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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 particulate 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_2O_5 as the radical precursor. N_2O_5 is generated from the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$, followed by the reactions $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ and $\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$. The synthesized N_2O_5 is collected and stored in a cold trap under dry conditions to minimize hydrolysis of N_2O_5 to nitric acid (HNO_3). This method has limitations that hinder widespread usage: specifically, long-term storage and handling of N_2O_5 at low temperature and under dry conditions is difficult, and the continuous generation of N_2O_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_2O_5 and NO_3 is required, such as OFR studies. The method is capable of continuous N_2O_5 generation in the gas phase at room temperature using a laminar flow reactor (LFR) that is coupled to a dark OFR. N_2O_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_2O_5 ” (where “i” stands for “injected”). We present experimental and model characterization of OFR- iN_2O_5 as a function of LFR and OFR conditions, and we demonstrate the application of OFR- iN_2O_5 to generate and characterize SOA from the β -pinene + NO_3 reaction.

2 Methods

2.1 N_2O_5 and NO_3 generation

Figure 1 shows a process flow diagram of the OFR- iN_2O_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_2O_5 (Wood et al., 2003; Boyd et al., 2015), although the LFR materials, flow rates,

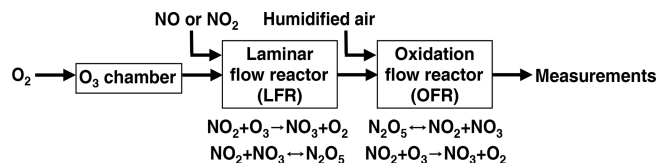


Figure 1. Process flow diagram of the OFR- iN_2O_5 technique used to generate nitrate radicals (NO_3).

and reagent concentrations were different. A compressed gas cylinder containing $1.00 \pm 0.02\%$ 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 $[\text{O}_3]$ accordingly achieves similar results. O_3 was generated by passing 1750–1800 $\text{cm}^3 \text{min}^{-1}$ of pure O_2 through a custom O_3 chamber housing a mercury fluorescent lamp (GPH212T5VH, Light Sources, Inc.) or 500–1800 $\text{cm}^3 \text{min}^{-1}$ O_2 through a corona discharge ozone generator (Enaly 1KNT). We used 1800 $\text{cm}^3 \text{min}^{-1}$ of O_2 carrier gas flow through the LFR ($Re \sim 110$, i.e., laminar flow) to achieve $\tau_{\text{LFR}} = 20$ s for reasons that are discussed in Sect. 3.1. The NO_2 mixing ratio entering the LFR, $[\text{NO}_2]_{0, \text{LFR}}$, was calculated from the NO_2 mixing ratio in the compressed gas mixture and the dilution ratio of 0–50 or 0–1300 $\text{cm}^3 \text{min}^{-1}$ gas flow into O_2 which was controlled using mass flow controllers. The O_3 mixing ratio entering the LFR, $[\text{O}_3]_{0, \text{LFR}}$, 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 (τ_{OFR}) was 120 ± 34 s ($\pm 1\sigma$), 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 $^\circ\text{C}$ 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_2O_5 characterization studies

In one set of experiments, the integrated NO_3 exposure ($\text{NO}_{3\text{exp}}$), defined here as the product of the average NO_3 concentration and τ_{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 NO_{3exp} 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 NO_{3exp} over the majority of the OFR-iN₂O₅ conditions that were investigated. Thus, experiments described in this paper used mixtures of tracers with bimolecular *k*_{NO₃} ranging from approximately 10⁻¹⁶ to 10⁻¹³ cm³ molecules⁻¹ s⁻¹ and *k*_{O₃} < 10⁻¹⁹ cm³ molecules⁻¹ s⁻¹ (Table S1). Acetonitrile was used as a nonreactive tracer. In “low O₃” experiments ([O₃]_{0, LFR} = 10 to 300 ppm) a mixture of acetonitrile, butanal, thiophene, 2,3-dihydrobenzofuran, and naphthalene-d₈ (C₁₀D₈), 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 (NO₃R_{ext}), which is the summed 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 C₁₀D₈. In “high O₃” experiments ([O₃]_{0, LFR} = 6100 to 7400 ppm), which generated higher NO_{3exp}, 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 NO₃R_{ext} ≈ 0.38 s⁻¹.

In another set of experiments that were conducted as part of the Aerosol Chemical Monitor Calibration Center (ACMCC) particulate organonitrates (*p*ON) 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, *p*ON were generated in a PAM OFR that used [O₃]_{0, LFR} = 150–160 ppm and [NO₂]_{0, LFR} : [O₃]_{0, 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):

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right) \left(\frac{1 - R(\lambda)}{d} \right) \quad (1)$$

where α(λ) is the absorption coefficient of the OFR sample in the instrument, *I*(λ) and *I*₀(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 %). *I*₀(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 *I*₀(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:

$$\alpha(\lambda) = [\text{NO}_2]\sigma_{\text{NO}_2} + [\text{NO}_3]\sigma_{\text{NO}_3} + [\text{O}_3]\sigma_{\text{O}_3} + p(\lambda) \quad (2)$$

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 NO₃ and N₂O₅ concentrations in the LFR and OFR. Inputs to the LFR-KinSim model were [O₃]_{0, LFR}, [NO₂]_{0, LFR}, RH = 1 %, $T = 24\text{ }^{\circ}\text{C}$, $\tau_{\text{LFR}} = 20\text{ s}$ (modeled as plug flow, see Sect. 3.1), and first-order wall loss rates of NO₃ and N₂O₅ ($k_{\text{wLFR}, \text{NO}_3}$ and $k_{\text{wLFR}, \text{N}_2\text{O}_5}$). Inputs to the OFR-KinSim model were [O₃], [NO₂], [NO₃], and [N₂O₅] output from the LFR scaled by a measured dilution factor of 4.4; RH and T measured in the OFR; $\tau_{\text{OFR}} = 120\text{ s}$, $k_{\text{wOFR}, \text{NO}_3}$, and $k_{\text{wOFR}, \text{N}_2\text{O}_5}$; and input VOC tracer concentrations and their k_{NO_3} values. Because the calculated N₂O₅ residence time in the OFR inlet ($\sim 0.04\text{ s}$) was short compared with the N₂O₅ decomposition timescale at $T = 23\text{--}25\text{ }^{\circ}\text{C}$ ($\sim 20\text{ s}$), potential thermal decomposition of N₂O₅ during the dilution step was not considered in the model.

2.2.1 LFR and OFR $k_{\text{w}, \text{NO}_3}$ and $k_{\text{w}, \text{N}_2\text{O}_5}$ values

Published $k_{\text{w}, \text{NO}_3}$ 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 2.22 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 $k_{\text{wLFR}, \text{NO}_3} = 0.15\text{ s}^{-1}$. Extrapolating this value to the OFR (20.32 cm i.d.) yielded $k_{\text{wOFR}, \text{NO}_3} = 0.02\text{ s}^{-1}$. At fixed OFR-iN₂O₅ conditions that are summarized in Table S3, varying $k_{\text{wLFR}, \text{NO}_3}$ between 0 and 0.3 s^{-1} changed the NO_{3exp} achieved in the OFR by 0.3 %. Results were even less sensitive to the $k_{\text{wOFR}, \text{NO}_3}$ assumed for the OFR because of its larger diameter and higher NO_{3Rext}.

Published $k_{\text{w}, \text{N}_2\text{O}_5}$ 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 $k_{\text{w}, \text{N}_2\text{O}_5} = 0.05\text{ s}^{-1}$, which was applied in the LFR-KinSim model. In preliminary OFR-KinSim modeling studies, we assumed $k_{\text{w}, \text{N}_2\text{O}_5} = 0.014\text{ s}^{-1}$ (Palm et al., 2017). However, as will be discussed in Sect. 3.3, $k_{\text{w}, \text{N}_2\text{O}_5}$ was humidity-dependent and required modifications to match measured NO_{3exp} values as a function of RH_{OFR}.

