Nitrate radical generation via continuous generation of dinitrogen pentoxide in a laminar flow reactor coupled to an oxidation flow reactor

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Abstract. Oxidation flow reactors (OFRs) are an emerging tool for studying the formation and oxidative aging of organic aerosols and other applications. The majority of OFR studies to date have involved the generation of the hydroxyl radical (OH) to mimic daytime oxidative aging processes. In contrast, the use of the nitrate radical (NO₃) in modern OFRs to mimic nighttime oxidative aging processes has been limited due to the complexity of conventional techniques that are used to generate NO₃. Here, we present a new method that uses a laminar flow reactor (LFR) to continuously generate dinitrogen pentoxide (N₂O₅) in the gas phase at room temperature from the NO₂ + O₃ and NO₂ + NO₃ reactions. The N₂O₅ is then injected into a dark Potential Aerosol Mass (PAM) OFR and decomposes to generate NO₃; hereafter, this method is referred to as “OFR-iN₂O₅” (where “i” stands for “injected”). To assess the applicability of the OFR-iN₂O₅ method towards different chemical systems, we present experimental and model characterization of the integrated NO₃ exposure, NO₃ : O₃, NO₂ : NO₃, and NO₂ : O₂ as a function of LFR and OFR conditions. These parameters were used to investigate the fate of representative organic peroxy radicals (RO₂) and aromatic alkyl radicals generated from volatile organic compound (VOC) + NO₃ reactions, and VOCs that are reactive towards both O₃ and NO₃. Finally, we demonstrate the OFR-iN₂O₅ method by generating and characterizing secondary organic aerosol from the β-pinene + NO₃ reaction.

1 Introduction

The importance of nitrate radicals (NO₃) as a nighttime oxidant is well established (Wayne et al., 1991; Brown and Stutz, 2012; Ng et al., 2017). In the atmosphere, NO₂ + O₃ is the primary source of NO₃, after which NO₃ exists in equilibrium with NO₂ and N₂O₅. Atmospheric nighttime NO₃ mixing ratios can vary by at least 2 orders of magnitude, ranging from 1 ppt or less in remote areas to 10–400 ppt in polluted urban regions (Finlayson-Pitts and Pitts Jr., 2000; Asaf et al., 2010; Warneck and Williams, 2012; Ng et al., 2017). Atmospheric organic compounds that are reactive towards NO₃ include isoprene and monoterpenes that are emitted from biogenic sources (including urban vegetation), phenols and methoxyphenols emitted from biomass burning, and polycyclic aromatic hydrocarbons (PAHs) emitted from combustion processes. NO₃ oxidation of these compounds...
generates oxygenated volatile organic compounds (OVOCs) and/or secondary organic aerosol (SOA), including particular organic nitrates or nitroaromatics. The importance of these sources and processes are likely to continue to increase for the foreseeable future due to climate change (Melaas et al., 2016; Short, 2017).

Laboratory studies have attempted to elucidate the mechanisms associated with NO$_3$-initiated oxidative aging processes in the gas and condensed phases and in environmental chambers and flow tubes. Traditional NO$_3$ generation techniques typically utilize N$_2$O$_5$ as the radical precursor. N$_2$O$_5$ is generated from the reaction NO + O$_3$ → NO$_2$ + O$_2$, followed by the reactions NO$_2$ + O$_3$ → NO$_3$ + O$_2$ and NO$_2$ + NO$_3$ → N$_2$O$_5$. The synthesized N$_2$O$_5$ is collected and stored in a cold trap under dry conditions to minimize hydrolysis of N$_2$O$_5$ to nitric acid (HNO$_3$). This method has limitations that hinder widespread usage: specifically, long-term storage and handling of N$_2$O$_5$ at low temperature and under dry conditions is difficult, and the continuous generation of N$_2$O$_5$ that is required for oxidation flow reactors (OFRs) or other continuous flow chambers is challenging. Thus, field studies investigating the NO$_3$-induced SOA formation potential of ambient air are extremely limited (Palm et al., 2017). Alternative NO$_3$ generation techniques that utilize reactions between chlorine atoms and chlorine nitrate (ClONO$_2$) or fluorine atoms and HNO$_3$ require cold storage of ClONO$_2$ and handling or generation of halogen species that are reactive towards organic compounds (Burrows et al., 1985).

To address issues associated with traditional NO$_3$ generation techniques, we developed and characterized a new method that is well suited to applications where a continuous source of N$_2$O$_5$ and NO$_3$ is required, such as OFR studies. The method is capable of continuous N$_2$O$_5$ generation in the gas phase at room temperature using a laminar flow reactor (LFR) that is coupled to a dark OFR. N$_2$O$_5$ injected into the OFR decomposes to generate NO$_3$ and initiate oxidation of reactive VOCs. Hereafter, we refer to this method as “OFR-iN$_2$O$_5$” (where “i” stands for “injected”). We present experimental and model characterization of OFR-iN$_2$O$_5$ as a function of LFR and OFR conditions, and we demonstrate the application of OFR-iN$_2$O$_5$ to generate and characterize SOA from the β-pinene + NO$_3$ reaction.

2 Methods

2.1 N$_2$O$_5$ and NO$_3$ generation

Figure 1 shows a process flow diagram of the OFR-iN$_2$O$_5$ method. Separate flows containing NO$_2$ and O$_3$ were input to a perfluoroalkoxy (PFA) tube with a 2.54 cm o.d. (outer diameter), a 2.22 cm i.d. (inner diameter), and a 152.4 cm length that was operated as an LFR. Previous studies used a similar process to generate N$_2$O$_5$ (Wood et al., 2003; Boyd et al., 2015), although the LFR materials, flow rates, and reagent concentrations were different. A compressed gas cylinder containing 1.00 ± 0.02 % NO$_2$ in N$_2$ (Praxair) was used to supply NO$_2$. While not used for this study, replacing NO$_2$ with NO to avoid NO$_2$-to-HNO$_3$ conversion inside the gas cylinder and increasing [O$_3$] accordingly achieves similar results. O$_3$ was generated by passing 1750–1800 cm$^3$ min$^{-1}$ of pure O$_2$ through a custom O$_3$ chamber housing a mercury fluorescent lamp (GPH212T5VH, Light Sources, Inc.) or 500–1800 cm$^3$ min$^{-1}$ O$_2$ through a corona discharge ozone generator (Enaly 1KNT). We used 1800 cm$^3$ min$^{-1}$ of O$_2$ carrier gas flow through the LFR (Re ∼ 110, i.e., laminar flow) to achieve t$_{LFR}$ = 20 s for reasons that are discussed in Sect. 3.1. The NO$_2$ mixing ratio entering the LFR, [NO$_2$]$_{0,LFR}$, was calculated from the NO$_2$ mixing ratio in the compressed gas mixture and the dilution ratio of 0–50 or 0–1300 cm$^3$ min$^{-1}$ gas flow into O$_2$ which was controlled using mass flow controllers. The O$_3$ mixing ratio entering the LFR, [O$_3$]$_{0,LFR}$, was measured using a 2B Technologies 106-MFT or a Teledyne M452 flow-through O$_3$ analyzer when generated from the mercury lamp or corona discharge source, respectively. The output of the LFR was mixed with a carrier gas containing 3.8 L min$^{-1}$ synthetic air and then injected into a Potential Aerosol Mass (PAM) OFR (Aerodyne Research, Inc.), which is a horizontal 13.3 L aluminum cylindrical chamber operated in continuous flow mode (Kang et al., 2007; Lambe et al., 2011, 2019) with 6.5 L min$^{-1}$ flow through the reactor. The mean residence time in the OFR (t$_{OFR}$) was 120 ± 34 s (±1σ), as obtained from measurements of 10 s pulsed inputs of NO$_2$ to the OFR obtained using a 2B Technologies Model 405 NO$_x$ analyzer (Fig. S1). Across all experiments, the relative humidity in the OFR (RH$_{OFR}$) was controlled in the range of 7–85 % at 23–25 °C by passing the carrier gas through a Nafion humidifier (Perma Pure LLC) or heated recirculating water bath (NESLAB Instruments, Inc.) prior to mixing with the LFR outflow. The O$_3$ mixing ratio at the exit of the OFR was measured with a 2B Technologies Model 106-M ozone analyzer.

