₂ : NO₃ ≈ 0.45 (Fig. 4). Multiple reactions may generate NO₂, including Reaction (R3), HNO₃ photolysis, and/or NO₃ photolysis as well as other reactions listed in Table S2. While NO₂ and/or HO₂ photolysis generated NO, its concentration was negligible in these experiments.
Atmos. Chem. Phys., 23, 13869–13882, 2023 https://doi.org/10.5194/acp-23-13869-2023

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 Table 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 7b shows time series of IN$_2$O$_5^-$ and IN$_2$O$_6^-$ signals measured with the CIMS. IN$_2$O$_5^-$ was formed from NO$_2$ + NO$_3$ → N$_2$O$_5$ reactions in the photoreactor and N$_2$O$_5$ + I$^-$ → IN$_2$O$_5^-$ reactions in the CIMS ion molecule reactor (IMR). As expected, IN$_2$O$_5^-$ followed a similar profile as NO$_2$ and NO$_3$. IN$_2$O$_6^-$ was either generated from NO$_3$ + NO$_3$ → N$_2$O$_6$ reactions in the photoreactor (Glass and Martin, 1970) followed by N$_2$O$_6$ + I$^-$ → IN$_2$O$_6^-$ reactions in the IMR or from the following series of reactions in the IMR: HNO$_3$ + IO$^-$ → NO$_3^-$ + HOI, HOI + NO$_3^-$ → INO$_3$ + OH$^-$, and INO$_3$ + NO$_3^-$ → IN$_2$O$_6^-$ (Ganske et al., 2019). To further explore the plausibility of N$_2$O$_6$ formation in this system, we conducted a theoretical investigation of the gas-phase NO$_3$ + NO$_3$ → N$_2$O$_5$ reaction and found that this reaction is exothermic, even more so than NO$_3$ + NO$_3$ → N$_2$O$_5$. Additional details regarding this analysis are provided in Sect. S1.

Figure 7c shows time series of IHNO$_2^-$, HNO$_2$NO$_3^-$, IHNO$_4^-$, and HNO$_4$NO$_3^-$ . These ions are associated with nitrous acid (HNO$_2$) and peroxynitric acid (HNO$_4$), respectively (Veres et al., 2015). Because rapid formation of HNO$_2$−4NO$_3^-$ ions was observed following Ce$^{(IV)}$ irradiation, and because IO$_x^-$ signals were relatively low (Sect. S2.1), we hypothesize that I$^+$ + NO$_3$ and/or I$^-$ + HNO$_3$ reactions were the main source of NO$_3^-$ (Lee et al., 2014; Dörich et al., 2021) and that subsequent competitive NO$_3^-$ + HNO$_2$−4 and I$^-$ + HNO$_2$−4 reactions in the IMR generated both IHNO$_2$−4 and HNO$_2$−4NO$_3^-$. HNO$_4$ was generated following the reactions HNO$_4$ + h$\nu$ → OH + NO$_2$, OH + NO$_3$ → HO$_2$ + NO$_2$, and HO$_2$ + NO$_2$ → HNO$_4$. This hypothesis is supported by the similarity between NO$_2$ and IHNO$_4^-$ time series coupled with the relatively constant concentrations of HO$_2$ generated via OH + OH → H$_2$O$_2$ and OH + H$_2$O$_2$ → HO$_2$ + H$_2$O reactions. H$_2$O$_2$, detected as IH$_2$O$_2^-$, also behaved similarly as HO$_2^-$(Fig. 7d).

HNO$_2^-$ had a different temporal profile than the other nitrogen oxides: IHNO$_2^-$ increased throughout the experiment, and HNO$_2$NO$_3^-$ increased and then decreased. We hypothesize that NO$_2$ + NO$_2$ → N$_2$O$_4$ and
N$_2$O$_4$ + H$_2$O → HNO$_2$ + HNO$_3$ reactions were the main source of HNO$_2$ (Sect. S2.2).