3 Results and discussion

3.1 LFR design considerations

The optimal LFR residence time (τ_{LFR}) was identified using model simulations of the injection of 300 ppm O₃ and NO₂ into the LFR followed by dilution and injection of the LFR output into an OFR operated with $\tau_{\text{OFR}} = 120\text{ s}$. Fig-

ure S2 plots the NO_{3exp} achieved in the OFR as a function of τ_{LFR} ranging from 1 to 60 s. Potential entry length effects that may have influenced results obtained below $\tau_{\text{LFR}} \approx 4\text{--}5\text{ s}$ were not considered in the model. Figure S2 shows that the maximum NO_{3exp} in the OFR was obtained at $\tau_{\text{LFR}} = 20\text{ s}$ at room temperature (unheated case); other NO_{3exp} values were normalized to this condition. Below $\tau_{\text{LFR}} = 20\text{ s}$, NO_{3exp} was suppressed due to higher NO₂ levels entering the OFR. Above $\tau_{\text{LFR}} = 20\text{ s}$, NO_{3exp} was suppressed due to lower N₂O₅ levels entering the OFR because of more extensive LFR wall loss.

In traditional studies of NO₃ oxidative aging processes that are conducted at low pressure and short residence time ($\tau \sim 1\text{ s}$), N₂O₅ is heated to generate a burst of NO₃ prior to injection into the system (Knopf et al., 2011). While not experimentally considered in this work, we modeled the NO_{3exp} achieved assuming complete thermal dissociation of N₂O₅ 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 N₂O₅ on NO_{3exp} was most significant at short τ_{LFR} , where [N₂O₅] at the exit of the LFR was higher due to less wall loss and room-temperature decomposition. For example, at $\tau_{\text{LFR}} = 8\text{ s}$, the modeled NO_{3exp} was 2.8 times higher in the complete-dissociation case than in the unheated case, whereas NO_{3exp} increased by factors of 2.3 and 1.5 at $\tau_{\text{LFR}} = 20$ and 60 s. Thus, a combination of reducing τ_{LFR} and heating N₂O₅ at the exit of the LFR increases NO_{3exp} and should be explored for future advanced implementations of OFR-iN₂O₅.

3.2 Example OFR-iN₂O₅ characterization studies

Figure 2a shows time series of O₃ and NO₂ concentrations during an OFR-iN₂O₅ characterization experiment where RH_{OFR} = 11 %, [O₃]_{0, LFR} = 280 ppm, and [NO₂]_{0, LFR} = 0 to 320 ppm. Figure 2b shows time series of acetonitrile (C₂H₃N), butanal (C₄H₈O), thiophene (C₄H₄S), 2,3-dihydrobenzofuran (C₈H₈O), and naphthalene-d₈ (C₁₀D₈) signals measured during the same period. Following NO₃ generation, the fractional decay of C₂H₃N, C₄H₈O, C₄H₄S, and C₈H₈O increased with increasing tracer k_{NO_3} , as expected. C₈H₈O was too reactive to measure any significant changes in its decay as a function of OFR-iN₂O₅ conditions, as shown in Fig. 2; however, maximum decay of C₄H₈O and C₄H₄S was observed at [NO₂]_{0, LFR} : [O₃]_{0, LFR} ≈ 0.7 in this experiment. Decay of naphthalene-d₈, which was influenced by both NO₃ and NO₂ concentrations (Table S1), was maximized at [NO₂]_{0, LFR} : [O₃]_{0, LFR} ≈ 0.3 to 1.1.

To confirm that the VOC degradation shown in Fig. 2b was due to reaction with NO₃, Fig. 3 shows IBBCEAS measurements of NO₃ obtained in separate OFR-iN₂O₅ characterization experiments that used [O₃]_{0, LFR} = 150–160 ppm and [NO₂]_{0, LFR} : [O₃]_{0, LFR} = 0.75 and 2.0. The maximum IBBCEAS signal observed at $\lambda = 662\text{ nm}$ indicated the presence of NO₃, as is evident from comparison with the

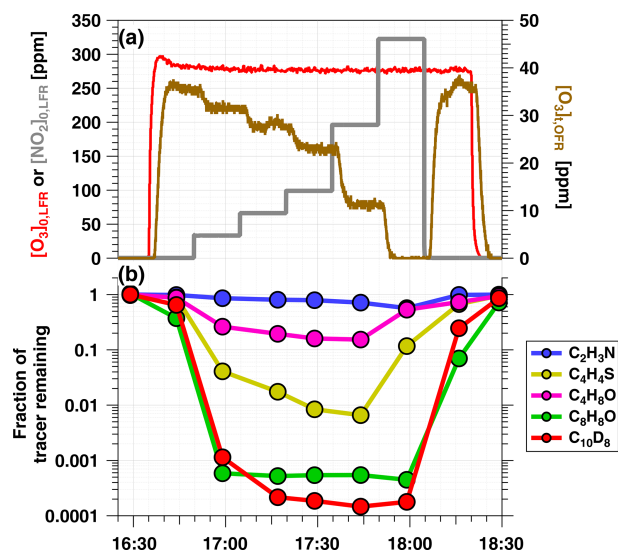


Figure 2. Time series from a representative OFR-iN₂O₅ characterization experiment conducted at RH_{OFR} = 11 % of (a) O₃ and NO₂ mixing ratios input to LFR (left axis) and O₃ measured at the exit of the OFR (right axis), and (b) VOC tracers measured with PTR-MS: acetonitrile (C₂H₃N), butanal (C₄H₈O), thiophene (C₄H₄S), 2, 3-dihydrobenzofuran (C₈H₈O), and naphthalene-d₈ (C₁₀D₈).

wavelength-dependent absorption cross section of NO₃ obtained by Orphal et al. (2003) and plotted in Fig. 3b. Additionally, Fig. S3 shows the relative rate coefficient obtained from the decay of C₄H₈O and C₄H₄S measured with PTR-MS. We measured a relative rate coefficient of 2.83, which is in agreement with a relative rate coefficient value of 3.22 ± 0.95 calculated from C₄H₈O + NO₃ and C₄H₄S + NO₃ rate coefficients (Atkinson, 1991; D’Anna et al., 2001). Ions corresponding to peroxy butyl nitrate, nitrothiophene, and nitronaphthalene-d₇, which are known NO₃ oxidation products of C₄H₈O, C₄H₄S, and C₁₀D₈, respectively (Atkinson et al., 1990; Jenkin et al., 2003; Saunders et al., 2003; Cabañas et al., 2005), were also detected with PTR-MS. Tracer decay experiments similar to the measurements shown in Fig. 2 were repeated over [O₃]_{0, LFR} ranging from 10 to 7400 ppm, [NO₂]_{0, LFR} ranging from 0 to 7200 ppm, and RH_{OFR} ranging from 7 % to 85 %. For experiments where [O₃]_{0, LFR} > 6000 ppm, NO_{3exp} was calculated from the decay of *o*-xylene because (1) *p*-cymene has a large ionized fragment at C₇H₉⁺ (thus interfering with detection of toluene), (2) NO₃ oxidation products were generated that interfered with detection of oxygenated tracers (butanol, benzaldehyde, and butanal), and (3) the remaining tracers that were used were too reactive towards NO₃ to accurately constrain NO_{3exp}.

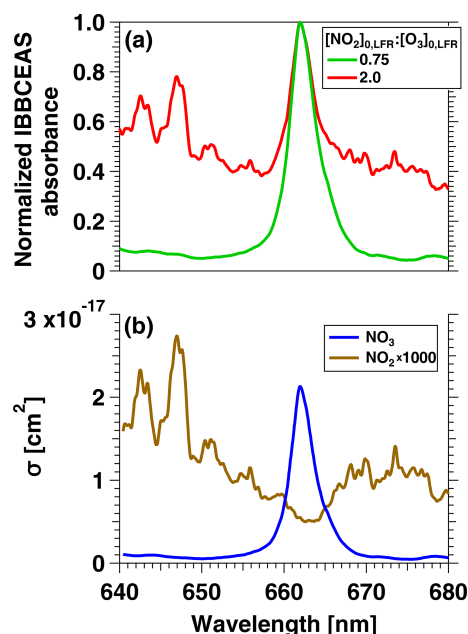


Figure 3. (a) IBBCEAS measurements of NO₂ and NO₃ absorbance obtained from an OFR-iN₂O₅ characterization experiment conducted at [O₃]_{0, LFR} = 150–160 ppm and [NO₂]_{0, LFR} : [O₃]_{0, LFR} = 0.75 and 2.0. (b) Absorption cross sections of NO₂ and NO₃ (Vandaele et al., 1998; Orphal et al., 2003).