2.1.1 OFR-iN$_2$O$_5$ characterization studies

In one set of experiments, the integrated NO$_3$ exposure (NO$_3$_exp), defined here as the product of the average NO$_3$ concentration and t$_{OFR}$, was characterized by measuring the decay of VOC tracers reactive towards NO$_3$ using...
a Tofwerk/Aerodyne Vocus proton transfer reaction time-of-flight mass spectrometer (PTR-MS; Krechmer et al., 2018). For this purpose, the tracer decay method is advantageous to direct NO₃ measurements at the OFR inlet and/or outlet, because potential NO₃ concentration gradients inside the OFR that might otherwise bias NO₃exp are accounted for. Tracers that were liquid at room temperature were injected into the OFR through a 10.2 cm length of 0.0152 cm i.d. Teflon tubing at a liquid flow rate of about 0.94 µL h⁻¹ using a syringe pump, prior to evaporation into a 2.4 L min⁻¹ N₂ carrier gas. In preliminary studies, tracers such as isoprene and β-pinene were too reactive towards NO₃ to facilitate accurate characterization of NO₃exp over the majority of the OFR-iN₂O₅ conditions that were investigated. Thus, experiments described in this paper used mixtures of tracers with bimolecular kNO₃, ranging from approximately 10⁻¹⁶ to 10⁻¹³ cm³ molecules⁻¹ s⁻¹ and kO₃, < 10⁻¹⁹ cm³ molecules⁻¹ s⁻¹ (Table S1). Acetonitrile was used as a nonreactive tracer. In “low O₂” experiments (O₃LFR = 10 to 300 ppm) a mixture of acetonitrile, butanal, triphenyl, 2,3-dihydrobenzofuran, and naphthalene-d₈ (C₁₀D₈₃), each with mixing ratios of approximately 660, 50, 56, 40, and 18 ppb, respectively, was used. For this tracer mixture, the total external NO₃ reactivity (NO₃Rext), which is the sum product of each tracer mixing ratio and its NO₃ rate constant, was approximately 0.07 s⁻¹. Naphthalene-d₈ was introduced by flowing 5 cm³ min⁻¹ N₂ through a Teflon tube packed with solid C₁₀D₈₃. In “high O₂” experiments (O₃LFR = 6100 to 7400 ppm), which generated higher NO₃exp, a mixture of acetonitrile (275 ppb), toluene (45 ppb), o-xylene (40 ppb), p-cymene (31 ppb), 1,2,4-trimethylbenzene (35 ppb), 1-butanol (53 ppb), benzaldehyde (47 ppb), butanal (53 ppb), and thiophene (56 ppb) was used, with NO₃Rext ≈ 0.38 s⁻¹.

In another set of experiments that were conducted as part of the Aerosol Chemical Monitor Calibration Center (ACMCC) particulate organonitrate (pON) experiment (Albinet et al., 2019), direct measurements of NO₃ generated via OFR-iN₂O₅ were performed using a newly developed “incoherent broad band cavity enhanced absorption spectroscopy” (IBBCEAS) technique (Cirtog et al., 2020; Fouqueau et al., 2020). The IBBCEAS instrument that was used measured absorption as a function of wavelength between λ = 640 and 680 nm, thereby allowing simultaneous measurements of NO₂ and O₃ along with NO₃. During this experiment, pON were generated in a PAM OFR that used [O₃]LFR = 150–160 ppm and [NO₂]LFR : [O₃]LFR = 0.75, 1.0, and 2.0. IBBCEAS has been used to measure trace NO₃ levels in laboratory and field studies (Venables et al., 2006; Kennedy et al., 2011) utilizing measurement principles that are described in detail by Fiedler et al. (2003) and Langridge et al. (2008). Briefly, measurements were conducted by exciting a high-finesse optical cavity formed by two high reflectivity mirrors with an incoherent broadband source centered on the λ = 662 nm absorption cross section of NO₃ (2 × 10⁻¹⁷ cm², Orphal et al., 2003). Photons resonate between the two mirrors, allowing an effective path length of up to 4.5 km inside the cavity. The absorption coefficient of the sample in the cavity, α(λ), was calculated using Eq. (1):

\[ \alpha(\lambda) = \left( \frac{L(\lambda)}{I(\lambda)} - 1 \right) \left( \frac{1 - R(\lambda)}{\lambda} \right) \]  

(1)

where α(λ) is the absorption coefficient of the OFR sample in the instrument, L(λ) and I₀(λ) were the measured transmitted intensities in the presence and absence of the sample, d = 61 cm was the distance between the cavity mirrors, and R(λ) was the mirror reflectivity (∼ 99.98 %). I₀(λ) was obtained by stopping the OFR sample through the instrument and flowing nitrogen from a cylinder (Air Liquide). A period of at least 30 s was allowed between the measurement of I₀(λ) and I(λ) to ensure the complete purge of the instrument. R(λ) was measured before each experiment using a certified calibration cylinder containing 600 ppb NO₂ in zero air (Air Liquide). Concentrations were calculated by applying a least square fit to the measured α(λ) considering the absorbing species in the sample:

\[ \alpha(\lambda) = [NO₂]σ_{NO₂} + [NO₃]σ_{NO₃} + [O₃]σ_{O₃} + p(\lambda) \]  

(2)

where NO₂, NO₃, and O₃ are the species absorbing in the spectral region of the instrument, α(λ) represents the respective absorption cross sections convoluted with the apparatus function (Vandaele et al., 1998; Voigt et al., 2001; Orphal et al., 2003), and p(λ) represents a cubic polynomial to correct baseline deformations due to small LED intensity variations. To avoid saturation of the IBBCEAS in these experiments, the OFR sample was diluted by a controlled dilution factor ranging from 9 to 41, and the detection response was deliberately lowered by reducing the optical path length. The sampling line and optical cavity were made of PFA. The residence time in the IBBCEAS sampling line and instrument ranged from 8.3 to 21.8 s. At these residence times, the calculated transmission efficiencies of NO₃ from the OFR to the IBBCEAS ranged from 0.3 % to 11 %, assuming a NO₃ wall loss rate constant of 0.27 s⁻¹ (Kennedy et al., 2011). Corrections to measured NO₃ and NO₂ values accounting for N₂O₅ thermal decomposition and sample dilution were applied to the IBBCEAS results presented in this paper.