Figure S13 shows time series of the same ions plotted in Fig. 7 following irradiation of a solution containing 0.5 M CAN and 3.0 M HNO$_3$ (I$_{369}$ = 7 x 10$^{15}$ photons cm$^{-2}$ s$^{-1}$). Here, 3.0 M HNO$_3$ was used because 6.0 M HNO$_3$ depleted the CIMS reagent ion too much (IHNNO$_5^-$ : I$^-$$\approx$ 15) to achieve signal-to-noise ratio that was sufficient for comparison to CAN / NaNO$_3$ mixtures (IHNNO$_5^-$ : I$^-$$\approx$ 3). The same gas-phase nitrogen oxides and reactive oxygen species were observed in this reaction system as with the irradiated CAN / NaNO$_3$ mixture. The relative yields of each compound plotted in Figs. 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 / HNO$_3$ mixtures decreased at a slower rate than the same compounds obtained from irradiated CAN / NaNO$_3$ mixtures. These trends may be due to different Ce(IV) composition (Fig. 3 and Sect. 3.2) and/or an enhanced rate of Ce(III) + NO$_3$ → Ce(IV) reactions in HNO$_3$ relative to NaNO$_3$ (Reaction R2).

3.6 OVOC–SOA generation from β-pinene + NO$_3$

To demonstrate proof of principle for NO$_3$-initiated oxidative aging studies, we generated NO$_3$ via irradiation of a mixture of 0.5 M CAN and 3.0 M HNO$_3$ (I$_{369}$ = 7 x 10$^{15}$ 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 + NO$_3$ oxidation products (Sect. 2.2). Figure 8a shows a spectrum of gas-phase β-pinene / NO$_3$ oxidation products detected between m/Q = 320 and 420, where the majority of the signal was observed; signals shown are unmodified (M + I$^-$$\approx$ 3) formulas. The largest ion detected was at m/Q = 356 (IC$_{10}$H$_{32}$NO$_{15}$), which represents a major first-generation dicarboxyl nitrate oxidation product with a relative abundance of 0.31 and a calculated saturation vapor pressure of 2 x 10$^{-7}$ atm (C$^*$ = 1900 µg m$^{-3}$; Claflin, 2018). Other ions corresponding to first-generation hydroxycarboxyl nitrate (IC$_{10}$H$_{17}$NO$_5^-$, C$^*$ = 95 µg m$^{-3}$), tricarboxyl nitrate (IC$_{10}$H$_{15}$NO$_6^-$, C$^*$ = 35 µg m$^{-3}$), hydroxycarboxyl nitrate (IC$_{10}$H$_{17}$NO$_5^-$, C$^*$ = 4.7 µg m$^{-3}$), and hydroxycarboxyl nitrate acid (IC$_{10}$H$_{17}$NO$_7^-$, C$^*$ = 0.29 µg m$^{-3}$) products were detected in addition to IC$_9$H$_{13}$NO$_5^-$ and a suite of additional previously characterized C$_8$ and C$_9$ organic nitrates (Nah et al., 2016; Takeuchi and Ng, 2019; Shen et al., 2021). The IC$_{10}$H$_{18}$N$_2$O$_5^-$ hydroxy dinitrate, which was also previously observed in FIGAERO-CIMS spectra of α-pinene / NO$_3$ SOA (Nah et al., 2016), was generated via an unknown reaction pathway. Overall, the high molar yield and vapor pressure of C$_{10}$H$_{15}$NO$_5$ (Claflin, 2018) are consistent with it having the highest relative abundance in the gas phase (Fig. 8a), whereas the other C$_{10}$ β-pinene oxidation products were semivolatile under our experimental conditions.

Figure 8. HR-ToF-CIMS spectra of gas-phase β-pinene / NO$_3$ oxidation products obtained following β-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$^-$$\approx$ 3) formulas.