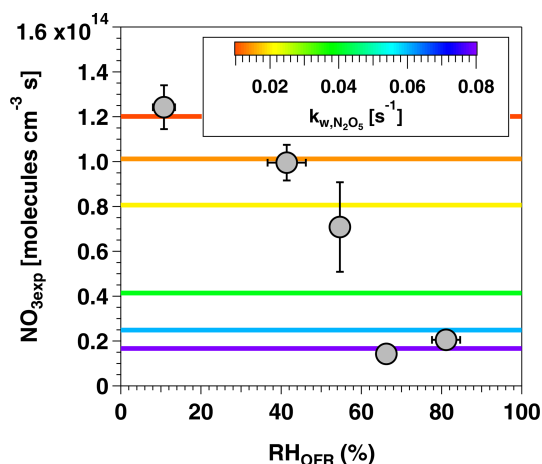


Figure 4. NO_{3exp} as a function of RH_{OFR} at [O₃]_{0, LFR} = 250 ppm and [NO₂]_{0, LFR} = 130 ppm. Horizontal lines represent N₂O₅ wall loss rate constants ranging from 0.01 to 0.08 s⁻¹ that were input to the OFR-iN₂O₅ KinSim mechanism (Table S2).

3.3 Effect of RH_{OFR}, [O₃]_{0, LFR}, and [NO₂]_{0, LFR} on NO_{3exp}

Figure 4 shows NO_{3exp} as a function of RH_{OFR} at [O₃]_{0, LFR} = 250 ppm and [NO₂]_{0, LFR} = 130 ppm. Under these conditions, NO_{3exp} decreased from 1.2×10^{14} to 2.0×10^{13} molecules cm⁻³ s as RH_{OFR} increased from 11 % to 81 %. We hypothesize that this result is due to more effi-

cient hydrolysis of N_2O_5 to HNO_3 on the wetted walls of the OFR at higher RH, thereby suppressing $\text{NO}_{3\text{exp}}$ relative to values obtained at lower RH conditions. In an attempt to model this behavior, $k_{\text{w},\text{N}_2\text{O}_5}$ values input to the model were adjusted as a function of RH_{OFR} . Figure 4 suggests that humidity-dependent $k_{\text{w},\text{N}_2\text{O}_5}$ values ranging from 0.01 to 0.08 s^{-1} were required to cover the range of measured $\text{NO}_{3\text{exp}}$. These values agreed within a factor of 2 or better with humidity-dependent $k_{\text{w},\text{N}_2\text{O}_5}$ 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 $\text{NO}_{3\text{exp}}$ as a function of $[\text{O}_3]_{0,\text{LFR}}$ for measurements with $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}} = 0.5 \pm 0.1$ and $\text{RH}_{\text{OFR}} = 11 \pm 2\%$. The equivalent ambient photochemical age shown on the right y axis was calculated assuming a 14 h average nighttime NO_3 mixing ratio of 30 ppt and a 10 h daytime NO_3 mixing ratio of 0 ppt (Asaf et al., 2010). $\text{NO}_{3\text{exp}}$ increased with increasing $[\text{O}_3]_{0,\text{LFR}}$ due to increased NO_3 production from higher $[\text{N}_2\text{O}_5]$. Over the range of measured conditions, increasing $[\text{O}_3]_{0,\text{LFR}}$ from 33 to 7092 ppm increased $\text{NO}_{3\text{exp}}$ from 6.4×10^{12} to 4.0×10^{15} molecules $\text{cm}^{-3}\text{ s}^{-1}$. The black line in Fig. 5 represents $\text{NO}_{3\text{exp}}$ modeled using the mechanism shown in Table S2. Measured and modeled $\text{NO}_{3\text{exp}}$ values agreed within a factor of 2 or better above $[\text{O}_3]_{0,\text{LFR}} \approx 40$ ppm, and the gain in $\text{NO}_{3\text{exp}}$ as a function of $[\text{O}_3]_{0,\text{LFR}}$ was highest between $[\text{O}_3]_{0,\text{LFR}} \approx 10$ and 300 ppm. Over this range of $[\text{O}_3]_{0,\text{LFR}}$, the NO_2 oxidation lifetime with respect to O_3 decreased from 115 to 4 s. Because $\tau_{\text{LFR}} = 20$ s, under this range of LFR conditions, the NO_2 lifetime in the LFR was long enough that high NO_2 levels exiting the LFR suppressed $\text{NO}_{3\text{exp}}$ in the OFR. In contrast, increasing $[\text{O}_3]_{0,\text{LFR}}$ from 300 to 7000 ppm decreased the NO_2 oxidation lifetime with respect to O_3 from 4 to 0.2 s, and $[\text{NO}_2]$ exiting the LFR was too low to significantly affect $\text{NO}_{3\text{exp}}$. To support this hypothesis, Fig. 6 plots $\text{NO}_{3\text{exp}}$ as a function of $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}}$ at $[\text{O}_3]_{0,\text{LFR}} = 250 \pm 20$ ppm and 6850 ± 400 ppm. Here, we incorporated $\text{NO}_{3\text{exp}}$ values obtained over $\text{RH}_{\text{OFR}} = 11\%$ to 81% for better statistics, and normalized each $\text{NO}_{3\text{exp}}$ value to the maximum $\text{NO}_{3\text{exp}}$ obtained at the same RH. Figure 6 shows that at $[\text{O}_3]_{0,\text{LFR}} = 250$ ppm, the maximum $\text{NO}_{3\text{exp}}$ was achieved at $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}} \approx 0.5$ to 0.7. Conversely, at $[\text{O}_3]_{0,\text{LFR}} = 6850$ ppm, the maximum $\text{NO}_{3\text{exp}}$ value was achieved at $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}} \approx 1.2$.

In a related set of experiments, IBBCEAS measurements of the $\text{NO}_2 : \text{NO}_3$ ratio at the exit of the OFR (obtained from Fig. 3a spectra) confirmed that significantly higher NO_2 levels were present in the OFR at higher $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}}$, as expected. For example, at $[\text{O}_3]_{0,\text{LFR}} = 150$ ppm and $[\text{NO}_2]_{0,\text{LFR}} = 112$ ppm, $\text{NO}_2 : \text{NO}_3 = 28$, whereas at $[\text{O}_3]_{0,\text{LFR}} = 160$ ppm and $[\text{NO}_2]_{0,\text{LFR}} = 320$ ppm, $\text{NO}_2 : \text{NO}_3 = 613$. $\text{NO}_2 : \text{NO}_3$, along with $\text{NO}_3 : \text{O}_3$ and $\text{NO}_2 : \text{O}_2$, has important implications for the fate of organic species in OFR- iN_2O_5 that are discussed in the following sections.