To demonstrate the application of OFR-iN₂O₅ to generate SOA, the chemical composition and mass concentration of β-pinene + NO₃ condensed-phase oxidation products was measured with an Aerodyne long-time-of-flight aerosol mass spectrometer (L-ToF-AMS) and/or an aerosol chemical speciation monitor (ACSM). A syringe pump was used to deliver β-pinene (10 %, v/v, in carbon tetrachloride or 50 %, v/v, in ethanol) into the carrier gas flow at liquid flow rates ranging from 0.94 to 19 µL h⁻¹. Results presented in this paper assume an AMS or ACSM collection efficiency of 0.5 (Middlebrook et al., 2012) and a relative ionization efficiency of particulate organics equal to 1.6 (Xu et al., 2018).
2.2 Photochemical model

We used the KinSim chemical kinetic solver to calculate concentrations of radical and oxidant species (Peng et al., 2015; Peng and Jimenez, 2017, 2019). The KinSim mechanism shown in Table S2 was adapted from Palm et al. (2017) to model NO$_3$ and N$_2$O$_5$ concentrations in the LFR and OFR. Inputs to the LFR-KinSim model were [O$_3$]$_{LFR}$, [NO$_2$]$_{LFR}$, RH = 1 %, $T$ = 24 °C, $\tau_{LFR} = 20$ s (modeled as plug flow, see Sect. 3.1), and first-order wall loss rates of NO$_3$ and N$_2$O$_5$ ($k_{w_{LFR},NO_3}$ and $k_{w_{LFR},N_2O_5}$). Inputs to the OFR-KinSim model were [O$_3$], [NO$_2$], [NO$_3$], and [N$_2$O$_5$] output from the LFR scaled by a measured dilution factor of 4.4; RH and $T$ measured in the OFR; $\tau_{OFR} = 120$ s, $k_{w_{OFR},NO_3}$, and $k_{w_{OFR},N_2O_5}$; and input VOC tracer concentrations and their $k_{NO_3}$ values. Because the calculated N$_2$O$_5$ residence time in the OFR inlet ($\approx 0.04$ s) was short compared with the N$_2$O$_5$ decomposition timescale at $T = 23–25$ °C ($\approx 20$ s), potential thermal decomposition of N$_2$O$_5$ during the dilution step was not considered in the model.

2.2.1 LFR and OFR $k_{w,NO_3}$ and $k_{w,N_2O_5}$ values

Published $k_{w,NO_3}$ values onto tubing with a 1 cm (Teflon) and a 4 cm (Pyrex) i.d. are 0.2 and 0.1 s$^{-1}$, respectively (Dubé et al., 2006; Wood et al., 2003), which bound the 2.2 cm i.d. of the LFR used in this study. Assuming $k_w$ is inversely proportional to the internal diameter of the tube, we assumed $k_{w_{LFR},NO_3} = 0.15$ s$^{-1}$. Extrapolating this value to the LFR (20.32 cm i.d.) yielded $k_{w_{OFR},NO_3} = 0.02$ s$^{-1}$. At fixed OFR-iN$_2$O$_5$ conditions that are summarized in Table S3, varying $k_{w_{LFR},NO_3}$ between 0 and 0.3 s$^{-1}$ changed the NO$_3$exp achieved in the OFR by 0.3 %. Results were even less sensitive to the $k_{w_{OFR},NO_3}$ for the OFR because of its larger diameter and higher NO$_3$$_{ext}$.

Published $k_{w,N_2O_5}$ values onto dry (RH $\approx 20$ %) Pyrex or PFA tubing with 4 and 7 cm i.d. are 0.04 and 0.009 s$^{-1}$, respectively (Wagner et al., 2008; Gržinić et al., 2015). Extrapolating these values to the LFR used here and then averaging them together yielded $k_{w,N_2O_5} = 0.05$ s$^{-1}$, which was applied in the LFR-KinSim model. In preliminary OFR-KinSim modeling studies, we assumed $k_{w,N_2O_5} = 0.014$ s$^{-1}$ (Palm et al., 2017). However, as will be discussed in Sect. 3.3, $k_{w,N_2O_5}$ was humidity-dependent and required modifications to match measured NO$_3$exp values as a function of RH$_{OFR}$.

3 Results and discussion

3.1 LFR design considerations

The optimal LFR residence time ($\tau_{LFR}$) was identified using model simulations of the injection of 300 ppm O$_3$ and NO$_2$ into the LFR followed by dilution and injection of the LFR output into an OFR operated with $\tau_{OFR} = 120$ s. Figure S2 plots the NO$_3$exp achieved in the OFR as a function of $\tau_{LFR}$ ranging from 1 to 60 s. Potential entry length effects that may have influenced results obtained below $\tau_{LFR} \approx 4–5$ s were not considered in the model. Figure S2 shows that the maximum NO$_3$exp in the OFR was obtained at $\tau_{LFR} = 20$ s at room temperature (unheated case); other NO$_3$exp values were normalized to this condition. Below $\tau_{LFR} = 20$ s, NO$_3$exp was suppressed due to higher NO$_2$ levels entering the OFR. Above $\tau_{LFR} = 20$ s, NO$_3$exp was suppressed due to lower N$_2$O$_5$ levels entering the OFR because of more extensive LFR wall loss.

In traditional studies of NO$_3$ oxidative aging processes that are conducted at low pressure and short residence time ($\tau \sim 1$ s), N$_2$O$_5$ is heated to generate a burst of NO$_3$ prior to injection into the system (Knopf et al., 2011). While not experimentally considered in this work, we modeled the NO$_3$exp achieved assuming complete thermal dissociation of N$_2$O$_5$ between the LFR and OFR – for example, by heating to 120 °C for 300 ms (Wood et al., 2003). Figure S2 suggests that the effect of heating N$_2$O$_5$ on NO$_3$exp was most significant at short $\tau_{LFR}$, where [N$_2$O$_5$] at the exit of the LFR was higher due to less wall loss and room-temperature decomposition. For example, at $\tau_{LFR} = 8$ s, the modeled NO$_3$exp was 2.8 times higher in the complete-dissociation case than in the unheated case, whereas NO$_3$exp increased by factors of 2.3 and 1.5 at $\tau_{LFR} = 20$ and 60 s. Thus, a combination of reducing $\tau_{LFR}$ and heating N$_2$O$_5$ at the exit of the LFR increases NO$_3$exp and should be explored for future advanced implementations of OFR-iN$_2$O$_5$.