Figure 9a shows a spectrum of condensed-phase β-pinene / NO$_3$ 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$^-$$\approx$ 3) formulas. To aid interpretation of the major features of the spectrum, bands of ion signals corresponding to IC$_{10}$H$_{15}$NO$_5^-$, IC$_{20}$H$_{32}$N$_2$O$_{10}$, and IC$_{20}$H$_{17}$N$_2$O$_{12}$ 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 (IC$_{10}$H$_{15}$NO$_5^-$), which is the condensed-phase component of the same tricarboxyl nitrate detected in the gas phase (Fig. 8a). IC$_{10}$H$_{15}$NO$_5^-$ and IC$_{10}$H$_{15}$NO$_7^-$ signals were also detected. The second-largest ion signal was measured at m/Q = 571 (IC$_{20}$H$_{32}$N$_2$O$_{12}$), an acetal dimer obtained from the condensed-phase reaction of two C$_{10}$H$_{17}$NO$_5$ monomers followed by H$_2$O elimination (Claflin and Ziemann, 2018). Similar accretion reactions between other C$_{10}$ organic nitrates yielded IC$_{20}$H$_{32}$N$_2$O$_{10}$ and IC$_{20}$H$_{32}$N$_2$O$_{10}$ signals. Likewise, reactions between C$_{10}$ monomers and C$_{20}$ dimers generated C$_{30}$ trimers detected between m/Q = 768–864 (IC$_{30}$H$_{47}$N$_3$O$_{12}$). The largest trimmer-related ion, IC$_{30}$H$_{47}$N$_3$O$_{12}$, was generated from C$_{10}$H$_{17}$NO$_4$ + C$_{20}$H$_{32}$NO$_8$ – H$_2$O or C$_{10}$H$_{17}$NO$_5$ + C$_{20}$H$_{32}$NO$_8$ – H$_2$O reactions (Claflin and Ziemann, 2018). A fourth cluster of ion signals at
Cluster of relation coefficients of 0.87 and 0.96 between the re-
mittance gas- and condensed-phase spectra. Clusters of
habit an overall high degree of similarity, with linear cor-
vironmental chamber (Takeuchi and Ng, 2019). The spec-
from NO
3
FIGAERO–HR-ToF-CIMS spectra of condensed-phase
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 and (b) thermal decomposition of N2O5 injected into the
Georgia Tech environmental chamber. Signals shown are unmod-
fied (M + I)− formulas. Bands of ion signals corresponding to
C10H15NO5, C20H32N2O3, and C30H47N3O3 oxidation products are
highlighted and colored by the number of oxygen atoms in their
chemical formulas.

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 > 30 β-pinene / NO3 oxidation
products. However, it seems plausible that these signals are
associated with tetramers.

To compare our results with those obtained using a con-
ventional NO3 generation method (room-temperature N2O5
thermal decomposition) in an environmental chamber study,
Figs. 8b and 9b show reference gas- and condensed-phase
FIGAERO–I−-CIMS spectra of OVOCs and SOA generated
from NO3 oxidation of β-pinene in the Georgia Tech envi-
ronmental chamber (Takeuchi and Ng, 2019). The spectra
obtained here and by Takeuchi and Ng (2019) ex-
hibit an overall high degree of similarity, with linear cor-
relation coefficients of 0.87 and 0.96 between the re-
spective gas- and condensed-phase spectra. Clusters of
IC10H15NO5, IC20H32N2O3, and IC30H47N3O3− ion signals are present in both Fig. 9a and b. The main differ-
ces between the gas-phase spectra shown in Figs. 8a and
9a were the different abundances of IC10H17NO4−, a first-
generation hydroxynitrate product (Claflin and Ziemann,
2018), and IC10H16N2O7−. Because C10H17NO4 is formed
from RO2 + RO2 reactions (DeVault et al., 2022) and is suf-
ciently volatile (C* = 750 µg m−3) to partition into the gas
phase (Claflin, 2018), differences in gas-phase C10H17NO4
and C10H16N2O7 yields were likely related to differences in
the relative importance of RO2 + RO2 versus RO2 + NO3
reaction pathways in the study by Takeuchi and Ng (2019)
compared to this work.

To further investigate the fate of RO2 generated from
VOC + NO3 reactions as a function of CAN irradiation con-
ditions, we calculated the fractional oxidative loss of generic
alkyl and acyl RO2 species due to reactions with HO2, NO3,
and NO2 (FRO2+HO2, FRO2+NO3, FRO2+NO2) using Eqs. (1)–
(3):

\[
F_{\text{RO}_2 + \text{HO}_2} = \frac{k_{\text{RO}_2 + \text{HO}_2}[\text{HO}_2]}{k_{\text{RO}_2 + \text{HO}_2}[\text{HO}_2] + k_{\text{RO}_2 + \text{NO}_3}[\text{NO}_3] + k_{\text{RO}_2 + \text{NO}_2}[\text{NO}_2]},
\]