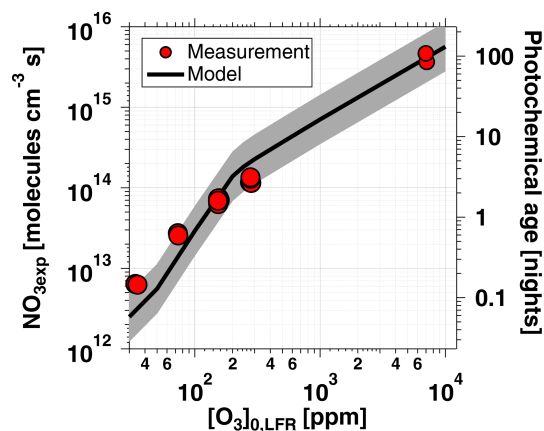


Figure 5. $\text{NO}_{3\text{exp}}$ as a function of $[\text{O}_3]_{0,\text{LFR}}$ for measurements with $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}} = 0.5 \pm 0.1$. Equivalent ambient photochemical age was calculated assuming a 14 h average nighttime NO_3 mixing ratio of 30 ppt and 10 h daytime average NO_3 mixing ratio of 0 ppt (Asaf et al., 2010). Model inputs were $k_{\text{w},\text{N}_2\text{O}_5} = 0.01\text{ s}^{-1}$ and $\text{NO}_3\text{R}_{\text{ext}} = 0.07\text{ s}^{-1}$ ($[\text{O}_3]_{0,\text{LFR}} < 1000$ ppm) or 0.38 s^{-1} ($[\text{O}_3]_{0,\text{LFR}} > 1000$ ppm). The shaded region encompasses model output scaled by factors of 0.5 and 2.

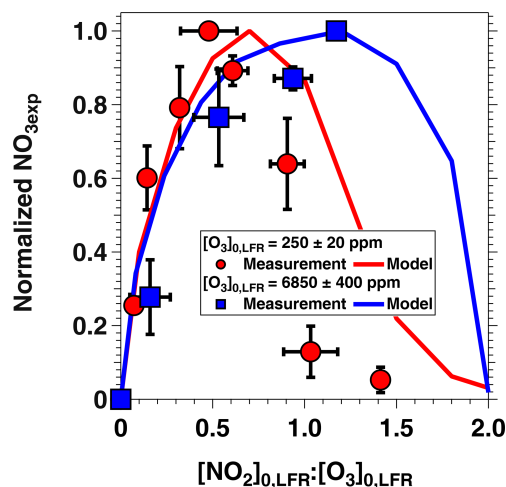


Figure 6. $\text{NO}_{3\text{exp}}$ as a function of $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}}$ at fixed $[\text{O}_3]_{0,\text{LFR}}$ values of 250 ± 20 and 6850 ± 400 ppm and $\text{RH}_{\text{OFR}} = 11\%$ to 81%. $\text{NO}_{3\text{exp}}$ values were normalized to the maximum $\text{NO}_{3\text{exp}}$ value obtained at the same RH.

3.4 Model characterization of OFR- $\text{iN}_2\text{O}_5 : \text{NO}_3 : \text{O}_3$, $\text{NO}_2 : \text{NO}_3$, and $\text{NO}_2 : \text{O}_2$

To examine OFR- iN_2O_5 performance over a wider range of conditions, Fig. 7 plots the mean $\text{NO}_{3\text{exp}}$, $[\text{O}_3]$, $\text{NO}_3 : \text{O}_3$, $\text{NO}_2 : \text{NO}_3$, and $\text{NO}_2 : \text{O}_2$ values obtained with the model as a function of $[\text{O}_3]_{0,\text{LFR}} = 10$ to 10^5 ppm (10%), for $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}} = 0.01, 0.1, 0.5, 1.0, 1.5, 1.8,$ and 2.0. Three observations are apparent from Fig. 7. First, at $[\text{O}_3]_{0,\text{LFR}} < 1000$ ppm and $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}} = 0.01$

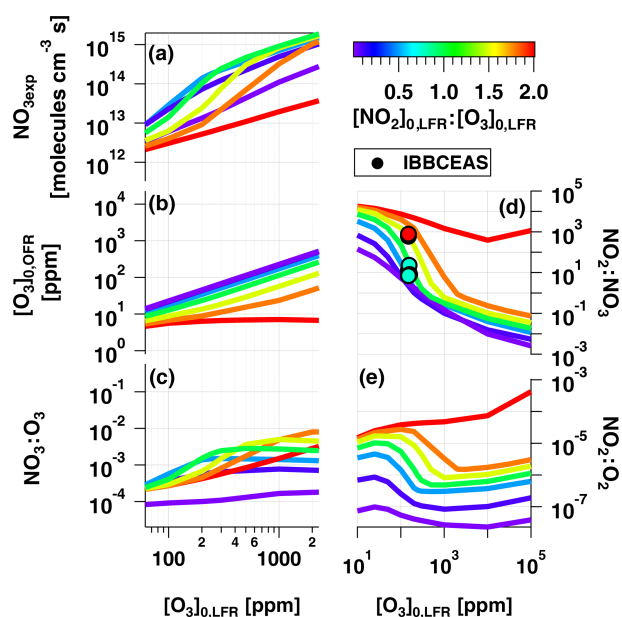


Figure 7. Modeled (a) NO_{3exp}, (b) [O₃], (c) NO₃:O₃, (d) NO₂:NO₃, and (e) NO₂:O₂ as a function of [O₃]_{0,LFR} = 10 to 10⁵ ppm, for [NO₂]_{0,LFR}:[O₃]_{0,LFR} = 0.01, 0.1, 0.5, 1.0, 1.5, 1.8, and 2.0. Model inputs were $k_{w,N_2O_5} = 0.01 \text{ s}^{-1}$, $NO_3R_{ext} = 0.07 \text{ s}^{-1}$. IBBCEAS-measured NO₂:NO₃ values are plotted in (d).

to 1.8, the maximum NO_{3exp} increased with [NO₂]_{0,LFR}:[O₃]_{0,LFR} prior to decreasing at [NO₂]_{0,LFR}:[O₃]_{0,LFR} > 1.0 (Fig. 7a). Above [O₃]_{0,LFR} ≈ 2000 ppm and below [NO₂]_{0,LFR}:[O₃]_{0,LFR} = 2.0, NO_{3exp} was less sensitive to [NO₂]_{0,LFR}:[O₃]_{0,LFR}. Second, the maximum NO₃:O₃ increased with increasing [NO₂]_{0,LFR}:[O₃]_{0,LFR} above [O₃]_{0,LFR} = 1000 ppm (Fig. 7c). Third, the [NO₂]_{0,LFR}:[O₃]_{0,LFR} = 2.0 case demonstrated unique behavior relative to the other cases because residual O₃ exiting the LFR was low (< 10 ppm) due to almost complete conversion of O₃ to O₂ inside the LFR (Fig. 7b). Consequently, the high residual [NO₂] suppressed NO_{3exp} by 1 to 2 orders of magnitude relative to [NO₂]_{0,LFR}:[O₃]_{0,LFR} < 2 cases (Fig. 7a) and generated enhanced NO₃:O₃, NO₂:NO₃, and NO₂:O₂ values. In addition, NO₂:NO₃ ratios obtained from IBBCEAS measurements at [O₃]_{0,LFR} = 150 to 160 ppm and [NO₂]_{0,LFR}:[O₃]_{0,LFR} = 0.75, 1.0 and 2.0 are shown in Fig. 7d. The measured NO₂:NO₃ values are comparable to, or lower than, the modeled NO₂:NO₃ values obtained under similar conditions and, therefore, broadly support using model results to further investigate the fate of (1) RO₂ formed from NO₃ oxidation of VOCs, (2) alkyl radicals that are reactive towards NO₂ and O₂, and (3) VOCs that are reactive towards O₃ and NO₃ in the following sections.

3.4.1 Fate of organic peroxy radicals (RO₂) formed from NO₃ + VOC reactions

Organic peroxy radicals (RO₂) react with NO, NO₂, NO₃, HO₂, or other RO₂ to generate alkoxy (RO) radicals, peroxy nitrates (RO₂NO₂), hydroperoxides or organic peroxides, and may additionally undergo autooxidation via sequential isomerization and O₂ addition. To investigate the fate of RO₂ as a function of OFR-iN₂O₅ conditions, we applied the methodology of Peng et al. (2019) by calculating the fractional oxidative loss of a generic alkyl or acyl RO₂ 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-iN₂O₅ conditions shown in Fig. 7, RO₂ reactions with NO, HO₂, and RO₂ were minor (< 1 %) loss pathways compared with reaction with NO₂ and NO₃. We conducted a model sensitivity analysis in which the RO₂ + RO₂ reaction rate was enhanced by increasing NO₃ R_{ext} from 0.07 to 0.7 s⁻¹ and increasing the RO₂ + RO₂ rate constant from 1 × 10⁻¹¹ to 1 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ (Berndt et al., 2018a, b). Despite these perturbations, the relative contribution of RO₂ + RO₂ reactions to total RO₂ loss remained < 1 % across this range of OFR-iN₂O₅ conditions.