3.2 Example OFR-iN$_2$O$_5$ characterization studies

Figure 2a shows time series of O$_3$ and NO$_2$ concentrations during an OFR-iN$_2$O$_5$ characterization experiment where RH$_{OFR} = 11$ %, [O$_3$]$_{LFR} = 280$ ppm, and [NO$_2$]$_{LFR} = 0$ to 320 ppm. Figure 2b shows time series of acetonitrile (C$_2$H$_3$N), butanal (C$_4$H$_8$O), thiophene (C$_4$H$_4$S), 2,3-dihydrobenzofuran (C$_8$H$_8$O), and naphthalene-d$_8$ (C$_10$H$_8$D$_8$) signals measured during the same period. Following NO$_3$ generation, the fractional decay of C$_2$H$_3$N, C$_4$H$_8$O, C$_4$H$_4$S, and C$_8$H$_8$O increased with increasing tracer $k_{NO_3}$, as expected. C$_8$H$_8$O was too reactive to measure any significant changes in its decay as a function of OFR-iN$_2$O$_5$ conditions, as shown in Fig. 2; however, maximum decay of C$_4$H$_8$O and C$_4$H$_4$S was observed at [NO$_2$]$_{LFR} : $[O_3]$$_{LFR}$ $\approx 0.7$ in this experiment. Decay of naphthalene-d$_8$, which was influenced by both NO$_3$ and NO$_2$ concentrations (Table S1), was maximized at [NO$_2$]$_{LFR} : $[O_3]$$_{LFR}$ $\approx 0.3$ to 1.1.

To confirm that the VOC degradation shown in Fig. 2b was due to reaction with NO$_3$, Fig. 3 shows IBBCEAS measurements of NO$_3$ obtained in separate OFR-iN$_2$O$_5$ characterization experiments that used [O$_3$]$_{LFR} = 150–160$ ppm and [NO$_2$]$_{LFR} : $[O_3]$$_{LFR} = 0.75$ and 2.0. The maximum IBBCEAS signal observed at $\lambda = 662$ nm indicated the presence of NO$_3$, as is evident from comparison with the
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Figure 2. Time series from a representative OFR-iN₂O₅ characterization experiment conducted at RH_OFR = 11 % of (a) O₃ and NO₂ mixing ratios input to LFR (left axis) and O₃ measured at the exit of the OFR (right axis), and (b) VOC tracers measured with PTR-MS: acetonitrile (C₂H₃N), butanal (C₄H₈O), thiophene (C₄H₄S), 2,3-dihydrobenzofuran (C₈H₈O), and naphthalene-d₈ (C₁₀D₈).

Figure 3. (a) IBBCEAS measurements of NO₂ and NO₃ absorbance obtained from an OFR-iN₂O₅ characterization experiment conducted at [O₃]₀,LFR = 150–160 ppm and [NO₂]₀,LFR: [O₃]₀,LFR = 0.75 and 2.0. (b) Absorption cross sections of NO₂ and NO₃ (Vandaele et al., 1998; Orphal et al., 2003).

Figure 4. NO₃_exp as a function of RH_OFR at [O₃]₀,LFR = 250 ppm and [NO₂]₀,LFR = 130 ppm. Horizontal lines represent N₂O₅ wall loss rate constants ranging from 0.01 to 0.08 s⁻¹ that were input to the OFR-iN₂O₅ KinSim mechanism (Table S2).

3.3 Effect of RH_OFR, [O₃]₀,LFR, and [NO₂]₀,LFR on NO₃_exp

Figure 4 shows NO₃_exp as a function of RH_OFR at [O₃]₀,LFR = 250 ppm and [NO₂]₀,LFR = 130 ppm. Under these conditions, NO₃_exp decreased from 1.2 × 10¹⁴ to 2.0 × 10¹³ molecules cm⁻³ s⁻¹ as RH_OFR increased from 11 % to 81 %. We hypothesize that this result is due to more effi-
cient hydrolysis of N₂O₅ to HNO₃ on the wetted walls of the OFR at higher RH, thereby suppressing NO₃exp relative to values obtained at lower RH conditions. In an attempt to model this behavior, kₖ₁, N₂O₅ values input to the model were adjusted as a function of RHOFR. Figure 4 suggests that humidity-dependent kₖ₁, N₂O₅ values ranging from 0.01 to 0.08 s⁻¹ were required to cover the range of measured NO₃exp. These values agreed within a factor of 2 or better with humidity-dependent kₖ₁, N₂O₅ values ranging from 0.014 to 0.040 s⁻¹ measured by Palm et al. (2017) in a similar OFR and were applied in subsequent model calculations.

Figure 5 shows NO₃exp as a function of [O₃]₀, LFR for measurements with [NO₂]₀, LFR : [O₃]₀, LFR = 0.5 ± 0.1 and RHOFR = 11 ± 2 %. The equivalent ambient photochemical age shown on the right y axis was calculated assuming a 14 h average nighttime NO₃ mixing ratio of 30 ppt and a 10 h daytime NO₃ mixing ratio of 0 ppt (Asaf et al., 2010). NO₃exp increased with increasing [O₃]₀, LFR due to increased NO₃ production from higher [N₂O₅]. Over the range of measured conditions, increasing [O₃]₀, LFR from 33 to 7092 ppm increased NO₃exp from 6.4 × 10¹² to 4.0 × 10¹⁵ molecules cm⁻³ s⁻¹. The black line in Fig. 5 represents NO₃exp modeled using the mechanism shown in Table S2. Measured and modeled NO₃exp values agreed within a factor of 2 or better above [O₃]₀, LFR ≈ 40 ppm, and the gain in NO₃exp as a function of [O₃]₀, LFR was highest between [O₃]₀, LFR = 10 and 300 ppm. Over this range of [O₃]₀, LFR, the NO₂ oxidation lifetime with respect to O₃ decreased from 115 to 4 s. Because tLFR = 20 s, under this range of LFR conditions, the NO₂ lifetime in the LFR was long enough that high NO₂ levels exiting the LFR suppressed NO₃exp in the OFR. In contrast, increasing [O₃]₀, LFR from 300 to 7000 ppm decreased the NO₂ oxidation lifetime with respect to O₃ from 4 to 0.2 s, and [NO₂] exiting the LFR was too low to significantly affect NO₃exp. To support this hypothesis, Fig. 6 plots NO₃exp as a function of [NO₂]₀, LFR : [O₃]₀, LFR at [O₃]₀, LFR = 250 ± 20 ppm and 6850 ± 400 ppm. Here, we incorporated NO₃exp values obtained over RHOFR = 11 % to 81 % for better statistics, and normalized each NO₃exp value to the maximum NO₃exp obtained at the same RH. Figure 6 shows that at [O₃]₀, LFR = 250 ppm, the maximum NO₃exp value was achieved at [NO₂]₀, LFR : [O₃]₀, LFR ≈ 0.5 to 0.7. Conversely, at [O₃]₀, LFR = 6850 ppm, the maximum NO₃exp value was achieved at [NO₂]₀, LFR : [O₃]₀, LFR ≈ 1.2.