(1)

\[
F_{\text{RO}_2 + \text{NO}_3} = \frac{k_{\text{RO}_2 + \text{NO}_3}[\text{NO}_3]}{k_{\text{RO}_2 + \text{HO}_2}[\text{HO}_2] + k_{\text{RO}_2 + \text{NO}_3}[\text{NO}_3] + k_{\text{RO}_2 + \text{NO}_2}[\text{NO}_2]},
\]

(2)

\[
F_{\text{RO}_2 + \text{NO}_2} = \frac{k_{\text{RO}_2 + \text{NO}_2}[\text{NO}_2]}{k_{\text{RO}_2 + \text{HO}_2}[\text{HO}_2] + k_{\text{RO}_2 + \text{NO}_3}[\text{NO}_3] + k_{\text{RO}_2 + \text{NO}_2}[\text{NO}_2]}
\]

(3)

Here, \(k_{\text{RO}_2 + \text{HO}_2}, k_{\text{RO}_2 + \text{NO}_3}, \) and \(k_{\text{RO}_2 + \text{NO}_2}\) are reaction rate coefficients for the corresponding RO2 + HO2, RO2 + NO3, and RO2 + NO2 forward reactions whose values are sum-
marized in Table S3. Several simplifying assumptions were
made. First, we assumed that RO2 + NO reactions were neg-
ligible. Second, we did not consider RO2 isomerization–
autoxidation and RO2 + RO2 reactions that are influenced
by external factors. Third, we set \(F_{\text{RO}_2 + \text{NO}_3} = 0\) for alkyl-
RO2-generated RO2NO3, which thermally decomposes on
timescales of seconds or less (Orlando and Tyndall, 2012).
Fourth, we assumed that vapor wall losses of acyl-RO2-
generated RO2NO2 were a minor RO2 sink because the
OFR residence time (\(t_{\text{OFR}} \approx 120 \text{ s} \)), Sect. 2.2) was signif-
icantly shorter than their estimated wall loss timescale
\((t_{\text{wall}} \approx 400 \text{ s}; \) Palm et al., 2016). Figure 10 shows calcu-
lated \(F_{\text{RO}_2 + \text{HO}_2}, F_{\text{RO}_2 + \text{NO}_3}, \) and \(F_{\text{RO}_2 + \text{NO}_2}\) values for
alkyl-RO2 and acyl-RO2 as a function of photon flux over the
range of NO3 generation conditions presented in Fig. 6. For alkyl-RO2, \(F_{\text{RO}_2 + \text{HO}_2}\) decreased and \(F_{\text{RO}_2 + \text{NO}_3}\) increased with increasing photon flux and decreasing
irradiation wavelength. On the other hand, for acyl-RO2,
\(F_{\text{RO}_2 + \text{NO}_2}\) 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 NO3 generation conditions (e.g., \(\lambda = 369 \text{ nm}\)
and \(I_{\text{369}} \approx 10^{16} \text{ photons cm}^{-2} \text{ s}^{-1}\)), our calculations sug-
that \(F_{\text{RO}_2 + \text{HO}_2} \approx F_{\text{RO}_2 + \text{NO}_3}\) for alkyl-RO2 (Fig. 10c)
and that \(F_{\text{RO}_2 + \text{HO}_2} \approx F_{\text{RO}_2 + \text{NO}_3} \approx F_{\text{RO}_2 + \text{NO}_2}\) for acyl-RO2 (Fig. 10g).
Because Ce(IV) irradiation already generates NO3 in aqueous solution, its performance is not hindered by humidity to the extent (if at all) as N2O3-based methods, where hydrolysis of N2O3 to HNO3 decreases the efficacy of the source. Additionally, the NO3 + H2O reaction rate in solution or on surfaces is slow in relation to other NO3 loss pathways (Jiang et al., 1992). Another advantage of Ce(IV) irradiation is that it does not involve the use of O3 as a reagent; therefore it eliminates the possibility of competing O3 and NO3 oxidation of compounds that are reactive towards both oxidants if NO2 + O3 reactions and/or online N2O3 synthesis are used as the NO3 source (Lambe et al., 2020). To identify optimal operating conditions for maximizing [NO3], we characterized concentrations of NO3 at [CAN] = 10−3 to 1 M, [HNO3] = 1.0 to 6.0 M, [NaNO3] = 1.0 to 4.8 M, a photon flux of 6.9 × 1014 to 1.0 × 1016 photons cm−2 s−1, and irradiation wavelengths of λ = 254, 313, 369, or 421 nm. With CAN/HNO3 mixtures, maximum [NO3] was achieved with [CAN] ≈ 0.5 M, [HNO3] ≈ 3.0 to 6.0 M, and I254 = 8 × 1015 photons cm−2 s−1 (4.3 mW cm−2). With CAN/NaNO3 mixtures, maximum [NO3] was achieved with [CAN] ≈ 1.0 M, [NaNO3] ≥ 1.0 M, and I254 ≈ 1 × 1016 photons cm−2 s−1 (7.8 mW cm−2). Thus, for applications such as environmental chambers or OFR studies of NO3-initiated oxidative aging processes, where significant NO3 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 NO3 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 NO3 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 NO3 generation techniques – especially in field studies – and it may therefore enable more widespread studies of NO3 oxidation chemistry. Adapting a photoreactor to operate with continuous injection of fresh Ce(IV) and photon flux. Overall, because Ce(IV) irradiation generates NO3 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 NO3 generation techniques – especially in field studies – and it may therefore enable more widespread studies of NO3 oxidation chemistry. Adapting a photoreactor to operate with continuous injection of fresh Ce(IV) and alternative photolytic NO3 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.