To investigate the relative importance of competing RO₂ + NO₂ and RO₂ + NO₃ pathways, we defined the fractional reactive loss of RO₂ due to NO₃, $F_{RO_2+NO_3}$:

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

Figure 8a and b show $F_{RO_2+NO_3}$ calculated for alkyl and acyl RO₂, respectively. To simplify the analysis, we assumed that the thermal decomposition of RO₂NO₂ species formed from RO₂ + NO₂ reactions was slow compared with τ_{OFR} . This assumption generates a lower limit $F_{RO_2+NO_3}$ value for the alkyl RO₂ case, where RO₂NO₂ decomposition occurs on timescales of seconds or less (Orlando and Tyndall, 2012) but has minimal influence on the acyl-RO₂ case due to higher thermal stability of peroxy acyl nitrates. For alkyl RO₂, Fig. 8a shows that $F_{RO_2+NO_3} = 0.5$ was achieved between [NO₂, O₃]_{0,LFR} = (125 ppm, 250 ppm) and (3240 ppm, 1800 ppm). For acyl RO₂, due to faster reaction with NO₂, Fig. 8b shows that $F_{RO_2+NO_3} = 0.5$ was achieved using [NO₂, O₃]_{0,LFR} = (350 ppm, 700 ppm) to (1.1 %, 0.6 %).

To investigate the feasibility of generating OFR-iN₂O₅ conditions where RO₂ loss is dominated by autooxidation, we calculated the lifetime of alkyl and acyl RO₂ (τ_{RO_2}) over the range of OFR-iN₂O₅ conditions shown in Fig. 7 and Fig. 8a and b. As shown in Fig. 8d and e, maximum τ_{RO_2} values of ≈ 1.4 s (alkyl) and 0.4 s (acyl) were obtained at [NO₂]_{0,LFR} ≈ 2 ppm and [O₃]_{0,LFR} ≈ 200 ppm. At lower [O₃]_{0,LFR}, τ_{RO_2} decreased due to a faster RO₂ + NO₂ reaction rate, and at higher [O₃]_{0,LFR}, τ_{RO_2} decreased due to a faster RO₂ + NO₃ reaction rate. Because RO₂ autooxidation

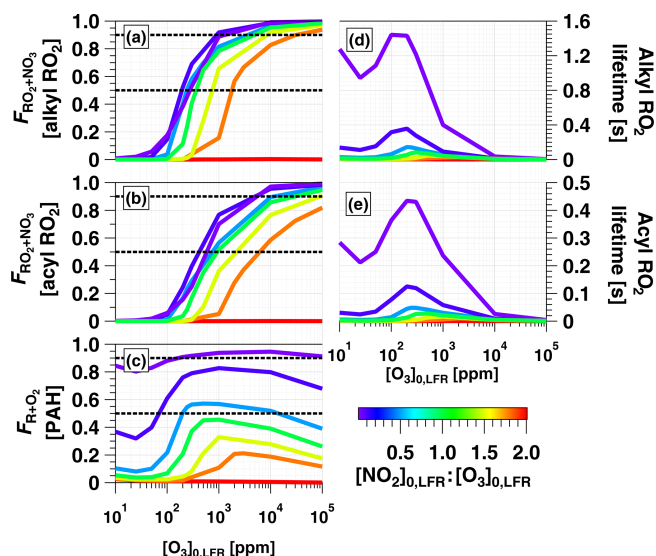


Figure 8. $F_{\text{RO}_2+\text{NO}_3}$ for (a) alkyl and (b) acyl RO_2 , and (c) $F_{\text{R}+\text{O}_2}$ over the same OFR- iN_2O_5 operating conditions and model inputs used to generate Fig. 7, with the corresponding lifetimes for (d) alkyl and (e) acyl RO_2 .

timescales range from 0.005 to 200 s depending on the specific RO_2 composition (Crouse et al., 2013), OFR- iN_2O_5 may achieve autooxidation-dominant conditions for some RO_2 but not for others.

3.4.2 Fate of aromatic alkyl radicals (R) formed from $\text{NO}_3 + \text{VOC}$ reactions

The majority of aromatic alkyl radicals (R) that are generated from NO_3 oxidation of VOCs quickly react with O_2 to generate RO_2 . However, NO_3 oxidation of a subset of aromatic VOCs generates R that react more slowly with O_2 , thereby enabling competing reactions with NO_2 . For example, the phenoxy radical ($\text{C}_6\text{H}_5\text{O}$) generated from NO_3 oxidation of phenol ($\text{C}_6\text{H}_5\text{OH}$) has $k_{\text{O}_2} : k_{\text{NO}_2} < 2.4 \times 10^{-9}$ (Platz et al., 1998), and the $\text{C}_{10}\text{H}_7\text{NO}_3$ radical that is generated from NO_3 oxidation of naphthalene (C_{10}H_8) has $k_{\text{O}_2} : k_{\text{NO}_2} < 4 \times 10^{-7}$ (Atkinson et al., 1994). Alkyl radicals generated from NO_3 oxidation of other PAHs may behave similarly to $\text{C}_{10}\text{H}_7\text{NO}_3$, but kinetic data are unavailable in the literature. To investigate the relative importance of competing $\text{R} + \text{NO}_2$ and $\text{R} + \text{O}_2$ reactions in these systems, we defined the fractional reactive loss of R with respect to O_2 , $F_{\text{R}+\text{O}_2}$:

$$F_{\text{R}+\text{O}_2} = \frac{k_{\text{R}+\text{O}_2}[\text{O}_2]}{k_{\text{R}+\text{O}_2}[\text{O}_2] + k_{\text{R}+\text{NO}_2}[\text{NO}_2]} \quad (4)$$

Figure 8c shows $F_{\text{R}+\text{O}_2}$ over the same OFR- iN_2O_5 operating conditions used to generate Fig. 7 and Fig. 8a and b. For $\text{C}_6\text{H}_5\text{O}$ (not shown), $F_{\text{R}+\text{O}_2} < 0.08$ over the entire range of OFR- iN_2O_5 conditions shown in Figs. 7e and 8c. For $\text{C}_{10}\text{H}_7\text{NO}_3$, $F_{\text{R}+\text{O}_2} \geq 0.5$ was achieved for the majority

of OFR- iN_2O_5 conditions where $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}} \leq 0.1$ and also between $[\text{NO}_2, \text{O}_3]_{0,\text{LFR}} = (100 \text{ ppm}, 200 \text{ ppm})$ and $(5000 \text{ ppm}, 10000 \text{ ppm})$. The use of $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}} \geq 1$ always generated conditions where the reaction rate of $\text{R} + \text{NO}_2$ exceeded $\text{R} + \text{O}_2$.