In a related set of experiments, IBBCEAS measurements of the NO₂ : NO₃ ratio at the exit of the OFR (obtained from Fig. 3a spectra) confirmed that significantly higher NO₂ levels were present in the OFR at higher [NO₂]₀, LFR : [O₃]₀, LFR, as expected. For example, at [O₃]₀, LFR = 150 ppm and [NO₂]₀, LFR = 112 ppm, NO₂ : NO₃ = 28, whereas at [O₃]₀, LFR = 160 ppm and [NO₂]₀, LFR = 320 ppm, NO₂ : NO₃ = 613. NO₂ : NO₃, along with NO₁ : O₃ and NO₂ : NO₃, has important implications for the fate of organic species in OFR-iN₂O₅ that are discussed in the following sections.

3.4 Model characterization of OFR-iN₂O₅ : NO₃ : O₃, NO₂ : NO₃, and NO₂ : O₂

To examine OFR-iN₂O₅ performance over a wider range of conditions, Fig. 7 plots the mean NO₃exp, [O₃], NO₃, NO₂ : NO₃, and NO₂ : O₂ values obtained with the model as a function of [O₃]₀, LFR = 10 to 10⁵ ppm (10 %), for [NO₂]₀, LFR : [O₃]₀, LFR = 0.01, 0.1, 0.5, 1.0, 1.5, 1.8, and 2.0. Three observations are apparent from Fig. 7. First, at [O₃]₀, LFR < 1000 ppm and [NO₂]₀, LFR : [O₃]₀, LFR = 0.01

Figure 5. NO₃exp as a function of [O₃]₀, LFR for measurements with [NO₂]₀, LFR : [O₃]₀, LFR = 0.5 ± 0.1. Equivalent ambient photochemical age was calculated assuming a 14 h average nighttime NO₃ mixing ratio of 30 ppt and 10 h daytime average NO₃ mixing ratio of 0 ppt (Asaf et al., 2010). Model inputs were kₖ₁, N₂O₅ = 0.01 s⁻¹ and NO₃Rexp = 0.07 s⁻¹ ([O₃]₀, LFR < 1000 ppm) or 0.38 s⁻¹ ([O₃]₀, LFR > 1000 ppm). The shaded region encompasses model output scaled by factors of 0.5 and 2.

Figure 6. NO₃exp as a function of [NO₂]₀, LFR : [O₃]₀, LFR at fixed [O₃]₀, LFR values of 250 ± 20 and 6850 ± 400 ppm and RHOFR = 11 % to 81 %. NO₃exp values were normalized to the maximum NO₃exp value obtained at the same RH.
to 1.8, the maximum NO$_3$exp increased with [NO$_2$]$_0$,LFR : [O$_3$]$_0$,LFR prior to decreasing at [NO$_2$]$_0$,LFR : [O$_3$]$_0$,LFR > 1.0 (Fig. 7a). Above [O$_3$]$_0$,LFR ≈ 2000 ppm and below [NO$_2$]$_0$,LFR : [O$_3$]$_0$,LFR = 2.0, NO$_3$exp was less sensitive to [NO$_2$]$_0$,LFR : [O$_3$]$_0$,LFR. Second, the maximum NO$_3$ : O$_3$ increased with increasing [NO$_2$]$_0$,LFR : [O$_3$]$_0$,LFR above [O$_3$]$_0$,LFR = 1000 ppm (Fig. 7c). Third, the [NO$_2$]$_0$,LFR : [O$_3$]$_0$,LFR = 2.0 case demonstrated unique behavior relative to the other cases because residual O$_3$ exiting the LFR was low (<10 ppm) due to almost complete conversion of O$_3$ to O$_2$ inside the LFR (Fig. 7b). Consequently, the high residual [NO$_2$]$_0$ suppressed NO$_3$exp by 1 to 2 orders of magnitude relative to [NO$_2$]$_0$,LFR : [O$_3$]$_0$,LFR < 2 cases (Fig. 7a) and generated enhanced NO$_3$ : O$_3$, NO$_2$ : NO$_3$, and NO$_2$ : O$_2$ values. In addition, NO$_2$ : NO$_3$ ratios obtained from IBBCAES measurements at [O$_3$]$_0$,LFR = 150 to 160 ppm and [NO$_2$]$_0$,LFR : [O$_3$]$_0$,LFR = 0.75, 1.0 and 2.0 are shown in Fig. 7d. The measured NO$_2$ : NO$_3$ values are comparable to, or lower than, the modeled NO$_2$ : NO$_3$ values obtained under similar conditions and, therefore, broadly support using model results to further investigate the fate of (1) RO$_2$ formed from NO$_3$ oxidation of VOCs, (2) alkyl radicals that are reactive towards NO$_2$ and O$_2$, and (3) VOCs that are reactive towards O$_3$ and NO$_3$ in the following sections.

### 3.4.1 Fate of organic peroxy radicals (RO$_2$) formed from NO$_3$ + VOC reactions

Organic peroxy radicals (RO$_2$) react with NO, NO$_2$, NO$_3$, HO$_2$, or other RO$_2$ to generate alkoxy (RO) radicals, peroxy nitrites (RO$_2$NO$_2$), hydroperoxides or organic peroxides, and may additionally undergo autooxidation via sequential isomerization and O$_2$ addition. To investigate the fate of RO$_2$ as a function of OFR-iN$_2$O$_5$ conditions, we applied the methodology of Peng et al. (2019) by calculating the fractional oxidative loss of a generic alkyl or acyl RO$_2$ to each of these species over the range of conditions shown in Fig. 7. Kinetic data from Orlando and Tyndall (2012) that were used in these calculations are summarized in Table S4. Under almost all OFR-iN$_2$O$_5$ conditions shown in Fig. 7, RO$_2$ reactions with NO, HO$_2$, and RO$_2$ were minor (<1%) loss pathways compared with reaction with NO$_2$ and NO$_3$. We conducted a model sensitivity analysis in which the RO$_2$ + RO$_2$ reaction rate was enhanced by increasing NO$_3$R$_{ext}$ from 0.07 to 0.7 s$^{-1}$ and increasing the RO$_2$ + RO$_2$ rate constant from $1 \times 10^{-11}$ to $1 \times 10^{-10} \text{cm}^3\text{molecule}^{-1} \text{s}^{-1}$ (Berndt et al., 2018a, b). Despite these perturbations, the relative contribution of RO$_2$ + RO$_2$ reactions to total RO$_2$ loss remained < 1% across this range of OFR-iN$_2$O$_5$ conditions.