4 Conclusions

Ce(IV) irradiation complements NO2 + O3 reactions and N2O3 thermal dissociation as a customizable photolytic NO3 source. Important method parameters were [CAN], [HNO3], or [NaNO3]; UV intensity; and irradiation wavelength. By contrast, important parameters for NO2 + O3 and N2O3 based methods are [O3], [NO2], temperature, and humidity. Because Ce(IV) irradiation already generates NO3 in aqueous solution, its performance is not hindered by humidity to the same extent (if at all) as N2O3-based methods, where hydrolysis of N2O3 to HNO3 decreases the efficacy of the source. Additionally, the NO3 + H2O reaction rate in solution or on surfaces is slow in relation to other NO3 loss pathways (Jiang et al., 1992). Another advantage of Ce(IV) irradiation is that it does not involve the use of O3 as a reagent; therefore it eliminates the possibility of competing O3 and NO3 oxidation of compounds that are reactive towards both oxidants if NO2 + O3 reactions and/or online N2O3 synthesis are used as the NO3 source (Lambe et al., 2020). To identify optimal operating conditions for maximizing [NO3], we characterized concentrations of NO3 at [CAN] = 10−3 to 1 M, [HNO3] = 1.0 to 6.0 M, [NaNO3] = 1.0 to 4.8 M, a photon flux of 6.9 × 1014 to 1.0 × 1016 photons cm−2 s−1, and irradiation wavelengths of λ = 254, 313, 369, or 421 nm. With CAN/HNO3 mixtures, maximum [NO3] was achieved with [CAN] ≈ 0.5 M, [HNO3] ≈ 3.0 to 6.0 M, and I254 = 8 × 1015 photons cm−2 s−1 (4.3 mW cm−2). With CAN/NaNO3 mixtures, maximum [NO3] was achieved with [CAN] ≈ 1.0 M, [NaNO3] ≥ 1.0 M, and I254 ≈ 1 × 1016 photons cm−2 s−1 (7.8 mW cm−2). Thus, for applications such as environmental chambers or OFR studies of NO3-initiated oxidative aging processes, where significant NO3 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 NO3 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 NO3 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 NO3 generation techniques – especially in field studies – and it may therefore enable more widespread studies of NO3 oxidation chemistry. Adapting a photoreactor to operate with continuous injection of fresh Ce(IV) and alternative photolytic NO3 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.

Figure 10. Fractional oxidative loss of alkyl and acyl organic peroxy radicals (RO3) due to reaction with H2O2, NO3, and NO2 (FR2O2+HO2, FR2O2+NO2, and FR2O3+NO2) generated following (a, e) λ = 254, (b, f) λ = 313, (c, g) λ = 369, and (d, h) λ = 421 nm irradiation of a mixture containing 0.5 M CAN and 6.0 M HNO3 as a function of photon flux ranging from 1 × 1014 to 1 × 1017 photons cm−2 s−1.