3.4.3 Fate of VOCs reactive towards O_3 and NO_3

We defined the fractional reactive loss of a VOC with respect to NO_3 , $F_{\text{VOC}+\text{NO}_3}$:

$$F_{\text{VOC}+\text{NO}_3} = \frac{k_{\text{VOC}+\text{NO}_3}[\text{NO}_3]}{k_{\text{VOC}+\text{NO}_3}[\text{NO}_3] + k_{\text{VOC}+\text{O}_3}[\text{O}_3]} \quad (5)$$

and we established $F_{\text{VOC}+\text{NO}_3} = 0.9$ as the criterion for NO_3 -dominated oxidative loss. Figure 9 plots $\text{NO}_3 : \text{O}_3$ at which $F_{\text{VOC}+\text{NO}_3} = 0.9$ for several classes of organic compounds with published k_{NO_3} and k_{O_3} values greater than 10^{-16} and $10^{-19} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, respectively. Therefore, this figure excludes compounds such as alkanes and monocyclic aromatics that react slowly with NO_3 and are essentially unreactive towards O_3 ($F_{\text{NO}_3} \approx 1$). $\text{NO}_3 : \text{O}_3$ values that correspond to $[\text{NO}_2]_{0,\text{LFR}}$ and $[\text{O}_3]_{0,\text{LFR}} = (2 \text{ ppm}, 200 \text{ ppm})$, $(150 \text{ ppm}, 300 \text{ ppm})$, and $(5400 \text{ ppm}, 3000 \text{ ppm})$ are represented by horizontal bands with upper and lower limit values calculated assuming $k_{\text{w},\text{N}_2\text{O}_5}$ values of 0.01 and 0.08 s^{-1} (Sect. 3.3). These LFR inputs generated OFR- iN_2O_5 conditions that maximize the RO_2 lifetime and $\text{NO}_3 : \text{O}_3$ at $[\text{NO}_2] : [\text{O}_3]_{0,\text{LFR}} = 0.5$ and 1.8, respectively (Figs. 7, 8). Figures 7 and 9 as well as kinetic data from the literature suggest that the injection of 2 ppm NO_2 and 200 ppm O_3 into the LFR was sufficient to achieve $F_{\text{VOC}+\text{NO}_3} \geq 0.9$ for phenols, PAHs with no double bonds, and mono- and sesquiterpenes with one double bond at low RH_{OFR} . Increasing $[\text{NO}_2]_{0,\text{LFR}}$ to 150 ppm and $[\text{O}_3]_{0,\text{LFR}}$ to 300 ppm additionally achieved $F_{\text{VOC}+\text{NO}_3} \geq 0.9$ for acenaphthylene, isoprene, and mono- and sesquiterpenes with one double bond at elevated RH_{OFR} . Further increasing $[\text{NO}_2]_{0,\text{LFR}}$ to 5400 ppm and $[\text{O}_3]_{0,\text{LFR}}$ to 3000 ppm achieved $F_{\text{VOC}+\text{NO}_3} \geq 0.9$ for $\geq \text{C}_3$ linear alkenes, unsaturated aldehydes, and mono- and sesquiterpenes with two double bonds at low RH_{OFR} . While $[\text{NO}_2, \text{O}_3] = [20 \%, 10 \%]$ (not shown) achieved $F_{\text{VOC}+\text{NO}_3} \geq 0.9$ for (E)-3-penten-2-one and ethene, the corresponding $\text{NO}_3_{\text{exp}} \approx 10^{14} \text{ molecules cm}^{-3} \text{ s}$ achieved at this condition (Fig. 7a) was insufficient to oxidize more than 1%–2% of the initial ethene concentration due to its slow NO_3 rate constant (Atkinson, 1991).

3.5 NO_3 estimation equation for OFR- iN_2O_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_{exp} as a function of readily measured experimental parameters, thereby providing a simpler alternative to detailed photochemical models for experimental planning

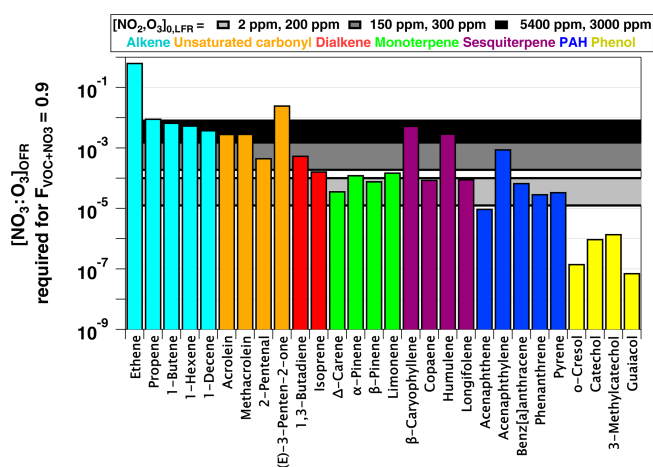


Figure 9. NO₃ : O₃ at which $F_{\text{VOC}+\text{NO}_3} = 0.9$ for representative VOCs with $k_{\text{NO}_3} > 10^{-16}$ and $k_{\text{O}_3} > 10^{-19}$ cm³ molecules⁻¹ s⁻¹ (Manion et al., 2015). Horizontal bands represent upper and lower limit values calculated assuming $k_w, \text{N}_2\text{O}_5 = 0.01$ and 0.08 s⁻¹.

and analysis. Here, we expand on those studies by deriving an NO_{3exp} estimation equation for OFR-iN₂O₅. Model results obtained from the base case of the model – a VOC reacting with NO₃ at 2.5×10^{-12} cm³ molecule⁻¹ s⁻¹ as a surrogate for NO₃R_{ext} – were used to derive the following equation that allows for the estimation of NO_{3exp} for OFR-iN₂O₅:

$$\begin{aligned} \log([\text{NO}_3]_{\text{exp}}) = & a + b \log[273.15 + T_{\text{OFR}}] + c \log[\tau_{\text{OFR}}] \\ & + d \log[\text{NO}_2]_{0, \text{LFR}} + e \log[\text{O}_3]_{0, \text{LFR}} \cdot T_{\text{OFR}} \\ & + f \log[k_{w, \text{OFR}, \text{N}_2\text{O}_5}] + \log\left(\frac{[\text{NO}_2]_{0, \text{LFR}}}{[\text{O}_3]_{0, \text{LFR}}}\right) \\ & \cdot (g (\log[\text{O}_3]_{0, \text{LFR}})^2 + h \log[\text{O}_3]_{0, \text{LFR}}) - \frac{[\text{NO}_2]_{0, \text{LFR}}}{[\text{O}_3]_{0, \text{LFR}}} \\ & \cdot (i + j \log[\text{O}_3]_{0, \text{LFR}}) + k \log(\text{NO}_3\text{R}_{\text{ext}}) \\ & + l \log[\text{NO}_2]_{0, \text{LFR}} \cdot T + m \log[\text{O}_3]_{0, \text{LFR}} \cdot \log k_{w, \text{OFR}, \text{N}_2\text{O}_5} \end{aligned} \quad (6)$$

The phase space of OFR-iN₂O₅ parameters for fitting Eq. (6) to the NO_{3exp} model results was defined as follows: [O₃]_{0, LFR} = 10–1000 ppm, [NO₂]_{0, LFR} = 10–1000 ppm, [NO₂]_{0, LFR} : [O₃]_{0, LFR} ≤ 2, NO₃R_{ext} = 1–200 s⁻¹, $k_{w, \text{OFR}, \text{N}_2\text{O}_5} = 0.01$ – 0.08 s⁻¹, $T_{\text{OFR}} = 0$ – 40 °C, and $\tau_{\text{OFR}} = 60$ – 300 s. The cases where [O₃]_{0, LFR} > 1000 ppm and/or [NO₂]_{0, LFR} : [O₃]_{0, 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 [O₃]_{0, LFR}, [NO₂]_{0, LFR} (11 values over 10–1000 ppm), NO₃R_{ext}, $k_w, \text{N}_2\text{O}_5$, and τ_{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

Table 1. Fit parameters for NO_{3exp} estimation equation (Eq. 6).

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

(Eq. 6) over three subphase spaces with the following additional constraints: (1) [NO₂]_{0, LFR} : [O₃]_{0, LFR} = 0–1 and NO₃R_{ext} = 20–200 s⁻¹; (2) [NO₂]_{0, LFR} : [O₃]_{0, LFR} = 0–1 and NO₃R_{ext} = 1–20 s⁻¹; and (3) [NO₂]_{0, LFR} : [O₃]_{0, 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_{3exp} and [NO₂]_{0, LFR} : [O₃]_{0, 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_{3exp} 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_y chemistry (Peng et al., 2018).