To investigate the relative importance of competing RO$_2$ + NO$_2$ and RO$_2$ + NO$_3$ pathways, we defined the fractional reactive loss of RO$_2$ due to NO$_3$, $F_{\text{RO}_2+\text{NO}_3}$:

$$F_{\text{RO}_2+\text{NO}_3} = \frac{k_{\text{RO}_2+\text{NO}_3}[\text{NO}_3]}{k_{\text{RO}_2+\text{NO}_2}[\text{NO}_3]+k_{\text{RO}_2+\text{NO}_3}[\text{NO}_2]}$$  (3)

Figure 8a and b show $F_{\text{RO}_2+\text{NO}_3}$ calculated for alkyl and acyl RO$_2$, respectively. To simplify the analysis, we assumed that the thermal decomposition of RO$_2$NO$_2$ species formed from RO$_2$ + NO$_2$ reactions was slow compared with $\tau_{\text{OFR}}$. This assumption generates a lower limit $F_{\text{RO}_2+\text{NO}_3}$ value for the alkyl RO$_2$ case, where RO$_2$NO$_2$ decomposition occurs on timescales of seconds or less (Orlando and Tyndall, 2012) but has minimal influence on the acyl-RO$_2$ case due to higher thermal stability of peroxyl acyl nitrates. For alkyl RO$_2$, Fig. 8a shows that $F_{\text{RO}_2+\text{NO}_3}$ = 0.5 was achieved between [NO$_2$, O$_3$]$_0$,LFR = (125 ppm, 250 ppm) and (3240 ppm, 1800 ppm). For acyl RO$_2$, due to faster reaction with NO$_3$, Fig. 8b shows that $F_{\text{RO}_2+\text{NO}_3} = 0.5$ was achieved using [NO$_2$, O$_3$]$_0$,LFR = (350 ppm, 700 ppm) to (1.1%, 0.6%).

To investigate the feasibility of generating OFR-iN$_2$O$_5$ conditions where RO$_2$ loss is dominated by autooxidation, we calculated the lifetime of alkyl and acyl RO$_2$ ($\tau_{\text{RO}_2}$) over the range of OFR-iN$_2$O$_5$ conditions shown in Fig. 7 and Fig. 8a and b. As shown in Fig. 8d and e, maximum $\tau_{\text{RO}_2}$ values of ≈1.4 s (alkyl) and 0.4 s (acyl) were obtained at [NO$_2$]$_0$,LFR ≈ 2 ppm and [O$_3$]$_0$,LFR ≈ 200 ppm. At lower [O$_3$]$_0$,LFR, $\tau_{\text{RO}_2}$ decreased due to a faster RO$_2$ + NO$_2$ reaction rate, and at higher [O$_3$]$_0$,LFR, $\tau_{\text{RO}_2}$ decreased due to a faster RO$_2$ + NO$_3$ reaction rate. Because RO$_2$ autooxidation...
3.4.2 Fate of aromatic alkyl radicals (R) formed from RO\textsubscript{2} may achieve autooxidation-dominant conditions for some VOCs generates R that react more slowly with O\textsubscript{3} from NO\textsubscript{2}.

The majority of aromatic alkyl radicals (R) that are generated during oxidation of a subset of aromatic VOCs may achieve autooxidation-dominant conditions for some RO\textsubscript{2} but not for others.

3.4.3 Fate of VOCs reactive towards O\textsubscript{3} and NO\textsubscript{3}

We defined the fractional reactive loss of a VOC with respect to NO\textsubscript{3}, \( F_{\text{VOC+NO}_3} \):

\[
F_{\text{VOC+NO}_3} = \frac{k_{\text{VOC+NO}_3}[\text{NO}_3]}{k_{\text{VOC+NO}_3}[\text{NO}_3] + k_{\text{VOC+O}_3}[\text{O}_3]}
\]

and we established \( F_{\text{VOC+NO}_3} = 0.9 \) as the criterion for NO\textsubscript{3}-dominated oxidative loss. Figure 9 plots NO\textsubscript{3} : O\textsubscript{3} at which \( F_{\text{VOC+NO}_3} = 0.9 \) for several classes of organic compounds with published \( k_{\text{NO}_3} \) and \( k_{\text{O}_3} \) values greater than \( 10^{-16} \) and \( 10^{-19} \) cm\(^3\) molecules\(^-1\) s\(^-1\), respectively. Therefore, this figure excludes compounds such as aromatics.

3.5 NO\textsubscript{3} estimation equation for OFR-iN\textsubscript{2}O\textsubscript{5}

Previous studies reported empirical OH exposure algebraic estimation equations for use with OFRs (Li et al., 2015; Peng et al., 2015, 2018; Lambe et al., 2019). These equations parameterize OH\textsubscript{exp} as a function of readily measured experimental parameters, thereby providing a simpler alternative to detailed photochemical models for experimental planning.
and analysis. Here, we expand on those studies by deriving an NO$_{3}$exp estimation equation for OFR-iN$_2$O$_5$. Model results obtained from the base case of the model—a VOC reacting with NO$_3$ at 2.5 $\times$ 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ as a surrogate for NO$_3$R$_{ext}$—were used to derive the following equation that allows for the estimation of NO$_{3}$exp for OFR-iN$_2$O$_5$:

$$\log([NO_3]_{exp}) = a + b \log(273.15 + T_{OFR}) + c \log(\tau_{OFR})$$

$$+ d \log([NO_2]_{LFR}) + e \log([O_3]_{LFR} \cdot T_{OFR})$$

$$+ f \log(k_{OFR}, N_2O_5) + \log \left( \frac{[NO_2]_{LFR}}{[O_3]_{LFR}} \right)$$

$$\cdot (g \log([O_3]_{LFR})^2 + h \log([O_3]_{LFR})^2 - [NO_2]_{LFR}$$

$$\cdot (i + j \log([O_3]_{LFR}) + k \log(NO_3R_{ext})$$

$$+ l \log([NO_2]_{LFR} \cdot T + m \log([O_3]_{LFR} \cdot \log(k_{OFR}, N_2O_5)$$