4 Conclusions

Ce(IV) irradiation complements NO2 + O3 reactions and N2O3 thermal dissociation as a customizable photolytic NO3 source. Important method parameters were [CAN], [HNO3], or [NaNO3]; UV intensity; and irradiation wavelength. By contrast, important parameters for NO2 + O3 and N2O3 based methods are [O3], [NO2], temperature, and humidity. Because Ce(IV) irradiation already generates NO3 in aqueous solution, its performance is not hindered by humidity to the same extent (if at all) as N2O3-based methods, where hydrolysis of N2O3 to HNO3 decreases the efficacy of the source. Additionally, the NO3 + H2O reaction rate in solution or on surfaces is slow in relation to other NO3 loss pathways (Jiang et al., 1992). Another advantage of Ce(IV) irradiation is that it does not involve the use of O3 as a reagent; therefore it eliminates the possibility of competing O3 and NO3 oxidation of compounds that are reactive towards both oxidants if NO2 + O3 reactions and/or online N2O3 synthesis are used as the NO3 source (Lambe et al., 2020). To identify optimal operating conditions for maximizing [NO3], we characterized concentrations of NO3 at [CAN] = 10−3 to 1 M, [HNO3] = 1.0 to 6.0 M, [NaNO3] = 1.0 to 4.8 M, a photon flux of 6.9 × 1014 to 1.0 × 1016 photons cm−2 s−1, and irradiation wavelengths of λ = 254, 313, 369, or 421 nm. With CAN/HNO3 mixtures, maximum [NO3] was achieved with [CAN] ≈ 0.5 M, [HNO3] ≈ 3.0 to 6.0 M, and I254 = 8 × 1015 photons cm−2 s−1 (4.3 mW cm−2). With CAN/NaNO3 mixtures, maximum [NO3] was achieved with [CAN] ≈ 1.0 M, [NaNO3] ≥ 1.0 M, and I254 ≈ 1 × 1016 photons cm−2 s−1 (7.8 mW cm−2). Thus, for applications such as environmental chambers or OFR studies of NO3-initiated oxidative aging processes, where significant NO3 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 NO3 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 NO3 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 NO3 generation techniques – especially in field studies – and it may therefore enable more widespread studies of NO3 oxidation chemistry. Adapting a photoreactor to operate with continuous injection of fresh Ce(IV) and alternative photolytic NO3 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 presented in this paper are available upon request. The KinSim mechanism used in this paper is included with the Supplement. The KinSim kinetic solver is freely available at https://gitlab.com/JimenezGroup/KinSim_Code (Peng and Jimenez, 2023).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-23-13869-2023-supplement.

Author contributions. ATL, BB, and PL conceived and planned the experiments. ATL, BB, MWA, and PL carried out the experiments. ATL conceived, planned, and carried out the KinSim model simulations. NO and PMZ conceived, planned, and carried out the quantum chemical calculations. ATL, BB, MT, NO, PMZ, MSC, DRW, and PL contributed to the interpretation of the results. ATL took the lead in writing the paper. All authors provided feedback on the paper.

Competing interests. At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics. The peer-review process was guided by an independent editor, and the authors also have no other competing interests to declare.

https://doi.org/10.5194/acp-23-13869-2023

Atmos. Chem. Phys., 23, 13869–13882, 2023
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Acknowledgements. Andrew T. Lambe thanks Anita Avery, Jordan Krechmer, Timothy Onasch (Aerodyne), and Shreya Suri (Georgia Tech) for experimental assistance; Evgeni Glebov (Russian Academy of Sciences) for sharing published UV–Vis spectra of CAN / CH₃CN mixtures; and the following colleagues for helpful discussions: Harald Stark, Manjula Canagaratna (Aerodyne), Steve Brown (NOAA CSL), Hartmut Herrmann (TROPOS), William Brune (Pennsylvania State University), Tyson Berg (Colorado State University), Lasse Moormann (Max Planck Institute for Chemistry), Uta Wille (University of Melbourne), and Burkhard Koenig (University of Regensburg). The authors thank the anonymous referee and Sergey A. Nizkorodov for their constructive comments during the paper review process.

Financial support. This work was supported by the Atmospheric Chemistry Program of the US National Science Foundation (grant nos. AGS-2131368, AGS2148439, AGS-2131458, AGS-2131084, and AGS-2147893).

Review statement. This paper was edited by Sergey A. Nizkorodov and reviewed by Sergey A. Nizkorodov and one anonymous referee.

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