NO₃R_{ext} of a system will change over the course of multiple generations of NO₃ oxidation due to changes in kinetic rate coefficients between different species and NO₃ (k_{NO_3}). The sensitivity of Eq. (6) to changes in NO₃R_{ext} depends in part on the relative magnitudes of NO₃R_{ext} and the internal NO₃ reactivity, NO₃R_{int}, which is approximately equal to $k_{\text{NO}_2+\text{NO}_3}[\text{NO}_2]$. If NO₃R_{int} ≫ NO₃R_{ext}, changes in NO₃R_{ext} would have minimal influence on Eq. (6). In one case study, we examined changes in NO₃R_{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, α-pinene to pinonaldehyde, sabinene to sabinaketone, and 3-carene to caronaldehyde. At the limit where 100% of each BVOC is converted to its carbonyl oxidation product, NO₃R_{ext} decreases by a factor of 200 or greater. Unsaturated organic nitrates that are generated from BVOC + NO₃ may also be reactive towards NO₃, but k_{NO_3} for these species are not available. In another case study, we examined changes in NO₃R_{ext} following conversion of

BVOCs to SOA. An effective k_{NO_3} for SOA was calculated using the following equation adapted from Lambe et al. (2009):

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

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

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

γ is the fraction of collisions between NO₃ and SOA resulting in reaction; D_p is the surface area-weighted mean particle diameter; ρ_p is the particle density; N_A is Avogadro's number; \bar{c} is the mean molecular speed of NO₃ ($3.2 \times 10^4 \text{ cm s}^{-1}$ at $T = 298 \text{ K}$); M_{SOA} is the mean molecular weight of the SOA; and $D_{\text{NO}_3} = 0.08 \text{ cm}^2 \text{ s}^{-1}$ is the NO₃ 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 $\rho_p = 1.4 \text{ g cm}^{-3}$, $M_{\text{SOA}} = 250 \text{ g mol}^{-1}$ (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 y axis. At the limit where 100% of a BVOC is converted to SOA, $\text{NO}_3 R_{\text{ext}}$ 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 $\text{NO}_3 R_{\text{ext}}$ decreases following NO₃ oxidation of BVOCs to carbonyl oxidation products and/or SOA. In this case, inputting $\text{NO}_3 R_{\text{ext}}$ of the BVOC precursor to Eq. (6) generates a lower limit to $\text{NO}_3 \text{exp}$ over multiple generations of NO₃ oxidation. Results for other systems will depend on the k_{NO_3} values of associated gas- and condensed-phase precursors and their oxidation products.

3.6 SOA generation from β -pinene + NO₃

To apply the OFR-iN₂O₅ technique to SOA formation studies, we generated SOA from β -pinene + NO₃ in the absence of seed particles using $[\text{O}_3]_{0, \text{LFR}} = 300 \text{ ppm}$, $[\text{NO}_2]_{0, \text{LFR}} = 150 \text{ ppm}$, and $\text{RH}_{\text{OFR}} \approx 1\%$. PTR-MS measurements confirmed the complete consumption of β -pinene, and numerous product ions were detected. The largest ions detected were $(\text{H}^+) \text{C}_9\text{H}_{14}\text{O}$ and $(\text{H}^+) \text{C}_{10}\text{H}_{14}$ which may correspond to nopinone ($\text{C}_9\text{H}_{14}\text{O}$) and fragmentation or decomposition products of $\text{C}_{10}\text{H}_{17}\text{NO}_4$, respectively (Hallquist et al., 1999; Clafin and Ziemann, 2018). The mass yield of SOA ranged from 0.03 to 0.39 over β -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 β -pinene mixing ratio,

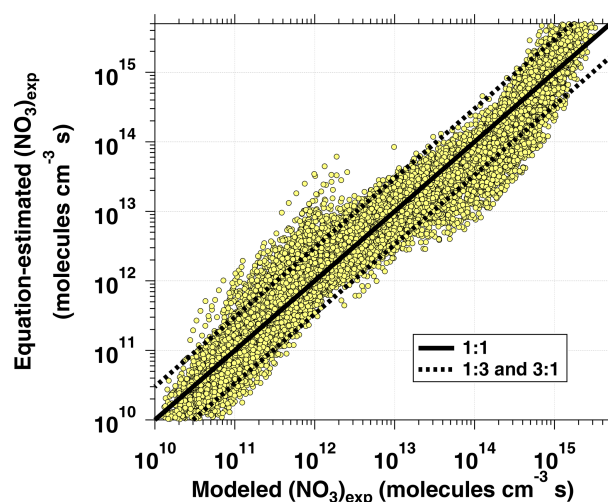


Figure 10. $\text{NO}_3 \text{exp}$ calculated from the estimation equation (Eq. 6 and Table 1) as a function of $\text{NO}_3 \text{exp}$ calculated from the full OFR-iN₂O₅ KinSim mechanism (Table S2). Solid and dashed lines correspond to the 1 : 1 and the 1 : 3, and 3 : 1 lines, respectively.

presumably due to the absence of seed particles in the OFR (Lambe et al., 2015). To compare the results obtained using OFR-iN₂O₅ with a conventional environmental chamber method, Fig. 11a and b show HR-ToF-AMS spectra of SOA generated from NO₃ oxidation of β -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, β -pinene + NO₃ 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^+ , which, along with the signal at NO_2^+ and $\text{NO}^+ : \text{NO}_2^+ = 6.7$, is consistent with the formation of particulate organic nitrates (Farmer et al., 2010). Signals observed at CHO^+ , $\text{C}_2\text{H}_3\text{O}^+$, and other $\text{C}_x\text{H}_y\text{O}_{>1}^+$ ions suggest the presence of other multifunctional oxidation products.

4 Conclusions

OFR-iN₂O₅ complements recently developed methods that enable NO_x-dependent photooxidation studies in OFRs such as OFR-iN₂O and OFR-iC₃H₇ONO (Lambe et al., 2017; Peng et al., 2018; Lambe et al., 2019) by enabling studies of nighttime NO₃-initiated oxidative aging processes. Important OFR-iN₂O₅ parameters are $[\text{O}_3]$, $[\text{NO}_2]$, $[\text{H}_2\text{O}]$, T , $\text{NO}_3 R_{\text{ext}}$, and τ_{OFR} . By contrast, important OFR-iN₂O and OFR-iC₃H₇ONO parameters are UV intensity, external OH reactivity (OHR_{ext}), τ_{OFR} , and either $[\text{O}_3] + [\text{H}_2\text{O}] + [\text{N}_2\text{O}]$ or $[\text{C}_3\text{H}_7\text{ONO}]$. Notably, $\text{NO}_3 R_{\text{ext}}$ is typically less significant in OFR-iN₂O₅ than OHR_{ext} in OFR-iN₂O or OFR-iC₃H₇ONO because (1) most compounds are less reactive

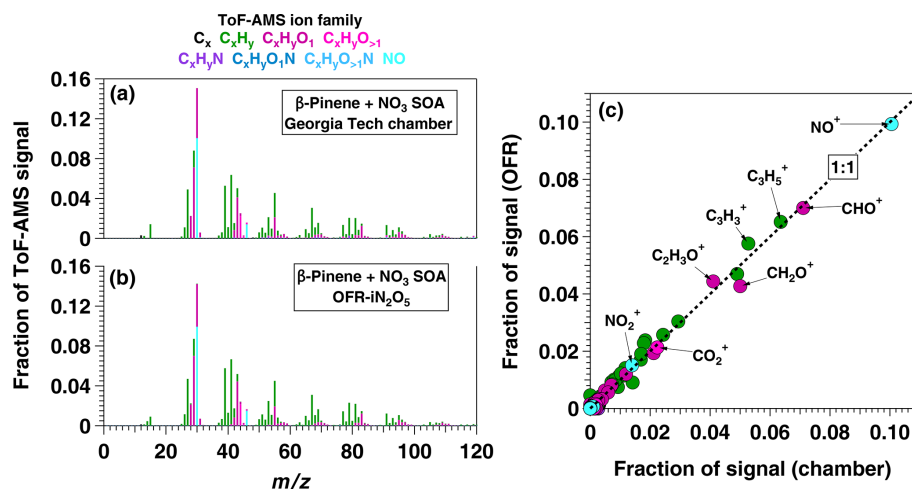


Figure 11. AMS spectra of SOA generated from NO_3 oxidation of β -pinene in (a) the Georgia Tech environmental chamber (Boyd et al., 2015) and (b) OFR- iN_2O_5 . The scatter plot in (c) shows spectra generated in the OFR and in the chamber plotted against each other.