$$\cdot (6)$$

The phase space of OFR-iN$_2$O$_5$ parameters for fitting Eq. (6) to the NO$_{3}$exp model results was defined as follows: $[O_3]_{LFR}$ = 10–1000 ppm, $[NO_2]_{LFR}$ = 10–1000 ppm, $[NO_2]_{LFR} / [O_3]_{LFR} \leq 2$, NO$_3$R$_{ext}$ = 1–200 s$^{-1}$, $k_{OFR}, N_2O_5$ = 0.01–0.08 s$^{-1}$, $\tau_{OFR}$ = 0–40 $\degree$C, and $\tau_{OFR}$ = 60–300 s. The cases where $[O_3]_{LFR} > 1000$ ppm and/or $[NO_2]_{LFR} / [O_3]_{LFR} > 2$ were not considered due to less practical interest. We explored 11, 11, 7, 4, and 5 logarithmically evenly distributed values in the ranges of $[O_3]_{LFR}$, $[NO_2]_{LFR}$ (11 values over 10–1000 ppm), NO$_3$R$_{ext}$, $k_{OFR}, N_2O_5$, and $\tau_{OFR}$, respectively. Due to significantly different chemical regimes in different parts of the phase space, fit coefficients that are reported in Table 1 were obtained by fitting the same functional form (Eq. 6) over three subphase spaces with the following additional constraints: (1) $[NO_2]_{LFR}, [O_3]_{LFR} = 0–1$ and NO$_3$R$_{ext}$ = 20–200 s$^{-1}$; (2) $[NO_2]_{LFR}, [O_3]_{LFR} = 0–1$ and NO$_3$R$_{ext}$ = 1–20 s$^{-1}$; and (3) $[NO_2]_{LFR}, [O_3]_{LFR} = 1–2$. For these three subspaces, 10080, 13440, and 5880 respective model cases were simulated. In Eq. (6), the terms involving the coefficients $g–j$ were included to reproduce the relationship between normalized NO$_3$exp and $[NO_2]_{LFR}, [O_3]_{LFR}$ shown in Fig. 5. Logarithms of first- and second-order terms were successively added until no further fit quality improvement was achieved. Figure 10 compares NO$_3$exp estimated from Eq. (6) and calculated from the model described in Sect. 2.2. The mean absolute value of the relative deviation was 49 % which is comparable to results obtained for previous estimation equations with significant NO$_3$ chemistry (Peng et al., 2018).

NO$_3$R$_{ext}$ of a system will change over the course of multiple generations of NO$_3$ oxidation due to changes in kinetic rate coefficients between different species and NO$_3$ ($k_{NO_3}$). The sensitivity of Eq. (6) to changes in NO$_3$R$_{ext}$ depends in part on the relative magnitudes of NO$_3$R$_{ext}$ and the internal NO$_3$ reactivity, NO$_3$R$_{int}$, which is approximately equal to $k_{NO_2+NO_3}[NO_2]$. If NO$_3$R$_{int} \gg NO_3$R$_{ext}$, changes in NO$_3$R$_{ext}$ would have minimal influence on Eq. (6). In one case study, we examined changes in NO$_3$R$_{ext}$ following conversion of biogenic VOCs (BVOCs) to gas-phase carbonyl oxidation products with known $k_{NO_3}$ values. Table S5 compares $k_{NO_3}$ of isoprene to methyl vinyl ketone and methacrolein, $\alpha$-pinene to pinonaldehyde, sabinene to sabinetalone, and 3-carene to caronalexde. At the limit where 100 % of each BVOC is converted to its carbonyl oxidation product, NO$_3$R$_{ext}$ decreases by a factor of 200 or greater. Unsaturated organic nitrates that are generated from BVOC + NO$_3$ may also be reactive towards NO$_3$, but $k_{NO_3}$ for these species are not available. In another case study, we examined changes in NO$_3$R$_{ext}$ following conversion of

### Table 1. Fit parameters for NO$_3$exp estimation equation (Eq. 6).

| Parameter | Subspace 1 values | Subspace 2 values | Subspace 3 values |
|-----------|-------------------|-------------------|-------------------|
| a | 61.0694 | -59.3835 | 246.416 |
| b | -20.1400 | 27.3434 | -122.229 |
| c | 0.795209 | 0.803508 | 0.581443 |
| d | -0.375825 | 1.18285 | 51.2355 |
| e | 0.0311034 | 0.00815681 | -0.66569 |
| f | 0.888193 | -0.0731138 | -0.0210958 |
| g | -0.379009 | 0.13199 | -0.346062 |
| h | 1.73605 | -0.422009 | -81.9221 |
| i | 0.14737 | 0.035132 | -22.4373 |
| j | 0.261402 | 0.311104 | 13.204 |
| k | -1.22009 | -0.323329 | -0.118988 |
| l | 0.00733645 | -0.004277 | 0.676436 |
| m | -0.957064 | -0.436977 | -0.3983 |

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BVOCs to SOA. An effective $k_{\text{NO}_3}$ for SOA was calculated using the following equation adapted from Lambe et al. (2009):

$$k_{\text{NO}_3} = \frac{3 \gamma \times \bar{c} \times M_{\text{SOA}} \times F_{\text{diff}}}{2 D_p \times \rho_p \times N_A},$$  
(7)

where $F_{\text{diff}}$ is a correction factor accounting for diffusion limitations to the particle surface in the transition regime (Fuchs and Sutugin, 1970),

$$F_{\text{diff}} = \frac{1 + 6 \times \frac{D_{\text{NO}_3}}{\varepsilon D_p}}{1 + 10.26 \times \frac{D_{\text{NO}_3}}{\varepsilon D_p} + 47.88 \times \left(\frac{D_{\text{NO}_3}}{\varepsilon D_p}\right)^2};$$  
(8)

$\gamma$ is the fraction of collisions between NO$_3$ and SOA resulting in reaction; $D_p$ is the surface area-weighted mean particle diameter; $\rho_p$ is the particle density; $N_A$ is Avogadro’s number; $\varepsilon$ is the mean molecular speed of NO$_3$ (3.2 $\times$ 10$^6$ cm s$^{-1}$ at $T = 298$ K); $M_{\text{SOA}}$ is the mean molecular weight of the SOA; and $D_{\text{NO}_3}$ = 0.08 cm$^2$ s$^{-1}$ is the NO$_3$ diffusion coefficient in air (Rudich et al., 1996). Figure S4 shows $k_{\text{SOA}+\text{NO}_3}$ as a function of $D_p$ ranging from 1 to 1000 nm, assuming $\rho_p$ = 1.4 g cm$^{-3}$, $M_{\text{SOA}}$ = 250 g mol$^{-1}$ (Nah et al., 2016), and an upper limit $\gamma = 0.1$ for BVOC-derived SOA (Ng et al., 2017). For reference, the range of slowest (isoprene) and fastest (humulene) known $k_{\text{BVOC}+\text{NO}_3}$ are indicated by the vertical blue line on the $\gamma$ axis. At the limit where 100% of a BVOC is converted to SOA, NO$_3$R$_{ex}$ decreases by a factor of 10 or greater depending on $k_{\text{BVOC}+\text{NO}_3}$ and $D_p$. Taken together, these results suggest that NO$_3$R$_{ex}$ decreases following NO$_3$ oxidation of BVOCs to carbonyl oxidation products and/or SOA. In this case, inputting NO$_3$R$_{ex}$ of the BVOC precursor to Eq. (6) generates a lower limit to NO$_3$exp over multiple generations of NO$_3$ oxidation. Results for other systems will depend on the $k_{\text{NO}_3}$ values of associated gas and condensed-phase precursors and their oxidation products.