towards NO_3 than OH ; (2) $\text{NO}_{3\text{exp}}$ is higher than OH_{exp} ; and (3) $(\text{NO}_3\text{R})_{\text{int}}$ of OFR- iN_2O_5 , which is dominated by the $\text{NO}_3 + \text{NO}_2$ reaction, is larger and easier to manipulate than the internal OH reactivity of OFR- iN_2O and OFR- $\text{iC}_3\text{H}_7\text{ONO}$, which is dominated by $\text{OH} + \text{HO}_2$ and $\text{OH} + \text{NO}_2$ reactions. To identify optimal OFR- iN_2O_5 conditions for different applications, we characterized $\text{NO}_{3\text{exp}}$, τ_{RO_2} , $F_{\text{RO}_2+\text{NO}_3}$, $F_{\text{R}+\text{O}_2}$, and $F_{\text{VOC}+\text{NO}_3}$ at $[\text{O}_3]_{0,\text{LFR}} = 10$ ppm to 10 %, $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}} = 0.01$ to 2.0, and $\text{RH}_{\text{OFR}} = 7\%$ to 85 %. Optimal $\text{NO}_{3\text{exp}}$ was achieved by minimizing $[\text{H}_2\text{O}]$ in the OFR and associated humidity-dependent N_2O_5 wall losses. This is contrary to most OFR techniques that are used to generate OH radicals, where optimal OH_{exp} is achieved by maximizing $[\text{H}_2\text{O}]$ and the associated OH production from the $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ reaction and/or H_2O photolysis at $\lambda = 185$ nm.

Figure 12 presents image plots that represent OFR- iN_2O_5 conditions suitable for generating optimal $\text{NO}_{3\text{exp}}$, $\text{NO}_3 : \text{O}_3$, $\text{NO}_2 : \text{NO}_3$, and τ_{RO_2} values at the lower and upper limit $k_{\text{w},\text{N}_2\text{O}_5}$ values that were measured. Most OFR- iN_2O_5 conditions using $[\text{O}_3]_{0,\text{LFR}} > 200$ ppm generated $\text{NO}_{3\text{exp}} > 1.5 \times 10^{12}$ molecules $\text{cm}^{-3} \text{s}$ (Fig. 12a, b), which is sufficient to oxidize isoprene and compounds with similar k_{NO_3} ; for reference, $\text{NO}_{3\text{exp}} > 1.6 \times 10^{11}$ molecules $\text{cm}^{-3} \text{s}$ is required to oxidize α -pinene. At $[\text{O}_3]_{0,\text{LFR}} > 200$ ppm and $[\text{NO}_2]_{0,\text{LFR}} : [\text{O}_3]_{0,\text{LFR}} > 0.5$, OFR- iN_2O_5 generated $\text{NO}_3 : \text{O}_3 > 10^{-3}$ at $k_{\text{w},\text{N}_2\text{O}_5} = 0.01 \text{ s}^{-1}$ (Fig. 12c), which achieved $F_{\text{VOC}+\text{NO}_3} > 0.9$ for mono- and sesquiterpenes with one double bond, most PAHs, and phenol/methoxyphenol species. Achieving $\text{NO}_3 : \text{O}_3 > 10^{-3}$ at $k_{\text{w},\text{N}_2\text{O}_5} = 0.08 \text{ s}^{-1}$ was more challenging (Fig. 12d). Increasing $[\text{O}_3]_{0,\text{LFR}}$ decreased $[\text{NO}_2] : [\text{NO}_3]$ and, therefore, increased $F_{\text{RO}_2+\text{NO}_3}$ (Fig. 12e, f). In contrast, decreasing $[\text{O}_3]_{0,\text{LFR}}$ or increasing $k_{\text{w},\text{N}_2\text{O}_5}$, and, consequently, $\text{NO}_{3\text{exp}}$, increased τ_{RO_2} (Fig. 12g, h), potentially allowing more time for the autooxidation processes

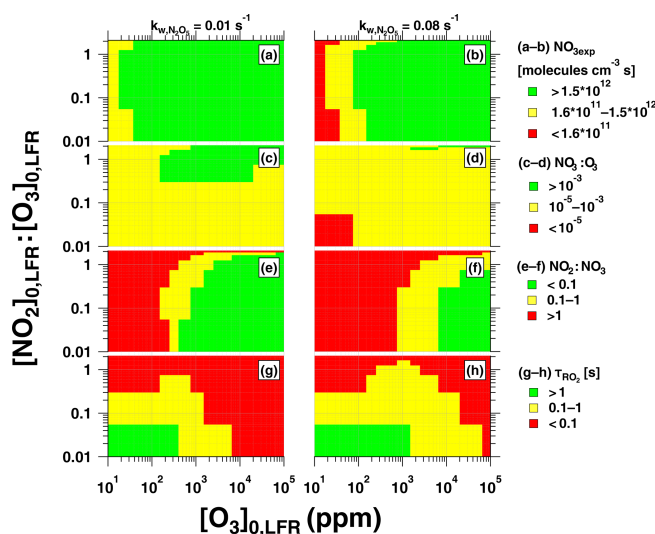


Figure 12. Summary of OFR- iN_2O_5 operating conditions suitable for maximum (a, b) $\text{NO}_{3\text{exp}}$, (c, d) $\text{NO}_3 : \text{O}_3$, (e, f) $\text{NO}_2 : \text{NO}_3$, and (g, h) τ_{RO_2} , assuming $k_{\text{w},\text{N}_2\text{O}_5} = 0.01$ and 0.08 s^{-1} .

to occur. The best overlap between OFR- iN_2O_5 conditions that achieved $F_{\text{RO}_2+\text{NO}_3} > 0.9$ and $\tau_{\text{RO}_2} > 1 \text{ s}$ was obtained with $[\text{NO}_2]_{0,\text{LFR}} \approx 2\text{--}3$ ppm and $[\text{O}_3]_{0,\text{LFR}} \approx 200\text{--}300$ ppm. Because atmospheric $\text{NO}_2 : \text{NO}_3$ is highly variable and often much larger than $\text{NO}_2 : \text{NO}_3$ achieved using OFR- iN_2O_5 (Brown et al., 2003; Stutz et al., 2004), simply attempting to maximize $F_{\text{RO}_2+\text{NO}_3}$ may not always be necessary and has trade-offs such as decreasing $\text{NO}_3 : \text{O}_3$ and $F_{\text{VOC}+\text{NO}_3}$. OFR- iN_2O_5 was more difficult to apply to species such as unsaturated carbonyls 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-iN₂O₅ can continuously generate N₂O₅ and NO₃ 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 N₂O₅ and HNO₃ concentrations that are generated using OFR-iN₂O₅ complicate the application of techniques such as iodide-adduct chemical ionization mass spectrometry due to efficient reactions between the iodide reagent ion and N₂O₅ or HNO₃ (Lee et al., 2014). Additionally, the humidity-dependent N₂O₅ wall loss rate must be accurately characterized to model the performance of a specific OFR-iN₂O₅ configuration. Future applications of OFR-iN₂O₅ will investigate the NO₃-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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Author contributions. ATL, ECW, and AA conceived and planned the experiments. ATL, JEK, FM, LRW, PLC, AA, and JEP carried out the experiments. MC and AF performed the IBBCEAS measurements and data analysis. AL, JLJ, and ZP conceived and planned the model simulations, and ATL and ZP carried out the model simulations. ATL, ECW, ZP, and JLJ contributed to the interpretation of the results. AL took the lead in writing the paper. All authors provided feedback on the paper.

Competing interests. The authors declare no competing interests.

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