3.6 SOA generation from $\beta$-pinene + NO$_3$

To apply the OFR-iN$_2$O$_5$ technique to SOA formation studies, we generated SOA from $\beta$-pinene + NO$_3$ in the absence of seed particles using [O$_3$]$_{0 \text{LFR}}$ = 300 ppm, [NO$_2$]$_{0 \text{LFR}}$ = 150 ppm, and RH$_{\text{OFR}}$ $\approx$ 1 %. PTR-MS measurements confirmed the complete consumption of $\beta$-pinene, and numerous product ions were detected. The largest ions detected were (H$^+$)C$_9$H$_{14}$O and (H$^+$)C$_{10}$H$_{14}$ which may correspond to nopinone (C$_9$H$_{12}$O) and fragmentation or decomposition products of C$_{10}$H$_{17}$NO$_4$, respectively (Hallquist et al., 1999; Claffin and Ziemann, 2018). The mass yield of SOA ranged from 0.03 to 0.39 over $\beta$-pinene mixing ratios ranging from 20 to 400 ppbv that were injected into the OFR. These yield values are broadly consistent with previous environmental chamber studies (Ng et al., 2017) but are lower than chamber SOA yields obtained at the same $\beta$-pinene mixing ratio, presumably due to the absence of seed particles in the OFR (Lambe et al., 2015). To compare the results obtained using OFR-iN$_2$O$_5$ with a conventional environmental chamber method, Fig. 11a and b show HR-ToF-AMS spectra of SOA generated from NO$_3$ oxidation of $\beta$-pinene in the Georgia Tech chamber (Boyd et al., 2015) and in the OFR, along with a scatter plot of relative ion abundances present in the two spectra (Fig. 11c). The same spectra are presented on a logarithmic scale in Fig. S5. As is evident, $\beta$-pinene + NO$_3$ SOA generated in the chamber and OFR exhibit a high degree of similarity (linear regression slope = 0.98 and $r^2 = 0.99$). The largest ion signal was observed at NO$_3^-$, which, along with the signal at NO$_3^+$ and NO$_3^+$: NO$_3^-$ = 6.7, is consistent with the formation of particulate organic nitrates (Farmer et al., 2010). Signals observed at CHO$^+$, C$_2$H$_4$O$^+$, and other C$_n$H$_x$O$_y^{+}$ ions suggest the presence of other multifunctional oxidation products.

4 Conclusions

OFR-iN$_2$O$_5$ complements recently developed methods that enable NO$_3$-dependent photooxidation studies in OFRs such as OFR-iN$_2$O and OFR-iC$_3$H$_7$ONO (Lambe et al., 2017; Peng et al., 2018; Lambe et al., 2019) by enabling studies of nighttime NO$_3$-initiated oxidative aging processes. Important OFR-iN$_2$O$_5$ parameters are [O$_3$], [NO$_2$], [H$_2$O], $T$, NO$_3$R$_{ex}$, and $r_{\text{OFR}}$. By contrast, important OFR-iN$_2$O$_5$ and OFR-iC$_3$H$_7$ONO parameters are UV intensity, external OH reactivity (OH$_{\text{ex}}$), $r_{\text{OFR}}$, and either [O$_3$] + [H$_2$O] + [NO$_2$] or [C$_3$H$_7$ONO]. Notably, NO$_3$R$_{ex}$ is typically less significant in OFR-iN$_2$O$_5$ than OH$_{\text{ex}}$ in OFR-iN$_2$O or OFR-iC$_3$H$_7$ONO because (1) most compounds are less reactive...
towards NO$_3$ than OH; (2) NO$_3$$^{\text{exp}}$ is higher than OH$_{\text{exp}}$; and (3) NO$_3$($R$)$_{\text{int}}$ of OFR-iN$_2$O$_5$, which is dominated by the NO$_3$ + NO$_2$ reaction, is larger and easier to manipulate than the internal OH reactivity of OFR-iN$_2$O$_5$ and OFR-iC$_3$H$_7$ONO, which is dominated by OH + HO$_2$ and OH + NO$_2$ reactions. To identify optimal OFR-iN$_2$O$_5$ conditions for different applications, we characterized NO$_3$$^{\text{exp}}$, $\tau$$_{R}$O$_2$, $F_{R}$$^{O_2}$+NO$_2$, $F_{R}$+O$_2$, and $F_{VOC}$+NO$_3$ at [O$_3$]$_{LFR}$ = 10 ppm to 10%, [NO$_2$]$_{LFR}$ : [O$_3$]$_{LFR}$ = 0.01 to 2.0, and RH$_{\text{OFR}}$ = 7% to 85%. Optimal NO$_3$$^{\text{exp}}$ was achieved by minimizing [H$_2$O] in the OFR and associated humidity-dependent N$_2$O$_5$ wall losses. This is contrary to most OFR techniques that are used to generate OH radicals, where optimal OH$_{\text{exp}}$ is achieved by maximizing [H$_2$O] and the associated OH production from the O($^1$D) + H$_2$O reaction and/or H$_2$O photolysis at $\lambda$ = 185 nm.

Figure 12 presents image plots that represent OFR-iN$_2$O$_5$ analysis at $\lambda$=185 nm. For the best overlap between OFR-iN$_2$O$_5$ conditions that achieved $F_{R}^{\text{RO}_2}$+NO$_3$ > 0.9 and $\tau$$_{R}$O$_2$ > 1 s was obtained with [NO$_2$]$_{LFR}$ ≈ 2–3 ppm and [O$_3$]$_{LFR}$ ≈ 200–300 ppm. Because atmospheric NO$_2$ : NO$_3$ is highly variable and often much larger than NO$_2$ : NO$_3$ achieved using OFR-iN$_2$O$_5$ (Brown et al., 2003; Stutz et al., 2004), simply attempting to maximize $F_{R}^{\text{RO}_2}$+NO$_3$ may not always be necessary and has trade-offs such as decreasing NO$_3$ : O$_3$ and $F_{VOC}$+NO$_3$. OFR-iN$_2$O$_5$ was more difficult to apply to species such as unsaturated carboxyls and mono- and sesquiterpenes with multiple double bonds that react more efficiently with O$_3$ than other VOCs; here, alternative NO$_3$ generation techniques that do not introduce O$_3$ to the OFR warrant consideration, even
though they are more difficult to implement (Palm et al., 2017).

Because OFR-iN$_2$O$_5$ can continuously generate N$_2$O$_5$ and NO$_3$ at room temperature, it is significantly easier to apply in continuous flow reactor studies than related techniques. However, in addition to the aforementioned considerations, high N$_2$O$_5$ and HNO$_3$ concentrations that are generated using OFR-iN$_2$O$_5$ complicated the application of techniques such as iodide-adduct chemical ionization mass spectrometry due to efficient reactions between the iodide reagent ion and N$_2$O$_5$ or HNO$_3$ (Lee et al., 2014). Additionally, the humidity-dependent N$_2$O$_5$ wall loss rate must be accurately characterized to model the performance of a specific OFR-iN$_2$O$_5$ configuration. Future applications of OFR-iN$_2$O$_5$ will investigate the NO$_3$-initiated OVOC and SOA formation potential of simple and complex precursors in laboratory and field studies.

**Code and data availability.** Data and KinSim mechanisms presented in this paper are available upon request. The KinSim kinetic solver is freely available at http://tinyurl.com/kinsim-release (Peng and Jimenez, 2020).

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